Simulation packages for rivers, estuaries and seas

D-HYDRO Suite

Dutch Delta System

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D-Water Quality Processes Library Description

Technical Reference Manual

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Processes Library Description

Detailed description of Processes

Technical Reference Manual

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telephone: +31 88 335 82 73
e-mail: Information
www: Deltares

For sales contact:
telephone: +31 88 335 81 88
e-mail: Sales
www: Sales & Support

For support contact:
telephone: +31 88 335 81 00
e-mail: Support
www: Sales & Support

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1 How to find your way in this manual

1.1 Introduction

This part of the D-Water Quality manual is called the Technical Reference Manual. It contains an overview of state variables, input parameters and output parameters and a detailed description of all processes included in the Processes Library for Delft3D and SOBEK. You should use detailed process descriptions in combination with the Processes Library Configuration Tool (PLCT) in order to connect state variables, input parameters, default values and output parameters to mathematical formulations.

Each process in the Processes Library is documented separately. Each process description starts with an introduction containing background and conceptual information, which precedes the following items:

Implementation	List of substances or other state variables for which the process is implemented, with references to other (auxiliary) processes used
Formulation	Detailed description of mathematical formulations and all process parameters and coefficients
Direction	Definition of the schematisations (1DV, 1DH, 2DV, 2DH, 3D) for which the process can be used
Directives for use	Tips for use of the process and for the quantification of input parameters
References	List of referenced literature
Parameter Tables	Tabulated lists of all input parameters and coefficients, and of output parameters (not included for some processes)

1.2 Overview

This manual provides process descriptions per group of substances. Within each group the proces descriptions have been ranked according to individual substances and the position in a processes cycle. Production comes first, and is followed by decomposition and removal. Additional processes that provide parameters to primary processes immediately follow the primary processes. Auxiliary processes that basically deliver additional output parameters take the last position.

Primary processes for a group of substances may affect the substances of another group as well, because they deliver mass fluxes for these substances. Typical examples are the processes that concern biomass or dead organic matter. These processes deliver fluxes for many other substances such as oxygen and nutrients. Auxiliary processes may provide additional input or output parameters, and do generally not deliver mass fluxes.

The Processes Library of D-Water Quality contains a comprehensive set of substances and processes, that covers a wide range of water quality parameters. In view of making the water quality module, D-Water Quality, available as open source modelling software, the Processes Library has been optimised into one coherent standard set of substances and processes for Delft3D. Usually only a part of this will be implemented in a specific water quality model. A selection can be made with Delft3D's user interface (PLCT). To facilitate the quick selection of substances and processes for a specific type of model such as a model for eutrophication or a model for dissolved oxygen Deltares intends to make available predefined sets. However, the manual is equally applicable to all selections, because the processes formulations are exactly the same for each selection.

The Processes Libary used for SOBEK still uses its own set of substances and processes,

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accessible in the form of pre-defined configurations. These configurations contain selections of substances and processes, on which this manual does not provide information. Parts of this manual that concern SOBEK only are indicated as such. Deltares intends to merge SOBEK's set of substances and processes with the standard set as described in this manual.

Present D-Water Quality has two standard options for the modelling of sediment-water interaction, a simplified approach and an advanced approach. The user interface supports only the simplified 'S1-S2' approach, for which additional substances represent two sediment layers. This manual includes the S1-S2 specific substances and processes. The comprehensive 'layered sediment' approach involves adding a sediment grid to the computational grid and including a sediment specific transport process. This is described in the addition manual 'Sediment Water Interaction'. The substances and processes are the same for water and sediment in the layered sediment approach as the formulations of the processes are generic. Processes turn out differently in water and sediment depending on local conditions, such as the dissolved oxygen concentration. Unless stated otherwise, a process description in this manual applies to the water column as well as the sediment. Presently the 'layered sediment' approach only applies to Delft3D.

The water quality processes are grouped under the following chapters:

- ◇ Oxygen and BOD (chapter 2)
- ◇ Nutrients (chapter 3)
- ◇ Primary producers (chapter 4)
- ◇ Light regime (chapter 6)
- ◇ Primary consumers and higher trophic levels (chapter 7)
- ◇ Organic matter (detritus) (chapter 8)
- ◇ Inorganic substances and pH (chapter 9)
- ◇ Organic micropollutants (chapter 10)
- ◇ Heavy metals and radio-active isotopes (chapter 11)
- ◇ Bacteria and viruses (chapter 12)
- ◇ Sediment and mass transport (chapter 13)
- ◇ Temperature (chapter 14)
- ◇ Various auxiliary processes (chapter 16)
- ◇ Deprecated processes descriptions (chapter 17)

Generic mass transport processes are dealt with together with the substances group "sediment" (chapter 13).

Remarks:

- ◇ Two different formats have been used for the process description. The original format and the improved format (as of 2000). The latter is more elaborate, has a different notation of parameters in formulations and provides tables with input and output parameters, facilitating the specification of parameter values in the input of models. Process descriptions according to the improved format usually concern the latest and most advanced versions of the processes. However, some of the process descriptions have not been updated for a long time, so that with regard to details they may not picture the actual situation. Process descriptions according to the original format may be incomplete and do not have the tables for the in- and output parameters.
- ◇ This manual may not be entirely complete with regard to substances and processes available in the Processes Library. Some processes are described in this manual that are not included in the standard set of processes, and are therefore not accessible in present D-Water Quality. This concerns the module the module MICROPHYT for microphytobenthos. Some processes are not described in this manual because they have not been integrated as they are under development such as module DEB for grazers

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(shell fish) and a module for aquatic macrophytes. All modules mentioned can be made available upon request.

◇ As the water quality module is open source software it also has a facility to modify the formulations of existing processes or to add new substances and processes. This is described in 'Open Processes Library, User Manual'.

1.3 Processes reference tables

Each process has a unique name, which is the way to get to the process you are interested in. The processes and their relation are listed in Table 1.1 to Table 16.1 from the Processes Library Tables manual

Table 1.1

Table 1.1 presents a list of the processes in the library together with the chapter where you can find the detailed description.

There are two ways to find the unique name of a process:

1 the report file of D-Water Quality $<*$.lsp$>$ tells you the name of a process
2 one of the following index-tables:

Table 2.1

This table is indexed on *substance* name and lists the associated water quality processes. When you model a substance find the associated processes in this table and refer to Table 1.1 to find the description of the water quality-processes involved.

Table 3.1 and Table 4.1

These tables are indexed on substance name and lists the associated transport processes. Table 3.1 lists the transport processes which calculate *velocities* and Table 4.1 lists the transport-processes which calculate *dispersions*. When you model a substance find the associated processes in these tables and refer to Table 1.1 to find the description of the transport-processes involved.

Table 5.1

This table is indexed on *flux* name and lists the *substances* and *water quality processes* associated. When you know the name of a flux (e.g. from D-Water Quality 4 post-processing) you can find in this table the substances which are influenced by this flux and the process which calculates this flux. Refer to Table 1.1 to find the description of the process involved.

Table 6.1 and Table 7.1

These tables are indexed on respectively *velocity* and *dispersion* name and lists the associated *substances* and *transport processes*. When you know the name of a velocity or dispersion (e.g. from D-Water Quality post-processing) you can find in this table the substances which are influenced and the process which calculates the velocity or dispersion. Refer to Table 1.1 to find the description of the transport process involved.

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Table 8.1 and Table 9.1

These tables are indexed on respectively *segment related* and *exchange related process-input* **that can be produced by other processes** and lists the process that can calculate the input-item. When you know the name of a process input item (e.g. from the detailed process description (Chapters 2 up to 16) or from the D-Water Quality list file $<*$.lsp$>$) find the name of the process that can calculate this item in this table. Refer to Table 1.1 to find a description of the process involved. You can also 'shop' through this list to find items worthwhile presenting.

Table 10.1 and Table 11.1

These tables are indexed on respectively *segment related* and *exchange-related process input* **that has a *default* value**. When you have the name of a process input item (e.g. from the detailed process description or from the D-Water Quality list file $<*$.lsp$>$) find the default value for this item in this table. Refer to Table 1.1to find a description of the process involved.

Table 12.1 and Table 13.1

These tables are indexed on respectively *segment related* and *exchange-related process input* **that has *no default* value** and can not be calculated by other processes. When you have the name of a process input item (e.g. from the detailed process description or from the D-Water Quality list file $<*$.lsp$>$) find the default value for this item in this table. Refer to Table 1.1 to find a description of the process involved.

Table 14.1 and Table 15.1

These tables are indexed on respectively *segment related* and *exchange related process-output* that is not used by other processes and lists the process that calculates the output item. When you have the name of a process output item (e.g. from the detailed process descriptions or from the D-Water Quality list file $<*$.lsp$>$) find the name of the process that can calculate this item in this table. Refer to Table 1.1 to find a description of the process involved. You can also 'shop' through this list to find items worthwhile presenting.

Table 16.1

This table is indexed on the processes and lists in which configurations of the Processes Library it is included (only relevant for SOBEK).

1.4 What's new?

This section gives a concise overview of new features in and restructuring of the Technical Reference Manual, which concerns the first open source version of D-Water Quality. In this version, the Processes Library has undergone modifications that resulted in a revised standard set of substances and processes, sofar as Delft3D is concerned. These modifications have been carried out to remove duplications and redundancies from the Processes Library and to integrate coherent clusters of smaller processes into larger units, which enhances the transparency of the Processes Library and reduces the risk of accidentally leaving out relevant processes in a model application. Extensions have been made as well to enlarge the modelling potential. The changes include:

- ◇ The definition of sub-sets of processes, called "configurations", has been removed.
- ◇ Processes which are not routinely used have been removed.
- ◇ The state variables (substances) *DetC, DetN, DetP, DetSi, OOC, OON, OOP* and *OOSi* have been replaced by *POC1, PON1, POP1, POC2, PON2, POP2* and *Opal*. All pro-

cesses dealing with the state variables *DetC, DetN, DetP, DetSi, OOC, OON, OOP* and *OOSi* representing organic matter have been removed.

- ◇ The processes dealing with the state variables *POC1-4, PON1-4, POP1-4* and *Opal* have been extended to include the precise formulations previously used for *DetX* and *OOX*.
- ◇ All processes dealing with resuspension, burial and digging for the state variables representing the S1-S2 sediment layers have been integrated in one single process per state variable called *S12TraXXXX*, where *XXXX* equals the state variable name (substance name). This single process makes use of the supporting processes *Res_DM, Bur_DM and Dig_DM*, where DM refers to total sediment dry matter.
- ◇ The state variables (substances) *GreenS*1 and *GreenS2*, representing Green algae after settling to the bed, have been removed. Green algae that settle are now instantaneously converted to detritus, just like the present practice with settling of BLOOM algae. Similarly, Diat algae that settle are now instantaneously converted to detritus.
- ◇ The state variables *DiatS1* and *DiatS2* now exclusively represent benthic algae (microphytobenthos), that may grow on the sediment. Settling water Diat algae are no longer converted into benthic *DiatS1* algae, while resuspending benthic *DiatS1* and *DiatS2* algae are no longer converted into water Diat algae.
- ◇ The previous processes *Salin* and *Chloride* have been replaced by the new *Salinchlor* process.
- ◇ The process *Tau* has been renamed to *CalTau*.
- ◇ The processes descriptions dealing with the algae module DYNAMO have been regrouped into two overall process descriptions for the water column and the sediment and one auxiliary process description.
- ◇ All processes dealing with the extinction of visible light (VL) are integrated in the overall process *Extinc_VLG*.
- ◇ The processes calculating aggregated parameters of organic pools (e.g. POC) in water and sediment have been integrated with the overall composition processes for water and sediment *Compos, S1_Comp* and *S2_Comp*.
- ◇ The processes calculating aggregated settling fluxes of organic matter have been integrated with the overall aggregated settling fluxes process *Sum_Sedim*.
- ◇ A host of new state variables (substances) has been included to extend the modelling potential of D-Water Quality, particularly relevant for the modelling of sediment-water interaction modelling and greenhouse gases. This includes state variables *VIVP, APATP* (phosphate minerals), *SO4* (sulfate), *SUD, SUP* (dissolved and particulate sulfide), *POC5, PON5, POP5* (non-transportable detritus, see below), *POS1, POS2, POS3, POS4, POS5, DOS* (particulate and dissolved organic sulfur), *FeIIIpa, FeIIIpc, FeIIId, FeS, FeS2, FeCO3, FeIId* (dissolved and particulate iron species) *TIC* (total inorganic carbon and alkalinity), *CH4* (methane). *TIC* replaces *CO2*. State variable *EnCoc* was added to represent bacterial pollutant Enterococci.
- ◇ Several new processes have been included to support the modelling of the new state variables. This includes *VIVIANITE, APATITE* (precipitation of phosphate), *CONSELAC* (consumption of oxygen, nitrate, iron and sulfate, and the production of methane in the mineralization of organic matter), *SPECSUD, OXIDSUD, SULPHOX, SPECSUDS1, SPECSUDS2, PRECSUL* (speciation, oxidation and precipitation of sulfide), *SPECIRON, IRONOX, IRONRED, PRIRON* (speciation, oxidation, reduction and precipitation of iron) *OXIDCH4, VOLATCH4, EBULCH4* (oxidation, volatilization and ebullition of methane), *SPECCARB, REARCO2, SATURCO2* (speciation and water-atmosphere exchange of dissolved inorganic carbon), and *EnCocMRT* (mortality of Enterococci).
- ◇ Process *LSEDTRA* has been added for the transport processes in sediment for the modeling of sediment-water interaction as based on the comprehensive layered sediment approach.
- ◇ A new module has been included for the mortality and (re-)growth of terrestrial drowned vegetation. This concerns additional state variables *VBNN*, where *NN* is a number from 01 to 09, and *POC5, PON5, POP5, POS5*, into which the non-transportable detrital biomass

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(stems, branches, roots) is released at mortality.

We used the old items automatic replacement functionality for other changes after the open source update.

◇ Within BLOOM there was a seasonal reflection coefficient encoded, that is actually only applicable at a latitude of ca 52 degrees north but could not be changed without recompiling the code. Therefore we added a reflection coefficient to the BLOOM parameters, and a new process Reflection that by default mimics the old BLOOM behaviour when the latitude is greater than 23 degrees north. When the latitude is greater than 23 degrees south, the seasonal pattern is inverted, and near the equator, between 23 degrees north and 23 degrees south, there is a fixed reflection constant.

1.5 Backward compatibility

The present version of open source D-Water Quality is generally backward compatible with the previous non open source version. However, there are a few non-backward compatible items in the Processes Library. With very few exceptions older input files of existing models are still supported. The input processor <delwaq1.exe> makes the necessary modifications and reports them in the <*.lsp> message file. Non-backward compatible items are printed as warnings with a reference number. These references are listed here.

1 void.
2 The concentration of detritus N, P and Si as well as OON, OOP, OOSi in the deep sediment boundary (layer "S3") are now specified directly as a solid phase concentration (FrDetNS3 in gN/gDM, FrDetPS3, FrDetSiS3, FrOONS3, FrOOPS3, FrOOSiS3). In previous versions, the carbon to X ratio was used (C-NDetCS3, C-PDetCS3, C-SDetCS3, C-NOOCS3, C-POOCS3, C-SOOCS3). If one of the latter constants has been detected in your input file, please replace by the appropriate new constant. Note: these numbers only have a meaning if the item SWDigS2 = 1.
3 The concentration of AAP in the deep sediment (layer "S3") is now specified directly as a solid phase concentration (FrAAPS3 in gP/gDM. In previous versions, the concentration in TIM was used (FrAAPTIMS3). If the latter constant has been detected in your input file, please replace by the new constant. Note: this number only has a meaning if the item SWDigS2 = 1.
4 The concentration of metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Va, Zn) in the deep sediment (layer "S3") is now specified directly as a solid phase concentration (e.g. QCdDMS3 in mg/kgDM). In previous versions, this concentration was specified via the concentrations in IM1, IM2, IM3, Phyt and POC (e.g. QCdIM1S3, QCdIM2S3, QCdIM3S3, QCdPHYTS3, QCdPOCS3). If one of the latter constants has been detected in your input file, please replace by the appropriate new constant. Note: these numbers only have a meaning if the item SWDigS2 = 1
5 The concentration of organic chemicals (153, Atr, BaP, Diu, Flu, HCB, HCH, Mef, OMP) in the deep sediment (layer "S3") is now specified directly as a solid phase concentration (e.g. QAtrDMS3 in mg/kgDM). In previous versions, this concentration was specified via the concentrations in Phyt and POC (e.g. QAtrPHYTS3, QAtrPOCS3). If one of the latter constants has been detected in your input file, please replace by the appropriate new constant. Note: these numbers only have a meaning if the item SWDigS2 = 1.
6 Where previously up to two substances represented biogenic silica (DetSi and OOSi), the Processes Library now uses just one substance (Opal). DELWAQ will automatically convert DetSi to Opal, and neglect OOSi. Biogenic silica formed within the model domain as a result of algae mortality will be released as Opal, will dissolve and will be available for uptake by algae. A problem exists if the user has specified an inflow of biogenic silica to the model domain in the form of the substance OOSi via boundary conditions and/or

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waste loads. This part of the biogenic silica will no longer dissolve, will not be available for algae and will not count in the output parameter total silica (TotSi). To avoid this problem, the user has to add the boundary concentrations and waste loads of OOSi to the boundary concentrations and waste loads of DetSi or Opal.

1.6 Modelling water and sediment layers

The processes library distinguishes two approaches to modelling the water and sediment compartments of a water system:

- The simpler approach is the so-called "S1/S2" approach, where an upper layer S1 is assumed to be at the top of the sediment and below it there is a layer S2. The layer S1 directly interacts with the water column and most of the sediment processes are located in this layer. The layer underneath, S2, is mostly inert and exchanges mass with the first layer via processes like burial and digging. In the process formulations specific substances are used to model the S1 and S2 layers. For instance: $IM1$ is the first inorganic matter fraction – the concentration of particulate matter in the water phase. Its counterpart in the S1 layer is called $IM1S1$" and in the S2 layer it is called "$IM1S2$".
- The alternative approach is the so-called "layered sediment" approach. With this approach all substances are present in both the water phase and the sediment layers (where the user can define the layout of the sediment layers themselves). This enables the library to treat all segments in the same way and reduces the number of individual substances. But above all it enables the detailed modelling of processes that take place in the sediment.

1.6.1 Usage notes

The presence of these two approaches has some consequences for the use of the processes library:

- To use the layered sediment approach you must define the sediment layers separately (see the separate manual for this, Deltares 2024). As there are no substances that are specific to the sediment anymore, substances like $IM1S1$ are not to be used.
- In the process formulations the bulk concentration is used for both the water phase and the sediment (both approaches). To accommodate for a uniform treatment, however, sometimes the pore water concentration is needed and therefore the *porosity* has been introduced even for processes that mostly work for the water phase. The convention there is:
  - The porosity is 1 for the water segments, in case of the layered sediment approach, and smaller than 1, typically around 0.4, for the sediment segments. In this case the porosity has to be specified explicitly for the sediment layers.
  - For the S1/S2 approach the porosity is simply 1, as then the distinction between bulk and pore-water concentrations is handled in an implicit way. The processes library provides this value as a default, so you should *not* specify it yourself.

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2 Oxygen and BOD

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2.1 Reaeration, the air-water exchange of DO

PROCESS: REAROXY

Dissolved oxygen (DO) in surface water tends to saturate with respect to the atmospheric oxygen concentration. However, oxygen production and consumption processes in the water column counteract saturation, causing a DO-excess or DO-deficit. The resulting super- or undersaturation leads to reaeration, the exchange of oxygen between the atmosphere and the water. Reaeration may cause an oxygen flux either way, to the atmosphere or to the water. The process is enhanced by the difference of the saturation and actual DO concentrations, and by the difference of the velocities of the water and the overlying air. Since lakes are rather stagnant, only the windspeed is important as a driving force for lakes. The reaeration rate tends to saturate for low windspeeds (< 3 m.s^{-1}). On the other hand, the stream velocity may deliver the dominant driving force for rivers. Both forces may be important in estuaries.

Extensive research has been carried out all over the world to describe and quantify reaeration processes, including the reaeration of natural surface water. Quite a few different models have been developed. The most generally accepted model is the “film layer” model. This model assumes the existence of a thin water surface layer, in which a concentration gradient exists bounded by the saturation concentration at the air-water interface and the water column average DO concentration. The reaeration rate is characterised by a water transfer coefficient, which can be considered as the reciprocal of a mass transfer resistance. The resistance in the overlying gas phase is assumed to be negligibly small.

Many formulations have been developed and reported for the water transfer coefficient. These formulations are often empirical, but most have a deterministic background. They contain the stream velocity or the windspeed or both. Most of the relations are only different with respect to the coefficients, the powers of the stream velocity and the windspeed in particular. Reaeration has been implemented in DELWAQ with ten different formulations for the transfer coefficient. Most of these relations have been copied or derived from scientific publications (WL | Delft Hydraulics, 1980b),(WL | Delft Hydraulics, 1978). The first two options are pragmatic simplifications to accommodate preferences of the individual modeller. All reaeration rates are also dependent on the temperature according to the same temperature function.

Implementation

Process REAROXY has been implemented in such a way, that it only affects the DO-budget of the top water layer. An option for the transfer coefficient can be selected by means of input parameter *SWRear* (= 0–7, 9–13). The DO saturation concentration required for the process REAROXY is calculated by an additional process SATUROXY.

The process has been implemented for substance OXY.

Table 2.1 provides the definitions of the parameters occurring in the formulations.

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Formulation

The reaeration rate has been formulated as a linear function of the temperature dependent mass transfer coefficient in water and the difference between the saturation and actual concentrations of DO as follows:

$$Rrear = klrear \times (Coxs - \max(Cox, 0.0))/H$$
$$klrear = klrear_{20} \times tcrear^{(T-20)}$$
$$klrear_{20} = \left(\frac{a \times v^b}{H^c}\right) + \left(d \times W^2\right)$$
$$Coxs = f\left(T, Ccl \text{ or } SAL\right) \quad \text{(delivered by SATUROXY)}$$
$$fsat = 100 \times \frac{\max(Cox, 0.0)}{Coxs}$$

with:

a, b, c, d	coefficients with different values for each reaeration options
Ccl	chloride concentration [gCl m^{-3}]
Cox	actual dissolved oxygen concentration [gO_2 m^{-3}]
$Coxs$	saturation dissolved oxygen concentration [gO_2 m^{-3}]
$fsat$	percentage of saturation [%]
H	depth of the water column [m]
$klrear$	reaeration transfer coefficient in water [m d^{-1}]
$klrear_{20}$	reaeration transfer coefficient at reference temperature 20 °C [m d^{-1}]
$tcrear$	temperature coefficient of the transfer coefficient [-]
$Rrear$	reaeration rate [gO_2 m^{-3} d^{-1}]
SAL	salinity [kg m^{-3}]
T	temperature [°C]
v	flow velocity [m s^{-1}]
W	wind speed at 10 m height [m s^{-1}]

Notice that the reaeration rate is always calculated on the basis of a positive dissolved oxygen concentration, whereas *OXY* may have negative values. Negative oxygen equivalents represent reduced substances.

Depending on the reaeration option, the transfer coefficient is dependent on either the flow velocity or the wind speed, or dependent on both. With respect to temperature dependency option *SWRear* = 10 is an exception. The respective formulation is not dependent on temperature according the above equations, but has its own temperature dependency on the basis of the Schmidt number. Information on the coefficients *a–d* and the applicability is provided below for each of the options.

SWRear = 0

The transfer coefficient is simplified to a constant, multiplied with the water depth *H*, using the transfer coefficient as input parameter. **So *klrear*$_{20}$ is to be provided as a value in [d^{-1}] in stead of in [m d^{-1}]!** Consequently, the coefficients are:

$$a = klrear_{20} \times H, \quad b = 0.0, \quad c = 0.0, \quad d = 0.0$$

SWRear = 1

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The transfer coefficient is simplified to a constant, using the transfer coefficient as input parameter. Consequently, the coefficients are:

$$a = klrear_{20}/H, \quad b = 0.0, \quad c = 0.0, \quad d = 0.0$$

SWRear = 2

The coefficients according to Churchill et al. (1962) are:

$$a = 5.026, \quad b = 0.969, \quad c = 0.673, \quad d = 0.0$$

The relation is valid for rivers, and therefore independent of wind speed.

SWRear = 3

The coefficients according to O' Connor and Dobbins (1956) are:

$$a = 3.863, \quad b = 0.5, \quad c = 0.5, \quad d = 0.0$$

The relation is valid for rivers, and therefore independent of wind speed.

SWRear = 4

The coefficients are the same as for option *SWRear = 3* according to O' Connor and Dobbins (1956), but coefficient a can be scaled using the transfer coefficient as input parameter. Consequently, the coefficients are:

$$a = 3.863 \times klrear_{20}, \quad b = 0.5, \quad c = 0.5, \quad d = 0.0$$

The relation is valid for rivers, and therefore independent of wind speed.

SWRear = 5

The coefficients according to Owens et al. (1964) are:

$$a = 5.322, \quad b = 0.67, \quad c = 0.85, \quad d = 0.0$$

The relation is valid for rivers, and therefore independent of wind speed.

SWRear = 6

The coefficients according to Langbein and Durum (1967) are:

$$a = 11.23, \quad b = 1.0, \quad c = 0.33, \quad d = 0.0$$

The relation is valid for rivers, and therefore independent of wind speed.

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SWRear = 7

The relation is according to O' Connor and Dobbins (1956) and Banks and Herrera (1977) as reported by WL | Delft Hydraulics (1980b), but the coefficients have been modified according WL | Delft Hydraulics (1978); *d = 0.3-0.6*) and later WL | Delft Hydraulics modelling studies for Dutch lakes. Consequently, the coefficients are:

$$a = 3.863, \quad b = 0.5, \quad c = 0.5, \quad d = 0.065 \times klrear_0$$

The relation is valid for rivers, lakes, seas and estuaries.

SWRear = 8

The option is presently void and should not be used.

SWRear = 9

The relation is according to Banks and Herrera (1977) as reported by WL | Delft Hydraulics (1980b), but the coefficients have been modified according to WL | Delft Hydraulics (1978); *d = 0.03–0.06*) and later modelling studies for Dutch lakes WL | Delft Hydraulics (1992c). Consequently, the coefficients are:

$$a = 0.3, \quad b = 0.0, \quad c = 0.0, \quad d = 0.028 \times klrear_0$$

The relation is valid for lakes and seas, and therefore independent of flow velocity. The relation takes into account that the mass transfer coefficient saturates at a lower boundary for low wind velocities ($W < 3$ m s^{-1}).

SWRear = 10

The relation according to Wanninkhof (1992) deviates from the previous relations with respect to temperature dependency, that is not included according to the above Arrhenius equation for *klrear*. The temperature dependency enters the relation in a scaling factor on the basis of the Schmidt number. Coefficient d had to be scaled from cm h^{-1} to m d^{-1}. Consequently, the coefficients are:

$$a = 0.0, \quad b = 0.0, \quad c = 0.0, \quad d = 0.0744 \times fsc$$

$$fsc = \left(\frac{Sc}{Sc_{20}} \right)^{-0.5}$$

$$Sc = d_1 - d_2 \times T + d_3 \times T^2 - d_4 \times T^3$$

with:

$d_{1\text{–}4}$	coefficients
fsc	scaling factor for the Schmidt number [-]
Sc	Schmidt number at the ambient temperature [g m^{-3}]
Sc_{20}	Schmidt number at reference temperature 20 °C [d^{-1}]
T	temperature [°C]

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The relation is valid for lakes and seas, and therefore independent of flow velocity.

The Schmidt number is the ratio of the kinematic viscosity of water (ν) and the molecular diffusion coefficient of oxygen in water (D). The appropriate constants to compute the Schmidt number in both seawater and fresh water are given in the table below.

Water system	$\mathbf{d_1}$	$\mathbf{d_2}$	$\mathbf{d_3}$	$\mathbf{d_4}$
Sea water Salinity $>$ 5 kg m^{-3}	1953.4	128.0	3.9918	0.050091
Fresh water Salinity $\leq$ 5 kg m^{-3}	1800.6	120.1	3.7818	0.047608

SWRear = 12 (SOBEK-only)

This relation is a hybrid combination of SWRear = 3 (O' Connor and Dobbins, 1956) and SWRear = 5 (Owens et al., 1964). This hybride formulation is developed for urban water management in The Netherlands. More information concerning the derivation of this hybrid relation can be found in Stowa (2002).

(O' Connor and Dobbins, 1956):

a = 3.93 , b = 0.5 , c = 0.5 , d = 0.0 if

$$v < \left(\frac{3.93}{5.32} H^{0.35}\right)^6 \tag{2.1}$$

(Owens et al., 1964):

a = 5.32 , b = 0.67 , c = 0.85 , d = 0.0 if

$$v < \left(\frac{3.93}{5.32} H^{0.35}\right)^6 \tag{2.2}$$

$$klrear_{20} = \max(klrear_{\min}, klrear_{20}) \tag{2.3}$$

with:

$klrear_{\min}$ minimum water transfer coefficient for oxygen [m.d^{-1}]

The relation is valid for rivers, and therefore independent of windspeed.

SWRear = 13

The relation according to Guérin (2006) and Guérin et al. (2007) deviates strongly from the previous relations, with respect to wind dependency, with respect to an additional forcing parameter, namely rainfall, and with respect to temperature dependency. The latter is not included according to the above Arrhenius equation for *klrear*. Like the relation described for

option 10, the temperature dependency enters the relation in a scaling factor on the basis of the Schmidt number. The relation for transfer coefficient is:

$$klrear = \left(a \times \exp\left(b_1 \times W^{b2}\right) + \left(c_1 \times P^{c2}\right)\right) \times fsc$$
$$fsc = \left(\frac{Sc}{Sc_{20}}\right)^{-0.67}$$
$$Sc = d_1 - d_2 \times T + d_3 \times T^2 - d_4 \times T^3$$

with:

a, b, c, d	coefficients
$klrear$	transfer coefficient in water [m d^{-1}]
P	precipitation, e.g. rainfall [mm h^{-1}]
Sc	Schmidt number at the ambient temperature [g m^{-3}]
Sc_{20}	Schmidt number at reference temperature 20 °C [d^{-1}]
T	temperature [°C]
W	windspeed at 10 m height [m s^{-1}]

The relation is valid for (tropical) lakes and therefore independent of stream velocity. The general coefficients have the following input names and values:

a	b_1	b_2	c_1	c_2
CoefAOXY	*CoefB1OXY*	*CoefB2OXY*	*CoefC1OXY*	*CoefC2OXY*
1.660	0.26	1.0	0.66	1.0

The Schmidt number is the ratio of the kinematic viscosity of water (ν) and the molecular diffusion coefficient of oxygen in water. The appropriate constants to compute the Schmidt number for fresh water are given in the table below (Guérin, 2006):

d_1	d_2	d_3	d_4
CoefD1OXY	*CoefD2OXY*	*CoefD3OXY*	*CoefD4OXY*
1800.06	120.10	3.7818	0.047608

Directives for use

- ◇ Options *SWRear = 0, 1, 4, 7, 9* provide the user with the possibility to scale the mass transfer coefficient *KLRear*. All other options contain fixed coefficients.
- ◇ When using option *SWRear = 0* the user should be aware that the mass transfer coefficient *KLRear* has the unusual dimension d^{-1}. Since high values of *KLRear* may cause numerical instabilities, the maximum *KLRear* value is limited to 1.0 day^{-1}.
- ◇ When using option *SWRear = 1* the user should be aware that the mass transfer coefficient *KLRear* has the standard dimension m d^{-1}.
- ◇ When using options *SWRear = 4, 7 or 9* you should be aware that the input parameter *KLRear*$_0$ is used as a dimensionless scaling factor. The default value of *KLRear*$_0$ is 1.0 in order to guarantee that scaling is not carried out when not explicitly wanted.
- ◇ The dependencies of *klrear*$_{20}$*/H* on *v*, *W* and *H* for options *SWRear = 2, 3, 5, 6, 7* are presented in Figure 2.1.

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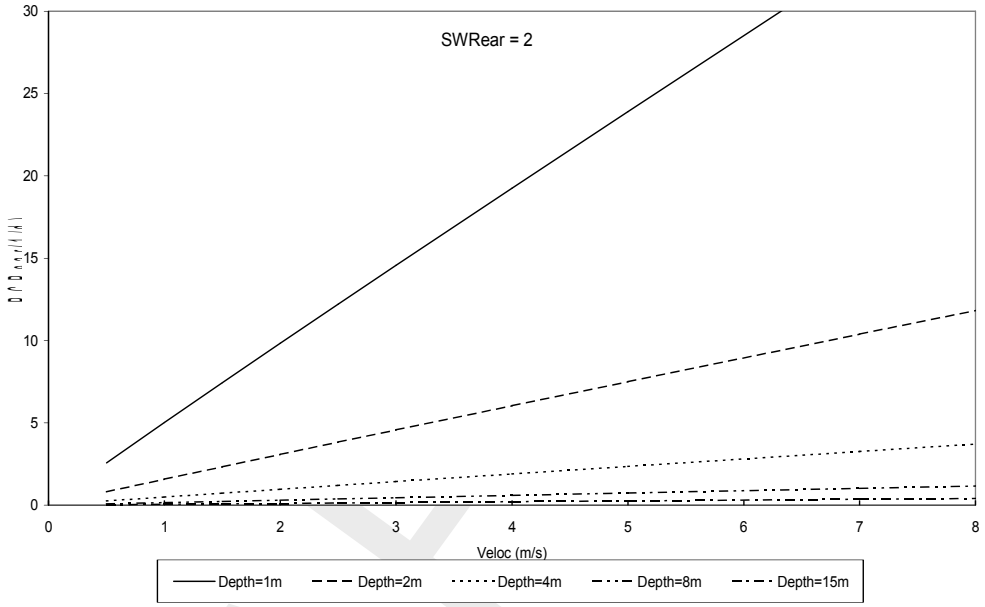

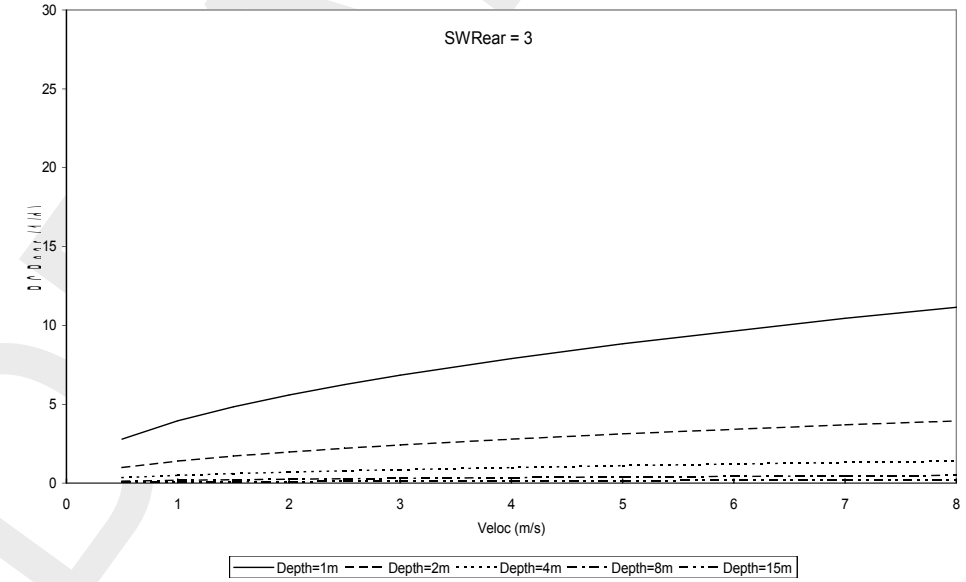

- ◇ The coefficients a–c_2 are input parameters for option *SWRear*=13 only. The default values are those for option 13.
- ◇ The coefficients d_{1-4} are input parameters for options *SWRear = 10, 13*. The default values are the freshwater values, which are the same for both options.

Table 2.1: *Definitions of the parameters in the above equations for REAROXY*

Name in formulas[1)]	**Name in in/output**	**Definition**	**Units**
Cox	*OXY*	concentration of dissolved oxygen	$gO_2\ m^{-3}$
Coxs	*SaturOXY*	saturation concentration dissolved oxygen from SATUROXY	$gO_2\ m^{-3}$
a	CoefAOXY	coefficients for option 13 only	-
b_1	CoefB1OXY		-
b_2	CoefB2OXY		-
c_1	CoefC1OXY		-
c_2	CoefC2OXY		-
d_1	CoefD1OXY	coefficients for options 10 and 13	-
d_2	CoefD2OXY		-
d_3	CoefD3OXY		-
d_4	CoefD4OXY		-
fsc	–	scaling factor for the Schmidt number	-
fsat	–	percentage oxygen saturation	%
H	*Depth*	depth of the water layer	m
$klrear_{20}$	*KLRear* (output)	water transfer coefficient for oxygen[1)]	$m\ d^{-1}$
$klrear_0$	*KLRear* (input)	input parameter to determine transfer coefficient (options 7 and 9)	$m\ d^{-1}$
tcrear	*TCRear*	temperature coefficient for reaeration	-
P	rain	rainfall	mm^{-1}
Rrear	–	reaeration rate	$gO_2\ m^{-3}\ d^{-1}$
SAL	*Salinity*	salinity	$kg\ m^{-3}$
Sc	–	Schmidt number for dissolved oxygen in water	-
SWRear	*SWRear*	switch for selection of options for transfer coefficient	-
T	*Temp*	temperature	°C
v	*Velocity*	flow velocity	$m\ s^{-1}$
W	*VWind*	wind speed at 10 m height	$m\ s^{-1}$

[1)] See directives for use concerning the dimension of *KLRear*.

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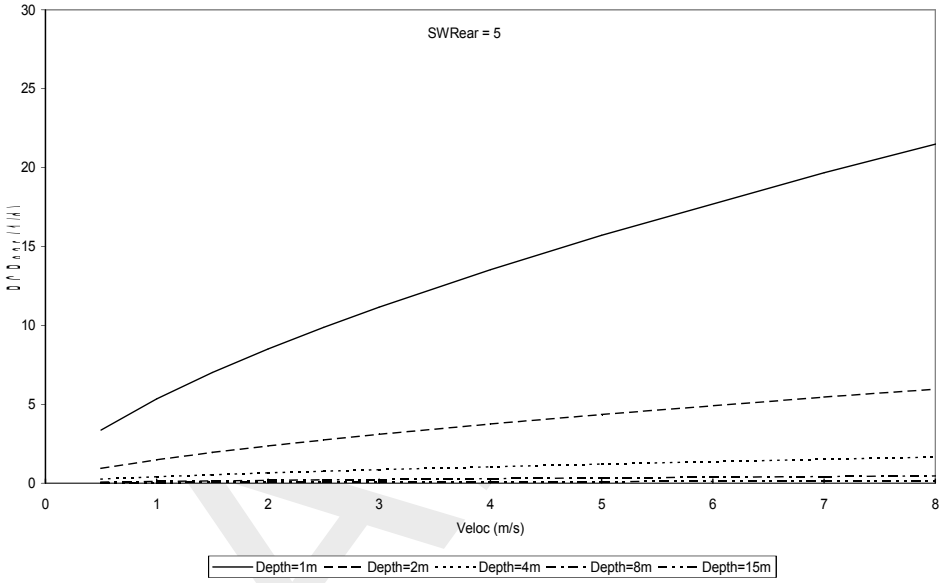
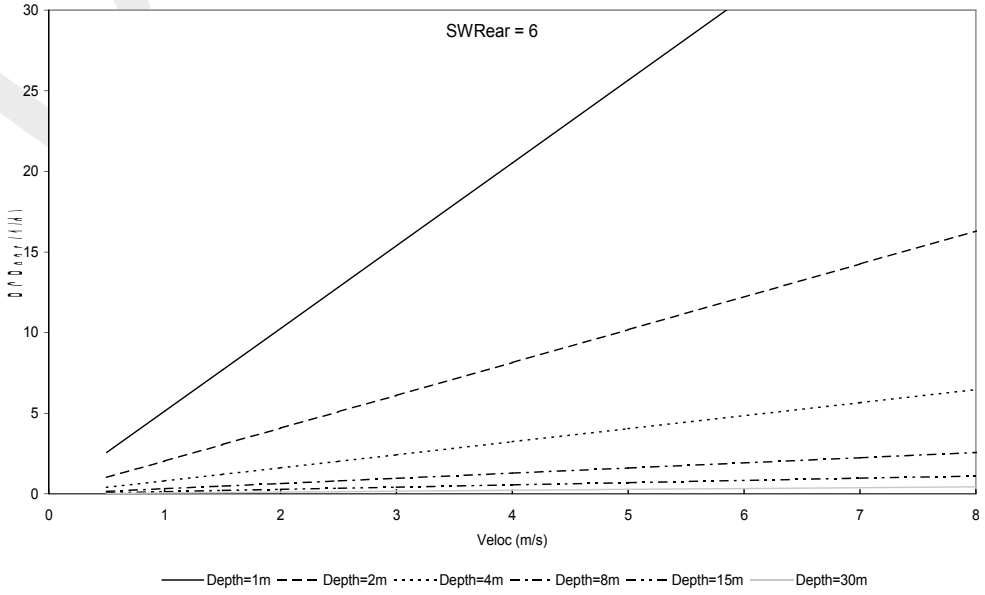

SWRear = 5
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
Veloc (m/s)
Depth=1m
Depth=2m
Depth=4m
Depth=8m
Depth=15m


SWRear = 6
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
Veloc (m/s)
Depth=1m
Depth=2m
Depth=4m
Depth=8m
Depth=15m
Depth=30m

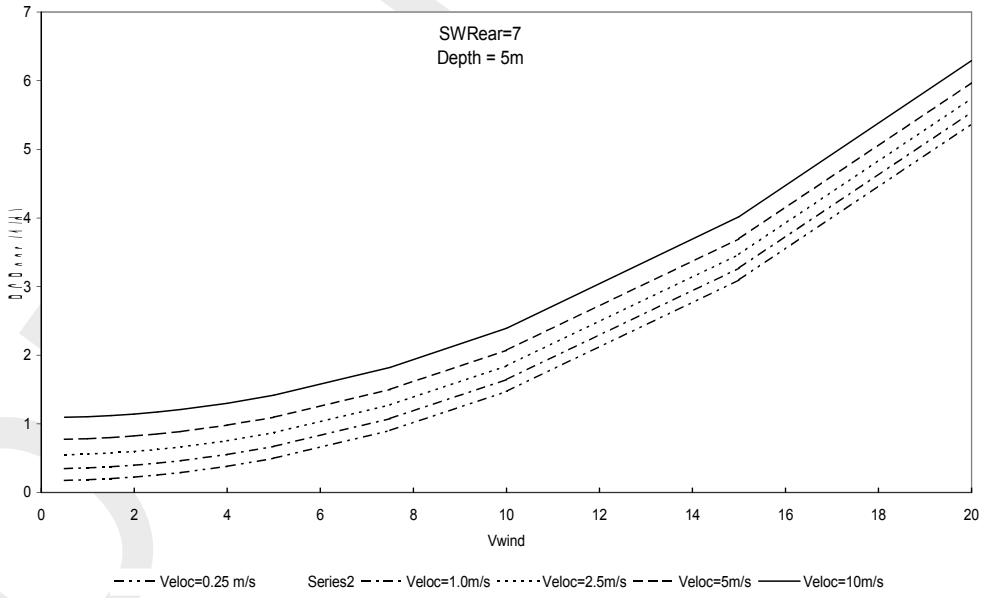


Figure 2.1: *The reaeration rate RCRear (=klrear$_{20}$/H) as a function of water depth, flow velocity and/or wind velocity for various options SWRear for the mass transfer coefficient klrear*

2.2 Dam reaeration, SOBEK only

PROCESS: DAMREAR

Water quality downstream of weirs improves as a result of reaeration. From this interest a lot of research on dam reaeration has been carried out in the United States and England in the sixties. Dam reaeration occurs because of an more intensive contact between air and water as a result of energy loss of the weir. The largest percentage change of the dissolved oxygen concentration occurs at the base of the weir (Gameson, 1957).

In the past reaeration at weirs and dams was described as a function of the difference of water levels up- and downstream of the structure. In formulations that are more commonly applicable other factors are taken into account as well. These are for example: temperature of the water, water quality, discharge over the structure, water depth behind the structure and characteristics of the structure, such as size, shape and construction material.

Implementation

Process damrear has been implemented in such a way, that it only affects the DO-budget of the top water layer. An option for the deficit ratio can be selected by means of input parameter *SWdrear* (= 0/1). The DO saturation concentration required for the process damrear is calculated by an additional process SATUROXY.

The process has been implemented for substance OXY.

Table 2.3 provides the definitions of the parameters occurring in the formulations.

Formulation

The amount of oxygen needed to reach a concentration Cox downstream of the weir is formulated as:

$$Rdrear = \frac{Cox - Cox_{t-1}}{\Delta t} \tag{2.4}$$

with:

$Rdrear$	oxygen reaeration rate as a result of dam reaeration [$gO_2.m^{-3}.d^{-1}$]
Cox	oxygen concentration [$gO_2.m^{-3}$]
Δt	timestep [d]

Almost all publications about dam aeration assume that the upstream oxygen deficit at a weir is partly neutralised as a result of dam aeration. Cox is determined as a function of the saturation concentration, the upstream concentration and the oxygen deficit ratio:

$$Cox = \frac{1}{fdrear}\left(Coxs(fdrear - 1) + Coxup\right) \tag{2.5}$$

with:

$fdraer$	oxygen deficit ratio [$-$]
$Coxs$	oxygen saturation concentration [$gO_2.m^{-3}$]
$Coxup$	oxygen concentration upstream of weir [$gO_2.m^{-3}$]

Dam reaeration is always calculated on the basis of a positive dissolved oxygen concentration, whereas OXY may have negative values. Negative oxygen values equivalents represent reduced substances.

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Notice that the reaeration rate is always calculated on the basis of a positive dissolved oxygen concentration, whereas *OXY* may have negative values. Negative oxygen equivalents represent reduced substances.

There are different options to calculate dam reaeration. Gameson developed a much quoted empirical formulation for the oxygen deficit ratio (*SWdrear* = 0). This formulation does not contain discharge over the structure and water depth behind the structure, while both parameters are both considered to be important. The formulation by Nakasone (*SWdrear* = 1) is a possible alternative which does take both parameters into account (Nakasone, 1975). A hybrid combination of both formulations is also available via *SWdrear* =1 (Stowa, 2002). In the latter case some coefficients get different values.

SWdrear = 0

$$fdrear = 1.0 + 0.38\, a\, b\, \Delta h\, (1 - 0.11\, \Delta h)\, (1 + 0.046\, T) \tag{2.6}$$

with:

a	water quality factor [$-$]
b	characteristic structure [$-$]
Δh	difference of water levels up- and downstream of the structure ($h_{up} - h_{down}$) [m]
h_{up}	water level upstream of structure [m]
h_{down}	water level downstream of structure [m]
T	water temperature [°C]

SWdrear = 1

Hybrid formulation for the oxygen deficit ratio of Gameson and Nakasone. If a and b are zero the oxygen deficit ratio according to Nakasone is calculated.

$$fdrear = 1 + (fdrearn - 1)\, a\, b\, (1 + 0.02(T - 20)) \tag{2.7}$$

$$fdrearn = \exp\left(0.0675\, \Delta h^{1.28}\, \left(\frac{3600\, Q}{L}\right)^{0.62}\, H^{0.439}\right) \tag{2.8}$$

with:

$fdrearn$	oxygen deficit ratio according to Nakasone [$-$]
Q	discharge over structure [$m^3\ s^{-1}$]
L	width of crest structure [m]
H	water depth [m]

The water quality factor is related to the BOD concentration:

$$a = \min\left(1.80, \frac{1.90}{Cbod^{0.44}}\right) \tag{2.9}$$

with:

$Cbod$	biological oxygen demand [$gO_2\ m^{-3}$]

Butts T. A and Evans (1983) studied reaeration at 54 small dams and en weirs in Illinois and determined the dam reaeration coefficient b (characteristic structure) for each structure. The structures could be subdivided into 9 categories with typical values for b (see Table 2.2). The

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b-values that were found vary from 1.05 for a sharp-crested straight slope face to 0.6 for round broad-crested straight slope face.

Table 2.2: *Factor 'b' (characteristic structure) for various structures.*

weir type	**b**
flat broad-crested regular step	0.70
flat broad-crested irregular step	0.80
flat broad-crested vertical face	0.80
flat broad-crested straight slope face	0.90
flat broad-crested curved face	0.75
round broad-crested straight slope face	0.60
sharp-crested straight slope face	1.05
sharp-crested vertical face	0.80
sluice gates with submerged discharge	0.05

Directives for use

- ◇ factor b (structure characteristic) is equal to the discharge coefficient Ce in the module Channel Flow of SOBEK Rural.
- ◇ In order to use the Nakasone formulation the following coefficient values should be used: $SWdRear = 1, Cbod = 1, b = 1/1.8, T = 20.$

Table 2.3: *Definitions of the parameters in the above equations for REAROXY*

Name in formulas[1)]	**Name in input**	**Definition**	**Units**
a	$-$	water quality factor	-
b	$Coefbi$	dam reaeration coefficient of structure i	-
$Cbod$	$CBOD5$	biological oxygen demand	$gO_2.m^{-3}$
Cox $Coxs$ $Coxup$	OXY $SaturOXY$ OXY	concentration of dissolved oxygen saturation conc. dissolved oxygen from saturoxy oxygen concentration upstream of weir	$gO_2.m^{-3}$ $gO_2.m^{-3}$ $gO_2\ m^{-3}$
$fdrear$ $fdrearn$	- -	oxygen deficit ratio oxygen deficit ratio according to Nakasone	- -

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Table 2.3: *Definitions of the parameters in the above equations for REAROXY*

Name in formulas[1)]	**Name in input**	**Definition**	**Units**
h_{up} h_{down}	$WtLvLSti$ $WtLvRSti$	Water level upstream of structure i (according to definition in schematisation) Water level downstream of structure i (according to definition in schematisation)	m m
H	$Depth$	depth of the top water layer	m
L	$Widthsti$	width of crest of structure i	m
Q	$DischSti$	discharge over structure i	m^3 s^{-1}
$Rdrear$	-	oxygen reaeration rate as a result of dam aeration	$gO_2.m^{-3}$ d^{-1}
Δt	$Delt$	timestep	d
T	$Temp$	temperature	°C

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2.3 Saturation concentration of DO

PROCESS: SATUROXY

The reaeration of oxygen proceeds proportional to the difference of the saturation and actual dissolved DO concentrations. The saturation concentration of DO is primarily a function of water temperature and salinity. The air pressure also affects the saturation concentration, but this effect is minor and can be taken into account in the temperature dependency.

The calculation of the saturation concentration has been implemented with two alternative formulations. Such formulations have been described by Weiss (1970), Fair et al. (1968), and Truesdale et al. (1955) and WL | Delft Hydraulics (1978).

Implementation

Process SATUROXY calculates the DO saturation concentration in water at ambient temperature and salinity required for the process REAROXY. The process has been implemented with two options for the formulations of the saturation concentration, that can be selected by means of input parameter *SWSatOxy* (=1, 2).

The process has been implemented for substance OXY.

Table 2.4 provides the definitions of the parameters occurring in the formulations.

Formulation

The saturation concentration (*SaturOxy*) has been formulated as the following functions of the temperature and the salinity.

For SWSatOxy = 1:

$$Coxs = \left(a - b\,T + (c\,T)^2 - (d\,T)^3\right)\ \left(1 - \frac{Ccl}{m}\right)$$

For SWSatOxy = 2:

$$Coxs = \exp\left(a + \frac{b}{T_f} + c\ \ln(T_f) + d\,T_f + SAL\,(m + n\,T_f + o\,T_f^2)\right)\ \frac{32\,000}{22\,400} \tag{2.10}$$

$$T_f = \left(\frac{T + 273}{100}\right) \tag{2.11}$$

with:

a, b, c, d, m, n, o	coefficients with different values for the two formulations
Ccl	chloride concentration [gCl m^{-3}]
$Coxs$	saturation dissolved oxygen concentration [gO_2 m^{-3}]
T	water temperature [°C]
T_f	temperature function [-]

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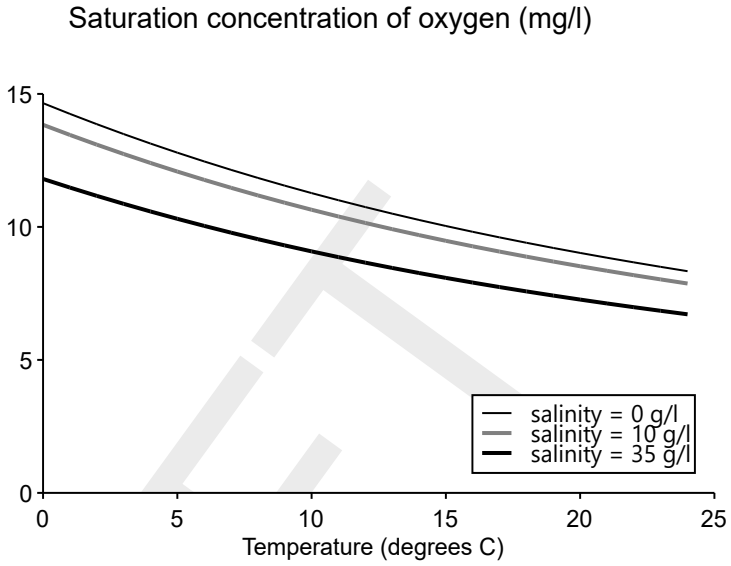

SAL salinity [kg m^{-3}]

The coefficients in both formulations are fixed. The values are presented in the table below.

SWSatOxy	a	b	c	d	m	n	o
1	14.652	0.41022	0.089392	0.042685	10^5	-	-
2	-173.4292	249.6339	143.3483	-21.8492	-0.033096	0.014259	-0.0017

Directives for use

◇ The chloride concentration *Cl* can either be imposed by you or simulated with the model. The salinity can be estimated from the chloride concentration with:

SAL = 1.805 $\times$ *Cl / 1 000*.

Additional references

WL | Delft Hydraulics (1980b)

Table 2.4: *Definitions of the parameters in the equations for SATUROXY*

Name in formulas	Name in input	Definition	Units
Coxs	*SaturOXY*	saturation concentration of oxygen in water	gO_2 m^{-3}
Ccl	*Cl*	chloride concentration	gCl m^{-3}
SAL	*Salinity*	salinity	kg m^{-3}
SWSatOxy	*SWSatOxy*	switch for selection options for saturation equation	-
T	*Temp*	water temperature	°C

T_f	–	temperature function	-

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2.4 Diurnal variation of DO

PROCESS: VAROXY

The phytoplankton models implemented in DELWAQ are subjected to *daily averaged* forcing functions. In particular, this is reflected by the choice of the input parameters for the subsurface light intensity model: the *daily averaged solar radiation* and the *day length*. However, in reality the gross primary production of phytoplankton is constrained to daytime. The same goes for the associated production of oxygen. On the contrary, the *respiration* process consumes oxygen all 24 hours of the day. The combination of gross production and respiration causes a rather strong diurnal variation of the dissolved oxygen concentration (DO). The process VAROXY modifies the daily DO-production by algae in such a way, that it is spread out over the period of daylight (day length) only.

Implementation

Process VAROXY can only be used in combination with the algae module BLOOM. This process produces the net primary production flux *dPrProdOxy* and the respiration flux *fRespTot*. The module D40BLO has the option parameter *SWOxyProd* for activation of the process VAROXY. For *SWOxyProd = 1* process VAROXY will be activated and the respiration flux will be used to calculate the gross production flux distribution over the day length. The respiration flux will be ignored for the DO-budget, when *SWOxyProd* has any other value.

Process VAROXY has been implemented for substance OXY.

Table 2.5 provides the definitions of the parameters occurring in the formulations.

Formulation

The net daily primary production and the respiration are added to obtain the gross production flux:

For SWOxyProd = 1: (diurnal variation)

$$Rgp_a = \frac{Fnp + Frsp}{H}$$

with:

Fnp	net primary production flux [gC m^{-2} d^{-1}]
$Frsp$	respiration flux [gC m^{-2} d^{-1}]
H	depth of the water column [m]
Rgp_a	daily average gross primary production rate [gC m^{-3} d^{-1}]

The distribution of the gross primary production over the day is shown in Figure 2.2. The shape of the production curve depends on day length *DL* and the times t_1 and t_2 which define the period of the maximum production during a day Rgp_{max}. The value of Rgp_{max} is calculated at the constraint that the integral of the production curve over 24 hours equals the daily averaged primary production Rgp_a. This results in:

$$Rgp_{max} = \frac{48 \times Rgp_a}{t_2 - t_1 + (DL \times 24)}$$

with:

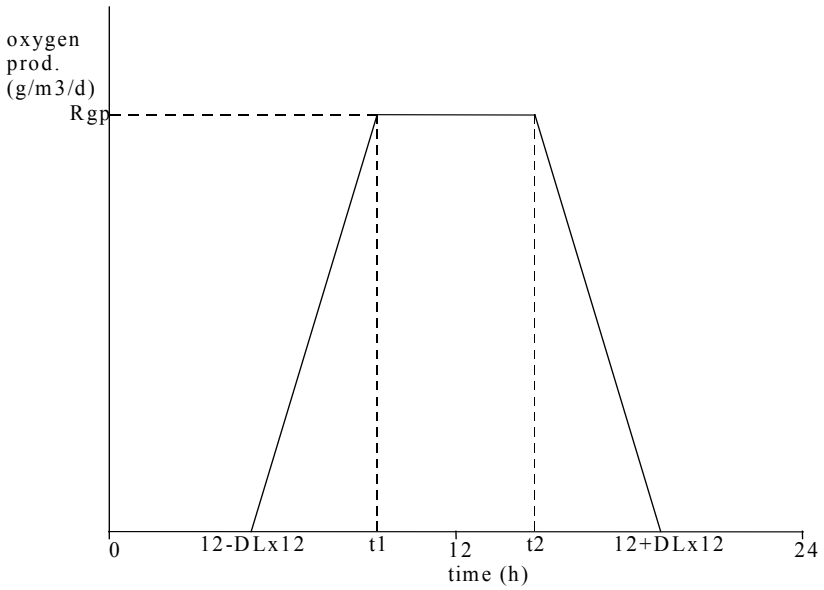

Figure 2.2: *The distribution of gross primary production over a day*

DL	day length, fraction of a day [-]
Rgp_{max}	maximal gross primary production rate during a day [gC m^{-3} d^{-1}]
t_1	time at which the maximal production is reached [h]
t_2	time at which the production starts to fade [h]

The net primary production as a function of the time in a day then follows from:

$$Rnp = \begin{cases} -\dfrac{Frsp}{H} & \text{for } t \leq (12 - 12\ DL) \\ \dfrac{Rgp_{max}}{(t_1 - (12 - 12\ DL))}\ (t - (12 - 12\ DL)) - \dfrac{Frsp}{H} & \text{for } (12 - 12\ DL) < t < t_1 \\ Rpg_{max} - \dfrac{Frsp}{H} & \text{for } t_1 \leq t \leq t_2 \\ Rpg_{max} - \dfrac{Rgp_{max}}{((12 + 12\ DL) - t_2)}\ (t - t_2) - \dfrac{Frsp}{H} & \text{for } t_2 < t < (12 + DL\ 12) \\ -\dfrac{Frsp}{H} & \text{for } t \geq (12 + 12\ DL) \end{cases}$$

with:

Rnp	net primary production (or respiration) rate during a day [gC m^{-3} d^{-1}]
t	actual time in a day [hr]

For SWOxyProd = 0: (no diurnal variation)

$$Rnp = 0.0$$

The conversion from the carbon fluxes of gross production and respiration into oxygen fluxes involves the multiplication of these fluxes with 2.67 gO_2/gC as defined in the stoichiometric matrix for the calculation of mass balances in DELWAQ.

Table 2.5: *Definitions of the parameters in the above equations for VAROXY*

Name in formulas	Name in in/output	Definition	Units
DL	*DayL*	day length, fraction of a day	-
Fnp	*fPPtot*	net primary production flux	gC m^{-2} d^{-1}
$Frsp$	*fResptot*	respiration flux	gC m^{-2} d^{-1}
H	*Depth*	thickness of the computational cell	m
$SWOxyProd$	*SWOxyProd*	switch for the option to activate process VAROXY	-
Rnp	–	net primary production (or respiration) rate during a day	gC m^{-3} d^{-1}
Rgp_a	–	average gross primary production rate during a day	gC m^{-3} d^{-1}
Rgp_{max}	–	maximal gross primary production rate during a day	gC m^{-3} d^{-1}
t	*Itime*	DELWAQ time	scu
t_1	*T1MXPP*	time at which the maximal production is reached	h
t_2	*T2MXPP*	time at which the production starts to fade	h
–	*AuxSys*	ratio between a day and system clock units (86400)	s d^{-1}
–	*Refhour*	time at the start of the simulation	h
t	*Time*	time in a day	h
t_1	*T1MXPP*	time at which the maximal production is reached	h
t_2	*T2MXPP*	time at which the production starts to fade	h

The actual time in a day is derived from system time, the time step and the start time of the simulation.

Directives for use

- ◇ The times of beginning and ending of the maximal primary production period on a day must satisfy the following constraints: $t_2 < (12 + 12\ DL)$ and $t_1 > (12 - 12\ DL)$.
- ◇ The actual time in a day is available as output parameter *ActualTime*.

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2.5 Calculation of daily minimal DO concentration

PROCESS: OXYMIN

The phytoplankton models implemented are subject to *daily averaged* forcing functions. This is reflected in particular by the choice of the input parameters for the subsurface light intensity model: the *daily averaged solar radiation* and the *day length*. However, in reality the gross primary production of phytoplankton and the associated production of oxygen are constrained to daytime. In contrast, *respiration* consumes oxygen all 24 hours of the day. The combination of gross production and respiration can cause a strong diurnal variation of the dissolved oxygen concentration (DO). The process OXYMIN computes the minimal DO-concentration that may occur during the day, when daily averaged forcing is used.

The actual minimal DO-concentration can be calculated with a mass balance on the basis of actual process rates. When dealing with daily average values, one has to settle for an estimate. Such an estimate can be made, either by neglecting all other processes but primary production and respiration, or by assuming that these other processes (mainly reaeration) exactly compensate for the DO-concentration change resulting from gross production and respiration on a daily basis. The truth lies in between these extremes. Whether option 1 or option 2 results in the lowest DO-minimum depends on production being larger or smaller than respiration. Since one does not want to overestimate DO-minima, the various options for estimation need to be combined in such a way that underestimation is prevented.

Implementation

Process OXYMIN can only be used in combination with the algae module DYNAMO, consisting of various production, respiration and mortality processes. The module delivers the net primary production fluxes and the respiration fluxes for two algae species (diatoms and non-diatoms, referred to as 'greens').

Process OXYMIN makes use of the substance OXY and calculates the minimum DO concentration that occurs during a 24-hour day (output parameter *OXYMIN*).

Table 2.6 provides the definitions of the parameters occurring in the formulations.

Formulation

When neglecting all processes but gross primary production and respiration, the minimal dissolved oxygen concentration in a day follows from half the DO-decrease during the night:

$$Cox_{min1} = Cox - 0.5 \times 2.67 \times Rrsp \times (1 - DL)$$

$$Rrsp = \sum_{i=1}^{2} (krsp_i \times Calg_i)$$

with:

$Calg$	algae biomass [gC m^{-3}]
Cox	average dissolved oxygen concentration [gO_2 m^{-3}]
Cox_{min1}	minimal dissolved oxygen concentration in a day for estimation method 1 [gO_2 m^{-3}]
DL	day length, fraction of a day [-]
$krsp$	algae respiration rate constant [d^{-1}]
$Rrsp$	total algae respiration rate [gC m^{-3} d^{-1}]

Table 2.6: *Definition of the parameters in the equations and the mode input for OXYMIN*

Name in formulas	Name in in/output	Definition	Units
$Calg_1$	*Green*	biomass of Green algae	gC m^{-3}
$Calg_2$	*Diat*	biomass of Diatoms	gC m^{-3}
Cox	*OXY*	average dissolved oxygen concentration	gO_2 m^{-3}
Cox_{min}	*OXYMIN*	minimal dissolved oxygen concentration in a day	gO_2 m^{-3}
DL	*DayL*	day length, fraction of a day	-
kgp_1	*RcGroGreen*	gross primary prod. rate constant of Green algae	d^{-1}
kgp_2	*RcGroDiat*	gross primary prod. rate constant of Diatoms	d^{-1}
$krsp_1$	*RcRespGreen*	algae respiration rate constant of Green algae	d^{-1}
$krsp_2$	*RcRespDiat*	algae respiration rate constant of Diatoms	d^{-1}
Rgp	–	total gross primary production rate	gC m^{-3} d^{-1}
$Rrsp$	–	total algae respiration rate	gC m^{-3} d^{-1}

i index for algae species (1-2)

When assuming that the other processes, reaeration in particular, compensate net production on a daily basis, the minimal dissolved oxygen concentration in a day follows from half the maximal DO-difference between day and night:

$$Cox_{min2} = Cox - 0.5 \times 2.67 \times Rgp \times (1 - DL)$$

$$Rgp = \sum_{i=1}^{2} (kgp_i \times Calg_i)$$

with:

Cox_{min2} minimal dissolved oxygen concentration in a day for estimation method 2 [gO_2 m^{-3}]
kgp gross primary production rate constant [d^{-1}]
Rgp total net primary production rate [gC m^{-3} d^{-1}]

In order to avoid overestimation of the DO-minimum, the minimal value is of both estimates is used in the model:

$$Cox_{min} = \min(Cox_{min1}, Cox_{min2})$$

Directives for use

◇ The process OXYMIN is used for presentation purposes only. The concentrations of the substance *OXY* and the parameter *OXYMIN* are both available for presentations.

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Table 2.7: *Definitions of the parameters in the above equations for POSOXY*

Name in formulas	Name in in/output	Definition	Units
Cox	*OXY*	equivalent dissolved oxygen concentration	$gO_2\ m^{-3}$
DO	–	positive dissolved oxygen concentration	$gO_2\ m^{-3}$

2.6 Calculation of actual DO concentration

PROCESS: POSOXY

DELWAQ allows negative dissolved oxygen concentrations (DO). Decomposition of dead organic matter continues, when DO has become depleted using other substances such as nitrate and sulfate as electron donors. A correct oxygen balance requires that these reduced substances produced at the anaerobic decomposition are taken into account. However, as not all reduced substances (for example sulfate) are included in DELWAQ, the reduced substances are includeed instead as negative oxygen equivalents. As it may be undesirable to show negative concentrations in the presentation of DO model results, process POSOXY determines the actual DO concentration, effectively setting negative concentrations to zero.

Implementation

Process POSOXY makes use of the substance OXY and generates the output parameter DO.

Table 2.7 provides the definitions of the parameters occurring in the formulations.

Formulation

The actual dissolved oxygen concentration follows from:

$$DO = \max\left(Cox, 0.0\right)$$

with:

DO	actual dissolved oxygen concentration [$gO_2\ m^{-3}$]
Cox	equivalent dissolved oxygen concentration [$gO_2\ m^{-3}$]

Directives for use

◇ The process POSOXY is used for presentation purposes only. The concentration of the substance OXY and the parameter DO are both available for output.

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Table 2.8: *Typical values for oxygen demanding waste waters (values in [mgO_2/l])*

Source	CBOD5	CBODu	NBODu	COD
Municipal waste (untreated)	100-400	220 (120-580)	220	
Combined sewer overflow (untreated)	170 (40-500)	220	-	
Separate urban runoff (untreated)	19 (2-80)	-	-	
Background natural water (excl. algae and detritus)	0			2-3
Background of natural water (incl. algae and detritus)	2-3			10

Data from Thomann and Mueller (1987).

Explanation: CBOD5 = 5-day CBOD; CBODu = ultimate CBOD

2.7 BOD, COD and SOD decomposition

PROCESS: BODCOD

Organic matter in natural waters includes a great variety of organic compounds usually present in minute concentrations, many of which elude direct isolation and identification. Collective parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total organic carbon (TOC) or dissolved organic carbon (DOC), are therefore often used to estimate the quantity of organic matter. Although often used they lack physiological meaning. The rates of microbial growth and the overall use of organic matter in multi-substrate media depend in a complex way on the activities of a great variety of different enzymes and on various mechanisms by which these activities are interrelated.

Discharges of wastes (municipal or industrial) and sewer overflows are principal inputs of oxygen demanding wastes. These discharges cause a chemical oxygen demand (COD), a carbonaceous bio-chemical oxygen demand (CBOD) and a nitrogenous biochemical oxygen demand (NBOD). CBOD represents the oxygen demanding equivalent of the complex carbonaceous material present in waste. Typical values for different waters are presented in Table 2.8.

2.7.1 Chemical oxygen demand

The chemical oxygen demand is a test that determines the organic matter content both in wastewater and natural waters. The oxygen equivalent of the organic matter that can be oxidized is measured using a strong chemical oxidizing agent in an acidic medium. Two chemicals are used: potassium dichromate (referred to as Cr-method) and potassium permanganate (referred to as Mn-method). The efficiency of the Cr-method is approximately 90 % whereas the Mn-method only yields around 50 % of the oxidizable carbon. COD cannot be measured accurately in samples containing more than 2 g l^{-1} Cl. There is no fixed relation between the results obtained with the Mn and Cr-method.

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2.7.2 Biochemical oxygen demand

Biochemical oxygen demand is the sum of carbonaceous and nitrogenous oxygen demand. This oxygen demand is determined by standard methods that measure the oxygen consumption of a filtered sample during a laboratory incubation within a period of time (usually 5-days at 20 °C in the dark). To obtain meaningful results the samples must be diluted in such a way that adequate nutrients and oxygen will be available during the incubation (Standard methods: APHA (1989)). A typical oxygen demand curve is presented in Figure 2.3. The CBOD is usually exerted first because of the time lag in the growth of the autotrophic nitrifying bacteria.

The heterotrophic carbonaceous oxidizing organisms are usually abundantly present in natural and sewage systems. The nitrifying bacteria convert ammonia to nitrate, a reaction that demands a lot of oxygen. These bacteria can be eliminated by pre-treatment with inhibitory agents, so that only the CBOD is measured. NBOD can then be obtained by the difference between BOD measurements in treated and untreated samples. Degradation of organic matter during BOD measurements is a complex reaction of sequential oxidation steps which finally results in CO_2 and H_2O. Simplification to first order kinetics is used frequently. Fresh organic matter is more susceptible to biochemical oxidation than older material. This preferential digestion causes residual material after treatment (either natural or anthropogenic) to be more resistant to further treatment (biochemical oxidation).

Figure 2.4 illustrates the relation between the amount of oxidizable carbonaceous material [gC m^{-3}] and the amount of oxygen consumed in the stabilisation of this organic material as a function of time. Note that it is assumed that 2.67 mg O_2 are used to oxidize 1 mg of carbon. The ratio between CBOD5 and CBODu depends on the decay rate of the organic material: $BOD5/BODu = (1 - \exp(-5 \times RcBodC))$. The higher the decay rate the more the ratio will reach unity. From the $BOD5/BODu$ ratio the decay rate (called bottle-decay rate) can be derived. The decomposition rate in rivers differs from the decomposition rate in laboratory bottles (Hydroscience, 1971 referenced within Thomann and Mueller (1987)). But information is scarce. Theoretically one would expect the decay rate to depend on the degree of treatment, significant trends were however not found (Hydroqual, 1983 referenced within Thomann and Mueller (1987)). $BOD5/BODu$ ratios reported in this study range from 0.8 for untreated to 0.3 for activated sludge.

2.7.3 Measurements and relations

Conversion of total BOD (TBOD) to CBOD can be tricky when nitrifying bacteria are present. During decomposition of organic material (proteins, urea) nitrogen can be liberated and subsequently be oxidized. Total BOD5 is often equal to CBOD5, due to the timelag of nitrifying bacteria: reproduction time of nitrifying bacteria is low (one day) compared to that of heterotrophic bacteria (hours). Nitrifying bacteria are present in soil but also in wastewaters and therefore in natural waters receiving wastewater. Industrial discharges (e.g. paper mills) are usually deficient in any nitrogen forms in which case TBOD can be used as CBOD.

The temperature dependence of bacteria mediated reactions is considerable. An often used value for the temperature coefficient is 1.04. For low temperatures however (below 20 °C) higher values up to 1.13 are suggested by Schroepfer et al. (1964) (referenced within Thomann and Mueller (1987)).

Empirical relations between water depth and or flow and the decay rate of BODC exist, for instance:

$$rate(20°C) = 0.3\ Depth^{-0.434} \quad [d^{-1}] \text{ for depths } < 2.5\ m. \tag{2.12}$$

For deeper water bodies the authors assume 0.33 m d^{-1}.

2.7.4 Accuracy

The BOD-test is a test in which much can go wrong: adequate bacterial seed is required, no toxic wastes are allowed, nitrifying bacteria should be considered and the dilution of the sample should be adequate. There is no standard against which the accuracy of the BOD-test can be measured. Inter laboratory precision on a glucose-glutamic acid mixture gave a standard deviation of 15 % (average level 175 mg l^{-1}). At lower values of BOD the error strongly increases for BOD values below 10 mg l^{-1}.

Implementation

All substances in this chapter are expressed as oxygen demand, so no direct connection with the carbon-cycle of phytoplankton is considered. DELWAQ considers two pools of CBOD with different decay rates (0.3 and 0.15 d^{-1}). These two pools can e.g. be used to keep track of waste from two different sources (with different treatment before entering the surface water). For NBOD and COD, one pool for each is implemented. Each pool (CBOD, CBOD_2, NBOD and COD) is characterized by a rate constant for decay, a coefficient for temperature dependence and a dependency of the ambient oxygen concentration.

Because for each pool different types of measurements exist, DELWAQ accepts two different measurements for each pool. For the biochemical pools CBOD, CBOD_2 and NBOD the standard measurement after 5 days as well as the measurement after ultimate time are accepted. For the chemical pool COD the Cr-method as well as the Mn-method are accepted. Thus waste loads measured by different methods do not have to be converted to one standard before they are entered into DELWAQ.

DELWAQ keeps track of the decay of each individual substance accepted by the system (CBOD5, CBODu, CBOD5_2, CBODu_2, COD_Cr, COD_Mn. NBOD5 and NBODu). The effects that individual decay fluxes cause on the oxygen balance are considered for the group as a whole (only one oxygen consumption flux, dOXYCODBOD, is calculated). The same aggregation is applied to the sediment (a description is given in documentation for the process Sediment Oxygen Demand, sod). For aggregation purposes, the biochemical substances are added to BOD5 and the chemical substances to COD (both parameters available for output). When using default settings (see also the Directives for use) the oxygen demand of detritus and part of the algae are added to these BOD and COD parameters (assuming that measurements of BOD and COD have been made in unfiltered samples and did therefore include the effect of algae and detritus).

You should be careful converting measurements to DELWAQ substances. There is a danger of 'double counting' the effect on the oxygen balance in the following situations:

- ◇ when one measurement of carbonaceous BOD is divided over the two BOD pools (CBOD and CBOD_2) the sum should equal 100% of the original measurement;
- ◇ when different measurements of one wasteload are added, they both affect the oxygen balance (e.g. when both COD_Cr and COD_Mn are measured, only one should be supplied as a wasteload). Measurements of BOD and COD of one wasteload may be added simultaneously; only one (chosen by you) will affect the oxygen balance;
- ◇ when measurements of oxygen demand include algae and detritus and simultaneously algae are modelled, their contribution to the oxygen demand is added to the BOD and COD pools.

The decay of biochemical as well as chemical oxygen demanding substances are modelled as

a first order process. If the water temperature drops below a critical value the decay is reduced to zero. The first order flux is corrected for water temperature and oxygen concentration. Below a critical oxygen concentration the oxygen function becomes equal to a user-defined level (default 0.3) while for above optimal oxygen concentration these functions have a value of 1.0. Linear interpolation of the oxygen functions is the default for intermediate oxygen concentrations. A higher order interpolation for intermediate values may also be applied.

One option is implemented for the calculation of the first order rate constant (correction by means of an 'aging function'). In this option the rate constant is made a function of the ratio between COD and BOD. This option is based on the fact that the COD/BOD ratio increases with the age of the decaying material. Of course both COD and BOD must be supplied for all boundaries and wasteloads to use this option in a meaningful way.

This process is implemented for CBOD5, CBODu, CBOD5_2, CBODu_2, COD_Cr, COD_Mn, NBOD5 and NBODu.

Formulation

Substance aggregation:

$$\begin{aligned}
BODu &= CBODu + CBODu_2 + CBOD5 \times \left(1 - \mathsf{e}^{-5 \times RcBOD}\right)^{-1} + \\
&\quad + CBOD5_2 \times \left(1 - \mathsf{e}^{-5 \times RcBOD_2}\right)^{-1} \\
BOD5 &= CBODu \times \left(1 - \mathsf{e}^{-5 \times RcBOD}\right) + CBODu_2 \times \left(1 - \mathsf{e}^{-5 \times RcBOD_2}\right) + \\
&\quad + CBOD5 + CBOD5_2 \\
COD &= \frac{COD_Cr}{EffCOD_Cr} + \frac{COD_Mn}{EffCOD_Mn} \\
NBOD &= NBODu + NBOD5 \times \left(1 - \mathsf{e}^{-5 \times RcBODN}\right)^{-1} \\
BODu_PHYT &= PHYT \times AlgFrBOD \times OXCCF \\
BOD5_PHYT &= BODu_PHYT \times BOD5/uPHYT \\
BODu_POC &= POC \times POCFrBOD \times OXCCF \\
BOD5_POC &= BODu_POC \times BOD5/\inf PO \\
BOD5 &= BOD5 + BOD5_POC + BOD5_PHYT \\
BODu &= BODu + BODu_POC + BODu_PHYT
\end{aligned}$$

Oxygen function for all biological oxygen demand:

$$\begin{aligned}
OXY &= \max(OXY, 0) \\
O2FuncBOD &= 1
\end{aligned}$$

for $(OXY) \geq OOXBOD$ then

$$O2FuncBOD = CFLBOD$$

for $(OXY) \leq COXBOD$ then

$$O2FuncBOD = (1 - CFLBOD) \times \left(\frac{(OXY) - COXBOD}{OOXBOD - COXBOD}\right)^{10^{CurvBOD}} + CFLBOD$$

Functions for calculation of rate constant ('aging function'):

$$AgeIndx = \frac{COD}{BOD5} \tag{2.13}$$

for $AgeIndx \leq LAgeIndx$:

$$AgeFun = UAgeFun \tag{2.14}$$

for $LAge < AgeIndx < LAgeIndx$:

$$AgeFun = (UAgeFun - LAgeFun) \times \exp\left(-\left(\frac{AgeIndx - LAgeIndx}{UAgeIndx}\right)^2\right) + LAgeFun \tag{2.15}$$

for $AgeIndx \geq LAgeIndx$:

$$AgeFun = LAgeFun \tag{2.16}$$

Decay fluxes:

$$\begin{aligned}
dCBOD5 &= RcBOD \times (CBOD5) \times TcBOD^{Temp-20} \times O2FuncBOD \times AgeFun \\
dCBODu &= RcBOD \times (CBODu) \times TcBOD^{Temp-20} \times O2FuncBOD \times AgeFun \\
dNBOD5 &= RcBODN \times (NBOD5) \times TcBOD^{Temp-20} \times O2FuncBOD \times AgeFun \\
dNBODu &= RcBODN \times (NBODu) \times TcBOD^{Temp-20} \times OFuncBOD \times AgeFun \\
dCBOD5_2 &= RcBOD_2 \times (CBOD5_2) \times TcBOD_2^{Temp-20} \times O2FuncBOD \times AgeFun \\
dCBODu_2 &= RcBOD_2 \times (CBODu_2) \times TcBOD_2^{Temp-20} \times O2FuncBOD \times AgeFun \\
dCOD_Cr &= RcCOD \times (COD_Cr) \times TcCOD^{Temp-20} \\
dCOD_Mn &= RcCOD \times (COD_Mn) \times TcCOD^{Temp-20}
\end{aligned}$$

Oxygen demand:

SWOxyDem = 0: BOD determining (default)

$$dOxyBODCOD = dCBOD5 + dCBOD5_2 + dCBODu + dCBODu_2 + dNBOD5 + dNBODu$$

SWOxyDem = 1: COD determining (option)

$$dOxyBODCOD = dCOD_Cr + dCOD_Mn$$

SWOxyDem = 2: BOD $\wedge$ COD determining (option)

$$\begin{aligned}
dOxyBODCOD = {} & dBOD5 + dCBOD5_2 + dCBODu + dCBODu_2 + \\
& + dNBOD5 + dNBODu + dCOD_Cr + dCOD_Mn
\end{aligned}$$

where:

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$CBOD5$	carbonaceous BOD (first pool) at 5 days [$gO_2\ m^{-3}$]
$CBOD5_2$	carbonaceous BOD (second pool) at 5 days [$gO_2\ m^{-3}$]
$CBODu$	carbonaceous BOD (first pool) ultimate [$gO_2\ m^{-3}$]
$CBODu_2$	carbonaceous BOD (second pool) ultimate [$gO_2\ m^{-3}$]
$AgeFun$	scaling function for decay rates [-]
$AgeIndx$	ratio of CBOD5 and COD [-]
$PHYT$	total phytoplankton concentration [$gC\ m^{-3}\ d^{-1}$]
$AlgFrBOD$	fraction of algae that contribute to BOD [-]
$BODu_PHYT$	calculated carbonaceous BOD at ultimate from PHYT [$gO_2\ m^{-3}$]
$BOD5/uPhyt$	ratio BOD5 to BOD_ultimate for PHYT [-]
$BOD5_PHYT$	calculated carbonaceous BOD at 5 days from PHYT [$gO_2\ m^{-3}$]
POC	total particulate organic carbon concentration [$gC\ m^{-3}\ d^{-1}$]
$POCFrBOD$	fraction of POC that contribute to BOD [-]
$BODu_POC$	calculated carbonaceous BOD at ultimate from POC [$gO_2\ m^{-3}$]
$BOD5/infPO$	ratio BOD5 to BOD_ultimate for POC [-]
$BOD5_POC$	calculated carbonaceous BOD at 5 days from POC [$gO_2\ m^{-3}$]
$BOD5$	calculated carbonaceous BOD at 5 days (incl. PHYT and POC) [$gO_2\ m^{-3}$]
$BODu$	calculated carbonaceous BOD at ultimate (incl. PHYT and POC) [$gO_2\ m^{-3}$]
COD	calculated chemical oxygen demand days [$gO_2\ m^{-3}$]
COD_Cr	COD concentration by the Cr-method [$gO_2\ m^{-3}$]
COD_Mn	COD concentration by the Mn-method [$gO_2\ m^{-3}$]
$COXBOD$	critical oxygen concentration: [$g\ m^{-3}$]
$CFLBOD$	value of the oxygen function for oxygen levels below the critical oxygen concentration [-]
$CurvBOD$	factor that determines the curvature [-] between COXBOD and OOXBOD (-1 $<$ CurvBOD $<$ 0)
$dCBOD5$	decay flux of CBOD5 [$gO_2\ m^{-3}\ d^{-1}$]
$dCBOD5_2$	decay flux of CBOD5_2 [$gO_2\ m^{-3}\ d^{-1}$]
$dCOD_Cr$	decay flux of COD_Cr [$gO_2\ m^{-3}\ d^{-1}$]
$dCBODu$	decay flux of CBODu [$gO_2\ m^{-3}\ d^{-1}$]
$dCBODu_2$	decay flux of CBODu_2 [$gO_2\ m^{-3}\ d^{-1}$]
$dCOD_Mn$	decay flux of COD_Mn [$gO_2\ m^{-3}\ d^{-1}$]
$dNBOD5$	decay flux of NBOD5 [$gO_2\ m^{-3}\ d^{-1}$]
$dNBODu$	decay flux of NBODu [$gO_2\ m^{-3}\ d^{-1}$]
$dOxyBODCOD$	oxygen consumption flux of BOD and COD species [$gO_2\ m^{-3}\ d^{-1}$]
$EffCOD_Cr$	efficiency of the Cr_method [-]
$EffCOD_Mn$	efficiency of the Mn_method [-]
$LAgeFun$	lower value of age function [-]
$LAgeIndx$	lower value of age index [-]
$NBOD$	calculated nitrogenous BOD at ultimate [$gO_2\ m^{-3}$]
$NBOD5$	nitrogenous BOD after 5 days [$gO_2\ m^{-3}$]
$NBODu$	nitrogenous BOD ultimate [$gO_2\ m^{-3}$]
$O2Func$	oxygen function for decay of CBOD [-]
$OXCCF$	oxygen to carbon ratio
$OOXBOD$	optimum oxygen concentration: above this value the oxygen function becomes 1.0 [$gO_2\ m^{-3}$]
OXY	oxygen concentration [$gO_2\ m^{-3}$]
$RcBOD$	reaction rate BOD (first pool) at 20 °C [d^{-1}]
$RcBOD_2$	reaction rate BOD_2 (second pool) at 20 °C [d^{-1}]
$RcBODN$	reaction rate BODN (second pool) at 20 °C [d^{-1}]
$RcCOD$	reaction rate COD (first pool) at 20 °C [d^{-1}]
$SWOxyDem$	switch that determines the oxygen consuming substance (0: BOD;

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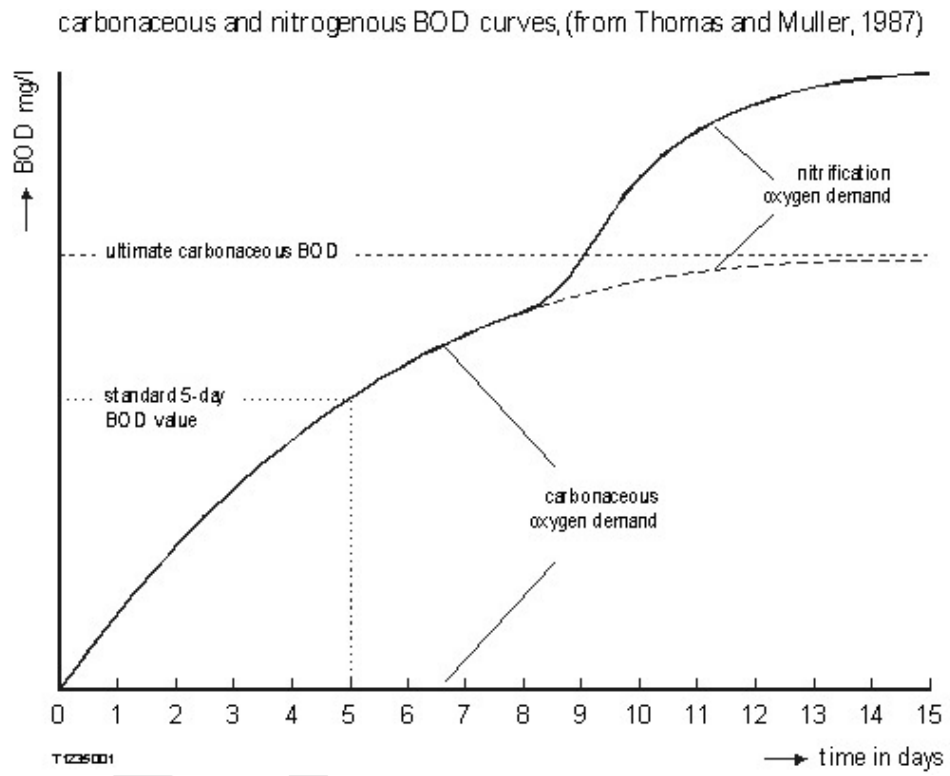

Figure 2.3: *A typical oxygen demand curve*

	1: COD; 2: COD+BOD) [-]
$TcBOD$	temperature coefficient BOD [-]
$TcBOD_2$	temperature coefficient BOD (second pool)[-]
$TcCOD$	temperature coefficient COD [-]
$Temp$	water temperature [°C]
$UAgeFun$	upper value of age function [-]
$UAgeIndx$	upper value of age index [-]

Directives for use

- ◇ To change the aging function from its default value (1.0) to the shape presented in Figure 2.6, change the value LAgeFun to 0.15.
- ◇ Disable the contribution of algae and detritus when filtered measurements of BOD are used as input. An easy way is to set AlgFRBOD and POCFrBOD to 0.
- ◇ The optimal oxygen concentration must be higher than the critical oxygen concentration (see Figure 2.5).
- ◇ By choosing a low (or negative) value for the optimal oxygen concentration, the oxygen function will have a value of 1.0 and thus not hamper the first order flux.
- ◇ By choosing a positive value for the minimum oxygen function level the oxygen function can have a user-defined value at oxygen concentrations below the critical oxygen concentration. This results in mineralisation of BODC when no oxygen is present (note that DELWAQ allows a negative oxygen concentration).
- ◇ The aging function (AgeFun) has a default value of 1.0. Adjust the value of LAgeFun to get functions as pictured in Figure 2.6.

Additional references

Metcalf and Eddy (1991), Stumm and Morgan (1987)

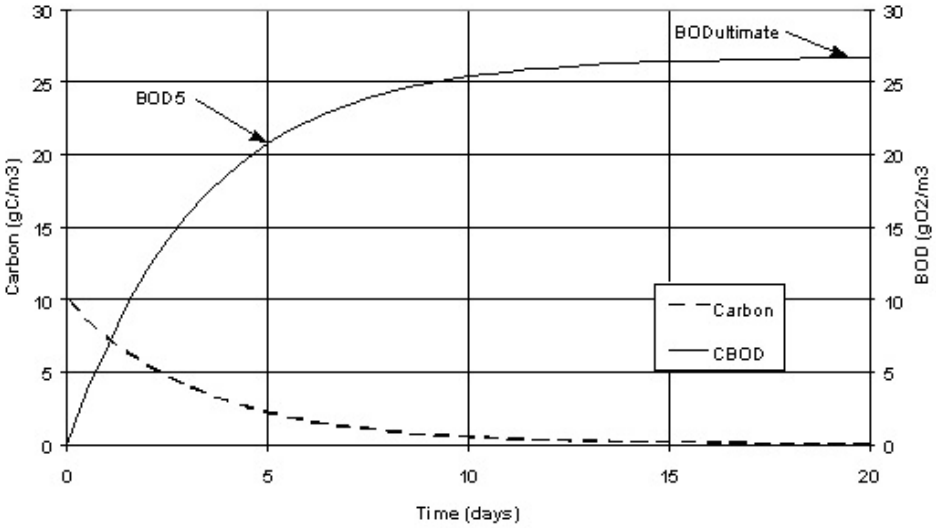

Figure 2.4: *The relation between the amount of oxidizable carbonaceous material [mgC/l], the amount of oxygen consumed in the stabilisation of this organic material after 5 days and after ultimate time*

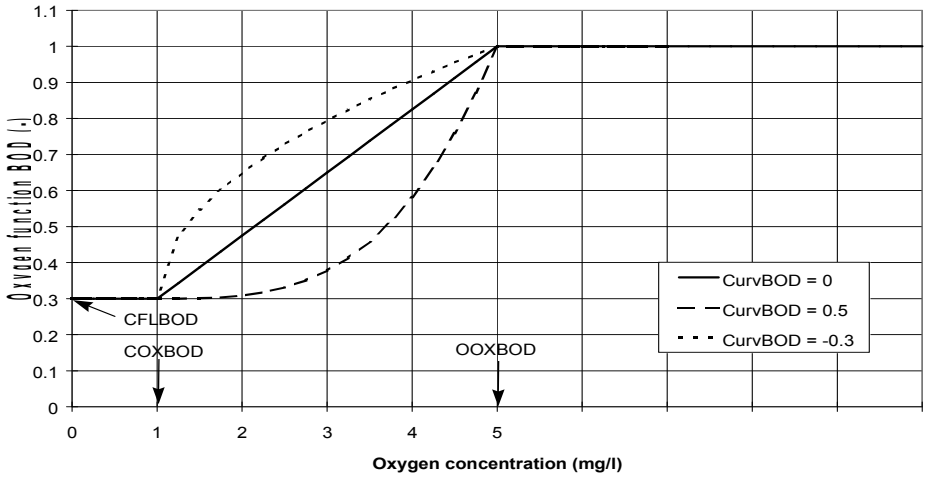

Figure 2.5: *Default and optional oxygen functions for decay of CBOD (O2FuncBOD)*

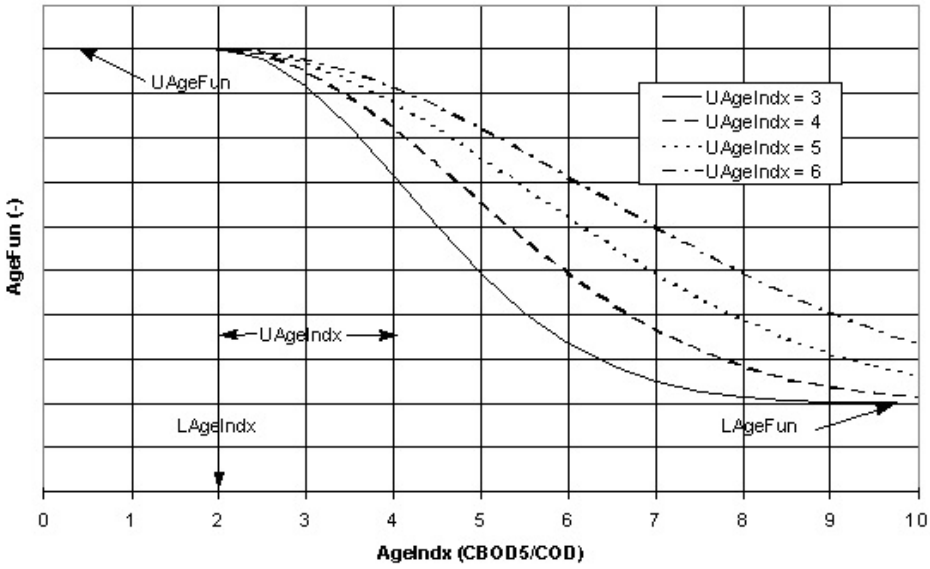

Figure 2.6: *Optional function for the calculation of the first order rate constant for BOD and NBOD*

2.8 Sediment oxygen demand

PROCESS: SEDOXYDEM

This process scales a user-defined sediment oxygen demand flux fSOD [gO_2 m^{-2} d^{-1}] to the dimensions required by DELWAQ. This parameter represents the sediment oxygen demand, as measured in the field. It is also possible to model a model substance SOD [gO_2], which equals the sum of BOD and COD components that accumulate in the sediment due to sedimentation. SOD represents the potential oxygen demand by BOD and COD components in the sediment. The actual flux is calculated according to the equations listed below.

Note that sediment oxygen demand is additional to the oxygen consumption caused by the oxidation of organic matter in the sediment (decay of substances DetCS1, DetCS2, OOCS1, OOCS2).

DELWAQ assumes that all mineralisation processes in the sediment lead to an instantaneous consumption of oxygen in the water column. In reality, mineralisation only causes a direct depletion of oxygen in the aerobic top layer of the sediment. The oxygen penetration depth in sediments is usually a few millimetres, or less.

Below the aerobic zone, reducing components, such as methane and hydrogen sulfide are formed. These components will be transported upwards by diffusion. In the aerobic zone, these components will react rapidly (instantaneously in the model) with oxygen. However, at relatively high mineralisation rates a part of the methane may disappear from the water column as gas bubbles, and not contribute to the sediment oxygen demand.

It is possible to introduce a methane-bubble correction term in DELWAQ, by specifying the appropriate value of constant (SwCH4bub) in the model input. The correction term accounts for the fraction of mineralized organic matter in the sediment that disappears as methane bubbles. The correction term is calculated by an algorithm, based on Di Toro et al. (1990).

Implementation

The process is implemented for DELWAQ substances oxygen (OXY) and sediment oxygen demand (SOD).

Formulations

If *SwCH4bub* $\neq 1$:

$$dSOD = \left(\frac{fSOD}{depth} + \frac{RcSOD \times TcSOD^{Temp-20} \times SOD}{Volume} \right) \times O2func$$

$$O2func = \begin{cases} 0 & \text{if } OXY < COXSOD \\ \frac{OXY - COXSOD}{OOXSOD - COXSOD} & \\ 1 & \text{if } OXY > OOXSOD \end{cases}$$

$$dOxSOD = dSOD$$

where

$fSOD$	user-specified sediment oxygen demand [gO_2 m^{-2} d^{-1}]
SOD	BOD/COD components, accumulated in sediment [gO_2]

$RcSOD$	decay rate of SOD in sediment [d^{-1}]
$TcSOD$	temperature coefficient SOD decay [-]
$depth$	depth of a DELWAQ segment [m]
$Volume$	volume of a DELWAQ segment [m^3]
$dSOD$	decay of SOD (DELWAQ flux) [gO_2 m^{-3} d^{-1}]
$dOxSOD$	oxygen consumption (DELWAQ flux) [gO_2 m^{-3} d^{-1}]
$O2func$	oxygen function for decay of SOD [-]
OXY	oxygen concentration in surface water [gO_2 m^{-3}]
$COXSOD$	critical oxygen concentration for SOD decay [gO_2 m^{-3}]
$OOXSOD$	optimal oxygen concentration for SOD decay [gO_2 m^{-3}]

If SwCH4bub = 1:

DELWAQ treats the methane bubble module as a black box. Reference is made to DiToro et al. (1990) for theoretical backgrounds on this algorithm. As well the oxygen demand by SOD (if modelled) as the oxygen consumption through the mineralisation of DetC and OOC in the sediment are corrected. The latter equals:

$$dOxMinSed = 2.67 \times (dMinDetCS1 + dMinDetCS2 + dMinOOCS1 + dMinOOCS2)$$

where:

$dOxMinSed$	oxygen consumption by mineralisation of DetC and OOC in sediment [gO_2 m^{-3} d^{-1}]
$dMinDetCS1$	mineralisation of DetC in sediment layer 1 [gC m^{-3} d^{-1}]
$dMinDetCS2$	mineralisation of DetC in sediment layer 2 [gC m^{-3} d^{-1}]
$dMinOOCCS1$	mineralisation of OOC in sediment layer 1 [gC m^{-3} d^{-1}]
$dMinOOCCS2$	mineralisation of OOC in sediment layer 2 [gC m^{-3} d^{-1}]

The methane module computes the flux of methane, escaping from the water column to the atmosphere. The flux is a function of $dSOD + dOxMinSed$.

$FlCH4$	methane bubble flux [gO_2 m^{-2} d^{-1}]

Additional output parameter:

$dCH4$	bubble flux expressed in DELWAQ units ($= FlCH4/depth$) [gO_2 m^{-3} d^{-1}]

Also the oxygen consumption by the sediment (*fSOD**) is computed by the algorithm, *fSOD** includes *dOxMinSed*! Because the contribution of *dOxMinSed* to the mass balance of oxygen is accounted for already by the mineralisation processes it has to be substracted from the sediment oxygen demand flux. A part of the methane does not escape to the atmosphere, but dissolves in the water column (*DifCH4bub, DifCH4dis*) where it is oxidized rapidly, causing no additional oxygen consumption.

The resulting DELWAQ flux for oxygen equals:

$$dOxSOD = \frac{fSOD^* + DifCH4bub + DifCH4dis}{Depth} - dOxMinSed$$

where:

$fSOD^*$	calculated total oxygen consumption in sediment [gO_2 m^{-2} d^{-1}]
$DifCH4bub$	oxygen consumption by CH_4 dissolving from bubbles [gO_2 m^{-2} d^{-1}]
$DifCH4dis$	oxygen consumption by CH_4 diffusing from sediment towards water column [gO_2 m^{-2} d^{-1}]

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Remarks:

- ◇ The methane bubble formulation was developed for a single layer water column (1D, 2DH). If it is used in a multi-layer application (1DV, 2DV, 3D) an error is introduced because *DifCH4bub* is entirely assigned to the bottom layer in stead of the total water column. This means an overestimation of the oxygen consumption in the bottom layer. Still, *FlCH4* will be computed correctly since the total depth (*TotalDepth*) is used in the methane bubble module.
- ◇ Field measurements of SOD represent the actual oxygen consumption of the sediment, and should not be corrected for methane bubble formation. Hence, do not use *fSOD* in combination with the methane bubble correction.
- ◇ The (escaping) methane bubble production *dCH4* is a fraction of the mineralisation of SOD + the mineralisation of DetC and OOC. It is possible that *dCH4* exceeds *dSOD*, for instance when you want to correct the oxygen consumption by DetC and OOC in the sediment, but does not want to use *SOD*.
- ◇ If *dCH4* $>$ *dSOD*, *dOxSod* will become negative, which means that it becomes a positive contribution to the mass balance of oxygen. In that case, *dOxSod* acts as a correction term for the oxygen consumption by DetC and/or OOC in the sediment.

Directives for use

- ◇ The constant *SwCH4bub* must be specified in the model input if you want to use the SOD module.
- ◇ If organic carbon in the sediment is modelled (DetCS1, OOCS1) oxygen from the water column is consumed during mineralisation. Take this sediment oxygen demand into account when using substance SOD.
- ◇ If switched on, the methane-bubble correction will also compensate for the oxygen consumption by DetCS1 etc.
- ◇ Usually, the DELWAQ substance SOD is only applied in studies which focus on oxygen problems, and where only measurements of (N)BOD and COD are available in stead of accurate measurements of particulate organic matter, phytoplankton etc.
- ◇ SOD is not a real bottom substance like IM1S1, DetCS1 etc, because all settled BOD species are lumped into this parameter. No distinction is made between SOD in the first or second sediment layer. It is not accounted for in the sediment composition routines, and it cannot be resuspended. Once settled it can only disappear by decay.
- ◇ In the current DELWAQ version the substance SOD and all BOD and COD species are expressed as oxygen equivalents.
- ◇ In earlier versions only one BOD related substance was distinguished, it was expressed as carbon (*BODC*, [gC m^{-3}]). Substance *BODC* may still be used, but will not be converted to SOD once sedimented.

Additional references

Thomann and Mueller (1987), Smits and Molen (1993), DiToro (1986)

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2.9 Production of substances: TEWOR, SOBEK only

2.9.1 Coliform bacteria – listing of processes

Table 2.9: *SOBEK-WQ processes for coliform bacteria.*

Process description	Process name
TEWOR Production Fluxes	PROD_TEWOR
Mortality of coli bacteria	(i)MRT[1)]

[1)] (i) $\in \{$ECOLI, FCOLI or TCOLI$\}$.

2.9.2 TEWOR-production fluxes

PROCESS: PROD_TEWOR

Production fluxes have been introduced for the TEWOR-module in SOBEK (Stowa, 2002). This module is used for water quality modelling of urban waters. The production fluxes can represent certain processes in the water column, for instance algae growth, that are not modelled explicitly.

Implementation

The process has been implemented for substances CBOD5, CBOD5_2, CBOD5_3, COD_Cr, OXY, DetN, NH4, NO3, Ecoli.

Table 2.10 provides the definitions of the parameters occurring in the formulations.

Formulation

The TEWOR-production fluxes are formulated as zeroth order fluxes.

$$Rtewor_i = ftewor_i \tag{2.17}$$

with:

$Rtewor_i$ TEWOR production flux (g i.m^{-3})
$ftewor_i$ TEWOR production flux (g i.m^{-3})

Directives for use

◇ The production fluxes were introduced for usage in the TEWOR subset. The fluxes can also be used in other applications.

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Table 2.10: *Definitions of the parameters in the above equations for PROD_TEWOR.*

Name in formulas	Name in input	Definition	Units
$Rtewor_i$	*dTEWORi*	TEWOR production flux	g.m^{-3}
$ftewor_i$	*fTEWORi*	TEWOR production flux	g.m^{-3}

2.9.3 Process TEWOR: Oxydation of BOD

PROCESS: DBOD_TEWOR

This module is an alternative process for the oxidation or mineralization of BOD that was introduced for the TEWOR-module in SOBEK (Stowa, 2002). This module is used for water quality modelling of urban waters. The prevailing process for the mineralization of BOD or COD in SOBEK-WQ is BODCOD.

Implementation

The process has been implemented for substances CBOD5, CBOD5_2 and CBOD5_3.

Table 2.11 provides the definitions of the parameters occurring in the formulations.

Formulation

The oxidation flux of BOD5 is a function of the BOD5 concentration and is limited by the oxygen concentration.

$$Rmin_i = kmin_i \times C5_i \times \frac{Cox}{Ksox + Cox} \tag{2.18}$$

The oxygen demand is a function of the ultimate BOD concentration, because the actual oxygen demand will be higher than the oxygen demand measured at 5 days.

$$Rox = \sum_i \frac{Rmin_i}{1 - exp(-5kmin_i)} \tag{2.19}$$

with:

$C5_i$	carbonaceous BOD (pool i) at 5 days [g O_2 m^{-3}]
Cox	dissolved oxygen [g O_2 m^{-3}]
$kmin_i$	oxidation reaction rate BOD (pool i) [d^{-1}]
$Ksox$	half saturation constant for oxygen limitation on oxidation of BOD [g O_2 m^{-3}]

Directives for use

◇ This process was introduced for usage in the TEWOR subset, but it can also be used in other applications.

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Table 2.11: *Definitions of the parameters in the above equations for DBOD_TEWOR.*

Name in formulas	**Name in input**	**Definition**	**Units**
$C5_i$	*CBOD5_i*	carbonaceous BOD (pool i) at 5 days	g O_2 m^{-3}
Cox	*OXY*	dissolved oxygen	g O_2 m^{-3}
Cu_i	*CBODu_i*	carbonaceous BOD (pool i) ultimate	g O_2 m^{-3}
$kmin_i$	*RCBOD_i*	oxidation reaction rate BOD (pool i)	d^{-1}
Ksox	*KMOX*	half saturation constant for oxygen limitation on oxidation of BOD	g O_2 m^{-3}

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3 Nutrients

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3.1 Nitrification

PROCESS: NITRIF_NH4

Nitrification is the microbial, stepwise oxidation of ammonium (and toxic ammonia) into nitrate, which requires the presence of oxygen. Several intermediate oxidation products are formed, but the final step from nitrite to nitrate is considered rate limiting. The accumulation of the intermediate products including toxic nitrite (NO_2^-) is negligible in systems with residence times longer than a few days.

Nitrification is highly sensitive to temperature. In contrast with the decomposition of detritus, which may proceed at a slow but measurable rate below 4°C, nitrification nearly comes to a halt at this temperature. This is connected with the fact that only a rather small number of specialised bacteria species are capable of nitrification. The decomposition of organic matter is performed by a very large number of species, including species that are adapted to low temperature environments.

Nitrifiers are predominantly sessile bacteria, that need readily available organic substrates. This implies that nitrification proceeds most actively at and in the oxidising top sediment layer.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process NITRIF_NH4 has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. The formation of intermediate products such as nitrite is not considered. Two options are available with respect to the formulation of the rate of nitrification. An option can be selected with parameter $SWVnNit$.

The process has been implemented for the following substances:

- ◇ NH4, NO3 and OXY.

Table 3.1 provides the definitions of the parameters occurring in the formulations.

Formulation

Nitrification can be described as a number of consecutive chemical reactions. The overall reaction equation is:

$$NH_4^+ + 2O_2 + H_2O \quad \Longrightarrow \quad NO_3^- + 2H_3O^+$$

Nitrification ultimately removes ammonium (ammonia) and oxygen from the water phase and produces nitrate. The process requires 4.57 gO_2 gN^{-1}.

The formulation according to Michaelis-Menten kinetics (SWVnNit = 1.0)

Nitrification is modelled as the sum of a zeroth order process and a process according to Michaelis-Menten kinetics Smits and Beek (2013). The rate of the last contribution is limited by the availability of ammonium and dissolved oxygen, and is also a function of the temperature.

The zeroth order rate may have different values for the sediment and the water column, and serves several purposes. It is used to account for the collapse of the process rate at low

temperatures. When the water temperature drops below a critical value, the zeroth order rate takes over. However, the zeroth order rate is set to zero, when the dissolved oxygen concentration drops below a critical value. The critical value in sediment layers should be equal to 0.0, whereas the critical dissolved oxygen concentration in the water column can be assigned a negative value. In that case, the zeroth order nitrification rate takes over from the Michelis-Menten process for the water column, when dissolved oxygen gets depleted and the temperature is still above the critical value. (Simulated DO can have a negative concentration, representing the DO-equivalent of reduced substances!) This feature in the nitrification formulations allows the occurrence of nitrification in a water column, in which the average dissolved oxygen concentration is zero or even negative. In this way it can be taken into account that the water column may not be homogeneously mixed in reality, and a surface layer with positive oxygen concentrations persists.

The nitrification rate is formulated as follows to accommodate the above features:

$$Rnit = k0nit + knit \times \left(\frac{Cam}{Ksam \times \phi + Cam}\right) \times \left(\frac{Cox}{Ksox \times \phi + Cox}\right)$$

$$knit = knit_{20} \times ktnit^{(T-20)}$$

$$\begin{aligned}
knit &= 0.0 && \text{if} \quad T < T_c \quad \text{or} \quad Cox \leq 0.0 \\
k0nit &= 0.0 \\
k0nit &= k0temp && \text{if} \quad T < T_c \quad \text{and} \quad Cox > 0.0 \\
k0nit &= k0ox && \text{if} \quad T \geq T_c \quad \text{and} \quad Cox \leq 0.0 \\
k0nit &= 0.0 && \text{if} \quad Cox \leq Coxc \times \phi
\end{aligned}$$

with:

Cam	ammonium concentration [gN.m$^{-3}_{\ell}$]
Cox	dissolved oxygen concentration ≥ 0.0 [g.m$^{-3}_{\ell}$]
$Coxc$	critical dissolved oxygen concentration [g.m$^{-3}_{w}$]
$knit$	Michaelis-Menten nitrification rate [gN.m$^{-3}_{\ell}$ d^{-1}]
$ktnit$	temperature coefficient for nitrification [-]
$k0nit$	zeroth order nitrification rate [gN.m$^{-3}_{\ell}$ d^{-1}]
$k0ox$	zeroth order nitrif. rate at negative average DO concentrations [gN.m$^{-3}_{\ell}$ d^{-1}]
$k0temp$	zeroth order nitrification rate at low temperatures [gN.m$^{-3}_{\ell}$ d^{-1}]
$Ksox$	half saturation constant for dissolved oxygen limitation [g.m$^{-3}_{w}$]
$Ksam$	half saturation constant for ammonium limitation [gN.m$^{-3}_{w}$]
T	temperature [°C]
Tc	critical temperature for nitrification [°C]
ϕ	porosity [-]

An important feature of MM-kinetics is that the process rate saturates at high concentrations of the substrate. The formulation turns into a first order kinetic process, when the ambient substrate concentration becomes small compared to the half saturation constant.

The formulation according to pragmatic kinetics (SWVnNit = 0.0)

Nitrification is modelled as the sum of a zeroth and a first order process. If the water temperature drops below a critical value, only the zeroth order flux remains. The first order flux is corrected for water temperature and oxygen concentration. Below a critical oxygen concentration the oxygen function for nitrification becomes equal to a user defined level (default zero),

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whereas for above an optimal oxygen concentration this function has a value of 1.0. Linear interpolation of the oxygen function is the default option for intermediate oxygen concentrations. A higher order interpolation for intermediate values may also be applied.

The nitrification rate is formulated as follows to accommodate the above features:

$$Rnit = k0nit + fox \times k1nit \times Cam$$

$$k1nit = \begin{cases} k1nit_{20} \times ktnit^{(T-20)} \\ 0.0 \qquad \text{if} \quad T < T_c \end{cases}$$

with:

Cam	ammonium concentration [gN m_w^{-3}]
fox	the oxygen limitation function [-]
$k1nit$	first order nitrification rate [d^{-1}]
$ktnit$	temperature coefficient for nitrification [-]
$k0nit$	zeroth order nitrification rate [gN m_w^{-3} d^{-1}]
T	temperature [°C]
T_c	critical temperature for nitrification [°C]

The oxygen limitation function reads:

$$fox = \begin{cases} foxmin & \text{if} \quad Cox \leq Coxc \\ (1 - foxmin) \times \left(\frac{Cox - Coxc}{Coxo - Coxc}\right)^{10^a} + foxmin & \text{if} \quad Coxc < Cox < Coxo \\ 1.0 & \text{if} \quad Cox \geq Coxo \end{cases}$$

with:

a	curvature coefficient [-]
Cox	dissolved oxygen concentration ≥ 0.0 [g m_w^{-3}]
$Coxo$	optimal dissolved oxygen concentration [g m_w^{-3}]
$Coxc$	critical dissolved oxygen concentration [g m_w^{-3}]
$foxmin$	minimal value of the oxygen limitation function [-]

The pragmatic oxygen limitation function for default parameter values is depicted in Figure 3.1.

SOBEK The formulation according to TEWOR (SWVnNit = 2.0)

Nitrification is modelled as a process according to Monod kinetics. The rate of the process is a function of the ammonium concentration and is limited by the availability of dissolved oxygen.

The nitrification rate is formulated as follows to accommodate the above features:

$$Rnit = knit \times Cam \times \left(\frac{Cox}{Ksox + Cox}\right) \tag{3.1}$$

with:

Cam	ammonium concentration [gN.m_ℓ^{-3}]
Cox	dissolved oxygen concentration ≥ 0.0 [g.m_ℓ^{-3}]
$knit$	First order nitrification rate [gN.m_ℓ^{-3}.d^{-1}]
$Ksox$	half saturation constant for dissolved oxygen limitation [g.m_w^{-3}]

An important feature of Monod-kinetics is that the process rate saturates at high concentrations of the substrate. The formulation turns into a first order kinetic process, when the ambient substrate concentration becomes small compared to the half saturation constant.

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Directives for use

- ◇ Formulation option $SWVnNit = 0.0$ is the default option for historical reasons.
- ◇ Care must be taken that the zeroth order reaction rates are given values, that are in proportion with the MM-kinetics or first-order kinetics. They should not deliver more than 20 % of the total rate at $T = 20$ °C, and average ammonium and DO concentrations. Using zeroth order kinetics may cause negative ammonium concentrations, when the time-step is too large!
- ◇ The critical temperature for nitrification $CTNit$ is approximately 4 °C.
- ◇ The rate $RcNit20$ will generally be much higher in the top sediment layer than in the overlying water. This is due to the sessile nature of nitrifiers. When the sediment is not explicitly modelled, one should take the nitrifying capacity of the sediment into account in the nitrification rate for the water column.

Concerning option $SWVnNit1.0$:

- ◇ For a start, the zeroth order rates $Rc0NitT$ and $Rc0NitOx$ and the critical DO concentration $CoxNit$ can be set to zero. The zeroth order rate for negative DO concentrations may not be relevant. If needed, the zeroth order rate for low temperatures can be quantified in establishing a good balance between summer and winter nitrification rates.
- ◇ The critical oxygen concentration should not be given negative values for sediment layers.
- ◇ Often nitrification has been modelled as a first-order (linear) process with respect to the ammonium concentration. The MM-kinetics can be made to behave like a first order process by assigning a value to $KsAmNit$ that is high compared to the ambient ammonium concentrations. By enlarging $RcNit20$ concurrently approximately the same rates can be obtained as for first order kinetics.

Concerning option $SWVnNit0.0$:

- ◇ The use of the curvature coefficient $CurvNit$ of the oxygen limitation function is described in WL | Delft Hydraulics (1994a). Linear interpolation between $COXNit$ and $OOXNit$ occurs, when $CurvNit$ is equal to 0.0, whereas the value -1 establishes maximal curvature.
- ◇ The optimal oxygen concentration $OOXNit$ must be higher than the critical oxygen concentration $COXNit$ (see Figure 3.1).
- ◇ The limitation function can be made inactive by choosing a low value for the optimal oxygen concentration $OOXNit$ (e.g. a negative value).
- ◇ By choosing a positive minimal value of the oxygen limitation function $CFLNit$ the limitation will have a user defined value at oxygen concentrations below the critical oxygen concentration. This may result in nitrification when the average dissolved oxygen concentration is negative.

Additional references

DiToro (2001), Smits and Molen (1993), WL | Delft Hydraulics (1997), Vanderborght et al. (1977)

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Table 3.1: *Definitions of the parameters in the above equations for NITRIF_NH4. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
a	$CurvNit$	curvature coefficient for the oxygen lim. function	-
Cam	$NH4$	ammonium concentration	gN $m^{-3}_{\mathscr{b}}$
Cox	OXY	dissolved oxygen concentration	g $m^{-3}_{\mathscr{b}}$
$Coxc$	$CoxNit$	critical DO concentration for nitrification	g $m^{-3}_{\mathscr{w}}$
$Coxo$	$OoxNit$	optimal DO concentration for nitrification	g $m^{-3}_{\mathscr{w}}$
$foxmin$	$CFLNit$	minimal value of the oxygen limitation function	-
$knit20$	$RcNit20$	MM- nitrification reaction rate at 20 °C	gN $m^{-3}_{\mathscr{b}}$ d^{-1}
$k1nit20$	$RcNit$	first order nitrification rate at 20 °C	d^{-1}
$ktnit$	$TcNit$	temperature coefficient for nitrification	-
$k0ox$	$Rc0NitOx$	zeroth order nitrification rate at negative DO	gN $m^{-3}_{\mathscr{b}}$ d^{-1}
$k0temp$	$Rc0NitT$	zeroth order nitrification rate at low temperatures	gN $m^{-3}_{\mathscr{b}}$ d^{-1}
$k0nit$	$Znit$	zeroth order nitrification rate	gN $m^{-3}_{\mathscr{b}}$ d^{-1}
$Ksam$	$KsAmNit$	half saturation constant for ammonium limitation	gN $m^{-3}_{\mathscr{w}}$
$Ksox$	$KsOxNit$	half saturation constant for DO limitation	g $m^{-3}_{\mathscr{w}}$
$Rnit$	–	nitrification rate	gN $m^{-3}_{\mathscr{b}}$ d^{-1}
-	$SWVnNit$	switch for selection of the process formulations (pragmatic kinetics = 0.0, MM-kinetics = 1.0)	-
T	$Temp$	temperature	°C
T_c	$CTNit$	critical temperature for nitrification	°C
ϕ	$POROS$	porosity	$m^3_{\mathscr{w}}$ $m^{-3}_{\mathscr{b}}$

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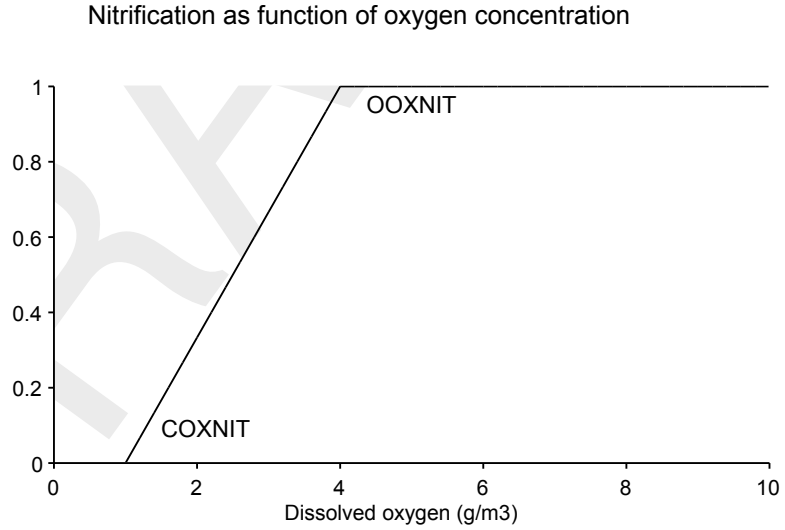

Figure 3.1: *Figure 1 Default pragmatic oxygen limitation function for nitrification (O2FuncNit, option 0).*

3.2 Calculation of NH3

PROCESS: NH3FREE

In rivers, estuaries and coastal seas near densely populated areas high loads of BOD and nutrients may cause conditions which favour high levels of unionised ammonia, especially in warm climates (Millero, 1995). Unionised, or free ammonia (NH_3) is toxic to fish.

NH_3 is the product of the dissociation of the ammonium (NH_4^+) ion:

$$NH_4^+ \Rightarrow NH_3 + H^+$$

The reaction is characterised by the equilibrium constant K :

$$K' = \frac{a_{NH_3} a_{H^+}}{a_{NH_4^+}}$$

where:

a_i	activity of species *i* [mol l^{-1}]

Rearranging this equation and taking logarithms ($pH = -\,^{10}\log(a_{H^+})$) results in:

$$\log\left(\frac{a_{NH_3}}{a_{NH_4^+}}\right) = \log K' + pH$$

Because DELWAQ computes concentrations rather than activities, a corrected equilibrium constant is introduced:

$$K = K' \frac{\gamma_{NH_4^+}}{\gamma_{NH_3}}$$

where:

γ_i	activity coefficient of species *i* [-]
K	equilibrium constant [mol l^{-1}], after correction for activities

Note that K is a function of the ionic strength of the solution (which determines g_i). Thus, K depends on salinity! Combination of the previous two equations yields:

$$\log \frac{(NH_3)}{(NH_4^+)} = logK + pH$$

This equation shows the relation between the ratio of unionised and ionised ammonia and the equilibrium constant. The equilibrium constant of this reaction depends strongly on temperature, increasing temperature favours the dissociation of NH_4^+ (Millero, 1995).

In DELWAQ, $totalNH_4$ is modelled as substance NH4, which is the sum of NH_4^+ and NH_3. The concentration of NH_3 is derived from the above equation and total NH_4 according to:

$$[NH_3] = \frac{\frac{[NH_3]}{[NH_4^+]}}{1 + \frac{[NH_3]}{[NH_4^+]}} \times (totalNH_4)$$

There are two options for calculating unionised ammonia. In the first option, the temperature dependency of K is computed in a semi-empirical way with a reprofunction for the dissociation constant, based upon the Netherlands' water quality standards which tabulate the maximum allowed total NH_4 concentration that yields a certain level of unionised ammonia, at different pH and T. In the second option, the value of the dissociation constant is calculated with a reprofunction dependent on salinity and temperature according to Millero (1995).

Implementation

The process has been implemented for the following substance:

- ◇ NH4

The process calculates additional substance NH3 (g.m^3), and is active in all types of computational elements.

Table 3.2 provides the definitions of the input parameters occurring in the formulations.

Formulation

The process is formulated as follows:

If NH3_Sw = 1 then

$$
\begin{aligned}
(totalNH_4) &= NH4 \times \frac{m^3}{l} \times \frac{1}{M} \\
\log K &= a + b \times T \\
(\mathsf{NH_3}) &= \frac{10^{logK+pH}}{1+10^{logK+pH}} \times (totalNH_4) \\
NH3 &= (\mathsf{NH_3}) \times M \times \frac{l}{m^3} \\
frNH3 &= \frac{(\mathsf{NH_3})}{(totalNH_4)}
\end{aligned}
$$

If NH3_Sw = 2 then

$$
\begin{aligned}
\ln K = &-6285.33/(T+273.15) + 0.0001635 \times (T+273.15) - 0.25444 \\
&+ (0.46532 - 123.7184/(T+273.15)) \times \sqrt{Sal} \\
&+ (-0.01992 + 3.17556/(T+273.15)) \times Sal
\end{aligned}
$$

$$
\rho = (1000.0 + 0.7 \times Sal/(1.0 - Sal/1000.0) - 0.0061 \times (T-4.0)^2)/1000.0
$$

$$
\begin{aligned}
(NH_4) &= NH4 \times \frac{m^3}{l} \times \frac{1}{M \times \rho} \\
(NH_3) &= (NH_4)/(1 + \frac{10^{-pH}}{K}) \\
NH3 &= (NH_3) \times M \times \rho \times \frac{l}{m^3}
\end{aligned}
$$

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where:

NH3_Sw	option parameter for calculation method [-]
NH3	concentration of ammonia [gN m^{-3}]
(NH_3)	molar concentration of ammonia [mol l^{-1}] or [mol kg^{-1} H_2O]
NH4	concentration of ammonium (DELWAQ substance) [gN m^{-3}]
(NH_4)	molar concentration of ammonium [mol l^{-1}] or [mol kg^{-1} H_2O]
a	coefficient a of reprofunction 1 [-]
b	coefficient b of reprofunction 1 [K^{-1}]
frNH3	fraction NH3 of NH4 [-]
K	dissociation constant [mol l^{-1}] or [mol kg^{-1} H_2O]
M	atomic weight of nitrogen (= 14) [g mol^{-1}]
pH	pH [-]
Sal	salinity [g kg^{-1}]
T	water temperature [°C]
ρ	density of water [kg l^{-1}]

[m^3] and [l] are the volume units (conversions between the standard volume unit in DELWAQ and the unit usually used in chemistry).

Directives for use

◇ Do not change the defaults of $KNH3rf1a$ and $KNH3rf1a$.

Table 3.2: *Definitions of the input parameters in the formulations for NH3FREE.*

Name in formulas	**Name in input**	**Definition**	**Units**
$NH4$	$NH4$	ammonium concentration	gN m^{-3}
$NH3_Sw$	$NH3_Sw$	option for calculation method (1=reprofunction 1; 2=Millero)	-
a b	$KNH3rf1a$ $KNH3rf1b$	coefficient a of reprofunction 1 coefficient b of reprofunction 1	- K^{-1}
pH	pH	acidity	-
Sal	$Salinity$	salinity	psu
T	$Temp$	temperature	°C

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3.3 Denitrification

PROCESS: DENWAT_NO3 AND DENSED_NO3

Denitrification is the microbial, stepwise reduction of nitrate into elemental nitrogen, which requires the absence of oxygen. The nitrogen produced may escape into the atmosphere. Denitrifiers use nitrate in stead of oxygen to oxidise organic matter. Several intermediate reduction products are formed, but the first step from nitrate to a nitrite is rate limiting. The accumulation of the intermediate products including toxic nitrite and various toxic nitrogen oxides is negligible in systems with residence times longer than a few days. The formation of intermediate products such as nitrite is not considered in the model.

Denitrification is highly sensitive to temperature. In contrast with the decomposition of detritus, which may proceed at a slow but measurable rate below 4 $^{\circ}$C, denitrification nearly comes to a halt at this temperature. This is connected with the fact that only a rather small number of specialised bacteria species are capable of denitrification. The decomposition of organic matter is performed by a very large number of species, including species that are adapted to low temperature environments.

Denitrifiers are predominantly sessile bacteria, that need readily available organic substrates and that can only actively survive in an anoxic environment. This implies that denitrification usually only proceeds in the lower part of the oxidising top sediment layer. It has been claimed, however, that denitrification may also be carried out in the water column by highly specialised bacteria, in anoxic pockets of suspended particles.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process DENWAT_NO3 has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. Process DENSED_NO3 is to be used in addition to DENWAT_NO3 only when the sediment is simulated according to the S1/2 option. When sediment layers are not simulated explicitly, this process takes care that denitrification in the sediment always proceeds, leading to the removal of nitrate from the water column. The alternative for denitrification by processes DENWAT_NO3and DENSED_NO3 is the denitrification by process CONSELAC (Consumption of electron acceptors), in which nitrate is one of the electron acceptors for the oxidation of organic detritus. When the "'layered sediment"' option is used CONSELAC should be used in stead of DENSED_NO3 and DENWAT_NO3.

Two options are available with respect to the formulation of the rate of nitrification. An option can be selected with parameter $SWVnDen$.

The processes have been implemented for the following substances:

- ◇ NO3 and OXY.

Tables 3.3 and 3.4 provide the definitions of the parameters occurring in the formulations.

Formulation

Denitrification can be described as a number of consecutive chemical reactions. The overall reaction equation is:

$$4NO_3^- + 4H_3O^+ \Longrightarrow 2N_2 + 5O_2 + 6H_2O$$

Denitrification ultimately removes nitrate from the water phase and produces elemental nitrogen. The process delivers 2.86 gO_2 gN^{-1}. The oxygen in nitrate used to oxidise organic matter is accounted for in the model using this stochiometric constant. The actual quantity of dissolved oxygen consumed for organic matter oxidation is therefore equal to the total oxygen demand minus the part delivered by nitrate.

The formulation according to Michaelis-Menten kinetics (SWVnDen = 1.0)
Denitrification is modelled as the sum of a zeroth order process and a process according to Michaelis-Menten kinetics. The rate of the latter contribution is a function of the nitrate concentration, the dissolved oxygen concentration and the temperature. The Michealis-Menten kinetic factor for dissolved oxygen is formulated as an inhibition factor. The denitrification rate has not been made proportional to the detritus concentration, since detritus is (almost) always abundantly present.

The zeroth order rate may have different values for the sediment and the water column, and serves several purposes. It is used to account for the collapse of the process rate at low temperatures. When the water temperature drops below a critical value, the zeroth order rate takes over. The zeroth order and Michealis-Menten rates are both set to zero, when the dissolved oxygen concentration rises above a critical value, and consequently, the environment is completely oxic. When the temperature is still above the critical temperature, the zeroth order denitrification rate may be assigned a substantially higher value than at low temperature. This feature in the denitrification formulations allows the occurrence of substantial denitrification in a water column or sediment layer, in which the average dissolved oxygen concentration is positive but below the critical concentration. In this way it can be taken into account that:

- ◇ the water column may not be homogeneously mixed in reality, and that near the sediment an oxygen depleted water layer persists; and
- ◇ denitrification can occur in a sediment environment that is oxic on the average, but does contain anoxic pockets at the same time.

The denitrification rate is formulated as follows to accommodate the above features:

$$Rden = k0den + kden \times \left(\frac{Cni}{Ksni \times \phi + Cni} \right) \times fox$$

$$fox = \begin{cases} 1.0 - \frac{Cox}{Ksox \times \phi + Cox} & \text{if } Cox \geq 0.0 \\ 1.0 & \text{if } Cox < 0.0 \end{cases}$$

$$\begin{aligned} kden &= kden_{20} \times ktden^{(T-20)} \\ kden &= 0.0 && \text{if } \; T < Tc \text{ or } Cox \geq Coxc \times \phi \\ k0den &= 0.0 \\ k0den &= k0temp && \text{if } \; T < Tc \text{ and } Cox < Coxc \times \phi \\ k0den &= k0ox && \text{if } \; T \geq Tc \text{ and } Cox < Coxc \times \phi \\ k0den &= 0.0 && \text{if } \; Cox \geq Coxc \times \phi \end{aligned}$$

with:

Cni	nitrate concentration [gN m_{ℓ}^{-3}]
Cox	dissolved oxygen concentration ≥ 0.0 [g m_{ℓ}^{-3}]

$Coxc$	critical dissolved oxygen concentration [g m_w^{-3}]
fox	oxygen inhibition function [-]
$kden$	Michaelis-Menten denitrification rate [gN m_b^{-3} d^{-1}]
$ktden$	temperature coefficient for denitrification [-]
$k0den$	zeroth order denitrification rate [gN m_b^{-3} d^{-1}]
$k0ox$	zeroth order denitrification rate at moderate DO concentrations [gN m_b^{-3} d^{-1}]
$k0temp$	zeroth order denitrification rate at low temperatures [gN m_b^{-3} d^{-1}]
$Ksni$	half saturation constant for nitrate limitation [gN m_w^{-3}]
$Ksox$	half saturation constant for dissolved oxygen inhibition [g m_w^{-3}]
T	temperature [°C]
Tc	critical temperature for denitrification [°C]
ϕ	porosity [-]

The oxygen inhibition function needs to be set to 1.0 at negative DO concentrations to avoid the function obtaining values higher than 1.0. (Simulated DO can have a negative concentration, representing the DO-equivalent of reduced substances!)

The formulation according to pragmatic kinetics (SWVnDen = 0.0)
Denitrification is modelled as the sum of a zeroth and a first order process. If the water temperature drops below a critical value, only the zeroth order flux remains. The first order flux is corrected for water temperature and oxygen concentration. Above a critical oxygen concentration the oxygen function for denitrification becomes equal to zero, whereas for below an optimal oxygen concentration this function has a value of 1.0. Linear interpolation of the oxygen functions is the default option for intermediate oxygen concentrations. A higher order interpolation for intermediate values may also be applied.

The denitrification rate is formulated as follows to accommodate the above features:

$$Rden = k0den + fox \times k1den \times Cni$$

$$k1den = \begin{cases} 0.0 & \text{if } T < T_c \\ k1den_{20} \times ktden^{(T-20)} & \end{cases}$$

with:

Cni	nitrate concentration [gN m_w^{-3}]
fox	the oxygen inhibition function [-]
$k1den$	first order denitrification rate [d^{-1}]
$ktden$	temperature coefficient for denitrification [-]
$k0den$	zeroth order denitrification rate [gN m_w^{-3} d^{-1}]
T	temperature [°C]
T_c	critical temperature for denitrification [°C]

The oxygen inhibition function reads:

$$fox = \begin{cases} 1.0 & \text{if } Cox \leq Coxo \\ \dfrac{Coxc - Cox}{Coxc - Coxo + (\mathrm{e}^a - \mathrm{e})\,(Cox - Coxo)} & \text{if } Coxo < Cox < Coxc \\ 0.0 & \text{if } Cox \geq Coxc \end{cases}$$

with:

a	curvature coefficient [-]
Cox	dissolved oxygen concentration ≥ 0.0 [g m_w^{-3}]
$Coxo$	optimal dissolved oxygen concentration [g m_w^{-3}]

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$Coxc$ critical dissolved oxygen concentration [g m_w^{-3}]

The pragmatic oxygen inibition function for default parameter values is depicted in Figure 3.2.

The above formulations for options 1 and 0 represent process DENWAT_NO3. Process DENSED_NO3 has been formulated in a much more simplified way with first-order kinetics with respect to the nitrate concentration. The deeper sediment is essentially reducing, leading to maximal denitrification in the sediment proportional to the nitrate concentration in the water column. DO inhibition has therefore been removed from the formulations. Only one zeroth order rate is used, the one associated with the critical temperature. The first-order reaction rate has to be provided in m.d-1, the zeroth order rate in [g.m^{-2} d^{-1}]. The resulting denitrification rate is divided by the depth of the water column H in order to obtain the rate in [g.m^{-3} d^{-1}].

Directives for use

- ◇ Formulation option $SWVnDen = 0.0$ is the default option for historical reasons.
- ◇ Care must be taken that the zeroth order reaction rates are given values, that are in proportion with the first-order kinetics. They should not deliver more than 20% of the total rate at T=20 °C, and moderate nitrate and DO concentrations. Using zeroth order kinetics may cause negative nitrate concentrations, when the time-step is too large!
- ◇ The critical temperature for denitrification $CTDen$ is approximately 4 °C.
- ◇ If denitrification actually occurs in the water column at all, the rate $RcDen20$ will generally be much higher in the top sediment layer than in the overlying water. This is due to the sessile nature of nitrifiers. When the sediment is not explicitly modelled, one should take the denitrifying capacity of the sediment into account in process DENSED_NO3.

Concerning option $SWVnDen1.0$:

- ◇ For a start, the zeroth order rates $Rc0DenT$ and $Rc0DenOx$ and the critical DO concentration $CoxDen$ can be set to zero. In a next step the zeroth order rate for low temperatures can be quantified in establishing a good balance between summer and winter nitrification rates. The zeroth order rate for moderate DO concentrations may not be relevant for the current case.
- ◇ The critical oxygen concentration should not be given a value higher than 2 g m_w^{-3} for physical reasons. A higher value might nevertheless be required to take the occurrence of denitrification in an inhomogeneous water column into account properly.
- ◇ Often denitrification has been modelled as a first-order (linear) process with respect to the nitrate concentration. The MM-kinetics can be made to behave like a first order process by assigning a value to $KsNiDen$ that is high compared to the ambient nitrate concentrations. By enlarging $RcDen20$ concurrently approximately the same rates can be obtained as for first order kinetics.

Concerning option $SWVnDen0.0$:

- ◇ Linear interpolation occurs for the oxygen inhibition function between $COXDen$ and $OOXDen$, when curvature coefficient $Curvat$ is equal to 1.0. Maximal curvature is established, when $Curvat$ is equal to 4.0
- ◇ The optimal oxygen concentration $OOXDen$ must be smaller than the critical oxygen concentration $COXDen$ (see Figure 3.2).
- ◇ The limitation function can be made inactive by choosing a high value for the optimal oxygen concentration $OOXDen$.

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Additional references

DiToro (2001), Smits and Molen (1993), WL | Delft Hydraulics (1997), Vanderborght et al. (1977)

Table 3.3: *Definitions of the parameters in the above equations for DENWAT_NO3. Volume units refer to bulk (b) or to water (w).*

Name in formulas	Name in input	Definition	Units
a	$Curvat$	curvature coefficient for the oxygen inhib. function	-
Cni	$NO3$	nitrate concentration	gN m_b^{-3}
Cox	OXY	dissolved oxygen concentration	g m_b^{-3}
$Coxc$	$CoxDen$	optimal DO concentration for denitrification	g m_w^{-3}
$Coxo$	$OoxDen$	critical DO concentration for denitrification	g m_w^{-3}
$kden_{20}$	$RcDen20$	MM- denitrification reaction rate at 20 °C	gN m_b^{-3} d^{-1}
$k1den_{20}$	$RcDenWat$	first order denitrification reaction rate at 20 °C	d^{-1}
$ktden$	$TcDenWat$	temperature coefficient for denitrification	-
$k0ox$	$Rc0DenOx$	zeroth order denitrification rate at moderate DO	gN m_b^{-3} d^{-1}
$k0temp$	$Rc0DenT$	zeroth order denitrification rate at low temperatures	gN m_b^{-3} d^{-1}
$k0den$	$ZDenWat$	zeroth order denitrification rate	gN m_b^{-3} d^{-1}
$Ksni$	$KsNiDen$	half saturation constant for nitrate limitation	gN m_w^{-3}
$Ksox$	$KsOxDen$	half saturation constant for DO inhibition	g m_w^{-3}
$Rden$	–	denitrification rate	gN m_b^{-3} d^{-1}
-	$SWVnDen$	switch for selection of the process formulations (pragmatic kinetics = 0.0, MM-kinetics = 1.0)	-
T	$Temp$	temperature	°C
T_c	$CTDen$	critical temperature for denitrification	°C
ϕ	$POROS$	porosity	m_w^3 m_b^{-3}

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Table 3.4: *Definitions of the parameters in the above equations for DENSED_NO3. Volume units refer to bulk ($\mathcal{b}$) or to water ($\mathcal{w}$).*

Name in formulas	Name in input	Definition	Units
Cni	$NO3$	nitrate concentration in the overlying water layer	gN m$^{-3}_{\mathcal{b}}$
H	$Depth$	depth of the overlying water layer	m
$kden_{20}$	$RcDenSed$	first-order denitrification reaction rate	m d^{-1}
$ktden$	$TcDenSed$	temperature coefficient for denitrification	-
$k0temp$	$Rc0DenSed$	zeroth order denitrification rate	gN m^{-2}
$Rden$	–	denitrification rate	gN m$^{-3}_{\mathcal{b}}$ d^{-1}
T	$Temp$	temperature	°C
T_c	$CTDen$	critical temperature for denitrification	°C

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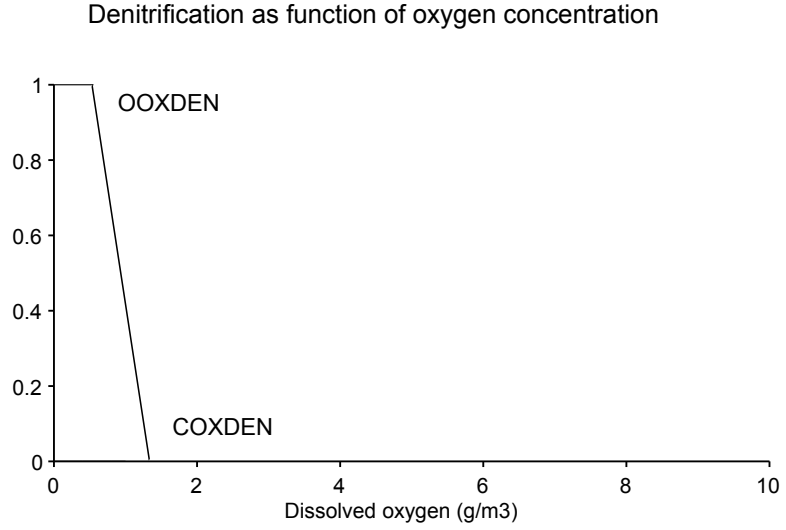

Figure 3.2: *Default pragmatic oxygen inhibition function for denitrification (O2Func, option 0).*

3.4 Adsorption of phosphate

PROCESS: ADSPO4AAP

Dissolved phosphate, mainly present as ortho-phosphate (mainly present as $H_2PO_4^-$), adsorbs onto suspended sediment, in particular to the iron(III)oxyhydroxides in sediment particles. Other adsorbing components are aluminium hydroxides and silicates, manganese oxides and organic matter. The fine sediment fraction (< 0.63 μm), containing more than 90 % of these components present in suspended sediment, basically accounts for the adsorption capacity of sediment.

The adsorption of phosphate onto sediment particles is highly pH dependent, since phosphate competes with OH^- for the adsorption sites. The adsorption decreases with increasing pH, which implies that alkalinity producing primary production by algae stimulates desorption, which in turn may stimulate primary production.

Moreover, the adsorption process is relatively weakly dependent on temperature and ionic strength (salinity). The effect of the latter has not been quantified very well and has therefore been ignored in the model formulations.

The adsorption of phosphate is also very sensitive to low dissolved oxygen concentrations. Iron(III) gets chemically reduced into iron(II), when dissolved oxygen has been depleted and the decomposition of detritus continues at anaerobic conditions. As a result, initially, iron(II) dissolves together with adsorbed substances, among which phosphate. Iron(II) will precipitate as sulfide and/or carbonate, the phosphate repartitions between the solution and the sediment particles, according to the decreased adsorption capacity.

The oxygen concentration dependency of the adsorption process has an enormous impact on the sorption of phosphate in the sediment. The sorption capacity of the oxidising top layer of the sediment is large, since oxidised iron(III) tends to accumulate in this layer. However, the sorption capacity of the reducing lower sediment layer is much smaller, since most of the iron may be present in its chemically reduced iron(II)-form. When the oxidising layer collapses due to intensified decomposition of organic matter, the phosphate release of the sediment into the overlying water may suddenly increase an order of magnitude. Consequently, linking the adsorption of phosphate to the presence of dissolved oxygen allows application of the same formulations to both the water column and the sediment.

Adsorption is fast and desorption of recently adsorbed phosphate is somewhat slower. Nevertheless, equilibrium is usually established within a few hours. Although process rates are high, the adsorption process has been formulated kinetically for pragmatic reasons. One reason is that this approach delivers the sorption flux. The present formulations, however, do not allow taking into account very slow desorption of phosphate from for instance river borne sediment/soil particles, that contain internally bound phosphate. The solid phase diffusion of phosphate proceeds very slow in such particles.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

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Implementation

Three different sets of formulations have been implemented in process ADSPO4AAP, from which a selection can be made using switch $SWAdsP$. The oxygen concentration dependent option $SWAdsP = 2$ is fully generic, meaning that it can be applied both to water layers and sediment layers. The adsorption of phosphate in the sediment is not considered, when phosphate in the sediment is modeled as a number of 'inactive' substances.

The process has been implemented for the following substances:

- ◇ dissolved PO4 and adsorbed AAP.

Table 3.5 provides the definitions of the parameters occurring in the formulations. The concentrations of adsorbing inorganic matter (Cim_{1-3}) and the dissolved oxygen concentration (Cox) can be either calculated by the model or imposed on the model via the input.

In case the S1-S2 option is applied for the sediment, slow desorption from AAPS1 and AAPS2 can be taken into account by processes DESO_AAPS1 and DESO_AAPS2 (see the formulations in section 8.4, Mineralization of detritus in the sediment (S1/2)).

Formulation

The three options regarding the formulation of the adsorption of phosphate to sediment particles range from ultimately simplified to rather complex pH- and DO dependent adsorption. The adsorption capacity of (suspended) inorganic sediment can be calculated in two different ways. The selection is made with switch parameter $SWVnAdsP$. The default version ($SWVnAdsP$=0.0) calculates the adsorption capacity from the total iron fraction in (suspended) inorganic sediment, whereas version ($SWVnAdsP$=1.0) calculates the adsorption capacity from the individual inorganic matter concentrations IM_{1-3} and pertinent iron fractions. For the eye of the user the versions are only different with respect to the names of several input parameters, see Table 3.5 and the directives for use.

Simplified equilibrium partitioning (SWAdsP = 0)
Instantaneous reversible equilibrium sorption is assumed. The adsorbed phosphate is quantified as a constant fraction of the total inorganic phosphate concentration, which implies a constant ratio between the dissolved and adsorbed phosphate concentrations:

$$Kdph = \frac{Cphd_e}{Cpha_e}$$

where:

$Cpha_e$	equilibrium adsorbed phosphate concentration [gP m$^{-3}_{\ell}$]
$Cphd_e$	equilibrium dissolved phosphate concentration [gP m$^{-3}_{\ell}$]
$Kdph$	distribution coefficient [-]

Consequently, adsorption in this formulation is not proportional to the sorption capacity of sediment.

The equilibrium adsorbed concentration follows from:

$$Cpha_e + Cphd_e = Cpha + Cphd$$

$$Cpha_e = \frac{Cpha + Cphd}{1 + Kdph}$$

where:

$Cpha$	the adsorbed phosphate concentration after the previous time-step [gP m^{-3}_{ℓ}]
$Cphd$	the dissolved phosphate concentration after the previous time-step [gP m^{-3}_{ℓ}]

The sorption rate is calculated as:

$$Rsorp = \frac{Cpha_e - Cpha}{\Delta t}$$

where:

Δt	computational time-step [d]

Simplified Langmuir adsorption (SWAdsP = 1)

The adsorption equilibrium can be considered as a chemical equilibrium described with the following simplified reaction equation:

$$ADS + P \Leftrightarrow ADSP$$

The kinetics of the reaction saturate with respect to the amount of adsorption sites (e.q. the adsorption capacity), which according to Langmuir can be taken into account with the following equilibrium equation:

$$Kads = \frac{Cpha_e \times \phi}{Cphd_e \times Cads_e}$$

where:

$Cads_e$	equilibrium concentration of free adsorption sites in P equivalents [gP m^{-3}_{ℓ}]
$Cpha_e$	equilibrium adsorbed phosphate concentration [gP m^{-3}_{ℓ}]
$Cphd_e$	equilibrium dissolved phosphate concentration [gP m^{-3}_{ℓ}]
$Kads$	adsorption equilibrium constant [m^3 gP^{-1}]
ϕ	porosity [-]

The free adsorbent is a fraction of the total adsorbent concentration. This fraction becomes infinitely small at an abundance of phosphate, which prevents the further increase of the concentration of adsorbed phosphate (see Fig. 3.3 and 3.4). The total adsorbent concentration $Cadst$ is proportional to the suspended sediment concentration. The proportionality factor is defined as the fraction reactive iron in suspended sediment:

$$Cadst = fcap \times \sum_{i=1}^{3}(ffe_i \times Cim_i)$$

$$fim_i = (ffe_i \times Cim_i) / \sum_{i=1}^{3}(ffe_i \times Cim_i)$$

where:

$Cadst$	total concentration of adsorption sites [gP m^{-3}_{ℓ}]
Cim_i	concentration of inorganic matter fractions i=1, 2, 3 [gDW.m^{-3}_{ℓ}]
fim_i	fraction of adsorbed phosphate bound to inorganic matter fractions i=1, 2, 3 [-]

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$fcap$	phosphate adsorption capacity of inorganic matter [gP gFe^{-1}]
ffe_i	fraction reactive iron(III) in inorganic matter fractions i=1, 2, 3 [gFe gDW^{-1}]

The fractions fim_i are available as output parameters to be used for the calculation of the settling of adsorbed phosphate connected with the settling of the inorganic matter fractions.

The equilibrium concentrations can be approximated with:

$$Cpha_e + Cphd_e = Cpha + Cphd \tag{3.2}$$
$$Cads_e = Cads = Cadst - Cpha \tag{3.3}$$

where:

$Cads$	the concentration of free ads. sites after the previous time-step [gP m$^{-3}_{\ell}$]
$Cpha$	the adsorbed phosphate concentration after the previous time-step [gP m$^{-3}_{\ell}$]
$Cphd$	the dissolved phosphate concentration after the previous time-step [gP m$^{-3}_{\ell}$]
e	index for the chemical equilibrium value

The above equations result in the following equation for the equilibrium adsorbed phosphate concentration:

$$Cpha_e = (Cpha + Cphd) / \left(1 + \frac{\phi}{Kads \times Cads}\right)$$

if $Cads < 0.0$ then $Cphae = 0.9 \times (31\,000 \times \phi) \times Cadst$

The above correction applies to a situation where imposed initial AAP would be larger than the adsorption capacity.

Considering (potentially) slow kinetics delivers for the sorption rate:

$$Rsorp = ksorp \times (Cphae - Cpha)$$

where:

$ksorp$	sorption reaction rate [d^{-1}]
$Rsorp$	adsorption or desorption rate [gP m$^{-3}_{\ell}$ d^{-1}]

Comprehensive Langmuir adsorption (SWAdsP = 2)

A more comprehensive description of the Langmuir adsorption equilibrium must include the dependency of the pH and the temperature with concentrations on a molar basis (Smits and Beek (2013)):

$$ADS(OH)_a + P \Leftrightarrow ADSP + a \times OH$$

$$Kads = \frac{Cpha_e \times OH^a}{Cphd_e \times Cads_e}$$

$$Kads = Kads_{20} \times ktads^{(T-20)}$$

$$OH = 10^{-(14-pH)}$$

where:

a	stochiometric reaction constant [-]

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$Cads_e$	equilibrium concentration of free adsorption sites [molFe l_w^{-1}]
$Cpha_e$	equilibrium adsorbed phosphate concentration [molP l_w^{-1}]
$Cphd_e$	equilibrium dissolved phosphate concentration [molP l_w^{-1}]
$Kads$	adsorption equilibrium constant [(mol l^{-1})$^{a-1}$]
$ktads$	temperature coefficient for adsorption [-]
OH	molar hydroxyl concentration [mol l_w^{-1}]
pH	acidity [-]
e	index for the chemical equilibrium value

The free adsorbent is a fraction of the total adsorbent concentration. The total adsorbent concentration $Cadst$ is proportional to the actual adsorption capacity of suspended sediment, which is coupled to the reactive iron(III) fraction, and the concentration suspended sediment. The actual adsorption capacity depends on the redox status of the total reactive iron fraction. Consequently, the total adsorbent concentration follows from:

$$Cadst = fcor \times \sum_{i=1}^{3}(ffe_i \times Cim_i) \times \frac{1}{56,000 \times \phi}$$

$$fcor = 1.0 \quad \text{if} \quad Cox \geq Coxc \times \phi$$
$$fcor = ffeox \quad \text{if} \quad Cox < Coxc \times \phi$$

$$fim_i = (ffe_i \times Cim_i) / \sum_{i=1}^{3}(ffe_i \times Cim_i)$$

where:

$Cadst$	total molar concentration of adsorption sites [molFe l_w^{-1}]
Cim_i	concentration of inorganic matter fractions i=1,2,3 [gDW m_b^{-3}]
Cox	dissolved oxygen concentration [g m_b^{-3}]
$Coxc$	critical dissolved oxygen concentration [g m_w^{-3}]
$fcor$	correction factor for the oxidised iron(III) fraction [-]
fim_i	fraction of adsorbed phosphate bound to inorganic matter fractions i=1, 2, 3 [-]
ffe_i	fraction of reactive iron in inorganic matter fractions i=1,2,3 [gFe gDW^{-1}]
$ffeox$	fraction of oxidised iron(III) in the reactive iron fraction [-]
ϕ	porosity [-]

The fractions fim_i are available as output parameters to be used for the calculation of the settling of adsorbed phosphate connected with the settling of the inorganic matter fractions.

The equilibrium concentrations can be approximated with:

$$Cpha_e + Cphd_e = \frac{(Cpha + Cphd)}{31\,000 \times \phi}$$

$$Cads_e = Cads = Cadst - \frac{Cpha}{31\,000 \times \phi}$$

where:

$Cads$	the concentration of free ads. sites after the previous time-step [molFe l_w^{-1}]
$Cpha$	the adsorbed phosphate concentration after the previous time-step [gP m_b^{-3}]
$Cphd$	the dissolved phosphate concentration after the previous time-step [gP m_b^{-3}]
e	index for chemical equilibrium value

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The above equations result in the following equation for the equilibrium adsorbed phosphate concentration:

$$Cpha_e = \frac{(Cpha + Cphd)}{31\,000 \times \phi \times \left(1 + \frac{OH^a}{Kads \times Cads}\right)}$$

Considering (potentially) slow kinetics delivers for the sorption rate:

$$Rsorp = ksorp \times (31\,000 \times \phi \times Cpha_e - Cpha)$$

where:

$ksorp$ sorption reaction rate [d^{-1}]

A positive value of the adsorption flux $Rsorp$ represents adsorption of $PO4$, a negative value represents desorption of $PO4$.

Directives for use

- Version $SWVnAdsP = 0.0$ uses $RcAdsPgem$ as input name for the sorption rate in the case of formulation option $SWAdsP = 2$.
  Version $SWVnAdsP = 0.0$ uses fr_Fe as input name for the fraction of reactive iron in inorganic matter in the cases of formulation options $SWAdsP = 1$ and 2.
- When using formulation option $SWAdsP = 0$, an indicative value for $KdPO4AAP$ is 0.5.
- Using data of Stumm and Morgan (1996) , it can be deduced that $KadsP_20$ and $a_OH - PO4$ may be approximately equal to respectively 3.8 (mole l^{-1})$^{a-1}$ and 0.2. These values relate to the sorption of ortho-phosphate onto $\alpha - FeOOH$ (goethite) within a pH range of 6 to 9, approximately at a temperature of 20 °C. Amorphous iron coating of sediment may have a much higher adsorption constant (≈1000).
- When dissolved oxygen (OXY) is not simulated, OXY must be imposed as the actual concentration times porosity for option 2 ($SWAdsP = 2$). This is necessary, because the formulations are based on simulated OXY, which is calculated internally as bulk concentration. The critical concentration $CrOXY$, however, is to be imposed as the actual concentration in (pore) water.
- When simulating the “inactive” substances in the sediment $AAPS1$ and $AAPS2$, the sorption process only affects AAP in the water column. However, slow desorption in the sediment can be taken into account with processes DESO_AAPS1 and DESO_AAPS2.
- AAP is also affected by settling and resuspension. The settling of AAP is coupled to the settling of inorganic matter fractions $IM1 - 3$, the fine inorganic matter fraction $IM1$ in particular since AAP is predominantly adsorbed to $IM1$. When $IM1 - 3$ are not modelled explicitly but imposed, the settling velocity of AAP should be equal to the settling velocity of the fine inorganic matter fraction $IM1$.
- The phosphorus fractions $FPIM1$, $FPIM2$ and $FPIM3$ ($= fim_i$) in the inorganic matter fractions are output parameters, that are used to correct the settling flux for differences in the settling velocities of $IM1 - 3$. The fractions add up to 1.
- The iron fraction in (suspended) sediment bound in redox stable minerals such as clay is not part of the reactive iron fraction. The reactive iron fraction is probably smaller than the redox sensitive iron fraction, because a part of this fraction is not available for surface reactions such as sorption.

Additional references

WL | Delft Hydraulics 1992a, WL | Delft Hydraulics (1997)

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Table 3.5: *Definitions of the parameters in the above equations for ADSPO4AAP. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
a	a_OH-PO4	stochiometric reaction constant for pH-dependency	-
Cim_i	IMi	conc. of inorg. matter fractions i = 1,2,3	gDW $m^{-3}_{\mathscr{b}}$
Cox	OXY	dissolved oxygen concentration	g $m^{-3}_{\mathscr{b}}$
$Coxc$	Cc_oxPsor	critical DO concentration for iron reduction	g $m^{-3}_{\mathscr{w}}$
$Cpha$	AAP	adsorbed phosphate concentration	gP $m^{-3}_{\mathscr{b}}$
$Cphd$	$PO4$	dissolved phosphate concentration	gP $m^{-3}_{\mathscr{b}}$
$fcap$	$MaxPO4AAP$	phosphate adsorp. capacity of inorg. matter	gP gFe^{-1}
fim_i	–	fraction ads. phosphate in inorg. matter fr. i = 1,2,3	-
ffe_i	fr_FeIMi	fraction react. iron in inorg. fr. i=1,2,3 ($SWVnAdsP$=1)	gFe gDW^{-1}
„	fr_Fe	fraction reactive iron in inorg. matter ($SWVnAdsP$=0)	gFe gDW
$ffeox$	fr_Feox	fraction oxidised iron(III) in the reactive iron fraction	-
$Kdph$	$KdPO4AAP$	distribution coefficient ($SWAdsP = 0$; see directives!)	-
$Kpads$	$KdPO4AAP$	adsorption eq. constant ($SWAdsP = 1$)	m^3 gP^{-1}
$Kads_{20}$	$KadsP_20$	molar adsorption equil. const. ($SWAdsP = 2$; see directives!)	$(mol\ l^{-1})^{a-1}$
$ksorp$	$RCAdPO4AAP$	sorption reaction rate ($SWVnAdsP = 1$)	d^{-1}
„	$RcAdsPgem$	sorption reaction rate ($SWVnAdsP = 0$)	d^{-1}
$ktads$	$TCKadsP$	temperature coefficient for adsorption	-
OH	–	hydroxyl concentration	mol l^{-1}
pH	pH	acidity	-
$Rsorp$	–	sorption rate	g $m^{-3}_{\mathscr{b}}$ d^{-1}
$SWAdsP$	$SWAdsP$	switch for selection of the formulation options	-
-	$SWVnAdsP$	switch for selection of the original (= 0.0) or the advanced (= 1.0) formulations	-
T	$Temp$	temperature	°C
ϕ	$POROS$	porosity	$m^3_{\mathscr{w}}$ $m^{-3}_{\mathscr{b}}$
Δt	$Delt$	computational time-step	d

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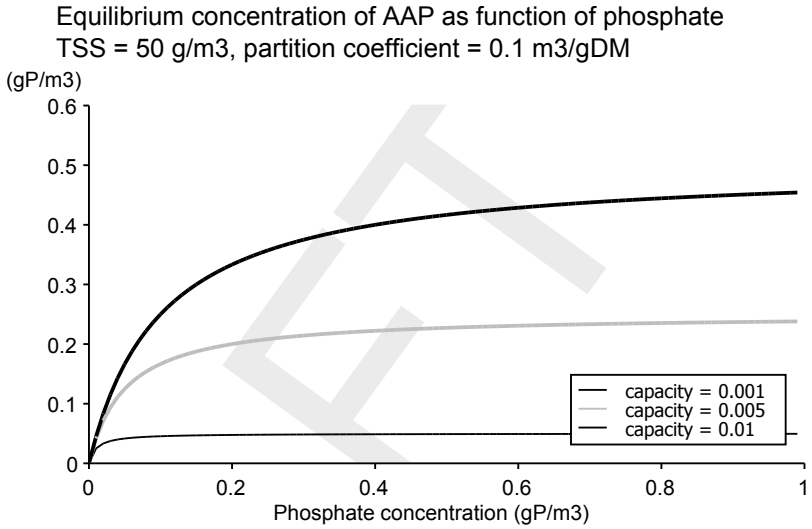

Figure 3.3: *Variation of the equilibrium concentration AAP (eqAAP) as a function of PO4 and the maximum adsorption capacity (MaxPO4AAP).*

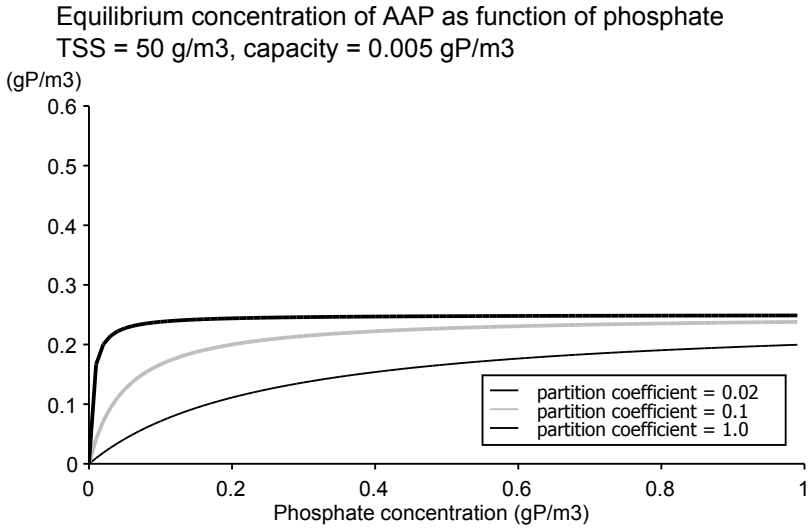

Figure 3.4: *Variation of the equilibrium concentration of AAP (eqAAP) as a function of PO4 and the partition coefficient of PO4 (KdPO4AAP).*

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3.5 Formation of vivianite

PROCESS: VIVIANITE

At reducing conditions phosphate may precipitate with iron(II) as vivianite (iron(II) phosphate: $Fe_3[PO_4]_2$). Vivianite is thermodynamically unstable at oxidising conditions. At the presence of dissolved oxygen iron(II) in vivianite is oxidised into iron(III), resulting in the subsequent dissolution of vivianite, the precipitation of iron(III)oxyhydroxides and the adsorption of phosphate to these minerals.

The precipitation of vivianite only occurs in a supersaturated solution at the absence of dissolved oxygen, and actually when also nitrate has depleted. These conditions usually only occur in the reducing sediment, just below an oxidising top layer. Precipitation is not only temperature dependent, but also pH dependent due to the acid-base equilibria to which both dissolved phosphate and iron are subjected. However, in a simplified approach the pH dependency may be ignored, since the pH is rather constant in the sediment.

Vivianite is transported to the oxidising top layer mainly by bioturbation. Oxidative dissolution of vivianite follows, a process the kinetics of which are not straight forward. The oxidation with dissolved oxygen seems to be a temperature dependent surface reaction mainly, due to the low solubility and slow dissolution of the mineral. The pH-dependency of the surface reaction seems to be rather weak and is therefore ignored.

Literature regarding sediment diagenesis as well as modelling exploits have provided indications for the formation of other stable phosphate minerals, hardly sensitive to the redox conditions. Such stable minerals most probably are apatite like calcium phosphate minerals. Another explanation for slow remobilisation of phosphate might be found in rather permanent inclusion of phosphate in various oxyhydroxides.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process VIVIANITE has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. The precipitation of phosphate in the sediment is not considered, when phosphate in the sediment is modeled as a number of 'inactive' substances.

The process has been implemented for the following substances:

- ◇ dissolved PO4 and VIVP.

Table 3.6 provides the definitions of the parameters occurring in the formulations. The dissolved oxygen concentration (Cox) can be either calculated by DELWAQ or imposed to DELWAQ via the input.

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Formulation

The precipitation and dissolution equilibrium of vivianite can be described with the following simplified reaction equation:

$$3\ \mathrm{Fe}^{2+} + 2\ \mathrm{PO}_4^{3-} \Leftrightarrow \mathrm{Fe}_3(\mathrm{PO}_4)_2$$

The precipitation rate is formulated with first-order kinetics, with the difference between the actual dissolved phosphate concentration and the equilibrium dissolved concentration as driving force (Smits and Beek (2013)):

$$Rprc = \begin{cases} frp \times kprc \times (\frac{Cphd}{\phi} - Cphde) \times \phi \\ 0.0 \qquad \text{if} \quad Rprc < 0.0 \end{cases}$$

$$kprc = kprc_{20} \times ktprc^{(T-20)}$$

$$frp = \begin{cases} 1.0 & \text{if} \quad Cox < Coxc \times \phi \\ frp = 0.0 & \text{if} \quad Cox \geq Coxc \times \phi \end{cases}$$

with:

Cox	dissolved oxygen concentration [g m_{ℓ}^{-3}]
$Coxc$	critical dissolved oxygen concentration [g m_w^{-3}]
$Cphd$	dissolved phosphate concentration [gP m_{ℓ}^{-3}]
$Cphde$	equilibrium dissolved phosphate concentration [gP m_w^{-3}]
frp	switch concerning the redox conditions for precipitation [-]
$kprc$	precipitation reaction rate [d^{-1}]
$ktprc$	temperature coefficient for precipitation [-]
$Rprc$	rate of precipitation [g m_{ℓ}^{-3} d^{-1}]
T	temperature [°C]
ϕ	porosity [-]

The dissolution of vivianite is probably characterised by two steps: a) the oxidation of dissolved Fe^{2+}, and b) the dissolution of vivianite at a very low Fe^{2+} concentration. The first depends on the dissolved oxygen concentration, the latter on the quantity of vivianite present. (However, the main driving force of the dissolution process might be the difference of the "equilibrium" Fe^{2+} concentration near the vivianite crystals and the average very low dissolved Fe^{2+} concentration.) The dissolution rate can be formulated pragmatically as follows:

$$Rsol = \begin{cases} frd \times ksol \times Cphpr \times \frac{Cox}{\phi} \\ 0.0 \qquad \text{if} \quad Rsol < 0.0 \end{cases}$$

$$ksol = ksol_{20} \times ktsol^{(T-20)}$$

$$frp = \begin{cases} 1.0 & \text{if} \quad Cox < Coxc \times \phi \\ frp = 0.0 & \text{if} \quad Cox \geq Coxc \times \phi \end{cases}$$

with:

$Cphpr$	precipitated phosphate concentration [gP m_{ℓ}^{-3}]
frd	switch concerning the redox conditions for dissolution [-]
$ksol$	dissolution reaction rate [m_w^3 gO_2^{-1} d^{-1}]

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$ktsol$	temperature coefficient for dissolution [-]
$Rsol$	rate of dissolution [g m_{ℓ}^{-3} d^{-1}]

The dissolution process must stop at the depletion of vivianite. Therefore, the dissolution flux is made equal to half the concentration of vivianite $VIVP$ divided with timestep Δt, when the flux as calculated with the above formulation is larger than $VIVP/\Delta t$.

Directives for use

- ◇ The formation of stable mineral "apatite" can also be included in the model. As an alternative, the user may ignore this substance and provide a (very) slow dissolution rate in the input for process VIVIANITE.
- ◇ The equilibrium dissolved phosphate concentration follows from the solubility product of vivianite, the dissolved Fe(II) concentration and the pH. Solubility products determined in the laboratory tend to underestimate the equilibrium concentration, since the mineral in natural sediment has lower stability due to the formation of amorphous, impure and coated vivianite. For similar reasons the actual reaction rates of precipitation and dissolution may deviate substantially from experimentally determined values. The following values are representative for fresh water sediments: $EqVIVDisP = 0.05$ gP m_{w}^{-3}, $RcPrecP20 = 0.8$ d^{-1}, $RcDissP20 = 0.005$ m^3 gO_2^{-1} d^{-1}.
- ◇ When DO is not simulated, OXY must be imposed as the actual concentration times porosity for option 2 ($SWAdsP = 2$). This is necessary, because the formulations are based on simulated DO, which is calculated internally as bulk concentration. The critical concentration $CrOXY$, however, is to be imposed as the actual concentration in (pore) water. $CrOXY$ is also used for the adsorption process ADSPO4AAP.
- ◇ When simulating the "inactive" substances in the sediment $AAPS1$ and $AAPS2$, the precipitation process only affects $PO4$ and $VIVP$ in the water column. $VIVP$ settles and ends up in $AAPS1$ and $AAPS2$.

Additional references

Santschi et al. 1990, Smits and Molen 1993, Stumm and Morgan 1996, WL | Delft Hydraulics 1997

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Table 3.6: *Definitions of the parameters in the above equations for VIVIANITE. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
Cox	OXY	dissolved oxygen concentration	g $m^{-3}_{\mathscr{b}}$
$Coxc$	Cc_oxPsor	critical DO concentration for iron reduction	g $m^{-3}_{\mathscr{w}}$
$Cphd$	$PO4$	dissolved phosphate concentration	gP $m^{-3}_{\mathscr{b}}$
$Cphde$	$EqVIVDisP$	equilibrium dissolved phosphate concentration	gP $m^{-3}_{\mathscr{w}}$
$Cphpr$	$VIVP$	precipitated vivianite phosphate concentration	gP $m^{-3}_{\mathscr{b}}$
frd	–	switch concerning redox conditions for dissolution	-
frp	–	switch concerning redox conditions for precipitation	-
$kprc_{20}$	$RcPrecP20$	vivianite precipitation reaction rate	d^{-1}
$ktprc$	$TcPrecipP$	temperature coefficient for precipitation	-
$ksol_{20}$	$RcDissP20$	vivianite dissolution reaction rate	$m^3_{\mathscr{w}}$ gO_2^{-1} d^{-1}
$ktsol$	$TcDissolP$	temperature coefficient for dissolution	-
$Rprc$	–	vivianite precipitation rate	g $m^{-3}_{\mathscr{b}}$ d^{-1}
$Rsol$	–	vivianite dissolution rate	g $m^{-3}_{\mathscr{b}}$ d^{-1}
T	$Temp$	temperature	°C
Δt	$Delt$	timestep	d
ϕ	$POROS$	porosity	$m^3_{\mathscr{w}}$ $m^{-3}_{\mathscr{b}}$

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3.6 Formation of apatite

PROCESS: APATITE

Phosphate may precipitate in various minerals that are stable under both oxidizing and reducing conditions. In literature regarding sediment diagenesis and sediment modelling, indications can be found for the formation of such stable minerals. As contrasting with vivianite that is only stable under reducing conditions, the identity of these stable minerals has not been determined unequivocally. The formation of pure calcium apatite in sediment may not be very likely due to the high pH required (calcium phosphate: Ca3[PO4]2); stable at pH$>$8.5). However, the co-precipitation of phosphate with several carbonates and sulfides and even the rather permanent inclusion of phosphate in various oxyhydroxides seem certainly possible, also at a pH of 7. Such a co-precipitation might be induced by the adsorption of phosphate on the surface of calcite-like minerals. For pragmatic reasons the stable phosphate minerals are named “apatite” in this documentation.

The precipitation of “apatite” only occurs in a supersaturated solution. Apatite is primarily formed in deeper sediment layers. It is exchanged among the sediment layers by means of bioturbation. Since supersaturation may not occur near the sediment-water interface, the apatite formed in deeper layers may dissolve slowly in the top sediment layer. The actual rate of the dissolution will be highly dependent on the dissolution of co-precipitated calcite-like minerals. Usually, these minerals do not dissolve significantly. Dissolution may then proceed very slowly by means of solid matter and surface diffusion of phosphate ions.

Precipitation is not only temperature dependent, but also pH dependent due to the acid-base equilibria to which both dissolved phosphate and calcite-like minerals are subjected. However, in a simplified approach the pH dependency may be ignored, since the pH is rather constant in the sediment.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process APATITE has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. The precipitation of phosphate in the sediment is not considered, when phosphate in the sediment is modeled as a number of ‘inactive’ substances.

The process has been implemented for the following substances:

- ◇ dissolved PO4 and APATP.

Table 3.7 provides the definitions of the parameters occurring in the formulations.

Formulation

Even when co-precipitating with calcite, the precipitation and dissolution equilibrium of apatite can be described with the following simplified reaction equation:

$$3\ \mathrm{Ca}^{2+} + 2\ \mathrm{PO}_4^{3-} \quad \Leftrightarrow \quad \mathrm{Ca}_3(\mathrm{PO}_4)_2$$

The calcium concentration is usually very constant in sediment pore water. Therefore, the precipitation rate is formulated with first-order kinetics, with the difference between the actual dissolved phosphate concentration and the equilibrium dissolved concentration as driving

force. In order to allow better control over the precipitation of apatite relative to the precipitation of vivianite the precipitation rate is formulated as follows (Smits and Beek (2013)):

$$Rprc = frr \times kprc \times \left(\frac{Cphd}{\phi} - Cphde \right) \times \phi$$

$$Rprc = 0.0 \quad \text{if} \quad Rprc < 0.0$$

$$kprc = kprc_{20} \times ktprc^{(T-20)}$$

with:

$Cphd$	dissolved phosphate concentration [gP m_{ℓ}^{-3}]
$Cphde$	equilibrium dissolved phosphate concentration [gP m_{w}^{-3}]
frr	ratio of the apatite and vivianite precipitation reaction rates [-]
$kprc$	precipitation reaction rate [d^{-1}]
$ktprc$	temperature coefficient for precipitation [-]
$Rprc$	rate of precipitation [g m_{ℓ}^{-3} d^{-1}]
T	temperature [°C]
ϕ	porosity [-]

The dissolution of apatite is driven by undersaturation in the pore water. The rate is dependent on the extent of undersaturation as well as the concentration of apatite. The dissolution rate is formulated pragmatically according to second-order kinetics as follows:

$$Rsol = ksol \times Cphpr \times \left(Cphde - \frac{Cphd}{\phi} \right)$$

$$Rsol = 0.0 \quad \text{if} \quad Rsol < 0.0$$

$$ksol = ksol_{20} \times ktsol^{(T-20)}$$

with:

$Cphpr$	precipitated phosphate concentration [gP m_{ℓ}^{-3}]
$ksol$	dissolution reaction rate [m_{w}^{3} gP^{-1} d^{-1}]
$ktsol$	temperature coefficient for dissolution [-]
$Rsol$	rate of dissolution [g m_{ℓ}^{-3} d^{-1}]

The dissolution process must stop at the depletion of apatite. Therefore, the dissolution flux is made equal to half the concentration of apatite $APATP$ divided with timestep Δt, when the flux as calculated with the above formulation is larger than $APATP/\Delta t$.

Directives for use

- ◇ The formation of vivianite should be included in the model too.
- ◇ The equilibrium dissolved phosphate concentration would follow from the solubility product of the mineral formed. Solubility products determined in the laboratory tend to underestimate the equilibrium concentration, since the mineral in natural sediment has lower stability due to the formation of amorphous, impure, co-precipitated and coated apatite. For similar reasons the actual reaction rates of precipitation and dissolution may deviate substantially from experimentally determined values. Since the identity of the phosphate mineral is poorly known, the equilibrium concentration and the reaction rates are typically calibration parameters. However, a good starting point can be found in equalising the equilibrium concentrations and the precipitation rates for vivianite and apatite, implying that $RatAPandVP = 1.0$. For a start the dissolution rate may be set at zero.

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◇ When simulating the “inactive” substances in the sediment $AAPS1$ and $AAPS2$, the precipitation process only affects $PO4$ and APATP in the water column. $APATP$ settles and ends up in $AAPS1$ and $AAPS2$.

Additional references

Santschi et al. (1990), Stumm and Morgan (1996), WL | Delft Hydraulics (1994b)

Table 3.7: *Definitions of the parameters in the above equations for APATITE. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
$Cphd$	$PO4$	dissolved phosphate concentration	gP $m^{-3}_{\mathscr{b}}$
$Cphde$	$EqAPATDisP$	equilibrium dissolved phosphate concentration	gP $m^{-3}_{\mathscr{w}}$
$Cphpr$	$APATP$	precipitated “apatite” phosphate concentration	gP $m^{-3}_{\mathscr{b}}$
frr	$RatAPandVP$	ratio of the apatite and vivianite precipitation rates	-
$kprc_{20}$	$RcPrecP20$	vivianite precipitation reaction rate	d^1
$ktprc$	$TcPrecipP$	temperature coefficient for precipitation	-
$ksol_{20}$	$RcDisAP20$	apatite dissolution reaction rate	$m^3_{\mathscr{w}}$ gP^{-1} d^{-1}
$ktsol$	$TcDissolP$	temperature coefficient for dissolution	-
$Rprc$	–	apatite precipitation rate	g $m^{-3}_{\mathscr{b}}$ d^{-1}
$Rsol$	–	apatite dissolution rate	g $m^{-3}_{\mathscr{b}}$ d^{-1}
T	$Temp$	temperature	°C
Δt	$Delt$	timestep	d
ϕ	$POROS$	porosity	$m^3_{\mathscr{w}}.m^{-3}_{\mathscr{b}}$

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3.7 Dissolution of opal silicate

PROCESS: DISSI

Opal silicate is produced by diatoms, that strengthen their cell walls with silicate skeletons. When diatom cells have died, the skeleton remains start to dissolve and settle on the sediment. The physical-chemical dissolution process continues in the sediment, since pore water is generally undersaturated with respect to opal silicate. However, the process is retarded strongly due to the adsorption of various substances such as metal ions (Fe, Al, Mn) onto the silicate frustules and due to coating of these frustules with iron and manganese minerals. Consequently, opal silicate is rather abundantly present in most sediments.

Dissolved silicate may adsorb onto iron and aluminium oxyhydroxides and silicates, and may also precipitate in extremely stable silicate minerals. However, adsorption is rather weak and reversible. Precipitation proceeds extremely slow. Both types of processes are rather poorly understood, and have been ignored in the model for all these reasons.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process DISSI has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. When silicate in the sediment is modeled as a number of 'inactive' substances $DETSiS1/2$ and $OOSiS1/2$, the dissolution of opal silicate in the sediment is formulated as simple first-order decomposition processes BMS1/2_(i) linked up with the decomposition of detritus.

The process has been implemented for the following substances:

- ◇ dissolved Si and Opal.

Table 3.8 provides the definitions of the parameters occurring in the formulations.

Formulation

The dissolution of opal silicate is formulated according to second-order (e.g. double first-order) or first-order kinetics. In the case of second-order kinetics the concentration of opal silicate and the difference between the actual dissolved silicate concentration and the equilibrium dissolved concentration determine the dissolution rate.

For option $SWDisSi$ = 0.0 the dissolution rate is formulated according to second order kinetics (Smits and Beek (2013)):

$$Rsol = ksol \times Csip \times (Cside - \frac{Csid}{\phi})$$

where:

$Csid$	dissolved silicate concentration [gSi $m^{-3}_{\mathscr{b}}$]
$Cside$	equilibrium dissolved silicate concentration [gSi $m^{-3}_{\mathscr{w}}$]
$Csip$	opal silicate concentration [gSi $m^{-3}_{\mathscr{b}}$]
$ksol$	dissolution reaction rate [$m^{3}_{\mathscr{w}}$ gSi^{-1} d^{-1}]
ϕ	porosity [-]

For option $SWDisSi$ = 1.0 the dissolution rate is formulated according to first order kinetics:

$$Rsol = ksol \times Csip$$

where:

$ksol$	dissolution reaction rate [d^{-1}]

In both cases the rate is dependent on temperature:

$$ksol = ksol_{20} \times ktsol^{(T-20)}$$

where:

$ksol$	dissolution reaction rate [m^3_w gSi^{-1} d^{-1} or d^{-1}]
$ktsol$	temperature coefficient for dissolution [-]
T	temperature [°C]

Directives for use

- ◇ The type of kinetics to be applied is selected with option parameter $SWDissi$ (=0.0 for second order kinetics, =1.0 for first order kinetics).
- ◇ The equilibrium dissolved silicate concentration follows from the solubility product of opal silicate and the pH. Solubility products determined in the laboratory tend to overestimate the equilibrium concentration, since the mineral in natural sediment has higher stability due to the formation of impurities and coatings. For similar reasons the actual reaction rates of dissolution may deviate substantially from experimentally determined values. The following values are representative for fresh water sediments: $EqDisSi$ = 10 gSi m^{-3}_w, $RcDisSi20$ = 0.09 d^{-1}.
- ◇ When simulating “inactive” substances in the sediment, the dissolution process only affects Si and $Opal$ in the water column. $Opal$ settles and ends up in $DETSiS1$ (and $DETSiS2$), subjected to first-order decomposition.

Additional references

Berner (1974), DiToro (2001), Schink and Guinasso (1978), Smits and Molen (1993), Stumm and Morgan (1996), Vanderborght et al. (1977), WL | Delft Hydraulics (1997)

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Table 3.8: *Definitions of the parameters in the above equations for DISSI. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	**Name in input**	**Definition**	**Units**
$Csid$	Si	dissolved silicate concentration	gSi $m^{-3}_{\mathscr{b}}$
$Cside$	Ceq_DisSi	equilibrium dissolved silicate concentration	gSi $m^{-3}_{\mathscr{w}}$
$Csip$	$Opal$	opal silicate concentration	gSi $m^{-3}_{\mathscr{b}}$
$ksol_{20}$	$RcDisSi20$	second order dissolution reaction rate, or first order dissolution rate	$m^3_{\mathscr{w}}$ gSi^{-1} d^{-1} d^{-1}
$ktsol$	$TcDisSi$	temperature coefficient for dissolution	-
$Rsol$	-	dissolution rate	g $m^{-3}_{\mathscr{b}}$ d^{-1}
$SWDissi$	$SWDissi$	option (=0.0 for second order, =1.0 for first order)	-
T	$Temp$	temperature	°C
ϕ	$POROS$	porosity	$m^3_{\mathscr{w}}$ $m^{-3}_{\mathscr{b}}$

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4 Primary producers

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4.1 Introduction to primary production

Within the processes library there are two distinct approaches to model primary production, that is, the growth and decay of phytoplankton. The first approach, called BLOOM, allows the user to model several groups of algae and types within these groups. While it is a very flexible method, it requires some understanding of the physiology of algae and the ecosystem that is being modelled. The second approach, called DYNAMO, is limited to two algal groups, "green algae" and "diatoms". As it is simpler, it may be easier to use (less coefficients with which to describe the properties of the algae, for instance). This simplicity also has a disadvantage, as the results will in general be less good than with a properly set up model using the BLOOM approach.

The two approaches are mutually exclusive: either use BLOOM or use DYNAMO, not both. This also holds, to a certain degree, to the input parameters. The parameters specific to algae have different names for the two approaches, but the environmental conditions, such as nutrient concentrations and irradiation, are described by the same parameters. For irradiation this requires some attention:

- The irradiation at the surface is always given as the total irradiation (correction for the photoactive fraction is done internally) in [W.m^{-2}].
- As BLOOM is based on the concept of optimising the biomass, its time step is typically 24 hours, you can use 12 and 6 hour time steps as well. The time step should be long enough to make sure that an equilibrium can be achieved. This has three consequences:
  - The irradiance for BLOOM has to be given as a *daily average*, not as hourly or even more frequent values.
  - BLOOM is usually called only once every few time steps of D-Water Quality itself. This is arranged via the parameter *TimMultBl*.
  - As the algae in BLOOM "see" an average amount of irradiation as they are transported over the vertical by mixing processes, the light intensity at the current location is not entirely representative for calculating the growth within the allotted time step. To account for this a special process is used, *VTRANS*. This has a parameter *PeriodVTRA* which controls the details. For most if not all situations, this parameter should be set to 24 hours.
- In contrast, the DYNAMO approach can handle irradiation time series at arbitrarily short intervals.

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4.2 Growth and mortality of algae (BLOOM)

PROCESS: BLOOM, BLOOM_P, ULVAFIX, ULVAFIX_P, PHY_BLO, PHY_BLO_P, DEPAVE, VTRANS, DAYLENGTH

Algae are subject to gross primary production, respiration, excretion, mortality, grazing, resuspension and settling. Net growth (biomass increase) is the result. Net primary production is defined as the gross primary production minus respiration. The phytoplankton module BLOOM includes specific formulations for these processes with the exception of excretion, grazing, resuspension and settling. Excretion is ignored. Grazing, resuspension and settling are similar for other phytoplankton modules in DELWAQ, and are therefore dealt with in separate process descriptions.

BLOOM considers different algae species groups. These groups may be defined as diatoms, green algae, bluegreen algae, flagellates, dinoflagellates, Phaeocystis, Ulva, etc. Diatoms differ from other species among other things by their dependency on dissolved silicon for growth. However, each group may be defined as being any other individual species. Each algae species (group) has several types, that are adapted to specific environments to cope with limiting resources. The types have different properties with respect to nutrient stoichiometry, chlorophyll content and process rates. Depending on which growth factor is currently limiting, the best adapted type of each group is selected. The relevant factors are nitrogen, phosphorus, silicon, carbon and energy (light), meaning that biomass stoichiometry depends on the availability of these factors. This mechanism enables BLOOM to describe phenotypical adaptation of algae under different growth conditions. BLOOM can simulate 30 algae species types (10 species $\times$ 3 types) at maximum. The default parameter values for several phytoplankton groups and types that have been modelled before can be read from a database with Delft3D.

BLOOM uses the technique of linear programming to calculate the optimum distribution of biomass over all algae types. The competition between the species is determined by the ratio of the resource requirement and the nett growth rate. Mathematically this is equivalent to maximizing the net growth rate of the total of all types. For a description of the use of this technique in bloom the user is referred to Los (2009), DBS (1991), and Los (1985). The solution of the optimisation is bound by several constraints: the available nutrient resources, the available amount of energy, the maximum growth rate and the maximum mortality rate.

BLOOM allows to account for mixotrophy and nitrogen fixation, by modification of the nutrient constraints. The amount of available nutrients for mixotrophic algae comprises both inorganic and organic nutrients. Nitrogen fixing algae are able to convert elementary nitrogen (dissolved N_2) into organic nitrogen.

The energy constraint concerns the energy obtained from ambient light intensity. It is expressed as the maximal extinction by phytoplankton where the light intensity is reduced due to self-shading, to a level where the growth rate equals the respiration rate. The relation between the growth rate and light intensity is determined by the light response curve. The light response curve is defined by the user as a table of growth efficiencies at different light intensities. It can be read from a database with Delft3D for the species that have been modelled and calibrated before with BLOOM. The light response curve can be derived from laboratory experiments. Light inhibition has not been included yet in the existing light response curves.

The processes growth, respiration and mortality are part of the constraints used in the optimisation technique. The process rates are corrected for temperature dependency before being used in the optimisation. Mortality is also corrected for salinity stress.

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DELWAQ determines the concentrations of substances from the transport and the process rates. Therefore the BLOOM process should calculate process rates for DELWAQ instead of an optimum species composition. These rates are therefore calculated from the change of biomass divided by the time step.

BLOOM has its own time step within the computational procedure of DELWAQ. Usually, BLOOM's time step is bigger than DELWAQ's time step used for the modelling of mass transport and the other water quality processes. A bigger time step reduces the computation time needed for a simulation. Using a bigger time step requires that the average water depth over BLOOM's time step is determined in view of light limitation. Therefore the process DEPAVE should be activated, calculating the average water depth during each BLOOM time step. This is particularly relevant for cases where the water depth varies significantly during a BLOOM time step such as tidal simulations.

A macro algae species like $Ulva$ or other macrophyte species can be included in BLOOM. This species may both be suspended in the water column and attached to the sediment. The process of resuspension of $Ulva$ is simulated with the process UlvaFix.

The algae processes affect a number of other DELWAQ substances apart from the algae biomass concentrations [gC m^{-3}]. Growth involves the uptake of inorganic nutrients [gN/P/Si/S/C m^{-3}] and the production of dissolved oxygen [gO_2 m^{-3}], and affects alkalinity (pH). Preferential uptake of ammonium over nitrate is included in the model. Mortality produces detritus [gC/N/P m^{-3}] and opal silicate [gSi m^{-3}]. The process rates for these substances are derived from the algae process rates by multiplication with the appropriate stoichiometric constants. These ratios reflect the chemical composition of the biomass of algae types.

All rates in BLOOM are daily averaged. The dissolved oxygen concentration is calculated on a daily average basis unless process VAROXY is included in the model. This process deduces the daily varying dissolved oxygen production rate from the daily average net primary production rate. The process VAROXY is described elsewhere in this manual.

Implementation

The algae module BLOOM can simulate maximally 30 algae species types. BLOOM has been implemented for the following substances:

- ◇ BLOOMALG01 – BLOOMALG30,
- ◇ POC1, PON1, POP1, POS1, POC2, PON2, POP2, POS2, Opal,
- ◇ NH4, NO3, PO4, Si, SO4 SUD, OXY, TIC and ALKA.

The module BLOOM is generic and can be applied for water as well sediment layers, although the algae in sediment layers have no primary production and are subject to mortality. It can also be used in combination with the sediment option S1/S2.

Process BLOOM (plus BLOOM_P) has auxiliary processes UlVAFIX (plus ULVAFIX_P), PHY_BLO (plus PHY_BLO_P), DEPAVE, VTRANS and DAYLENGTH. ULVAFIX adds specific parameters for the "inactive" algae species Ulva. PHY_BLO generates additional output for BLOOM, the overall organic carbon (PHYT), dry matter (ALGDM) and nutrients concentrations (ALGN, ALGP, ALGSi) and the chlorophyll-a concentration (Chlfa). DEPAVE determines the average water depth that algae experience during a time step, which is relevant for tidal water systems. VTRANS produces "tracers" that allow for the determination of average light intensity for algae as resulting from vertical mixing.

Table 4.1 and Table 4.2 provide the definitions of the parameters occurring in the user-defined

input and output. The (default) coefficients for the selected algal types are stored in the file <bloom.spe> which needs to be available in the work directory (see also the end of "Directives for use").

Formulation

In the first four sections formulations are presented for the constraints for growth as included in the optimisation technique (linear programming). This technique delivers the algae biomasses of all species groups and types at the end of a time step by means of solving a set of linear equations and constraints, thereby maximising the total net growth. The constraints are:

1 the nutrient constraints;
2 the energy constraints;
3 the growth constraints; and
4 the mortality constraints.

The rates of growth, production, respiration and mortality are derived from the change of the algae biomasses over a time step. The following sections deal with the formulations for these rates and constraints, and specific additional output. The final sections describe the process of resuspension of $Ulva$ (or other macrophytes) called Ulvafix, and the process DEPAVE, that calculates the averaged depth during a BLOOM time step.

Nutrient constraints

The solution of the linear programming method for the calculation of biomasses of autotrophic algae should satisfy the following set of nutrient balances:

$$Ctnut_k = Cnut_k + \sum_{i=1}^{n} (anut_{k,i} \times Calg_i) - Cnutc_k$$

with:

$anut_{k,i}$	stoichiometric constant of nutrient k originating from dissolved inorganic nutrient over organic carbon in algae biomass [gN/P/Si gC^{-1}], an, aph or asi
$Calg_i$	algae biomass concentration [gC m^{-3}]
$Cnut_k$	concentration of dissolved inorganic nutrient k [gN/P/Si m^{-3}]
$Cnutc_k$	threshold concentration of dissolved inorganic nutrient k [gN/P/Si m^{-3}]
$Ctnut_k$	concentration of total available nutrient k [gN/P/Si m^{-3}]
i	index for algae species type [-]
k	index for nutrients, 1 = nitrogen, 2 = phosphorus, 3 = silicon, 4 = carbon [-]
n	number of algae species types, equal to 15 [-]

Additional requirements are that $Calg_i \geq 0.0$ and $Cnut_k \geq 0.0$. The total available nutrient concentration includes the total dissolved inorganic nutrients and nutrients in phytoplankton. The dissolved nitrogen concentration is the sum of the concentrations of ammonium and nitrate. The threshold concentration is the dissolved nutrient concentration below which algae are no longer able to withdraw this nutrient from the ambient water. The threshold is ignored for total dissolved inorganic carbon (TIC).

Some algae (especially dinoflagellates) are able to use detritus as an additional food source, when resources of dissolved nutrients are low. For these so-called mixotrophic algae the nutrient constraints are modified in a way that more nutrients are available to these algae. Extra constraints are added for the nutrients detritus nitrogen and detritus phosphorus. The

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dissolved nutrient constraints are modified as follows:

$$Cdet2_k = Cdet1_k + \sum_{i=1}^{n} (ad_{k,i} \times Calg_i)$$

$$Ctnut_k = Cnut_k + \sum_{i=1}^{n} ((anut_{k,i} - ad_{k,i}) \times Calg_i) - Cnutc_k$$

with:

$ad_{k,i}$	stoichiometric constant of a nutrient originating from detritus over org. carbon in algae biomass [gN/P gC^{-1}], adn, $adph$ or $adsi$
$Cdet1_k$	concentration of a detritus nutrient at t_1, the beginning of a time step [gN/P mS^{-3}]
$Cdet2_k$	concentration of a detritus nutrient at t_2, the end of a time step [gN/P m^{-3}]
k	index for nutrients, 1 = nitrogen, 2 = phosphorus [-]

Note that these formulations are equivalent to the formulations for autotrophic algae when the stochiometric constants $ad_{k,i}$ obtain the value zero.

Some other algae are able to use elementary nitrogen (N_2) dissolved in the water as a nutrient source. This is established in the constraint in a similar way. Extra nutrient constraints are added to describe the uptake of N_2 by nitrogen fixative algae:

$$Cen2 = Cen1 + \sum_{i=1}^{n} (aen_i \times Calg_i)$$

$$Ctnut_1 = Cnut_1 + \sum_{i=1}^{n} ((anut_{1,i} - aen_i) \times Calg_i) - Cnutc_1$$

with:

aen_i	stoichiometric constant of nitrogen orig. from el. nitrogen in algae biomass [gN gC^{-1}]
$Cen1$	concentration of elementary nitrogen at t_1, the beginning of a time step [gN m^{-3}]
$Cen2$	concentration of elementary nitrogen at t_2, the end of a time step [gN m^{-3}]

The concentration of dissolved elementary nitrogen is assumed never to be limiting, so both concentrations are infinite. Notice that these formulations reduce to the formulations for autotrophic algae when the stoichiometric constants aen_i obtain the value zero.

The limitation of phytoplankton by total dissolved inorganic carbon is only included in BLOOM's optimisation algorithm, when option parameter $SwTICdummy$ has a value 10.0 or higher (default value = 0.0). Alternatively, carbon limitation can be taken into account for BLOOM in a simplified way by scaling of the overall growth rates with a simple limitation factor. This factor, a multiplier on the growth rate, increases linear from zero at TIC = 0.0 to 1.0 at TIC = $KCO2$. The factor is equal to 1.0 for higher TIC.

Sulfur is not a constraint, because it has been included in BLOOM only in the form of the sulfur stored in biomass, assuming that sulfate is always amply available. Sulfate is just taken up proportional to biomass produced and is released from algae biomass on the basis of a constant species independent stoichiometric ratio set at 0.0175 gS/gC.

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Energy constraints (light)

Energy in light (solar radiation) becomes limiting through self shading when the total extinction exceeds the maximum at which growth is just balanced by respiration and mortality. For each type a specific value of the total extinction coefficient $eamax_i$ exists, at which this is the case. On the other hand the total extinction coefficient cannot be smaller than a certain extinction coefficient $eamin_i$, which is equal to the background extinction coefficient augmented with a small contribution by the minimum algae concentation. Hence the extinction coefficient must satisfy the following condition as an additional constraint for the solution of the linear programming method for the calculation of biomasses of algae:

$$eat = \sum_{i=1}^{n} (ea_i \times Calg_i)$$

$$eamin_i \leq eat \leq eamax_i$$

$$eamin_i = eatmin_i - eb$$

$$eamax_i = eatmax_i - eb$$

$$eb = et - eat$$

with:

ea_i	specific extinction coefficient of an algae species type [m^2 gC^{-1}]
eat	total extinction coefficient of all algae [m^{-1}]
eb	extinction by other substances than algae [m^{-1}]
et	total extinction coefficient [m^{-1}]
$eamin_i$	minimum extinction coefficient of algae i connected with background extinction [m^{-1}]
$eatmin_i$	minimum total extinction coefficient connected with background extinction [m^{-1}]
$eamax_i$	maximum extinction coefficient of algae i needed to avoid self shading [m^{-1}]
$eatmax_I$	maximum total extinction coefficient needed to avoid self shading of algae i [m^{-1}]

At a certain critical level of self shading the respective algae species is no longer able to have net growth. The maximally allowed extinction coefficient $eatmax_i$ for algae species type i is determined as the extinction where the light intensity allows for a gross production rate that exactly compensates for the mortality and respiration rates. Gross production is formulated as a potential specific rate multiplied with a light efficiency factor. This factor Ef is a function of the light intensity, the amount of available light ($0.0 \leq Ef \leq 1.0$) The critical efficiency at which no net growth or mortality occurs follows from:

$$Efc_i = \frac{krsp_i + kmrt_i}{kgp_i}$$

with:

Ef	light efficiency factor [-]
Efc_i	critical light efficiency factor [-]
kgp_i	specific growth rate [d^{-1}]
$kmrt_i$	specific mortality rate [d^{-1}]
$krsp_i$	specific maintenance respiration rate [d^{-1}]

Once the critical efficiency factor is known, the pertinent critical light intensity (the total available amount of light) can be obtained from the efficiency versus photosynthic light intensity table in input file <bloominp.frm>. The maximum extinction coefficient $eatmax_i$ is calculated from this critical light intensity and the light intensity at the top of a water compartment

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(layer) which must be provided as a daily average intensity. The calculation uses the depth integrated law of Lambert-Beer, which can be described with the following exact solution:

$$Ia_i = \frac{(1-fr) \times fpa \times Itop \times (1 - \exp(-eatmax_i \times Ha))}{eatmax_i \times Ha}$$

$$Ia_i = f(Efc_i)$$

with:

fpa	fraction of photosinthetically active light in visible light, = 0.45 [-]
fr	fraction of visible light reflected at the water surface [-]
Ha	timestep average depth of a water compartment or water layer [m]
Ia_i	critical depth average intensity of photosynthetic light [W m^{-2}]
$Itop$	visible light intensity at the top of a water compartment/layer [W m^{-2}]
z	depth [m]

The fraction of visible light reflected at the water surface fr is approximately 0.1 depending on the time in a year. Both fr and fpa are allocated fixed values in BLOOM.

The maximal extinction coefficient is found via transformation of the integral.

The specific rates of growth, maintenance respiration and mortality are formulated as functions of temperature:

$$kgp_i = kpg_i^0 \times ktpg_i^T \quad \text{for} \quad TFPMxAlg(i) = 1.0$$

$$kgp_i = kpg_i^0 \times (T - ktpg_i) \quad \text{for} \quad TFPMxAlg(i) = 0.0$$

$$kgp_i \geq 0.0$$

$$krsp_i = krsp_i^0 \times ktrsp_i^T$$

$$kmrt_i = kmrt_i^0 \times ktmrt_i^T \quad \text{for all algae except macro algae (Ulva)}$$

$$kmrt_i = kmrt_i^0 \quad \text{for Ulva when} \quad T < 25.0$$

$$kmrt_i = kmrt_i^0 \times (T - 25) \quad \text{for Ulva when} \quad T \geq 25.0$$

with:

kgp^0	growth rate at 0 °C [d^{-1}], or per degree centigrade [°C^{-1} d^{-1}]
$ktgp$	temperature coefficient for growth [-], or temperature at which kgp_0 is equal to zero
$kmrt^0$	specific mortality rate at 0 °C or at temperatures < 25 °C [d^{-1}], or per degree centigrade at temperatures > 25 °C [°C^{-1} d^{-1}]
$ktmrt$	temperature coefficient for mortality [-]
$krsp^0$	specific maintenance respiration rate at 0 °C [d^{-1}]
$ktrsp$	temperature coefficient for maintenance respiration [-]
T	water temperature [°C]

Growth respiration is not modelled explicitly but is included in the growth rate.

Algal mortality is caused by temperature dependent natural mortality, salinity stress mortality, and grazing by consumers. The last process is either thought to be part of the overall mortality rate imposed or modelled explicitly apart from BLOOM. The modelling of grazers is described elsewhere in this manual. Salinity driven mortality is described with a sigmoidal function of chlorinity (NIOO/CEMO, 1993)

$$kmrt_i^0 = \frac{m2_i - m1_i}{1 + \exp(b1_i \times (Ccl - b2_i))} + m1_i$$

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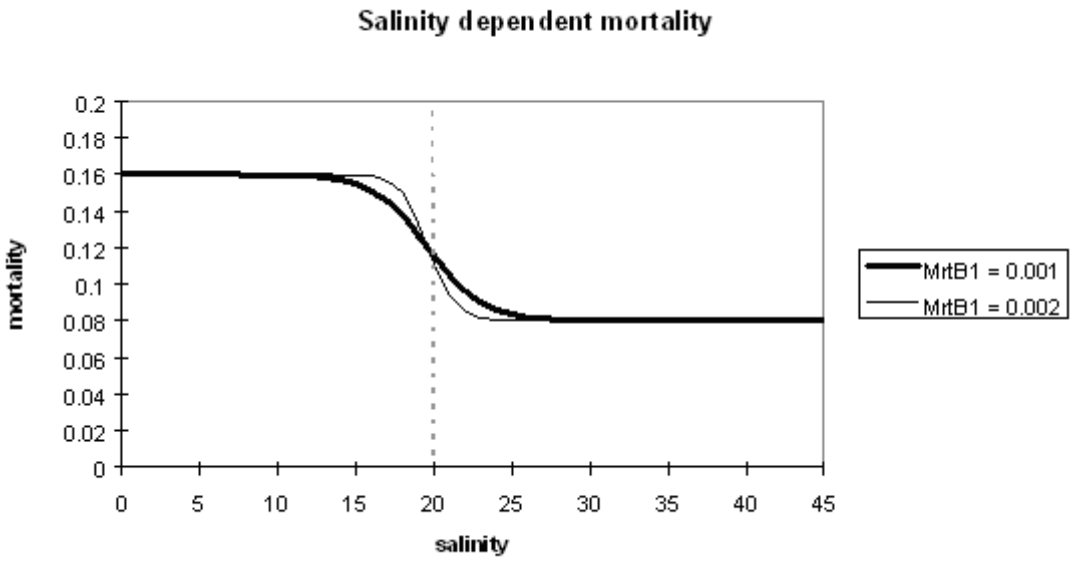

Figure 4.1: *Example of the salinity dependent mortality function. m1 = 0.08 d^{-1}; m2 = 0.16 d^{-1}; b2 = 11000 (equivalent with 20 ppt salinity) [gCl m^{-3}]; b1 = 0.001 and 0.002 m^3 gCl^{-1}.*

with:

$b1_i$	coefficient 1 of salinity stress function [$g^{-1}.m^3$]
$b2_i$	coefficient 2 of salinity stress function [$g.m^{-3}$]
$m1_i$	rate coefficient 1 of salinity stress function [d^{-1}]
$m2_i$	rate coefficient 2 of salinity stress function [d^{-1}]
Ccl	chloride concentration [g m^{-3}]

$m1$ and $m2$ are the end members of the above function, meaning that the function obtains the value $m1$ at high Ccl, and the value $m2$ for low Ccl. The mortality rate increases with decreasing chloride concentration, when $m2$ is larger than $m1$. This situation which applies to marine algae is depicted in the example of Figure 4.1. The mortality rate increases with increasing chloride concentration, when $m1$ is larger than $m2$. This situation applies to fresh water algae.

Growth constraints

The maximum biomass of a species can also be limited by the maximum growth under the given environmental conditions. The maximum increase of the biomass is determined by:

1 the initial biomass; and
2 the net growth rate.

To simplify the formulation a single growth constraint for all types (i) within each species (j) is considered by the model. The maximum growth rate of the energy limited type (E-type) is used as maximum growth rate of the species. Furthermore, since rapidly growing species have a low mortality rate, the mortality is ignored in the computation of the growth constraint. The growth constraint for species j applying to all types of this species is computed as:

$$Calgmax_i = Calg1_i \times \exp\left((kgp_i \times Ef_i - krsp_i) \times \Delta tb\right)$$

$$Calgmax_j = \sum_{i=l}^{m} Calgmax_i$$

$$Calgmax_j = \begin{cases} Calgmax_j & \text{if } Calgmax_j \geq Calgc_j \\ 0 & \text{if } Calgmax_j < Calgc_j \end{cases}$$

$$\sum_{i=l}^{m} (Calg2_i) \leq Calgmax_j$$

$$\Delta tb = ft \times \Delta t$$

with:

$Calgmax$	maximum concentration of an algae species or type at time t_2, the end of a timestep [gC m^{-3}]
$Calgc$	threshold biomass concentration of an algae species at time t_1, the beginning of a timestep [gC m^{-3}]
$Calg_1$	biomass concentration of algae species j at time t_1 [gC m^{-3}]
$Calg_2$	biomass concentration of algae species j at time t_2 [gC m^{-3}]
ft	ratio of the BLOOM timestep and the DELWAQ timestep ≥ 1.0 [-]
Ef	light efficiency factor [-]
kgp	potential specific growth rate of the fastest growing type of an algae species [d^{-1}]
$krsp$	specific maintenance respiration rate of the fastest growing type of an algae species [d^{-1}]
Δt	time step in DELWAQ [d]
Δtb	time interval, the time step in BLOOM [d]
j	index for algae species [-]
i	index for algae species type [-]
l	index of the first algae type for species j [-]
m	index of the last algae type for species j, $= l-1+$ number of types species $j-1$ [-]

For each species a minimum level $Calgc$ is defined in the model. If the actual biomass is lower, this threshold level is used instead. This enables the growth of a new species when the conditions become favourable to this species.

The production efficiency factor Ef is determined from the table in the input file "bloominp.frm" using the actual visible light intensity corrected with fpa and $(1 - fr)$. The average light intensity Ia within a water layer is derived from the light intensity at the top of this layer as calculated according to the above integrated attenuation function of Lamber-Beer using the actual total extinction coefficient et. Itop is delivered by process CalcRad, described elsewhere in this manual.

Mortality constraints

As in the case of growth the mortality of each algae species is also constrained within the model to prevent a complete removal within a single time step. The minimum biomass value of a species is obtained when there is no production, but only mortality. This minimum biomass depends on:

1 the initial biomass; and
2 the mortality rate.

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This minimum value is computed for each individual algae type i, but the model takes the summation of all types within a species. This way the maximum possible mortality cannot be exceeded, but transitions between types remain possible. Thus the following equation is included:

$$Calgmin_i = Calg1_i \times e^{(-kmrt_i \times \Delta tb)}$$

$$Calgmin_j = \sum_{i=l}^{m} (Calgmin_i)$$

$$Calgmin_j = \begin{cases} Calgmin_j & \text{if} \quad Calgmin_j \geq Calgc_j \\ 0 & \text{if} \quad Calgmin_j < Calgc_j \end{cases}$$

$$\sum_{i=l}^{m} (Calg2_i) \geq Calgmin_j$$

with:

$Calgmin$	minimum concentration of an algae species type at time t_2, the end of a time step [gC m^{-3}]
$Calg_1$	biomass concentration of an algae species type at time t_1 [gC m^{-3}]
$Calg_2$	biomass concentration of an algae species type at time t_2 [gC m^{-3}]
$kmrt$	specific mortality rate of an algae species type [d^{-1}]

Since mortality is computed according to a negative exponential function, the minimum biomass level is always positive, in other words a species can never disappear completely. For numerical reasons, however, a base level is included in the model as indicated in relation to the growth constraints.

Growth, production, mortality and respiration rates

The algae processes lead to the production of algae biomass (C, N, P, Si, S), detritus (C, N, P, S), opal silicate and dissolved oxygen, and to the consumption of nutrients (N, P, Si, C, S). In case of mixotrophic algae there is also the consumption of detritus. Nitrogen fixative algae have an additional nitrogen uptake from elementary nitrogen. DELWAQ requires the rates of all processes that affect the mass balances in the model, which renders the nitrogen fixation rates per se superfluous. The rates are deduced from the changes of the algae biomasses over a time step. The mass balances for algae types are based on the following growth, respiration and mortality rates:

$$\begin{aligned}
Rgr_i &= \frac{Calg2_i - Calg1_i}{\Delta tb} \\
Rgr_{on,i} &= Rgr_i \times (an_i + adn_i + aen_i) \\
Rgr_{op,i} &= Rgr_i \times (aph_i + adph_i) \\
Rgr_{osi,i} &= Rgr_i \times asi_i \\
Rgp_i &= Rgr_i + Rrsp_i + Rmrt_i \\
Rnp_i &= Rgp_i - Rrsp_i \\
Rrsp_i &= krsp_i \times \frac{(Calg2_i + Calg1_i)}{2} \\
Rmrt_i &= kmrt_i \times \frac{(Calg2_i + Calg1_i)}{2}
\end{aligned}$$

with:

$Calg1_i$	algae biomass concentration at t_1, the beginning of a time step [gC m^{-3}]
$Calg2_i$	algae biomass concentration at t_2, the end of a time step [gC m^{-3}]
$krsp$	specific respiration rate [d^{-1}]
$kmrt$	specific mortality rate [d^{-1}]
Rgp	gross primary production rate [gC.m^{-3} d^{-1}]
Rgr	growth rate for organic carbon [gC.m^{-3} d^{-1}]
Rgr_{on}	growth rate for organic nitrogen [gN m^{-3}.d^{-1}]
Rgr_{op}	growth rate for organic phosphorus [gP m^{-3} d^{-1}]
Rgr_{osi}	growth rate for "organic" silicate [gSi m^{-3} d^{-1}]
$Rmrt$	mortality rate [gC m^{-3} d^{-1}]
Rnp	net primary production rate [gC m^{-3} d^{-1}]
$Rrsp$	respiration rate [gC m^{-3} d^{-1}]
Δtb	time interval, the time step in BLOOM [d]
i	index for species group 1-4 [-]

The consumption rate for inorganic carbon is equal to the algae biomass growth rate Rgr. The consumption and production rates for dissolved oxygen, nutrients and detritus for each algae species type are derived from the above rates as follows:

$$Rprd_{ox,i} = \left(\left(\frac{an_i}{an_i + adn_i} \right) \times Rnp_i + Raut_i \right) \times aox_i$$

$$Rcns_{am,i} = Rnp_i \times an_i \times fam$$

$$Rcns_{ni,i} = Rnp_i \times an_i \times (1 - fam)$$

$$Rcns_{ph,i} = Rnp_i \times aph_i$$

$$Rcns_{si,i} = Rnp_i \times asi_i$$

$$Rcns_{s,i} = Rnp_i \times as_i$$

$$Rfix_i = Rnp_i \times aen_i$$

$$Rcns_{oc1,i} = Rnp_i \times \left(\frac{adn_i}{an_i + adn_i} \right)$$

$$Rcns_{on1,i} = Rnp_i \times adn_i$$

$$Rcns_{op1,i} = Rnp_i \times adph_i$$

$$Raut_i = faut_i \times Rmrt_i$$

$$Raut_{am,i} = Raut_i \times an_i$$

$$Raut_{ph,i} = Raut_i \times aph_i$$

$$Raut_{si,i} = Raut_i \times asi_i$$

$$Raut_{s,i} = Raut_i \times as_i$$

$$Rprd_{oc1,i} = Rmrt_i \times (1 - faut_i) \times fdet_i$$

$$Rprd_{on1,i} = Rmrt_i \times an_i \times (1 - faut_i) \times fdet_i$$

$$Rprd_{op1,i} = Rmrt_i \times aph_i \times (1 - faut_i) \times fdet_i$$

$$Rprd_{osi1,i} = Rmrt_i \times asi_i \times (1 - faut_i) \times fdet_i$$

$$Rprd_{os1,i} = Rmrt_i \times as_i \times (1 - faut_i) \times fdet_i$$

$$Rprd_{oc2,i} = Rmrt_i \times (1 - faut_i) \times (1 - fdet_i)$$

$$Rprd_{on2,i} = Rmrt_i \times an_i \times (1 - faut_i) \times (1 - fdet_i)$$

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$$Rprd_{op2,i} = Rmrt_i \times aph_i \times (1 - faut_i) \times (1 - fdet_i)$$
$$Rprd_{osi2,i} = Rmrt_i \times asi_i \times (1 - faut_i) \times (1 - fdet_i)$$
$$Rprd_{os2,i} = Rmrt_i \times as_i \times (1 - faut_i) \times (1 - fdet_i)$$

with:

aen	stoichiometric constant of nitrogen originating from elementary nitrogen in algae biomass [gN gC^{-1}]
an	stoichiometric constant for ammonium/nitrate over carbon in algae biomass [gN gC^{-1}]
adn	stoichiometric constant for detritus nitrogen over carbon in algae biomass [gN gC^{-1}]
aph	stoichiometric constant for phosphate over carbon in algae biomass [gP gC^{-1}]
$adph$	stoichiometric constant for detritus phosphorus over carbon in algae biomass [gP gC^{-1}]
aox	stoichiometric constant for oxygen over carbon in algae biomass [gO$_2$ gC^{-1}]
asi	stoichiometric constant for silicon over carbon in algae biomass [gSi gC^{-1}]
as	stoichiometric constant for sulfur over carbon in algae biomass [gS.gC^{-1}]
fam	fraction of ammonium in the consumed nitrogen nutrients [-]
$fdet$	fraction of dead algae biomass allocated to fast decomposing detritus [-]
$faut$	fraction of dead algae biomass autolysed [-]
$Raut$	autolysis rate for dead algae biomass (organic carbon) [gC m^{-3} d^{-1}]
$Raut_{am}$	autolysis rate for ammonium [gN m^{-3} d^{-1}]
$Raut_{ph}$	autolysis rate for phosphate [gP m^{-3} d^{-1}]
$Raut_{si}$	autolysis rate for silicate [gSi m^{-3} d^{-1}]
$Raut_s$	autolysis rate for sulfide [gS m^{-3} d^{-1}]
$Rcns_{am}$	consumption rate for ammonium [gN m^{-3} d^{-1}]
$Rcns_{ni}$	consumption rate for nitrate [gN m^{-3} d^{-1}]
$Rcns_{ph}$	consumption rate for phosphate [gP m^{-3} d^{-1}]
$Rcns_{si}$	consumption rate for silicate [gSi m^{-3} d^{-1}]
$Rcns_s$	consumption rate for sulfate [gS m^{-3} d^{-1}]
$Rcns_{oc1}$	consumption rate for detritus carbon [gC m^{-3} d^{-1}]
$Rcns_{on1}$	consumption rate for detritus nitrogen [gN m^{-3} d^{-1}]
$Rcns_{oph1}$	consumption rate for detritus phosphorus [gP m^{-3} d^{-1}]
$Rfix$	nitrogen fixation (consumption) rate [gN m^{-3} d^{-1}]
$Rprd_{ox}$	net production rate for dissolved oxygen [gO$_2$ m^{-3} d^{-1}]
$Rprd_{oc1}$	production rate for fast decomposing detritus carbon POC1 [gC m^{-3} d^{-1}]
$Rprd_{on1}$	production rate for fast decomposing detritus nitrogen PON1 [gN m^{-3} d^{-1}]
$Rprd_{op1}$	production rate for fast decomposing detritus phosphorus POP1 [gP m^{-3} d^{-1}]
$Rprd_{osi1}$	production rate for particulate soluble silicate OPAL [gSi m^{-3} d^{-1}]
$Rprd_{os1}$	production rate for fast decomposing detritus sulfur POS1 [gS m^{-3} d^{-1}]
$Rprd_{oc2}$	production rate for slowly decomposing detritus carbon POC2 [gC m^{-3} d^{-1}]
$Rprd_{on2}$	production rate for slowly decomposing detritus nitrogen PON2 [gN m^{-3} d^{-1}]
$Rprd_{op2}$	production rate for slowly decomposing detritus phosphorus POP2 [gP m^{-3} d^{-1}]
$Rprd_{osi2}$	production rate for particulate soluble silicate OPAL [gSi m^{-3} d^{-1}]
$Rprd_{os2}$	production rate for slowly decomposing detritus sulfur POS2 [gS m^{-3} d^{-1}]

The stoichiometric constants for oxygen and sulfur over carbon aox_i and as_i are not input parameters. In the model for all algae species they are fixed and equal to 2.67 and 0.0175, respectively.

The overall production and consumption rates required for DELWAQ are derived simply by adding up the above rates for all algae species types.

The fraction of ammonium in nitrogen nutrients consumed fam simply follows from the total demand for the nitrogen nutrients and the current ammonium and nitrate concentrations. If the demand is not covered by ammonium alone, the model allocates the additional demand to nitrate.

Output

BLOOM delivers some additional output parameters, such as the overall concentrations of algae biomass, indicators for the active limiting factors, and the rates of total net primary production, respiration and nitrogen fixation. The algae biomass concentrations expressed in various units are:

$$Calgt = \sum_{i=1}^{n} (Calg_i)$$

$$Cadm = \sum_{i=1}^{n} (adm_i \times Calg_i)$$

$$Cchf = 1000 \times \sum_{i=1}^{n} (achf_i \times Calg_i)$$

$$Can = \sum_{i=1}^{n} ((an_i + adn_i + aen_i) \times Calg_i)$$

$$Caph = \sum_{i=1}^{n} ((aph_i + adph_i) \times Calg_i)$$

$$Casi = \sum_{i=1}^{n} (asi_i \times Calg_i)$$

with:

$achf$	stoch. constant for chlorophyll-a over carbon in algae biomass [gChf gC^{-1}]
adm	stoch. constant for dry matter over carbon in algae biomass [gDM gC^{-1}]
$Calgt$	total algae biomass concentration [gC m^{-3}]
Can	total concentration of nitrogen in algae biomass [gN m^{-3}]
$Caph$	total concentration of phosphorus in algae biomass [gP m^{-3}]
$Casi$	total concentration of silicon in algae biomass [gSi m^{-3}]
$Cadm$	total algae biomass concentration on a dry matter basis [gDM m^{-3}]
$Cchf$	total chlorophyll-a concentration [mgChf m^{-3}]

The limiting factors concern inorganic and detrital nitrogen, inorganic and detrital phosphorus, dissolved silicon, dissolved inorganic carbon, energy (light), growth and mortality. The active factors for each timestep are delivered by the optimisation method.

The rates of total net primary production, mortality and nitrogen fixation are:

$$Rnpt = \sum_{i=1}^{n} \left(\frac{Rnp_i}{H} \right)$$

$$Rrspt = \sum_{i=1}^{n} \left(\frac{Rrsp_i}{H} \right)$$

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$$Rfixt = \sum_{i=1}^{n} \left(\frac{Rfix_i}{H} \right)$$

with:

$Rfixt$	total nitrogen fixation rate [gN m^{-2} d^{-1}]
$Rrspt$	total algal maintenance respiration rate [gC m^{-2} d^{-1}]
$Rnptt$	total algal primary production rate [gC m^{-2} d^{-1}]

Process UlvaFix

Macro algae such as $Ulva$ and similarly behaving macrophytes which can be described with BLOOM may both be suspended in the water column and attached to the sediment. Two states are distinguished for such a species, one suspended type and one attached type. These different states are modelled as different species groups. The two states form a pair in the sense that biomass can be transferred from the attached type to the suspended state and vise versa WL | Delft Hydraulics 1998. This “resuspension” or “detachment” process is due to elevated water flow velocity, and requires the sediment shear stress caused by water flow. The shear stress can be imposed on the model as a time series or calculated from the flow field (a velocity array), which is described elsewhere in this manual. “Resettling” or “reattachment” to the sediment occurs at the decrease of shear stress.

The characteristics of the pair of types will be identical, except for an additional model parameter $SDMixAlg(i)$ that indicates the position of the algae in the water column. This parameter has the default value of 1.0 for the suspended type, meaning that the algae are mixed over the complete water column. For the attached type, $SDMixAlg(i)$ has a small negative value, for example -0.25, meaning that the algae are mixed over the lower 25 % of the water column. The calculation of the energy constraint for this algae type takes into account that the attached type “observes” the light intensity in the lower part of the water column.

The parameter $FixAlg(i)$ defines for each algae type, whether it belongs to a pair of attached and suspended types. At the default value of 0.0 an algae type is considered a normal suspended algae species. If the parameter obtains a positive value (1.0, 2.0, etc.), it is the suspended type of a pair. For the attached type of this pair $FixAlg(i)$ must have the same but negative value.

Based on the ratio of the actual shear stress and a critical shear stress the fraction of the algae biomass which is attached to the sediment is calculated as follows:

$$fat = af - \frac{\tau}{\tau_c}$$

$$0.0 \leq fat \leq 1.0$$

with:

af	attachment affinity coefficient [-]
$Calg_i$	biomass concentration of the suspended algae species type [gC m^{-3}]
$Calg - j$	biomass concentration of the attached algae species type [gC m^{-3}]
fat	target fraction of attached algae type [-]
τ	shear stress at the sediment water interface [Pa]
τc	critical shear stress for resuspension [Pa]

The resuspension and settling rates for algae biomass are then calculated in such a way, that the concentrations of suspended and attached algae will tend to agree with the calculated target distribution:

if $fat \geq \frac{Calg_j}{Calg_i}$:

$$Rres_j = \frac{((1.0 - fat) \times (Calg_i + Calg_j)) - Calg_i}{\Delta t}$$

$$Rres_i = -Rres_j$$

if $fat < \frac{Calg_j}{Calg_i}$:

$$Rset_i = \frac{Calg_j - (fat \times (Calg_i + Calg_j))}{\Delta t}$$

$$Rres_j = -Rset_i$$

with:

$Rres_j$	resuspension rate of the attached algae species j [gC m^{-3} d^{-1}]
$Rset_j$	settling rate of the attached algae species j [gC m^{-3} d^{-1}]
$Rres_i$	resuspension rate of the suspended algae species i [gC m^{-3} d^{-1}]
$Rset_i$	settling rate of the suspended algae species i [gC m^{-3} d^{-1}]
Δtb	time interval, the timestep in BLOOM [d]

In case macro algae attached to sediment are included in the model BLOOM produces additional output in the form of the fraction of biomass attached to the sediment and the algae biomasses per m^2 (derived from the concentrations and the water depth).

Process: DEPAVE

When BLOOM's time step is bigger than DELWAQ's time step the average depth for BLOOM should be calculated using the process DEPAVE. DEPAVE calculates a running average of the DEPTH within a BLOOM timestep according to:

$$Ha_{nt} = \frac{(nt - 1) \times Ha_{nt-1} + H_{nt}}{nt} \quad \text{for} \quad nt \leq ft$$

with:

ft	ratio of the BLOOM time step and the DELWAQ time step ≥ 1.0 [-]
nt	counter for number of DELWAQ time steps made in current BLOOM time step [-]
Ha	average water depth for the current BLOOM time step [m]
Ha_{nt}	running average water depth at DELWAQ time step nt in the current BLOOM time step [m]
H_{nt}	water depth at DELWAQ time step nt [m]

The depth averaging is activated or deactivated according to the value of option parameter $SWDepAve$ in the process DEPAVE.

Directives for use

- ◇ The variable $TimMultBl$ is a multiplication factor for the transport time step, that enables bloom to use a bigger time step then the transport. With the process decomposition method also for the other water quality processes a larger time step than the transport

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time step can be used. bloom was set up to calculate algae processes on a daily (average) scale. Suitable time steps for bloom are in the range of 6 hours to 2 days. The value of $TimMultBl$ should be an integer, not less than one. When the time step of bloom is larger than the time step of the water quality processes, nutrient levels rise between the bloom time steps and drop when a bloom computation is performed. Output should therefore only be generated at time steps where a bloom computation has been performed. At times teps in between the nutrient levels are not accurate.

- ◇ The bloom module will only be used if the name `bloomalg01` is specified in the delwaq input. N.B. the rate constants for growth, mortality and maintenance respiration must be supplied for a standard temperature of 0 °C, instead of 20 °C as in the other delwaq modules.
- ◇ The flux of algae mortality to slowly decomposing detritus is calculated as the total mortality flux, minus the autolysis and the flux to fast decomposing detritus. If slowly decomposing detritus ($POC2$) is not modelled, the sum of $FrAutAlg(i)$ and $FrDetAlg(i)$ should equal to 1.0 for each algae type. In no case the sum should exceed one.
- ◇ The specific extinction of bloom-algae can not be set equal to zero, or the calculation will stop with the error message that the model cannot divide by zero.
- ◇ Mixotrophic nitrogen and phosphorus algae types can be defined by providing a positive value for the coefficients $XNCRAlg(i)$ and $XPCRAlg(i)$ respectively. These coefficients must be equal to 0.0 for autotrophic algae. The sum of the stoichiometric constants $NCRAlg(i)$ and $XNCRAlg(i)$, or $PCRAlg(i)$ and $XPCRAlg(i)$, of the mixotrophic algae types should be equal to the real overall stoichiometric constant for nitrogen, or phosphorus. The distribution of the nutrients regarding their origin, that is the ratio of both constants, should be chosen in such a way, that a realistic amount of nutrients in detritus is consumed by the mixotrophic type. It is very well possible, that the results will not show high biomass for the mixotrophic type, even if the nutrients become completely depleted. Other types of the same group may be more efficient in the use of the nutrients, once they have been made available by the mixotrophic types. The production of the mixotrophic types can be calculated by division of the nutrient uptake by the prescribed stoichiometry ($XNCRAlg(i)$ and $XPCRAlg(i)$).
- ◇ It is possible to describe nitrogen fixation by algae types by providing a positive value for the coefficient $FNCRAlg(i)$. These coefficients must be equal to 0.0 for autotrophic and mixotrophic algae. Again the sum of the stoichiometric constants $NCRAlg(i)$ and $FNCRAlg(i)$ of the nitrogen fixative algae types should be equal to the real overall stoichiometric constant for nitrogen. Nitrogen fixation is not limited by the availability of the nutrient (N2), but by the fixation capacity of the algae. Therefore, the values of $FNCRAlg(i)$ and $PPMaxAlg(i)$ should be chosen in such a way, that a realistic nitrogen fixation rate will be used. Furthermore, the primary production rate $PPMaxAlg(i)$ will be lower than for the autotrophic types, because nitrogen fixation costs more energy than the uptake of dissolved nutrients. Maximum nitrogen fixation is in the order of 25 kgN ha^{-1} y^{-1} $\sim 0.006\,8$ gN m^{-2} d^{-1} (Ross, 1995). If $PPMaxAlg(i)$ is set to be 0.1 1/d (after temperature correction) on average during the growing season, the depth is 2.0 meters and the biomass of the nitrogen fixing group is 10 gC m^{-3}, then the maximum realistic value of $FNCRAlg(i)$ can be calculated as 0.006 8 / $(10 \times 0.1 \times 2)$ = 0.0034 gN gC^{-1}.
- ◇ Changes in salinity can induce extra algae mortality. Marine algae suffer from extra mortality when they are exposed to fresh water and vice versa, fresh water algae die in a marine environment. The effect in bloom depends on the relative magnitudes of coefficients $MND(i)m1$ and $MND(i)m2$. The salinity effect on mortality can be inactivated by allocating the same value to $MND(i)m1$ and $MND(i)m2$.
- ◇ The current implementation of BLOOM allows for only one macro algae of macrophyte species, whereas in parameter naming $Ulva$ was taken as a reference. With the default value of 2.0 for $FixGrad$ the target attached fraction fat is equal to 1.0, when shear stress Tau is less than $TauCrUlva$, and equql to 0.0 when Tau is more than two times $TauCrUlva$. This can be modified by changing the value of $FixGrad$.

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- ◇ When (macro) algae from the bottom are resuspended their biomass is converted to the algae type with the corresponding positive value of the parameter FixAlg(i). So the biomass of the type with the value of FixAlg(i) = -1.0 is converted to the type with the value of FixAlg(i) = +1.0.
- ◇ Biomass of the algae species attached to the sediment (one of a pair) is expressed in [gC m^{-2}], since this state variable is modelled as an "inactive" substance.
- ◇ Usually the observed light intensity, also indicated as irradiation or solar radiation, is expressed in [J cm^{-2} $week^{-1}$]. Notice that the light intensity has to be provided in [W m^{-2}].
- ◇ Always make sure that the light input (observed solar radiation) is consistent with the light related parameters of BLOOM. This concerns the use of either visible light or the photosynthetic fraction of visible light. BLOOM assumes total visible light observed just above the water surface. It carries out corrections for the fraction of photosynthetically active light (45 %) and reflection (approximately 10 % depending on the point of time in a year). The input incident light time series should have been corrected for cloudiness.
- ◇ Carbon limitation can be taken account according to options, through the advanced BLOOM optimisation approach and through the simplified growth scaling approach. For the advanced approach the input parameter $SwTICdummy$ (default value = 0.0) needs to be allocated a value of 10.0 or higher. The limitation parameter $KCO2$ of the simplified approach has a default value of 0.0, implying no limitation by carbon, which must not be modified when applying the advanced approach. When using the simplified approach, an appropriate value of $KCO2$ for limitation is 1.0 gC.m^3.
- ◇ The sulfur content of algae will only be taken into account automatically, when $SO4$, SUD, $POS1$ and $POS2$ are actually modelled.

In 2019 the code of BLOOM underwent a major overhaul. The code was modernised, and a lot of obsolete code was removed, while maintaining the same results, and having the same functionality. Also the dependency on the <bloominp.d09> file was removed. The <bloominp.d09> allowed for several settings that could not be done otherwise. We preserved most of these settings by adding new parameters to the BLOOM process that can be set through the Delwaq input. An overview of these settings can be found in Table 4.3.

Additional references

Molen et al. (1994a), WL | Delft Hydraulics (1992c), Los (1985), DBS (1994), DBS (1991), Los (2009)

Table 4.1: *Definitions of the input parameters in the formulations for BLOOM.*

Name in formulas	Name in input	Definition	Units
$Calg_i$	$BLOOMALG(i)$	biomass concentration of algae species type i	gC m^{-3}
Cam	$NH4$	ammonium concentration	gN m^{-3}
Ccl	Cl	chloride concentration	gCl m^{-3}
Cni	$NO3$	nitrate concentration	gN m^{-3}
Cph	$PO4$	phosphate concentration	gP m^{-3}
Csi	Si	dissolved inorganic silicate concentration	gSi m^{-3}
$Cnutc_1$	$ThrAlgNH4$	threshold concentration for uptake of ammonium	gN m^{-3}

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Table 4.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
$Cnutc_2$	$ThrAlgNO3$	threshold concentration for uptake of nitrate	gN m^{-3}
$Cnutc_3$	$ThrAlgPO4$	threshold concentration for uptake of phosphorus	gP m^{-3}
$Cnutc_4$	$ThrAlgSi$	threshold concentration for uptake of silicate	gSi m^{-3}
–	$PON1$ or $DetN$	concentration of nitrogen in fast decomp. detritus	gN m^{-3}
–	$POP1$ or $DetP$	concentration of phosphorus in fast decomp. detritus	gP m^{-3}
–	$SpecAlg(i)3$	species identification number of types	-
$achf_i$	$ChlaCAlg(i)$	algae type spec. stoch. const. chlorophyll over carbon	gChf gC^{-1}
adm_i	$DMCFAlg(i)$	algae type spec. stoch. const. dry matter over carbon	gDM gC^{-1}
an_i	$NCRAlg(i)$	algae type spec. stoch. const. nutr. nitrogen / carbon	gN gC^{-1}
adn_i	$XNCRAlg(i)$	algae type spec. stoch. const. detr. nitrogen / carbon	gN gC^{-1}
aen_i	$FNCRAlg(i)$	algae type spec. stoch. const. elem. nitrogen / carbon	gN gC^{-1}
aph_i	$PCRAlg(i)$	algae type spec. stoch. const. nutr. phos. / carbon	gP gC^{-1}
$adph_i$	$XPCRAlg(i)$	algae type spec. stoch. const. detr. phos. / carbon	gP gC^{-1}
asi_i	$SCRAlg(i)$	algae type spec. stoch. const. for silicon over carbon	gSi gC^{-1}
$m1_i$	$Mort0Alg(i)$	algae type spec. rate coefficient 1 of salinity stress	d^{-1}
$m2_i$	$Mort2Alg(i)$	algae type spec. rate coefficient 2 of salinity stress	d^{-1}
$b1_i$	$MrtB1Alg(i)$	algae type spec. coefficient 1 of salinity stress function	$g^{-1}.m^3$
$b2_i$	$MrtB2Alg(i)$	algae type spec. coefficient 2 of salinity stress function	g m^{-3}
ea_i	$ExtVlAlg(i)$	algae species type specific extinction coefficient	m^2 gC^{-1}
$KCO2$	$KCO2$	limitation constant for carbon	gC m^3
$faut_i$	$FrAutAlg(i)$	fraction of dead algae biomass autolised	-

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Table 4.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
$fdet_i$	$FrDetAlg(i)$	fr. of dead algae biomass allocated to fast dec. detritus	-
–	$SDMixAlg(i)$	distribution of an algae type over the water column	-
–	$FixAlg(i)$	identifier for pairs of algae types attaching to sediment (0 =not applying, > 0 = suspended, < 0 = attached)	-
–	$SWBlOutput$	option for specific BLOOM output (0 = no, 1 = yes)	-
–	$SWOxyProd$[2]	option for calc. oxygen conc. (0 = daily av., 1 = daily var.)	-
–	$SWDepAve$	option depth aver. over BLOOM timestep (0 = off, 1 = on)	-
H	$Depth$	depth of a water compartment or water layer	m
Ha	$BloomDepth$	average depth during a BLOOM timestep	m
V	$Volume$	volume of a water compartment or water layer	m^3
DL	$DayL$	daylength, fraction of a day	-
et	$ExtVl$[4]	total extinction coefficient of visible light	m^{-1}
eat	$ExtVlPhyt$[4]	extinction coefficient of all agae species types	m^{-1}
$Itop$	Rad	light intensity at top of layer or compartment	W m^{-2}
kgp_i^0	$PPMaxAlg(i)$	algae type spec. pot. gross primary prod. rate at 0 °C	d^{-1}
$ktgp_i$	$TcPMxAlg(i)$	algae type spec. temperature coeff. for primary prod.	- or °C
–	$TFPMxAlg(i)$	option temperature dep. of prod. (0 = linear, 1 = exp.)	-
$krsp_i^0$	$MRespAlg(i)$	algae type spec. maintenance respiration rate at 0 °C	d^{-1}
–	$MrtExAlg(i)$	algae type spec. extra rapid mortality rate	d^{-1} °C^{-1}
$ktmrt_i$	$TcMrtAlg(i)$	algae type spec. temperature coefficient for mortality	-
$ktrsp_i$	$TcRspAlg(i)$	algae type spec. temperature coef. for maint. resp.	-
T	$Temp$	water temperature	°C
af	$FixGrad$	attachment affinity coefficient	-
τ	Tau	shear stress at the sediment water interface	Pa

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Table 4.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
τc	$TauCrUlva$	critical shear stress for resuspension	Pa
ft	$TimMultBl$	ratio of the BLOOM timestep and the DELWAQ timestep	-
Δt	$Delt$	time interval, that is the DELWAQ timestep	d

[1](i) indicates algae species types 01-15. Biomass of algae species attached to the sediment is expressed in [gC.m^{-2}].

[2]For $SWOXYProd = 1.0$ process VAROXY is used to calculated the daily varying dissolved oxygen concentration (see description elsewhere in the manual).

[3]The species identification number needs to be an integer that is equal for all types that belong to the same species.

[4]These parameters are calculated by processes ExtinaBVL and Extinc_VL.

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Table 4.2: *Definitions of the output parameters for BLOOM.*

Name in formulas	**Name in output**[1]	**Definition**	**Units**
$Calgt_i$	$Phyt$	total algae biomass concentration	gC m^{-3}
Cdm_i	$AlgDM$	total algae biomass conc. on a dry matter basis	gDM m^{-3}
$Cchf_i$	$Chlfa$	total chlorophyll-a concentration	mgChf m^{-3}
Can_i	$AlgN$	total concentration of nitrogen in algae biomass	gN m^{-3}
$Caph_i$	$AlgP$	total concentration of phosphorus in algae biomass	gP m^{-3}
$Casi_i$	$AlgSi$	total concentration of silicon in algae biomass	gSi m^{-3}
–	$Limit\ Nit$ or Lim_IN	indicator for limitation by inorganic nitrogen	-
–	Lim_DetN	indicator for limitation by detrital nitrogen	-
–	Lim_FixN	indicator for limitation by nitrogen fixation	-
–	$Limit\ Pho$ or Lim_IP	indicator for limitation by inorganic phosphorus	-
–	Lim_DetP	indicator for limitation by detrital phosphorus	-
–	$Limit\ Sil$ or Lim_Si	indicator for limitation by silicon	-
–	$Limit\ E$ or Lim_light	indicator for limitation by energy (light)	-
–	Lim_inhib	indicator for limitation by photo inhibition	-
–	$Limit\ Gro$ or Lim_GALG	indicator for limitation by growth can be split into species specific $Lim_G(i)$	-
–	$Limit\ Mor$ or Lim_MALG	indicator for limitation by mortality can be split into species specific $Lim_M(i)$	-
$Rnpt$	$fPPtot$	total net primary production	gC m^{-2} d^{-1}
$Rrspt$	$fResptot$	total maintenance respiration	gC m^{-2} d^{-1}
$Rfixt$	$fFixNUpt$	total uptake of nitrogen by fixation	gN m^{-2} d^{-1}
–	$RcPPAlg(i)$	algae type specific net primary production rate	d^{-1}
–	$RcMrtAlg(i)$	algae type specific net primary mortality rate	d^{-1}
–	$frFixedAlg$	fraction of algae fixed to the sediment bed	-
–	$BLALG(i)m2$	algae type specific biomass per m^2	gC m^{-2}

[1](i) indicates the algae species types that are used.

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Table 4.3: *Former d09 settings for BLOOM.*

Name in input	Definition	Default	Unit
SWBlSolInt	Switch between solar iradiation being given as total iradiation (0) or PAR (0)	0	-
SWBlObject	Switch between objective growth (1) or biomass (0)	1	-
BlTemLim	Temperature below which growth stops	2.5	°C
BlBasMor	Base mortality	0.01	1/day
SWBlGroChk	Switch to put on growth check	1	-
BlBioBas	Minimum biomass for growth	50.0	gDW/m3
SWBlMorChk	Switch to put on mortality check	1	-
BlTopLev	Top level	2.5	gDW/m3
SWBloomOut	Switches on writing BLOOM debug information. By using a parameter, function, or segment function, this can be switched on for specific periods or locations in the model	0	-

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4.3 Bottom fixation of BLOOM algae types

PROCESS: ULVAFIX

Some macrophytes which can be described with BLOOM, can occur both suspended and fixed to the bottom. An example of such a macrophyte is ulva. Such macrophytes can be modelled by BLOOM by defining for each algae type two types: one fixed and one suspended. The characteristics of the two types will be identical, except for the parameter indicating the relative mixing depth, SDMixAlgi. This parameter has the default value of 1.0 for the suspended type, meaning that the algae are mixed over the complete water column. For the fixed type, this parameter has a small negative value, e.g. -0.25, meaning that the algae are mixed over the lower 25 % of the water column. The flow field should be supplied in a velocity array, which has been made inactive for the fixed algae types. The exchange of algae between the fixed and suspended state depends on the bottom shear stress.

Implementation

The parameter FixAlgi defines for each algae type, whether it is part of a combination of fixed and suspended types or not. If FixAlgi has the default value of 0, this type is omitted from the further analysis. If the value of FixAlgi is a positive number, it is the suspended type of a combination. For the fixed type of the combination the value of FixAlgj should be the same number, but negative.

Based on comparison of the actual shear stress with the critical shear stress the fraction of the total concentration which is fixed to the bottom is calculated. The fluxes are then calculated in such a way, that the concentrations of suspended and fixed algae will be in accordance with the calculated fraction.

This process is implemented for all BLOOM algae types. The current maximum number of BLOOM algae types is 15.

i = 1 to 15, suspended type
j = 1 to 15, fixed type forming a pair with i

Formulation

The fraction of the total concentration, which is fixed to the bottom is calculated from the ratio between the actual and the critical bottom shear stress:

$$frFixedAlg = FixGrad - \frac{Tau}{TauCrUlva} \text{ with } frFixedAlg = [0, 1]$$

The flux for the suspended type is then calculated as:

$$dResSedi = ((1 - frFixedAlg) \times (BloomAlgi + BloomAlgj) - BloomAlgi)/Delt$$

And for the fixed type as:

$$dResSedj = (frFixedAlgae \times (BloomAlgi + BloomAlgj) - BloomAlgj)/Delt$$

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Directives for use

◇ For a complete description of the application of DELWAQ for the analysis of ulva see the documentation of project number T2162, regarding Venice Lagoon (WL | Delft Hydraulics, 1998).

With the default value of 2.0 for FixGrad the fraction fixed is 1.0 when Tau is less than TauCrUlva and 0.0 when Tau is more than two times TauCrUlva. This can be modified by changing the value of FixGrad.

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4.4 PROTIST: growth, mortality and interaction of a protist community

PROCESS: PROT_DIA, PROT_GRE, PROT_CM, PROT_NCM, PROT_ZOO, PHY_PROT

Protists are unicellular eukaryotes and they form the base marine pelagic foodwebs. A protist community consists of different protist functional types (PFT) that can be grouped into three broad trophic categories: phytoplankton, mixoplankton and protozooplankton. Phytoplankton, such as diatoms and green algae (phototrophic non-diatoms), are defined as protists that can only utilize the photo-osmotrophic pathways. They cover their energy requirements through the photosynthetic fixation of inorganic carbon and their nutrient requirements through the uptake of dissolved inorganic nutrients. Protozooplankton are defined as protists that can only utilize the phagotrophic pathways. They cover their energy and nutrient requirements through the assimilation of prey. In contrast to phytoplankton and protozooplankton, mixoplankton can utilize the photo-, osmo- and phagotrophic pathways simultaneously (Flynn et al., 2019). They can be divided into constitutive mixoplankton (CM) and non-constitutive mixoplankton (NCM) (Mitra et al., 2016). CMs have the constitutive ability to perform photosynthesis and they can uptake dissolved inorganic nutrients as well as assimilate prey. NCMs need to acquire the photosynthetic machinery from their prey. They cover their nutrient requirements mainly through the assimilation of prey (Stoecker et al., 2017).

The process PROTIST simulates the growth and mortality of the protist community while taking the trophic modes of protists into account. PROTIST can thus be used to simulate primary production in marine pelagic ecosystems. The process PROTIST combines model equations from Flynn (2001), Flynn and Mitra (2009) and Flynn (2021), which are summarized in a model called SAPPM (Switchable Acclimative Protist Plankton - Model). The SAPPM equations were adapted to work in the Delft3D-WAQ environment and to separate between the stand-alone version of the model (SAPPM) and the Delft3D-WAQ implementation, the name PROTIST was applied.

The SAPPM equations are based on first principles that were implemented unchanged in PROTIST. Firstly, the growth of protists is not only determined by the external availability of resources such as light, nutrients and prey, but also by the protists' internal stoichiometry. The internal nutrient quotas of the protists regulate the protists' affinity to uptake nutrients (Grover, 1991), synthesize chlorophyll-a (Davey et al., 2008) and assimilate prey (Mitra and Flynn, 2005). Secondly, the trophic modes of protists determine the interactions within protist communities (Flynn et al., 2019). However, some changes were needed for the equations to run stably and efficiently as a Delft3D-WAQ module:

1. the nutrient uptake equations were described using continuous functions (instead of coupled conditional statements as in Flynn (2021)).
2. the uptake of dissolved amino acids was not implemented, as Delft3D-WAQ does not simulate dissolved amino acids explicitly due to the lack of validation data.
3. the assimilation of dissolved organic carbon was not implemented, as all protist functional types (PFT) can assimilate dissolved organic carbon (DOC) (Stoecker et al., 2017), so it is not a distinguishing pathway between the PFTs.
4. PROTIST enables multiple PFTs to interact with, compete against and graze on each other.

To gather global information, such as the total chlorophyll concentration, the process PHY_PROT is available (*cf* Section 4.8).

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4.4.1 Implemented protist functional types (PFT)

Processes PRODIA, PROGRE, PROTCM, PRONCM and PROZOO have been implemented for the PROTIST substances, i.e. the different PFTs. Each PFT consists of state variables (SV) that describe carbon (C), nitrogen (N) and phosphorus (P) biomass. Chlorophyll-a (Chl) is an additional SV for phototrophic protists. Diatoms contain an additional SV to describe the silica (Si) content. This makes PROTIST fully stoichiometrically variable. The PFTs require either light and/or prey and/or nutrients. Figure 4.2 visualizes the SVs required for PROTIST and the interactions between the different SVs.

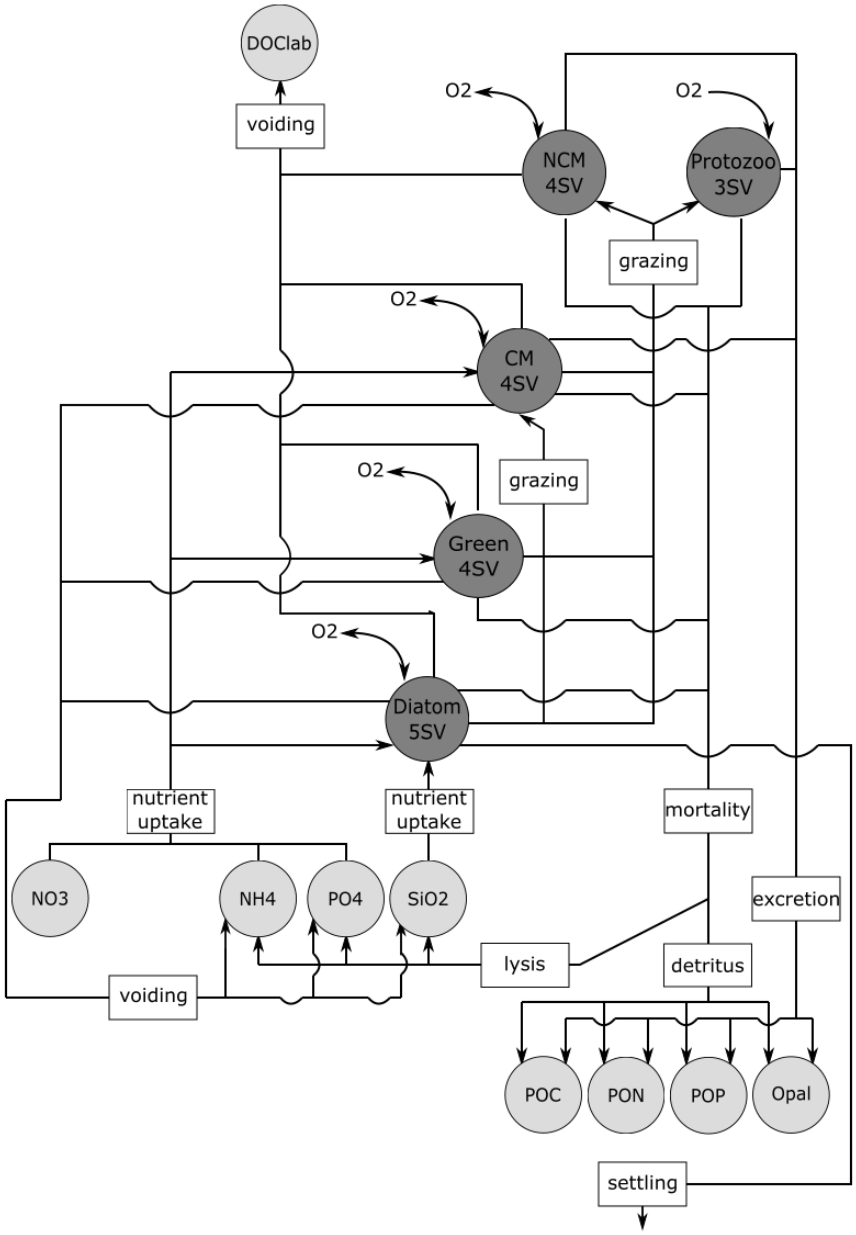

Figure 4.2: *Conceptual visualization of the module PROTIST. The lightgrey circles are abiotic state variables (SV) and the darkgrey circles the protist functional types (PFT). Each PFT consists of multiple SVs. The arrows and the labels depict the interaction between the PFTs as well as the interactions between the abiotic SVs and the PFTs. DOClab stands for labile dissolved organic carbon.*

There are physiological processes that are common to every PFT (growth, mortality, inter-

nal nutrient status) as well as physiological processes that are only used by certain PFTs (nutrient uptake, photosynthesis and phagotrophy). The different physiological processes are summarized in four modules which can be found in the fortran source file protistFunctions.f90.

4.4.1.1 Diatoms

The processes PRODIA, PROSED, PROATT and EXTINAPRO have been implemented for the PFT diatoms. The PFT diatoms are defined as phytoplankton that utilize silica. Diatoms are described with five SVs, i.e., five PROTIST substances. There are two diatoms species implemented that can be parameterized to differ from each other in size or fitness.

- ◇ diatC_1, diatChl_1, diatN_1, diatP_1, diatSi_1
- ◇ diatC_2, diatChl_2, diatN_2, diatP_2, diatSi_2

The diatom SVs increase over time through the uptake of nutrients (up_{NH4}, up_{NO3}, up_{PO4}, up_{Si}), the fixation of carbon ($Cfix$) and the synthesis of chlorophyll-a ($synChl$). The diatom SVs decrease over time through predation ($Pred$), mortality (mrt), the leakage of photosynthate ($Cleak$), the voiding of excess nutrients or carbon ($Nout$, $Pout$, $Cvoid$), the degradation of chlorophyll-a ($degChl$) and respiration ($totR$). The following equations provide the conservation equations for the PFT diatom.

$$\frac{dDiat_{C,i}}{dt} = dCfix - dCleak - dCvoid - dCresp - dAutC - dDetC - \sum Pred \quad (4.1)$$

$$\frac{dDiat_{N,i}}{dt} = dNH4up + dNO3up - dNH4out - dAutN - dDetN - \sum Pred \quad (4.2)$$

$$\frac{dDiat_{P,i}}{dt} = dPup - dPout - dAutP - dDetP - \sum Pred \quad (4.3)$$

$$\frac{dDiat_{Si,i}}{dt} = dSiup - dAutSi - dDetSi - \sum Pred \quad (4.4)$$

$$\frac{dDiat_{Chl,i}}{dt} = dChlsyn - dChldeg - dAutChl - dDetChl - \sum Pred \quad (4.5)$$

where:

$\frac{dDiat_{X,i}}{dt}$ rate of change for diatom carbon, nitrogen, phosphate, silica and chlorophyll state variable [gX m^{-3} d^{-1}]

The units and description of the fluxes can be found in table 4.7.

4.4.1.2 Green algae

The processes PROGRE, PROATT and EXTINAPRO have been implemented for the PFT green algae. The PFT green algae are defined as phytoplankton that do not utilize silica. Green algae are described with four SVs, i.e., four PROTIST substances. There are two green algae species implemented that can be parameterized to differ from each other in size or fitness.

- ◇ greenC_1, greenChl_1, greenN_1, greenP_1

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◇ greenC_2, greenChl_2, greenN_2, greenP_2

The green algae SVs increase over time through the uptake of nutrients (up_{NH4}, up_{NO3}, up_{PO4}), the fixation of carbon ($Cfix$) and the synthesis of chlorophyll-a ($synChl$). The green algae SVs decrease over time through predation ($Pred$), mortality (mrt), the leakage of photosynthate ($Cleak$), the voiding of excess nutrients or carbon ($Nout$, $Pout$, $Cvoid$), the degradation of chlorophyll-a ($degChl$) and respiration ($totR$). The following equations provide the conservation equations for the PFT green algae.

$$\frac{dGreen_{C,i}}{dt} = dCfix - dCleak - dCvoid - dCresp - dAutC - dDetC - \sum Pred \quad (4.6)$$

$$\frac{dGreen_{N,i}}{dt} = dNH4up + dNO3up - dNH4out - dAutN - dDetN - \sum Pred \quad (4.7)$$

$$\frac{dGreen_{P,i}}{dt} = dPup - dPout - dAutP - dDetP - \sum Pred \quad (4.8)$$

$$\frac{dGreen_{Chl,i}}{dt} = dChlsyn - dChldeg - dAutChl - dDetChl - \sum Pred \quad (4.9)$$

where:

$\frac{dGreen_{X,i}}{dt}$ rate of change for green algal carbon, nitrogen, phosphate and chlorophyll state variable [gX m^{-3} d^{-1}]

The units and description of the fluxes can be found in table 4.7.

4.4.1.3 Protozooplankton

The process PROZOO has been implemented for the PFT protozooplankton. The PFT protozooplankton are defined as protists that are only capable of phagotrophy. Protozooplankton are described using three SVs, i.e., three PROTIST substances.

◇ zooC_1, zooN_1, zooP_1

The protozooplankton SVs increase over time through the assimilation of prey ($assC$, $assN$, $assP$). The protozooplankton SVs decrease over time through mortality (mrt - includes implicit grazing by higher trophic levels through use of a quadratic closure function), the voiding of unassimilated prey ($POCout$, $PONout$, $POPout$) and respiration ($totR$).

$$\frac{dZoo_C}{dt} = dCeat - dPOCout - dCresp - dAutC - dDetC \quad (4.10)$$

$$\frac{dZoo_N}{dt} = dNeat - dPONout - dAutN - dDetN \quad (4.11)$$

$$\frac{dZoo_P}{dt} = dPeat - dPOPout - dAutP - dDetP \quad (4.12)$$

where:

$\frac{dZoo_X}{dt}$ rate of change for protozooplankton carbon, nitrogen and phosphate state variable [gX m^{-3} d^{-1}]

The units and description of the fluxes can be found in table 4.7.

4.4.1.4 Constitutive Mixoplankton (CM)

The processes PROTCM, PROATT and EXTINAPRO have been implemented for the PFT constitutive mixoplankton. The PFT CM are defined as mixoplankton that are primarily phototrophic, but are also capable of phagotrophy. CMs require four SVs, i.e., four PROTIST substances. There are two CM species implemented that can be parameterized to differ from each other in size or fitness.

- ◇ cmC_1, cmChl_1, cmN_1, cmP_1
- ◇ cmC_2, cmChl_2, cmN_2, cmP_2

The CM SVs increase over time through the uptake of nutrients (up_{NH4}, up_{NO3}, up_{PO4}), the fixation of carbon ($Cfix$), the synthesis of chlorophyll-a ($synChl$) and the assimilation of prey ($assC$, $assN$, $assP$). The CM SVs decrease over time through predation ($Pred$), mortality (mrt), the leakage of photosynthate ($Cleak$), the voiding of excess nutrients or carbon ($Nout$, $Pout$, $Cvoid$), the voiding of unassimilated prey ($POCout$, $PONout$, $POPout$), the degradation of chlorophyll-a ($degChl$) and respiration ($totR$).

$$\frac{dCM_{C,i}}{dt} = dCfix + dCeat - dCleak - dCvoid - dPOCout - dCresp - dAutC - dDetC - \sum Pred \quad (4.13)$$

$$\frac{dCM_{N,i}}{dt} = dNH4up + dNO3up + dNeat - dNH4out - dPONout - dAutN - dDetN - \sum Pred \quad (4.14)$$

$$\frac{dCM_{P,i}}{dt} = dPup + dPeat - dPout - dPOPout - dAutP - dDetP - \sum Pred \quad (4.15)$$

$$\frac{dCM_{Chl,i}}{dt} = dChlsyn - dChldeg - dAutChl - dDetChl - \sum Pred \quad (4.16)$$

where:

$\frac{dCM_X}{dt}$ rate of change for protozooplankton carbon, nitrogen, phosphate and chlorophyll state variable [gX m^{-3} d^{-1}]

The units and description of the fluxes can be found in table 4.7.

4.4.1.5 Non-Constitutive Mixoplankton

The processes PROTNCM, PROATT and EXTINAPRO have been implemented for the PFT non-constitutive mixoplankton. The PFT NCM are defined as mixoplankton that are primarily phagotrophic, but are also capable of enslaving the photosynthetic machinery of their phototrophic prey. NCMs require 4 SVs, i.e., four PROTIST substances:

- ◇ ncmC_1, ncmChl_1, ncmN_1, ncmP_1

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While NCMs have been shown to also uptake inorganic nutrients, the percentage of uptake is negligible compared to the acquisition of nutrients from prey (Schoener and McManus, 2017). The NCM SVs increase over time through the assimilation of prey ($assC$, $assN$, $assP$), the uptake of chloroplasts ($upChl$) and the fixation of carbon ($Cfix$). The NCM SVs decrease over time through predation ($Pred$), mortality (mrt), the leakage of photosynthate ($Cleak$), the voiding of unassimilated prey ($POCout$, $PONout$, $POPout$), the loss of chlorophyll-a ($lossChl$) and respiration ($totR$).

$$\frac{dNCM_C}{dt} = dCfix + dCeat - dCleak - dCvoid - dPOCout - dCresp - dAutC - dDetC - \sum Pred \quad (4.17)$$

$$\frac{dNCM_N}{dt} = dNeat - dPONout - dAutN - dDetN - \sum Pred \quad (4.18)$$

$$\frac{dNCM_P}{dt} = dPeat - dPOPout - dAutP - dDetP - \sum Pred \quad (4.19)$$

$$\frac{dNCM_{Chl}}{dt} = dChlup - dChldeg - dAutChl - dDetChl - \sum Pred \quad (4.20)$$

where:

$\frac{dCM_X}{dt}$ rate of change for protozooplankton carbon, nitrogen, phosphate and chlorophyll state variable [gX m^{-3} d^{-1}]

The units and description of the fluxes can be found in table 4.7.

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4.4.2 Formulations

4.4.2.1 Cellular status

For each PFT the cellular quota, the maximum growth rate, the mortality rate, the basal respiration rate, the total respiration rate, the carbon-specific growth rate as well as the cellular nutrient status of nitrogen, phosphate and silica need to be calculated. Table 4.9 summarizes the description of the auxiliaries and section 4.4.8.2 provides the detailed mathematical equations.

The cellular quotas (NC, PC, SC) describe the ratio of the respective protist nutrient SVs to the protist carbon SVs according to Droop (1974). The maximum growth rate (UmT) as well as the mortality rate (mrt) are calculated using the Q10 approach (Van't Hoff, 1884). The basal respiration rate (BR) is defined as a fraction of maximum growth rate (Geider and Osborne, 1989). The total respiration is the sum of the metabolic cost ($redco$) of nitrate reduction ($upNO3$) (Flynn and Flynn, 1998), the anabolic cost (AR) of nitrogen utilization ($upNH4$, $assN$) (Wirtz and Pahlow, 2010), the foraging costs for prey (SDA, $assC$) (Pahlow and Prowe, 2010) and the basal respiration (BR) (Geider and Osborne, 1989).

Furthermore, the nutrient status for nitrogen (NCu), phosphate (PCu) and silica (SCu - only for diatoms) is calculated. The nutrient status returns values between 0 (severely deprived of the respective nutrient) and 1 (at the optimal nutrient quota). The form of the functions depends on the protist's physiology to store the respective nutrient (see fig. 4.3). As protist cells store nitrogen in a form that is not physiologically active (Andersen et al., 1991), the nutrient status for nitrogen (NCu - see fig. 4.3) is a linear function between the minimum and maximum quota. The nutrient status for phosphate (PCu - see fig. 4.3) is calculated using a sigmoidal function to mimic the storage of phosphate as polyphosphate within the cell (Lin et al., 2016). The cellular status of silica (SCu - see fig. 4.3) is a function of the external silica availability, as incorporated silica is not accessible by the cells anymore (Martin-Jézéquel et al., 2003). Applying Liebig's law of minimum (Liebig, 1840), the limiting nutrient ($NPCu$ or $NPSiCu$ - for diatoms) is determined by the minimum nutrient status within the cell.

To ensure that the nitrogen:carbon and phosphate:carbon quotas do not exceed the maximum nutrient quota between time steps, cellular nitrogen and phosphate is voided as soon as the cellular nutrient quota exceeds the maximum nutrient quota ($Nout$ and $Pout$). This does not occur for silica, as incorporated silica cannot be dispelled from the cell walls of diatoms (Martin-Jézéquel et al., 2003). If the nitrogen:carbon quota falls below the minimum nitrogen:carbon quota, then carbon is voided ($Cvoid$).

4.4.2.2 Uptake

In general, the uptake of dissolved inorganic nutrients ($upNH4$, $upNO3$, upP, $upSi$) is a combination of the external availability of the nutrients and the acquisition capability, which depends on the internal nutrient status (Grover, 1991; Moreno and Martiny, 2018). This is achieved by enhancing or repressing the optimal nutrient uptake via sigmoidal functions (see fig. 4.4). Table 4.10 summarizes the description of the auxiliaries and section 4.4.8.3 provides the detailed mathematical equations.

The nutrient uptake at the optimal nutrient quota is regulated via the Michaelis-Menten function and scaled to the maximum growth rate and the optimal nutrient:carbon quota. For the uptake of NH_4^+ and NO_3^-, the optimum nutrient uptake is also scaled to the relative growth feasible with the respective nutrient. If the cellular nutrient quota is below the optimum nutrient quota (i.e. nutrient stressed), the nutrient uptake is enhanced until the maximum nutrient uptake is reached (Goldman and Glibert, 1982; Perry, 1976). If the cellular nutrient quota is

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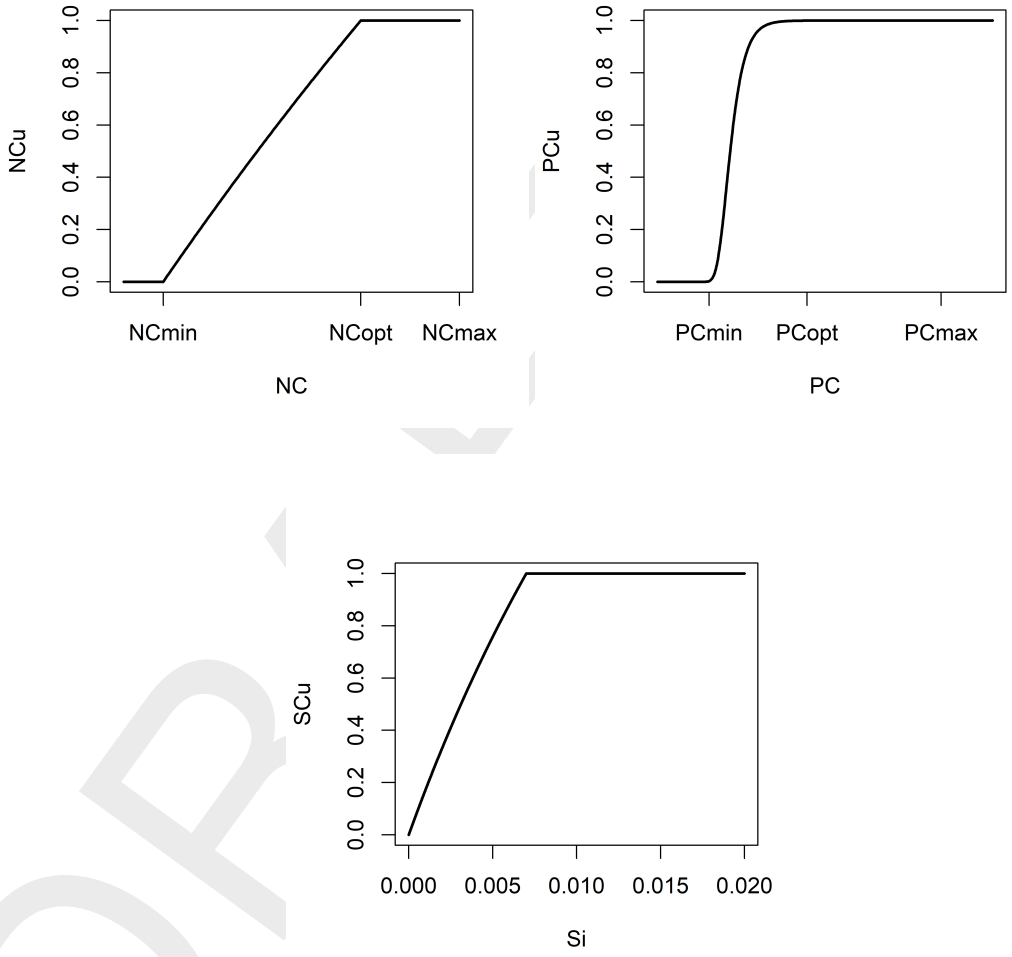

Figure 4.3: *Visualization of the internal nutrient status for a) nitrogen NCu [-], b) phosphate PCu [-] and c) silica SCu [-] (modified from Flynn (2021)). A value of 1 denotes that the internal nutrient stores are optimal, a value of 0 that the internal nutrient stores are completely depleted. The figures display that while NCu decreases linearly as soon as the optimal quota is not reached, PCu does not. These functions mathematically describe that nitrogen cannot be stored within the cell, while phosphate as polyphosphate can.*

above the optimum nutrient quota, the nutrient uptake for NH_4^+ and PO_4^{3-} are repressed (Wirtz and Pahlow, 2010), while the nutrient uptake for NO_3^- (Dugdale et al., 2007; Domingues et al., 2011) and silica are stopped all together. Furthermore, the uptake of nitrogen is a function of the cellular phosphate:carbon quota resulting in a decrease of the cellular nitrogen:carbon quota during phosphate stress (Pahlow and Oschlies, 2009).

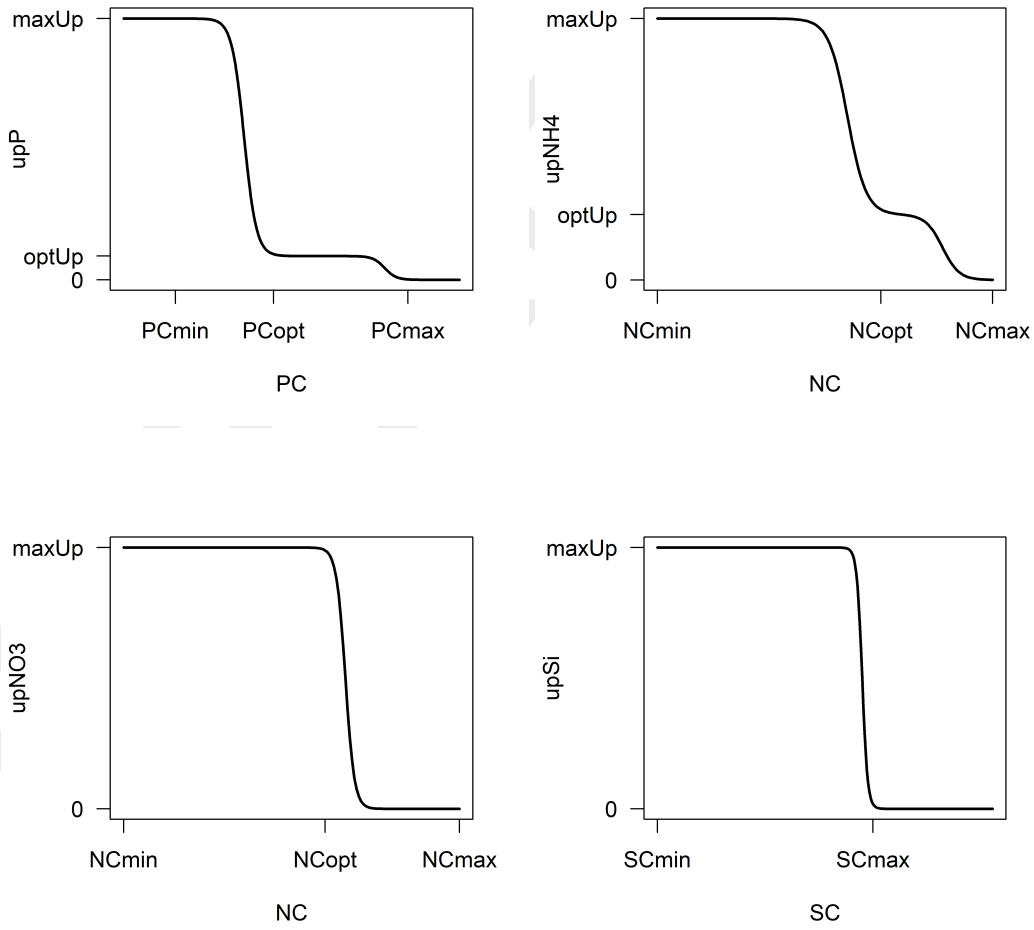

Figure 4.4: *Visualization of the nutrient uptake for a) phosphate (upP [gP gC^{-1} d^{-1}]), b) ammonium ($upNH4$ [gN gC^{-1} d^{-1}]), c) nitrate ($upNO3$ [gN gC^{-1} d^{-1}]) and d) silica ($upSi$ [gSi gC^{-1} d^{-1}]) (modified from Flynn (2021)). The figures display that the uptake of phosphate and ammonium is repressed once the optimum cellular status is reached, while the uptake of nitrate and silica is stopped all together after the optimum quota is passed.*

4.4.2.3 Phototrophy

The photosynthesis equations are based on the photosynthesis-irradiance curve that requires three input parameters: the maximum photosynthetic rate ($PSqm$), the chlorophyll-a specific initial slope (α^{Chl}) and photon flux density (PFD) (Jassby and Platt, 1976). Table 4.11 summarizes the description of the auxiliaries and section 4.4.8.4 provides the detailed mathematical equations.

The maximum rate of photosynthesis covers the basal respiration (BR), the maximum growth rate (UmT), the leakage of photosynthate as DOC ($PSDOC$) (Thornton, 2014) and the costs of reducing nitrate ($redco$ and AR) (Dugdale et al., 2007) which (with the exception of basal respiration) are all influenced by the nitrogen quota of the cell (NCu) (Droop, 1974; Thornton, 2014; Flynn and Flynn, 1998). Furthermore, the maximum rate of photosynthesis depends on the organism's physiology, i.e. their capability to overcompensate the photosynthetic rate ($relPS$) (Geider, 1993). The maximum photosynthetic rate along with the initial slope (α^{Chl}) and the photon flux density (PFD) are used to calculate gross photosynthesis ($Cfix$) using the Smith equation (Smith, 1936). The net photosynthesis rate ($netPS$) is determined by subtracting the loss through leakage ($Cleak$).

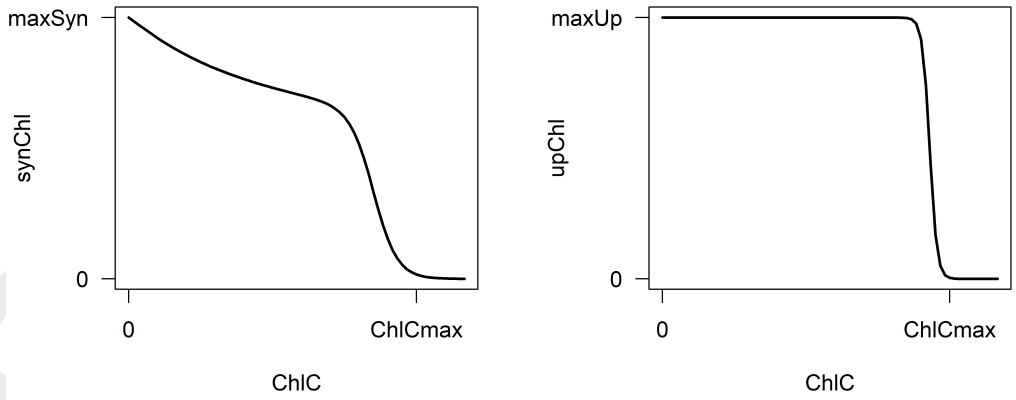

Figure 4.5: *Visualization of the a) synthesis of chlorophyll-a for diatoms, green algae and CMs (synChl)and b) the uptake of chloroplasts by NCMs from their prey (upChl). The figures display that the synthesis of chlorophyll-a is repressed depending on the amount of carbon fixed and that NCMs can uptake chloroplasts until a maximum chlorophyll-a:carbon is reached.*

Primarily phototrophic organisms such as diatoms, green algae and CMs can regulate their chlorophyll-a synthesis ($synChl$ - see fig. 4.5) (Geider and Piatt, 1986). If the cell is nutrient limited or the cell fixed too much carbon, the synthesis of chlorophyll-a is repressed (Moreno and Martiny, 2018). Under low light, the synthesis of chlorophyll-a is enhanced (Sukenik et al., 1987). Chlorophyll-a is also decomposed with a linear relationship to the nitrogen status ($degChl$) (Wirtz and Pahlow, 2010). Primarily phagotrophic organisms such as NCMs cannot produce their own chloroplasts, so they acquire them from prey ($upChl$). This acquisition is limited by a maximum chlorophyll-a:carbon quota via a sigmoidal function (see fig. 4.5). Those acquired chloroplasts are subsequently lost at a fixed linear rate ($lossChl$) (Ghyoot et al., 2017).

4.4.2.4 Phagotrophy

The phagotrophic functions can be divided into four subsections: determining the prey capture, determining the prey quality, determining the predator ingestion rate and determining the predator assimilation rate. Table 4.12 summarizes the description of the auxiliaries and section 4.4.8.5 provides the detailed mathematical equations.

The prey capture depends on the motility of predator and prey as well as the density of the prey. The motility (mot) is derived from a linear regression by Flynn and Mitra (2016) that uses the organisms' equivalent spherical diameter as an input. The density of the prey ($nrPrey$) is calculated from the cellular carbon content ($Ccell$) and the current carbon protist state variable ($protC$). The motility of predator and prey as well as the density of prey are input parameters to determine the encounter rate (enc) according to the empirical Rothschild equation (Rothschild and Osborn, 1988). This encounter rate multiplied with the optimum capture rate ($optCR$) of the predator and the predator specific prey handling index (PR) determines the amount of specific prey the predator can capture. This is summed over all prey items ($sumCP$). As mixoplankton do not have the same capacity to ingest prey in the dark as in light (Skovgaard, 1996; Anderson et al., 2018), a light-dependent inhibition curve ($inhLight$ - sigmoidal curve) is multiplied with the encounter rate and limits the capture of prey depending on the light availability. The light-dependent inhibition curve takes the photon flux density as well as the parameter $relPhag$ (fraction of prey that can be ingested in the dark) as input.

The prey quality determines the assimilation efficiency ($opAE$) of the predator. A decrease in prey quality leads to a decrease in assimilation efficiency (Elser et al., 2000). The nutrient quota of the captured prey is compared against the nutrient quota of the predator. This returns a value between minimum (AEo) and the maximum assimilation efficiency (AEm see solid, black line in figure 4.6).

The predator ingestion rate ($ingC$ - see figure 4.6) at very low prey densities is limited by the amount of prey ($sumCP$) that can be captured and at very high prey densities by the predator's satiation ($ingSat$) (Flynn and Mitra, 2016). This satiation ingestion rate is calculated using a Holling type II curve (Holling, 1959) scaled to its maximum ingestion rate ($maxIng$). The maximum ingestion covers the maximum growth rate and basal respiration rate taking the quality of the captured prey into account. The ingestion of the other prey nutrients ($ingN$, $ingP$) is referenced to the carbon ingestion and the prey nutrient quota.

The predator assimilation rate ($assC$) is determined by taking the carbon specific ingestion rate and limiting it to the assimilation efficiency. The assimilation of the other prey nutrients ($assN$, $assP$) is referenced to the carbon assimilation and the optimum predator nutrient quota. Non-assimilated prey is voided as particulate organics, i.e. $POCout$, $PONout$ and $POPout$.

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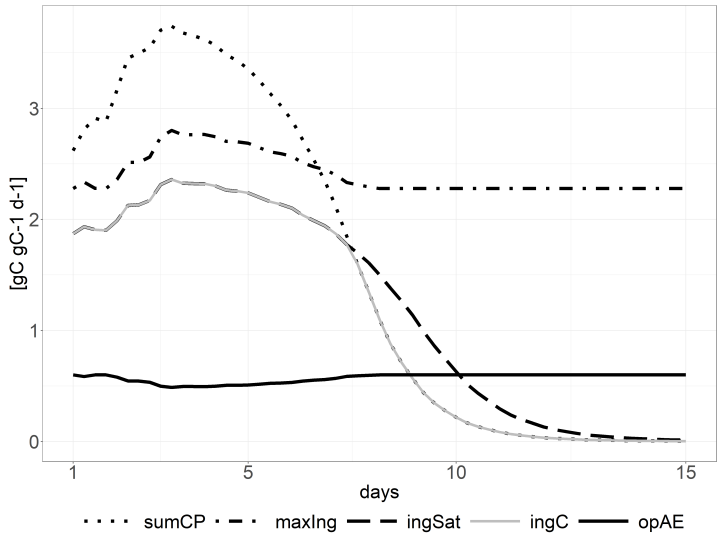

Figure 4.6: *Visualization of the ingestion rate. The ingestion increases with decreasing prey quality ($opAE$ - solid, black line), while the actual ingestion ($ingC$ - solid, grey line) is limited either by the satiation rate ($ingSat$ - dashed, black line) or by the amount of captured prey ($sumCP$ - dotted, black line).*

4.4.3 Directives for use

- ◇ Unlike the BLOOM and DYNAMO modules for algal growth, each PFT is characterised by several state variables or constituents. For the diatoms the state variables represent carbon, nitrogen, phosphorus, silica and chlorophyll. For the non-diatiom algae, silica is missing and for the protozooplankton chlorophyll is not needed. A PFT can only be properly modelled if all these constitutents are modelled as substances. The constituents are used to model the changing stoichiometry of the PFTs.
  It is advised to initialise the constituents in such a way that the ratio of the constituent concentrations to the carbon concentration is between the lower and upper bounds for the stoichiometric ratio. If not, the process will develop the concentrations towards either limit, but a realistic stoichiometry is more appropriate.
- ◇ For information on the parameterization of different PFTs please see Schneider et al. (2021)
- ◇ The PFT non-constitutive mixoplankton is implemented technically, but has not been tested in a ecosystem setting as it is difficult to parameterize the NCM due to lack of literature and in-situ data (as of 12/2021)

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4.4.4 State variables

Table 4.4: *List of all model state variables (SV), their description and unit.*

SV name in formulae	SV name in input	SV description	unit
	PO4	initial DIP	gP m^{-3}
	NH4	initial NH_4^+	gN m^{-3}
	NO3	initial NO_3^-	gN m^{-3}
	Si	initial Si	gSi m^{-3}
	Opal	Opal-Si	gSi m^{-3}
	POC1	POC1 (fast decomposing fraction)	gC m^{-3}
	PON1	PON1 (fast decomposing fraction)	gN m^{-3}
	POP1	POP1 (fast decomposing fraction)	gP m^{-3}
	DOClab	labile DOC	gC m^{-3}
	OXY	oxygen	gO2 m^{-3}
protC	greenC_i	green algae C-biomass of species i	gC m^{-3}
protChl	greenChl_i	green algae Chl-biomass of species i	gChl m^{-3}
protN	greenN_i	green algae N-biomass of species i	gN m^{-3}
protP	greenP_i	green algae P-biomass of species i	gP m^{-3}
protC	diatC_i	diatom C-biomass of species i	gC m^{-3}
protChl	diatChl_i	diatom Chl-biomass of species i	gChl m^{-3}
protN	diatN_i	diatom N-biomass of species i	gN m^{-3}
protP	diatP_i	diatom P-biomass of species i	gP m^{-3}
protSi	diatSi_i	diatom Si-biomass of species i	gSi m^{-3}
protC	cmC_i	CM C-biomass of species i	gC m^{-3}
protChl	cmChl_i	CM Chl-biomass of species i	gChl m^{-3}
protN	cmN_i	CM N-biomass of species i	gN m^{-3}
protP	cmP_i	CM P-biomass of species i	gP m^{-3}
protC	zooC	protozooplankton C-biomass	gC m^{-3}
protN	zooN	protozooplankton N-biomass	gN m^{-3}
protP	zooP	protozooplankton P-biomass	gP m^{-3}
protC	ncmC	NCM C-biomass	gC m^{-3}
protChl	ncmChl	NCM Chl-biomass	gChl m^{-3}
protN	ncmN	NCM N-biomass	gN m^{-3}

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Table 4.4 – continued from previous page

SV name in formulae	**SV name in input**	**SV description**	**unit**
protP	ncmP	NCM P-biomass	gP m^{-3}

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4.4.5 Parameters

Table 4.5: *List of all model parameters for a generic PFT, their description, unit and default value. Default parameter values labeled with a * are important parameters to modify in order to simulate different PFTs. Please see Schneider et al. (2021) for more information on the choice of parameter values. Dmensionless parameters are denoted with [-].*

Name in formulae	Name in input	parameter description	unit	value
AEm	AEm_{Xi}	maximum assimilation efficiency (AE) for PFT X, species i	-	0.6
AEo	AEo_{Xi}	minimum AE for PFT X, species i	-	0.3
alpha	$alpha_{Xi}$	alpha for photosynthesis in protist for PFT X, species i	gC $gChl^{-1}$ m^2 $umol^{-1}$ photon	7.00E-06 *
abcoChl	$abcChl_{Xi}$	light absorbance coefficient for chlorophyll for PFT X, species i	m^2 $gChl^{-1}$	20
Ccell	$Ccell_{Xi}$	C content of protist cell for PFT X, species i	pgC $cell^{-1}$	543.995 *
ChlCmax	$ChlCm_{Xi}$	maximum cellular Chl:C ratio for PFT X, species i	gChl gC^{-1}	0.06 *
ChlCmin	$ChlCo_{Xi}$	minimum cellular Chl:C ratio for PFT X, species i	gChl gC^{-1}	0.001
CR	CR_{Xi}	catabolic respiration quotient for PFT X, species i	-	0.05
degChl	$degChl_{Xi}$	Chl degradation for PFT X, species i	d^{-1}	0.72
FrAut	$FrAut_{Xi}$	fraction of mortality to autolysis for PFT X, species i	-	0.3
FrDet	$FrDet_{Xi}$	fraction of mortality to detritus for PFT X, species i	-	0.7
kAE	kAE_{Xi}	control of AE in response to prey quality for PFT X, species i	-	1000
KtNH4	$KtNH4_{Xi}$	Kt for NH_4^+ transport for PFT X, species i	gN m^{-3}	0.007
KtNO3	$KtNO3_{Xi}$	Kt for NO_3^- transport for PFT X, species i	gN m^{-3}	0.007
KtP	KtP_{Xi}	Kt for DIP transport for PFT X, species i	gP m^{-3}	0.031
KtSi	$KtSi_{Xi}$	Kt for DiSi transport for PFT X, species i	gSi m^{-3}	0.028
MrtRT	$MrtRT_{Xi}$	mortality at reference temperature for PFT X, species i	-	0.035 *

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Table 4.5 – continued from previous page

Name in formulae	Name in input	parameter description	unit	value
Mphoto	$Mphoto_{Xi}$	acclimation rate to light for PFT X, species i	-	0.5
NCmax	NCm_{Xi}	N:C that totally represses NH_4^+ transport for PFT X, species i	gN gC^{-1}	0.2 *
NCmin	NCo_{Xi}	minimum N-quota for PFT X, species i	gN gC^{-1}	0.05 *
NCopt	$NCopt_{Xi}$	N:C for growth under optimal conditions for PFT X, species i	gN gC^{-1}	0.15 *
NO3Cmax	$NO3Cm_{Xi}$	N:C that totally represses NO_3^- transport for PFT X, species i	gN gC^{-1}	0.16 *
NO3Copt	$NO3Copt_{Xi}$	N:C for growth on NO_3^- under optimal conditions for PFT X, species i	gN gC^{-1}	0.15 *
optCR	$optCR_{Xi}$	proportion of prey captured by starved Zoo for PFT X, species i	-	0.1
PCmax	PCm_{Xi}	PC maximum quota for PFT X, species i	gP gC^{-1}	0.05 *
PCmin	PCo_{Xi}	PC minimum quota for PFT X, species i	gP gC^{-1}	0.005 *
PCoNCm	$PCoNCm_{Xi}$	maximum NC when PC is minimum (PCu = 0) for PFT X, species i	gN gC^{-1}	0.12 *
PCoNCop	$PCoNCop_{Xi}$	optimum NC when PC is minimum (PCu = 0) for PFT X, species i	gN gC^{-1}	0.1 *
PCopt	$PCopt_{Xi}$	PC optimum quota for PFT X, species i	gP gC^{-1}	0.024 *
PSDOC	$PSDOC_{Xi}$	proportion of current PS being leaked as DOC for PFT X, species i	-	0.1
Q10	$Q10_{Xi}$	Q10 for UmRT for PFT X, species i	-	1.8
r	r_{Xi}	radius of nutrient repleted protist cell for PFT X, species i	um	10.0 *
redco	$redco_{Xi}$	C respired to support nitrate reduction for NH_4^+ for PFT X, species i	gC gN-1	1.71
relPhag	$relPhag_{Xi}$	relative phagotrophy in night:day for PFT X, species i	-	0.5 *
relPS	$relPS_{Xi}$	relative PSmax:Umax on phototrophy for PFT X, species i	-	1.0 *
relUmNH4	$ReUmNH4_{Xi}$	max. growth rate supported by NH_4^+:Umax for PFT X, species i	-	0.9

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Table 4.5 – continued from previous page

Name in formulae	**Name in input**	**parameter description**	**unit**	**value**
relUmNO3	ReUmNO3$_{Xi}$	max. growth rate supported by NO_3^-:Umax for PFT X, species i	-	0.8
RT	RT$_{Xi}$	reference temperature for UmRTfor PFT X, species i	deg C	10
SDA	SDA$_{Xi}$	specific dynamic action for PFT X, species i	-	0.3
UmRT	UmRT$_{Xi}$	maximum growth rate at reference T for PFT X, species i	d^{-1}	0.7 *
SCmax	SCm$_{Xi}$	absolute maximum Si:C (diatom) for PFT X, species i	gSi gC^{-1}	0.2
SCmin	SCo$_{Xi}$	minimum Si:C (diatom) for PFT X, species i	gSi gC^{-1}	0.02
SCopt	SCopt$_{Xi}$	optimum Si:C for (diatom) growth for PFT X, species i	gSi gC^{-1}	0.1

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4.4.6 Auxiliaries

Table 4.6: *List of all model auxiliaries for a generic PFT, their description and unit.*

name in formulae	name in input	auxiliary description	unit
NC	NC_{Xi}	cellular nitrogen:carbon ratio for PFT X, species i	gN gC^{-1}
PC	PC_{Xi}	cellular phosphate:carbon ratio for PFT X, species i	gP gC^{-1}
SC	SC_{Xi}	cellular silica:carbon ratio for PFT X, species i	gSi gC^{-1}
ChlC	$ChlC_{Xi}$	cellular chlorphyll:carbon ratio for PFT X, species i	gChl gC^{-1}
UmT	UmT_{Xi}	temperature dependent maximum growth rate for PFT X, species i	gC gC^{-1} d^{-1}
BR	BR_{Xi}	temperature dependent basal respiration rate for PFT X, species i	gC gC^{-1} d^{-1}
NCu	NCu_{Xi}	cellular nitrogen status for PFT X, species i	-
PCu	PCu_{Xi}	cellular phosphate status for PFT X, species i	-
SCu	SCu_{Xi}	cellular silica status for PFT X, species i	-
NPCu	$NPCu_{Xi}$	Liebig nutrient limitation for PFT X, species i	-
mot	mot_{Xi}	motility of the protist for PFT X, species i	m s^{-1}
upP	upP_{Xi}	uptake rate of phosphate for PFT X, species i	gP gC^{-1} d^{-1}
upNH4	$upNH4_{Xi}$	uptake rate of ammonium for PFT X, species i	gN gC^{-1} d^{-1}
upNO3	$upNO3_{Xi}$	uptake rate of nitrate for PFT X, species i	gN gC^{-1} d^{-1}
upSi	$upSi_{Xi}$	uptake rate of silica for PFT X, species i	gSi gC^{-1} d^{-1}
upChl	$upChl_{Xi}$	uptake rate of chlorphyll for PFT X, species i	gChl gC^{-1} d^{-1}
PSqm	$PSqm_{Xi}$	maximum photosynthetic rate for PFT X, species i	gC gC^{-1} d^{-1}
PS	PS_{Xi}	gross photosynthetic rate for PFT X, species i	gC gC^{-1} d^{-1}
Cfix	$Cfix_{Xi}$	net photosynthetic rate for PFT X, species i	gC gC^{-1} d^{-1}
synChl	$synChl_{Xi}$	synthesis rate of chlorophyll-a for PFT X, species i	gChl gC^{-1} d^{-1}

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Table 4.6 – continued from previous page

name in formulae	name in input	auxiliary description	unit
degChl	$degChl_{Xi}$	degradation rate of chlorphyll for PFT X, species i	gChl gC^{-1} d^{-1}
sumCP	$sumCP_{Xi}$	rate of all potential prey captures for PFT X, species i	gC gC^{-1} d^{-1}
ingNC	$ingNC_{Xi}$	rate of captured nitrogen:carbon for PFT X, species i	gN gC^{-1} d^{-1}
ingPC	$ingPC_{Xi}$	rate of captured phosphate:carbon for PFT X, species i	gP gC^{-1} d^{-1}
ppNC	$ppNC_{Xi}$	ratio of captured prey nitrogen: predator nitrogen for PFT X, species i	-
ppPC	$ppPC_{Xi}$	ratio of captured prey nitrogen: predator nitrogen for PFT X, species i	-
stoichP	$stoichP_{Xi}$	limiting nutrient in prey for PFT X, species i	-
opAE	$opAE_{Xi}$	assimilation efficiency of predator for PFT X, species i	-
maxIng	$maxIng_{Xi}$	maximum ingestion rate for PFT X, species i	gC gC^{-1} d^{-1}
ingSat	$ingSat_{Xi}$	satiation ingestion rate for PFT X, species i	gC gC^{-1} d^{-1}
ingC	$ingC_{Xi}$	ingestion rate of prey carbon for PFT X, species i	gC gC^{-1} d^{-1}
assC	$assC_{Xi}$	assimilation rate of prey carbon for PFT X, species i	gC gC^{-1} d^{-1}
ingN	$ingN_{Xi}$	ingestion rate of prey nitrogen for PFT X, species i	gN gC^{-1} d^{-1}
ingP	$ingP_{Xi}$	ingestion rate of prey phosphate for PFT X, species i	gP gC^{-1} d^{-1}
assN	$assN_{Xi}$	assimilation rate of prey nitrogen for PFT X, species i	gN gC^{-1} d^{-1}
assP	$assP_{Xi}$	assimilation rate of prey phosphate for PFT X, species i	gP gC^{-1} d^{-1}
totR	$totR_{Xi}$	total respiration rate for PFT X, species i	gC gC^{-1} d^{-1}
Cu	Cu_{Xi}	carbon-specific growth rate for PFT X, species i	gC gC^{-1} d^{-1}
mrtAut	$mrtAut_{Xi}$	mortality rate autolysis for PFT X, species i	gC gC^{-1} d^{-1}
mrtDet	$mrtDet_{Xi}$	mortality rate detritus for PFT X, species i	gC gC^{-1} d^{-1}
IInh	$IInh_{Xi}$	light inhibition factor for PFT X, species i	-

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Table 4.6 – continued from previous page

name in formulae	**name in input**	**auxiliary description**	**unit**
capPrey	capPrey$_{Xi}$	potential C-specific capture of prey for PFT X, species i	gC gC^{-1} d^{-1}

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4.4.7 Fluxes

Table 4.7: *List of all model fluxes for a generic PFT, their description and unit.*

name in formulae	name in input	flux description	unit
dNH4up	dNH4up$_{Xi}$	uptake of NH_4^+ into algal biomass for PFT X, species i	gN m^{-3} d^{-1}
dNO3up	dNO3up$_{Xi}$	uptake of NO_3^- into algal biomass for PFT X, species i	gN m^{-3} d^{-1}
dPup	dPup$_{Xi}$	uptake of PO_4^{3-} into algal biomass for PFT X, species i	gP m^{-3} d^{-1}
dSiup	dSiup$_{Xi}$	uptake of Si into algal biomass for PFT X, species i	gSi m^{-3} d^{-1}
dCfix	dCfix$_{Xi}$	contribution to biomass growth from C-fixation for PFT X, species i	gC m^{-3} d^{-1}
dChlsyn	dChlsyn$_{Xi}$	synthesis Chl rate of change for PFT X, species i	gChl m^{-3} d^{-1}
dChldeg	dChldeg$_{Xi}$	degradation Chl rate of change for PFT X, species i	gChl m^{-3} d^{-1}
dChlup	dChlup$_{Xi}$	acquistion of prey Chl by NCM for PFT X, species i	gChl m^{-3} d^{-1}
dCresp	dCresp$_{Xi}$	total respiration rate for PFT X, species i	gC m^{-3} d^{-1}
dCleak	dCleak$_{Xi}$	release of DOC for PFT X, species i	gC m^{-3} d^{-1}
dCvoid	dCvoid$_{Xi}$	voiding of C as DOC if NC falls below NCmin for PFT X, species i	gC m^{-3} d^{-1}
dNH4out	dNH4out$_{Xi}$	NH_4^+ release by regeneration for PFT X, species i	gN $^{-3}$ d^{-1}
dPout	dPout$_{Xi}$	PO_4^{3-} release by regeneration for PFT X, species i	gP $^{-3}$ d^{-1}
dCeat	dCeat$_{Xi}$	assimilation of C from prey for PFT X, species i	gC m^{-3} d^{-1}
dNeat	dNeat$_{Xi}$	assimilation of N from prey for PFT X, species i	gN m^{-3} d^{-1}
dPeat	dPeat$_{Xi}$	assimilation of P from prey for PFT X, species i	gP m^{-3} d^{-1}
dPOCout	dPOCout$_{Xi}$	rate of voiding of C as particulates for PFT X, species i	gC m^{-3} d^{-1}
dPONout	dPONout$_{Xi}$	rate of voiding of N as particulates for PFT X, species i	gN m^{-3} d^{-1}
dPOPout	dPOPout$_{Xi}$	rate of voiding of P as particulates for PFT X, species i	gP m^{-3} d^{-1}

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Table 4.7 – continued from previous page

name in formulae	name in input	flux description	unit
dAutC	dAutC$_{Xi}$	protist-C mortality through Autolysis for PFT X, species i	gC m^{-3} d^{-1}
dDetC	dDetC$_{Xi}$	protist-C mortality through Detritus for PFT X, species i	gC m^{-3} d^{-1}
dAutN	dAutN$_{Xi}$	protist-N mortality through Autolysis for PFT X, species i	gN m^{-3} d^{-1}
dDetN	dDetN$_{Xi}$	protist-N mortality through Detritus for PFT X, species i	gN m^{-3} d^{-1}
dAutP	dAutP$_{Xi}$	protist-P mortality through Autolysis for PFT X, species i	gP m^{-3} d^{-1}
dDetP	dDetP$_{Xi}$	protist-P mortality through Detritus for PFT X, species i	gP m^{-3} d^{-1}
dAutSi	dAutSi$_{Xi}$	protist-Si mortality through Autolysis for PFT X, species i	gSi m^{-3} d^{-1}
dDetSi	dDetSi$_{Xi}$	protist-Si mortality through Detritus for PFT X, species i	gSi m^{-3} d^{-1}
dAutChl	dAutChl$_{Xi}$	protist-Chl mortality through Autolysis for PFT X, species i	gChl m^{-3} d^{-1}
dDetChl	dDetChl$_{Xi}$	protist-Chl mortality through Detritus for PFT X, species i	gChl m^{-3} d^{-1}
dD1C	dYiC$_{Xi}$	mortality of prey Y, species i through predator X, species i	gC m^{-3} d^{-1}
dD1Chl	dYiChl$_{Xi}$	mortality of prey Y, species i through predator X, species i	gChl m^{-3} d^{-1}
dD1N	dYiN$_{Xi}$	mortality of prey Y, species i through predator X, species i	gN m^{-3} d^{-1}
dD1P	dYiP$_{Xi}$	mortality of prey Y, species i through predator X, species i	gP m^{-3} d^{-1}
dD1Si	dYiSi$_{Xi}$	mortality of prey Y, species i through predator X, species i	gSi m^{-3} d^{-1}

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$$dNH4up = protC \cdot upNH4 \tag{4.21}$$
$$dNO3up = protC \cdot upNO3 \tag{4.22}$$
$$dPup = protC \cdot upP \tag{4.23}$$
$$dSiup = protC \cdot upSi \tag{4.24}$$
$$dCfix = protC \cdot Cfix \tag{4.25}$$
$$dChlsyn = protC \cdot synChl \tag{4.26}$$
$$dChldeg = protC \cdot degChl \; or \; protC \cdot degChl_{NCM} \tag{4.27}$$
$$dChlup = protC \cdot (ingC \cdot \frac{capPrey}{sumCP}) \cdot \frac{preyChl}{preyC} \cdot upChl \tag{4.28}$$
$$dCresp = protC \cdot totR \tag{4.29}$$
$$dCleak = protC \cdot (PS - Cfix) \tag{4.30}$$
$$dCvoid = protC - protN/NCmin \tag{4.31}$$
$$dNH4out = max(0.0, protN - protC \cdot NCmax) \tag{4.32}$$
$$dPout = max(0.0, protP - protC \cdot PCmax) \tag{4.33}$$
$$dCeat = protC \cdot assC \tag{4.34}$$
$$dNeat = protC \cdot assN \tag{4.35}$$
$$dPeat = protC \cdot assP \tag{4.36}$$
$$dPOCout = protC \cdot (ingC - assC) \tag{4.37}$$
$$dPONout = protC \cdot (ingN - assN) \tag{4.38}$$
$$dPOPout = protC \cdot (ingP - assP) \tag{4.39}$$
$$dAutC = protC \cdot mrt \cdot FrAut \tag{4.40}$$
$$dDetC = protC \cdot mrt \cdot FrDet \tag{4.41}$$
$$dAutN = protN \cdot mrt \cdot FrAut \tag{4.42}$$
$$dDetN = protN \cdot mrt \cdot FrDet \tag{4.43}$$
$$dAutP = protP \cdot mrt \cdot FrAut \tag{4.44}$$
$$dDetP = protP \cdot mrt \cdot FrDet \tag{4.45}$$
$$dAutSi = protSi \cdot mrt \cdot FrAut \tag{4.46}$$
$$dDetSi = protSi \cdot mrt \cdot FrDet \tag{4.47}$$
$$dAutChl = protChl \cdot mrt \cdot FrAut \tag{4.48}$$
$$dDetChl = protChl \cdot mrt \cdot FrDet \tag{4.49}$$
$$dD1C = protC \cdot (ingC \cdot \frac{capPrey}{sumCP}) \tag{4.50}$$
$$dD1Chl = dD1C \cdot (preyChl/preyC) \tag{4.51}$$
$$dD1N = dD1C \cdot (preyN/preyC) \tag{4.52}$$
$$dD1P = dD1C \cdot (preyP/preyC) \tag{4.53}$$
$$dD1Si = dD1C \cdot (preySi/preyC) \tag{4.54}$$
$$\tag{4.55}$$

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4.4.8 Modules

4.4.8.1 Module base functions

This module provides the equations for basic mathematical functions that are used to describe physiological processes such as internal nutrient status of the cell or nutrient uptake by the cell. Thus, these functions are called by the other modules.

$$normalize(x, x_{min}, x_{max}) = \frac{x - x_{min}}{x_{max} - x_{min}}$$

$$gompertz(L, b, x) = L \cdot exp(-b \cdot exp(-k \cdot x))$$

$$monod(R, kt) = \frac{R}{R + kt}$$

$$logistic(L, k, b, x) = \frac{L}{(1.0 + exp(-k * (x - x_0)))}$$

Table 4.8: *List of all parameters for the mathematical functions listed above.*

parameter	parameter description	unit
L	upper asymptote	-
b	displacement along the x-axis	-
k	growth rate of gompetz curve	-
R	resource	-
kt	half-saturation constant	-
x_0	value at sigmoid's midpoint	-

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4.4.8.2 Module cellular status

Table 4.9: *Summary of the auxiliaries in the module cellular status.*

auxiliary	description	unit	origin	eq. #
NC	cellular carbon quota for nitrogen	gN gC^{-1}	Flynn 2001	4.56
PC	cellular carbon quota for phosphate	gP gC^{-1}	Flynn 2001	4.57
SC	cellular carbon quota for silica	gSi gC^{-1}	Flynn 2001	4.58
$ChlC$	cellular carbon quota for chlorophyll-a	gChl gC^{-1}	Flynn 2001	4.59
UmT	maximum possible growth rate at the current temperature	d^{-1}	Flynn 2021	4.60
BR	basal respiration at the current temperature	d^{-1}	Flynn 2001	4.62
$totR$	total respiration taking metabolic, anabolic and foraging costs into account.	gC gC^{-1} d^{-1}	Flynn 2021	4.68
Cu	net carbon specific growth rate taking phagotrophic and phototrophic carbon sources into account	gC gC^{-1} d^{-1}	Flynn 2021	4.68
NCu	cellular nitrogen status (1 = saturated; 0 = limited) determined using a linear relationship.	-	modified from Flynn 2021	4.64
PCu	cellular phosphate status (1 = saturated; 0 = limited) determined using a Gompertz curve	-	modified from Flynn 2021	4.66
SCu	cellular silica status (1 = saturated; 0 = limited)	-	Flynn 2021	4.66
$DOCvoid$	voiding of DOC if minimum quota is reached	gC gC^{-1}	Flynn 2021	4.63
mrt	mortality rate	gC gC^{-1}	Flynn 2021	4.61

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$$NC = \frac{protN}{protC} \tag{4.56}$$

$$PC = \frac{protP}{protC} \tag{4.57}$$

$$SC = \frac{protSi}{protC} \tag{4.58}$$

$$ChlC = \frac{protChl}{protC} \tag{4.59}$$

$$UmT = UmRT \cdot Q10^{\frac{Temp-RT}{10}} \tag{4.60}$$

$$mrt = mrtRT \cdot Q10^{\frac{Temp-RT}{10}} \tag{4.61}$$

$$BR = UmT \cdot CR \tag{4.62}$$

$$DOCvoid = \{NC < NCmin, protC - \frac{protN}{NCmin}, 0.0\} \tag{4.63}$$

$$NCu = min(1.0, max(0.0, normalizeNC, NCmin, NCmax)) \tag{4.64}$$

$$PCu = gompertz(1.0, 6.0, 10.0, normalize(PC, PCmin, PCmax)) \tag{4.65}$$

$$SCu = min((monod(Si, ktSi) \cdot \frac{SCopt}{SCmin}), 1.0) \tag{4.66}$$

$$totR = (redco \cdot upNO3) + AR \cdot (upNH4 + upNO3 + assN \cdot SDA) + (assC \cdot SDA) + BR \tag{4.67}$$

$$Cu = Cfix + assC - totR \tag{4.68}$$

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4.4.8.3 Module uptake

Table 4.10: *Summary of the auxiliaries in the module uptake.*

Auxiliary	Description	Unit	Origin	Eq. #
upP	uptake of phosphate described using the monod function and enhanced or repressed using two logistic sigmoid functions.	gP gC^{-1} d^{-1}	modified from Flynn 2021	4.69
$upNH4$	uptake of ammonium described using the monod function and enhanced or repressed using two logistic sigmoid functions.	gN gC^{-1} d^{-1}	modified from Flynn 2021	4.70
$upNO3$	uptake of nitrite described using the monod function and enhanced using a logistic sigmoid functions.	gN gC^{-1} d^{-1}	modified from Flynn 2021	4.71
$upSi$	uptake of silica described using the monod function and enhanced using a logistic sigmoid functions.	gSi gC^{-1} d^{-1}	modified from Flynn 2021	4.72

P uptake

$$
\begin{aligned}
APin_P &= logistic(1.0, -16.0, 0.7, normalize(PC, PCmin, PCopt)) \\
APde_P &= logistic(1.0, -40.0, 0.9, normalize(PC, PCmin, PCmax)) \\
upP_{opt} &= monod(P, ktP) \cdot UmT \cdot PCopt \\
upP &= upP_{opt} \cdot APin_P \cdot 10.0 + upP_{opt} \cdot APde_P
\end{aligned}
\tag{4.69}
$$

NH_4^+ uptake

$$
\begin{aligned}
NCPopt &= ((PCu < NCu), PCoNCop + PCu \cdot (NC - PCoNCop), NC) \\
APin_{NH4} &= logistic(1.0, -24.0, 0.85, normalize(NC, NCmin, NCPopt)) \\
NCPopt &= ((PCu < NCu), PCoNCm + PCu \cdot (NC - PCoNCm), NC) \\
APde_P &= logistic(1.0, -40.0, 0.85, normalize(NC, NCmin, NCPmax)) \\
upNH4_{opt} &= monod(NH4, ktNH4) \cdot UmT \cdot NCopt \cdot relUm_{NH4} \\
upNH4 &= upNH4_{opt} \cdot APin_{NH4} \cdot 3.0 + upNH4_{opt} \cdot APde_{NH4}
\end{aligned}
\tag{4.70}
$$

NO_3^- uptake

$$
\begin{aligned}
NCPm &= ((PCu < NCu), PCoNCm + PCu \cdot (NC - PCoNCm), NC) \\
APde_{NO3} &= logistic(1.0, -55.0, 0.9, normalize(NC, NCmin, NCPm)) \\
upNO3_{opt} &= monod(NO3, ktNO3) \cdot UmT \cdot NCopt \cdot relUm_{NO3} \\
upNO3 &= upNO3_{opt} \cdot APde_{NO3}
\end{aligned}
\tag{4.71}
$$

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Si uptake

$$APde_{Si} = logistic(1.0, -80.0, 0.95, normalize(SC, SCmin, SCmax))$$
$$upSi_{opt} = monod(Si, ktSi) \cdot UmT \cdot SCopt$$
$$upSi = upSi_{opt} \cdot APde_{Si} \quad (4.72)$$

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4.4.8.4 Module phototrophy

Table 4.11: *Summary of the auxiliaries in the module phototrophy.*

Auxiliary	Description	Unit	Origin	Eq. #
$PSqm$	maximal attainable photosynthetic rate under optimum light (plateau of the PE-curve)	gC gC^{-1} d^{-1}	Flynn 2001	4.74
$atten$	attenuation of light by water + plankton chlorophyll	-	Flynn 2001	process: Prot_Atte
PS	carbon fixation through photosynthesis at current light and current cellular status	gC gC^{-1} d^{-1}	Flynn 2001	4.75
$Cfix$	net carbon fixation taking leakage into account	gC gC^{-1} d^{-1}	Flynn 2001	4.75
$synChl$	synthesis of chlorophyll-a	gChl gC d^{-1}	modified from Flynn 2021	4.77
$degChl$	degradation of chlorophyll-a	gChl gC^{-1} d^{-1}	Flynn 2021	4.77
$degChl_{NCM}$	loss of chlorophyll-a	gChl gC^{-1} d^{-1}	Ghyoot et al. 2017	4.78
$upChl$	uptake of chlorophyll-a from prey	gChl gC^{-1} d^{-1}	modified from Ghyoot et al. 2017	4.80

$$PSqm = [UmT \cdot relPS \cdot (1 + PSDOC) + NCm \cdot UmT \cdot \cdot(redco + AR)]NCu + BR \quad (4.73)$$

$$X = \frac{\alpha^{Chl} \cdot ChlC \cdot PFD \cdot 24.0 \cdot 60.0 \cdot 60.0}{PSqm}$$

$$PS = (PSqm \cdot (log(X + sqrt(1.0 + X^2)) - log(X \cdot exat + sqrt(1.0 + (X \cdot exat)^2))))/(atten) \quad (4.74)$$

$$Cfix = PS \cdot (1.0 - PSDOC) \quad (4.75)$$

$$synChl = ChlCmax \cdot UmT \cdot NPSiCu \cdot M \cdot (1.0 - \frac{Cfix}{PSqm}) \cdot logistic(0.95, -24.0, 0.85, normalize(ChlC, ChlCmin, ChlCmax)) \quad (4.76)$$

$$degChl = (min(ChlC, ChlCmax) \cdot UmT \cdot (1.0 - NPSiCu)) \quad (4.77)$$

$$degChl_{NCM} = constant \quad (4.78)$$

$$upChl = logistic(1.0, -80, 0.93, normalize(ChlC, 0.0, ChlCmax)) \quad (4.79)$$

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4.4.8.5 Module phagotrophy

Table 4.12: *Summary of the auxiliaries in the module phagotrophy.*

Auxiliary	Description	Unit	Origin	Eq. #
mot	motility of the protists	m s^{-1}	Flynn and Mitra 2016	4.80
$nrPrey$	density of prey in segment	nr cells m^{-3}	modified from Flynn 2021	4.82
enc	encounter rate	(prey predator)$^{-1}$ d^{-1}	Rothschild and Osborn 1988	4.84
$capPrey$	potential C-specific capture of prey	gC gC^{-1} d^{-1}	Flynn 2021	4.84
$sumCP$	captured prey	gC gC^{-1} d^{-1}	Flynn 2021	4.85
$opAE$	assimilation efficiency	-	Flynn 2021	4.90
$maxIng$	maximum ingestion rate	gC gC^{-1} d^{-1}	Flynn 2021	4.90
$satIng$	saturation ingestion rate	gC gC^{-1} d^{-1}	Flynn 2021	4.91
$ingC$	actual carbon ingestion rate	gC gC^{-1} d^{-1}	Flynn 2021	4.92
$ingNut_i$	nutrient ingestion rate	gNut gC^{-1} d^{-1}	Flynn 2021	4.93, 4.94
$assC$	carbon assimilation rate	gC gC^{-1} d^{-1}	Flynn 2021	4.95
$assNut_i$	nutrient assimilation rate	gNut gC^{-1} d^{-1}	Flynn 2021	4.96, 4.97

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$$mot = 1e^{-6} \cdot (38.542 \cdot (r \cdot 2)^{0.5424}) \quad (4.80)$$

$$lightInh = sigmoidLogistic((1 - relPhag), 10.0, 1.0, PFD) + (1.0 - (1 - relPhag)) \quad (4.81)$$

$$nrPrey = lightInh \cdot 1e12 \cdot \frac{preyC}{CcellPrey} \quad (4.82)$$

$$encPrey = (24.0 \cdot 60.0 \cdot 60.0) \cdot \pi \cdot (\frac{rPrey}{1E6} + \frac{rProt}{1E6})^2 \cdot nrPrey \cdot ((vel_{prey}^2 + 3 \cdot vel_{pred}^2 + 4 \cdot wTurb^2) \cdot ((vel_{pred}^2 + wTurb^2)^{-0.5})) \cdot 3.0^{-1.0} \quad (4.83)$$

$$capPrey = encPrey \cdot PR \cdot optCR \cdot \frac{CcellPrey}{CcellPred} \quad (4.84)$$

$$sumCP = sum(capPrey) \quad (4.85)$$

$$ingNC = \frac{capPrey}{sumCP} \cdot \frac{preyN}{preyC} \quad (4.86)$$

$$ingPC = \frac{capPrey}{sumCP} \cdot \frac{preyP}{preyC} \quad (4.87)$$

$$stoichP = min(\frac{ingNC}{NCopt}, \frac{ingPC}{PCopt}, 1.0) \quad (4.88)$$

$$opAE = (AEo + (AEm - AEo) \cdot monod(stoichP, kAE) \cdot (1.0 + kAE)) \cdot stoichP \quad (4.89)$$

$$maxIng = \frac{UmT + BR}{1.0 - SDA} \cdot \frac{1}{opAE} opAE \quad (4.90)$$

$$satIng = maxIng \cdot monod(sumCP, \frac{maxIng}{4}) \quad (4.91)$$

$$ingC = min(ingSat, sumCP) \quad (4.92)$$

$$ingN = ingC \cdot ingNC \quad (4.93)$$

$$ingP = ingC \cdot ingPC \quad (4.94)$$

$$assC = ingC \cdot opAE \quad (4.95)$$

$$assN = assC \cdot NCopt \quad (4.96)$$

$$assP = assC \cdot PCopt \quad (4.97)$$

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4.5 PROTIST: light attenuation

PROCESS: EXTINAPRO

4.5.1 Implementation

The phototrophic organisms of the protist community attenuate light and thus add to the overall extinction of light in the water column. The phototrophic PFTs of PROTIST attenuate light via their variable chlorophyll content, i.e. the PROTIST substances

- ◇ diatChl_1, greenChl_1, cmChl_1, ncmChl_1
- ◇ diatChl_2, greenChl_2, cmChl_2

The process is calculated using the already existing EXTINA subroutine using the equation

$$EXTALG = EXTALG + BIOMAS * EXTCF.$$

where:

$EXTALG$ extinction by phytoplankton [1/m]
$BIOMAS$ chlorophyll biomass of phototrophic protists [gChl m^{-3}]
$EXTCF$ light absorbance coefficient for chlorophyll [m^2 g Chl^{-1}]

Table 4.13: *Definitions of the input parameters EXTINAPRO.*

Name in formulas	Name in input	Definition	Units
NALG	nrSpProt	nr of species to be modelled	(-)
ISWFIX	SW_fixin_n	switch possible scaling of input	(-)
depth	Volume	volume of computational cell	(m^{-3})
EXTCF	abcoChl_D1	Light absorbance coefficient for chlorophyll	m^2 g Chl^{-1}
	abcoChl_D2	Light absorbance coefficient for chlorophyll	m^2 g Chl^{-1}
	abcoChl_G1	Light absorbance coefficient for chlorophyll	m^2 g Chl^{-1}
	abcoChl_G2	Light absorbance coefficient for chlorophyll	m^2 g Chl^{-1}
	abcoChl_C1	Light absorbance coefficient for chlorophyll	m^2 g Chl^{-1}
	abcoChl_C2	Light absorbance coefficient for chlorophyll	m^2 g Chl^{-1}
	abcoChl_N1	Light absorbance coefficient for chlorophyll	m^2 g Chl^{-1}
BIOMAS	diatChl_1	diatom cellular-Chl mass	gChl m^{-3}
	diatChl_2	diatom cellular-Chl mass	gChl m^{-3}
	greenChl_1	green cellular-Chl mass	gChl m^{-3}
	greenChl_2	green cellular-Chl mass	gChl m^{-3}
	cmChl_1	CM cellular-Chl mass	gChl m^{-3}

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Table 4.13 – continued from previous page

Name in formulas	Name in input	Definition	Units
	cmChl_2	CM cellular-Chl mass	gChl m^{-3}
	ncmChl_1	NCM cellular-Chl mass	gChl m^{-3}

Table 4.14: *Definitions of the output parameters EXTINAPRO.*

Name in formulas	Name in input	Definition	Units
EXTALG	ExtVlPhyt	VL extinction by phytoplankton	(1/m)

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4.6 PROTIST: light availability

PROCESS: PROT_ATTE

4.6.1 Implementation

The phototrophic organisms of the protist community use light for photosynthesis. The light required for the subroutines Prot_Dia, Prot_Gre, Prot_CM, Prot_NCM must be in photon flux density. The transformation from radiation in W m^2 (user input) to PAR (photosynthetic active radiation, light between 400-700 nm) to photon flux density (PFD) is calculated in this process. Furthermore, the overall extinction is used to calculate the light attenuation.

$$PARRAD = RAD * 0.45$$

$$PFD = PARRAD * 4.57$$

where:

RAD solar radiation [W/m^2]
$PARRAD$ photosynthetic active radiation [W/m^2]
PFD photon flux density [(umol photon m^{-2})]

Table 4.15: *Definitions of the input parameters EXTINAPRO.*

Name in formulas	Name in input	Definition	Units
RAD	Rad	irradiation at the segment upper-boundary	(W/m^2)
ExtVl	ExtVl	total extinction coefficient visible light	(1/m)
depth	Depth	depth of segment	(m)

Table 4.16: *Definitions of the output parameters EXTINAPRO.*

Name in formulas	Name in input	Definition	Units
PFD	PFD	photon flux density	μmol photon m^{-2}
atten	atten	attenuation of light by water + plankton chlorophyll	-
exat	exat	exponent of attenuation	-
PARRAD	PARRAD	photosynthetic active radiation	W/m^2

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4.7 PROTIST: sedimentation of diatom substances

PROCESS: PROSEDD

4.7.1 Implementation

The settling of diatoms is implemented for all diatom substances. A specific fraction of the diatom substances settles with a specific velocity which in the current implementation is removed from the diatom substances, enters the sediment (THIS STILL NEEDS TO BE IMPLEMENTED!!!).

- ◇ diatC_1, diatN_1, diatP_1, diatSi_1, diatChl_1
- ◇ diatC_2, diatN_2, diatP_2, diatSi_2, diatChl_2

The potential sedimentation is calculated using

$$PotSed_X = ZSedDiat + (VSedDiat * diat_X) * PSed$$

where:

$PotSed_X$ potential sedimentation in X which is carbon, nitrogen, phosphate, chlorophyll or silica [gX m-2 d-1]
$VSedDiat$ sedimentation velocity Diatoms [m/d]
$ZSedDiat$ zeroth-order sedimentation flux Diatoms [gC/m^2/d]
$diat_X$ diatom state variable X which is carbon, nitrogen, phosphate, chlorophyll or silica [()]
$PSed$ sedimentation probabality [(-)]

Table 4.17: *Definitions of the input parameters EXTINAPRO.*

Name in formulas	Name in input	Definition	Units
	maxNrSp_D	total nr species (DON'T CHANGE)	(-)
	nrSp_D	nr of species user wants to model	(-)
	nrSpCon_S	nr of species dependent items	(-)
	nrInd_S	nr of species independent items	(-)
	DELT	timestep for processes	(d)
	MinDepth	minimum layer thickness for sedimentation/resuspension	(m)
	TaucSDiat	critical shear stress for sedimentation Diatoms	(N/m^2)
	Tau	total bottom shear stress	(N/m^2)
	Depth	depth of segment	(m)
diatC	diatC_1	C-biomass	gC m^{-3}

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Table 4.17 – continued from previous page

Name in formulas	Name in input	Definition	Units
diatChl	diatChl_1	Chl-biomass	gChl m^{-3}
diatN	diatN_1	N-biomass	gN m^{-3}
diatP	diatP_1	P-biomass	gP m^{-3}
diatSi	diatSi_1	Si-biomass	gSi m^{-3}
ZSedDia	ZSedDia_1	zeroth-order sedimentation flux Diatoms	gC/m^2 d^{-1}
VSedDia	VSedDia_1	sedimentation velocity Diatoms	(m/d)
diatC	diatC_2	C-biomass	gC m^{-3}
diatChl	diatChl_2	Chl-biomass	gChl m^{-3}
diatN	diatN_2	N-biomass	gN m^{-3}
diatP	diatP_2	P-biomass	gP m^{-3}
diatSi	diatSi_2	Si-biomass	gSi m^{-3}
ZSedDia	ZSedDia_2	zeroth-order sedimentation flux Diatoms	gC/m^2 d^{-1}
VSedDia	VSedDia_2	sedimentation velocity Diatoms	(m/d)

Table 4.18: *Definitions of the output parameters EXTINAPRO.*

Name in formulas	Name in input	Definition	Units
PSed	PSedDiat_1	sedimentation probability <0-1> Diatoms	(-)
MaxSed_C	fSedC_1	sedimentation flux for diatC_1	gC m^{-2} d^{-1}
MaxSed_Chl	fSedChl_1	sedimentation flux for diatChl_1	gChl m^{-2} d^{-1}
MaxSed_N	fSedN_1	sedimentation flux for diatN_1	gN m^{-2} d^{-1}
MaxSed_P	fSedP_1	sedimentation flux for diatP_1	gP m^{-2} d^{-1}
MaxSed_Si	fSedSi_1	sedimentation flux for diatSi_1	gSi m^{-2} d^{-1}
PSed	PSedDiat_2	sedimentation probability <0-1> Diatoms	(-)
MaxSed_C	fSedC_2	sedimentation flux for diatC_1	gC m^2 d^{-1}
MaxSed_Chl	fSedChl_2	sedimentation flux for diatChl_1	gChl m^2 d^{-1}
MaxSed_N	fSedN_2	sedimentation flux for diatN_1	gN m^2 d^{-1}
MaxSed_P	fSedP_2	sedimentation flux for diatP_1	gP m^2 d^{-1}
MaxSed_Si	fSedSi_2	sedimentation flux for diatSi_1	gSi m^2 d^{-1}

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4.8 Global output of PROTIST

The process Phy_Prot can be used to sum the carbon content, nutrient content, chlorophyll content of the various PFTs as well as a sum of the nett primary production orginitaing from all the phototrophic PFTs. As the protist types are all represented by a full set of constituents, there is no need to provide stoichiometric constants, like it is for the DYNAMO and BLOOM modules

The table below summarises the output of this process. Note that the unit for the total concentration of chlorophyll is mg chlfa m $^{-3}$ instead of g chlfa m^{-3} as for the other state variables per PFT. Total chlorophyll, as calculated, has a different unit so that it is in line with the chlorophyll value made available by DYNAMI and BLOOM.

Table 4.19: *Summed outputs from the process Phhy_Prot.*

Name in output	**Definition**	**Units**
Phyt	Total carbon concentration of PFTs	gC m^{-3}
AlgN	Total nitrogen concentration of PFTs	gN m^{-3}
AlgP	Total phosphorus concentration of PFTs	gP m^{-3}
AlgSi	Total silica concentration of diatoms	gSi m^{-3}
Chlfa	Total chloropyll concentration of PFTs	mg chlfa m^{-3}
NPP	Nett primary production by phototrophic PFTs	gC m^{-3} d^{-1}

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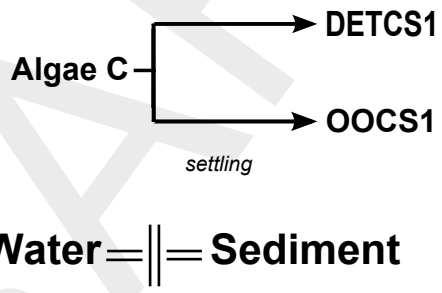
4.9 Settling of phytoplankton

PROCESS: SED(I), SEDPHBLO, SEDPHDYN, CALVS(I)

Live algae biomass settles on the sediment. The biomass components (C,N,P,Si,S) become parts of algae biomass or detritus in the sediment. The fate of settled biomass depends on the option for sediment modelling. The destinations in the sediment are:

1 the biomasses of the same algae species X_i as in the water column when sediment layers are actually simulated (layered sediment approach); or
2 DET(C,N,P,Si)S1 and OO(C,N,P,Si)S1 for the S1/2 approach (sulfur is not covered for S1/2).

When the S1/2 approach is followed phytoplankton biomass is allocated to the sediment detritus pools as follows:



For DYNAMO algae biomass only settles in DETC/N/P/Si/S1.

Implementation

Processes SEDALG and SEDPHBLO have been implemented for the BLOOM substances:

◇ BLOOMALG01-BLOOMALG30.

Processes SEDDIAT, SED_GRE and SEDPHDYN have been implemented for the DYNAMO substances:

◇ Diat and Green

Processes SED(i) deliver the settling rates of individual algae species biomass (C). Process SEDPHBLO delivers the settling rates of total algae biomass (C) and the nutrients in algae biomass (C,N,P,Si,S), for which BLOOM provides the stochiometric ratios. Process SEDPHDYN delivers the settling rate of total algae biomass (C) and calculates the settling rates of the nutrients in algae biomass (C,N,P,Si) for DYNAMO using input parameters for the stochiometric ratios.

Processes CALVSALG may be used to modify the input settling velocity of BLOOM algae for shear stress and/or flocculation, which requires alternative input parameters $V0Sed(i)$. Processes CALVS_Diat and CALVSGreen do the same for DYNAMO algae.

Internally in DELWAQ, the above processes for BLOOM set up the same processes for the individual algae species, using species specific settling velocities.

Table 4.20 provides the definitions of the input parameters occurring in the formulations.

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Formulation

The settling rate of the organic carbon components is described as the sum of zero-order and first-order kinetics. The settling rates are zero, when the shear stress exceeds a certain critical value, or when the water depth is smaller than a certain critical depth Krone (1962). The rates are calculated according to:

$$Rset_i = ftau_i \times \frac{Fset_i}{H}$$

$$if H < Hmin \; Fset_i = 0.0$$

$$else$$

$$Fset_i = \min\left(Fset'_i, \frac{Cx_i \times H}{\Delta t}\right)$$

$$Fset'_i = Fset0_i + s_i \times Cx_i$$

$$if \tau = -1.0 \; ftau = 1.0$$

$$else$$

$$ftau_i = \max\left(0.0, \left(1 - \frac{\tau}{\tau c_i}\right)\right)$$

where:

Cx	concentration of the biomass of an algae species [gC m^{-3}]
$Fset0$	zero-order settling flux of an algae species [gC m^{-2} d^{-1}]
$Fset$	settling flux of an algae species [gC m^{-2} d^{-1}]
$ftau$	shearstress limitation function [-]
H	depth of the water column [m]
$Hmin$	minimal depth of the water column for resuspension [m]
$Rset$	settling rate of an algae species [gC m^{-3} d^{-1}]
s	settling velocity of an algae species [m d^{-1}]
τ	shearstress [Pa]
τc	critical shearstress for settling of an algae species [Pa]
Δt	timestep in DELWAQ [d]
i	index for algae species (i)

The settling of organic nutrients in algae biomass is coupled to the settling of organic carbon in algae biomass as follows:

$$Rsn_{j,i} = fs_{j,i} \times Rset_i$$

where:

$fs_{j,i}$	stochiometric ratio of nutrient j in algae species i [gX gC^{-1}]
$Rsn_{j,i}$	settling rate of nutrient j in algae species i [gX m^{-3} d^{-1}]
i	index for algae species (i)
j	index for nutrient (j)

Directives for use

- ◇ Tau can be simulated with process CALTAU. If not simulated or imposed Tau will have the default value -1.0, which implies that settling is not affected by the shear stress. For specific input parameters, see the process description of CALTAU.
- ◇ Settling does not occur, when $Depth$ (acutally the water layer thickness) is smaller than the minimum thickness $MinDepth$ for settling, which has a default value of 0.1 m. When desired $MinDepth$ may be given a different value.

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◇ The settling fluxes $fSedAlg$ (gDM m^{-2}.d^{-1}) and $fSedPhyt$ (gC m^{-2}.d^{-1}) are available as additional output parameters.

Table 4.20: *Definitions of the input parameters in the above equations for SED(i), SEDPHBLO and SEDPHDYN.*

Name in formulas	Name in input	Definition	Units
Cx_i^1	$BLOOM(i)$[1] or (i)[1]	concentration of biomass of algae species i, for BLOOM or DYNAMO	gC m^{-3}
$Fset0_I$	$ZSed(i)$	zero-order settling flux of algae species i	gC m^{-2} d^{-1}
$fs_{j,i}$	$NCR(i)$	stoch. ratio N in algae species i for BLOOM	gN gC^{-1}
	$PCR(i)$	stoch. ratio P in algae species i for BLOOM	gP gC^{-1}
	$SCR(i)$	stoch. ratio Si in algae species i for BLOOM	gSi gC^{-1}
	$SuCr(i)$	stoch. ratio S in algae species i for BLOOM	gS gC^{-1}
	or		
	$NCrat(i)$	stoch. ratio N in algae species i for DYNAMO	gN gC^{-1}
	$PCrat(i)$	stoch. ratio P in algae species i for DYNAMO	gP gC^{-1}
	$SCrat(i)$	stoch. ratio Si in algae species i for DYNAMO	gSi gC^{-1}
	$SuCrat(i)$	stoch. ratio S in algae species i for DYNAMO	gS gC^{-1}
H	$Depth$	depth of the overlying water compartment	m
$Hmin$	$MinDepth$	minimum layer thickness for settling and resuspension	m
s_i	$VSed(i)$	input or calc. settling velocity algae species i	m d^{-1}
	or		
	$V0Sed(i)$	basic settling velocity of algae species i	m d^{-1}
τ	Tau	shear stress	Pa
τc_i	$TaucS(i)$	critical shear stress for settling of algae species i	Pa
Δt	$Delt$	timestep in DELWAQ	d

[1]) (i) is equal to one of the algae species names, BLOOM specific names connected to ALG01-30, or Diat and Green.

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4.10 Production and mortality of algae (DYNAMO)

PROCESS: GROMRT_(I), TF_(I), NL(I), DL_(I), RAD_(I), PPRLIM, NUTUPT_ALG, NUTREL_ALG

The primary production of algae is limited by nutrient availability, light and temperature. Mortality is a function of temperature and salinity. DYNAMO applies so-called Monod kinetics for the growth of algae biomass, and for the competition of two species, green algae and diatoms.

Implementation

Processes GROMRT_(i), TF_(i), NL(i), DL_(i), RAD_(i), PPRLIM, NUTUPT_ALG and NUTREL_ALG have been implemented for the following substances:

- ◇ Diat and Green
- ◇ NH4, NO3, PO4 and Si

Table 4.21 provides the definitions of the input parameters occurring in the formulations.

Formulation

The production and mortality of algae biomass (organic carbon)

The primary production rate is formulated as follows:

$$
\begin{aligned}
Rnp_i &= knp_i \times Calg_i \\
knp_i &= kgp_i - krsp_i \\
kgp_i &= fdl_i \times frad_i \times fnut_i \times ftp_i \times kpp_{i,20} \\
ftp_i &= ktp_i^{(T-20)}
\end{aligned}
$$

where:

$Calg$	concentration of algae biomass [gC m^{-3}]
fdl	daylength limitation function [-]
$fnut$	nutrient limitation function [-]
$frad$	light limitation function [-]
ftp	production temperature function [-]
kgp	gross primary production rate constant [d^{-1}]
knp	net primary production rate constant [d^{-1}]
kpp_{20}	potential maximum production rate constant at 20 °C [d^{-1}]
$krsp$	total respiration rate constant [d^{-1}]
ktp	temperature constant for production [-]
Rnp	net primary production rate [gC m^{-3} d^{-1}]
T	water temperature [°C]
i	index for algae species

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The limitation function for nutrients is given by:

$$fnut_i = Min(fn_i, fp_i, fsi_i)$$
$$fn_i = \frac{Cnn}{Cnn + Ksn_i}$$
$$fp_i = \frac{Cph}{Cph + Ksp_i}$$
$$fsi_i = \frac{Csi}{Csi + Kssi_i}$$
$$Cnn = Cam + \frac{Cni}{fan_i}$$

where:

Cam	concentration of ammonium [gN m^{-3}]
Cni	concentration of nitrate [gN m^{-3}]
Cnn	concentration of preferred nutrient nitrogen [gN m^{-3}]
Cph	concentration of dissolved phosphate [gP m^{-3}]
Csi	concentration of dissolved silicate [gSi m^{-3}]
fan	preference of ammonium over nitrate [-]
$fnut$	nutrient limitation function [-]
fn	nitrogen limitation function [-]
fp	phosphorus limitation function [-]
fsi	silicon limitation function [-]
Ksn	half saturation constant for nutrient nitrogen [gN m^{-3}]
Ksp	half saturation constant for phosphate [gP m^{-3}]
$Kssi$	half saturation constant for silicate [gSi m^{-3}]
i	index for algae species

The limitation functions for daylength and light are given by:

$$fdl_i = \frac{\min(DL, DLo_i)}{DLo_i}$$

if $(Is/Io_i) \geq 1.0$ **and** $(Ib/Io_i) \geq 1.0$ **then** $frad_i = 1.0$

if $(Is/Io_i) \geq 1.0$ **and** $(Ib/Io_i) < 1.0$ **then**

$$frad_i = \frac{1 + \ln(Is/Io_i) - (Is/Io_i) \times e^{(-et \times H)}}{et \times H}$$

if $(Is/Io_i) < 1.0$ **then**

$$frad_i = \frac{Is}{Io_i} \times \frac{1 - e^{(-et \times H)}}{et \times H}$$

$$Io_i = ftp_i \times Io_{i,20}$$
$$Ib_i = Is_i \times e^{(-et \times H)}$$

where:

DL	daylength, fraction of a day [-]
DLo	optimal daylength [d]
et	total extinction coefficient [m^{-1}]
fdl	daylength limitation function [-]
$frad$	light limitation function [-]
ftp	production temperature function [-]
H	water depth [m]

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Io	optimal light intensity [W m^{-2}]
Io_{20}	optimal light intensity [W m^{-2}]
Ib	light intensity at the bottom [W m^{-2}]
Is	light intensity at water surface [W m^{-2}]
i	index for algae species

Note that the value of Io_i is corrected for temperature. This results in a dependency of $frad_i$ of Is as presented in Figure 4.8 (Harris, 1986). This means that at a constant value for light intensity, the light limitation is less important at lower temperatures. The above formulations do not consider the availability of nutrients. However, primary production can not larger than the available quantities of nutrients allow for. The primary production rate is corrected for available nutrients as follows:

$$Rnp_{max,1} = \min(\frac{\max(Cni + Cam, 0.0)}{an_1 \times \Delta t}, \frac{\max(Cph, 0.0)}{ap_1 \times \Delta t})$$

$$Rnp_{max,2} = \min(\frac{\max(Cni + Cam, 0.0)}{an_2 \times \Delta t}, \frac{\max(Cph, 0.0)}{ap_2 \times \Delta t}, \frac{\max(Csi, 0.0)}{asi_2 \times \Delta t})$$

$$Rnp_{max} = \max(Rnp_{max,1}, Rnp_{max,2})$$

$$Rnp = \max(Rnp_1, Rnp_2)$$

if $Rnp > Rnp_{max}$ **then**

$$Rnp_{c,2} = \min(\frac{Rnp_{max}}{Rnp} \times Rnp_2, Rnp_{max,2})$$

$$Rnp_{c,1} = Rnp_{max} - Rnp_{c,2}$$

$$\Delta Rnp_2 = Rnp_{c,2} - Rnp_2$$

$$\Delta Rnp_1 = Rnp_{c,1} - Rnp_1$$

else

$$Rnp_{c,1} = Rnp_1 \ \ and \ \ Rnp_{c,2} = Rnp_2$$

$$\Delta Rnp_{c,1} = 0.0 \ \ and \ \ \Delta Rnp_{c,2} = 0.0$$

where:

an	stoichiometric constant for N over C in algae biomass [gN gC^{-1}]
ap	stoichiometric constant for P over C in algae biomass [gP gC^{-1}]
asi	stoichiometric constant for Si over C in algae biomass [gSi gC^{-1}]
Cam	concentration of ammonium [gN m^{-3}]
Cni	concentration of nitrate [gN m^{-3}]
Cph	concentration of dissolved phosphate [gP m^{-3}]
Csi	concentration of dissolved silicate [gSi m^{-3}]
Rnp	total or partial net primary production rate [gC m^{-3} d^{-1}]
ΔRnp	correction of the net primary production rate [gC m^{-3} d^{-1}]
Δt	computational timestep [d]
c	index for corrected net primary production
max	index for maximum net primary production
1	index for green algae
2	index for diatoms

The respiration rate is formulated as follows:

$$krsp_i = fgr_i \times kgp_i + ftm_i \times (1 - fgr_i) \times kmr_{i,20}$$

where:

fgr	growth respiration factor [-]

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ftm	mortality temperature function [-]
kmr_{20}	maintenance respiration constant at 20 °C [d^{-1}]
$krsp$	total respiration rate constant [d^{-1}]
i	index for algae species

The mortality rate is formulated as follows:

$$Rmrt_i = ftm_i \times kmrt_{i,20} \times Max((Calg_i - Calgmin_i), 0.0)$$

$$ftm_i = ktm_i^{(T-20)}$$

if $S < Smin_i$ **then** $kmrt_{i,20} = kmrt_{min,i,20}$

if $S > Smax_i$ **then** $kmrt_{i,20} = kmrt_{max,i,20}$

else

$$kmrt_{i,20} = kmrt_{min,i,20} + \frac{(S - Smin_i)}{(Smax_i - Smin_i)} \times (kmrt_{max,i,20} - kmrt_{min,i,20})$$

where:

$Calg$	concentration of algae biomass [gC m^{-3}]
$Calgmin$	minimum concentration of algae biomass [gC m^{-3}]
ftm	mortality temperature function [-]
$kmrt_{20}$	mortality rate constant at 20 °C [d^{-1}]
$kmrt_{min,20}$	minimum mortality rate constant at 20 °C [d^{-1}]
$kmrt_{max,20}$	maximum mortality rate constant at 20 °C [d^{-1}]
ktm	temperature constant for mortality [-]
$Rmrt$	mortality rate [gC m^{-3} d^{-1}]
S	ambient salinity [psu] or [g kg^{-1}]
$Smin$	salinity limit for minimum mortality [psu] or [g kg^{-1}]
$Smax$	salinity limit for maximum mortality [psu] or [g kg^{-1}]
T	water temperature [°C]
i	index for algae species

Uptake and release of nutrients

Nutrients are taken up (consumed) proportional to net primary production as follows:

$$Ruam_i = fram \times \sum_i^{n=2}(an_i \times Rnp_{c,i})$$

$$Runi_i = (1 - fram) \times \sum_i^{n=2}(an_i \times Rnp_{c,i})$$

$$Rup_i = \sum_i^{n=2}(ap_i \times Rnp_{c,i})$$

$$Rusi_i = \sum_i^{n=2}(asi_i \times Rnp_{c,i})$$

where:

an	stoichiometric constant for N over C in algae biomass [gN gC^{-1}]
ap	stoichiometric constant for P over C in algae biomass [gP gC^{-1}]
asi	stoichiometric constant for Si over C in algae biomass [gSi gC^{-1}]
$fram$	fraction of N consumed as ammonium [-]

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$Ruam$	ammonium uptake rate [gN m^{-3} d^{-1}]
$Runi$	nitrate uptake rate [gN m^{-3} d^{-1}]
Rup	phosphate uptake rate [gP m^{-3} d^{-1}]
$Rusi$	silicate uptake rate [gSi m^{-3} d^{-1}]
Rnp	net primary production rate [gC m^{-3} d^{-1}]
c	index for corrected net primary production
i	index for algae species

Algae prefer ammonium over nitrate. The fraction of N consumed as ammonium follows from:

if $Cam \ < Cam_c$ **then**

$$fram = \frac{Cam}{Cam + Cni}$$

else

$$Run = \sum_{i}^{n=2} (an_i \times Rnp_{c,i})$$

if $(Cam - Cam_c) \ \geq \ (Run \times \Delta t)$ **then** $\quad fram = 1.0$

if $(Cam - Cam_c) \ < \ (Run \times \Delta t)$ **then**

$$fram = \frac{(Cam - Cam_c) + (Cam_c/(Cam_c + Cni)) \times (Run \times \Delta t - Cam + Cam_c)}{Run \times \Delta t}$$

where:

an	stoichiometric constant for N over C in algae biomass [gN gC^{-1}]
Cam	concentration of ammonium [gN m^{-3}]
Cam_c	critical concentration of ammonium [gN m^{-3}]
Cni	concentration of nitrate [gN m^{-3}]
$fram$	fraction of N consumed as ammonium [-]
Rnp	net primary production rate [gC m^{-3} d^{-1}]
Run	required nitrogen uptake in a timestep [gC m^{-3} d^{-1}]
Δt	computational timestep [d]
c	index for corrected net primary production
i	index for algae species

The mortality flux is divided among three pools: dissolved inorganic substances (autolysis), fast decomposing detritus and medium slow decomposing detritus. Organic carbon and nutri-

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ents are released proportional to mortality as follows:

$$Ran = fra_i \times \sum_i^{n=2}(an_i \times Rmrt_i)$$

$$Rap = fra_i \times \sum_i^{n=2}(ap_i \times Rmrt_i)$$

$$Rasi = fra_i \times \sum_i^{n=2}(asi_i \times Rmrt_i)$$

$$Rmc_1 = \frac{frpoc_1}{(1 - fra_i)} \times \sum_i^{n=2}(Rmrt_i)$$

$$Rmn_1 = frpoc_1 \times \sum_i^{n=2}(an_i \times Rmrt_i)$$

$$Rmp_1 = frpoc_1 \times \sum_i^{n=2}(ap_i \times Rmrt_i)$$

$$Rmsi_1 = frpoc_1 \times \sum_i^{n=2}(asi_i \times Rmrt_i)$$

$$Rmc_2 = (1 - \frac{frpoc_1}{(1 - fra_i)}) \times \sum_i^{n=2}(Rmrt_i)$$

$$Rmn_2 = (1 - frpoc_1 - fra_i) \times \sum_i^{n=2}(an_i \times Rmrt_i)$$

$$Rmp_2 = (1 - frpoc_1 - fra_i) \times \sum_i^{n=2}(ap_i \times Rmrt_i)$$

$$Rmsi_2 = (1 - frpoc_1 - fra_i) \times \sum_i^{n=2}(asi_i \times Rmrt_i)$$

where:

an	stoichiometric constant for N over C in algae biomass [gN gC^{-1}]
ap	stoichiometric constant for P over C in algae biomass [gP gC^{-1}]
asi	stoichiometric constant for Si over C in algae biomass [gSi gC^{-1}]
fra	fraction released by autolysis [-]
$frpoc_1$	fraction released to detritus POC/N/P1 or OPAL [-]
Ran	nitrogen NH4 release due to autolysis [gN m^{-3} d^{-1}]
Rap	dissolved phosphate PO4 release due to autolysis [gP m^{-3} d^{-1}]
$Rasi$	dissolved silicate Si release due to autolysis [gSi m^{-3} d^{-1}]
Rmc_1	detritus C release to POC1 due to mortality [gC m^{-3} d^{-1}]
Rmc_2	detritus C release to POC2 due to mortality [gC m^{-3} d^{-1}]
Rmn_1	detritus N release to PON1 due to mortality [gN m^{-3} d^{-1}]
Rmn_2	detritus N release to PON2 due to mortality [gN m^{-3} d^{-1}]
Rmp_1	detritus P release to POP1 due to mortality [gP m^{-3} d^{-1}]
Rmp_2	detritus P release to POP2 due to mortality [gP m^{-3} d^{-1}]
$Rmsi_1$	silicate release to OPAL due to mortality [gSi m^{-3} d^{-1}]
$Rmsi_2$	silicate release to OPAL due to mortality [gSi m^{-3} d^{-1}]

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$Rmrt$	mortality rate [gC m^{-3} d^{-1}]
i	index for algae species

Note that the the release of medium slow decaying detritus is calculated as the residual from autolysis and release as fast decaying detritus. (If the respective fractions do not add up to 1, the rest is assigned to the medium slow decaying detritus.)

Directives for use

- ◇ Because the limitation function for radiation ($frad_i$) depends on temperature, the product of kgp_i depends differently on temperature than might be expected at first sight. The temperature dependency conform to literature (Harris, 1986) is presented in Figure 4.7.
- ◇ The value of $SalM2$ should be greater than the value of $SalM1$. If $SalM1 = -1$ then the procedure described above is not applied. In that case the mortality rate equals $Mort0(i)$.
- ◇ Always make sure that the radiation input is coherent with the saturated radiation. Undepleted solar radiation ranges from 100 to 500 W m^{-2} at altitudes around 50° North/South. At other altitudes these values must be corrected. However, these values should be corrected for e.g. clouds and the wavelength spectrum (0.45 is a frequently used value).

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Table 4.21: *Definitions of the input parameters in the above equations for GROMRT_(i), TF_(i), NL(i), DL_(i), RAD_(i), PPRLIM, NUTUPT_ALG and NUTREL_ALG. $(i) = Green$ or $Gree$ for green algae (input names maximum 10 letters long!), and $(i) = Diat$ for diatoms.*

Name in formulas	Name in input	Definition	Units
$Calg_i$	(i)	concentration algae biomass (i)	gC m^{-3}
$Calgmin_i$	$Min(i)$	minimum conc. algae species (i)	gC m^{-3}
an_i	$NCRat(i)$	stoich. constant N over C in algae (i)	gN gC^{-1}
ap_i	$PCRat(i)$	stoich. constant P over C in algae (i)	gN gC^{-1}
asi_i	$SCRat(i)$	stoich. constant Si over C in algae (i)	gN gC^{-1}
Cam	$NH4$	concentration of ammonium	gN m^{-3}
Cam_c	$NH4Crit$	critical conc. of ammonium for uptake	gN m^{-3}
Cni	$NO3$	concentration of nitrate	gN m^{-3}
Cph	$PO4$	concentration of dissolved phosphate	gP m^{-3}
Csi	Si	concentration of dissolved silicate	gSi m^{-3}
DL	$DayL$	daylength, fraction of a day	-
DLo_i	$OptDL(i)$	optimal daylength for algae species (i)	-
et	$ExtVL$	total extinction coefficient	m^{-1}
fan_i	$PrfNH4(i)$	pref. ammonium over nitrate for algae (i)	-
fgr_i	$GResp(i)$	growth respiration factor for algae (i)	-
fra_i	$FrAut(i)$	fraction released by autolysis for algae (i)	-
$frpoc_1$	$FrDet(i)$	fraction released to detritus POC/N/P1 or OPAL for algae (i)	-
H	$Depth$	water depth	m
Is	Rad	light intensity at water surface	W m^{-2}
$Io_{i,20}$	$RadSat(i)$	optimal light int. at 20 °C for algae (i)	W m^{-2}
$kmr_{i,20}$	$MResp(i)$	maint. resp. const. at 20 °C of algae (i)	d^{-1}
$kmrt_{min,i,20}$	$Mort0(i)$	min. mort. constant at 20 °C of algae (i)	d^{-1}
$kmrt_{max,i,20}$	$MortS(i)$	max. mort. constant at 20 °C of algae (i)	d^{-1}
$kpp_{i,20}$	$PPMax(i)$	max. prod. constant at 20 °C of algae (i)	d^{-1}
ktm_i	$TCDec(i)$	temp. constant for mortality of algae (i)	-
ktp_i	$TCGro(i)$	temp. constant for production of algae (i)	-
Ksn_i	$KmDIN(i)$	half satur. const. nitrogen for algae (i)	gN m^{-3}
Ksp_i	$KmP(i)$	half satur. const. phosphate for algae (i)	gP m^{-3}
$Kssi_i$	$KmSi(i)$	half satur. const. silicate for algae (i)	gSi m^{-3}
S	$Salinity$	salinity	psu
$Smin_i$	$SalM1(i)$	salinity limit for Mort0 of algae (i)	psu
$Smax_i$	$SalM2(i)$	salinity limit for MortS of algae (i)	psu
T	$Temp$	water temperature	°C

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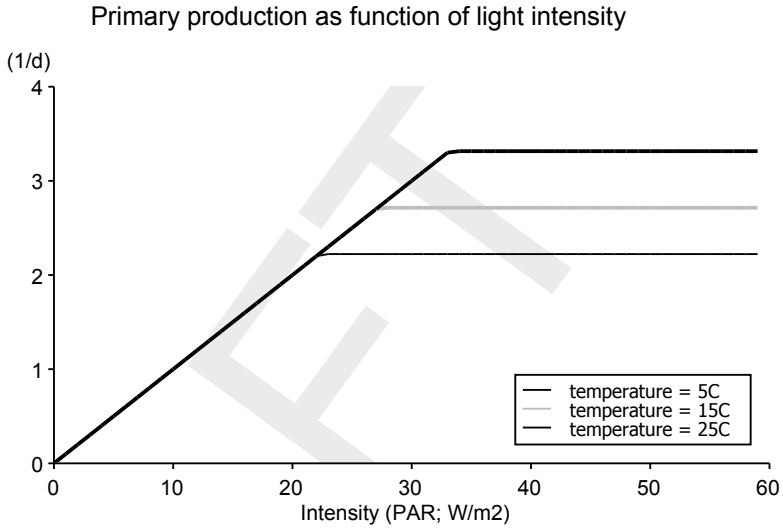

Figure 4.7: *Primary production rate of algae species i as a function of temperature and radiation.*

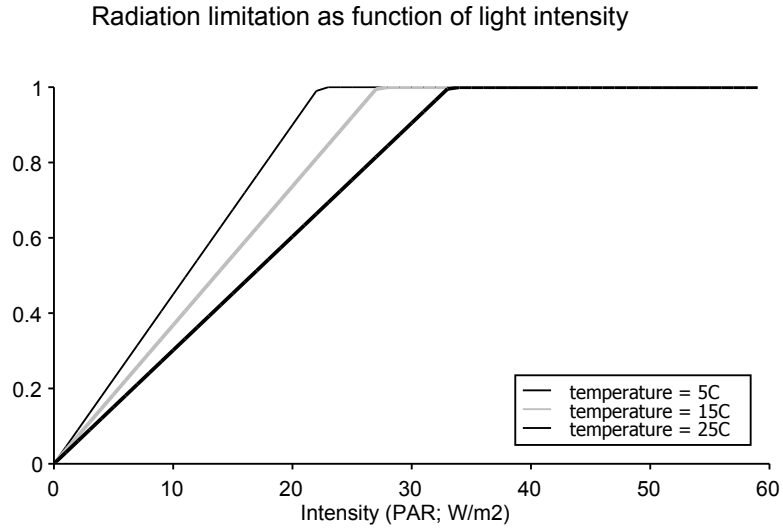

Figure 4.8: *Limitation function for radiation ($frad_i$) for algae species i as a function of radiation (Is,RAD) at different temperature ranging from 5 to 25 °C.*

4.11 Computation of the phytoplankton composition (DYNAMO)

PROCESS: PHY_DYN

Process PHY_DYN computes the total concentrations of the nutrients in biomass from the contributions of individual algae species. Additionally the processes deliver the total concentration of algae biomass expressed in various units among which chlorophyll-a. The concentrations of nutrients in algae biomass are used to calculate the concentrations of a number of aggregate substances with auxiliary process COMPOS.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

PHY_DYN has been implemented for the following substances:

- ◇ Diat and Green

The process does not directly influence state variables, since they do not generate mass fluxes.

Tables 4.22–4.23 provide the definitions of the input and output parameters occurring in the formulations.

Formulation

The total concentrations of algae biomass components follow from:

$$Calgt_1 = \sum_{i=1}^{n} Calg_i$$

$$Calgt_2 = \sum_{i=1}^{n} (fdm_i \times Calg_i)$$

$$Calgn = \sum_{i=1}^{n} (an_i \times Calg_i)$$

$$Calgp = \sum_{i=1}^{n} (ap_i \times Calg_i)$$

$$Calgsi = \sum_{i=1}^{n} (asi_i \times Calg_i)$$

$$Cchf = \sum_{i=1}^{n} (achf_i \times Calg_i)$$

where:

$achlf$	stochiometric ratio of chlorophyll-a in organic matter [mgChf gC^{-1}]
an	stochiometric ratio of nitrogen in organic matter [gN gC^{-1}]
ap	stochiometric ratio of phosphorus in organic matter [gP gC^{-1}]
asi	stochiometric ratio of silicate in organic matter [gSi gC^{-1}]
$Calg$	concentration of biomass of algae species i [gC m$^{-3}_{\mathscr{b}}$]

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$Calgn$	concentration of organic nitrogen in algae biomass [gC m^{-3}_{ℓ}]
$Calgp$	concentration of organic phosphorus in algae biomass [gC m^{-3}_{ℓ}]
$Calgsi$	concentration of silicate in algae biomass [gC m^{-3}_{ℓ}]
$Calgt_1$	total concentration of algae biomass [gC m^{-3}_{ℓ}]
$Calgt_2$	total concentration of algae biomass [gDM m^{-3}_{ℓ}]
$Cchl$	concentration of chlorophyll-a [mgChf m^{-3}_{ℓ}]
fdm	dry matter conversion factor [gDM gC^{-1}]
i	index for algae species [-]
n	number of algae species, 6 for MONALG and GEMMPB, 2 for DYNAMO [-]

Table 4.22: *Definitions of the input parameters in the above equations for PHY_DYN. (i) is a substance name, $Green$ or $Diat$. Volume units refer to bulk (ℓ) or to water (w).*

Name in formulas	**Name in input**[1]	**Definition**	**Units**
an_i	$Ncrat(i)$	stochiometric ratio of nitrogen in algae species (i)	gN gC^{-1}
ap_i	$PCrat(i)$	stochiometric ratio of phosphorus in algae species (i)	gP gC^{-1}
asi_i	$SCrat(i)$	stochiometric ratio of silicate in algae species (i)	gSi gC^{-1}
$achf_1$	$GrToChl$	stochiometric ratio of chlorophyll-a in green algae	gChl gC^{-1}
$achf_2$	$DiToChl$	stochiometric ratio of chlorophyll-a in diatoms	gChl gC^{-1}
$Calg_i$	(i)	concentration of biomass in algae species (i)	gC m^{-3}_{ℓ}
fdm_i	$DMCF(i)$	dry matter conversion factor for algae species (i)	gDM gC^{-1}
n	$NAlgDynamo$	number of algae species in DYNAMO, default=2, this should not be changed	-

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Table 4.23: *Definitions of the output parameters in the above equations for PHY_DYN. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	**Name in input**[1]	**Definition**	**Units**
$Calgt_1$	$Phyt$	total algae biomass carbon concentration	gC $m^{-3}_{\mathscr{b}}$
$Calgt_2$	$AlgDM$	total algae biomass dry matter concentration	gDM $m^{-3}_{\mathscr{b}}$
$Calgn$	$AlgN$	concentration of organic nitrogen in algae biomass	gN $m^{-3}_{\mathscr{b}}$
$Calgp$	$AlgP$	concentration of organic phosphorus in algae biomass	gP $m^{-3}_{\mathscr{b}}$
$Calgsi$	$AlgSi$	concentration of silicate in algae biomass	gSi $m^{-3}_{\mathscr{b}}$
$Cchf$	$Chlfa$	chlorophyll-a concentration	mgChf $m^{-3}_{\mathscr{b}}$

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4.12 Production and mortality of benthic diatoms S1/2 (DYNAMO)

PROCESS: GROMRT_DS1, TF_DIAT, DL_DIATS1, RAD_DIATS1, MRTDIAT_S1, MRTDIAT_S2, NRALG_S1

The primary production of algae in the sediment e.g. microphytobenthos is implemented for benthic diatoms in sediment layer S1. Mortality of the diatoms occurs in layers S1 and S2.

Hints for use

- Do not combine the benthic diatoms described here (DiatS1) with the MPBENTHOS process and the associated microphytobenthos types. This would lead to unforeseen competition and the processes were not designed for such a combination.

Implementation

Processes GROMRT_DS1, TF_DIAT, DL_DIATS1, RAD_DIATS1, MRTDIAT_S1, MRTDIAT_S2 and NRALG_S1 have been implemented for the following substances:

- DiatS1
- NH4, NO3, PO4 and Si

These processes have been implemented for benthic diatoms according to the S1/2 approach for the sediment, and can not be used for the layered sediment approach. The processes affect the upper sediment layer S1, with one exception. The mortality process MRTDIAT_S2 affects layer S2.

The mineralisation rate for detrital nutrients are delivered by processes BMS1_DetN, BMS1_DetP and BMS1_DetSi.

Table 4.24 provides the definitions of the input parameters occurring in the formulations.

Formulation

The production and mortality of diatom biomass (organic carbon)

The primary production rate is formulated as follows:

$$
\begin{aligned}
Rnp &= \frac{knp \times Malg}{A \times H} \\
knp &= kgp - krsp \\
kgp &= fdl \times frad \times fnut \times ftp \times kpp_{20} \\
ftp &= ktp^{(T-20)}
\end{aligned}
$$

where:

A	surface area [m^2]
fdl	daylength limitation function [-]
$fnut$	nutrient limitation function [-]
$frad$	light limitation function [-]
ftp	production temperature function [-]
H	water depth [m]
kgp	gross primary production rate constant [d^{-1}]

knp	net primary production rate constant [d^{-1}]
kpp_{20}	potential maximum production rate constant at 20 °C [d^{-1}]
$krsp$	total respiration rate constant [d^{-1}]
ktp	temperature constant for production [-]
$Malg$	quantity of diatom biomass [gC]
Rnp	net primary production rate [gC m^{-3} d^{-1}]
T	water temperature [°C]

The limitation function for nutrients is given by:

$$fnut = Min(fn, fp, fsi, 1.0)$$

$$fn = \frac{(Rmn_{S1} \times (1 - frnb) + (Cnn/(Cnn + Ksn)) \times (Cnn/\Delta t)) \times A \times H}{an \times kpn \times Malg}$$

$$fp = \frac{(Rmp_{S1} + (Cph/(Cph + Ksp)) \times (Cph/\Delta t)) \times A \times H}{ap \times kpn \times Malg}$$

$$fsi = \frac{(Rmsi_{S1} + (Csi/(Csi + Kssi)) \times (Csi/\Delta t)) \times A \times H}{asi \times kpn \times Malg}$$

$$Cnn = Cam + Cni$$

where:

A	surface area [m^2]
an	stoichiometric constant for N over C in diatom biomass [gN gC^{-1}]
ap	stoichiometric constant for P over C in diatom biomass [gP gC^{-1}]
asi	stoichiometric constant for Si over C in diatom biomass [gSi gC^{-1}]
Cam	concentration of ammonium [gN m^{-3}]
Cni	concentration of nitrate [gN m^{-3}]
Cnn	concentration of nutrient nitrogen [gN m^{-3}]
Cph	concentration of dissolved phosphate [gP m^{-3}]
Csi	concentration of dissolved silicate [gSi m^{-3}]
$fnut$	nutrient limitation function [-]
fn	nitrogen limitation function [-]
fp	phosphorus limitation function [-]
fsi	silicon limitation function [-]
$frnb$	fraction of mineralisation rate N allocated to bacteria in sediment [-]
H	water depth [m]
Ksn	half saturation constant for nutrient nitrogen [gN m^{-3}]
Ksp	half saturation constant for phosphate [gP m^{-3}]
$Kssi$	half saturation constant for silicate [gSi m^{-3}]
$Malg$	quantity of diatom biomass [gC]
Rmn_{S1}	mineralisation rate for DETNS1 [gN m^{-3} d^{-1}]
Rmp_{S1}	mineralisation rate for DETPS1 [gP m^{-3} d^{-1}]
$Rmsi_{S1}$	mineralisation rate for DETSiS1 [gSi m^{-3} d^{-1}]

The limitation functions for daylength and light are given by:

$$fdl = \frac{\min(DL, DLo)}{DLo}$$

$$frad = \begin{cases} 1.0 & \text{if } (Is/Io) \geq 1.0 \\ \dfrac{Ib}{Io} & \text{if } (Ib/Io) < 1.0 \end{cases}$$

where:

DL	daylength, fraction of a day [-]
DLo	optimal daylength [-]
fdl	daylength limitation function [-]
$frad$	light limitation function [-]
Io	optimal light intensity [W m^{-2}]
Ib	light intensity at the bottom [W m^{-2}]

The above formulations do consider the availability of nutrients, and the uptake of nutrients beyond availability is prevented.

The respiration rate is formulated as follows:

$$krsp = fgr \times kgp + ftm \times (1 - fgr) \times kmr_{20}$$

where:

fgr	growth respiration factor [-]
ftm	mortality temperature function [-]
kmr_{20}	maintenance respiration constant at 20 °C [d^{-1}]
$krsp$	total respiration rate constant [d^{-1}]

The mortality rate is formulated as follows:

$$Rmrt = \frac{ftm \times kmrt_{20} \times Malg}{A \times H}$$

$$ftm = ktm^{(T-20)}$$

where:

A	surface area [m^2]
ftm	mortality temperature function [-]
H	water depth [m]
$kmrt_{20}$	mortality rate constant at 20 °C [d^{-1}]
ktm	temperature constant for mortality [-]
$Malg$	quantity of diatom biomass [gC]
$Rmrt$	mortality rate [gC m^{-3} d^{-1}]
T	water temperature [°C]

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Uptake and release of nutrients

Algae in the sediment primarily consume dissolved nutrients released by the mineralisation of detritus in the sediment. It is assumed that algae are able to take up all nutrients released. Uptake from the water column occurs when the mineralisation flux is not large enough to sustain maximal production. Ammonium from the water column is consumed until the concentration drops below a critical low concentration. Then nitrate is consumed too. The nutrients are taken up (consumed) proportional to net primary production as follows:

$$
\begin{aligned}
Ruam &= fram \times Run \\
Runi &= (1 - fram) \times Run \\
Run_{S1} &= Min(an \times Rnp, (1 - frnb) \times Rmn_1) \\
Run &= Max((an \times Rnp - Run_{S1}), 0.0) \\
Rup_{S1} &= Min(ap \times Rnp, Rmp_{S1}) \\
Rup &= Max((ap \times Rnp - Rup_{S1}), 0.0) \\
Rusi_{S1} &= Min(asi \times Rnp, Rmsi_{S1}) \\
Rusi &= Max((asi \times Rnp - Rusi_{S1}), 0.0)
\end{aligned}
$$

where:

an	stoichiometric constant for N over C in algae biomass [gN gC^{-1}]
ap	stoichiometric constant for P over C in algae biomass [gP gC^{-1}]
asi	stoichiometric constant for Si over C in algae biomass [gSi gC^{-1}]
$fram$	fraction of N consumed as ammonium [-]
$frnb$	fraction of mineralisation rate N allocated to bacteria in sediment [-]
$Ruam$	ammonium uptake rate from the water column [gN m^{-3} d^{-1}]
$Runi$	nitrate uptake rate from the water column [gN m^{-3} d^{-1}]
Run	nitrogen uptake rate from the water column [gN m^{-3} d^{-1}]
Run_{S1}	nitrogen uptake rate from mineralisation DETNS1 [gN m^{-3} d^{-1}]
Rup	phosphate uptake rate from the water column [gP m^{-3} d^{-1}]
Rup_{S1}	phosphate uptake rate from mineralisation DETPS1 [gP m^{-3} d^{-1}]
$Rusi$	silicate uptake rate from the water column [gSi m^{-3} d^{-1}]
$Rusi_{S1}$	silicate uptake rate from mineralisation DETSiS1 [gSi m^{-3} d^{-1}]
Rmn_{S1}	mineralisation rate for DETNS1 [gN m^{-3} d^{-1}]
Rmp_{S1}	mineralisation rate for DETPS1 [gP m^{-3} d^{-1}]
$Rmsi_{S1}$	mineralisation rate for DETSiS1 [gSi m^{-3} d^{-1}]
Rnp	net primary production rate [gC m^{-3} d^{-1}]

Algae prefer ammonium over nitrate. The fraction of N consumed as ammonium follows from:

$$
\begin{aligned}
&if\ Cam\ < Cam_c\ then\ fram = \frac{Cam}{Cnn} \\
&if\ (Run \times \Delta t)\ \leq\ (Cam - Cam_c)\ then\ fram = 1.0 \\
&\quad else \\
&\quad fram = \frac{(Cam - Cam_c) + (Cam_c/(Cam_c + Cni)) \times (Run \times \Delta t - Cam + Cam_c)}{Run \times \Delta t}
\end{aligned}
$$

where:

an	stoichiometric constant for N over C in diatom biomass [gN gC^{-1}]
Cam	concentration of ammonium [gN m^{-3}]
Cam_c	critical concentration of ammonium [gN m^{-3}]
Cni	concentration of nitrate [gN m^{-3}]

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Cnn	concentration of nutrient nitrogen DIN [gN m^{-3}]
$fram$	fraction of N consumed as ammonium [-]
Rnp	net primary production rate [gC m^{-3} d^{-1}]
Run	nitrogen uptake rate from the water column [gC m^{-3} d^{-1}]
Δt	computational timestep [d]

The mortality flux is divided among three pools: dissolved inorganic substances (autolysis) in the water column, fast decomposing detritus and slow decomposing detritus in the sediment (layer S1). Organic carbon and nutrients are released proportional to mortality as follows:

$$
\begin{aligned}
Ran &= fra \times an \times Rmrt \\
Rap &= fra \times ap \times Rmrt \\
Rasi &= fra \times asiRmrt \\
Rmc_1 &= \frac{frdet_1}{(1-fra)} \times Rmrt \\
Rmn_1 &= frdet_1 \times an \times Rmrt \\
Rmp_1 &= frdet_1 \times ap \times Rmrt \\
Rmsi_1 &= frdet_1 \times asi \times Rmrt \\
Rmc_2 &= (1 - \frac{frdet_1}{(1-fra)}) \times Rmrt \\
Rmn_2 &= (1 - frdet_1 - fra) \times an \times Rmrt \\
Rmp_2 &= (1 - frdet_1 - fra) \times ap \times Rmrt \\
Rmsi_2 &= (1 - frdet_1 - fra) \times asi \times Rmrt
\end{aligned}
$$

where:

an	stoichiometric constant for N over C in algae biomass [gN gC^{-1}]
ap	stoichiometric constant for P over C in algae biomass [gP gC^{-1}]
asi	stoichiometric constant for Si over C in algae biomass [gSi gC^{-1}]
fra	fraction released by autolysis [-]
$frdet_1$	fraction released to detritus DetXS1 [-]
Ran	nitrogen NH4 release due to autolysis [gN m^{-3} d^{-1}]
Rap	dissolved phosphate PO4 release due to autolysis [gP m^{-3} d^{-1}]
$Rasi$	dissolved silicate Si release due to autolysis [gSi m^{-3} d^{-1}]
Rmc_1	detritus C release to DetCS1 due to mortality [gC m^{-3} d^{-1}]
Rmc_2	detritus C release to OOCS1 due to mortality [gC m^{-3} d^{-1}]
Rmn_1	detritus N release to DetNS1 due to mortality [gN m^{-3} d^{-1}]
Rmn_2	detritus N release to OONS1 due to mortality [gN m^{-3} d^{-1}]
Rmp_1	detritus P release to DetPS1 due to mortality [gP m^{-3} d^{-1}]
Rmp_2	detritus P release to OOPS1 due to mortality [gP m^{-3} d^{-1}]
$Rmsi_1$	silicate release to DetSiS1 due to mortality [gSi m^{-3} d^{-1}]
$Rmsi_2$	silicate release to OOSiS1 due to mortality [gSi m^{-3} d^{-1}]
$Rmrt$	mortality rate [gC m^{-3} d^{-1}]

Note that the the release of medium slow decaying detritus is calculated as the residual from autolysis and release as fast decaying detritus. (If the respective fractions do not add up to 1, the rest is assigned to the medium slow decaying detritus.)

Directives for use

- ◇ The nutrient-carbon ratios for diatoms in the sediment are the same as for diatoms in the water column.

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Table 4.24: *Definitions of the input parameters in the above equations for GROMRT_$DS1$, TF_$DIAT$, DL_$DIAT$, RAD_$DIATS1$, MRTDIAT_$S1$, MRTDIAT_$S2$ and NRALG_$S1$.*

Name in formulas	Name in input	Definition	Units
$Malg$	$DiatS1$	quantity of benthic diatom biomass	gC m^{-3}
A	$Surf$	surface area	m^2
an	$NCRatDiat$	stoich. const. N over C in diatom biomass	gN gC^{-1}
ap	$PCRatDiat$	stoich. const. P over C in diatom biomass	gN gC^{-1}
asi	$SCRatDiat$	stoich. const. Si over C in diatom biomass	gN gC^{-1}
Cam	$NH4$	concentration of ammonium	gN m^{-3}
Cam_c	$NH4Crit$	critical conc. of ammonium for uptake	gN m^{-3}
Cni	$NO3$	concentration of nitrate	gN m^{-3}
Cph	$PO4$	concentration of dissolved phosphate	gP m^{-3}
Csi	Si	concentration of dissolved silicate	gSi m^{-3}
DL	$DayL$	daylength, fraction of a day	-
DLo	$OptDLDiaS1$	optimal daylength for benthic diatoms	-
fgr	$GRespDiaS1$	growth respiration factor	-
fra	$FrAutDiatS$	fraction released by autolysis	-
$frdet_1$	$FrDetDiatS$	fraction released to detritus DetC/N/P/SiS1	-
$frnb$	$FrMinS1Bac$	frac. min. N allocated to sediment bacteria	-
H	$Depth$	water depth	m
Ib	Rad	light intensity at water surface	W m^{-2}
Io	$RadSatDiS1$	optimal light intensity for benthic diatoms	W m^{-2}
kmr_{20}	$MRespDiaS1$	maint. resp. const. at 20 °C of diatoms	d^{-1}
$kmrt_{20}$	$MrtSedDiat$	mortality constant at 20 °C of diatoms	d^{-1}
kpp_{20}	$PPMaxDiaS1$	max. prod. constant at 20 °C of diatoms	d^{-1}
ktm	$TCDecDiat$	temp. constant for mortality of diatoms	-
ktp	$TCGroDiat$	temp. constant for production of diatoms	-
Ksn	$KmDINDiaS1$	half satur. const. nitrogen for diatoms	gN m^{-3}
Ksp	$KmPDiatS1$	half satur. const. phosphate for diatoms	gP m^{-3}
$Kssi$	$KmSiDiatS1$	half satur. const. silicate for diatoms	gSi m^{-3}
Rmn_S1	$dMinDetNS1$	mineralisation rate for DETNS1	gN m^{-3} d^{-1}
Rmp_S1	$dMinDetPS1$	mineralisation rate for DETPS1	gP m^{-3} d^{-1}
$Rmsi_S1$	$dMinDetSiS$	mineralisation rate for DETSiS1	gSi m^{-3} d^{-1}
T	$Temp$	water temperature	°C
Δt	$Delt$	computational timestep	d

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4.13 The development of microphytobenthos (MPBENTHOS)

PROCESS: MICROPHYT, MPB1TEMP, MPB2TEMP, MPB1LLIM, MPB2LLIM, MPB1NLIM, MPB2NLIM, MPBNUT

The microphytobenthos consists of unicellular eukaryotic algae and cyanobacteria that grow within the upper several millimeters of illuminated sediments, typically appearing only as a subtle brownish or greenish shading. Microphytobenthos biomass are subject to gross primary production, respiration, excretion, mortality, grazing, resuspension and settling. Net primary production is defined as gross primary production minus respiration. The algae module 'MPBENTHOS' includes specific formulations for these processes with the exception of grazing, resuspension and settling.

Carbon fixation and growth are not always synonymous. Photosynthesis is a prerequisite but not a sufficient condition for growth because all cell materials, not just carbon must be assimilated before a cell division can occur. Photosynthesis is here defined as photo-chemical carbon fixation, growth as increase in biomass (dry weight); it requires a balanced uptake of all essential elements in addition to carbon and is usually followed by a cell division. Under certain conditions carbon fixation may continue, although actual growth is prohibited by for example a nutrient limitation; in that case the surplus amount of fixed carbon must be excreted by the cell.

The microphytobenthos module considers two different benthic diatoms species groups: epipelic diatoms and epipsammic diatoms. Epipelic diatoms are capable of vertical migration to the surface to increase their access to irradiance. Epipsammic diatoms cannot actively migrate through the sediment as they grow attached to sand grains.

The effect of nutrient availability on growth rates is formulated according to Monod kinetics. The growth rate is corrected for sub-optimal growth conditions by multiplication with the minimum of the limiting factors for nutrient availability and light. Furthermore the growth rate is corrected for temperature and inorganic carbon availability. Growth, respiration, excretion and mortality rates are all based on first-order kinetics with respect to algae biomass.

The benthic algae processes affect a number of other model substances apart from the biomass concentrations [gC m^{-3}]. Growth involves the uptake of inorganic nutrients [gN/P/Si m^{-3}] and the production of dissolved oxygen [gO_2 m^{-3}]. Preferential uptake of ammonium over nitrate is included in the model according to McCarthy et al. (1977). Respiration consumes dissolved oxygen. Excretion and mortality produce detritus [gC/N/P m^{-3}] and opal silicate [gSi m^{-3}]. The process fluxes concerning these substances are derived from the algae process fluxes by means of multiplication with stochiometric constants. These ratios reflect the chemical composition of the benthic algae biomass.

The availability of light at and in the top sediment layer depends on the solar irradiance and the extinction of light both in the water column and the sediment. The tidal phase is taken into account through time varying depth and extinction.

Hints for use

- ◇ Do not combine the benthic diatoms of DYNAMO (DiatS1) with the MPBENTHOS process and the associated microphytobenthos types. This would lead to unforeseen competition and the processes were not designed for such a combination.
- ◇ For the migration of epipelic diatoms the "Emersion" process is used. The output of this process is used to detect if the segment (adjacent to the bottom) is dry or not and thus

whether migration is assumed to happen. Therefore you should always turn this process on to take advantage of the difference between the two types of benthic diatoms.

Implementation

The microphytobenthos module has been implemented as several different processes. The main process, where the growth, respiration, excretion and mortality fluxes for both groups of algae are calculated is proces MPBENTHOS. The nutrient limitation, light limitation and temperature limitation for each of the groups of algae are calculated in different processes: MPB1NLim, MPB2NLim, MPB1LLim, MPB2LLim, MPB1Temp and MPB2Temp respectively.

When modelling the sediment with the S1 approach, the nutrient concentrations in the sediment are not explicitly simulated. In that case the process MPBNUT calculates nutrient concentrations in the sediment, based on steady-state concentrations at mineralisation and diffusion rates during the time step.

The process MPBENTHOS has been formulated in a way that holds for both water and sediment. It can be used in combination with both DYNAMO and BLOOM, but for now it is recommended to be used in combination with DYNAMO, since it is based on similar equations as DYNAMO (see 4.1.

MPBENTHOS has been implemented for the following substances:

for water and sediment layers (the "layered sediment" or "Delwaq-G" approach),

- ◇ MPB1peli, MPB2psam, POC1, PON1, POP1, Opal, NH4, NO3, PO4, Si, OXY, TIC and Alka.

for the S1 sediment approach,

- ◇ MPB1peli, MPB2psam, MPB1peliS1, MPB2psamS1, DETCS1, DETNS1, DETPS1, DETSiS1, NH4, NO3, PO4, Si, OXY, TIC and Alka.

Sulfur is not considered by MPBENTHOS.

The simulation mode is selected by means of a switch input parameter $SwMPBGEM$ (0 = layered sediment, 1 = S1).

Tables 4.25 to 4.27 provide the definitions of the parameters occurring in the user-defined input and output.

Formulation

Formulations are subsequently presented for primary production, respiration, excretion and mortality. The processes lead to the consumption or production of nutrients and dissolved oxygen, or to the production of detritus components. The resulting process rates and considerations on schematisation in space and time are presented in the final two sections.

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Primary production

Gross primary production is formulated as a temperature dependent first order process limited by light, nutrient and inorganic carbon availability:

$$\begin{aligned} Rgp_i &= kpmax_i \times Calg_i \\ kpmax_i &= kpmax_{i,20} \times ftmp_i \times \min(fnut_i, flt_i) \times f_{CO_2} \\ ftmp_i &= ktpg_i^{(T-20)} \\ Calg_i &= \max\left(Calg_i, Calg_{\min}\right) \end{aligned}$$

with:

$Calg$	algal biomass concentration [gC m^{-3}]
$Calg_{\min}$	minimal algal biomass concentration, a threshold value [gC m^{-3}]
flt	light limitation factor [-]
$fnut$	Monod nutrient limitation factor [-]
$ftmp$	temperature limitation factor for production [-]
f_{CO2}	limitation factor for inorganic carbon [-]
$kgmax$	potential gross primary production rate [d^{-1}]
$kgmax_{20}$	potential gross primary production rate at 20 °C [d^{-1}]
$ktgp$	temperature coefficient for primary production [-]
Rgp	gross primary production rate [gC m^{-3} d^{-1}]
T	water temperature [°C]
i	index for species group 1-2 [-]

When the S1 approach is used the algae biomass is modelled as the mass per square meter (gC/m^2) per segment instead of concentrations (g/m^3). In the S1 approach the volumetric concentration is calculated by assuming that the benthic algae are evenly distributed over the mixing depth for microphytobenthos z_m. For both the Delwaq-G and S1 approaches an output parameter is available to express the concentration in the unit gC/m^2. In the S1 approach this parameter is calculated in the process S1_Comp. In the Delwaq-G approach this parameter is calculated in the process 'MPBENTHOS'.

Nutrient limitation

PROCESS: MPB1NLIM, MPB2NLIM

The nutrient limitation factor can be described in various ways. Limiting factors for separate nutrients are sometimes multiplied, assuming that all nutrient concentrations simultaneously affect the growth rate. However it is often assumed that only one nutrient can be limiting at a time. This is approached by using only the minimum value of all limitation factors for separate nutrients. For the 'MPBENTHOS' module we have adopted the latter approach, better known as Liebigs approach.

Algae can use two inorganic sources of nitrogen, although many prefer ammonium. Consequently, the limitation factor must consider both the availability of and affinity for ammonium

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and nitrate. The following nutrient limitation factor takes all this into account:

$$Cnn_i = Cam + \frac{Cni}{PrfNH_i}$$
$$fn_i = \frac{Cnn_i}{(Knn_i + Cnn)}$$
$$fp_i = \frac{Cp}{(Kp_i + Cp)}$$
$$fsi_i = \frac{Csi}{(Ksi_i + Csi)}$$
$$fnut_i = \min(fn_i, fp_i, fsi_i)$$

with:

fn	nitrogen specific nutrient limitation factor [-]
fp	phosphate specific nutrient limitation factor [-]
fsi	silicate specific nutrient limitation factor [-]
Cam	ammonium concentration [gN m^{-3}]
Cni	nitrate concentration [gN m^{-3}]
Cnn	concentration of nitrogen corrected for preference [gN m^{-3}]
Cph	phosphate concentration [gP m^{-3}]
Csi	dissolved inorganic silicate concentration [gSi m^{-3}]
Knn	half saturation constant for nitrogen (preferred) [gN m^{-3}]
Kph	half saturation constant for phosphate [gP m^{-3}]
Ksi	half saturation constant for silicate [gSi m^{-3}]
$PrfNH$	ammonium preference over nitrate [-]

Calculation of nutrient concentrations in sediment

PROCESS: MPBNUT

The calculation of the nutrient limitation factors requires information about the nutrient concentrations in the sediment. These concentrations are available when Delwaq-G is applied. In case of the S1 approach the nutrient concentrations in the sediment are not calculated by the sediment module. Therefore, an alternative process to estimate these nutrient concentrations has been developed for microphytobenthos: MPBNUT. The nutrient concentrations in the sediment are estimated in a very simplified way on the basis of steady-state mass balances for the benthic algae production layer. The balances only consider mineralisation fluxes and diffusion fluxes. The conversion of a part of the ammonium into nitrate by nitrification is taken into account. The effects of the overlying water nutrient concentrations, the limitative effect of nutrient diffusion from deeper sediment layers, and the porosity effect are ignored. It is assumed that all mineralised nutrients become available instantly in the layer where microphytobenthos is mixed homogeneously: z_m. The nutrient concentrations are calculated in MPBNUT with the following formulations:

$$Cam = z_m \times \frac{Fam}{D}$$
$$Cni = z_m \times \frac{Fni}{D}$$
$$Cph = z_m \times \frac{Fph}{D}$$

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$$Csi = z_m \times \frac{Fsi}{D}$$

$$Fni = frnit \times ktnit^{(T-20)} \times Ram \times H$$

$$Fam = Ram \times H - Fni$$

$$Fph = Rph \times H$$

$$Fsi = Rsi \times H$$

with:

Cam	ammonium concentration in pore water of the sediment toplayer [gN m^{-3}]
Cni	nitrate concentration in pore water of the sediment toplayer [gN m^{-3}]
Cph	phosphate concentration in pore water of the sediment toplayer [gP m^{-3}]
Csi	diss. silicate concentration in pore water of the sediment toplayer [gSi m^{-3}]
D	dispersion constant [m^2 d^{-1}]
Fam	return flux of ammonium from the sediment [gN d^{-1} m^{-2}]
Fni	nitrification flux in the sediment [gN d^{-1} m^{-2}]
Fph	mineralisation phosphate flux in the sediment [gP d^{-1} m^{-2}]
Fsi	dissolution silicate flux in the sediment [gSi d^{-1} m^{-2}]
H	depth of the overlying water compartment [m]
$ktnit$	temperature coefficient of nitrification [-]
$frnit$	fraction of nitrogen mineralisation rate nitrified [-]
Ram	mineralisation rate in sediment for ammonium, per volume water [gN d^{-1} m^{-3}]
Rph	mineralisation rate in sediment for phosphate, per volume water [gP d^{-1} m^{-3}]
Rsi	dissolution rate of silicate in sediment per volume water [gSi d^{-1} m^{-3}]
z_m	depth of the top sediment layer where microphytobenthos is mixed almost homogeneously [m]

Light limitation

PROCESS: MPB1LLIM, MPB2LLIM

Primary production is limited when the light availability is less than the optimal radiation for an algae species. Below this optimal radiation light limitation is a saturating function of light availability. Photoinhibition is typically not observed for microphytobenthos. The formulation of Webb et al. (1974), as fitted by McIntyre and Cullen (1995) is used for description of the production-light relation:

$$flt_i = 1 - e^{(-I_z/I_{sat,i})}$$

with:

flt	light limitation factor [-]
I_z	light intensity at depth z_j and time t_k [W m^{-2}]
$I_{sat,i}$	Saturation light intensity [W m^{-2}]
$kpmax$	maximal gross production rate [d^{-1}]
i	index for species group 1-2 [-]

This relation between light intensity and the light limitation factor (or efficiency) is formulated similarly for epipelic and epipsammic diatoms, although parameter values can be chosen differently. However the availability of light is different for the two types of microphytobenthos. Epipelic diatoms can migrate to the surface during emersion of the tidal flat and experience

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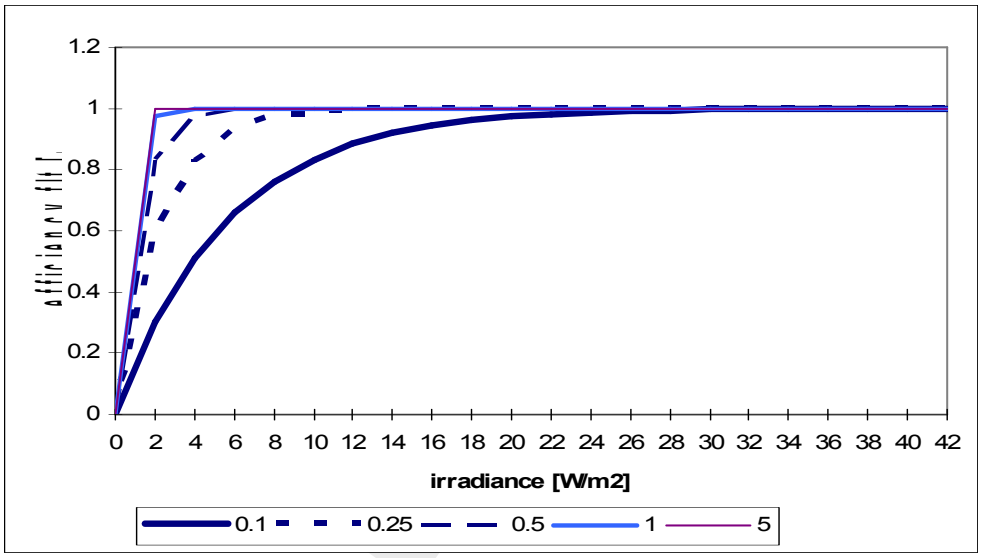

Figure 4.9: *Relation between light intensity and primary production efficiency flt for different values of the intial slope factor s.*

solar light intensity. In the model the epipelic microphytobenthos does not physically migrate between the different segment layers. Instead part of the population in each layer is exposed to solar light intensity (I_0: light intensity at the sediment surface, without extinction by sediment or water). At greater depths in the sediment the ability of the microphytobenthos to reach the surface decreases, due to the increase of the distance to the surface. In the 'MPBENTHOS' module this is simulated as a depth varying fraction of the population that is exposed to sunlight intensity I_0 during emersion. The fraction of the population that does not reach the surface is considered to receive only the light penetrating into their segment layer, similarly to epipsammic diatoms. The result is a vertical profile of microphytobenthos density in the sediment, with higher densities near the surface and decreasing densities at greater depths. The model user can specify the fraction of the population that experiences sunlight intensity I_0 (representing the percentage that reaches the surface during emersion) with the following function:

$$0.5\,(\cos(\pi \times \min(\max(0, ((z - d1)/(d2 - d1))), 1)) + 1)$$

with:

z	depth in the sediment [m]
$d1$	depth above which all epipelic microphytobenthos reach the surface during emersion [m]
$d2$	depth below which no epipelic microphytobenthos reaches the surface during emersion [m]

Figure 4.10 illustrates the resulting vertical profiles of the fraction of the population able to reach the surface during emersion for different values of d1 and d2.

For epipsammic microphytobenthos the availability of light is determined by the penetration of light into the sediment. The light climate in sediments is complicated due to the scattering and absorption processes by the sediment particles and algae (Kühl and Jörgensen, 1994; Kühl et al., 1994). It is difficult to derive a general formulation from the scattered measurements. As a first approximation, it can be assumed that scalar irradiance at the sediment surface is appr. 120–200 % of incident radiation, depending on the grain size and the diatom biomass; attenuation coefficients also depend on grain size and diatom abundance, in a typical range of 2–6 mm^{-1}. Over the daytime downwelling incident light at the sediment surface varies due

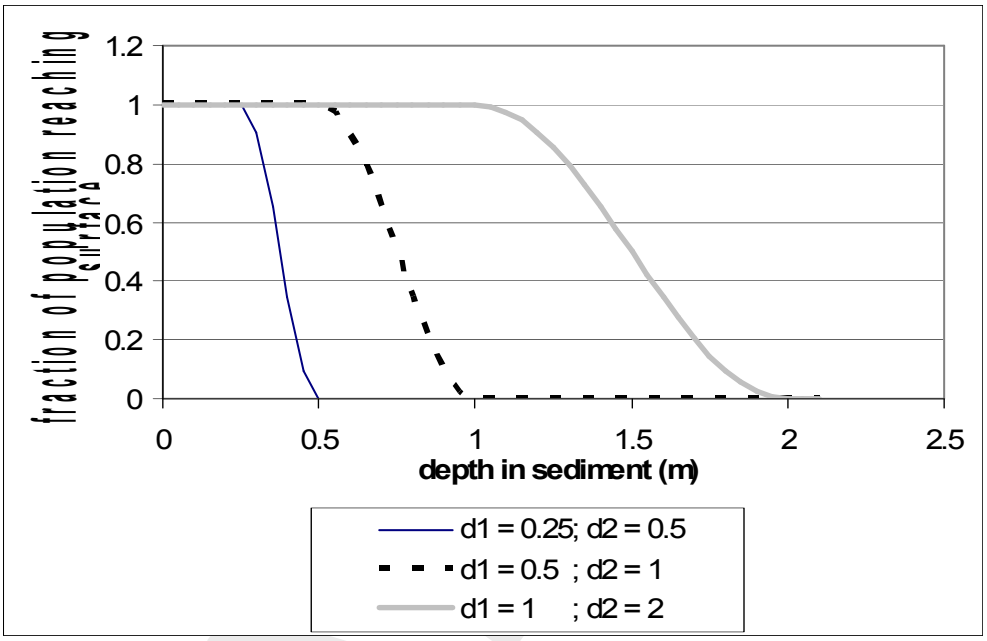

Figure 4.10: *vertical profiles in the sediment of the percentage of the population able to reach the surface during emersion for different values of d1 and d2 (×0.01 m).*

to variation in the sunlight, depth of the water column and attenuation in the water column. We assume that the extinction of light in the sediment can be approached with the Lambert-Beer formulation, similarly to the extinction of light in the water. To account for the effect of scattering the surface irradiance is multiplied with an enhancement factor. Ambient scalar light at time t and depth z is then given by:

$$I_z = I_0 e^{-kz}$$

$$I_0 = a \times I_s$$

with:

a	amplification factor for scalar irradiance due to scattering by sed. particles [-]
k	total extinction coefficient of visible light within the sediment [m^{-1}]
I_0	light intensity at depth zo (the sediment-water interface) [W m^{-2}]
I_s	solar light intensity [W m^{-2}]
z	sediment depth [m]

If a tidal flat emerges above the water, no extinction in water takes place. When the hydrodynamic calculation does not allow for dry segments and maintains a minimum water level in each segment, then the user can specify that if the water level reaches this threshold minimum water level z_T , the segment is considered to be emersed. In that case the extinction in the remaining water above the sediment is ignored.

In the model it is assumed that epipsammic microphytobenthos is uniformly distributed over the mixing depth z_m. This mixing depth can be specified by the modeller, based on an estimation of the euphotic depth and vertical mixing. The growth efficiency is integrated over depth z_m. The integration is performed numerically, by splitting up depth z_m in 10 layers. The sum of the efficiencies calculated in these 10 layers is divided by 10, to obtain the averaged efficiency. If the depth of the top layer in the Delwaq-G approach is smaller than z_m, then the integration is performed over the layer depth instead of depth z_m.

McIntyre and Cullen (1995) showed that maximal production and initial slope both increase with depth in the sediment. This is most probably caused by dark adaptation after long periods of burial. This effect of depth in sediment on the initial slope and maximum production is not included in the model.

Carrying capacity

Microphytobenthos typically shows logistic growth curves. Reasons for the apparent biomass maximum may be CO_2 limitation, direct competition, or other density dependent factors that may come into play in densely populated sediment surfaces. The effect of these factors is implemented as a logistic growth curve, which is effective only in the sediment layers. The controlling input parameter is the carrying capacity of the system K [gC/m^3].

$$f_{CO_2} = \frac{K - C_{alg_i}}{K}$$

. In practice this parameter is better expressed as the amount of algae per square meter, hence the input parameter is expressed as g/m^2. Internally, its value is divided by the thickness of the euphotic depth, z_m, so that a concentration results.

Respiration

Algal respiration consists of maintenance respiration and growth respiration. Maintenance respiration is corrected for temperature effects. Growth respiration is defined as a fraction of the gross primary production rate. The total respiration rate is given by:

$$Rrsp_i = krsp_i \times Calg_i + frsp_i \times Rgp_i$$

$$krsp_i = krsp_{i,20} \times ktrsp_i^{(T-20)}$$

with:

$frsp$	fraction of gross production respired [-]
$krsp$	maintenance respiration rate [d^{-1}]
$krsp_{20}$	maintenance respiration rate at 20 °C [d^{-1}]
$ktrsp$	temperature coefficient for maintenance respiration [-]
$Rrsp$	total respiration rate [gC m^{-3} d^{-1}]

Excretion

Excretion of organic carbon is a function of nutrient stress. Excretion increases with increasing nutrient limitation. It is modelled as a fraction of the gross primary production according to a formulation by Klepper et al. (1994):

$$Rexc_i = fexc_i \times (1 - fnut_i) \times Rgp_i$$

with:

$fexc$	fraction of gross production excreted due to nutrient limitation [-]
$Rexc$	total excretion rate [gC m^{-3} d^{-1}]

Correction of nett growth to total availability of nutrients

The nett growth rate is calculated as the gross primary production minus respiration. This may be an overestimation of the growth rate, because the availability of nutrients may not be large enough to sustain the calculated growth rate. In the Delwaq-G sediment approach the availability of nutrients is calculated as the total amount of inorganic nutrients in the segment

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at the start of the time step. If the time step of the simulation is small enough the growth rate will decrease due to decreasing nutrient concentrations. In that case the nett growth rate will not exceed the total available amount of nutrients. However, if the time step is large the decrease of the nutrient concentrations during the time step can be so large that the growth rate calculated at the beginning of the time step, is not representative anymore for the growth rate during the entire time step. Although this is basically a numerical problem, an extra check is included in the model to prevent negative nutrient concentrations.

In case of the S1 sediment approach there is no information on the nutrient concentrations in the sediment. In this case the availability of nutrients is determined by the mineralisation flux. Furthermore, in the process routine the nitrogen consumption is exclusively restricted to ammonia. The reason for this is that the mineralisation flux is assigned to ammonia only. If the algae in the process routine were to consume both ammonia and nitrate, a deficit of nitrate would occur.

The growth rate is adjusted to the maximal growth rate allowed by the nutrient availability. The available amount of the limiting nutrient is divided over the two groups of microphytobenthos according to their fraction (fbi) of the total nutrient uptake if nutrients would not be limiting. The correction factor is an output parameter so that one can check whether the correction has taken place. There is one output parameter per nutrient (N, P, Si) to show which of the nutrients was limiting, due to the time step being too large.

$$fb_i = \frac{Rgp_i \times anut}{\sum_{i=1}^{2} Rgp_i \times anut}$$

Delwaq-g sediment approach:

$$Rgp_i = \frac{(fb_i \times Cnut/(dt \times anut_i)) + \left(krsp_{i,20} \times ktrsp_i^{T-20} \times Calg_i\right)}{(1 - frsp_i)}$$

S1 sediment approach:

$$Rgp_i = \frac{(fb_i \times Rmin/anut_i) + \left(krsp_{i,20} \times ktrsp_i^{T-20} \times Calg_i\right)}{(1 - frsp_i)}$$

with:

$anut$	stoch. constant of the limiting nutrient in microphytobenthos group i, (parameters: an, aph or asi for N, P and Si respectively) [gN/P/Si gC^{-1}]
fb	fraction of total nutrient requirement of groups 1 and 2 [-] (parameters: fmn, fmp or fms for N, P and Si respectively)
$Rmin$	mineralisation rate in the sediment of the limiting nutrient [gN/P/Si m^{-3} d^{-1}]
i	index for species group 1-2 [-]

The nett growth rates, respiration rates and excretion rates are recalculated along with the corrected value of the gross production rate.

Mortality

The mortality of benthic algae in the model comprises temperature dependent natural mortality and grazing. The temperature dependent physiological mortality is modelled by a first-order process. In absence of explicitly modelled sediment grazers, grazing mortality can be modelled with a second-order term, which may be more typical for grazing mortality. The total mortality is modelled with the following formulation:

$$Rmrt_i = kmrt1_i \times Calg_i + kmrt2_i \times Calg_i^2$$

$$kmrt1_i = kmrt1_{i,20} \times ktmrt_i^{(T-20)}$$

$$kmrt2_i = kmrt2_{i,20} \times ktmrt_i^{(T-20)}$$

with:

$kmrt1$	physiological mortality process rate [d^{-1}]
$kmrt2$	pseudo grazing mortality process rate [m^3 gC^{-1} d^{-1}]
$kmrt1_{20}$	physiological mortality process rate at 20 °C [d^{-1}]
$kmrt2_{20}$	pseudo grazing mortality process rate at 20 °C [d^{-1}]
$ktmrt$	temperature coefficient for mortality [-]
$Rmrt$	total mortality rate [gC m^{-3} d^{-1}]

Consumption and production

The consumption and production rates for nutrients and dissolved oxygen are derived from the production rate as follows:

$$Rprd_{ox,i} = (Rgp_i - Rrsp_i - Rexc_i) \times 2.67$$

$$Rcns_{am,i} = (Rgp_i - Rrsp_i) \times an_i \times \frac{fam_i}{fn_i}$$

$$Rcns_{ni,i} = (Rgp_i - Rrsp_i) \times an_i \times \frac{1 - fam_i}{fn_i}$$

$$Rcns_{ph,i} = (Rgp_i - Rrsp_i) \times aph_i$$

$$Rcns_{si,i} = (Rgp_i - Rrsp_i) \times asi_i$$

$$Rprd_{oc,i} = Rmrt_i$$

$$Rprd_{on,i} = Rmrt_i \times an_i$$

$$Rprd_{op,i} = Rmrt_i \times aph_i$$

$$Rprd_{osi,i} = Rmrt_i \times asi_i$$

with:

an	stochiometric constant for nitrogen over carbon in algae biomass [gN gC^{-1}]
aph	stochiometric constant for phosphorus over carbon in algae biomass [gP gC^{-1}]
aox	stochiometric constant for oxygen in CO_2 [gO_2 C^{-1}]
asi	stochiometric constant for silicon over carbon in algae biomass [gSi gC^{-1}]
$Rcns_{am}$	net consumption rate for ammonium [gN. m^{-3} d^{-1}]
$Rcns_{ni}$	net consumption rate for nitrate [gN. m^{-3} d^{-1}]
$Rcns_{ph}$	net consumption rate for phosphate [gP m^{-3} d^{-1}]
$Rcns_{si}$	net consumption rate for silicate [gSi m^{-3} d^{-1}]
$Rprd_{ox}$	net production rate for dissolved oxygen [gO_2 m^{-3} d^{-1}]
$Rprd_{oc}$	net production rate for detritus organic carbon [gC m^{-3} d^{-1}]
$Rprd_{on}$	net production rate for detritus organic nitrogen [gN. m^{-3} d^{-1}]
$Rprd_{op}$	net production rate for detritus organic phosphorus [gP m^{-3} d^{-1}]
$Rprd_{osi}$	net production rate for opal silicate [gSi m^{-3} d^{-1}]

Notice that fam and fn are used to calculate the preference for ammonium uptake. The ratio of the ammonium specific limitation factor and the overall nitrogen limitation factor defines the fraction of nitrogen obtained from ammonium.

Notice also that the immediate release of inorganic nutrients caused by autolysis at the mortality of algae is ignored.

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Schematisation in space and time (Delwaq-G)

The microphytobenthos module has been developed in a way that allows for different levels of detail regarding spatial and temporal schematisation. If one intends to model variations of for example oxygen concentrations in the sediment during the day the microphytobenthos module can be run with a timestep of minutes to hours. There are several reasons why it can be more practical to model microphytobentos at a time step of a day instead. On the one hand it saves simulation time, on the other hand the competition for nutrients between microphytobenthos and pelagic algae can only be modelled correctly if the microphytobenthos module and the module for pelagic phytoplankton run at the same time step. The BLOOM module is often run with a timestep of one day, resulting in nutrient uptake by pelagic algae once per day. If microphytobenthos takes up nutrients every transport time-step it obtains an unrealistic advantage in the competition for nutrients. It is possible to run different processes at different time steps. If the microphytobenthos module is run with a time step of one day the limitation functions for light and temperature can be calculated at a smaller time step (e.g. the transport time step) and integrated and averaged to obtain the limitation functions per day.

Directives for use

- ◇ Always make sure that the light input (observed solar radiation) is consistent with the light related parameters of microphytobenthos. This concerns the use of either visible light or the photosynthetic fraction of visible light (approximately 45 %).
- ◇ Apart from availability of light and inorganic nutrients, the overall biomass of the microphytobenthos in the sediment layer can be controlled using the carrying capacity of the system K.

Additional references

WL | Delft Hydraulics (1997), O' Neill et al. (1989)

Table 4.25: *Definitions of the input parameters in the formulations for microphytobenthos.*

Name in formulas	Name in input	Definition	Units
an_i	$MPB(i)NCrat$	group specific stoch. const. for nitrogen over carbon	gN gC^{-1}
aph_i	$MPB(i)PCrat$	group spec. stoch. const. for phosphorus over carbon	gP gC^{-1}
asi_i	$MPB(i)SiCrat$	group specific stoch. const. for silicon over carbon	gSi gC^{-1}
Cam	$NH4$	ammonium concentration	gN m^{-3}
Cni	$NO3$	nitrate concentration	gN m^{-3}
Cph	$PO4$	phosphate concentration	gP m^{-3}
Csi	Si	dissolved inorganic silicate concentration	gSi m^{-3}
$Calg_1$	$MPB1peli$	concentration of epipelic benthic diatoms (in water)	gC m^{-3}
	$MPB1peliS1$	concentration of epipelic diatoms (in sediment)	gC m^{-2}

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Table 4.25 – continued from previous page

Name in formulas	Name in input	Definition	Units
$Calg_2$	$MPB2psam$	concentration of epipsammic benthic diatoms (in water)	gC m^{-3}
	$MPB2psamS1$	concentration of epipsammic diatoms (in sediment)	gC m^{-2}
$Calg_{\min}$	$MPB(i)Tresh$	minimal algal biomass conc., a threshold value	gC m^{-3}
Knn_i	$KNMPB(i)$	group specific half saturation constant for nitrogen	gN m^{-3}
Kph_i	$KPMPB(i)$	group specific half saturation constant for phosphate	gP m^{-3}
Ksi_i	$KSMPB(i)$	group specific half saturation constant for silicate	gSi m^{-3}
$PrfNH_i$	$PrfNH4MPB(i)$	group specific preference for ammonium over nitrate	-
a	a_enh	ampl. factor for irradiance due to scatter by sediment	-
$I_{sat,i}$	$RadSatMPB(i)$	saturation light intensity for group i	W m^{-2}
k	$ExtVlSed$	total extinction coefficient of visible light in sediment	m^{-1}
m	Nr_dz	number of depth intervals in a sediment layer	-
I_s	Rad	light int. at the top of a sed. layer when $SwMPBGEM = 0$	W m^{-2}
I_s	$Radbot$	light int. at the bottom of the lower water layer when $SwMPBGEM = 1$	W m^{-2}
$fexc_i$	$MPB(i)b_ex$	group spec. frac. gross prod. excr. at abs. of nutr. lim.	-
$frsp_i$	$MPB(i)r_pr$	group specific fraction of gross production respired	-
$kpmax_{i,20}$	$MPB(i)Pmax20$	group spec. potential gross primary prod. rate at 20 °C	d^{-1}
$kmrt1_{i,20}$	$MPB(i)m1_20$	group spec. physiological mort. process rate at 20 °C	d^{-1}
$kmrt2_{i,20}$	$MPB(i)m2_20$	group spec. pseudo grazing mort. process rate at 20 °C	m^3 gC^{-1} d^{-1}
$krsp_{20}$	$MPB(i)r_mt20$	group spec. maintenance respiration rate at 20 °C	d^{-1}

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Table 4.25 – continued from previous page

Name in formulas	Name in input	Definition	Units
$ktpmax_i$	$MPB(i)ktgp$	group spec. temperature coefficient for primary prod.	-
$ktmrt_i$	$MPB(i)mt$	group spec. temperature coefficient for mortality	-
$ktrsp_i$	$MPB(i)rt$	group spec. temperature coefficient for maintenance resp.	-
$kmrt_{w,i}$	$MPB(i)MorSed$	group spec. mortality process rate in the water column	d^{-1}
K	$MPB(i)Ccap$	Carrying capacity for MPB(i) (*)	gC m^{-2}
T	$Temp$	sediment (overlying water) temperature	°C
z_T	$Zthreshold$	threshold water depth, representing emersion	m
z_m	$Zsed$	euphotic depth for microphytobenthos	m

[1](i) indicates species groups 1 or 2.

(*) The carrying capacity is expressed as grams per square meter in the input, but it is converted to a concentration by dividing it by z_m.

Table 4.27: *Definitions of the output parameters for microphytobenthos.*

Name in formulas	Name in input	Definition	Units
flt_i	$MPB(i)flt$	group specific light limitation factor	-
fn_i	$MPB(i)fnit$	group spec. nitrogen limitation factor	-
fp_i	$MPB(i)fpho$	group spec. phosphorus limitation factor	-
fsi_i	$MPB(i)fsi$	group spec. silica limitation factor	-
$fnut_I$	$MPB(i)fnut$	group specific total nutrient limitation factor	-
$ftmp_i$	$MPB(i)ftmp$	group specific temperature limitation factor	-
f_{CO2}	$MPB(i)fc$	group specific inorganiccarbon limitation factor	-
fmn	$MPB(i)fmn$	correction factor for insuffient nitrogen	-
fmp	$MPB(i)fmp$	correction factor for insuffient phosphorus	-

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Table 4.27 – continued from previous page

Name in formulas	Name in input	Definition	Units
fms	$MPB(i)fms$	correction factor for insuffient silicate	-
$Rcns_{am,i}$	$FMPBiNH4UP$	group specific net consumption rate for ammonium	gN m^{-3} d^{-1}
$Rcns_{ni,i}$	$FMPBiNO3UP$	group specific net consumption rate for nitrate	gN m^{-3} d^{-1}
$Rcns_{ph,i}$	$FMPBiPO4UP$	group specific net consumption rate for phosphate	gP m^{-3} d^{-1}
$Rcns_{si,i}$	$FMPBiSIUP$	group specific net consumption rate for silicate	gSi m^{-3} d^{-1}
$Rexc_i$	$FMPBiHH4UP$	group specific excretion rate	gC m^{-3} d^{-1}
Rgp_i	$FMPBiHH4UP$	group specific gross primary production rate	gC m^{-3} d^{-1}
$Rmrt_i$	$FMPBiMOR$	group specific total mortality rate	gC m^{-3} d^{-1}
$Rprd_{oc}$	$FMPBiPOC1$	group specific net prod. rate for detritus org. carbon	gC m^{-3} d^{-1}
$Rprd_{on}$	$FMPBiPON1$	group specific net prod. rate for detritus org. nitrogen	gN m^{-3} d^{-1}
$Rprd_{op}$	$FMPBiPOP1$	group spec. net prod. rate for detr. org. phosphorus	gP m^{-3} d^{-1}
$Rprd_{osi}$	$FMPBiOPAL$	group specific net production rate for opal silicate	gSi m^{-3} d^{-1}
$Rprd_{ox}$	$FMPBiOXY$	group specific net production rate for opal silicate	gO_2 m^{-3} d^{-1}
$Rrsp_i$	$FMPBiRES$	group specific total respiration rate	gC m^{-3} d^{-1}
For S1:			
Cam	$NH4S1$	ammonium concentration in top sediment layer	gN m^{-3}
Cni	$NO3S1$	nitrate concentration in top sediment layer	gN m^{-3}
Cph	$PO4S1$	phosphate concentration in top sediment layer	gP m^{-3}
Csi	$SiS1$	dissolved silicate concentration in top sediment layer	gSi m^{-3}
$Calg_i$	$MPB(i)S1M3$	biomass concentration of benthic algae	gC m^{-3}

[1](i) indicates species groups 1 or 2.

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Table 4.26: *Definitions of the input parameters for the calculation of nutrient concentrations in the sediment in case of the S1 sediment approach.*

Name in formulas	Name in input	Definition	Units
A	$Surf$	surface area of the sediment in a water compartment	m^2
$frnit$	$FrNO3$	fraction of ammonium mineralirate conv. into nitrate	-
D	DIF	dispersion coeffcient at the sediment-water interface	$m^2\ d^{-1}$
H	$Depth$	depth of a water compartment or layer	m
$ktnit$	$TcNit$	temperature coefficient of nitrification	-
$Rmin$	$dMinDetNS1$	sed. min. rate for ammonium in case of S1-stand-alone	$gN\ m^{-3}\ d^{-1}$
(for N)	$dGEMSEDNH4$	sed. prod. rate for ammonium in case of GEMSED	$gN\ m^{-3}\ d^{-1}$
$Rmin$	$dGEMSEDNO3$	sed. prod. rate for nitrate in case of GEMSED	$gN\ m^{-3}\ d^{-1}$
(for P)	$dMinDetPS1$	sed. min. rate for phosphate in case of S1-stand-alone	$gP\ m^{-3}\ d^{-1}$
$Rmin$	$dGEMSEDPO4$	sed. min. rate for phosphate in case of GEMSED	$gP\ m^{-3}\ d^{-1}$
(for Si)	$dMinDetSiS1$	sed. diss. rate for silicate in case of S1-stand-alone	$gSi\ m^{-3}\ d^{-1}$

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4.14 Mortality and re-growth of terrestrial vegetation (VEGMOD)

PROCESSES: VBMORT(I), VB(I)_MRT3W, VB(I)_MRT3S, VBGROWTH(I), VB(I)UPT, VB(I)_UPT3D, VB(I)AVAILN, VBSTATUS(I)

The vegetation sub-model simulates the effects of the drowning and re-growth of vegetation in water systems such as (man-made) reservoirs on water quality. The design of the module is generic to allow for a comprehensive processes content, but only the most essential formulations for growth and mortality have been included. Starting from a standing stock of biomasses for a number of vegetation cohorts (types, species, etc.), mortality due to inundation leads to the allocation of organic matter (C, N, P, S) to the POX1–3 and POX5 fractions in water and sediment. Re-growth in areas run dry may lead to the building up of a standing stock of new vegetation biomass, the nutrients for which are withdrawn from the sediment.

A cohort is treated as a homogeneous entity in the model in terms of variables (state variable, coefficients and mass fluxes). The number of vegetation cohorts in the model is limited to a maximum of 9. Various cohorts may be present in the same model grid cell. The total biomasses of the cohorts are modelled as inactive substances expressed in grams carbon per m^2. These not transported state variables only exist in the lower water layer. Additional output parameters provide total biomass for each cohort expressed in tonnes C per ha. The concurrent organic nutrients (nitrogen, phosphorus, sulfur) in vegetation biomass are not modelled as separate state variables, but as quantities derived from the carbon state variables using stoichiometric ratio's.

Each cohort of vegetation consists of the following above-ground and below-ground compartments: 1) stems, 2) foliage, 3) branches, 4) roots, 5) fine roots. The fractions of biomass of these compartments for each vegetation cohort imposed as allocation factors are used to calculate the fluxes of biomass turned over into the various detritus pools in the layers of the water column and the sediment (Figure 4.11). Nutrients are stored in the compartments in agreement with compartment-specific stoichiometric constants.

Mortality starts after a lag time following inundation and proceeds according to a first-order decay of living biomass. Foliage and fine roots are allocated to the detritus pools in the water and sediment layers according to vegetation height and rooting depth.

Growth is calculated from a predefined growth curve, and will stop once a certain target biomass is achieved (Figure 4.12). Growth may be limited by the quantities of nutrients available in the sediment according to rooting depth. Nitrogen is taken from ammonium (NH4, preferred) and nitrate (NO3), phosphorus from dissolved and adsorbed phosphate (PO4, preferred, and AAP), and sulfur from sulfate (SO4, preferred) and dissolved sulfide (SUD). Carbon is taken up from the atmosphere. For each vegetation cohort (re-)growth may be prevented or allowed by means of two "option" parameters. In this way it can be manipulated that initially present types do not (re-)grow.

Implementation

The processes of vegetation module VEGMOD have been implemented for the following substances:

- ◇ VB01, VB02, VB03, VB04, VB05, VB06, VB07, VB08, VB09
- ◇ POC1, PON1, POP1, POS1, POC2, PON2, POP2, POS2, POC3, PON3, POP3, POS3, POC5, PON5, POP5, POS5
- ◇ NH4, NO3, PO4, AAP, SO4, SUD

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- ◇ Processes VBMORT(i) calculate the mortality rates and the detritus release rates.
- ◇ Processes VB(i)_MRT3W and VB(i)_MRT3S distribute the release rates among water and sediment layers.
- ◇ Processes VBGROWTH(i) calculates the growth rates as based on available nutrients in the sediment.
- ◇ Processes VB(i)AVAILN determine the available quantities of the nutrients (N, P, S), whereas processes VB(i)UPT and VB(i)_UPT3D calculate the nutrient uptake rates for the sediment layers.
- ◇ Processes VBSTATUS(i) keep record of the inundation time, and set the option parameters for growth and mortality (*SWVB(i)Gro* and *SWVB(i)Mrt*). (i) is the number of a vegetation cohort (01–09).

Table 4.28 provides the definitions of the input parameters occurring in the formulations, and Table 4.29 provides the output parameters.

Formulation

(Re-)Growth

The growth curve of a vegetation cohort is defined by 4 parameters; minimum biomass, maximum target biomass, cohort age where 50 % of maximum biomass is achieved and a factor for the shape of the growth curve (Figure 4.12). The "target" attainable biomass is thus a function of the age of the vegetation cohort. The actual biomass growth in each time step of the simulation is determined from the "target" attainable biomass for the current age and the actual biomass. The calculation of growth starts with determination of the total attainable biomass of each vegetation cohort as resulting from the growth curve:

$$Mveg_{a,i} = \frac{(Mveg_{min,i} - Mveg_{max,i})}{1 + \exp\left(sf_i \times (ag_i - ag_{hb,i})/ag_{hb,i}\right)} + Mveg_{max,i}$$

where:

ag	age of vegetation [d]
ag_{hb}	age of vegetation when half of attainable biomass is reached [d]
$Mveg_a$	attainable biomass in all compartments [gC.m^{-2}]
$Mveg_{max}$	maximum biomass in all compartments [gC.m^{-2}]
$Mveg_{min}$	minimum biomass in all compartments [gC.m^{-2}]
sf	shape factor of the growth function [-]
i	index for vegetation cohorts (1–9)

The initial vegetation biomass at the start of the simulation ($t = 0$) is computed from the amount of vegetation biomass dry matter per ha. Optionally, a percentage of surface coverage may be used in the calculation of initial biomass according to:

$$Mveg_i = fa_i \times Mveg_{0,i}/\mathrm{dmc_i}$$

where:[1]

dmc	dry matter carbon ratio [gDM.gC^{-1}]
fa	percentage of area coverage [%]
$Mveg$	actual biomass in all compartments [gC.m^{-2}]
$Mveg_0$	initial biomass in all compartments [tDM.ha^{-1}]

[1] The use of a percentage rather than a fraction allows the implicit conversion of the unit [tDM.ha^{-1}] to the unit [gC.m^{-2}].

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If growth takes place (*SWVB(i)Gro* = 1.0), the potential (or target) growth rate of biomass per vegetation cohort results from:

$$Rgr_{p,i} = (Mveg_{a,i} - Mveg_i)/\Delta t$$

where:

Rgr_p	potential growth rate of biomass in all compartments [gC.m^{-2}.d^{-1}]
Δt	computational time step [d]

In a final step the growth is corrected for nutrient limitation. In case of nutrient limitation, the above potential growth rates $Rgr_{p,i}$ are reduced to actual growth rates Rgr_i in proportion with the available quantity of the growth limiting nutrient. These actual growth rates are calculated from the potential growth rates multiplied with the ratio of the available quantity of the most limiting nutrient and the quantity of this nutrient needed to sustain the potential growth rates ($NutLimVB(i)$).

When inundation occurs, the vegetation stops growing ($SWVB(i)Gro = 0.0$), and the vegetation age remains constant at the current age until inundation is over. When vegetation growth is limited by a shortage of nutrients, vegetation growth and age are reduced accordingly. Initial age is calculated from the initial biomass using the formulation of the growth curve. Age is reset to zero if the vegetation dies (see below).

Uptake of nutrients

Nutrients (N, P and S) are taken up by vegetation from the sediment within rooting depth, whereas carbon is taken up from the atmosphere. The total uptake rates are computed using vegetation cohort and biomass compartment specific carbon to nutrient ratios. The total uptake rates are distributed among the sediment layers within rooting depth proportional to the quantities of the nutrients available in the layers (grid cells). The nutrient uptake rates result from:

$$Rup_{lin} = fn_{ln} \times Rgr_i \times \sum_{j=1}^{5} \left(fb_{ij}/vn_{lij} \right) / H$$

$$Rup_{t,l} = \sum_{i=1}^{9} \left(\sum_{n=1}^{nr} \left(Rup_{iln} \right) \right)$$

where:

fb	fraction of biomass in a compartment [-]
fn	fraction of total available nutrient in a layer [-]
H	sediment layer thickness [-]
Rgr	growth rate of biomass in all compartments [gC.m^{-2}.d^{-1}]
Rup	uptake rate of nutrients in all compartments [gN/P/S.m^{-3}.d^{-1}]
$Rupt$	total uptake rate of nutrients in all compartments [gN/P/S.m^{-3}.d^{-1}]
vn	carbon nutrient ratio in vegetation biomass [gC.gN/P/S^{-1}]
l	index for nutrient (1=nitrogen, 2=phosphorus, 3=sulfur)
i	index for vegetation cohorts (1–9)
j	index for biomass compartments (1=stem, 2=foliage, 3=branches, 4=roots, 5=fine roots)
n	index for a sediment layer (nr = number of layer within rooting depth)

The quantities of available nutrients are derived from the nutrient concentrations (*Cam, Cni, Cph, Cap, Csu, Csud*) in the sediment layers within rooting depth. When not enough nutrient

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is available to sustain potential growth, the growth rates have been reduced proportionally (see above). In order to avoid numerical errors when all available nutrient would be depleted the maximum fraction of the available nutrients that can be taken up in a time step can be made smaller than 1.0 by means of input parameter *VBFrMaxU*.

Mortality and detritus release

The onset of mortality from the start of the simulation can be imposed optionally, using option parameter *IniVB(i)Dec*=1.0. If the duration of inundation exceeds a lag time defined as the critical number of subsequent days with inundation, the vegetation cohorts in the inundated area will start to die:

$$\text{if } \; SwEmersion = 0.0 \;\; then \;\; ti = ti + \Delta t \;\; else \;\; ti = 0.0$$

$$\text{if } \; ti > ti_{c,i} \;\; then \;\; ag_i = 0.0 \;\; and \;\; SwVB_iMrt \; = \; 0.0$$

where:

ag	age of biomass [d]
ti	inundation period, the number of successive days of inundation [d]
ti_c	critical inundation period, the mortality lag time [d]
$SwEmersion$	switch for emersion/inundation (0 = yes, 1 = no)
$SwVB_iMrt$	switch for mortality (0 = yes, 1 = no)
Δt	computational time step [d]
i	index for vegetation cohorts (1–9)

The lag time for mortality due to inundation is input to the model and not a function of local conditions such as the dissolved oxygen concentration. The duration of inundation prior to the simulation start time ti_0 can be imposed.

Mortality results in the decrease of vegetation biomass and the transfer of vegetation biomass to the particulate detritus fractions. Detritus from foliage, stems and branches goes to water layers, detritus from fine roots and roots to sediment layers. The detritus release rates for each sediment grid cell are computed using vegetation cohort and biomass compartment specific carbon to nutrient ratios and the fraction of biomass allocated to a water or sediment layer. This fraction is derived from vegetation height and rooting depth and the fractions of biomass allocated to each of the five biomass compartments (see below). The mortality rate of the vegetation biomass and the release rates of organic nutrients follow from:

$$Rmrt_i = kmrt_i \times Mveg_i$$
$$Rmrd_{klij} = fh_i \times fd_{kij} \times fb_{ij} \times Rmrt_i/(vn_{lij} \times H)$$

where:

fb	fraction of biomass in a compartment [-]
fd	fraction of biomass released into a specific detritus fraction [-]
fh	fraction of biomass in a layer [-]
H	water layer or sediment layer thickness [-]
$kmrt$	mortality rate constant [d^{-1}]
$Mveg$	actual biomass in all compartments [$gC.m^{-2}$]
$Rmrd$	release rate of detritus [$gC/N/P/S.m^{-3}.d^{-1}$]
$Rmrt$	mortality rate of biomass [$gC.m^{-2}.d^{-1}$]
vn	carbon nutrient ratio in vegetation biomass [$gC.gC/N/P/S^{-1}$]
k	index for detritus fraction (1 = POX1, 2 = POX2, 3 = POX3, 5 = POX5)
l	index for carbon and nutrient (0 = carbon, 1 = nitrogen, 2 = phosphorus, 3 = sulfur)

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i	index for vegetation cohorts (1–9)
j	index for biomass compartments (1 = stem, 2 = foliage, 3 = branches, 4 = roots, 5 = fine roots)

The fractions fd for foliage and fine roots to POX1–3 are derived from input parameters. The fractions fd for stems, branches and large roots to POX5 are equal to 1.0.

Vertical distribution of the detritus release rates

In order to obtain vertical distributions of the detritus release rates, the biomass compartments of each vegetation cohort are distributed virtually among the layers (grid cells) in each water-sediment column. A distinction is made between the compartments in above-ground biomass (foliage, branches, stems) and the compartments in below-ground biomass (roots, fine roots). Above-ground biomass of each cohort has a vegetation height. Below-ground biomass of each cohort has a rooting depth. Based on these parameters, the number of water layers and sediment layers involved in the distribution are determined. Water layers above vegetation height and sediment layers below rooting depth have zero biomass, and therefore zero detritus release.

The distribution is determined from the total above-ground or the total below-ground biomass per m^2 using a distribution shape constant. The total above-ground and total below-ground biomass is derived from the total biomass of a vegetation cohort and the biomass fractions in the five compartments. The shape constant is given by:

$$Fs_i = \frac{Cveg_i(z_{max,i})}{\left(Mveg_{p,i}/H_{max,i}\right)}$$

where:

Fs	shape constant for vertical distribution of biomass [-]
$Cveg(z_{max})$	above-ground or under-ground biomass at z_{max} [gC.m^{-3}]
$Mveg_p$	above-ground or under-ground biomass [gC.m^{-2}]
H_{max}	vegetation height (positive) or rooting depth (negative) [m]
z_{max}	water depth (positive) at vegetation height or sediment (negative) depth at rooting depth [m]
i	index for vegetation cohorts (1–9)

The value of shape constant Fs varies from 0 to 2. When $Fs = 0$ the biomass $Cveg$ is zero at zmax, when $Fs = 1$ biomass $Cveg$ is homogeneously distributed (constant over depth), and when $Fs = 2$ biomass $Cveg$ is zero at the sediment. For values of Fs between 0 and 1 biomass decreases towards vegetation height or rooting depth. For Fs-values between 1 and 2 the biomass decreases towards the sediment. The effects of Fs on the distribution appear from Figure 4.13.

A linear distribution function is formulated using two constants, a and b. Both are fixed when Fs is fixed because the integral of the biomass distribution must equal the total biomass. The vertical distribution within the water column or the sediment column follows from:

$$\begin{aligned} Cveg_i(z) &= a_i \times z + b_i \\ a_i &= \frac{Mveg_{p,i}}{H_{max,i}} \times \frac{(2 - 2 \times Fs_i)}{(H_t - z_{max,i})} \\ b_i &= \frac{Mveg_{p,i}}{H_{max,i}} \times \frac{(Fs_i \times (z_{max,i} + H_t) - 2 \times z_{max,i})}{(H_t - z_{max,i})} \end{aligned}$$

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The biomass fraction fh_i in a layer n between z_n and z_{n+1} follows from:

$$\int_{z_n}^{z_{n+1}} (Cveg_i(z)/Mveg_i)\, dz = \frac{A}{2}\left(z_{n+1}^2 - z_n^2\right) + B\left(z_{n+1} - z_n\right)$$

$$fh_i = \begin{cases} \int_{z_n}^{z_{n+1}} \left(Cveg_i(z)/Mveg_i\right) dz & \text{if } z_n > z_{max,i} \\ \int_{z_n}^{z_{max,i}} \left(Cveg_i(z)/Mveg_i\right) dz & \text{if } z_n \leq z_{max,i} \end{cases}$$

with:

$$\int_{z_n}^{z_{n+1}} (Cveg_i(z)/Mveg_i)\, dz = \frac{A}{2}\left(z_{n+1}^2 - z_n^2\right) + B\left(z_{n+1} - z_n\right)$$

where:

$Cveg(z)$	above-ground or under-ground biomass at water or sediment depth z [gC.m^{-3}]
fh	fraction of biomass in a water or sediment layer [-]
H_t	total water depth or total sediment depth [m]
$Mveg$	biomass in all compartments [gC.m^{-2}]
$Mveg_p$	above-ground or under-ground biomass [gC.m^{-2}]
z	water depth (positive) or sediment depth (negative) at bottom of a layer [m]
i	index for vegetation cohorts (1–9)

For $Fs = 1$ the integral reduces to:

$$fh_i = \frac{Mveg_{p,i}}{Mveg_i} \times \frac{(z_{n+1} - z_n)}{H_{max,i}} \qquad \text{if} \quad z_n > z_{max,i}$$

$$fh_i = \frac{Mveg_{p,i}}{Mveg_i} \times \frac{(z_{max,i} - z_n)}{H_{max,i}} \qquad \text{if} \quad z_n < z_{max,i} \;\; and \;\; z_{n+1} > z_{max,i}$$

Directives for use

1 Two options are available for the input of initial vegetation biomasses. For *SwIniVB(i)=1.0* the model expects percentual coverage and initial biomass in tDM.ha^{-1} for each vegetation type. For *SwIniVB(i)=0.0* the model expects biomasses in tDM.ha^{-1} for each vegetation type for each grid cell.

2 The input for initial biomasses may be generated as a GIS map representing each model grid cell, for instance based on a satellite image.

3 The option for the vertical distribution of biomass and detritus fluxes *SWDisVB(i)* overlaps the distribution shape factor *FfacVB(i).* If *FfacVB(i)*=1.0 *SWDisVB(i)* must equal 1.0 as well. The linear and exponential distributions (*SWDisVB(i)*=2.0 or 3.0) are not fully implemented.

4 The option parameter *IniVB(i)Dec* can be used to impose mortality from the start of the simulation. Default value 0.0 implies “no” mortality, value 1.0 causes mortality from the start.

5 The maximum fraction of the available nutrients that can be taken up in a time step *VBFrMaxU* ($<$1.0) has a default value of 0.5. To avoid too strong nutrient limitation its value can be increased, but one should verify that this does not cause numerical errors.

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Table 4.28: *Definitions of the input parameters in the above equations for VBMORT(i), VB(i)_MRT3W, VB(i)_MRT3S, VBGROWTH(i), VB(i)UPT, VB(i)_UPT3D, VB(i)AVAILN and VBSTATUS(i).*

Name in formulas[1]	**Name in input**[1]	**Definition**	**Units**
ag_{hb}, *i*	*HlfAgeVb(i)*	age of veg. when half of attainable biomass is reached	d
Cam	*NH4*	concentration of ammonium	gN.m^{-3}
Cni	*NO3*	concentration of nitrate	gN.m^{-3}
Cph	*PO4*	concentration of dissolved phosphate	gP.m^{-3}
Cap	*AAP*	concentration of adsorbed phosphate	gP.m^{-3}
Csu	*SO4*	concentration of sulfate	gS.m^{-3}
Csud	*SUD*	concentration of dissolved sulfide	gS.m^{-3}
dmc_i	*DMcfVB(i)*	dry matter carbon ratio	gDM.gC^{-1}
fa_i	*IniCovVB(i)*	percentage of area coverage	%
fb_{ij}	*F1VB(i)*	fraction of biomass in compartment 1 (stems)	-
	F2VB(i)	fraction of biomass in comp. 2 (foliage)	-
	F3VB(i)	fraction of biomass in comp. 3 (branches)	-
	F4VB(i)	fraction of biomass in comp. 4 (roots)	-
	F5VB(i)	fraction of biomass in comp. 5 (fine roots)	-
fd_{1i2}	*FfolPOC1*	biomass fraction 2 (foliage) to detr. POX1	-
fd_{2i2}	*FfolPOC2*	biomass fraction 2 (foliage) to detr. POX2	-
fd_{1i5}	*FfrootPOC1*	biomass fraction 2 (fine roots) to detr. POX1	-
fd_{2i5}	*FfrootPOC2*	biomass fraction 2 (fine roots) to detr. POX2	-
Fs	*FfacVB(i)*	shape constant for vertical distr. of biomass	-
H	*Depth*	water layer or sediment layer thickness	m
H_{max}	*VegHeVB(i)*	vegetation height (positive)	m
H_{max}	*RootDeVB(i)*	rooting depth (negative)	m
H_t	*TotalDepth*	total water depth or total sediment depth	m
z	*LocalDepth*	depth to the bottom of a water layer	m
z	*LocSedDept*	depth to the bottom of a sediment layer	m
-	*Surf*	surface area of a grid cell	m^{-2}
-	*Volume*	volume of a grid cell	m^{-3}
$kmrt_i$	*RcMrtVB(i)*	mortality rate constant	d^{-1}
Mveg	*VB(i)*	vegetation biomass in all five compartments	gC.m^{-2}
$Mveg_0$	*IniVB(i)*	initial biomass in all five compartments	tDM.ha^{-1}
$Mveg_{max,i}$	*MaxVB(i)*	maximum biomass in all five compartments	gC.m^{-2}

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Name in formulas[1]	Name in input[1]	Definition	Units
$Mveg_{min,i}$	*MinVB(i)*	minimum biomass in all five compartments	gC.m^{-2}
sf_i	*SfVB(i)*	shape factor of the growth function	-
SWEmersion	*SWEmersion*	switch for inundation (0 = yes, 1 = no)	-
SWDisVB(i)	*SWDisVB(i)*	option vert. distr. (1=const., 2=linear, 3=exp.)	-
SwIniVB(i)	*SwIniVB(i)*	option init. biomass (0=biomass,1=coverage)	-
IniVB(i)Dec	*IniVB(i)Dec*	option mort. at start of simul. (0=no, 1=yes)	-
SwRegrVB(i)	*SwRegrVB(i)*	option for re-growth (0=no, 1=yes)	-
VBFrMaxU	*VBFrMaxU*	max. fr. of nutrients taken up in a time step	-
vn_{1ij}	*CNF1VB(i)*	carbon nitrogen ratio in comp. 1 (stems)	gC.gN^{-1}
	CNF2VB(i)	carbon nitrogen ratio in comp. 2 (foliage)	gC.gN^{-1}
	CNF3VB(i)	carbon nitrogen ratio in comp. 3 (branches)	gC.gN^{-1}
	CNF4VB(i)	carbon nitrogen ratio in comp. 4 (roots)	gC.gN^{-1}
	CNF5VB(i)	carbon nitrogen ratio in comp. 5 (fine roots)	gC.gN^{-1}
vn_{2ij}	*CPF1VB(i)*	carbon phosphorus ratio in comp. 1 (stems)	gC.gP^{-1}
	CPF2VB(i)	carbon phosphorus ratio in comp. 2 (foliage)	gC.gP^{-1}
	CPF3VB(i)	carbon phos. ratio in comp. 3 (branches)	gC.gP^{-1}
	CPF4VB(i)	carbon phosphorus ratio in comp. 4 (roots)	gC.gP^{-1}
	CPF5VB(i)	carbon phos. ratio in comp. 5 (fine roots)	gC.gP^{-1}
vn_{3ij}	*CSF1VB(i)*	carbon sulfur ratio in comp. 1 (stems)	gC.gS^{-1}
	CSF2VB(i)	carbon sulfur ratio in comp. 2 (foliage)	gC.gS^{-1}
	CSF3VB(i)	carbon sulfur ratio in comp. 3 (branches)	gC.gS^{-1}
	CSF4VB(i)	carbon sulfur ratio in comp. 4 (roots)	gC.gS^{-1}
	CSF5VB(i)	carbon sulfur ratio in comp. 5 (fine roots)	gC.gS^{-1}
$ti_{c,i}$	*CrnsfVB(i)*	critical inundation period, mortality lag time	d
$ti_{0,i}$	*Initnsfd*	inundation period prior to sim. start time	d
Δt	*Delt*	computational time step	d

[1)] *i=1–9* or *(i)*=01–09 is the vegetation cohort number; *j=1–5* is the biomass compartment number.

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Table 4.29: *Definitions of the additional output parameters for VBMORT(i), VB(i)_MRT3W, VB(i)_MRT3S, VBGROWTH(i), VB(i)UPT, VB(i)_UPT3D, VB(i)AVAILN and VBSTATUS(i).*

Name in formulas[1]	**Name in output**[1]	**Definition**[2]	**Units**
ti_i	*AgeVB(i)*	age of vegetation biomass	d
-	*fNVB(i)UP*	N vegetation uptake flux	$gN.m^{-2}.d^{-1}$
	fPVB(i)UP	P vegetation uptake flux	$gP.m^{-2}.d^{-1}$
	fSVB(i)UP	S vegetation uptake flux	$gS.m^{-2}.d^{-1}$
	fN1VB(i)UPy	ammonium N vegetation uptake flux	$gN.m^{-2}.d^{-1}$
	fN2VB(i)UPy	nitrate N vegetation uptake flux	$gN.m^{-2}.d^{-1}$
	fP1VB(i)UPy	dissolved phosphate P vegetation uptake flux	$gP.m^{-2}.d^{-1}$
	fP2VB(i)UPy	adsorbed phosphate P vegetation uptake flux	$gP.m^{-2}.d^{-1}$
	fS1VB(i)UPy	sulfate S vegetation uptake flux	$gS.m^{-2}.d^{-1}$
	fS2VB(i)UPy	dissolved sulfide S vegetation uptake flux	$gS.m^{-2}.d^{-1}$
-	*fC1VB(i)P5*	C flux from biomass comp. 1 to detritus POC5	$gC.m^{-3}.d^{-1}$
	fN1VB(i)P5	N flux from biomass comp. 1 to detritus POC5	$gN.m^{-3}.d^{-1}$
	fP1VB(i)P5	P flux from biomass comp. 1 to detritus POC5	$gP.m^{-3}.d^{-1}$
	fS1VB(i)P5	S flux from biomass comp. 1 to detritus POC5	$gS.m^{-3}.d^{-1}$
	fC2VB(i)P1	C flux from biomass comp. 2 to detritus POC1	$gC.m^{-2}.d^{-1}$
	fN2VB(i)P1	N flux from biomass comp. 2 to detritus POC1	$gN.m^{-2}.d^{-1}$
	fP2VB(i)P1	P flux from biomass comp. 2 to detritus POC1	$gP.m^{-2}.d^{-1}$
	fS2VB(i)P1	S flux from biomass comp. 2 to detritus POC1	$gS.m^{-2}.d^{-1}$
	fC2VB(i)P2	C flux from biomass comp. 2 to detritus POC2	$gC.m^{-2}.d^{-1}$
	fN2VB(i)P2	N flux from biomass comp. 2 to detritus POC2	$gN.m^{-2}.d^{-1}$
	fP2VB(i)P2	P flux from biomass comp. 2 to detritus POC2	$gP.m^{-2}.d^{-1}$
	fS2VB(i)P2	S flux from biomass comp. 2 to detritus POC2	$gS.m^{-2}.d^{-1}$
	fC2VB(i)P3	C flux from biomass comp. 2 to detritus POC3	$gC.m^{-2}.d^{-1}$
	fN2VB(i)P3	N flux from biomass comp. 2 to detritus POC3	$gN.m^{-2}.d^{-1}$
	fP2VB(i)P3	P flux from biomass comp. 2 to detritus POC3	$gP.m^{-2}.d^{-1}$
	fS2VB(i)P3	S flux from biomass comp. 2 to detritus POC3	$gS.m^{-2}.d^{-1}$
	fC3VB(i)P5	C flux from biomass comp. 3 to detritus POC5	$gC.m^{-3}.d^{-1}$
	fN3VB(i)P5	N flux from biomass comp. 3 to detritus POC5	$gN.m^{-3}.d^{-1}$
	fP3VB(i)P5	P flux from biomass comp. 3 to detritus POC5	$gP.m^{-3}.d^{-1}$
	fS3VB(i)P5	S flux from biomass comp. 3 to detritus POC5	$gS.m^{-3}.d^{-1}$
	fC4VB(i)P5	C flux from biomass comp. 4 to detritus POC5	$gC.m^{-3}.d^{-1}$
	fN4VB(i)P5	N flux from biomass comp. 4 to detritus POC5	$gN.m^{-3}.d^{-1}$
	fP4VB(i)P5	P flux from biomass comp. 4 to detritus POC5	$gP.m^{-3}.d^{-1}$
	fS4VB(i)P5	S flux from biomass comp. 4 to detritus POC5	$gS.m^{-3}.d^{-1}$

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Name in formulas[1]	Name in output[1]	Definition[2]	Units
	fC5VB(i)P1	C flux from biomass comp. 5 to detritus POC1	gC.m^{-2}.d^{-1}
	fN5VB(i)P1	N flux from biomass comp. 5 to detritus POC1	gN.m^{-2}.d^{-1}
	fP5VB(i)P1	P flux from biomass comp. 5 to detritus POC1	gP.m^{-2}.d^{-1}
	fS5VB(i)P1	S flux from biomass comp. 5 to detritus POC1	gS.m^{-2}.d^{-1}
	fC5VB(i)P2	C flux from biomass comp. 5 to detritus POC2	gC.m^{-2}.d^{-1}
	fN5VB(i)P2	N flux from biomass comp. 5 to detritus POC2	gN.m^{-2}.d^{-1}
	fP5VB(i)P2	P flux from biomass comp. 5 to detritus POC2	gP.m^{-2}.d^{-1}
	fS5VB(i)P2	S flux from biomass comp. 5 to detritus POC2	gS.m^{-2}.d^{-1}
	fC5VB(i)P3	C flux from biomass comp. 5 to detritus POC3	gC.m^{-2}.d^{-1}
	fN5VB(i)P3	N flux from biomass comp. 5 to detritus POC3	gN.m^{-2}.d^{-1}
	fP5VB(i)P3	P flux from biomass comp. 5 to detritus POC3	gP.m^{-2}.d^{-1}
	fS5VB(i)P3	S flux from biomass comp. 5 to detritus POC3	gS.m^{-2}.d^{-1}
Rgr_i	*fVB(i)*	actual vegetation biomass growth rate	gC.m^{-2}.d^{-1}
NutLimVB(i)	*NutLimVB(i)*	nutrient limitation factor for growth (≤ 1.0)	-
-	*VB(i)ha*	vegetation biomass density	tC.ha^{-1}
	VB(i)Aha	attainable vegetation biomass density	tC.ha^{-1}
-	*VB(i)Navail*	available nutrient N within rooting depth	gN.m^{-2}
	VB(i)Pavail	available nutrient P within rooting depth	gP.m^{-2}
	VB(i)Savail	available nutrient S within rooting depth	gS.m^{-2}
-	*SWVB(i)Dec*	switch continuation mortality (0 = no, 1 = yes)	-
SWVB(i)Gro	*SWVB(i)Gro*	switch for growth (0 = no, 1 = yes)	-
SWVB(i)Mrt	*SWVB(i)Mrt*	switch for mortality (0 = no, 1 = yes)	-

[1] *(i)*=01–09 is the vegetation cohort number; *j=1–5* is the biomass compartment number.

[2] Vegetation biomass compartments are 1=stems, 2=foliage, 3=branches, 4=roots and 5=fine roots.

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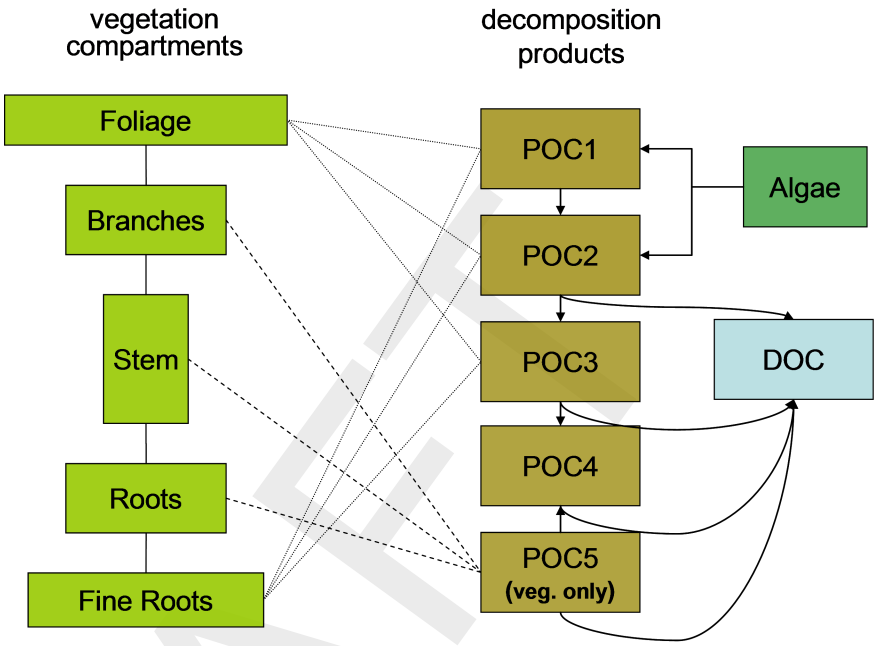

Figure 4.11: *Interactions between the compartments of a vegetation cohort (left side, green) and the detritus fractions POC1–5/DOC in the model (particulate fractions brown, dissolved fraction blue). Similar schemes apply to PON1–5/DON, POP1–5/DOP and POS1–5/DOS.*

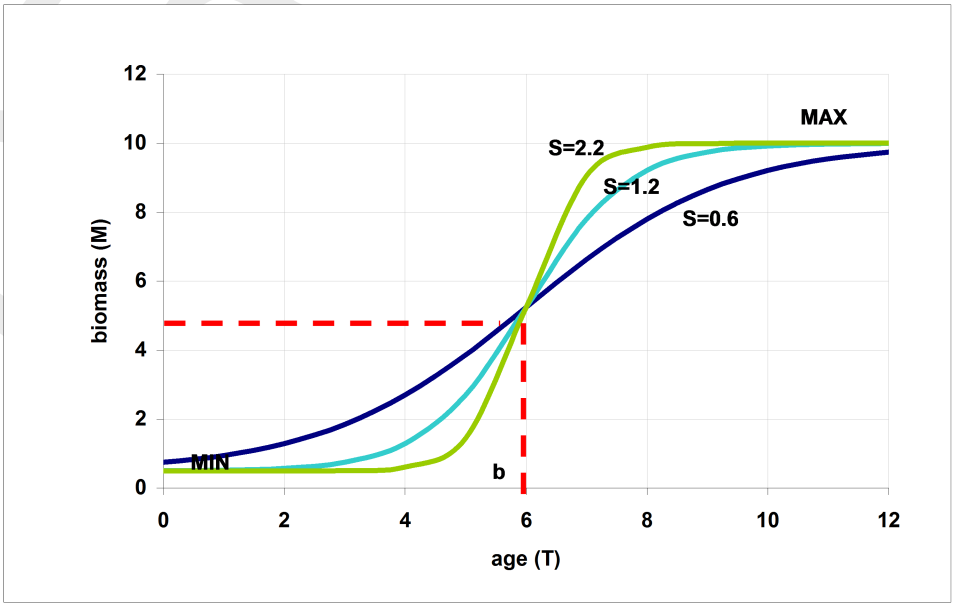

Figure 4.12: *The growth curve of a vegetation cohort (y-axis) as a function of it's age is a function of 4-parameters: minimum biomass (MIN), maximum target biomass (MAX), cohort age where 50 % of maximum biomass is achieved (b) and a factor indicating how 'smooth' the growth curve is (s).*

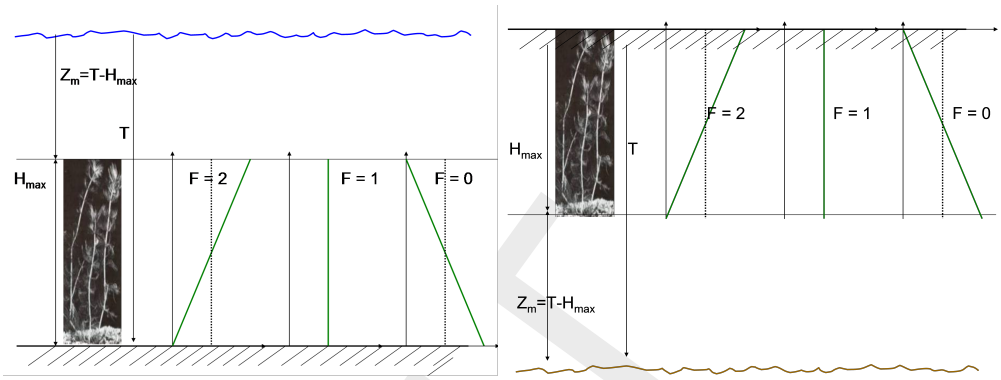

Figure 4.13: *The effect of shape constant $Fs(F)$ on the distribution of vegetation biomass above the sediment (a) and vegetation biomass in the sediment (b). The symbols used are explained in the text ($T = H_t$).*

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5 Macrophytes

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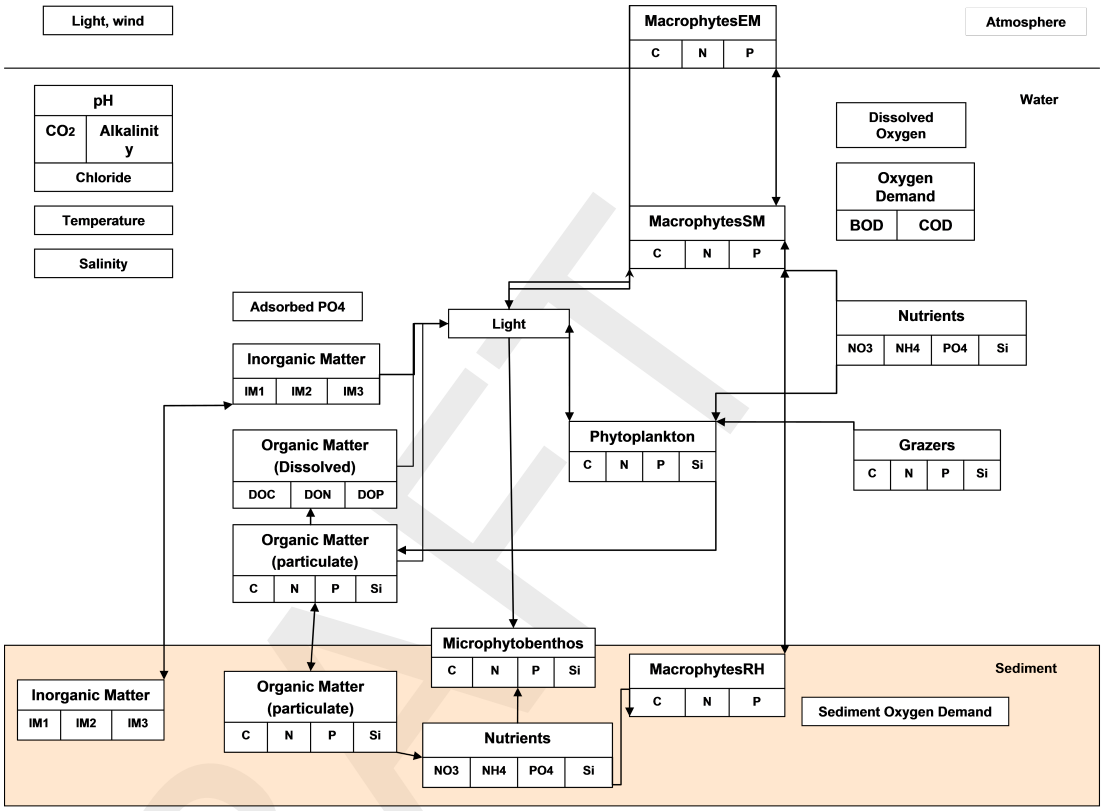

Figure 5.1: *Interactions between the nutrient cycles and the life cycle of macrophytes.*

5.1 Framework of the macrophyte module

5.1.1 Relation macrophyte module and other DELWAQ processes

Many processes are acknowledged to be of importance to the development of macrophytes and their interaction with the environment:

- ◇ Light climate
- ◇ Sedimentation and resuspension
- ◇ Nutrient dynamics
- ◇ Oxygen and carbon cycles
- ◇ Diurnal processes
- ◇ Food web structures
- ◇ Chemical processes within the root zone

Figure 5.1 gives an overview of the most important fluxes that exist within and between macrophytes and their abiotic surroundings. It also indicates which relevant processes are already included in D-Water Quality and which fluxes (and processes within macrophytes/ macrophyte stands) are newly included in the D-Water Quality macrophyte module. The internal processes of transport between different functional parts of macrophytes (being emerged, submerged and root sections of the plant) play an important role too. The development of biomass is directly linked to the fluxes between the macrophyte stands and the open water plus sediment as modelled in D-Water Quality (e.g. nutrient uptake for growth, uptake of CO_2).

5.1.2 Growth forms

In the Macrophytes Module macrophytes can be described based on their growth forms by selecting to include sections of the plants: emerged, submerged and root sections. Five growth forms have been selected as examples (Figure 5.2). For each category a few species growing in Western Europe are given as examples.

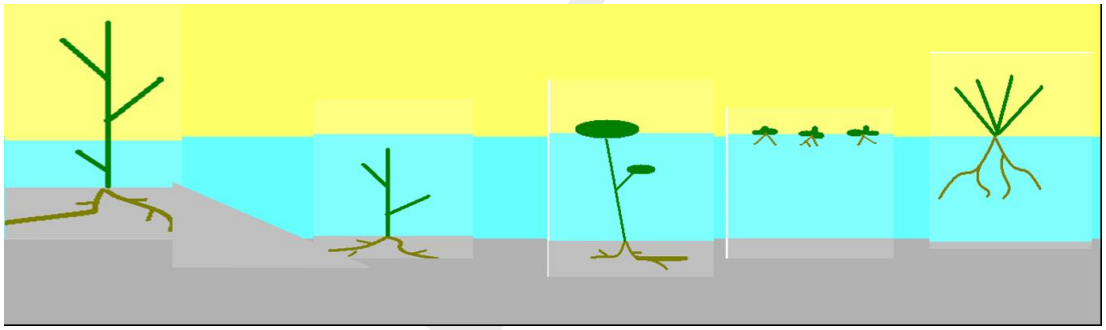

Figure 5.2: *The different macrophytes growth forms that can be modeled with the Macrophyte Module.*

The different macrophytes growth forms that can be modeled with the Macrophyte Module.

1. Helophytes like the common reed *Phragmites australis*, the cattail or *Typhaceae* family and the arrowhead *Sagittaria saggittifolia*.
2. Eloidids: The submerged angiosperms like the sago pondweed *Potamogeton pectinatus*, the common waterweed *Elodea canadensis* and the Eurasian water-milfoil *Myriophyllum spicatum*.
3. Charids: The submerged macro-algae like the stoneworts *Chara sp. Chara sp.* can also be modeled with the BLOOMmodule, which models the phytoplankton production in D-Water Quality). The coefficients concerning this species are also given separately from the other submerged species.
4. Lemnids: The emerged, non-rooted species like the lesser duckweed *Lemna minor*, the star duckweed *Lemna gibba* and the water fern *Azolla filiculoides*.
5. The emerged rooted species like the *Nympheaceae* family: the white water lily *Nymphea alba*, the spatter-dock *Nuphar lutea* and the yellow floating-heart *Nymphoides peltata*.

The distinction between emerged and submerged macrophytes is especially important because they have different interactions with water quality processes. The major changes concern the nutrient uptake strategies, the dependence on light availability and the sedimentation/erosion processes (Calow and Petss, 1992; Barko and Smart, 1981; Scheffer, 1998). Emerged sections of macrophytes can fully cover the water surface and thereby block light penetration and aeration, though oxygen is still released of course into the water via photosynthesis. Submerged macrophytes on the other hand, are strongly dependent on the light climate and growth is limited through shading. They too can shade lower parts, but influence on aeration processes is not modelled. During their life cycle or seasons some plants may change strategy from submerged to emerged (e.g. *Nympheaceae*). Thus, a good understanding of the life cycle is essential when they are to be included in the macrophyte modelling.

Note that the emerged, non-rooted species can also be affected by drift due to winds. This process is not included in the macrophyte module.

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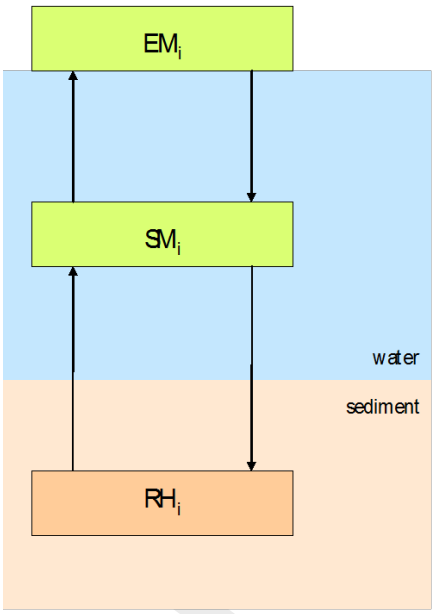

Figure 5.3: *The abbreviations for the parts of the vegetation that are used in the equations.*

5.1.3 Plant parts

In the formulas a single species i can consist of emerged parts and/or submerged parts and/or root-rhizome parts. The emerged part is indicated by EM$_i$, the submerged part by SM$_i$ and the root-rhizome by RH$_i$. Please note that EM$_i$, SM$_i$ and RH$_i$ refer to the same species i. This is illustrated in Figure 5.3. The submerged section SM$_i$ can be subdivided over multiple layers in case of a vertically differentiated model (see (Deltares, 2024)).

5.1.4 Usage note

There can be a strong variation in some of the coeffcients (when adopting those from literature) due to local settings. Especially the coefficient values concern the macrophytes nutrients uptake and release, the life span and the macrophytes density are prone to local variation. We recommend appropriate validation of the module for each new application.

5.1.5 Different macrophyte growth forms

This section provides a detailed description of the various forms in which aquatic macrophytes can grow.

Emerged macrophytes

Emerged macrophytes take up nutrients from the roots and the rhizome exclusively (Granéli and Solander, 1988). They contribute to removing some important quantities of nutrients from the sediment, because of that they are often called helophytes filters. Nevertheless some researchers suspect that they are not directly taking up nutrients, but that the epiphytic community that they often shelter is responsible for it. Because of these properties, emerged plants are often grown and harvested in the area of Waste Water Treatment Plants (WWTP) in order to remove the excess of nutrients. But the nutrients are translocated from shoots and leaves to rhizome and roots during autumn, so the harvesting is only efficient if done before this translocation (Meuleman and al., 2002). The decomposition of the organic matter, and especially of the rhizome (*), which contains a lot of carbohydrates reserves, is slow for the emerged plant since they have tissue resistance to microbiological attacks (Granéli and Solander, 1988).

As their growth is not limited by light extinction, they can reach some very dense stands stage. Their rhizome, stems, and leaves also contribute to the limitation of the wave and wind impact and therefore to the stabilization of the sediment in the area where they grow; emerged plants are also acting as a sediment trap (Coops, 1996). Moreover those plants are also a source of feeding and a refuge for a lot of bird species.

Water type and habitat: shoreline or even wet ground, out of water of marshy shores; marshes, ponds, lakes, ditches, streams and estuaries with running or standing waters.

Submerged macrophytes

In general submerged macrophytes take up most of the nutrients from the rhizome and roots system and little directly from the water (Eugelink, 1998; Granéli and Solander, 1988). It has been demonstrated that in the case of *Myriophyllum exalbescens* there is an uptake by the leaves but that the foliar uptake of Phosphorus goes much faster when the concentration in the water increases (Marte and Hartman, 1974). The mineralization of the organic matter is quite fast since the roots of the submerged plants are finer compared to the emerged plants, and don't have a storage system like the emerged plants. Their growth can be limited by light availability even in shallow lakes. On the other hand their roots, leaves and stems contributes to the increase of the resistance to the water flow and consequently to the increase of sedimentation of suspended particles. The result is the maintenance of water transparency, a factor which itself influences the probability of colonization by submerged macrophytes. The increase of sedimentation concern notably the nutrients associated with particles: therefore nutrients are buried in the sediment layer faster and consequently the amount of nutrients in the water remains lower than in more open deep water bodies.

Many submerged plants like the pondweeds are a very important source of food for the wildlife.

Water type: alkaline fresh to brackish, running or standing water (for *Potamogeton sp.*)
Habitat: usually found entirely underwater. Can grow from shallow water to depths greater than ten meters in case of very clear water.

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Submerged macroalgae

The plant-like macroalgae like the Characeae family do not have a real root system and take up more nitrogen from the water than from the sediment, (Vermeer and al., 2003) and there are indications that the water nutrient concentration can be lowered widely by their presence. In certain cases they seem to improve the water transparency significantly, especially because they are stabilizing the sediment and therefore limiting its resuspension (see section II.2.B. on submerged plants). They grow faster than the submerged plants. Besides, Characeae have the peculiarity to disperse by detaching from the substrate and emerging above water with the current. In the already existing BLOOM module (*) of Delwaq, Chara sp. is modeled in this particular growth form whereas in the macrophyte module, Chara sp. is modeled as an emerged "rooted" plant at which a very small root biomass is attributed, since in the reality the root system is very reduced and it tends to lie on or just above the sediment. Chara sp. will be included in the submerged plant category in the Macrophyte module, but since it possesses some special features and coefficient, the set of coefficient has been defined properly in the table 8 in section II.3.C.

Water type: Fresh to brackish hard water.
Habitat: They are found from shallow water to very deep areas in clear water. Their presence is generally a sign of good 'health' of the ecosystem.

Emerging non-rooted macrophytes

Emerging non rooted macrophytes, like duckweeds, take up nutrients from the water column and are also able to transform the diazote directly from the atmosphere. They usually grow in rather nutrient-rich waters and can remove a lot of nutrients from the water during their growth that they release during the decay phase. These plants can grow and reproduce very quickly when the environmental conditions are adequate, and they have a very short life span (*) compared to the other macrophytes: the Lemnids can decompose to 50 % of the original biomass within 10 to 20 days (Anonymous, 1992).

As their name indicates, the emerging-non-rooted plants are laying in the surface of the water and consequently can block the light up to 99 percent. They might over compete with the submerged plant, but they are more often found on the shore, in between other macrophytes. In the model they are not considered to be light-limited, even if in the reality they can sometimes be seen forming layers on top of each other and consequently auto-competing for the light, which is necessary for the photosynthesis.

The emergent non-rooted plants are an important source of feeding for the water fowls.

Water type: Still and slow moving waters in many nutrient-rich freshwater.
Habitat: Often found along the shoreline. Sometimes form extensive green mats on the water surface.

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Emerged and submerged-rooted macrophytes

Emergent-rooted macrophytes take up most of the nutrients from the sediment by the rhizome and roots system which is very developed.

They block the light penetration in the water by multiplication on top of the water column, so that no submerged species are able to grow below these plants since no photosynthesis is possible in absence of light. The Nympheaceae can sometimes grow on top of each other and auto-compete for light, but they are not limited by light availability in the model. [TODO: Rudy's remark]

The seeds constitute a direct food source for birds like waterfowls and the leaves for mammals like beavers, muskrats, porcupines and deer and provides spawning habitat for fishes (Aquatic Plant Identification Manual for Washington's Freshwater Plants, year?).

Water type: shallow, still or slowly moving water in ponds, lakes, swamps, rivers, canals and ditches.
Habitat: They often form a band along the shallow lake in rich organic sediment.

Emerging submerged non-rooted macrophytes

These plants have emerged parts, while their root system is in the water, but there are exceptions since for example the water soldier (*Stratiotes aloides*) has a submerged phase in winter and is only ermergent in summer (see beginning of section II.2.). It requires specific conditions like peat soil and large humic layer, which could correspond to a filling-up stage of the water body. Moreover the life cycle is rather complex since the shoots formed by vegetative reproduction sink on the ground in winter and float again in early summer (Pot, 2003). Other classifications like the one from Dodds (2002), adapted from Riener (1984) put this category in the emergent unattached growth form.

Water type and Habitat: stagnant water with organic sediment.

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5.2 Growth of submerged and emerged biomass of macrophytes

PROCESS: MACROPHYTI

The start of the growing season depends on the water temperature and the light climate under water. The growth function differs for emerged and submerged vegetation. In both cases the potential growth is limited by several factors: light climate, nutrient availability, water temperature. The growth of submerged macrophytes can stop at a certain maximum due to light limitation by means of self shading (Calado and Duarte, 2000). The growth of submerged macrophytes will stop when a maximum amount of biomass is reached. In order to get a quick start at the beginning of the growing season, the growth of submerged macrophytes depends on the sum of the submerged biomass at the beginning of the growing season and the biomass stored in the rhizomes.

The growth rate is calculated via the following formula:

If $EM_i < MaxEM_i$

$$\begin{aligned} GrowthEM_i =& (EM_i + RH_i) \times MaxGrowthEM_i \times LimLightEM_i \\ & \times LimTEM_i \times LimAgeEM_i \end{aligned} \tag{5.1}$$

Else

$$GrowthEM_i = 0$$

If $SM_i < MaxSM_i$

$$\begin{aligned} GrowthSM_i =& (SM_i + RH_i) \times MaxGrowthSM_i \times LimLightSM_i \\ & \times LimTSM_i \times LimAgeSM_i \end{aligned}$$

Else

$$GrowthSM_i = 0$$

where:

SM_i	Biomass of submerged (SM) species i	[g C·m^{-2}]
$GrowthSM_i$	Growth of SM species i	[g C·m^{-2}·d^{-1}]
$MaxGrowthSM_i$	Potential growth rate of SM species i	[d^{-1}]
$LimLightSM_i$	Light limitation factor SM species i	[-]
$LimTSM_i$	Temperature limitation factor SM species i	[-]
EM_i	Biomass of emerged species (EM) i	[g C·m^{-2}]
$GrowthEM_i$	Growth of EM species i	[g C·m^{-2}·d^{-1}]
$MaxEM_i$	Maximum biomass of EM species i	[g C·m^{-2}]
$MaxGrowthEM_i$	Potential growth rate of EM species i	[d^{-1}]
$LimNutEM_i$	Nutrient limitation factor EM species i	[-]
$LimTEM_i$	Temperature limitation factor EM species i	[-]

The limitation factors are explained in the following subsections.

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5.2.1 Nutrient limitation

The growth of *emerged non-rooted vegetation*, such as duck weeds (e.g. *Lemna spp.*) can be limited by low dissolved nitrogen and phosphorus concentrations in surface water (Anonymous, 1992). The growth of rooted vegetation is not limited by nutrients, for the Dutch shallow eutrophic lakes situation (REF). For aquatic macroalgae such as *Chara* and other species uptaking nutrients predominantly from the water column nutrients can become limiting, although in naturally eutrophic systems such as the Netherlands this is not very likely (REF). The limitation function computed on the basis of a half saturation concentration.

$$\begin{aligned} LimNH4EM_i &= \frac{NH4}{NH4 + NH4hsEM_i} \\ LimNO3EM_i &= \frac{NO3}{NO3 + NO3hsEM_i} \\ LimPO4EM_i &= \frac{PO4}{PO4 + NO3hsEM_i} \\ LimNutEM_i &= \min(LimPO4EM_i, \max(LimNH4EM_i, LimNO3EM_i)) \end{aligned} \tag{5.2}$$

where:

NH4	Ammonia concentration	[g N·m^{-3}]
NH4hsEM$_i$	Half saturation concentration NH4 for growth of EM species i	[g N·m^{-3}]
LimNH4EM$_i$	Ammonium limitation factor for EM species i	[-]
NO3	Nitrate concentration	[g N·m^{-3}]
NO3hsEM$_i$	Half saturation concentration NO3 for growth of EM species i	[g N·m^{-3}]
LimNO3EM$_i$	Nitrate limitation factor for EM species i	[-]
PO4	Ortho-phosphorus concentration	[g P·m^{-3}]
PO4hsEM$_i$	Half saturation concentration PO4 for growth EMi	[g N·m^{-3}]
LimPO4EM$_i$	Phosphorus limitation factor for EM species i	[-]
LimNutEM$_i$	Nutrient limitation factor for EM species i	[-]

5.2.2 Uptake of carbon, nitrogen and phosphorus from rhizomes

The energy stored in the rhizome/root system in the form of glucose (carbon) is the first source for the growth of submerged vegetation in early spring. When the nitrogen in the rhizomes is exhausted, the vegetation will switch to the uptake of nutrients via the roots (see also Subsection 5.2.8). Uptake is regarded as negative translocation. The uptake of carbon and nutrients from the rhizome continues until a certain minimum biomass has been reached. The total uptake of nutrients from the sediment by all modelled macrophyte types is then used for calculating the nutrient content of the sediment.

If $(GrowthEM_i + GrowthSM_i) \times dt < (RH_i - RHmin_i)$

$$\begin{aligned} CtranslocRHtoEM_i &= GrowthEM_i \\ CtranslocRHtoSM_i &= GrowthSM_i \end{aligned} \tag{5.3}$$

Else

$$\begin{aligned} CtranslocRHtoEM_i &= 0 \\ CtranslocRHtoSM_i &= 0 \end{aligned}$$

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If $(GrowthEM_i \times NCratEM_i + GrowthSM_i \times NCrateSM_i) \times dt < (NRH_i - NRHmin_i)$

$$\begin{aligned} NtranslocRHtoEM_i &= GrowthEM_i \times NCratEM_i \\ NtranslocRHtoSM_i &= GrowthSM_i \times NCratSM_i \end{aligned} \tag{5.4}$$

Else

$$\begin{aligned} NtranslocRHtoEM_i &= 0 \\ NtranslocRHtoSM_i &= 0 \end{aligned}$$

If $(GrowthEM_i \times PCratEM_i + GrowthSM_i \times PCrateSM_i) \times dt < (PRH_i - PRHmin_i)$

$$\begin{aligned} PtranslocRHtoEM_i &= GrowthEM_i \times PCratEM_i \\ PtranslocRHtoSM_i &= GrowthSM_i \times PCratSM_i \end{aligned} \tag{5.5}$$

Else

$$\begin{aligned} PtranslocRHtoEM_i &= 0 \\ PtranslocRHtoSM_i &= 0 \end{aligned}$$

where:

RH_i	Rhizome species $_i$	[g C·m^{-2}]
$RHmin_i$	Critical biomass of RH species i	[g C·m^{-2}]
dt	Timestep of computation	[d]
$CtranslocRHtoEM_i$	Translocation of C from RH to EM species i	[g C·m^{-2}·d^{-1}]
$CtranslocRHtoSM_i$	Translocation of C from RH to SM species i	[g C·m^{-2}·d^{-1}]
NRH_i	Nitrogen content of rhizome	[g N·m^{-2}]
$NRHmin_i$	Critical nitrogen content of RH species i	[g N·m^{-2}]
$NtranslocRHtoEM_i$	Translocation of N from RH to EM species i	[g N·m^{-2}·d^{-1}]
$NtranslocRHtoSM_i$	Translocation of N from RH to SM species i	[g N·m^{-2}·d^{-1}]
$NCratEM_i$	Nitrogen-carbon ratio of EM species i	[g N·g C^{-1}]
$NCratSM_i$	Nitrogen-carbon ratio of SM species i	[g N·g C^{-1}]
PRH_i	Phosphorus content of RH species i	[g P·m^{-2}]
$PRHmin_i$	Critical phosphorus content of RH species i	[g P·m^{-2}]
$PtranslocRHtoEM_i$	Translocation of P from RH to EM species i	[g P·m^{-2}·d^{-1}]
$PtranslocRHtoSM_i$	Translocation of P from RH to SM species i	[g P·m^{-2}·d^{-1}]
$PCratEM_i$	Phosphorus-carbon ratio of EM species i	[g P·g C^{-1}]
$PCratSM_i$	Phosphorus-carbon ratio of SM species i	[g P·g C^{-1}]

5.2.3 Daylength limitation

The daylength function for macrophytes differs from the method that is applied for algae. The daylength limitation function for macrophytes becomes zero below a certain threshold value:

If $DL < MinDLEM_i$

$$LimDLEM_i = 0 \tag{5.6}$$

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If $MinDLEM_i < DL < OptDLEM_i$

$$LimDLEM_i = \frac{DL - MinDLEM_i}{OptDLEM_i - MinDLEM_i} \tag{5.7}$$

If $DL > OptDLEM_i$

$$LimDLEM_i = 1 \tag{5.8}$$

The daylength limitation functions are the same for submerged macrophytes:

If $DL < MinDLSM_i$

$$LimDLSM_i = 0 \tag{5.9}$$

If $MinDLSM_i < DL < OptDLSM_i$

$$LimDLSM_i = \frac{DL - MinDLSM_i}{OptDLSM_i - MinDLSM_i} \tag{5.10}$$

If $DL > OptDLSM_i$

$$LimDLSM_i = 1 \tag{5.11}$$

	DL	Daylength	[d]
	LimDLEM$_i$	Daylength limitation factor for EM species i	[-]
	LimDLSM$_i$	Daylength limitation factor for SM species i	[-]
where:	OptDLEM$_i$	Optimum daylength for EM species i	[d]
	OptDLSM$_i$	Optimum daylength for SM species i	[d]
	MinDLEM$_i$	Minimum daylength for EM species i	[d]
	MinDLSM$_i$	Minimum daylength for SM species i	[d]

5.2.4 Temperature limitation

Growth rates increase when the water temperature exceeds 20 °C and decreases when the water temperature drops below 20 °C. Below a certain critical temperature, the growth stops altogether.

If $T > TcritEM_i$

$$LimTEM_i = K_{T20} EM_i^{T-20}$$

Else

$$LimTEM_i = 0 \tag{5.12}$$

If $T > TcritSM_i$

$$LimTSM_i = K_{T20} SM_i^{T-20}$$

Else

$$LimTSM_i = 0 \tag{5.13}$$

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where:

T	Temperature	[°C]
TcritEM$_i$	Critical temperature for growth EM species i	[°C]
LimTEM$_i$	Temperature limitation factor for EM species i	[-]
K$_{T20}$EM$_i$	Temperature coefficient for EM species i	[-]
TcritSM$_i$	Critical temperature for growth SM species i	[°C]
LimTEM$_i$	Temperature limitation factor for SM species i	[-]
KT$_{20}$SM$_i$	Temperature coefficient for SM species i	[-]

5.2.5 Decay of emerged and submerged biomass

The decay of emerged and submerged biomass occurs during the autumn and winter. The decay flux is temperature dependent. The decay is limited to the autumn and winter, the process is regulated by the daylength function that is also used for the growth process.

$$\begin{aligned} DecayEM_i =& K1DecayEM_i \times EM_i \times (1 - LimDLEM_i) \times K_{DecayT20} EM_i^{T-20} \\ DecaySM_i =& K1DecaySM_i \times SM_i \times (1 - LimDLSM_i) \times K_{DecayT20} SM_i^{T-20} \end{aligned} \tag{5.14}$$

where:

DecayEM$_i$	Decay of emerged part of species i (EM$_i$)	[g C ·m^{-2}·d^{-1}]
K1decayEM$_i$	First order autumn decay constant of EM$_i$	[d^{-1}]
K$_{DecayT20}$EM$_i$	Temperature constant for decay of EM$_i$	[-]
DecaySM$_i$	Decay of submerged part of species i (SM$_i$)	[d^{-1}]
K1decaySM$_i$	First order autumn decay constant of SM$_i$	[d^{-1}]
K$_{DecayT20}$SM$_i$	Temperature constant for decay of SM$_i$	[-]

5.2.5.1 Hints for use

- ◇ A sudden collaps of the vegetation can be modelled by means of a high first order decay rate during a short period of time.
- ◇ Some plants remain present over wintertime. This can be modelled by means of a low decay rate.

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5.2.6 Growth of the rhizomes/root system

The below-ground biomass of macrophytes consists of organs for uptake of nutrients from the soil (root) and in some cases also storage organs (rhizomes). In plants where both primary roots and rhizomes are present the biomass of the rhizomes will be relatively large. Part of the decaying vegetation becomes dead organic matter and part of the carbon and nutrients is stored in the rhizomes. The rhizome/root system has its own nitrogen-carbon ratios and phosphorus-carbon ratios. The rhizome/root system grows predominantly during the late summer and autumn in case the macrophyte stores nutrients in the below-ground system (REF) and translocated these from above-ground systems to below-ground systems. All carbon related substances are produced in the above-ground system, and translocation from these to the rhizome/root system is modelled as follows.

For emerged vegetation:

$$\begin{aligned} CtranslocEMtoRH_i =& DecayEM_i \times FrEMtoRH_i \\ NtranslocEMtoRH_i =& CtranslocEMtoRH_i \times \min(NCRatRH_i, NCRatEM_i) \\ PtranslocEMtoRH_i =& CtranslocEMtoRH_i \times \min(PCRatRH_i, PCRatEM_i) \end{aligned} \tag{5.15}$$

For submerged vegetation:

$$\begin{aligned} CtranslocSMtoRH_i =& DecaySM_i \times FrSMtoRH_i \\ NtranslocSMtoRH_i =& CtranslocSMtoRH_i \times \min(NCRatRH_i, NCRatSM_i) \\ PtranslocSMtoRH_i =& CtranslocSMtoRH_i \times \min(PCRatRH_i, PCRatSM_i) \end{aligned} \tag{5.16}$$

In the current model implementation, the rhizome/root system will not decay. Instead, the fraction of the decaying emerged and submerged biomass that is not translocated to the rhizome/root system (FrEMtoRH$_i$) is converted into organic matter (POC).

In the above formulae:

CtranslocEMtoRH$_i$	Translocation of C from EM to RH species i [g C·m^{-2}d^{-1}]
FrEMtoRH$_i$	Fraction of EM that becomes RH species i [-]
NtranslocEMtoRH$_i$	Translocation of N from EMi to RHi [g N·m^{-2}d^{-1}]
NCratRH$_i$	Nitrogen-carbon ratio of RH species i [g N·g C^{-1}]
NCratEM$_i$	Nitrogen-carbon ratio of EM species i [g N·g C^{-1}]
PtranslocEM$_i$	Translocation of P from EMi to rhizomes [g P·m^{-2}d^{-1}]
PCratRH$_i$	Phosphorus-carbon ratio of EM species i [g P·g C^{-1}]
PCratEM$_i$	Phosphorus-carbon ratio of EM species i [g P·g C^{-1}]
CtranslocSMtoRH$_i$	Translocation of C from EM to RH species i [g C·m^{-2}d^{-1}]
FrSMtoRH$_i$	Fraction of SM that becomes RH species i [-]
NtranslocSMtoRH$_i$	Translocation of N from EMi to RHi [g N·m^{-2}d^{-1}]
NCratSM$_i$	Nitrogen-carbon ratio of EM species i [g N·g C^{-1}]
PtranslocSM$_i$	Translocation of P from EMi to rhizomes [g P·m^{-2}d^{-1}]
PCratSM$_i$	Phosphorus-carbon ratio of EM species i [g P·g C^{-1}]

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5.2.7 Formation of particulate organic carbon

D-Water Quality has two different routines for the fractioning and decay of organic material. The first method is the DetC-OOC approach. The second approach is the POC-approach that is illustrated in Figure 8.1. This is the approach taken in the macrophytes module.

When the emerged and submerged vegetation starts to die in autumn, some of the carbon and nutrients are stored in the rhizomes while the remaining part becomes particulate organic matter, distributed over three different fractions (see Figure 8.1). The ratio of the three particulate organic carbon fractions is a user-defined parameter. The following equation is a recalculation of the fractions in order to guarantee mass conservation in the computations:

$$FrPOCxEM_i = \frac{FrPOCxEM_i}{FrPOC1EM_i + FrPOC2EM_i + FrPOC3EM_i} \tag{5.17}$$

(x = 1, 2 or 3) and equivalently for the submerged biomass (SM_i).

The production of particulate organic carbon is calculated by:

$$\begin{aligned} ProdPOCxEM_i =& (DecayEM_i - CtranslocEMtoRH_i) \times FrPOCxEM_i + \\ & (DecaySM_i - CtranslocSMtoRH_i) \times FrPOCxSM_i \end{aligned} \tag{5.18}$$

The production of particulate organic nitrogen amnd phosphorus is calculated by:

$$\begin{aligned} ProdPONxEM_i =& (DecayEM_i \times NCratEM_i - NtranslocEMtoRH_i) \times FrPOCxEM_i + \\ & (DecaySM_i \times NCratEM_i - NtranslocSMtoRH_i) \times FrPOCxSM_i \\ ProdPOPxEM_i =& (DecayEM_i \times PCratEM_i - PtranslocEMtoRH_i) \times FrPOCxEM_i + \\ & (DecaySM_i \times PCratEM_i - PtranslocSMtoRH_i) \times FrPOCxSM_i \end{aligned} \tag{5.19}$$

where:

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POC1	Particulate organic carbon, fraction 1	[g C·m^{-3}]
POC2	Particulate organic carbon, fraction 2	[g C·m^{-3}]
POC3	Particulate organic carbon, fraction 3	[g C·m^{-3}]
FrPOC1EM$_i$	Fraction of decaying EMi that becomes POC1	[-]
FrPOC2EM$_i$i	Fraction of decaying EMi that becomes POC2	[-]
FrPOC3EM$_i$i	Fraction of decaying EMi that becomes POC3	[-]
FrPOC1SM$_i$i	Fraction of decaying SMi that becomes POC1	[-]
FrPOC2SM$_i$i	Fraction of decaying SMi that becomes POC2	[-]
FrPOC3SM$_i$i	Fraction of decaying SMi that becomes POC3	[-]
ProdPOC1$_i$i	POC1 production from decaying vegetation i	[g C·m^{-2}·d^{-1}]
ProdPOC2$_i$i	POC2 production from decaying vegetation i	[g C·m^{-2}·d^{-1}]
ProdPOC3$_i$i	POC3 production from decaying vegetation i	[g C·m^{-2}·d^{-1}]
PON1	Particulate organic nitrogen, fraction 1	[g N·m^{-3}]
PON2	Particulate organic nitrogen, fraction 2	[g N·m^{-3}]
PON3	Particulate organic nitrogen, fraction 3	[g N·m^{-3}]
ProdPON1$_i$i	PON1 production from decaying vegetation i	[g N·m^{-2}·d^{-1}]
ProdPON2$_i$i	PON2 production from decaying vegetation i	[g N·m^{-2}·d^{-1}]
ProdPON3$_i$i	PON3 production from decaying vegetation i	[g N·m^{-2}·d^{-1}]
POP1	Particulate organic phosphorus, fraction 1	[g P·m^{-3}]
POP2	Particulate organic phosphorus, fraction 2	[g P·m^{-3}]
POP3	Particulate organic phosphorus, fraction 3	[g P·m^{-3}]
ProdPOP1$_i$i	POP1 production from decaying vegetation i	[g P·m^{-2}·d^{-1}]
ProdPOP2$_i$i	POP2 production from decaying vegetation i	[g P·m^{-2}·d^{-1}]
ProdPOP3$_i$i	POP3 production from decaying vegetation i	[g P·m^{-2}·d^{-1}]

5.2.8 Uptake of nitrogen and phosphorus from sediment

The phosphorus in the rhizomes is the first source for the growth of submerged vegetation. When the phosphorus in the rhizomes is exhausted, the vegetation will switch to the uptake of phosphorus via the roots.

$$\begin{aligned} Nuptakesediment =& GrowthEM_i \times NCratEM_i - NtranslocRHtoEM_i + \\ & GrowthSM_i \times NCratSM_i - NtranslocRHtoSM_i \\ Puptakesediment =& GrowthEM_i \times PCratEM_i - PtranslocRHtoEM_i + \\ & GrowthSM_i \times PCratSM_i - PtranslocRHtoSM_i \end{aligned} \tag{5.20}$$

where:

Nuptakesediment	Uptake of nitrogen from the sediment	[g N·m^{-2}]
Puptakesediment	Uptake of phosphorus from the sediment	[g P·m^{-2}]

5.2.8.1 Hints for use

The sediment should contain enough nutrients to support the growth of macrophytes. In this model, the growth of macrophytes is NOT limited by a lack of nutrients in the sediment.

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The release of dissolved nutrients depends on the decay of organic matter, containing nitrogen and phosphorus. On the long run, the amount of organic matter in the sediment depends on the production of organic matter in the lake. It is therefore possible that the nutrient pool in the sediment is exhausted by the macrophytes.

5.2.9 Uptake of nitrogen and phosphorus from water

Nitrogen can only be taken up from the water by the emerged non-rooted vegetation. The growth of emerged vegetation is limited at low phosphorus and nitrogen concentrations. The following equations describe the uptake of nutrients on the basis of the growth rate and the nutrient-carbon ratios. At low nutrient concentrations the growth will be limited.

If $NH4 < NH4critEM_i$

$$FrNH4EM_i = \frac{NH4}{NH4 + NO3}$$

Else

$$FrNH4EM_i = 1 \tag{5.21}$$

$$\begin{aligned} NH4uptakeEM_i &= GRowthEM_i \times NCratEM_i \times FrNH4EM_i \\ NO3uptakeEM_i &= GRowthEM_i \times NCratEM_i \times (1 - FrNH4EM_i) \\ PO4uptakeEM_i &= GRowthEM_i \times PCratEM_i \end{aligned} \tag{5.22}$$

where:

NH4critEM$_i$	Critical NH4 concentration for uptake by EMi	[g N·m^{-2}·d^{-1}]
NH4uptakeEM$_i$	Ammonium uptake by emerged vegetation	[g N·m^{-2}·d^{-1}]
NO3uptakeEM$_i$	Nitrate uptake by emerged vegetation	[g N·m^{-2}·d^{-1}]
PO4uptakeEM$_i$	Ortho-phosphorus uptake by emerged vegetation	[g P·m^{-2}·d^{-1}]
FrNH4EM$_i$	Fraction of NH4 in total nitrogen uptake	[-]

5.2.10 Oxygen production and consumption

When macrophytes grow, they produce oxygen during the production of biomass. The stoichiometric ratio between O_2 production [g O_2] and CO_2 uptake g C] is 2.67 (**<empty citation>**).

The assumption is made, that the oxygen produced by emerged macrophytes escapes to the atmosphere immediately. The oxygen that is produced by submerged macrophytes dissolves in the water:

$$O2productionSM_i = 2.67 \times CuptakeSM_i \tag{5.23}$$

Since respiration is not modelled explicitly, the consumption of oxygen in water in the macrophyte model is limited to the oxygen that is involved in the decay of organic matter.

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5.2.11 Net growth of emerged and submerged vegetation and rhizomes

All the growth and loss processes together give the net growth of the three parts of the vegetation:

$$\begin{aligned}
\frac{EM_i}{dt} =& GrowthEM_i - GrazeEM_i - HarvestEM_i - DecayEM_i \\
\frac{SM_i}{dt} =& GrowthSM_i - GrazeSM_i - HarvestSM_i - DecaySM_i \\
\frac{RH_i}{dt} =& CtranslocEMtoRH_i + CtranslocSMtoRH_i - CtranslocRHtoEM_i \\
& CtranslocRHtoSM_i - GrazeRH_i \\
\frac{NRH_i}{dt} =& NtranslocEMtoRH_i + NtranslocSMtoRH_i - NtranslocRHtoEM_i \\
& NtranslocRHtoSM_i - GrazeNRH_i \\
\frac{PRH_i}{dt} =& PtranslocEMtoRH_i + PtranslocSMtoRH_i - PtranslocRHtoEM_i \\
& PtranslocRHtoSM_i - GrazePRH_i
\end{aligned} \tag{5.24}$$

In these formulae grazing and harvesting terms have been included (see Section 5.4).

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5.3 Maximum biomass per macrophyte species

PROCESS: MAXMACRO

With so-called Habitat Suitability Indices (HSI) the occurrence of a particular growth form at a certain location can be indicated. The HSI's should vary between 0 and 1, in which 0 implies that the habitat is not suitable for the species, and 1 implies that the habitat is very suitable (optimal) for the species. It can be computed in the dedicated software tool HABITAT for instance. When the HSI equals 1 for a particular growth form, this growth form can reach its potential biomass. When the HSI equals 1 for several growth forms, the maximum biomass for each growth form is computed by weighing the HSI by the total index for all species.

5.3.1 Implementation

The maximum biomass for each growth form and for each species is calculated as follows:

If $\sum_i HSI_i > 0$:

$$MaxEM_i = \frac{HSI_i \times PotEM_i}{\sum_i HSI_i} \qquad (5.25)$$
$$MaxSM_i = \frac{HSI_i \times PotSM_i}{\sum_i HSI_i}$$

Else

$$MaxEM_i = 0$$
$$MaxSM_i = 0$$

where:

EM_i	Emerged biomass of macrophyte species i	[g C $\cdot$ m^{-2}]
HSI_i	Habitat Suitability Index for species i	[-]
i	Subscript for species	[-]
$MaxEM_i$	Maximum biomass for EM species i	[g C $\cdot$ m^{-2}]
$PotEM_i$	Potential biomass for EM species i	[g C $\cdot$ m^{-2}]
SM_i	Submerged biomass of macrophyte species i	[g C $\cdot$ m^{-2}]
$MaxSM_i$	Maximum biomass for SM species i	[g C $\cdot$ m^{-2}]
$PotSM_i$	Potential biomass for SM species i	[g C $\cdot$ m^{-2}]

5.3.2 Hints for use

The competition between macrophyte species is not modelled as such. The species composition is fully determined by the user defined Habitat Suitability Indices. Table 5.1 shows some examples.

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Table 5.1: *Computation of the maximum biomass of three macrophyte species as a function of the Habitat Suitability Index.*

example 1	parameter	Name	units	species 1	species 2	species 3
	HSI	Habitat Suitability Index	[-]	1	0	0
	PotEM	Potential biomass	g/m^2	1000	1000	1000
	MaxEM	Maximum biomass	g/m^2	1000	0	0
example 2	parameter	Name	units	species 1	species 2	species 3
	HSI	Habitat Suitability Index	[-]	1	1	1
	PotEM	Potential biomass	g/m^2	1000	1000	1000
	MaxEM	Maximum biomass	g/m^2	333	333	333
example 3	parameter	Name	units	species 1	species 2	species 3
	HSI	Habitat Suitability Index	[-]	0.2	0.3	0.5
	PotEM	Potential biomass	g/m^2	1000	1000	1000
	MaxEM	Maximum biomass	g/m^2	200	300	500
example 4	parameter	Name	units	species 1	species 2	species 3
	HSI	Habitat Suitability Index	[-]	0.2	0.3	0.5
	PotEM	Potential biomass	g/m^2	500	1000	250
	MaxEM	Maximum biomass	g/m^2	100	300	125

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5.4 Grazing and harvesting

PROCESS: GRZMACII AND HRVMACII

Grazing by birds and fishes, and mowing of vegetation as a management option both create a decrease in the biomass of macrophytes. The characteristics of the grazing/moving depend not only on the species but also on the season. The model contains both a zero order and a first order flux for harvesting and grazing. The first order grazing/harvesting depends on the amount of vegetation. The grazing and harvesting slows down when the macrophytes are gone. The zero order grazing flux is independend of the amount of vegetation, until all vegetation has gone.

In general one can define a process coefficient as a global value that is valid for the entire model, or as a local value for specific location. The global value can either be constant or varying in time.

Grazing and harvesting during a certain period of time can be defined by several methods:

- ◇ As a time varying, first order grazing/harvesting pressure. Every day a certain portion of the vegetation is being eaten until the vegetation is gone.
- ◇ As a time varying, zero order grazing/harvesting function. During a certain episode, the birds eat a constant amount of vegetation.
- ◇ Depth of vegetation: for some species of birds e.g. Bewick Swans the grazing is limited by the depth of the lake. Feeding on the tubers of Potamogeton pectinatus, these birds need to be able to reach the bottom without diving down (< 0.4 m) **LiteratureReference**.

Both fluxes can also be defined locally, but not varying in time.

5.4.1 Grazing

Birds can exert a constant or a first order grazing pressure on the vegetation. The vegetation is removed from the lake, until all vegetation has been eaten. Grazing stops, when the amount of vegetation that could be eaten within one time step, exceeds the amount vegetation that is available. Birds can eat the emerged and submerged vegetation, as well as the rhizomes of for instance *P. pectinatus* **REF**.

If $EM_i > (K0GrazeEM_i + K1GrazeEM_i \times EM_i) \times dt$:

$$GrazeEM_i = K0GrazeEM_i + K1GrazeEM_i \times EM_i \tag{5.26}$$

Else

$$GrazeEM_i = 0$$

If $SM_i > (K0GrazeSM_i + K1GrazeSM_i \times SM_i) \times dt$:

$$GrazeSM_i = K0GrazeSM_i + K1GrazeSM_i \times SM_i \tag{5.27}$$

Else

$$GrazeSM_i = 0$$

If $RH_i > (K0GrazeRH_i + K1GrazeRH_i \times RH_i) \times dt$:

$$GrazeRH_i = K0GrazeRH_i + K1GrazeRH_i \times RH_i \tag{5.28}$$
$$GrazeNRH_i = GrazeRH_i \times \frac{NHR_i}{RH_i}$$
$$GrazePRH_i = GrazeRH_i \times \frac{PHR_i}{RH_i}$$

Else

$$GrazeRH_i = 0$$
$$GrazeNRH_i = 0$$
$$GrazePRH_i = 0$$

where:

GrazeEM$_i$	Grazing of EM species i	[g C·m^{-2}·d^{-1}]
K0GrazeEM$_i$	Zero order grazing constant of EM species i	[g C·m^{-2}·d^{-1}]
K1GrazeEM$_i$	First order grazing constant o fEM species i	[d^{-1}]
dt	time step of the simulation	[d]
GrazeSM$_i$	Grazing of SM species i	[g C·m^{-2}·d^{-1}]
K0GrazeSM$_i$	Zero order grazing constant of SM species i	[g C·m^{-2}·d^{-1}]
K1GrazeSM$_i$	First order grazing constant of SM species i	[d^{-1}]
RH$_i$	Rhizome species i	[g C·m^{-2}]
GrazeRH$_i$	Grazing of RH species i	[g C·m^{-2}·d^{-1}]
K0GrazeRH$_i$	Zero order grazing of RH species i	[g C·m^{-2}·d^{-1}]
K1GrazeRH$_i$	First order grazing constant of RH species i	[d^{-1}]
GrazeNRH$_i$	Grazing of RH species i, nitrogen component	[g N·m^{-2}·d^{-1}]
GrazePRH$_i$	Grazing of RH species I, phosphorus component	[g P·m^{-2}·d^{-1}]

5.4.2 Hints for use

The grazing can be estimated on the basis of the number of birds, the period during which they are eating somewhere, the area of the lake and the amount of macrophytes each bird eats. An example equation for the estimation of the grazing pressure for emerged vegetation could look like:

$$K0GrazeEM_i = \frac{birds \times fooddemand}{area} \tag{5.29}$$

where:

birds	Number of birds in the colony	[-]
fooddemand	Amount of vegetation per bird per day	[g C·d·-1]
area	Lake area where the colony of birds is feeding	[m^2]

The grazing of submerged vegetation by birds is limited to a maximum depth. If this is the case, the grazing function can be applied locally in the shallow areas in the model schematisation.

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5.4.3 Harvesting

Harvesting can be used as a management practise to reduce nuicance biomass (e.g. to improve recreational values) or to remove nutrients from the system. Both emerged and submerged vegetation can be removed from the water system. The harvesting can be modelled as a constant and /or a first order flux. The modelled harvesting stops, when all vegetation is removed from the lake.

IF $EM_i > (K0HarvestEM_i + K1HarvestEM_i \times EM_i) \times dt$:

$$HarvestEM_i = K0HarvestEM_i + K1HarvestEM_i \times EM_i$$

ELSE

$$HarvestEM_i = 0$$

IF $SM_i > (K0HarvestSM_i + K1HarvestSM_i \times SM_i) \times dt$:

$$HarvestSM_i = K0HarvestSM_i + K1HarvestSM_i \times SM_i$$

ELSE

$$HarvestSM_i = 0$$

where:

K0HarvestEMi	Zero order harvesting of emerged vegetation	[g C·m^{-2}·d^{-1}]
K1HarvestEMi	First order harvesting constants of emerged vegetation	[d^{-1}]
dt	Time step of computation	[d]
HarvestEMi	Harvesting of emerged vegetation	[g C·m^{-2}·d^{-1}]
K0HarvestSMi	Zero order harvesting of submerged vegetation	[g C·m^{-2}·d^{-1}]
K1HarvestSMi	First order harvesting constant of submerged vegetation	[d^{-1}]
HarvestSMi	Harvesting of submerged vegetation	[g C·m^{-2}·d^{-1}]

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5.5 Light limitation for macrophytes

PROCESS: RAD_SMII

For the submerged parts of the macrophytes the light limitation is determined from the light intensity at the tip of the submerged parts.

Implementation

The limitation ($frad$) is expressed as the ratio between the light intensity at the tip and the satuaration light intensity:

$$frad = \min(1, \frac{Itop}{Isat_{ii}}) \tag{5.30}$$

where:

$frad$	light limitation factor	[-]
$Itop$	light intensity at the tip of the submerged part	[-]
$Isat_{ii}$	light intensity at which saturation occurs for submerged macrophyte ii	[-]

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5.6 Vegetation coverage

PROCESS: COVERAGE

When a water body is covered by emerged macrophytes, the reaeration with oxygen and the light intensity in the water are decreased. The parameter $fcov$ for the coverage of the surface water is an existing model coefficient, that is already used in the computation of the reaeration flux. On the basis of the model for emerged macrophytes, the coverage can be computed. The coverage with emerged macrophytes is assumed to be 100 % when the actual emerged biomass reaches the maximum emerged biomass. The parameter is used in the model equations for light intensity near the water surface.

5.6.1 Implementation

The growth of submerged vegetation can be limited by the underwater light climate. This depends on the dissolved and suspended matter in the water (both organic and inorganic) **VanDuinEtAl2001** as well as on the shading due to emerged vegetation that covers the surface of the water. The growth of emerged vegetation is not limited by light in this model, although several authors report that selfshading can occur. In the light extinction function in D-Water Quality, the coverage by emerged vegetation is included via the following function:

$$Itop_1 = Is \times (1 - fcov) \tag{5.31}$$

where:

$Itop_1$	light intensity at the surface of the water layer (layer 1)	[W·m^{-2}]
Is	light intensity at the water surface	[W·m^{-2}]
fcov	fraction of the water surface covered by vegetation	[-]

The light intensity of the subsequent layers is computed according by the process CalcRad, see also Figure 5.4:

$$Itop_n = Ibot_{n-1} \tag{5.32}$$

$$Ibot_n = Itop_n \times e^{-ExvVl_n \times H_n} \tag{5.33}$$

where:

ExtVL$_n$	extinction of visible light in layer n	[m^{-1}]
Itop	light intensity at the top of a water layer	[W·m^{-2}]
Ibot	light intensity at the bottom of a water layer	[W·m^{-2}]
H	thickness of the water layer, $z_{n-1} - z_n$	[m]
n	index for water layers	[-]

When there is only one water layer (compartment), the depth is equal to the water depth.

In the case that sediment layers are actually modelled the light intensities at the top and the bottom of these layers are calculated in a slightly modified way:

$$Ibot_n = a \times Itop_n \times e^{-ExvVl_n \times H_n} \tag{5.34}$$

where:

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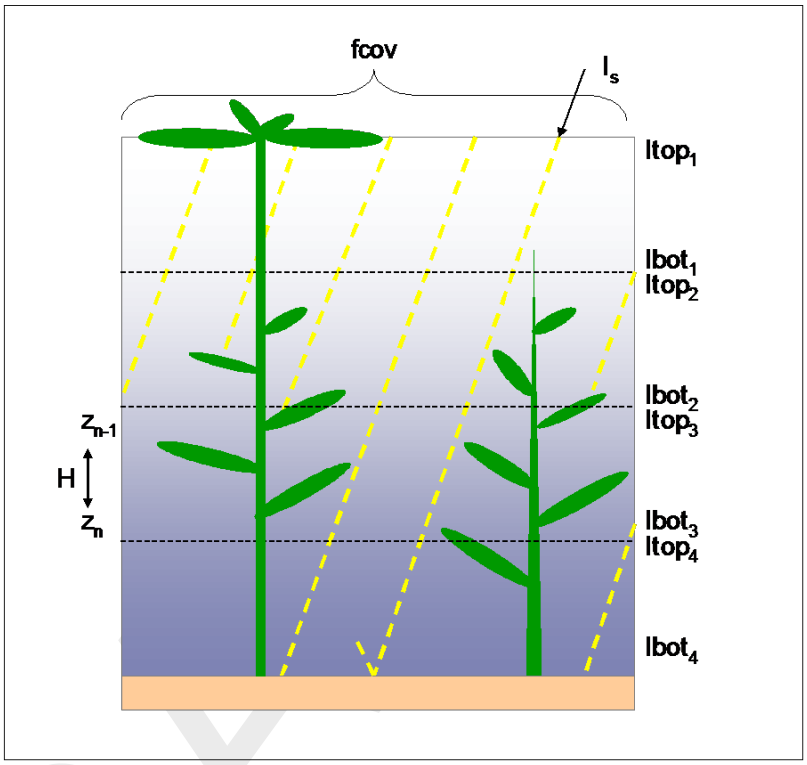

Figure 5.4: *The light intensity under water – explanation of the variables in the light intensity functions.*

a amplification factor by scattering by sediment particles [-]

The coverage $fcov$ is calculated via:

$$fcov = \sum_i \frac{EM_i}{MaxEM_i} \tag{5.35}$$

where:

CoverageEM$_i$	Coverage with emerged vegetation	[-]
CoverageSM$_i$	Coverage with submerged vegetation	[-]
fcov	Total coverage on the basis of all emerged species	[-]
EM$_i$	Actual biomass emerged vegetation	[g·m^{-2}]
SM$_i$	Actual biomass submerged vegetation	[g·m^{-2}]
MaxEM$_i$	Maximum biomass emerged vegetation	[g·m^{-2}]
MaxSM$_i$	Maximum biomass submerged vegetation	[g·m^{-2}]

5.7 Vertical distribution of submerged macrophytes

PROCESS: MACDISII

The actual location of the submerged biomass in the water column is species specific. Some species are evenly distributed over the water column, where others tend to concentrate in the top layers.

The macrophytes biomass is administratively located in the bottom water layer. If the model is layered (1Dv, 2Dv, 3D), the biomass is distributed over the vertical layers to provide input for the modules that require such a distribution, in particular the vertical distribution of light extinction.

5.7.1 Implementation

This process is implemented for different types of macrophytes, indicated by "ii" throughout this document.

The vertical distribution of the macrophyte biomass is calculated from the following input items (for submerged macrophyte species ii):

Id in process	Symbol used	Description
Depth	D	depth of segment, layer thickness [m]
TotalDepth	T	total depth water column [m]
LocalDepth	L	depth from water surface to bottom of segment [m]
SMii	M_T	submerged macrophyte biomass in water column [gC/m^2]
SwDisSMii		type of macrophyte shape function (1: linear, 2: exponential)
HmaxSMii	H_{max}	maximum height of macrohyte [m]
FfacSMii	F	parameter F in shape function [-]

Figure 5.5 provides an overview of the geometrical quantities used in the calculation. Note that the vertical co-ordinate z is defined in a downward direction, with a value of zero at the water surface.

The vertical distribution of the submerged macrophytes *m(z)* (in g/m^3) is represented either by a linear or by an exponential function.

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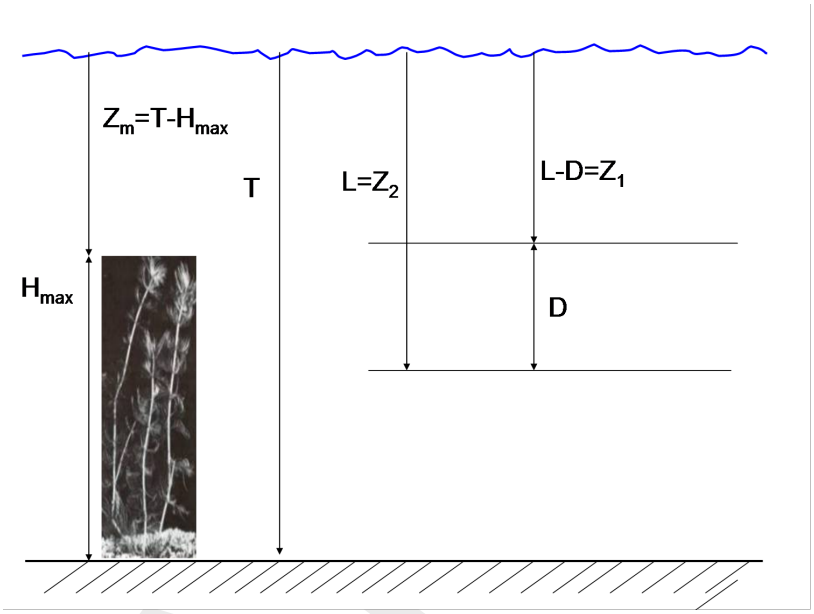


Figure 5.5: *Definition of the quantities used for determining the linear vertical distribution.*

5.7.1.1 Linear distribution (SwDisSMii=1)

The shape function is defined by means of one dimensionless parameter F with a value ranging from 0 to 2. For $F = 0$, the biomass approaches zero at the top of the plant, for $F = 1$ the biomass is distributed homogeneously and for $F = 2$, the biomass approaches zero near the bed. Values between 0 and 1 result in a decreasing biomass from bottom to top. Values between 1 and 2 result in an increasing biomass from bottom to top.

The biomass distribution $m(z)$ can be expressed by means of two constants A and B, which are formulated in terms of the total biomass M_T and the shape parameter F:

$$
\begin{aligned}
m(z) &= Az + B \\
A &= \frac{M_T}{H_{max}} \frac{2 - 2F}{T - z_m} \\
B &= \frac{M_T}{H_{max}} \frac{F(z_m + T) - 2z_m}{T - z_m}
\end{aligned}
\tag{5.36}
$$

It is easy to derive that for $F = 1$, $A = 0$ and $B = M_T/H_{max}$.

Consequently, the algorithm to calculate the biomass in a layer from $z = Z_1$ to $z = Z_2$ proceeds as follows:

If $z_m > z_2$ (layer above top of plant): $M_{12} = 0$

If $z_m < z_1$ (layer entirely below top of plant): $M_{12} = \int_{Z_1}^{Z_2} m(z)dz$

Else (top of plant inside layer): $M_{12} = \int_{Z_m}^{Z_2} m(z)dz$

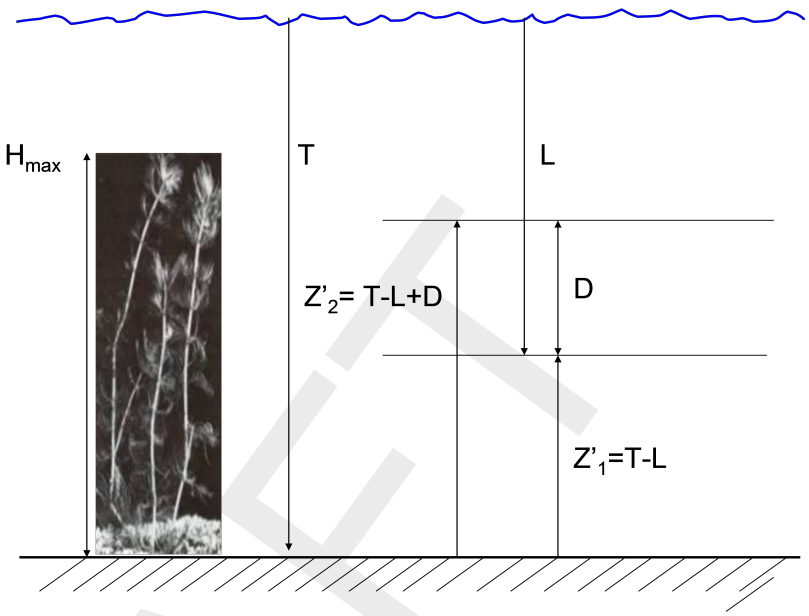


Figure 5.6: *Definition of the quantities used for determining the exponential vertical distribution.*

By integrating the mass distribution function we can derive the biomass in the layer, e.g.:

$$\int_{Z_1}^{Z_2} m(z)dz = \frac{A}{2}(Z_2^2 - Z_1^2) + B(Z_2 - Z_1) \tag{5.37}$$

The module calculates the following output items for submerged macrophyte species ii:

FrBmSMii	Fraction of the macrophyte biomass in present layer [-]
BmLaySMii	Macrophyte biomass density in present layer [gC/m^3]

The fraction of the biomass in a layer from $z = Z_1$ to $z = Z_2$ is calculated as M_{12}/M_T.

5.7.1.2 Exponential distribution (SwDisSMii=2)

The exponential shape function is defined on an inverse vertical co-ordinate *z'*, which is defined as (see also Figure 5.6):

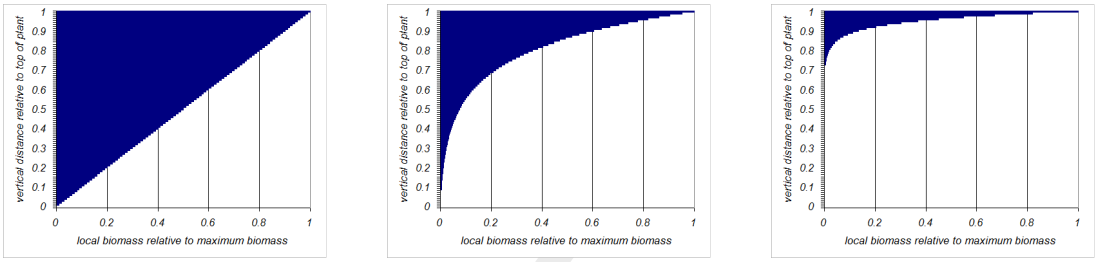
$$z' = T - z \tag{5.38}$$

The value of z' equals 0 at the bottom and it equals H_{max} at the tip of the plant.

The mass distribution function is defined as follows:

$$m(z') = A \cdot \left(e^{Fz'/H_{max}} - 1\right) \tag{5.39}$$

The shape function is defined by means of one parameter F. The constant *A* is determined by requiring that the integrated mass equals the total mass M_T. A value of F approaching 0 defines a linear distribution. Increasing values of F define a stronger and stronger concentration of the biomass near the plant tip (see Figure 5.7). The value of A can be determined as:



(a) *F = 0.001* ***(b)*** *F = 5* ***(c)*** *F = 20*

Figure 5.7: *Examples of the exponential vertical distribution for three values of the shape parameter F.*

$$A = \frac{M_T}{H_{max}\left(\frac{e^F - 1}{F} - 1\right)} \tag{5.40}$$

Consequently, the algorithm to calculate the biomass in a layer from $z' = Z'_1$ to $z' = Z'_2$ proceeds as follows:

If $Z'_1 > H_{max}$ (layer above top of plant): $M_{12} = 0$

If $Z'_2 < H_{max}$ (layer entirely below top of plant): $M_{12} = \int_{Z'_1}^{Z'_2} m(z')dz'$

Else (top of plant inside layer): $M_{12} = \int_{Z'_1}^{H_{max}} m(z')dz'$

By integrating the mass distribution function we can derive the biomass in the layer, e.g.:

$$\int_{Z'_1}^{Z'_2} m(z')dz' = A \cdot \left(H_{max}\frac{e^{FZ'_2/H_{max}} - e^{FZ'_1/H_{max}}}{F} - (Z'_2 - Z'_1)\right) \tag{5.41}$$

5.7.2 Hints

The module uses a work array ("IBotSeg") which is filled during the first call. This work array contains the segment number of the bottom segment that lies beneath each segment not located in the bottom layer. This tells each segment where the biomass in the segment administratively resides, as biomass can only exist in the bottom segment but is 'distributed' vertically in a post-processing step. Note that in a 2Dh or 1D model this work array is trivial; every segment is the bottom segment of the whole water column.

For an exponential biomass distribution, the value of F can range from a small positive number to infinite. The table below provides the share of the biomass of the plant present in the upper 10 % of the plant height, as a function of F:

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F	Share of biomass in top 10%
0.1	19
2	26
4	36
6	46
8	55
10	63
15	78
20	87
25	93
30	96

The maximum allowable value for F is 50 – this is a numerical limitation, because otherwise the numbers could become too large.

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6 Light regime

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6.1 Light intensity in the water column

PROCESS: CALCRAD, CALCRADDAY

Sunlight penetrates in water where it is absorbed and scattered by water itself and the substances present in the water column. The absorption and scattering properties of water determine its turbidity, its transparency and its apparent colour. The penetration of visible light in water is relevant for processes and ecological functions in the water column that depend on the amount of light, its spectral distribution and water clarity such as the heat balance of the water body, primary production (growth rates of phytoplankton, microphytobenthos and submerged macrophytes), photolysis, capture of prey by predating birds and fish, underwater visibility for humans etc. Next to this the magnitude and spectral distribution of the reflected proportion of the sunlight observed by optical sensors (reflectance) is relevant for optical retrieval of water quality properties such as concentrations of suspended particles or algae.

Penetration of (visible) light is quantified in terms of the downward attenuation (extinction) coefficient commonly referred to as Kd (see 6.2). Due to absorption and scattering the underwater light intensity reduces with depth compared to the intensity of light at the water surface. Theoretically (Lambert-Beer law) the profile for one light colour (monochromatic light of one wavelength) is an exponential function with distance travelled in water. Visible light (or photosynthetically active radiation, PAR) however is a spectrum with various wavelengths (400 700nm) and the resulting downward attenuation profile of visible light is therefore not one exponential function, although usually, and successfully, approximated as such using one Kd(PAR) value. Theoretically the attenuation depth profile of visible light should be described as a summation of several exponential curves, each representing one light colour and one associated Kd. The latter is referred to as the "spectral" approach unlike the one Kd PAR approach.

In the D-Water Quality process library both the averaged over PAR approach (default) and the spectral approach (UITZICHT) are available.

Vertical extinction coefficient (Kd, et) and Secchi depth (Sd) and are optical parameters used as a measure of the turbidity condition of a water system. The Secchi depth is a measure of the clarity of a water system and is often measured as standard by water managers. It is the depth at which the "Secchi disk" is just visible from the surface, see Section 6.6.

The extinction coefficient is calculated by process Extinc_VLG (see Section 6.2) and contains contributions of algae biomass, particulate organic detritus, dissolved organic matter, suspended inorganic matter, submerged macrophytes and water itself, including non-specifically accounted substances.

Implementation

Process CALCRAD delivers the intensity of total visible light (solar radiation) at the top and the bottom of the water and sediment layers in the model. The time-base of solar radiation to be provided in the input (RadSurf) is not prescribed, typically daily or hourly. The process DAYRAD may convert actual daily averaged radiation provided in the input to actual hourly radiation. It assumes a clear sky distribution of sunlight over the day based on latitude and date and time. All processes use the same light intensity at the water surface as input . All processes have been implemented in a generic way, meaning that they apply to water layers as well as sediment layers. Table 6.1 provides the definitions of the parameters occurring in the user-defined input and output parameters.

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Formulation

The light intensities at the top or bottom of a water layer or compartment follow from:

$$Itop_1 = (1 - \alpha) \cdot Is$$
$$Itop_i = Ibot_{i-1}$$
$$Ibot_i = Itop_i \times e^{(-et_i \times H_i)}$$

with:

et	extinction coefficient [m^{-1}]
H	thickness of the water layer [m]
Is	light intensity at the water surface, above the surface [W.m^{-2}]
$Itop$	light intensity at the top of a water layer [W.m^{-2}]
$Ibot$	light intensity at the bottom of a water layer [W.m^{-2}]
i	index for water layer [-]

When there is only one water layer (compartment) the depth is equal to water depth.

In the case that sediment layers are actually modelled the light intensities at the top and the bottom of these layers are calculated in a slightly modified way:

$$Ibot_i = a \times Itop_i \times e^{(-et_i \times H_i)}$$

with:

a	amplification factor due to scattering by sediment particles [-]
H	thickness of a sediment layer [m]
$Itop$	light intensity at the top of a sediment layer [W.m^{-2}]
$Ibot$	light intensity at the bottom of a sediment layer [W.m^{-2}]
i	index for sediment layer [-]

$Itop$ at the sediment-water interface is equal to $Ibot$ of the lower water layer.

Directives for use

- ◇ The radiation intensity at the water surface (RadSurf) is the total solar radiation intensity or global radiation (uv, visible and infra-red) as measured for instance with a pyranometer.
- ◇ The light intensity may be corrected for reflection via the process REFLECTION.
- ◇ Above water solar or global radiation at latitudes around 50° (such as the Netherlands) reaches peak value in summer of 900 $W.m^{-2}$. Daily averaged values (over daylight hours) range from 70-270 $W.m^{-2}$ (winter-summer). Averaged over the full day (24 hours) these values are lower (30-200 $W.m^{-2}$).
- ◇ The light intensity may be corrected for reflection via the process REFLECTION. The process estimates the percentage of the incident solar radiation reflected. The reflection coefficient (Albedo coefficient) depends on the latitude and angle of incidence. It is common practice to use a constant value of 6% for the globe.
- ◇ The actual relation between PAR and total radiation intensity is complicated as it depends subtly on the circumstances notably direct and diffuse light conditions (and the measurement technique), but a good approximation for PAR (400-700nm) is 45% of the total radiation intensity. Note that visible light can penetrate over up to distances of 30 meters, depending on the transparency of the water. The Secchi depth (m), is a measure of the transparency of the water. The infra-red (IR) part of the radiation hardly penetrates the water.
- ◇ Always make sure that the light input (observed solar radiation) is consistent with the light-related parameters of the primary producer modules used:

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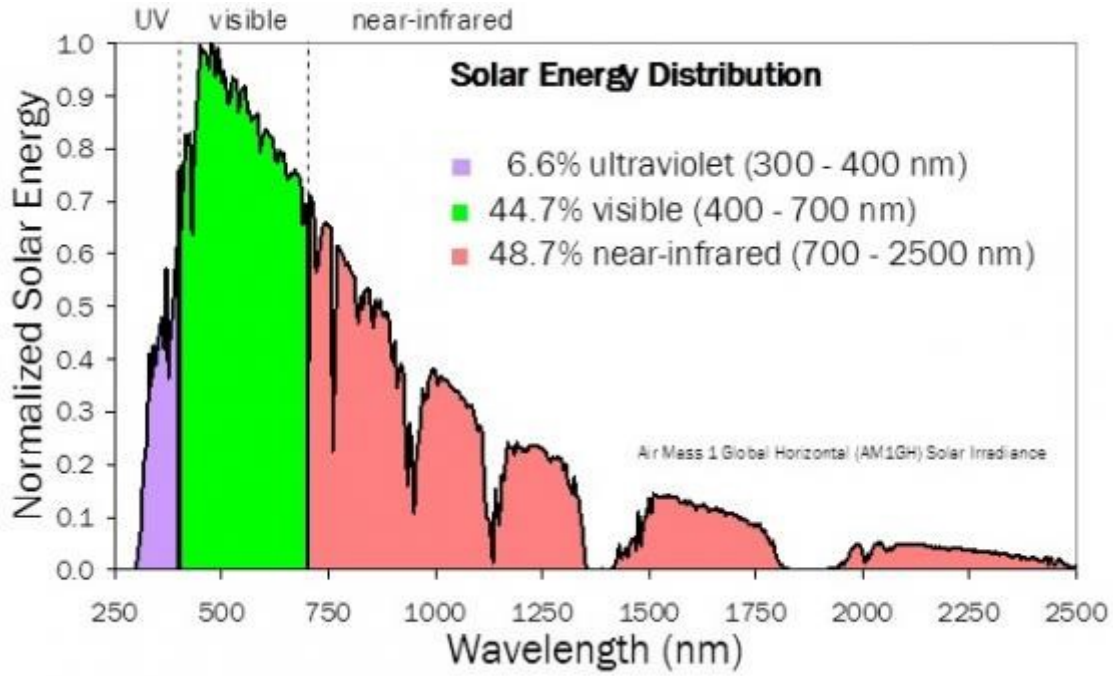

Figure 6.1: *Solar energy as function of the wave length.*

- The DYNAMO module expects PAR (photosynthetic active radiation).
- The BLOOM module expects total light, averaged over the whole day (24 hours).
- DYNAMO may use the daily average radiation or the instantaneous radiation (PAR!) varying over the day if irradiation data are available within the day.
- Bloom may use PAR (daily averaged!) radiation when SWBlSolInt set to 1 (default =0)
- Temperature models need total radiation and perform better using higher resolution data

BLOOM corrects the visible light intensity (irradiation) for the fraction light that can be used by algae (45%). Often, available irradiation data is expressed in J.cm^{-2}.week-1 (PAR or TotalRAD) . Notice that irradiation must be provided in $W.m^{-2}$. To convert PAR J.cm^{-2}.week^{-1}, multiply with 0.016534 and 1/0.45. To convert TotalRAD (J.cm^{-2}.week^{-1}, only multiply with 0.016534.
If radiation data are expressed in J.cm^{-2}.day^{-1} multiply with $10^4 cm^2/m^2$ and with 1/86400 day/s (10000 * 1/86400 = 0.011574) to obtain the required input unit for radiation $W/m2$.

◇ DYNAMO may use the daily average radiation or the instantaneous radiation varying over the day if irradiation data are avaiable within the day.

Additional references

WL | Delft Hydraulics (1991a)

Table 6.1: *Definitions of the input parameters in the formulations for CALCRAD.*

Name in formulas	Name in input	Definition	Units
a	a_enh	amplification factor due to scattering by suspended particles	-
et	$ExtVl$	total extinction coefficient of visible light	m^{-1}
Is	$Radsurf$	light intensity at water surface	$W.m^{-2}$
z_1	$Depth$	thickness of a water or sediment layer	m

Table 6.2: *Definitions of the output parameters for CALCRAD.*

Name in formulas	Name in output	Definition	Units
$Itop$	Rad	light intensity at the top of a water or sediment layer	$W.m^{-2}$
$Ibot$	$RadBot$	light intensity at the bottom of a water or sediment layer	$W.m^{-2}$

Table 6.3: *Definitions of the input parameters in the formulations for CALCRADDAY.*

Name in formulas	Name in output	Definition	Units
a	*a_enh*	amplification factor due to scattering by sed. particles	-
et	*ExtVl*	total extinction coefficient of visible light	m^{-1}
Is	*DayRadsurf*	light intensity at the water surface	$W.m^{-2}$
H	*Depth*	thickness of a water or sediment layer	m
α	*fRefl*	fraction of light that is reflected	-

Table 6.4: *Table IV Definitions of the output parameters for CALCRADDAY.*

Name in formulas	Name in output	Definition	Units
Itop	*DayRad*	light intensity at the top of a water or sediment layer	$W.m^{-2}$
Ibot	*DayRadBot*	light intensity at the bottom of a water or sediment layer	$W.m^{-2}$

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6.2 Extinction coefficient of the water column

PROCESS: EXTINABVL, EXTPHGVL, EXTPHDVL, EXTPODVL, EXTPOGVL, EXTINC_VL

With extinction coefficient we refer to the diffuse (opposite to beam) attenuation of irradiance (light as measured under water with a flat collector looking vertically upward). The extinction coefficient (ExtVL, K_d, ϵ_T) is a measure of the decrease or attenuation of the amount of available light in downward direction and is expressed in m^{-1}. The extinction coefficient is used to calculate remaining underwater light (see Section 6.1).

The extinction coefficient has a direct relationship to light available to aquatic plants and algae. Secchi depth (Section 6.6) is a measure for transparency and by the nature of the measurement largely determined by scattering of incident light. High scattering values result in low transparency but not necessarily in low available light because scattered light remains available to aquatic plants and algae. The extinction coefficient correctly considers the loss of light scattering (and absorption) and is therefore used in all the light dependent growth modules in D-Water Quality, among others the algae model BLOOM. Growth modules use light that algae and aquatic plants can use for photosynthesis, viz. PAR (Photosynthetically Available Radiation) in the range of 400-700 nm wavelength. Other parts of the light spectrum are also relevant for other modules eg. infrared (ir) part for temperature modules. Note that extinction coefficients are strongly wavelength dependent (see below).

The extinction coefficient is classified as an apparent optical property (as is e.g. transparency or water colour) meaning that (Preisendorfer, 1961) its value does not, like for inherent properties, depends on the water composition only but varies with changes in the direction and intensity of underwater light. Inherent optical properties (IOPs) are, for example, the absorption and scattering properties of water (Rijkeboer et al. 1997). Thus, the extinction coefficient cannot be directly determined from inherent optical properties of the water without knowing the geometry of the light field for which either extensive radiative transfer modelling is required or, as presented here, simplifying assumptions are used.

Light modelling as presented here is classified as a forward model in which inherent optical properties (absorption and scattering of water) are translated to apparent (light) properties such as extinction, transparency, colour and reflection. Remote sensing does the opposite (and is therefore called a backward model) as apparent properties, remotely observed, are used to estimate the inherent properties of water ultimately to be translated to water quality concentrations. Both type of models need absorption and scattering coefficients per unit weight of the component (so called SIOPs) for their modelling. For example, the SIOP for light absorption by chlorophyll is the absorption coefficient per $mg.L^{-1}$ of chlorophyll.

D-Water Quality contains two implementations for the parametrization of the extinction coefficient (ϵ_T) which is used to calculate attenuation (Section 6.1).

- ◇ *Linear* approach (Section 6.2.1) based on linear relations between specific absorption coefficients lumped over PAR (or more in general over the spectrum of interest).
- ◇ A *spectral* approach (which is non-linear, Section 6.2.2) based on inherent optical properties, including scattering, differentiated by wavelength in the PAR spectrum.

Both methods calculate Kd-PAR, but the latter is more advanced and has a more physical foundation. The spectral method should produce more reliable results notably for deeper and less turbulent waters, better results for Secchi depth and is more suitable for comparison

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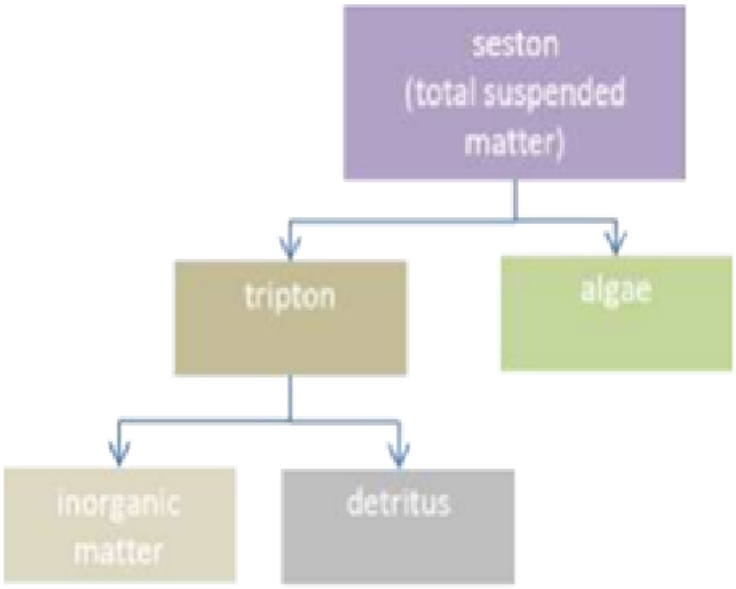

Figure 6.2: *Hierarchical representation of the different forms of suspended matter.*

with or integration with remote sensing products as it has the ability to predict water leaving radiance (as it includes upward reflection) and is spectrally detailed.

When using the spectral approach, the modelled Kd decreases with water depth which is in line with physics and with measurements of underwater light against depth (common practice when calculating Kd from measurements is to a priori assume a constant Kd over depth).

6.2.1 Linear parameterization of the extinction coefficient

In the linear approach the total extinction coefficient of visible light is calculated as the sum of partial extinction coefficients. These partial extinction coefficients (m^{-1}) are the contributions from the five optically active substances, see below, and are each calculated from the product of their concentration ($g.m^{-3}$) and a substance specific extinction coefficient ($m^2.g^{-1}$). Water contributes through a fixed background extinction. All non-specifically mentioned substances can be accounted for applying a specific extinction coefficient for salinity.

The optically active substance components are phytoplankton, non-living particulate matter (NAP, tripton), coloured dissolved organic substances (CDOM or humic acids, fulvic acids, gilvin, yellow substance etc.) and water. The hierarchy of the particulate part (seston or total suspended matter, TSM) is shown below.

See the Section Implementation below for the substances from the process library included. Note that detritus is modelled as POC1-4 and inorganic matter as IM1-3.

Implementation

The total extinction coefficient for the water column is delivered by three processes the names of which depend on the algae module and the detritus mode selected. Processes ExtinaBVL (or ExtPh(i)VL) and ExtPO(i)VL provide the overall extinction coefficients of respectively algae biomass and detritus. Process Extinc_VL adds the various coefficients up in order to obtain the total extinction coefficient. The processes do not deliver process rates and, therefore, do not affect mass balances.

For the extinction due to macrophytes the process Extinc_VLG is used.

Process ExtinaBVL has been implemented for the BLOOM algae:

◇ BLOOMALG01 - BLOOMALG15.

Process ExtPhDVL has been implemented for the DYNAMO algae:

◇ Diat and Green.

Process ExtPhGVL has been implemented for the MONALG algae:

◇ MND1Diat-m, MND2Flag-m, MND3Diat-f and MND4Flag-f.

Process ExtPODVL has been implemented for the detritus substances (DetX mode):

◇ DetC and OOC.

Process ExtPOGVL has been implemented for the detritus substances (POX mode):

◇ POC1, POC2, POC3 and DOC.

Process Extinc_VL has been implemented for all these substances.

Tables 6.5 to 6.11 provide the definitions of the parameters occurring in the user-defined input and output.

Formulation

The total extinction coefficient is calculated as the sum of five contributions:

$$\epsilon_t = \epsilon_{at} + \epsilon_{dt} + \epsilon_{st} + \epsilon_{ot} + \epsilon_b$$

with:

ϵ_{at}	overall extinction coefficient of algae biomass [m^{-1}]
ϵ_b	background extinction coefficient [m^{-1}]
ϵ_{dt}	overall extinction coefficient of detritus [m^{-1}]
ϵ_{st}	overall extinction coefficient of suspended inorganic matter [m^{-1}]
ϵ_{ot}	overall extinction coefficient of other substances as a function of salinity [m^{-1}]
ϵ_t	total extinction coefficient [m^{-1}]

The background extinction coefficient is an input parameter. The other contributions are determined according to:

$$\epsilon_{at} = \sum_{i=1}^{n} (\epsilon_{a,i} \times Calg_i)$$

$$\epsilon_{dt} = \sum_{j=1}^{m} (\epsilon_{d,j} \times Cdet_j)$$

$$\epsilon_{st} = \sum_{k=1}^{3} (\epsilon_{s,k} \times Cim_k)$$

$$\epsilon_{ot} = \epsilon_o \times (1 - SAL/SAL_{max})$$

with:

$Calg_j$	biomass concentration of algae species group j [gCm^{-3}]
$Cdet_j$	concentration of detritus component j [gCm^{-3}]
Cim_k	concentration of suspended inorganic matter fraction k [gCm^{-3}]
ϵ_a	specific extinction coefficient of an algae species type [m^2gC^{-1}]
ϵ_d	specific extinction coefficient of a detritus component [m^2gC^{-1}]
ϵ_o	spec. ext. coefficient of other substances on the basis of relative salinity [m^{-1}]
ϵ_s	spec. ext. coefficient of a suspended inorganic matter fraction [m^2gDM^{-1}]
SAL	actual salinity [$g \cdot kg^{-1}$] $\approx$ [gl^{-1}]
SAL_{max}	maximum salinity [$g \cdot kg^{-1}$] $\approx$[gl^{-1}]
i	index for algae species [-]
j	index for detritus components [-]
k	index for suspended inorganic matter fractions [-]
n	number for algae species, =15 for BLOOM, =2 for DYNAMO, =4 for MONALG [-]
m	number of detritus components, =2 for DetX, =4 for POX [-]

Besides the total extinction coefficient, the processes deliver the overall extinction coefficients of algae biomass, detritus and suspended inorganic matter.

Directives for use

- ◇ To use the linear model make sure the constant SW_Uitz is set to zero.
- ◇ Dissolved organic matter (fulvic and humic acids) may be modelled as substance DOC or accounted for in the background extinction coefficient, or in a salinity related extinction coefficient.
- ◇ Dominant contributions to the extinction are different for saline and fresh water. Among other things, in fresh water a relatively large contribution come from dissolved fulvic and humic acids, whereas saline water as a rule contains very small quantities of these substances. This is due to photochemical oxidation of these substances and long residence time. It is also conceivable that marine suspended sediment has a specific extinction coefficient that is different from the coefficient of riverine suspended sediment. Where river water is mixed with saline water in estuaries, the background extinction changes from a relatively high value in the river to a low value in the sea. The opposite applies to salinity. It has been shown that the background extinction coefficient in estuaries can be described empirically as a function of salinity Rijkswaterstaat/RIKZ 1991. For this reason such a relation has been incorporated in process Extinc_VLG .

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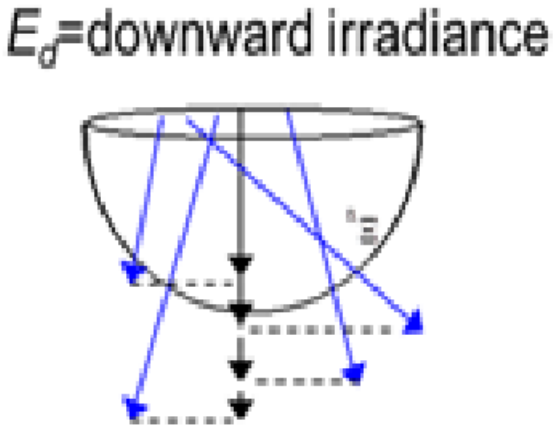

Figure 6.3: *Sketch of the downward irradiation.*

6.2.2 Spectral parameterization of the extinction coefficient (Kd-PAR, et) using UITZICHT

Underwater light is removed from the incoming light by absorption and scattering by coloured water components including phytoplankton and suspended or dissolved organic matter. The direction of the light can be changed by scattering of light by particles in the water. Scattering increases the pathlength travelled by light and therefore increases the probability of light being absorbed. For the particles in water the scattering is mainly in the forward direction. A small fraction of light scatters backwards, causing the reflection of water.

Buiteveld published a peer-reviewed article (Buiteveld 1995) on a $K_d(\lambda)$ parameterisation for lakes. Buiteveld aimed at a generic method dubbed UITZICHT ('UITdoving ZICHTbaar licht' which means extinction of visible light) valid for different Dutch lakes where field data were available that could replace the hitherto empirical linear regression-based approaches for a bulk Kd-PAR.

Formulation

The attenuation of light over depth is determined by absorption and scattering. The attenuation of an infinitely narrow beam of light falling perpendicular to the water surface, the beam attenuation coefficient ($c(\lambda)$, m^{-1}), is equal to the sum of the absorption coefficient ($a(\lambda)$, m^{-1}) and the scattering coefficient ($b(\lambda)$), m^{-1}):

$$c(\lambda) = a(\lambda) + b(\lambda)$$

However, attenuation of the total light field relevant for water quality and ecology encompasses more than a single beam: it relates to the total amount of all light available for viewing under water or for photosynthesis. Figure 6.3 shows in black the downward irradiance E_d [Wm^{-2}] which in fact is a vertical projection of the light field (blue) integrated over the hemisphere.

The empirical relationship below considers the directional structure of the incident light including absorption and scattering per wavelength, this gives a more accurate description of the extinction coefficient:

$$\epsilon_{total}(\lambda) = \frac{1}{\cos(\alpha)} \sqrt{a(\lambda)^2 + (0.425 \cdot cos(\alpha) - 0.19) \cdot a(\lambda) \cdot b(\lambda)} \tag{6.1}$$

Where $\cos(\alpha)$ is the cosine of the refracted solar light just beneath the surface relative to the zenith angle and $a(\lambda)$ and $b(\lambda)$ are respectively the wavelength dependent absorption and scattering coefficients, see below. The coefficients in the equation (0.425 and -0.19) can

be regarded as coefficients that determine the relative contribution of scattering to vertical attenuation of irradiance.

As introduced above, a and b are the total spectral absorption and scatter by the constituents of respectively absorption coefficients $a(\lambda)$ [m^{-1}] and total scattering coefficient $b(\lambda)$ [$m^{-}1$] for various optical substances indicated by the subscript.

The total absorption and scattering coefficients per wavelength are the sum of the individual coefficients of the individual components, for absorption this yields:

$$\begin{aligned} a(\lambda) &= a(\lambda)_{water} + a(\lambda)_{CDOM} + a(\lambda)_{phyt} + a(\lambda)_{detritus} \\ &\quad + a(\lambda)_{inorganic\ particulate\ matter} \end{aligned}$$

and for scattering:

$$b(\lambda) = b(\lambda)_{water} + b(\lambda)_{NAP} + b(\lambda)_{phyt} + b(\lambda)_{CDOM}$$

Note that absorption by inorganic particulate matter and scatter by CDOM are presumed negligible.

$a(\lambda)$	total absorption coefficient [m^{-1}]
$a(\lambda)_{water}$	absorption coefficient for water [m^{-1}]
$a(\lambda)_{cdom}$	absorption coefficient for coloured dissolved organic matter [m^{-1}]
$a(\lambda)_{phyt}$	absorption coefficient for algae [m^{-1}]
$a(\lambda)_{detritus}$	absorption coefficient for detritus (the fraction of suspended matter that absorbs) [m^{-1}]
$b(\lambda)$	total scattering coefficient [m^{-1}]
$b(\lambda)_{water}$	scattering coefficient for water [m^{-1}]
$b(\lambda)_{phyt}$	scattering coefficient for algae [m^{-1}]
$b(\lambda)_{NAP}$	scattering coefficient for suspended matter (i.e. glow residue or inorganic particulate matter and detritus. This is the fraction of suspended matter that scatters) [m^{-1}]

Thus, the total absorption and scattering coefficients can be calculated if the IOPs of the various substances in the water (and water per se) are known, in UITZICHT these are:

Water

A standard set for the absorption and scattering coefficients of water is Smith & Baker (1988) and Prieur & Sathyendranath (1981). Values are tabulated in the code for 5 nm intervals.

CDOM

CDOM is the optically measurable component of dissolved organic matter in water. Traditional methods of measuring CDOM include UV-visible spectroscopy. The absorption spectrum has characteristic gradient, the height of which depends on the concentration. Because of this, the value $a(380)_{CDOM}$ or $a(440)_{CDOM}$ is often taken as a measure of the absorption of coulored dissolved organic matter. The wavelength dependence of the CDOM absorption coefficient is represented by a measured absorption coefficient at 380 nm:

$$a(\lambda)_{CDOM} = a(380)_{CDOM} \cdot e^{-k_h(380)} \tag{6.2}$$

$$a(380)_{CDOM} = \epsilon_d \cdot DOC \tag{6.3}$$

$a(380nm)_{CDOM}$	absorption by CDOM at 380 nm wavelength [m^{-1}]
k_h	input constant [nm^{-1}]

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Figure 6.4: *Absoprtion of light by humic acids as a function of the wave length.*

DOC	dissolved organic carbon (DOC) [$gC.m^{-3}$]
ϵ_d	specific extinction coefficient for DOC [$m^2.gC^{-1}$]

Values for k_h are commonly between 0.01 and 0.025 are common (Bricaud et al. 1981). The wavelength dependency follows from the constant k_h. A graph of this absorption (m^{-1}) is given below for a $a(380)_{CDOM}$ of 5.0 m^{-1} and a k_h of 0.014 nm^{-1}.

Chlorophyll

Algae absorb and scatter light. The assumption in is that the absorption and scattering spectra have an inverse gradient, which asserts that the gradient of the beam attenuation coefficient is constant. Algae (not species specific) are expressed as the sum of chlorophyll they represent.

$$\begin{aligned} c_{phyt} &= a(550)_{phyt} + 0.12 \cdot C_{Chla}^{0.63} \cdot K_{phyt} \\ a(\lambda)_{phyt} &= (0.058 + 0.018 C_{Chla}) \cdot e(\lambda)_{chl} \cdot K_{phyt} \\ b_{phyt}(\lambda) &= C_{phyt} - a_{phyt}(\lambda) \end{aligned}$$

where:

c_{phyt}	beam attenuation coefficient for algae [m^{-1}]
$a(\lambda)_{phyt}$	specific absorption coefficient for algae [$nm \cdot m^{-1}$]
$b(\lambda)_{phyt}$	specific scattering coefficient for algae [$nm \cdot m^{-1}$]
k_{phyt}	correction factor [-]
C_{Cha}	concentration of chlorophyll-a [$mg.m^{-3}$]
$e(\lambda)_{chl}$	specific absorption coefficient for algae [$nm \cdot m^{-2} \cdot mg^{-1}$], tabulated

However, in D-Water Quality, this the contribution for living algae based on their summed chlorophyll is not used. Instead, the effect of living algae is computed in the same way as described for the simple extinction module (ϵ_{at} = partial extinction coefficient of algae biomass (ExtVlPhyt) calculated by process EXTINABVLP (module EXTINA).

Suspended matter (tripton, NAP)

Suspended solids (also called "seston") can be divided into an inorganic part (glow residue) and an organic part (algae and detritus). Absorption and reflection of algae are described in the previous paragraph so seston is corrected for the algae content leaving tripton or non-algae particles (NAP), the sum of inorganic matter and detritus, in formulae are:

$$\begin{aligned} C_{NAP}\ (or\ tripton) &= C_{seston} - w_{chf} \cdot C_{chlfa} \\ C_{detritus} &= C_{NAP} - C_{TIM} \end{aligned}$$

where:

$C_{detritus}$	concentration detritus, [mgl^{-1}]
C_{seston}	concentration total suspended matter, [mgl^{-1}]
C_{TIM}	total particulate inorganic matter or glow residue, [mgl^{-1}]
w_{chf}	conversion of chlorophyll to dry weight algae (i.e. 0.07 - 0.1 [gmg^{-1}])
C_{NAP}	concentration TIM + detritus, known as tripton, [mgl^{-1}]
C_{chlfa}	concentration of chlorophyll-a, [μgl^{-1}]

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From an empirical relationship, the following equation for the non algae particles of suspended matter (tripton, so including inorganic matter) the beam attenuation, $c(\lambda)$, was derived:

$$C_{NAP}(\lambda) = k_1 C_{NAP}^{k_2}(400/\lambda)$$

where:

k_1, k_2	optimalisation constants
C_{NAP}	$C_{detritus} + C_{TIM}$
C_{TIM}	sum of the three fractions of inorganic matter (IM1-3)

The scattering of detritus and total particulate inorganic matter is:

$$b_{NAP}(\lambda) = c_{NAP}(\lambda) - a_{detritus}(\lambda)$$

The absorption by detritus is wavelength dependent and is described by an inverse relationship with wavelength:

$$a_{detritus}(\lambda) = k_3 C_{detritus}(400/\lambda)$$

where:

$C_{detritus}$	sum of the four POC fractions(POC1-4), scaled by the factor $dmpoc$
k_3	optimisation constant
$dmpoc$	averaged dry matter to carbon ratio in all POC fractions [$gDMgC^{-1}$]

Note that inorganic material (TIM) does not contribute to absorption and that detritus (sum of the POC fractions) does contribute to both absorption and scattering.

Integration over PAR

The irradiance at a given wavelength and depth can be calculated using the total extinction coefficient with:

$$E_z(\lambda) = E_0(\lambda) \cdot e^{-\epsilon_{total}(\lambda)z} \tag{6.4}$$

where:

z	depth, [m]
$E_z(\lambda)$	irradiance at depth z [Wm^{-2}]
$E_0(\lambda)$	irradiance just below the water surface [Wm^{-2}]
ϵ_{total}	total extinction coefficient [m^{-1}]

For $E_0(\lambda)$ the theoretical irradiance spectrum of the sun above water is used, derived from Planck's radiation law with a (black body) temperature of around 6000 K. The visual part of this curve is shown below (red curve) and is, as a reference, compared to the Standard Table for Reference Solar Spectral Distributions (blue). The relative value of the different wavelengths is of importance (see below), not the absolute values. The module uses a resolution of 5 nm. Symbol E_0 is used (instead of I_0) as we moved to quantum irradiance, [$\mu mol \cdot m^{-2}s^{-1}nm^{-1}$]. It should be noted that a radiometer signal relates to the flux of energy, [$Wm^{-2}nm^{-1}$], in discrete wavebands, whereas PAR is expressed as the density of photons, [μmol photons $m^{-2}s^{-1}$], in the PAR domain (400–700 nm).

$E_z(\lambda)$ is integrated over PAR at two different depths following:

$$E_{z1} = \sum_{\lambda=400}^{700} E_0(\lambda) e^{-\epsilon_{total}(\lambda)z_1} \tag{6.5}$$

$$E_{z2} = \sum_{\lambda=400}^{700} E_0(\lambda) e^{-\epsilon_{total}(\lambda)z_2}$$

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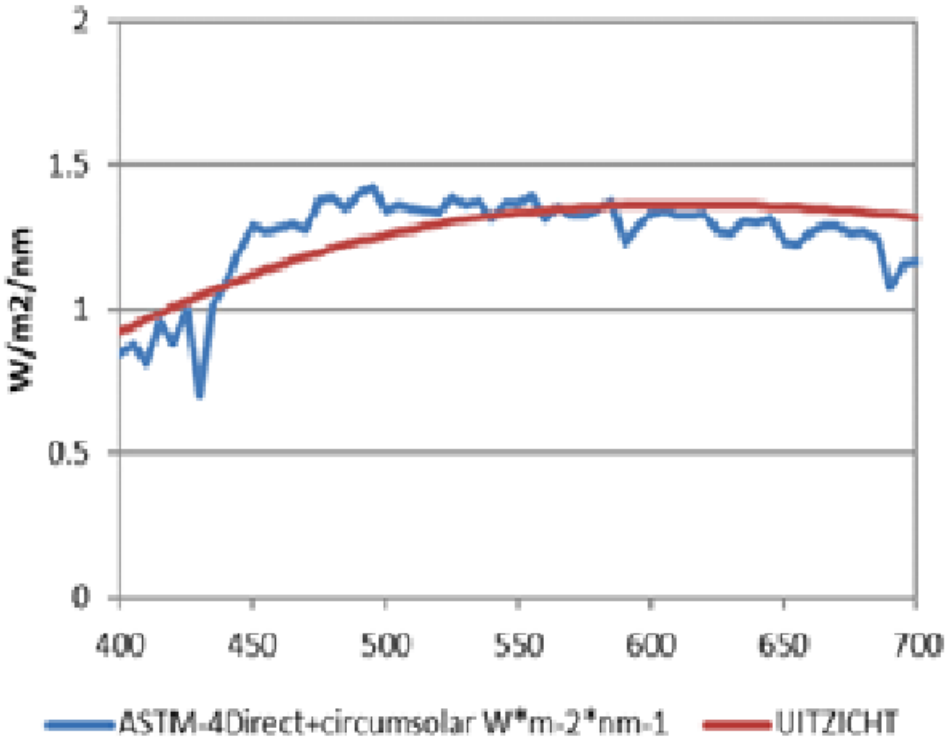

Figure 6.5: *Approximation of the solar spectrum by UITZICHT.*

representing the amount irradiance at depths z_1 and z_2 respectively.

Then the extinction coefficient that would cause the total light level thus obtained at z_2, given the total light level at z_1 is:

$$\epsilon_{(PAR)} = \frac{1}{z2 - z1} \cdot ln(\frac{Ez_1}{Ez_2}) \tag{6.6}$$

With increasing depth, light frequencies with higher extinction coefficients have vanished and the spectrum of light is shifted towards the frequencies with lower extinction coefficients. In fact $\epsilon(PAR)$ is defined as the local slope of the logarithm of E and varies with depth, since not all wavelengths in the light field are attenuated similarly. This causes the spectrum of E to change over the vertical. The increasingly blue hue of water with increasing depth is due to this effect, since pure water absorption is strongest in the red parts of the spectrum. So Kd(PAR) is not constant with depth, even in a homogeneous water body.

The beam attenuation coefficient ($c(\lambda)$, [m^{-1}]), must also be integrated over PAR as it is required for the Secchi depth calculation (section 6.6). The calculation for $c_{(PAR)}$ is analogous to the calculation for $\epsilon_{(PAR)}$ explained above. First $c(\lambda)$ is obtained from summing $a(\lambda)$ and $b(\lambda)$, Then, $\epsilon_{total}(\lambda)$ is replaced by $c(\lambda)$ in equation 6.5. Finally, $c_{(PAR)}$ is calculated for two depths (equations 6.5 and 6.6) where z_1 is the depth where a 10 % light level is reached for 550 nm and $z_2 = z_1 + 0.1\ m$. For the calculation of z_1 equation 6.4 is rewritten and ϵ_{total} is

used:

$$z_1 = -\ln\left(\frac{E_z(\lambda_0)}{E_0(\lambda_0}\right)/\epsilon_{total}(\lambda_0)$$
$$\frac{E_z(\lambda_0)}{E_0(\lambda_0)} = 10\,\%$$

where $\lambda_0 = 550$nm

Additional references

Rijkswaterstaat/RIKZ (1990), Rijkswaterstaat/RIKZ (1991)

Table 6.5: *Definitions of the input parameters in the formulations for ExtinaBVL*

Name in formulas	Name in input/output	Definition	Units
$Calg_i$	*BLOOMALG(I)*	biomass concentration of algae species type I	$gC.m^{-3}$
$\epsilon_{a,i}$	*ExtVlAlg(i)*	algae species type specific extinction coefficient	$m^2.gC^{-1}$
n	*NAlgBloom*	number of algae species groups	

1 (i) indicates algae species types 01-15.
2 The default values are fixed and must not be changed! The indicator also refers to additional input in the form of *FixAlg(i).*
3 These input parameters are added in order to convert the biomass of algae species attached to the sediment from gC.m-2 to gC.m-3.

Table 6.6: *Definitions of the input parameters in the formulations for ExtPhDVL*

Name in formulas	Name in input/output	Definition	Units
$Calg_1$	*Diat*	biomass concentration of diatoms	$gC.m-3$
$Calg_2$	*Green*	biomass concentration of green algae	$gC.m-3$
$\epsilon a, 1$	*ExtVlDiat*	specific extinction coefficient for diatoms	$m2.gC^{-1}$
$\epsilon a, 2$	*EXtVlGreen*	specific extinction coefficient for green algae	$m2.gC^{-1}$
n	*NAlgDynamo*	number of algae species groups	

1 The default values are fixed and must not be changed!

Directives for use (specific to UITZICHT)

In the current application the energy in the above-water radiation (RadSurf, I_0) is distributed over the PAR spectrum using a standard daylight spectrum. The spectrum is independent on weather conditions (e.g. cloudiness).

Table 6.7: *Definitions of the input parameters in the formulations for ExtPhGVL*

Name in formulas	Name in input/output	Definition	Units
$Calg_1$	*MND1Diat-m*	biomass concentration of marine diatoms	$gC.m-3$
$Calg_2$	*MND1Flag-m*	biomass concentration of marine flagellates	$gC.m-3$
$Calg_3$	*MND1Diat-f*	biomass concentration of fresh water diatoms	$gC.m-3$
$Calg_4$	*MND1Flag-f*	biomass concentration of fresh water flagellates	$gC.m-3$
$\epsilon_{a,i}$	*ExtVlMND(i)*	algae species type specific extinction coefficient	$m^2.gC^{-1}$
n	*NAlgGEMWK*	number of algae species groups	

1 (i) indicates algae species types 1-4.
2 The default values are fixed and must not be changed!

Table 6.8: *Definitions of the input parameters in the formulations for ExtPODVL*

Name in formulas	Name in input/output	Definition	Units
$Cdet_1$	*DetC*	concentration of detritus component DetC	$gC.m^{-3}$
$Cdet_2$	*OOC*	concentration of detritus component OOC	$gC.m^{-3}$
$\epsilon_{d,1}$	*ExtVlDetC*	specific extinction coefficient of detritus DetC	$m^2.gC^{-1}$
$\epsilon_{d,2}$	*ExtVlOOC*	specific extinction coefficient of detritus OOC	$m^2.gC^{-1}$
n	*NPOCDynamo*	number of detritus components	

1 The default values are fixed and must not be changed!

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Table 6.9: *Definitions of the input parameters in the formulations for ExtPOGVL*

Name in formulas	Name in input/output	Definition	Units
$Cdet_1$	*DOC*	concentration of detritus component DOC	$gC.m^{-3}$
$Cdet_2$	*POC1*	concentration of detritus component POC1	$gC.m^{-3}$
$Cdet_3$	*POC2*	concentration of detritus component POC2	$gC.m^{-3}$
$Cdet_4$	*POC3*	concentration of detritus component POC3	$gC.m^{-3}$
$\epsilon_{d,1}$	*ExtVlDOC*	specific extinction coefficient of detritus DOC	$m^2.gC^{-1}$
$\epsilon_{d,2}$	*ExtVlPOC1*	specific extinction coefficient of detritus POC1	$m^2.gC^{-1}$
$\epsilon_{d,3}$	*ExtVlPOC2*	specific extinction coefficient of detritus POC2	$m^2.gC^{-1}$
$\epsilon_{d,4}$	*ExtVlPOC3*	specific extinction coefficient of detritus POC3	$m^2.gC^{-1}$
n	*NPOCDOCGem*	number of detritus components	

1 The default values are fixed and must not be changed!

Table 6.10: *Definitions of the output parameters for ExtinaBVL (or ExtPh(i)VL), ExtPO(i)VL and Extinc_VL*

Name in formulas	Name in output	Definition	Units
ϵ_{at}	*ExtVlPhyt*	overall extinction coefficient of algae biomass	m^{-1}
ϵ_{dt}	*ExtVlOSS*	overall extinction coefficient of detritus	m^{-1}
ϵ_{st}	*ExtVlISS*	overall extinction coefficient of suspended inorg. matter	m^{-1}
ϵ_t	*ExtVl*	total extinction coefficient	m^{-1}

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Table 6.11: *Definitions of the additional parameters used in the UITZICHT module*

Name in formulas	Name in output	Definition	Units
C_{TIM}	IM1	inorganic matter (IM1)	[$gDMm^{-3}$]
	IM2	inorganic matter (IM2)	[$gDMm^{-3}$]
	IM3	inorganic matter (IM3)	[$gDMm^{-3}$]
$C_{detritus}$	POC1	POC1 (fast decomposing fraction)	[gCm^{-3}]
	POC2	POC2 (medium decomposing fraction)	[gCm^{-3}]
DOC	DOC	Dissolved Organic Carbon (DOC)	[gCm^{-3}]
ed	ExtVlDOC	VL specific extinction coefficient DOC	[m^2gC^{-1}]
z_1	UitZDEPT1	Z1 (depth)	[m]
z_2	UitZDEPT2	Z2 (depth)	[m]
K_{phyt}	UitZCORCH	CORa correction factor	[-]
k_3	UitZC_DET	C3 coeff. absorption ash weight & detritus	[-]
k_1	UitZC_GL1	C1 coeff. absorption ash weight & detritus	[-]
k_2	UitZC_GL2	C2 coeff. absorption ash weight & detritus	[-]
k_h	UitZHELHM	Hel_h constant	[nm^{-1}]
$alpha$	UitZangle	Angle of incidence solar radiation	[°]
$dmpoc$	DMCFDetC	DM:C ratio DetC	[$gDMgC^{-1}$]
$C_{detritus}$	POC3	POC3 (slow decomposing fraction)	[gCm^{-3}]
$C_{detritus}$	POC4	POC4 (particulate refractory fraction)	[gCm^{-3}]

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This daylight spectrum changes from just above to just below water and subsequently with water depth due to specific absorption of certain wavelengths. When using UITZICHT the user has to provide the depth at which UITZICHT determines $\epsilon_{(PAR)}$ (UITZ_Depth, default 1 m), this is the euphotic depth and is not coupled to the actual water depth. In pure water the depth at which $K_d - PAR$ is calculated determines its value, small depths yield higher values (as red light attenuates stronger) and at larger depth the calculated $K_d - PAR$ is based on blue light and thus has a lower value. UITZICHT was developed for application in depth-averaged models (having homogeneous concentrations of substances over depth).

In 3D model applications the UITZICHT implementation (at present) is the same. In each vertical model grid cell $K_d(PAR)$ is based on the default euphotic depth (default 1 m). This gives the same results as (an equally deep vertically averaged model) provided the optically active substances are homogeneously distributed over depth. The latter condition is generally not fulfilled, however, in 3D model applications studying e.g. salt intrusion, silt resuspension and floating algae scums. In that case the current implementation is conceptually incorrect for 3D models.

In the current implementation, in each vertical model grid cell the amount of light energy remaining at the top of that cell (RAD) is assumed to have the same spectral composition as daylight the water surface. Of course this is a simplification. To correct this, module CalcRad should be adapted to calculate attenuation of coloured or spectral components, rather than only visible light).

Extinction from algae (self shading) is calculated by Bloom (ExtinaBVL). This routine uses a linear approach and overrules the spectral calculation based on total chlorophyl which is available in UITZICHT.

All growth models in D-Water Quality use the total light energy in the PAR spectrum for their growth function. So, although the spectral light model can output spectral components, K_d integrated over PAR ($K_d - PAR$) is used for the attenuation of light energy with depth. The $K_d - PAR$ determined by UITZICHT better match the actual spectrum at each waterdepth though (when all above mentioned omissions are resolved).

To relate K_d to the light available for primary production in the water column of vertically mixed models, the interval ($z_2 - z_1$) over which K_d is determined should preferably correspond to the depth of the euphotic zone (1% of surface light intensity). In 3D set z_1 and z_2 to segment upper and lower depth.

The UITZICHT allows no detail in size distributions of particles. Coarser particles have a lower specific extinction coefficient because the number of particles is lower per unit of weight and because their absorbing surface area is lower per unit of weight. The number of particles is linearly related with the scattering ability of the water as measured with turbidity measurements. In UITZICHT this is one function and even the effects of inorganic particles and organic particles are related. In systems where particles of different sizes are present, this approach may be unsuitable.

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6.3 Variable solar radiation during the day

PROCESS: DAYRAD

The light intensity during the day varies due to the different angles of the sun in relation to the earth surface, which depends on latitude as well as season. This module calculates light intensity (solar radiance, irradiance) at any moment during the day, as a function of latitude on earth, the average intensity over the day, the time of the day, and day of the year. The variation of light intensity during the day is relevant for the simulation of both primary producers and bacterial pollutants. For microphytobenthos, depending for their light supply on the period that a tidal flat is emerged, the light intensity during the emersion period is very relevant for their primary production. For coli bacteria the decay rates are so high and influenced by light intensity, that the variation of solar irradiance during the day can have a significant impact on the concentration patterns.

Implementation

Process DAYRAD calculates the light intensity at any moment during the day. It is used in combination with process CALCRADDAY, that provides light intensities at the top and the bottom of water and sediment layers for daily varying light intensity. Currently, DAYRAD can not be used for the simulation of bacterial pollutants.

Table 6.12 and Table 6.13 provide the definition of the input and output parameters.

Formulation

The formulations used to calculate the solar intensity are based on the constant radiance from the sun (1367 W m^{-2}) and the angle between the sun and the earth surface. The resulting solar irradiance can be corrected for measured daily averaged irradiance, or for cloudiness. The following formulations are used for the calculation of the maximum solar irradiance at time t at day d and latitude ϕ:

$$E_t = I_0 \frac{\bar{R}^2}{R^2} \left(\sin\delta \sin\phi + \cos\delta \cos\phi \cos\omega\right)$$

where:

$$\begin{aligned}
\delta = {} & 0.006918 - \\
& 0.399921 \times \cos(1 \times \eta \times d) - \\
& 0.006758 \times \cos(2 \times \eta \times d) - \\
& 0.002697 \times \cos(3 \times \eta \times d) + \\
& 0.070257 \times \sin(1 \times \eta \times d) + \\
& 0.000907 \times \sin(2 \times \eta \times d) + \\
& 0.001480 \times \sin(3 \times \eta \times d)
\end{aligned}$$

$$\eta = \frac{2\pi}{366}$$

$$\frac{\bar{R}^2}{R^2} = 1 + 0.033 \cos(\eta d)$$

$$\omega = |12 - h| \times \frac{\pi}{12}$$

and:

E_t	maximum solar irradiance at time t [W.m^{-2}]
I_0	sun constant = 1367 [W.m^{-2}]
d	day of the year (1-366; 1 = 1 January, 365 = 31 December) [d]
$\frac{\bar{R}^2}{R^2}$	relative difference of distance earth-sun compared to average distance [-]
δ	angle between sun and earth surface at specific day [rad]
ω	angle between sun and earth surface at hour h [rad]
h	hour of the day [h]
ϕ	latitude [rad]

The parameters above are calculated from the input parameters as follows:

$$d = \left(\frac{ITIME}{86400} + RefDay \right)$$

$$h = 24.0 \times \left((\frac{ITIME}{86400} + RefDay) \text{mod} 1.0 \right)$$

$$\phi = \frac{Latitude}{360} \times 2\pi$$

where:

$ITIME$	DELWAQ time [scu]
$Latitude$	latitude of area of interest [degrees]
$RefDay$	day at start of the simulation [d]
$Reftime$	time of day at the start of the simulation [h]

The maximum solar irradiance at any time during the day is corrected for the effects of clouds and extinction in the atmosphere with measured data of the daily averaged light intensity. The calculated function of irradiance over the day is scaled with the ratio between maximum solar irradiance and measured light intensity. This requires the maximum solar irradiance expressed as the total irradiance over the day. Integration of the formulation for Et above for a day results in the following expression for the maximum average irradiance over the day E_d [W.m^{-2}].

$$E_d = \frac{I_0}{\pi} \times \frac{\bar{R}^2}{R^2} \times (\omega_0 \sin\delta \sin\phi + \cos\delta \cos\phi \sin\omega_0)$$

where:

$$\omega_0 = \arccos(-tg\delta \times tg\phi)$$

Correction of the maximum irradiance at time t (E_t [W m^{-2}]) for cloudiness and atmospheric absorption by using the measured average light intensity ($Radsurf$ [W m^{-2}]) is formulated as follows:

$$Dayrad = E_t \times \frac{Radsurf}{E_d}$$

Directives for use

◇ The light intensity at the water surface $RadSurf$ is the total visible light intensity (solar radiation) or the photosynthetic active light intensity (PAR). See section Light intensity in the water column for more information.

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References

Velds (1992)

Table 6.12: *Definitions of the input parameters in the formulations for DAYRAD.*

Name in formulas	Name in output	Definition	Units
$Radsurf$	$RadSurf$	daily average observed light intensity at water surface	W.m^{-2}
$Latitude$	$Latitude$	thickness of a water or sediment layer	degrees
$RefDay$	$RefDay$	time at the start of the simulation	-

Table 6.13: *Definitions of the output parameters for DAYRAD.*

Name in formulas	Name in output	Definition	Units
$DayRad$	$DayRadSurf$	actual light intensity at water surface as varying over the day	W.m^{-2}

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6.4 Computation of day length

PROCESS: DAYLENGTH

This module calculates the length of a day (sunrise to sunset) as a function of latitude on earth. As an example, of the results for four different latitudes are shown in Figure 6.6.

Implementation

The process is only implemented for DayL

Formulation

$$
\begin{aligned}
E &= 0.01721420632 \\
Declin &= 0.006918 - \\
&\quad 0.399921 \times \cos(1 \times E \times DayNr) - \\
&\quad 0.006758 \times \cos(2 \times E \times DayNr) - \\
&\quad 0.002697 \times \cos(3 \times E \times DayNr) + \\
&\quad 0.070257 \times \sin(1 \times E \times DayNr) + \\
&\quad 0.000907 \times \sin(2 \times E \times DayNr) + \\
&\quad 0.001480 \times \sin(3 \times E \times DayNr) \\
Tmp &= \frac{-0.01454389765 - \sin(Declin) \times \sin(LatRad)}{\cos(Declin) \times \cos(LatRad)}
\end{aligned}
$$

If $Tmp > 1.0$

$$DayL = 0.0 \tag{6.7}$$

If $Tmp < -1.0$

$$DayL = 1.0 \tag{6.8}$$

Else

$$DayL = 7.639437268 \times \arccos(Tmp)/24 \tag{6.9}$$

ITIME	DELWAQ time [scu]
Latitude	latitude of area of interest [degr]
LatRad	latitude of area of interest [rad]
DayNr	number of the day for the calculation of the day length (1=1 January, 365 = 31 December) [-]
RefDay	day of the year at start of the simulation [d]
DayL	daylength (fraction of a day - sunrise to sunset) [-]
Tmp	temporarily variable for calculation [d]

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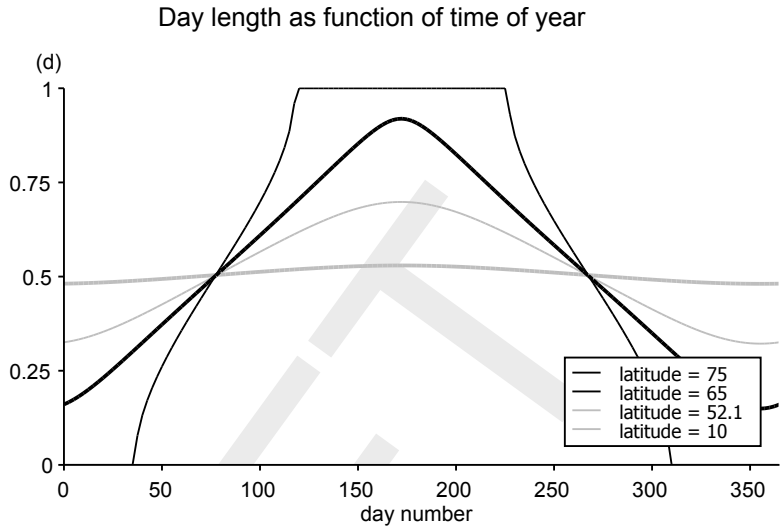

Figure 6.6: *Day length calculated by the module DAYL for the latitudes 10 °, 52.1°, 65° and 75° . The latitude of 52.1° refers to De Bilt, The Netherlands*

Directives for use

◇ The reference date and time for a DELWAQ calculation is not necessarily the first of January. At the start of a DELWAQ calculation the default day number calculated by the module DAYL equals 0 (based on variable $ITIME$ which equals 0.0 at that time). The day length module can compute the actual day number at the start of a calculation based on the T0-string. E.g. when a run starts at the first of April (T0-string is set to 01-04-XXXX), the variable $RefDay$ is computed to be $31 + 28 + 31 + 1 = 91$). Leap years are accounted for, so for a leap year $RefDay = 92$ for this example.
Alternatively, $RefDay$ can be specified in the input by the user.

Additional references

Velds (1992)

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6.5 Light reflection at the surface

PROCESS: REFLECTION

Light will be reflected at the water surface depending on the incidence angle and the presence of wind waves. While this latter effect is ignored, the incidence angle is take into account via this process.

Implementation

To estimate the reflection a simple procedure is used:

- ◇ If the latitude is between -23 and 23°, then the reflection is set to 0.05 (5%), irrespective of the time of year.
- ◇ Otherwise the reflection is estimated based on the week number since mid winter (1 january for the northern hemisphere, 1 july for the southern hemisphere):

Week	Fraction reflected
< 4	0.10
$4 - 13$	0.08
$14 - 17$	0.06
$18 - 31$	0.05
$32 - 35$	0.06
$36 - 45$	0.08
> 45	0.10

The reflected fraction is then applied to the irradiation in the process CALCRAD.

Table 6.14: *Definitions of the input parameters in the formulations for REFLECTION.*

Name in formulas	Name in input	Definition	Units
–	$Latitude$	Latitude of the model area in degrees	-
–	$RefDay$	Day number of the reference date (as it appears in the T0-string)	-

Table 6.15: *Definitions of the output parameters for CALCRAD.*

Name in formulas	Name in output	Definition	Units
–	$fRefl$	Fraction of light that is reflected	-

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6.6 Computation of Secchi depth

PROCESS: SECCHI

The Secchi depth is a measure for the transparency of water, and is measured with a Secchi disk. The transparency depends on the extinction of visible light in the water column. The euphotic zone for algae is approximately 2.5 times the Secchi depth.

Process SECCHI may apply an alternative advanced sub-model of the extinction coefficient called UITZICHT. This sub-model takes the detailed optical properties of a water column into account.

Implementation

The auxiliary process SECCHI has been implemented for the following substances:

◇ IM1, IM2, IM3, POC1, POC2, POC3, POC4.

Table 6.16 provides the definitions of the parameters occurring in the formulations.

Formulation

Two methods are available to compute the Secchi depth (SD).

For SW_Uitz = 0.0 (UITZICHT not applied) the Poole-Atkins relation is applied:

$$SD = \frac{a_{pa}}{\epsilon_t}$$

where:

a_{pa}	Poole-Atkins constant (1.7-1.9) [-]
ϵ_t	total extinction coefficient [m^{-1}]
SD	Secchi depth [m]

For SW_Uitz = 1.0 the auxiliary process UITZICHT is applied for the calculation of the Secchi depth based on a background extinction and the concentrations of (in)organic suspended matter, chlorophyll and dissolved organic matter (fulvic and humic acids). In this case, the Secchi depth is calculated as:

$$SD = \frac{\Gamma}{c_{PAR} + K_{PAR}}$$

where:

Γ	constant representing the water transparency [-]
c_{PAR}	beam attenuation coefficient [m^{-1}]
K_{PAR}	vertical extinction coefficient [m^{-1}]

Directives for use

◇ The concentrations of $IM1, IM2, IM3, POC1, POC2, POC3$ and $POC4$ are only used if auxiliary process UITZICHT is applied for the calculation of the total extinction coefficient.

◇ UITZICHT is applied when SW_Uitz = 1.0. In that case a number of additional input parameters are needed, among which $ExtVLODS$ (partial extinction coefficient dissolved

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organic matter) calculated by process $Extinc_VLG$ and $Chlfa$ calculated by the active phytoplankton module.

Table 6.16: *Definitions of the parameters in the above equations for SECCHI, exclusive of input parameters for auxiliary process UITZICHT.*

Name in formulas	Name in input	Definition	Units
a_{pa}	$PAConstant$	Poole-Atkins constant	-
ϵ_t	$ExtVl$	total extinction coefficient	m^{-1}
SW_Uitz	Sw_Uitz	option parameter: if 0.0 no UITZICHT (default), if 1.0 UITZICHT is applied	-

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7 Primary consumers and higher trophic levels

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7.1 Grazing by zooplankton and zoobenthos (CONSBL)

PROCESS: CONSBL

The consumption of algae and detritus by zooplankton and zoobenthos is called grazing. Grazers have a certain preference with respect to the components of their food, meaning that they consume certain algae species rather than other algae species, and rather phytoplankton than detritus. The four nutrient components in the model (organic carbon, nitrogen, phosphorus and silicon), are all required for grazers. The consumption process involves ingestion (uptake) and digestion of food components, egestion of detritus, excretion of nutrients, and growth and respiration. Grazer biomass eventually returns to detritus due to mortality. Net biomass growth or decline and net detritus mineralisation are the results of grazing.

The grazing module uses a so-called 'forcing function' approach. The user needs to specify the biomass development of filterfeeders (benthic and zooplankton) over the year. Based on this biomass the grazing rate on phytoplankton and detritus is simulated. The simulation takes into account the filtration, assimilation, respiration, mortality and excretion by the filter feeders. Whenever the nutrient availability is insufficient to sustain the specified biomass development, the filterfeeder biomass in the model is corrected. A lower biomass, that can be sustained, is assumed in the model in that case. Inorganic nutrients and detritus are released by the filterfeeders, due to excretion, respiration and mortality. For pelagic filterfeeders these substances are released to the water column. For benthic filterfeeders the detritus is released to the sediment.

CONSBL can be applied for up to five types of grazers, which may be species groups or individual species of zooplankton and zoobenthos. An important difference between the two species groups is that zoobenthos is only active in the lower water layer. The egestion of digested algae and detritus by grazers in the form of faecal pellets implies the production of detritus. This detritus may be released in the water column or added to the sediment detritus pool. The last option can be effectuated in the model for all zoobenthos groups.

Due to respiration nutrients (N/P/Si) are released into the water column. The effect of respiration on the dissolved oxygen budget is ignored in the model.

The process formulations of CONSBL have been described in more detail by WL | Delft Hydraulics (1990), WL | Delft Hydraulics (1992c), and Molen et al. (1994b).

The advantage of a forcing function over a dynamic grazing model is that the grazer biomass is controlled. Even state-of-the-art dynamic simulation of grazers is still subject to problems of stability and limited accurateness. However, imposing forcing functions demands for reliable and rather frequently measured grazer biomass data.

Implementation

Process CONSBL has been implemented for maximally five species groups of grazers. The input and output parameter names of the first group refer to zooplankton. The names of the parameters of the second group concern zoobenthos, and more specifically mussel type grazers. The other three groups have generic names. However, the names have only been selected in this way for easy recognition of simulated grazer species groups. The formulations are equal for the five groups, which means that the user eventually defines the nature of each grazer group.

Pelagic and benthic grazers are modelled in the same way. The only differences between

pelagic and benthic grazers are the unit and the fate of produced detritus. Zooplankton biomass needs to be imposed in [g m^{-3}], whereas zoobenthos biomass must to be provided in [g m^{-2}]. The selection is made using option parameter $(i)UnitSWS$. Selection of [g m^{-2}] implies that the grazer biomass in water layers without sediment surface is made equal to zero. The parameter $(i)FrDetBot$ determines whether detritus produced by the grazers is released into the water column ($(i)FrDetBot = 0$) or to the sediment ($(i)FrDetBot = 1$).

CONSBL has been formulated in a generic way and can be applied for water as well as sediment layers (layered sediment). It can also be used in combination with the sediment option S1/2. Detritus produced by grazers is deposited in the water column or in DETCS1 (etc.).

CONSBL has been implemented for the following substances:

for BLOOM,

- ◇ ALGC, ALGN, ALGP, ALGSi, BLOOMALG01-BLOOMALG30, MPB1peli, MPB2Psam, POC1, PON1, POP1, OPAL, DETCS1, DETNS1, DETPS1, DETSiS1, NH4, NO3, PO4, Si, OXY, TIC and ALKA

for DYNAMO,

- ◇ GREEN, DIAT, MPB1peli, MPB2Psam, POC1, PON1, POP1, OPAL, DETCS1, DETNS1, DETPS1, DETSiS1, NH4, NO3, PO4, Si, OXY, TIC and ALKA

Sulfur is not considered by CONSBL.

Currently, grazing of microphytobenthos is limited to the pelagic fraction, grazing of the benthic fraction is not included.

Table 7.1 and Table 7.2 provide the definitions of the parameters occurring in the user-defined input and output.

Formulation

The mass fluxes caused by grazing are calculated taking the following steps:

1. conversion of the biomass forcing function input to the desired units;
2. adjustment (if necessary) of the imposed grazer biomass according growth and mortality constraints;
3. calculation of the consumption rates for detritus and algae;
4. calculation of the rates of food assimilation and detritus production;
5. correction of the assimilation rates for respiration;
6. adjustment of the grazer biomass;
7. calculation of the detritus production rates according to the food availability constraints;
8. evaluation of the total conversion rates as additional output parameters; and
9. evaluation of the grazer biomass concentrations as additional output parameters.

The next sections deal with each of these steps.

1. Conversion of units

The forcing function formulations are based on the imposed grazer biomass expressed in [gC m^{-3}]. However, benthic grazer biomass is usually expressed in [gC m^{-2}]. The input to the model contains option parameters $(i)UnitSW$, with which the grazer biomass unit

can be selected for each grazer species group. When $(i)UnitSW = 0.0$ the model assumes that biomass concentrations provided in the input are expressed in [gC m^{-3}]. When $(i)UnitSW = 1.0$ the model assumes that biomass concentrations provided in the input are expressed in [gC m^{-2}]. In that case the concentrations are converted to [gC m^{-3}] by means of divison by the water depth H.

2. Adjustment of grazer biomass according to growth and mortality constraints

The imposed grazer biomasses are adjusted according to growth and mortality constraints in a step by step way. The grazer biomass at the end of a timestep (t_2) is diminished when the maximal growth rate does not support the imposed biomass increase with respect to the biomass at the beginning of a timestep (t_1). The grazer biomass at t_2 is augmented when the maximal natural mortality rate does not allow the imposed biomass decrease with respect to the biomass at t_1. The grazer biomass in the next timestep is adjusted accordingly as follows:

when $Cgri2_i \geq Cgr1_i$,

$$Cgrc_i = Cgr1_i \times (1 + kgr_i \times \Delta t)$$

$$\begin{array}{ll} Cgr2_i = Cgrc_i & \text{if} \quad Cgri2_i > Cgrc_i \\ Cgr2_i = Cgri2_i & \text{if} \quad Cgri2_i \leq Cgrc_i \end{array}$$

$$kgr_i = kgr_{i,20} \times e^{ktgr_i \times (T-20)}$$

when $Cgri2_i < Cgr1_i$,

$$Cgrc_i = Cgr1_i \times (1 - kmrt_i \times \Delta t)$$

$$\begin{array}{ll} Cgr2_i = Cgrc_i & \text{if} \quad Cgri2_i < Cgrc_i \\ Cgr2_i = Cgri2_i & \text{if} \quad Cgri2_i \geq Cgrc_i \end{array}$$

$$kmrt_i = kmrt_{i,20} \times e^{ktgr_i \times (T-20)}$$

with:

$Cgr1_i$	grazer biomass concentration at t_1 [gC m^{-3}]
$Cgr2_i$	grazer biomass concentration at t_2 [gC m^{-3}]
$Cgrc_i$	grazer biomass concentration constraint at t_2 [gC m^{-3}]
$Cgri2_i$	imposed grazer biomass concentration at t_2 [gC m^{-3}]
kgr	maximal growth rate [d^{-1}]
kgr_{20}	maximal growth rate at 20 °C [d^{-1}]
$ktgr$	temperature coefficient of growth [-]
$kmrt$	maximal natural mortality rate [d^{-1}]
$kmrt_{20}$	maximal natural mortality rate at 20 °C [d^{-1}]
$ktmrt$	temperature coefficient of mortality [-]
T	water temperature [°C]
Δt	timestep [d]
i	index for grazer species group 1-5 [-]

3. Consumption rates

The consumption rate of the grazers is limited by the filtration rate at low food availability and by the uptake rate at high food availability. The filtration rate and the uptake rate are equal at a certain food concentration $Cfdci$. The total food availability is defined as the sum of

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the concentrations of detritus and phytoplankton groups, adjusted by a preference factor for each food source. The preference factor accounts for the suitability of the food source for the grazers. Certain phytoplankton species and detritus fractions are more difficult to filtrate and digest for the grazers than others.

$$Cfd_i = fdpr_i \times Cdet_1 + \sum_{j=1}^{m} (fapr_i \times Calg_j)$$

with:

$Calg_j$	biomass concentration of algae species group j [gC m^{-3}]
Cfd_i	food concentration available to grazer species group i [gC m^{-3}]
$Cdet_1$	detritus organic carbon concentration [gC m^{-3}]
$fdpr_i$	preference of a grazer species group i for detritus [-]
$fapr_{i,j}$	preference of a grazer species group i for algae species group j [-]
m	number of algae groups, different for (BLOOM) and (DYNAMO) [-]
i	index for grazer species groups (at most 5) [-]
j	index for algae species groups (depends on whether BLOOM is used or DYNAMO) [-]

The maximal filtration rate and the maximal uptake rate are defined as:

$$kfil_i = Cgr1_i \times ksfil_i \times \frac{Cfd_i}{Ksfd_i + Cfd_i}$$

$$ksfil_i = ksfil_{i,20} \times e^{ktfil_i \times (T-20)}$$

$$kup_i = \frac{Cgr1_i \times kmup_i}{Cfd_i}$$

$$kmup_i = kmup_{i,20} \times e^{ktup_i \times (T-20)}$$

with:

$kfil$	filtration rate [d^{-1}]
$ksfil$	maximal specific filtration rate [m^3 gC^{-1} d^{-1}]
$ksfil_{20}$	maximal specific filtration rate at 20 °C [m^3 gC^{-1} d^{-1}]
$ktfil$	temperature coefficient for filtration [-]
kup	uptake rate [d^{-1}]
$kmup$	maximal uptake rate [d^{-1}]
$kmup^20$	maximal uptake rate at 20 °C [d^{-1}]
$ktup$	temperature coefficient for uptake [-]
$Ksfd$	half saturation constant for uptake [gC m^{-3}]
i	index for grazer species groups 1–5 [-]

The consumption of detritus and algae biomass by grazing is derived from the maximum uptake rate when the available food concentration is equal or larger than a certain critical amount. This amount is the biomass cencentration for which the filtration rate and the maximal uptake rate are equal:

$$Cfdc_i = \frac{kmup_i}{ksfil_i} \times \frac{Ksfd_i + Cfd_i}{Cfd_i}$$

with:

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$Cfdc_i$ critical concentration of food for grazer group i [gC m^{-3}]

The consumption process rate is equal to either the filtration or the uptake rate according to:

$$kcns_i = kfil_i \quad \text{if} \quad Cfdi < Cfdci$$
$$kcns_i = kup_i \quad \text{if} \quad Cfdi \geq Cfdci$$

with:

$kcns_i$ consumption process rate of grazer group i [d^{-1}]

So far, all rates are referring to organic carbon as a nutrient to grazers. Since the nutrient stochiometry of food is also important to grazers, the nutrient fluxes connected with grazing have to be taken into account in the model. The consumption rates for the nutrient components of detritus and the biomass of an algae species for a grazer group are:

$$Rdcns1_{k,i} = fdpr_i \times kcns_i \times Cdet_k$$

$$Racns_{k,i,j} = fapr_{i,j} \times kcns_i \times anut_{k,j} \times Calg_j$$

with:

$anut_{k,j}$ stochiometric const. of nutr. k over org. carbon in algae j [gC/N/P/Si gC^{-1}]
$Cdet_k$ detritus concentration for nutrient k [gC/N/P/Si m^{-3}]
$fdpr_i$ preference of a grazer species group i for detritus [-]
$fapr_{i,j}$ preference of a grazer species group i for algae species group j [-]
$Racns_{k,i,j}$ cons. rate of grazer group i for nutrient k in algae j [gC/N/P/Si m^{-3} d^{-1}]
$Rdcns1_{k,i}$ gross cons. rate of grazer group i for nutrient k in detritus [gC/N/P/Si m^{-3} d^{-1}]
i index for grazer species groups 1–5 [-]
j index for algae species groups 1–15 (BLOOM) or 1–2 (DYNAMO) [-]
k index for nutrients, 1 = carbon, 2 = nitrogen, 3 = phosphorus, 4 = silicon [-]

4. Assimilation and production of detritus

Consumed food is either assimilated into grazer biomass, respired or egested as detritus (fecal pellets). For benthic grazers part of the egested detritus is deposited at the sediment and is therefore added to the sediment detritus pool. If respiration is ignored the total rates of food assimilation, net detritus consumption and sediment detritus production caused by grazing are as follows:

$$Ras1_{k,i} = (1 - fdet_i) \times Rdcns1_{k,i} + \sum_{j=1}^{m} ((1 - falg_{i,j}) \times Racns_{k,i,j})$$

$$Rdcns2_{k,i} = (1 - fdet_i) \times Rdcns1_{k,i} + \sum_{j=1}^{m} ((1 - falg_{i,j} \times (1 - fsed_i)) \times Racns_{k,i,j})$$

$$Rsdpr1_{k,i} = fdet_i \times fsed_i \times Rdcns1_{k,i} + \sum_{j=1}^{m} (falg_{i,j} \times fsed_i \times Racns_{k,i,j})$$

with:

$falg_{i,j}$ egested fraction of algae j consumed by grazer i, = 1-yield [-]
$fdet_i$ egested fraction of detritus consumed by grazer i, = 1-yield [-]

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$fsed_i$ fraction of detritus egested by grazer i added to the sediment detritus pool [-]
$Ras1_{k,i}$ total food assimilation rate for nutrient k for grazer group i [gC/N/P/Si m^{-3} d^{-1}]
$Rdcns2_{k,i}$ net cons. rate of grazer group i for nutrient k in detritus [gC/N/P/Si m^{-3} d^{-1}]
$Rsdpr1_{k,i}$ total nutrient k in detr. prod. at the sediment for all grazers [gC/N/P/Si m^{-3} d^{-1}]

5. Assimilation corrected for respiration (nutrient excretion)
The food assimilation rates as calculated above are available for the growth of the grazer biomass. However, the actual assimilation of specific organic nutrients may be lower because of the difference in the nutrient stochiometries of grazers, algae and detritus. The most limiting nutrient determines the actual assimilation rates for all nutrients. The remaining portions of the other nutrients are egested as detritus in addition to the detritus production calculated above.

Moreover, due to growth respiration and maintenance respiration part of the assimilated biomass is converted back into inorganic nutrients. In order to calculate the nett assimilation rate the gross assimilation rate needs to be corrected for respiration.

The actual assimilation rates and the respiration rates follow from:

$$Ras2_{1,i} = \min_{k=1-4} (Ras1_{k,i}/bnut_{k,i})$$

$$Rrsp1_{k,i} = bnut_{k,i} \times frsp1_i \times Ras2_{1,i}$$
$$Rrsp2_{k,i} = bnut_{k,i} \times krsp2_i \times Cgr1_i$$
$$Rrsp_{k,i} = Rrsp1_{k,i} + Rrsp2_{k,i}$$
$$Ras3_{k,i} = Ras2_{k,i} - Rrsp_{k,i}$$
$$frsp1_i = frsp1_{i,20} \times e^{ktrsp1_i \times (T-20)}$$
$$krsp2_i = krsp2_{i,20} \times e^{ktrsp2_i \times (T-20)}$$

with:

$bnut_{k,i}$ stochiometric const. of nutr. k over org. carbon in grazer i [gC/N/P/Si gC^{-1}]
$Cgr1_i$ grazer biomass concentration at t_1 [gC m^{-3}]
$frsp1_i$ growth respiration fraction [-]
$frsp1_{i,20}$ growth respiration fraction at 20 °C [-]
$ktrsp1$ temperature coefficient for growth respiration [-]
$krsp2_i$ maintenance respiration rate [d^{-1}]
$krsp2_{i,20}$ maintenance respiration rate at 20 °C [d^{-1}]
$ktrsp2$ temperature coefficient for maintenance respiration [-]
$Rrsp_{k,i}$ total respiration rate for nutrient k and grazer i [gC/N/P/Si m^{-3} d^{-1}]
$Rrsp1_{k,i}$ growth respiration rate for nutrient k and grazer i [gC/N/P/Si m^{-3} d^{-1}]
$Rrsp2_{k,i}$ maintenance respiration rate for nutrient k and grazer i [gC/N/P/Si m^{-3} d^{-1}]
$Ras2_{k,i}$ actual nutrient k in food ass. rate for grazer group i [gC/N/P/Si m^{-3} d^{-1}],
$Ras3_{k,i}$ actual nutrient k in food ass. rate for grazer group i [gC/N/P/Si m^{-3} d^{-1}], diminished with growth respiration

6. Correction of grazer biomass for the food constraint
Grazers can not assimilate more food than is available. The food that is available to a grazer group on a daily basis is equal to $Ras3_{1,i}$. Consequently, the net growth rate of a grazer group should not exceed the actual food assimilation rate. If the imposed grazer biomass at

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t_2 is larger than supported by food assimilation, it must be diminished in order to meet the food constraint. The corrected grazer biomass $Cgr2c_i$ follows from:

$$Rgr1_i = \frac{(Cgr2_i - Cgr1_i \times (1 - krsp2_i \times \Delta t))}{\Delta t}$$

if $Rgr1_i > Ras3_{1,i}$,

$$Cgr2c_i = Cgr1_i \times (1 - krsp2_i \times \Delta t) + Ras3_{1,i} \times \Delta t$$

$$Rgr_i = Ras3_{1,i}$$

if $Rgr1_i \leq Ras3_{1,i}$,

$$Cgr2c_i = Cgr2_i$$

$$Rgr_i = Rgr1_i$$

with:

$Cgr1_i$	grazer biomass concentration at $t1$ [gC m^{-3}]
$Cgr2_i$	grazer biomass concentration at $t2$ [gC m^{-3}]
$Cgr2c_i$	corrected grazer biomass concentration at t2 [gC m^{-3}]
Rgr_i	actual growth rate for grazer group i [gC m^{-3} d^{-1}]
$Rgr1_i$	imposed growth rate for grazer group i [gC m^{-3} d^{-1}]
Δt	timestep [d]

Notice that Rgr_i is negative in the case of net mortality within a timestep at the decrease of grazer biomass.

7. Correction of detritus consumption and production rates for the food constraint

The total rates of food assimilation, net detritus consumption and sediment detritus production caused by grazer group i calculated above need to be corrected for changes in grazer biomass resulting from the food constraint. In case of mortality the grazer biomass decrease needs to be added to the detritus production rates. The corrected rates are:

$$Ras_{k,i} = bnut_{k,i} \times Rgr_i$$

$$Rdcns_{k,i} = Rdcns2_{k,i} + (1 - fsed_i) \times (Ras3_{k,i} - Ras_{k,i})$$

$$Rsdpr_{k,i} = Rsdpr2_{k,i} + fsed_i \times (Ras3_{k,i} - Ras_{k,i})$$

with:

$Ras_{k,i}$	nutrient k in food assimilation rate for grazer group i [gC/N/P/Si m^{-3} d^{-1}],
$Rdcns_{k,i}$	net cons. rate of grazer group i for nutrient k in detritus [gC/N/P/Si m^{-3} d^{-1}]
$Rsdpr_{k,i}$	nutrient k in detr. prod. at the sediment for grazer i [gC/N/P/Si m^{-3} d^{-1}]

Notice that these relations hold even in case of mortality within a timestep. $Ras_{k,i}$ is negative in that case and adds up to the detritus rates.

8. Total algae, detritus and inorganic nutrient conversion rates

The total rates of algae consumption, net detritus consumption, sediment detritus production and inorganic nutrient excretion caused by grazing are:

$$Racns_{k,j} = \sum_{i=1}^{n} (Racns_{k,i,j})$$

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$$Rtacns_k = \sum_{j=1}^{m} (Racns_{k,j})$$

$$Rtas_k = \sum_{i=1}^{n} (Ras_{k,i})$$

$$Rtdcns_k = \sum_{i=1}^{n} (Rdcns_{k,i})$$

$$Rtsdpr_k = \sum_{i=1}^{n} (Rsdpr_{k,i})$$

$$Rtrsp_k = \sum_{i=1}^{n} (Rrsp_{k,i})$$

with:

$Racns_{k,j}$	total consumption rate for nutrient k in algae group j [gC/N/P/Si m^{-3} d^{-1}]
$Rtacns_k$	total consumption rate for nutrient k in algae [gC/N/P/Si m^{-3} d^{-1}]
$Rtas_k$	total food assimilation rate for nutrient k [gC/N/P/Si m^{-3} d^{-1}]
$Rtdcns_k$	total consumption rate for nutrient k in detritus [gC/N/P/Si m^{-3} d^{-1}]
$Rtrsp_k$	total release rate for inorganic nutrient k by respiration [gC/N/P/Si m^{-3} d^{-1}]
$Rtsdpr_k$	total nutrient k in detr. prod. at the sediment for all grazers [gC/N/P/Si m^{-3} d^{-1}]
n	number of grazer species groups (5; [-])
m	number of algae species groups (2 for DYNAMO or 15 for BLOOM; [-])
i	index for grazer species groups [-]
j	index for algae species groups [-]
k	index for nutients, 1 = carbon, 2 = nitrogen, 3 = phosphorus, 4 = silicon [-]

9. Grazer biomass concentrations

CONSBL delivers some additional output parameters in the form of the biomass concentrations of the grazer species groups per volume of (sediment overlying) water. The output values of these parameters may deviate from the imposed biomass time series because of two reasons. The biomass may have been adjusted as described above in order to obey the growth, mortality and food constraints. The other reason is connected with interpolation over time. The output biomasses are input biomasses for t_1 at the beginning of the next timestep:

$$Cgr1_i = Cgr2c_i / fs_i$$

with:

fs_i	scaling factor for the biomass of grazer group i [-]

The scaling factor fs_i may be used to scale the grazer biomass up or down for calibration purposes. When the grazer has been indicated as zoobenthos group with option parameter $(i)UnitSw$, the biomass is expressed in [gC m^{-2}] by means of multiplication with water depth H.

Directives for use

- ◇ The proces rates in connection with grazing have a temperature basis of 20 oC. That means that input values have to be corrected when provided for another temperature basis.

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- ◇ The user needs to make a decision about how to route produced detritus in the model using the input parameters $(i)FrDetBot$. When $(i)FrDetBot = 0.0$ all detritus by grazers will be allocated to the sediment overlying water compartment (layer). All produced detritus will be added to the sediment detritus pools when $(i)FrDetBot = 1.0$.
- ◇ Grazers in CONSBL consume algae biomass and detritus from the water column only in the case of the S1-S2 option for the sediment.
- ◇ The constraints imposed on grazer biomass in relation to maximal growth or maximal mortality imply that the first adjustment of the input biomass affects the next adjustment, and so forth. When composing the input biomass time series the user should be aware of this step by step adjustment of the grazer biomasses. When differences between the imposed and adjusted time series turn out to be large or systematic, the user may want to revise the input time series in order to ensure realistic calculations of grazing pressure on algae by the model.
- ◇ The food preference parameters $(i)ALGPR(j)$ and $(i)DETPR$ are to be considered weigth factors, that must always be smaller than or equal to 1.0 the default value.
- ◇ The scaling factors $(i)GRZML$ may be used to scale the grazer biomass up or down for calibration purposes. The factors have the default value 1.0.
- ◇ $SwDetTyp$ needs to be equal to 1.0 (default) as it refers to an option for detritus substances input that does no longer exist.

Additional references

WL | Delft Hydraulics (1997), Scholten and Tol (1994),

Table 7.1: *Definitions of the input parameters in the formulations for CONSBL.*

Name in formulas	Name in input	Definition	Units
$anut_{2,1}$	$NCratGreen$	green algae spec. stoch. constant nitrogen over carbon	gN gC^{-1}
$anut_{2,2}$	$NCratDiat$	diatoms spec. stoch. constant nitrogen over carbon	gN gC^{-1}
$anut_{2,3}$	$MPB1NCrat$	epipelic diatoms spec. stoch. constant nitrogen over carbon	gN gC^{-1}
$anut_{2,4}$	$MPB2NCrat$	epipsammic diatoms spec. stoch. constant nitrogen over carbon	gN gC^{-1}
$anut_{2,j}$	$NCRAlg(j)$	BLOOM algae group spec. stoch. const. nitr. over carb.	gN gC^{-1}
$anut_{3,1}$	$PCratGreen$	green algae spec. stoch. constant phos. over carbon	gP gC^{-1}
$anut_{3,2}$	$PCratDiat$	diatoms spec. stoch. constant phosphorus over carbon	gP gC^{-1}
$anut_{3,3}$	$MPB1PCrat$	epipelic diatoms spec. stoch. constant phosphorus over carbon	gP gC^{-1}
$anut_{3,4}$	$MPB2PCrat$	epipsammic diatoms spec. stoch. constant phosphorus over carbon	gP gC^{-1}
$anut_{3,j}$	$PCRAlg(j)$	BLOOM algae group spec. stoch. const. phos. over carb.	gP gC^{-1}

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Table 7.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
$anut_{4,3}$	$SCratGreen$	green algae spec. stoch. constant silicon over carbon	gSi gC^{-1}
$anut_{4,4}$	$SCratDiat$	diatoms spec. stoch. constant silicon over carbon	gSi gC^{-1}
$anut_{4,1}$	$MPB1SCrat$	epipelic diatoms spec. stoch. constant silicon over carbon	gSi gC^{-1}
$anut_{4,2}$	$MPB2SCrat$	epipsammic diatoms spec. stoch. constant silicon over carbon	gSi gC^{-1}
$anut_{4,j}$	$SCRAlg(j)$	BLOOM algae group spec. stoch. const. sil. over carb.	gSi gC^{-1}
$Cgri2_1$	$Zooplank$	biomass concentration of zooplankton	gC m^{-3} or $^{-2}$
$Cgri2_2$	$Mussel$	biomass concentration of mussel type zoobenthos	gC m^{-3} or $^{-2}$
$Cgri2_3$	$Grazer3$	biomass concentration of grazer type 3	gC m^{-3} or $^{-2}$
$Cgri2_4$	$Grazer4$	biomass concentration of grazer type 4	gC m^{-3} or $^{-2}$
$Cgri2_5$	$Grazer5$	biomass concentration of grazer type 5	gC m^{-3} or $^{-2}$
$Calg1$	$Green$	biomass concentration of green algae (DYNAMO)	gC m^{-3}
$Calg2$	$Diat$	biomass concentration of diatoms (DYNAMO)	gC m^{-3}
$Calgj$	$BLOOMALG(j)$	biomass concentration of a BLOOM algae group	gC m^{-3}
$Cdet1$	$POC1$	detritus organic carbon concentration	gC m^{-3}
$Cdet2$	$PON1$	detritus nitrogen concentration	gN m^{-3}
$Cdet3$	$POP1$	detritus phosphorus concentration	gP m^{-3}
$Cdet4$	$Opal$	opal silicate concentration	gSi m^{-3}
H	$Depth$	depth of a water compartment (layer)	m
–	$(i)UnitSW$	group spec. option for biomass unit (1=g m^{-2}, 0=g m^{-3})	-
T	$Temp$	water temperature	°C
V	$Volume$	volume of a water comp. (layer) or sediment layer	m^3
Δt	$DELT$	time interval, that is the DELWAQ timestep	d
$bnut_{1,i}$	$(i)GRZSTC$	stoch. constant for carbon over carbon in grazer i	gC gC^{-1}

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Table 7.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
$bnut_{2,i}$	$(i)GRZSTN$	stoch. constant for nitrogen over carbon in grazer i	gN gC^{-1}
$bnut_{3,i}$	$(i)GRZSTP$	stoch. constant for phosphorus over carbon in grazer i	gP gC^{-1}
$bnut_{4,i}$	$(i)GRZSTSi$	stoch. constant for silicon over carbon in grazer i	gSi gC^{-1}
$fapr_{i,1}$	$(i)ALGPRGrn$	preference of grazer i for green algae (DYNAMO)	-
$fapr_{i,2}$	$(i)ALGPRDiat$	preference of grazer i for diatoms (DYNAMO)	-
$fapr_{i,1}$	$(i)ALGPRPeli$	preference of grazer i for epipelic benthic diatoms	-
$fapr_{i,2}$	$(i)ALGPRPsam$	preference of grazer i for epipsammic benthic diatoms	-
$fapr_{i,j}$	$(i)ALGPR(j)$	preference of grazer i for BLOOM algae group j	-
$fdpr_i$	$(i)DETPR$	preference of grazer i for detritus	-
$falg_{i,1}$	$(i)ALGFFGrn$	egested fraction of green algae consumed by grazer i	-
$falg_{i,2}$	$(i)ALGFFDiat$	egested fraction of diatoms consumed by grazer i	-
$falg_{i,1}$	$(i)ALGFFPeli$	egested fraction of epipelic diatoms consumed by grazer i	-
$falg_{i,2}$	$(i)ALGFFPsam$	egested fraction of epipsammic diatoms consumed by grazer i	-
$falg_{i,j}$	$(i)ALGFF(j)$	egested fraction of algae j consumed by grazer i	-
$fdet_i$	$(i)DETFF$	egested fraction of detritus consumed by grazer i	-
$fsed_i$	$(i)FrDetBot$	fr. of produced detr. by grazer i to sediment detr. pool	-
fs_i	$(i)GRZML$	scaling factor for the biomass of grazer i	-
$frsp1_{i,20}$	$(i)GRZRE$	growth respiration fraction for grazer i at 20 °C	-
$kgr_{i,20}$	$(i)GRZGM$	maximal growth rate of grazer i at 20 °C	d^{-1}
$kmup_{i,k,20}$	$(i)GRZRM$	maximal uptake rate of grazer i at 20 °C	d^{-1}
$kmrt_{i,20}$	$(i)GRZMM$	maximal mortality rate of grazer i at 20 °C	d^{-1}

continued on next page

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Table 7.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
$krsp2_{i,20}$	$(i)GRZSE$	maintenance respiration rate for grazer i at 20 °C	d^{-1}
$Ksfd_i$	$(i)GRZMO$	half saturation constant for food uptake by grazer i	gC m^{-3+}
$ksfil_{i,20}$	$(i)GRZFM$	maximal specific filtration rate of grazer i at 20 °C	m^3 gC^{-1} d^{-1}
$ktfil$	$(i)TMPFM$	temperature coefficient of filtration for grazer i	$°C^{-1}$
$ktgr$	$(i)TMPGM$	temperature coefficient of growth for grazer i	$°C^{-1}$
$ktmrt$	$(i)TMPMM$	temperature coefficient of mortality for grazer i	$°C^{-1}$
$ktrsp1$	$(i)TMPRE$	temperature coeff. of growth respiration for grazer i	$°C^{-1}$
$ktrsp2$	$(i)TMPSE$	temperature coeff. of maintenance resp. for grazer i	$°C^{-1}$
$ktup$	$(i)TMPRM$	temperature coefficient of uptake for grazer i	°C-1

[1](i) indicates grazer species groups 1–5, respectively Z for zooplankton, M for mussel type zoobenthos, G3, G4 and G5 for user defined groups.

[2](j) indicates BLOOM algae species groups 1–30.

Table 7.2: *Definitions of the output parameters for CONSBL.*

Name in formulas	Name in output	Definition	Units
$Cgr1_1$	$CZooplank$	biomass concentration of zooplankton	gC $m^{-3 \text{ or } -2}$
$Cgr1_2$	$CMussel$	biomass concentration of mussel type zoobenthos	gC $m^{-3 \text{ or } -2}$
$Cgr1_3$	$CGrazer3$	biomass concentration of grazer type 3	gC $m^{-3 \text{ or } -2}$
$Cgr1_4$	$CGrazer4$	biomass concentration of grazer type 4	gC $m^{-3 \text{ or } -2}$
$Cgr1_5$	$CGrazer5$	biomass concentration of grazer type 5	gC $m^{-3 \text{ or } -2}$

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7.2 Grazing by zooplankton and zoobenthos (DEBGRZ, DEBGRP)

PROCESS: DEBGRZ, DEBGRP

The consumption of algae and detritus by zooplankton and zoobenthos is called grazing. Grazer related processes are filtration, ingestion, and digestion of food components, (pseudo)faeces production and respiration, as well as growth and mortality.

The grazer module DEBGRZ simulates grazing using a fully dynamic approach, which contrasts with the semi-dynamic approach of the CONSBL routine. The grazing module is based on the Dynamic Energy Budget (DEB) theory. DEB-theory is a modelling framework based on first principles and simple physiology-based rules that describe the uptake and use of energy and nutrients and the consequences for physiological organization throughout an organism's life cycle Kooijman (2010). DEB models are generic models of organism growth, and can be used for basically any species or life stage. The aspect that makes DEB framework unique and separates it from more traditional "net production" models, is its compartmented energy storage or reserve dynamics.

The DEBGRZ module is originally set up for (passive) shellfish, but can also be used for other benthic or suspended filter feeders as well as for (active) pelagic filter feeders, but note that the organisms are described by multiple state variables such that the exchange of active organisms between grid cells may lead to changes in the ratios of their state variables.

Note: Since the PROTIST module represents algae via separate pools of carbon, nitrogen, phosphorus, silica and chlorophyll, a separate process module was made to accommodate for this configuration. This process module is called DEBGRP. It works in much the same way as DEBGRZ, but please note that the algae modules BLOOM, DYNAMO and PROTIST should not be mixed.

DEBGRP has been set up in the same way as DEBGRZ, so that in this chapter DEBGRP is synonymous to DEBGRZ, when the PROTIST algal module is used.

The different representation, via separate pools, means that the ratios carbon to nutrients are not input parameters but rather derived from the respective pools.

Implementation

The module allows for maximally 5 different grazer populations or cohorts, which may belong to different species (groups), and which may be simulated separately or simultaneously. Physiological parameter settings determine which species (group) is simulated. Option parameter SWBen specifies whether the grazers are pelagic (i.e. passively transported by the water, SWBEN=0), benthic (fixed to the bottom, SWBEN=1), or suspended (fixed to some structure at any vertical position in the water column, SWBEN=2). Parameter FrDetBot determines whether dead material is released into the water column (FrDetBot = 0) or ends up in the sediment (FrDetBot = 1). Parameter SFSusp determines whether (or to what extent) the grazers are deposit feeders or filterfeeders. Finally, the option parameter SwV1 determines whether the simulated grazers represent a cohort (i.e. a group of equal individuals with individual sizes that increase over time, SwV1=0) or to a (simplified) population (i.e. a group of different individuals with an overall size distribution that is constant over time, SwV1=1).

Cohorts ($(i)_SwV1 = 1$) are described by four state variables:

1 total structural biomass ($(i)_V$),
2 total energy biomass ($(i)_E$),

3 total gonadal biomass ($(i)_R$), and
4 the number of individuals ($(i)_N$).

For simplified populations ($(i)_SwV1 = 0$) the number of individuals becomes a derived variable instead of a state variable, such that only three state variables remain. For pelagic (active) grazers, initial values for all state variables need to be specified in units per volume [m^{-3}], whereas for benthic or suspended grazers the initial values must be provided in units per surface area [m^{-2}]. Note that the initial length of organisms in cohorts is defined by the combination of structural volume and number of individuals.

By default the first grazer corresponds to a simplified population of mussels (Mussel), the second to a simplified population of mesozooplankton (Zoopl), and the three remaining grazers to cohorts of small, medium, and large shellfish (Grazer3, Grazer4, Grazer5). Note that Grazer3 and Grazer4 have been configured to represent sedentary organisms and Grazer5 has been configured to represent organisms that are transported along with the water flow.

DEBGRZ can be used in combination with any of the sediment options, being stand-alone, S1/2 and S1 in combination with SWITCH or GEMSED. It is necessary to select the detritus substances using option parameter SwDetTyp. DetX is selected for SwDetTyp = 0:0, POX for SwDetTyp = 1:0.

DEBGRZ has been implemented for the following substances:

for BLOOM,

◇ ALGC, ALGN, ALGP, ALGSi, MPB1peli, MP2psam, BLOOMALG01-BLOOMALG30, POC1, PON1, POP1, OPAL, DETCS1, DETNS1, DETPS1, DETSiS1, NH4, NO3, PO4, Si, OXY, TIC and ALKA

for DYNAMO,

◇ GREEN, DIAT, PB1peli, MP2psam, POC1, PON1, POP1, OPAL, DETCS1, DETNS1, DETPS1, DETSiS1, NH4, NO3, PO4, Si, OXY, TIC and ALKA

for PROTIST,

◇ Diatoms: DIAT1 (diatC_1, diatChl_1, diatN_1, diatP_1, diatSi_1), DIAT2 (diatC_2, diatChl_2, diatN_2, diatP_2, diatSi_2)
◇ Green algae: GREEN1 (greenC_1, greenChl_1, greenN_1, greenP_1), GREEN2 (greenC_2, greenChl_2, greenN_2, greenP_2)
◇ Constitutive mixoplankton: CM1 (cmC_1, cmChl_1, cmN_1, cmP_1), CM2 (cmC_2, cmChl_2, cmN_2, cmP_2)
◇ Non-consitutive mixoplankton: NCM1 (ncmC_1, ncmChl_1, ncmN_1, ncmP_1), NCM2 (ncmC_2, ncmChl_2, ncmN_2, ncmP_2)
◇ Protozooplankton: ZOO1 (zooC_1, zooN_1, zooP_1), ZOO2 (zooC_2, zooN_2, zooP_2)
◇ POC1, PON1, POP1, OPAL, DETCS1, DETNS1, DETPS1, DETSiS1, NH4, NO3, PO4, Si, OXY, TIC and ALKA

Sulfur is not considered by DEBGRZ. In addition for DEBGRP: benthic diatoms are not currently considered.

Currently, grazing of microphytobenthos is limited to the pelagic fraction, grazing of the benthic fraction is not included.

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Table 7.3 and Table 7.4 provide the definitions of the parameters occurring in the user-defined input and output.

Formulation

The mass fluxes caused by grazing are described in the following sections:

1 Individual dynamics
   - 1.1 Filtration, ingestion, and assimilation
   - 1.2 Growth and maintenance
   - 1.3 Maturity and reproduction
   - 1.4 Respiration
   - 1.5 Temperature dependency

2 From individuals to populations
   - 2.1 Standard approach: isomorphs
   - 2.2 Simplified approach: V1-morphs
   - 2.3 Total grazer rates of change
   - 2.4 Total algae, detritus and inorganic nutrient rates of change
   - 2.5 Total grazer biomass and other derived variables;

1. Individual dynamics

Although the DEBGRZ module calculates state variables that refer to the total population or cohort, the heart of the code is based on DEB theory (Kooijman (2010)) which is formulated at the individual level. Some additions have been made to the standard DEB equations to incorporate filterfeeding-specific aspects. These additions are not new but have been included before in other shellfish modelling studies using DEB, such as Bacher and Gangnery (2006), Pouvreau et al. (2006), and Rosland et al. (2009).

1.1 Filtration, uptake and assimilation

Shellfish are filter feeders for whom the relation between food uptake and food density can be described by a Holling Type II response curve Holling (1959) that is adjusted for the negative influence of inorganic matter in the filtration capacity of bivalves Kooijman (2006). The negative effect of inorganic matter can be compensated for by higher food concentrations (competitive inhibition):

$$f_i = \frac{Cfd_i}{Ksfd'_i + Cfd_i}$$

in which

$$Ksfd'_i = Ksfd_i \left(1 + \frac{Ctim}{Kstim_i}\right)$$

with:

Cfd_i	food concentration available to grazer i [gC m^{-3}]
$Ctim$	concentration of inorganic matter [g m^{-3}]
f_i	scaled functional response of grazer i [-]
$Ksfd_i$	half saturation constant for food uptake by grazer i [gC m^{-3}]
$Ksfd'_i$	half saturation constant for food uptake by grazer i adjusted for the negative influence of inorganic matter [gC m^{-3}]
$Kstim_i$	half saturation constant for the negative effect of inorganic matter on food uptake [gC m^{-3}]
i	index for grazer species groups 1–5 [-]

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The food concentration available to grazer i is the summed concentration of all edible particles. Some particles are too small and pass through the filtering apparatus, which (passive) selection mechanism is implemented in the model by a preference coefficient for each of the food components:

$$Cfd_i = fdpr_i \times Cdet_1 + \sum_{j=1}^{m}(fapr_i \times Calg_j)$$

with:

Cfd_i	food concentration available to grazer species group i [gC m^{-3}]
$Calg_j$	biomass concentration of algae species group j [gC m^{-3}]
$Cdet_1$	detritus organic carbon concentration [gC m^{-3}]
$fdpr_i$	preference of a grazer species group i for detritus [-]
$fapr_{i,j}$	preference of grazer type i for algae type j [-]
m	number of algae groups, different for (BLOOM) and (DYNAMO) [-]
i	index for grazer species groups (at most 5) [-]
j	index for algae species groups (depends on whether BLOOM is used or DYNAMO) [-]

According to the DEB theory, the energy ingestion rate is defined as:

$$Pupte = kuptm_{i,20} \times f_i \times V_i^{\frac{2}{3}} \times kT_i$$

with:

f_i	scaled functional response of grazer type i [-]
$kuptm_{i,20}$	maximum surface-area-specific ingestion rate of grazer i at 20 °C [J cm^{-2} d^{-1}]
kT_i	Arrhenius rate of change of chemical reaction processes due to temperature (see section 1.5) [-]
$Pupte_i$	energy ingestion rate [J ind^{-1} d^{-1}]
V_i	structural biovolume of an individual grazer of type i [cm^3 ind^{-1}]

In the DEBGRZ module the carbon uptake rates are derived from the energy ingestion rate by means of the energy-to-carbon conversion factor cec. Also, they are increased by the indigestible fractions of algae $falg$ and detritus $fdet$. These indigestible fractions do not contribute to the ingested energy since they are assumed to be low in energy, but they do contribute to the amount of ingested carbon. Hence, these fractions implicitly define the carbon specific energy content of each food component.

$$Puptd_{i,j} = Pupte_i \times \frac{cec_i}{(1 - fdet_i)}$$

$$Pupta_{i,j} = Pupte_i \times \frac{cec_i}{(1 - falg_{i,j})}$$

with:

cec_i	energy to carbon conversion factor [gC J^{-1}]
$fdet_i$	egested fraction of detritus consumed by grazer i [-]
$falg_{i,j}$	egested fraction of algae j consumed by grazer i [-]
$Pupte_i$	energy ingestion rate of grazer i [J ind^{-1} d^{-1}]
$Puptd_i$	uptake rate of detritus for grazer i [gC ind^{-1} d^{-1}]
$Pupta_{i,j}$	uptake rate of algal species j for grazer i [gC ind^{-} d^{-1}]

Filtration rates are derived from the carbon uptake rates by increasing them by pseudofaeces losses. These losses stem from active selection, which is incorporated in the module by

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means of the ingestion-efficiency coefficient κ_I. This coefficient defines the fraction of the filtered food that is actually ingested, while the remaining part $(1 - fie)$ is excreted as pseudofaeces. Although pseudofaeces and faeces may have different characteristics with respect to sedimentation and mineralization, these differences are not (yet) taken into account in this module, and both products end up in the same detritus pool. But note that the stoichiometry of detritus will vary according to its constituents, and that its mineralisation rate depends on this stoichiometry.

$$Pfild_{i,j} = Puptd_{i,j}/\kappa_{I,i}$$

$$Pfila_{i,j} = Pupta_{i,j}/\kappa_{I,i}$$

$$Pfildn_{k,i} = Pfild_i \times Cdet_k/Cdet_1$$

$$Pfilan_{k,i,j} = Pfila_{k,i} \times anut_{k,j}$$

$$Pfiln_{k,i} = Pfildn_{k,i} + \sum_{j=1}^{m}(Pfilan_{k,i,j})$$

with:

$anut_{k,j}$	stoichiometric constant of algal species j for nutrient k [gC/gN/gP/gSi gC^{-1}]
$Cdet_k$	detritus organic carbon concentration [gC m^{-3}]
$\kappa_{I,i}$	ingestion efficiency coefficient of grazer i [-]
$Pfild_i$	filtration rate of detritus for grazer i [gC ind^{-1} d^{-1}]
$Pfila_{i,j}$	filtration rate of algal species j for grazer i [gC ind^{-} d^{-1}]
$Pfildn_{k,i}$	filtration rate of nutrient k from detritus for grazer i [gC ind^{-} d^{-1}]
$Pfilan_{k,i}$	filtration rate of nutrient k from algal species j for grazer i [gC ind^{-1} d^{-1}]
$Pfiln_{k,i}$	filtration rate of nutrient k for grazer i [gC ind^{-1} d^{-1}]

Assimilation rates are determined from the filtration rates through correction for the faecal fractions and ingestion efficiencies. In addition, assimilation rates are corrected for the differences in the nutrient stochiometries of grazers, algae and detritus: the most limiting nutrient determines the actual assimilation rates for all nutrients. The remaining portions of the other nutrients are egested as detritus, as are the indigestible fractions. Optionally, an additional and constant efficiency loss can be included by means of the assimilation-efficiency coefficient κ_A:

$$Pa1_{k=1,i} = \times\kappa_{I,i}\times\kappa_{A,i}\times\left((1 - fdet_i) \times Pfildn_{k,i} + \sum_{j=1}^{m}((1 - falg_{i,j}) \times \kappa_{I,i} \times Pfilan_{k,i,j})\right)$$

$$Pa1_{k=2-4,i} = \kappa_{I,i} \times \kappa_{A,i}\left(\times Pfildn_{k,i} + \sum_{j=1}^{m}(Pfilan_{k,i,j})\right)$$

$$Pa2_{k,i} = \min_{k=1-4}(Pa1_{k,i}/bnut_{k,i})$$

$$Pdef_{k,i} = Puptn_{k,i} - Pa2_{k,i}$$

with:

$bnut_{k,i}$	stoch. constant for nutrient k over carbon in grazer i [gC/gN/gP/gSi gC^{-1}]
$fdet_i$	egested fraction of detritus consumed by grazer i [-]
$falg_{i,j}$	egested fraction of algae j consumed by grazer i [-]

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$\kappa_{I,i}$	ingestion efficiency coefficient of grazer i [-]
$\kappa_{A,i}$	assimilation efficiency coefficient of grazer i [-]
$Pa1_{k,i}$	potential assimilation rate of nutrient k [gC/gN/gP/gSi ind^{-1} d^{-1}]
$Pa2_{k,i}$	actual assimilation rate of nutrient k [J ind^{-1} d^{-1}]
$Pdef_{k,i}$	faeces production rate of nutrient k [gC/gN/gP/gSi ind^{-1} d^{-1}]

1.2 Growth and maintenance

Assimilated energy is incorporated into a reserve pool from which it is mobilized and then used for maintenance, growth, development and reproduction. The catabolic or energy mobilization rate is defined as follows:

$$Pc_i = \frac{E_i/V_i}{\kappa_i \times E_i/V_i + keg_i} \times \frac{\kappa_{A,i} \times kuptm_{i,20} \times kT_i \times keg_i}{kem_i} \times V_i^{\frac{2}{3}} + kpm_i \times V_i \times kT_i$$

with:

$\kappa_{A,i}$	assimilation efficiency coefficient of grazer i [-]
κ	fraction of mobilized energy to growth and maintenance of grazer i [-]
keg_i	volume-specific costs for growth of grazer i [J cm^{-3}]
kem_i	maximum energy density of grazer i [J cm^{-3}]
$kuptm_{i,20}$	maximum surface area-specific ingestion rate of grazer i at 20 °C [J cm^2 d^{-1}]
$kpm_{i,20}$	volumetric costs of maintenance for grazer i at 20 °C [J cm^{-3} d^{-1}]
kT_i	Arrhenius rate of change of chemical reaction processes due to temperature (see section 1.5)[-]
Pc_i	energy mobilization rate of grazer i [J ind^{-1} d^{-1}]
V_i	structural biovolume of individual grazer of type i [cm^3 ind^{-1}]
E_i	energy reserves of individual grazer of type i [J cm^{-3}]

A constant fraction κ of the mobilized energy is allocated to growth and maintenance. The maintenance rate is determined by the structural volume and the volume specific maintenance costs. The remaining energy flux will be used for growth. When the energy required for maintenance is higher than the energy available for growth and maintenance, maintenance is paid from structural volume. This will require additional overhead costs which we assume to be proportional to those required for growth, and will result in shrinking of the organism.

$$Pm_i = kpm_i \times V_i \times kT_i$$

$$Pg_i = (\kappa_i \times Pc_i - Pm_i)$$

if $Pg_i > 0$,

$$Pv_i = \kappa_{G,i} \times Pg_i$$

if $Pg_i \leq 0$,

$$Pv_i = (1 + (1 - \kappa_{G,i})) \times Pg_i$$

$$Pm_i = Pm_i + \text{abs}((1 - \kappa_{G,i}) \times Pg_i)$$

in which:

$$\kappa_{G,i} = \frac{cvc_i}{keg_i \times cec_i}$$

with:

cec_i	conversion coefficient from energy to carbon of grazer i [gC J^{-1}]
cvc_i	conversion coefficient from volume to carbon of grazer i [gC cm^{-3}]

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κ_i	fraction of mobilized energy to growth and maintenance [-]
$\kappa_{G,i}$	growth efficiency [-]
keg_i	volume specific costs for growth of grazer i [J cm^{-3}]
kpm_i	volumetric costs of maintenance for grazer i at 20 °C [J cm^{-3} d^{-1}]
kT_i	Arrhenius rate of change of chemical reaction processes due to temperature for grazer i [-]
Pg_i	energy flux to growth of grazer i [J ind^{-1} d^{-1}]
Pm_i	maintenance rate of grazer i [J ind^{-1} d^{-1}]
Pc_i	energy mobilization flux of grazer i [J ind^{-1} d^{-1}]
Pv_i	growth rate of structural biovolume of grazer i [cm^3 ind^{-1} d^{-1}]
V_i	structural biovolume of individual grazer of type i [cm^3 ind^{-1}]

1.3 Maturity and reproduction

The fraction $(1 - \kappa)$ of the mobilized energy Pc goes to maturation, maturity maintenance, and reproduction. These fluxes differ between adults and juveniles. The transition of juvenile to adult occurs at a fixed volume Vp. For juveniles, the maturity maintenance costs are proportional to their actual structural volume, while for adults they are proportional to the volme at puberty. Juveniles use all of the remaining energy for development of reproductive organs and regulation systems. When juveniles have too little energy available for development and/or maturity maintenance, these processes simply stop without further consequence. Adults, which do not have to invest in development anymore, use the remaining energy flux Pr for production of gonadal tissue R. When adults have too little energy available for maturity maintenance, gonadal tissue will be used instead. This will entail overhead costs that are proportional to those for production of gonads.

$$Pjj_i = \frac{1-\kappa_i}{\kappa_i} \times kpm_i \times V_i \times fjuv_i \times kT_i$$

$$Pja_i = \frac{1-\kappa_i}{\kappa_i} \times kpm_i \times Vp_i \times fadult_i \times kT_i$$

$$Prj_i = (1-\kappa_i)Pc_i \times fjuv_i - Pjj_i$$

$$Pra_i = (1-\kappa_i)Pc_i \times fadult_i - Pja_i$$

if $Pra_i > 0$,

$$Pr_i = \kappa_{R,i} \times Pra_i$$

if $Pra_i \leq 0$,

$$Pr_i = (1 + (1-\kappa_{R,i})) * Pra_i$$

$$Pja_i = Pja_i + \text{abs}((1-\kappa_{R,i}) * Pra_i)$$

with:

$fadult$	adult fraction of cohort/population of grazer type i [-]
$fjuv_i$	juvenile fraction of cohort/population of grazer type i [-]
κ_i	fraction of mobilized energy to growth and maintenance [-]
$\kappa_{R,i}$	reproduction efficiency [-]
$kpm_{i,20}$	volumetric costs of maintenance for grazer i at 20 °C [J cm^{-3} d^{-1}]
Pjj_i	maturity maintenance flux of juvenile grazers of type i [J ind^{-1} d^{-1}]
Pja_i	maturity maintenance flux of adult grazers of type i [J ind^{-1} d^{-1}]
Prj_i	maturity development flux of juvenile grazers of type i [J ind^{-1} d^{-1}]
Pra_i	energy flux to reproduction of adult grazers of type i [J ind^{-1} d^{-1}]

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Pr_i	gonadal production rate of adult grazers of type i [J ind^{-1} d^{-1}]
Pc_i	energy mobilization flux of grazer type i [J ind^{-1} d^{-1}]
V_i	structural biovolume of individual grazer of type i [cm^3 ind^{-1}]
Vp_i	biovolume at start of reproductive age for individual grazer of type i [cm^3 ind^{-1}]

Spawning events occur when enough energy has been allocated into the gonads ($GSI > GSIupr$) and when the water temperature is above a threshold value ($T > Tspm$). Gonads are released from the buffer at a certain rate per day $kspr_i$ until the temperature drops below the threshold value or the GSI drops below an lower threshold value $GSIlwr$.

$$Pspw_i = kspr_i \times R_i + \kappa_{R,i} \times max(Pra_i, 0.)$$

where:

$$GSI_i = \frac{cec_i \times R_i}{cvc_i \times fadult \times V_i + cec_i \times fadult_i \times E_i + cec_i \times R_i}$$

with:

cec_i	conversion coefficient from energy to carbon of grazer i [gC J^{-1}]
cvc_i	conversion coefficient from volume to carbon of grazer i [gC cm^{-3}]
$fadult$	adult fraction of population [-]
$\kappa_{R,i}$	fraction of reproduction flux to gonadal tissue [-]
$kspr_i$	gonadal release rate at spawning for grazer i [d^{-1}]
Pra_i	energy flux to reproduction of adult grazers of type i [J ind^{-1} d^{-1}]
GSI_i	gonadal somatic index of grazer type i [-]
V_i	structural biovolume of individual grazer of type i [cm^3 ind^{-1}]
E_i	energy reserves of individual grazer of type i [J ind^{-1}]
R_i	gonadal reserves of individual grazer of type i[J ind^{-1}]
$Pspw_i$	spawning rate of grazer type i [J ind^{-1} d^{-1}]

1.4 Respiration

Respiration is the sum of the maintenance rate, maturation flux, development flux, and overhead costs for reproduction and growth:

$$Pres_i = Pm_i + Pjj_i + Pja_i + Prj_i + (1-\kappa_{G,i}) \times \text{max}(Pg_i, 0.) + (1-\kappa_{R,i}) \times \text{max}(Pra_i, 0.)$$

with

$\kappa_{G,i}$	growth efficiency [-]
$\kappa_{R,i}$	reproduction efficiency [-]
Prj_i	development flux of grazer type i [J ind^{-1} d^{-1}]
Pm_i	maintenance rate of grazer type i [J ind^{-1} d^{-1}]
Pja_i	maturation flux of grazer type i [J ind^{-1} d^{-1}]
Pjj_i	energy flux to maturity maintenance of grazer type i [J ind^{-1} d^{-1}]
$Pres_i$	respiration rate of grazer type i [J ind^{-1} d^{-1}]

1.5 Temperature dependency It is assumed that all physiological rates are affected by temperature in the same way. This temperature effect is based on an Arrhenius type relation, which describes the rates at ambient temperature T as follows:

$$kT = e^{\left(\frac{Ta_i}{Tref+273} - \frac{Ta_i}{T+273}\right)} \times \frac{1 + e^{\left(\frac{Tal_i}{Tref+273} - \frac{Tal_i}{Tl_i}\right)} + e^{\left(\frac{Tah_i}{Th_i} - \frac{Tah_i}{Tref+273}\right)}}{1 + e^{\left(\frac{Tal_i}{T+273} - \frac{Tal_i}{Tl_i}\right)} + e^{\left(\frac{Tah_i}{Th_i} - \frac{Tah_i}{T+273}\right)}}$$

with:

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kT_i	Arrhenius rate of change of chemical reaction processes due to temperature [-]
T	water temperature [°C]
Ta_{ref}	reference temperature (set to 20°C) [°C]
Ta_i	Arrhenius temperature for grazer i [K]
Tah_i	Arrhenius temperature for rate of decrease at upper boundary for grazer i [K]
Tal_i	Arrhenius temperature for rate of decrease at lower boundary for grazer i [K]
Tl_i	Lower temperature boundary for grazer i [K]
Th_i	Upper temperature boundary for grazer i [K]

2. From individuals to populations The equations above apply to growth and reproduction of individual organisms. The DEBGRZ module provides two approaches to scale up the equations to the population level.

2.1 Default approach: isomorphs The default, and most straightforward, approach to scale up the individual dynamics to the population level is by grouping the individuals into various age classes (cohorts). Each cohort consists of a number of equal individuals following the same growth trajectory. The total number of individuals in a cohort is included as an additional state variable. This number is the resultant of its rates of change: the recruitment rate and the mortality rate.

Recruitment is not included as a dynamic process but can be included by (manual) initialization of a new cohort. Mortality is implemented as a first order decrease of the number of individuals in the cohort. A distinction is made between natural mortality and harvesting, where harvesting does not depend on temperature and harvested material will leave the system, while natural mortality does depend on temperature and will end up in the local detritus pool. Both mortality rates may be made dependable on the size of the individuals by setting $kmrt1B$ and $kmrt2B$ unequal 0:

$$kmrt1_i = kmrt1_i^{1,20} \times L_i^{klmrt1_i} \times kT_i$$

$$kmrt2_i = kmrt2_i^{1} \times L_i^{klmrt2_i}$$

in which:

$$L_i = V_i^{1/3}/kshp_i$$

with

$kmrt1_i$	mortality rate [d^{-1}]
$kmrt2_i$	harvesting rate [d^{-1}]
$kmrt1_i^{1,20}$	reference mortality rate of grazer i for individuals of 1 cm at 20 [d^{-1}]
$kmrt2_i^{1}$	reference harvesting rate of grazer i for individuals of 1cm [d^{-1}]
$klmrt1_i$	length dependency coefficient of mortality rate [-]
$klmrt2_i$	length dependency coefficient of harvesting rate [-]
$kshp_i$	shape coefficient for grazer i [-]
kT_i	Arrhenius rate of change of chemical reaction processes due to temperature [-]
L_i	individual length of grazer i [cm]
V_i	structural biovolume of individual grazer of type i [cm^3 ind^{-1}]

Note that in this approach starvation will lead to a decrease in the structural volume, but not to enhanced mortality. Starvation occurs when the growth rate Pg becomes negative.

2.2 Simplified approach: V1-morphs
An alternative, simplified, approach to scale up the individual growth model to the population level is available in the DEBGRZ module. In this approach the difference between individuals

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and the population is eliminated, and the population is considered as a whole. This approach requires some additional assumptions, but requires less state variables, which makes the model easier to initialize, calibrate and/or analyse. This makes it specifically suitable when only little information is available about the population size- or age distribution, or when the model objective is system-oriented rather than grazer-oriented.

implementation and consequences of the V1-morph approach:

- ◇ The alternative approach is implemented by modeling the organisms as so-called "V1-morphs". V1-morphs are a specific class of shape-changing organisms that have a constant surface-to-volume ratio (Kooijman (2010)). The corresponding assumption is that the size distribution of the population remains constant.
- ◇ A surface-to-volume ratio is achieved by making the body size L an input parameter instead of an output parameter ($L = Lref$). Note that reference length L_{ref} erpresents the average length (weighted by structural body volume) and thus characterizes the population size composition, which makes it an important parameter affecting the physiological behaviour of the whole population.
- ◇ As a result of the constant size L_{ref}, the structural body volume per individual V becomes constant as well ($V = (Lref/kshp)^3$). Note that individual energy reserves E and gonads R will remain dynamic state variables that may vary over time.
- ◇ Also, the number of individuals is no longer a dynamic state variable but can now be derived from the total structural biomass $Cgrv$ divided by the individual length V and is provided as output variable: $Cgrn = Cgrv/V = Cgrv/(Lref \times kshp)^3$.
- ◇ For V1-morphs, starvation ($Pg \leq 0$) will lead to a decrease in the number of individuals $Cgrn$, and thus to an increased mortality (while for isomorphs, it leads to shrinking of the individual structural body volume).
- ◇ In the V1-morph approach, recruitment can be implemented by a first order increase. Hence, mortality and recruitment may be combined into one net (mortality) rate. Underlying assumption is that the larvae prefer settling at locations where conspecifics are already present.
- ◇ Reproduction related processes depend on a critical volume Vp at which the transition from juvenile to adult occurs. For V1-morphs, it is assumed that a fraction $Vp/(Vp + Vref)$ of the population consists of juveniles, while the remaining fraction consists of adults. This fraction depends on the reference size relative to the critical volume as follows:

$$
\begin{aligned}
fjuv_i &= \frac{Vp}{Vp + Vref} && \text{if} \quad SwV1 = 1 \\
fjuv_i &= 0 && \text{if} \quad (SwV1 = 0 \text{and} V_i > V_p) \\
fjuv_i &= 1 && \text{if} \quad (SwV1 = 0 \text{and} V_i \leq V_p) \\
fadult_i &= 1 - fjuv_i
\end{aligned}
$$

2.3 Total grazer rates

The total mass fluxes for the whole cohort or population are calculated by multiplying the individual energy fluxes by the number of individuals in the cohort or population and converting them to mass fluxes. Note that isomorphs only grow in terms of their individual size, while V1-morphs only grow with respect to their number of individuals. This results in the following rates of change for each of the state variables of grazer i:

$$Rgrv_i = cec_i \times Pv_i \times Cgrn_i$$

$$Rgre_i = cec_i \times (Pa2_i - Pc_i) \times Cgrn_i$$

$$Rgrr_i = cec_i \times Pr_i \times Cgrn_i$$

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$$Rgrn_i = 0 \quad \text{if} \quad SwV1 = 0$$
$$Rgrn_i = cec_i \times (Pv_i / V_i) \times Cgrn_i \quad \text{if} \quad SwV1 = 1$$

$$Rmrv_i = cvc_i \times (kmrt1_i + kmrt2_i) \times V_i \times Cgrn_i$$
$$Rmre_i = cvc_i \times (kmrt1_i + kmrt2_i) \times E_i \times Cgrn_i$$
$$Rmrr_i = cvc_i \times (kmrt1_i + kmrt2_i) \times R_i \times Cgrn_i$$
$$Rmrn_i = (kmrt1_i + kmrt2_i) \times Cgrn_i$$

with

$Cgrn_i$	number of individuals of grazer type i [# m^{-3}] or [$^{-2}$]
cec_i	conversion coefficient from energy to carbon of grazer i [gC J^{-1}]
cvc_i	conversion coefficient from volume to carbon of grazer i [gC cm^{-3}]
$kmrt1_i$	mortality rate of grazer type i [d^{-1}]
$kmrt2_i$	harvesting rate of grazer type i [d^{-1}]
$Pa2_{k,i}$	actual assimilation rate of nutrient k for grazer type i [J ind^{-1} d^{-1}]
Pc_i	energy mobilization flux of grazer type i [J ind^{-1} d^{-1}]
Pv_i	growth rate of structural biovolume of grazer type i [cm^3 d^{-1}]
Pr_i	gonadal production rate of adult grazers of type i [J ind^{-1} d^{-1}]
$Rgrv_i$	total growth rate of structural volume of grazer i
$Rgre_i$	total growth rate of energy reserves of grazer i
$Rgrr_i$	total growth rate of structural volume of grazer i
$Rgrn_i$	total increase rate of number of individuals due to growth of grazer i
$Rmrv_i$	total decrease rate of structural volume due to growth of grazer i [d^{-1}]
$Rmre_i$	total decrease rate of energy reserves due to mortality of grazer i [d^{-1}]
$Rmrr_i$	total decrease rate of gonadal reserves due to mortality of grazer i [d^{-1}]
$Rmrn_i$	total decrease rate of number of individuals due to mortality of grazer i [d^{-1}]
V_i	structural biovolume of individual grazer of type i [cm^3 ind^{-1}]
E_i	energy reserves of individual grazer of type i [J ind^{-1}]
R_i	gonadal reserves of individual grazer of type i [J ind^{-1}]

2.4 Total algae, detritus and inorganic nutrient rates of change

Uptake rate for each of the algal species and detritus are:

$$Racns_{k,j} = Puptdn_{k,i} \times Cgrn_i$$

$$Rdcns_{k,j} = Puptan_{k,i,j} \times Cgrn_i$$

with

$Cgrn_i$	number of individuals of grazer type i [# m^{-3} or $^{-2}$]
$Puptdn_{k,i}$	uptake rate of nutrient k from detritus for grazer i [gC ind$^-$ d^{-1}]
$Puptan_{k,i}$	uptake rate of nutrient k from algal species j for grazer i [gC ind^{-1} d^{-1}]
$Racns_{k,j}$	total consumption rate for nutrient k in algae group j [gC/N/P/Si m^{-3} d^{-1}]
$Rdcns_{k,j}$	total consumption rate for nutrient k in detritus [gC/N/P/Si m^{-3} d^{-1}]
i	index for grazer species groups [-]
j	index for algae species groups [-]
k	index for nutients, 1 = carbon, 2 = nitrogen, 3 = phosphorus, 4 = silicon [-]

The detritus production rates for each of the nutrients are the sum of the natural mortality fluxes from the three body compartments (structural volume, energy reserves and gonads) and the spawning flux (survival of spawned eggs is assumed to be negligible). The fraction $fsus$ determines to what extend the material ends up in the detritus in the water column or

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in the sediment. Spawned material, and (pseudo)faeces end up in the pelagic detritus pool, while respired nutrients end up as ammonia and phosphate:

$$Rmrt_{i,k} = (Rmrv_i + Rmre_i + Rmrr_i) \times fsus_i \times bnut_{k,i}$$

$$Rmrts1_{i,k} = (Rmrv_i + Rmre_i + Rmrr_i) \times fsed_i \times bnut_{k,i}$$

$$Rres_{i,k} = cec_i \times Pres_i \times Cgrn_i \times bnut_{k,i}$$

$$Rdef_{i,k} = cec_i \times Pdef_{i,k} \times Cgrn_i$$

$$Rspw_{i,k} = cec_i \times Pspw_i \times Cgrn_i \times bnut_{k,i}$$

The release rate for inorganic nutrients by respiration is as follows:

$$Rres_{i,k} = cec_i \times Pres_{i,k} \times Cgrn_i$$

with

$bnut_{k,i}$	stoch. constant for nutrient k over carbon in grazer i [gC/gN/gP/gSi gC^{-1}]
$Cgrn_i$	number of individuals of grazer type i [# m^{-3}] or [$^{-2}$]
cec_i	conversion coefficient from energy to carbon of grazer i [gC J^{-1}]
$Pres_i$	respiration rate of grazer type i [J ind^{-1} d^{-1}]
$Pspw_i$	spawning rate of grazer type i [J ind^{-1} d^{-1}]
$Pdef_{k,i}$	defaecation rate of nutrient k [gC/gN/gP/gSi ind^{-1} d^{-1}]
$Rres_{i,k}$	release rate of inorganic nutrient k by respiration [gC/N/P/Si m^{-3} d^{-1}]
$Rspw_{i,k}$	detritus production of nutrient k by spawning [J ind^{-1} d^{-1}]
$Rdef_{k,i}$	detritus production rate of nutrient k by defaecation [gC/gN/gP/gSi ind^{-1} d^{-1}]
i	index for grazer species groups [-]
j	index for algae species groups [-]
k	index for nutients, 1 = carbon, 2 = nitrogen, 3 = phosphorus, 4 = silicon [-]

2.5 Total grazer biomass and other derived variables

The total carbon biomass, ash-free dry weight and wet weight of the population or cohort are defined as follows:

$$Cgrc_i = (cec_i \times (E_i + R_i) + cvc_i \times V_i) \times Cgrn_i$$

$$Cgrd_i = Ccgr_i / cawc_i$$

$$Cgwr_i = Ccgr_i / cwwc_i$$

with:

$Cgrn_i$	Total number of individuals of grazer i [# m^{-3}] or [$^{-2}$]
$Cgrc_i$	Total carbon biomass of grazers [gC]
$Cgrd_i$	Total ash free dry weight of zooplankton [gAFDW]
$Cgrw_i$	Total wet weight of zooplankton [gWW]
cec_i	conversion coefficient from energy to carbon of grazer i [gC J^{-1}]
cvc_i	conversion coefficient from volume to carbon of grazer i [gC cm^{-3}]
$cdwc_i$	conversion coefficient from ash free dry weight to carbon for grazer i [gC gAFDW^{-1}]
$cwwc_i$	conversion coefficient from wet weight to carbon for grazer i [gC gWW^{-1}]
V_i	structural biovolume of individual grazer of type i [cm^3 ind^{-1}]
E_i	energy reserves of individual grazer of type i [J ind^{-1}]
R_i	gonadal reserves of individual grazer of type i [J ind^{-1}]

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Individual length may be derived from the individual structural volume and the shape coefficient as follows:

$$L_i = V_i^{1/3}/kshp_i$$

with

$kshp_i$	shape coefficient of grazer type i [-]
L_i	length of individual grazer of type i [cm]
V_i	structural biovolume of individual grazer of type i [cm^3 ind^{-1}]

The scaled energy density is a measure for the condition of the organisms, which can be expressed as the energy density relative to the maximum energy density. Similarly, the gonadal-somatic index is a measure for the reproductive state of the organism, and is defined as the ratio of the gonadal biomass over the total biomass:

$$Es_i = E_i/(V_i \times kem_i)$$

$$GSI_i = \frac{cec_i \times R_i}{cvc_i \times fadult \times V_i + cec_i \times fadult_i \times E_i + cec_i \times R_i}$$

with:

$fadult$	adult fraction of population of grazer i [-]
GSI_i	Gonadal Somatic Index of grazer type i [J ind^{-1}]
cec_i	conversion coefficient from energy to carbon of grazer i [gC J^{-1}]
cvc_i	conversion coefficient from volume to carbon of grazer i [gC cm^{-3}]
kem_i	maximum energy density for grazer i [J cm^{-3}]
Es_i	scaled energy density of grazer i [-]
V_i	structural biovolume of individual grazer of type i [cm^3 ind^{-1}]
E_i	energy reserves of individual grazer of type i [J ind^{-1}]
R_i	gonadal reserves of individual grazer of type i [J ind^{-1}]

Directives for use

- ◇ The proces rates in connection with grazing have a temperature basis of 20 oC. That means that input values have to be corrected when provided for another temperature basis.
- ◇ Parameter values for a range of species can be found on the "add my pet" page at http://www.bio.vu.nl/thb/ → DEB → Laboratory. If parameter values are not available for a certain species, this page also contains instructions on how to construct a new (and consistent) set of parameter values.
- ◇ The initial length of isomporphs is determined from the inital carbon biomass and number of individuals.
- ◇ Benthic and suspended grazers (SwBen>0) are fixed to a specific vertical location in the water column. Therefore, they may not be present in all vertical layers. In this case, any output (both state and derived variables) that is aggregated over a monitoring area, should be multiplied by the number of layers included in the monitoring area. Output values in single segment locations do not have to be corrected. Note that this correction is necessary for all passive substances.
- ◇ The PROTIST algal groups give rise to names for the various process parameters like: $M_PrDiat1$ for the preference DEB mussels for PROTIST diatoms of species 1, $M_PrDiat2$ for species 2 etc. The parameter names connecting to the PROTIST species use the following "infixes": $diat1$, $diat2$, $green1$, $green2$, $cm1$, $cm2$, $ncm1$, $ncm2$ and $zoo1$, $zoo2$.

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Additional references

Table 7.3: *Definitions of the input parameters in the formulations for DEBGRZ.*

Name in formulas	Name in input	Definition	Units
$anut_{2,1}$	$NCratGreen$	green algae spec. stoch. constant nitrogen over carbon	gN gC^{-1}
$anut_{2,2}$	$NCratDiat$	diatoms spec. stoch. constant nitrogen over carbon	gN gC^{-1}
$anut_{2,3}$	$MPB1NCrat$	epipelic diatoms spec. stoch. constant nitrogen over carbon	gN gC^{-1}
$anut_{2,4}$	$MPB2NCrat$	epipsammic diatoms spec. stoch. constant nitrogen over carbon	gN gC^{-1}
$anut_{2,j}$	$NCRAlg(j)$	BLOOM algae group spec. stoch. const. nitr. over carb.	gN gC^{-1}
$anut_{3,1}$	$PCratGreen$	green algae spec. stoch. constant phos. over carbon	gP gC^{-1}
$anut_{3,2}$	$PCratDiat$	diatoms spec. stoch. constant phosphorus over carbon	gP gC^{-1}
$anut_{3,3}$	$MPB1PCrat$	epipelic diatoms spec. stoch. constant phosphorus over carbon	gP gC^{-1}
$anut_{3,4}$	$MPB2PCrat$	epipsammic diatoms spec. stoch. constant phosphorus over carbon	gP gC^{-1}
$anut_{3,j}$	$PCRAlg(j)$	BLOOM algae group spec. stoch. const. phos. over carb.	gP gC^{-1}
$anut_{4,1}$	$SCratGreen$	green algae spec. stoch. constant silicon over carbon	gSi gC^{-1}
$anut_{4,2}$	$SCratDiat$	diatoms spec. stoch. constant silicon over carbon	gSi gC^{-1}
$anut_{4,1}$	$MPB1SCrat$	epipelic diatoms spec. stoch. constant silicon over carbon	gSi gC^{-1}
$anut_{4,2}$	$MPB2SCrat$	epipsammic diatoms spec. stoch. constant silicon over carbon	gSi gC^{-1}
$anut_{4,j}$	$SCRAlg(j)$	BLOOM algae group spec. stoch. const. sil. over carb.	gSi gC^{-1}
		Note: for PROTIST the stoichiometry is calculated	
$Cgrv_1$	$Zoopl_V$	structural biomass concentration of zooplankton	gC m^{-3} or $^{-2}$
$Cgre_1$	$Zoopl_E$	energy reserve biomass concentration of zooplankton	gC m^{-3} or $^{-2}$
$Cgrr_1$	$Zoopl_R$	gonadal biomass concentration of zooplankton	gC m^{-3} or $^{-2}$

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Name in formulas	Name in input	Definition	Units
$Cgrn_1$	$Zoopl_N$	number of individuals (density) of zooplankton	# m^{-3} or $^{-2}$
$Cgrv_2$	$Mussel_V$	structural biomass concentration of mussel	gC m^{-3} or $^{-2}$
$Cgre_2$	$Mussel_E$	energy reserve biomass concentration of mussel	gC m^{-3} or $^{-2}$
$Cgrr_2$	$Mussel_R$	gonadal biomass concentration of mussel	gC m^{-3} or $^{-2}$
$Cgrn_2$	$Mussel_N$	number of individuals (density) of mussel	# m^{-3} or $^{-2}$
$Cgrv_3$	$Grazer3_V$	structural biomass concentration of grazer type 3	gC m^{-3} or $^{-2}$
$Cgre_3$	$Grazer3_E$	energy reserve biomass concentration of grazer type 3	gC m^{-3} or $^{-2}$
$Cgrr_3$	$Grazer3_R$	gonadal biomass concentration of grazer type 3	gC m^{-3} or $^{-2}$
$Cgrn_3$	$Grazer3_N$	number of individuals (density) of grazer type 3	# m^{-3} or $^{-2}$
$Cgrv_4$	$Grazer4_V$	structural biomass concentration of grazer type 4	gC m^{-3} or $^{-2}$
$Cgre_4$	$Grazer4_E$	energy reserve biomass concentration of grazer type 4	gC m^{-3} or $^{-2}$
$Cgrr_4$	$Grazer4_R$	gonadal biomass concentration of grazer type 4	gC m^{-3} or $^{-2}$
$Cgrn_4$	$Grazer4_N$	number of individuals (density) of grazer type 4	# m^{-3} or $^{-2}$
$Cgrv_5$	$Grazer5_V$	structural biomass concentration of grazer type 5	gC m^{-3} or $^{-2}$
$Cgre_5$	$Grazer5_E$	energy reserve biomass concentration of grazer type 5	gC m^{-3} or $^{-2}$
$Cgrr_5$	$Grazer5_R$	gonadal biomass concentration of grazer type 5	gC m^{-3} or $^{-2}$
$Cgrn_5$	$Grazer5_N$	number of individuals (density) of grazer type 5	# m^{-3} or $^{-2}$
$Calg1$	$Green$	biomass concentration of green algae (DYNAMO)	gC m^{-3}
$Calg2$	$Diat$	biomass concentration of diatoms (DYNAMO)	gC m^{-3}
$Calgj$	$BLOOMALG(j)$	biomass concentration of a BLOOM algae group	gC m^{-3}
	$diatC_1$	Carbon content for PROTIST diatom 1	gC m^{-3}

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Table 7.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
	$diatChl_1$	Chlorophyll content for PROTIST diatom 1	gChl m^{-3}
	$diatN_1$	Nitrogen content for PROTIST diatom 1	gN m^{-3}
	$diatP_1$	Phosphorus content for PROTIST diatom 1	gP m^{-3}
	$diatSi_1$	Silica content for PROTIST diatom 1	gSi m^{-3}
	$diatC_2$	Carbon content for PROTIST diatom 2	gC m^{-3}
	$diatChl_2$	Chlorophyll content for PROTIST diatom 2	gChl m^{-3}
	$diatN_2$	Nitrogen content for PROTIST diatom 2	gN m^{-3}
	$diatP_2$	Phosphorus content for PROTIST diatom 2	gP m^{-3}
	$diatSi_2$	Silica content for PROTIST diatom 2	gSi m^{-3}
	$greenC_1$	Carbon content for PROTIST green algae 1	gC m^{-3}
	$greenChl_1$	Chlorophyll content for PROTIST green algae 1	gChl m^{-3}
	$greenN_1$	Nitrogen content for PROTIST green algae 1	gN m^{-3}
	$greenP_1$	Phosphorus content for PROTIST green algae 1	gP m^{-3}
	$greenC_2$	Carbon content for PROTIST green algae 2	gC m^{-3}
	$greenChl_2$	Chlorophyll content for PROTIST green algae 2	gChl m^{-3}
	$greenN_2$	Nitrogen content for PROTIST green algae 2	gN m^{-3}
	$greenP_2$	Phosphorus content for PROTIST green algae 2	gP m^{-3}
	cmC_1	Carbon content for PROTIST const. mix. 1	gC m^{-3}
	$cmChl_1$	Chlorophyll content for PROTIST const. mix. 1	gChl m^{-3}
	cmN_1	Nitrogen content for PROTIST const. mix. 1	gN m^{-3}
	cmP_1	Phosphorus content for PROTIST const. mix 1	gP m^{-3}
	cmC_1	Carbon content for PROTIST const. mix. 2	gC m^{-3}

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Name in formulas	Name in input	Definition	Units
	$cmChl_2$	Chlorophyll content for PROTIST const. mix. 2	gChl m^{-3}
	cmN_2	Nitrogen content for PROTIST const. mix. 2	gN m^{-3}
	cmP_2	Phosphorus content for PROTIST const. mix 2	gP m^{-3}
	$ncmC_1$	Carbon content for PROTIST non-const. mix. 1	gC m^{-3}
	$ncmChl_1$	Chlorophyll content for PROTIST non-const. mix. 1	gChl m^{-3}
	$ncmN_1$	Nitrogen content for PROTIST non-const. mix. 1	gN m^{-3}
	$ncmP_1$	Phosphorus content for PROTIST non-const. mix 1	gP m^{-3}
	$ncmC_2$	Carbon content for PROTIST non-const. mix. 2	gC m^{-3}
	$ncmChl_2$	Chlorophyll content for PROTIST non-const. mix. 2	gChl m^{-3}
	$ncmN_2$	Nitrogen content for PROTIST non-const. mix. 2	gN m^{-3}
	$ncmP_2$	Phosphorus content for PROTIST non-const. mix 2	gP m^{-3}
	$zooC_1$	Carbon content for PROTIST protozooplankton 1	gC m^{-3}
	$zooN_1$	Nitrogen content for PROTIST protozooplankton 1	gN m^{-3}
	$zooP_1$	Phosphorus content for PROTIST protozooplankton 1	gP m^{-3}
	$zooC_2$	Carbon content for PROTIST protozooplankton 2	gC m^{-3}
	$zooN_2$	Nitrogen content for PROTIST protozooplankton 2	gN m^{-3}
	$zooP_2$	Phosphorus content for PROTIST protozooplankton 2	gP m^{-3}
$Cdet1$	$POC1$	detritus organic carbon concentration	gC m^{-3}
$Cdet2$	$PON1$	detritus nitrogen concentration	gN m^{-3}
$Cdet3$	$POP1$	detritus phosphorus concentration	gP m^{-3}
$Cdet4$	$Opal$	opal silicate concentration	gSi m^{-3}
$Ctim$	$Opal$	concentration of inorganic matter	g m^{-3}

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Name in formulas	Name in input	Definition	Units
H	$Depth$	depth of a water compartment (layer)	m
–	$(i)UnitSW$	group spec. option for biomass unit (1=g m^{-2}, 0=g m^{-3})	-
–	$(i)_SwV1$	group spec. option for upscaling (0=isomorphs(cohort), 1=V1morphs (population))	-
T	$Temp$	water temperature	°C
$bnut_{1,i}$	$(i)_TC$	stoch. constant for carbon over carbon in grazer i	gC gC^{-1}
$bnut_{2,i}$	$(i)_TN$	stoch. constant for nitrogen over carbon in grazer i	gN gC^{-1}
$bnut_{3,i}$	$(i)_TP$	stoch. constant for phosphorus over carbon in grazer i	gP gC^{-1}
$bnut_{4,i}$	$(i)_TSi$	stoch. constant for silicon over carbon in grazer i	gSi gC^{-1}
$fapr_{i,1}$	$(i)_ALGPRGrn$	preference of grazer i for green algae (DYNAMO)	-
$fapr_{i,2}$	$(i)_ALGPRDiat$	preference of grazer i for diatoms (DYNAMO)	-
$fapr_{i,3}$	$(i)_ALGPRMPB1$	preference of grazer i for epipelic benthic diatoms	-
$fapr_{i,4}$	$(i)_ALGPRMPB2$	preference of grazer i for epipsammic benthic diatoms	-
$fapr_{i,j}$	$(i)_ALGPR(j)$	preference of grazer i for BLOOM algae group j	-
	$(i)_Diat1$	preference of grazer i for PROTIST diatoms 1	-
	$(i)_Diat2$	preference of grazer i for PROTIST diatoms 2	-
	$(i)_Green1$	preference of grazer i for PROTIST green algae 1	-
	$(i)_Green2$	preference of grazer i for PROTIST green algae 2	-
	$(i)_cm1$	preference of grazer i for PROTIST const. mix. 1	-
	$(i)_cm2$	preference of grazer i for PROTIST const. mix. 2	-

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Table 7.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
	$(i)_ncm1$	preference of grazer i for PROTIST non-const. mix. 1	-
	$(i)_ncm2$	preference of grazer i for PROTIST non-const. mix. 2	-
	$(i)_zoo1$	preference of grazer i for PROTIST protozooplankton 1	-
	$(i)_zoo2$	preference of grazer i for PROTIST protozooplankton 2	-
$fdpr_i$	$(i)_DETPR$	preference of grazer i for detritus	-
$falg_{i,1}$	$(i)_ALGFFGre$	egested fraction of green algae consumed by grazer i	-
$falg_{i,2}$	$(i)_ALGFFDia$	egested fraction of diatoms consumed by grazer i	-
$falg_{i,3}$	$(i)_ALGFFMPB1$	egested fraction of epipelic diatoms consumed by grazer i	-
$falg_{i,4}$	$(i)_ALGFFMPB2$	egested fraction of epipsammic diatoms consumed by grazer i	-
$falg_{i,j}$	$(i)_ALGFF(j)$	egested fraction of algae j consumed by grazer i	-
	$(i)_FFDiat1$	egested fraction of PROTIST diatoms 1 consumed by grazer i	-
	$(i)_FFDiat2$	egested fraction of PROTIST diatoms 2 consumed by grazer i	-
	$(i)_FFGreen1$	egested fraction of PROTIST greens 1 consumed by grazer i	-
	$(i)_FFGreen2$	egested fraction of PROTIST greens 2 consumed by grazer i	-
	$(i)_FFcm1$	egested fraction of PROTIST const.mix. 1 consumed by grazer i	-
	$(i)_FFcm2$	egested fraction of PROTIST const.mix. 2 consumed by grazer i	-
	$(i)_FFncm1$	egested fraction of PROTIST non-const.mix. 1 consumed by grazer i	-
	$(i)_FFncm2$	egested fraction of PROTIST non-const.mix. 2 consumed by grazer i	-
	$(i)_FFzoo1$	egested fraction of PROTIST protozoopl. 1 consumed by grazer i	-
	$(i)_FFzoo2$	egested fraction of PROTIST protozoopl. 2 consumed by grazer i	-

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Table 7.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
$fdet_i$	$(i)_DETFF$	egested fraction of detritus consumed by grazer i	-
$fsed_i$	$(i)_FrDetBot$	fr. of mortality flux of grazer i to sediment detr. pool	-
$fsus_i$	$(i)_FrDetBot$	fr. of mortality flux of grazer i to sediment detr. pool	-
$\kappa_{I,i}$	$(i)_kappaI$	fr. of filtered food ingested by grazer i	-
$\kappa_{A,i}$	$(i)_kappaA$	fr. of ingested food assimilated by grazer i	-
κ_i	$(i)_kappa$	fr. of mobilized energy to growth and maintenance of grazer i	-
$\kappa_{R,i}$	$(i)_kappaR$	fr. of reproduction flux to gonadal tissue of grazer i	-
cec_i	$(i)_cEC$	conversion coefficient from energy to carbon biomass of grazer i	gC J^{-1}
cvc_i	$(i)_cVC$	conversion coefficient from volume to carbon biomass of grazer i	gC cm^{-3}
$cdwc_i$	$(i)_cDWC$	conversion coefficient from carbon biomass to ash free dry weight for grazer i	gC $gAFDW^{-1}$
$cwwc_i$	$(i)_cWWC$	conversion coefficient from carbon biomass to wet weight for grazer i	gC gWW^{-1}
$GSIupr_i$	$(i)_GSIupr$	energy threshold to start spawning for grazer i	-
$GSIlwr_i$	$(i)_GSIlwr$	energy threshold to stop spawning for grazer i	-
keg_i	$(i)_EG$	volume-specific costs for growth of grazer i	J cm^{-3}
kem_i	$(i)_EM$	maximum energy density of grazer i	J cm^{-3}
$kuptm_{i,20}$	$(i)_JXm$	maximum surface-area-specific ingestion rate of grazer i at 20 °C	J cm^2 d^{-1}
$kmrt1_{i,1,20}$	$(i)_rMor$	reference mortality rate of grazer i for individuals of 1cm at 20 °C	d^{-1}
$kmrt2_{i,1}$	$(i)_rHrv$	reference harvesting rate of grazer i for individuals of 1cm	d^{-1}
$klmrt1_i$	$(i)_cMor$	length dependency coefficient for mortality rate of grazer i	-
$klmrt2_i$	$(i)_cHrv$	length dependency coefficient for harvesting rate of grazer i	-

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Table 7.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
$kpm_{i,20}$	$(i)_PM$	volumetric costs of maintenance for grazer i at 20 °C	J cm^{-3} d^{-1}
$kspr_i$	$(i)_Rspw$	gonadal release rate at spawning for grazer i	d^{-1}
$kshp_i$	$(i)_Shape$	shape coefficient for grazer i	-
$Ksfd_i$	$(i)_Xk$	half saturation constant for food uptake by grazer i	gC m^{-3}
$Kstim_i$	$(i)_Yk$	half saturation constant for the negative effect of inorganic matter on food uptake by grazer i	gC m^{-3}
$Lref_i$	$(i)_Lref$	reference length of individual grazer of type i (only for V1morphs)	cm
Ta_i	$(i)_Ta$	Arrhenius temperature for grazer i	K
Tal_i	$(i)_Tal$	Arrhenius temperature for rate of decrease at upper boundary for grazer i	K
Tah_i	$(i)_Tah$	Arrhenius temperature for rate of decrease at lower boundary for grazer i	K
Tl_i	$(i)_Tl$	Lower temperature boundary of tolerance range for grazer i	K
Th_i	$(i)_Th$	Upper temperature boundary of tolerance range for grazer i	K
$Tspm_i$	$(i)_MinSTmp$	minimum spawning temperature for grazer i	K
Vp_i	$(i)_Vp$	biovolume at start of reproductive age for grazer i	cm^3 ind^{-1}

[1](i) indicates grazer species groups 1–5, respectively Z for zooplankton, M for mussel type zoobenthos, G3, G4 and G5 for user defined groups.

[2](j) indicates BLOOM algae species groups 1–30.

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Table 7.4: *Definitions of the output parameters for DEBGRZ.*

Name in formulas	**Name in output**	**Definition**	**Units**
L_i	$(i)_L$	Individual length of grazer i	cm
Es_i	$(i)_Escaled$	Scaled energy density, which is a measure for the condition of the organism	-
GSI_i	$(i)_GSI$	Gonadal Somatic Index of grazer type i	-
V_i	$(i)_Vind$	Structural biovolume of individual grazer of type i	cm^3 ind^{-1}
E_i	$(i)_Eind$	Energy reserves of individual grazer of type i	J ind^{-1}
R_i	$(i)_Rind$	Gonadal reserves of individual grazer of type i	J ind^{-1}
$Cgrc_i$	$(i)_TotBiomass$	Total carbon biomass concentration of grazer type i	gC $m^{-3 \text{ or } -2}$
$Cgrd_i$	$(i)_TotAFDW$	Total ash free dry weight concentration of grazer type i	gAFDW $m^{-3 \text{ or } -2}$
$Cgrw_i$	$(i)_TotWW$	Wet weight concentration of grazer i	gWW $m^{-3 \text{ or } -2}$
$Cgrc_i$	$(i)_Biomass$	Total carbon biomass of grazer i	gC
$Cgrd_i$	$(i)_AFDW$	Total ash free dry weight of grazer i	gAFDW
$Cgrw_i$	$(i)_WW$	Total wet weight of grazer i	gWW

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8 Organic matter (detritus)

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8.1 Decomposition of detritus

PROCESS: DECFAST, DECMEDIUM, DECSLOW, DECREFR, DECDOC AND DECPOC5

Being natural dead organic matter, detritus is produced when algae and higher plants die off. Detritus may also arise from organic matter present in discharged wastewater. The microbial decomposition of detritus into its basic inorganic components such as carbon dioxide, ammonium, phosphate and sulfide is called mineralization. During the decomposition process the organic matter is gradually converted into material that is more resistant to microbial breakdown. In other words, the decomposition rate decreases at the increase of the age of detritus. This is caused by both the difference in degradability of the numerous chemical components in detritus and the (bio)chemical conversion of readily degradable components into less readily degradable components. Eventually, refractory organic matter results, that is subjected to very slow decomposition. Humic matter may not be decomposed at all, when stored under chemically reducing conditions. The decomposition of humic matter only continues significantly when exposed to oxygen, especially when solar radiation is available to speed up the process by means of photo-oxidation.

The slowing down of the decomposition process over time can be modelled by means of the distinction of several detritus fractions, each having a different decomposition rate. The resulting model will show a decreasing overall decomposition rate, when no new detritus is added to the initial detritus pools. Adding “fresh” detritus brings along the question how this detritus must be allocated to the existing detritus pools. This can be done by i) distributing the fresh detritus among the detritus fractions according to fixed ratios, and/or by ii) converting a more readily degradable fraction into a more refractory fraction proportional to the decomposition rates.A combination of these options has been implemented in the model. The fresh detritus from algae is added to both the fast and medium slow decomposing detritus fractions according to fixed ratios. The fresh detritus from submerged and emerging terrestrial vegetation is added to all detritus fractions according to user defined ratios. However, all organic matter in stems (incl. branches) and roots is by definition allocated to one and the same organic “detritus” fraction, that has been included in DELWAQ specifically for this purpose. The detritus from waste water can be allocated to the organic fractions via the loads.

Detritus consists of both particulate and dissolved components. The dissolved components can be allocated to two categories:

1 highly degradable dissolved substances, such as amino acids and sugars, and
2 highly refractory dissolved substances such as humic and fulvic acids.

Category 1 is taken into account in the model by means of the autolysis of fresh detritus, which is implemented in connection with the algae mortality process (detritus production). Autolysis leads to the instantaneous release of inorganic nutrients present in autolysed algal biomass. Category 2 demands for the definition of a refractory dissolved detritus fraction, being produced from particulate detritus.

The decomposition rates depend on the availability of nutrients (N, P), as well as on the redox conditions. Both aspects are connected with the needs and the efficiency of bacteria in performing the decomposition process. The availability of nutrients can be taken into account by interpolating the decomposition rate between a maximal value and a minimal value proportional to the nutrient contents of the detritus.

The redox-dependency is caused by the fact that the energy gain of decomposition (oxidation)

decreases going from aerobic decomposition, to denitrification, to sulfate reduction and finally to methanogenesis. In principle, these processes are mutually exclusive. Only one of them may occur at the same time and the same place. Consequently, the decomposition rate has been made a function of the presence of the various electron acceptors, dissolved oxygen and nitrate in particular.

Carbon, nitrogen, phosphorus and sulfur in detritus are considered as separate state variables in the model (sulfur can be ignored). The mineralization of organic nitrogen and organic phosphorus is fast, compared to the mineralization of organic carbon, when the organic matter is rich in these nutrients. During the decomposition process detritus becomes less rich in nutrients, until eventually the minimal nutrients contents of refractory organic matter (humic matter) have been established. In order to take this preferential nutrient stripping into account, the decomposition rates of organic nitrogen, phosphorus and sulfur have been made a function of the nutrient stochiometry of refractory detritus.

The rate of mineralization is also a function of the temperature. Decomposition rates tend to decrease progressively at temperatures below 4 $^{\circ}$C. Because the decomposition of organic matter is performed by a very large number of species, including species that are adapted to low temperature environments, the effect is not nearly as strong as in the case of nitrification. The present model ignores the “near-freezing” effect, which means that imposing a discontinuity at a critically low temperature is not possible when using the processes described here.

Volume units refer to bulk ($\mathcal{b}$) or to water ($\mathcal{w}$).

Implementation

Processes DECFST, DECMEDIUM, DECSLOW, DECREFR, DECPOC5 and DECDOC for the decomposition of organic matter have been implemented in a generic way, meaning that they can be applied both to water layers and sediment layers. The processes can also be used in combination with one of the other options for mineralization in the sediment (BMS1_i and BMS2_i).

The processes have been implemented for the following substances:

- ◇ POC1, PON1, POP1, POS1, POC2, PON2, POP2, POS2, POC3, PON3, POP3, POS3, POC4, PON4, POP4, POS4, POC5, PON5, POP5, POS5, DOC, DON, DOP, DOS, NH4, PO4 and SUD.

POC/N/P/S5 must be defined as inactive substances (= substances that are not transported), and should be used for stem and root ”detritus” from vegetation only. As opposed to all other conversion processes, the decomposition of POC5 continues in grid cells when running dry.

Table 8.1 and Table 8.2 provide the definitions of the input parameters occurring in the formulations.

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Formulation

The biochemical decomposition of dead organic matter (detritus) is described here as the mineralization and conversion of five particulate fractions and the mineralization of one dissolved fraction. Each mineralization flux for the particulate fractions has one or two proportional conversion fluxes. The overall decomposition (loss) flux of the fractions is the sum of the mineralization and the conversion fluxes. The fractions are produced, converted and mineralized according to the following schemes:

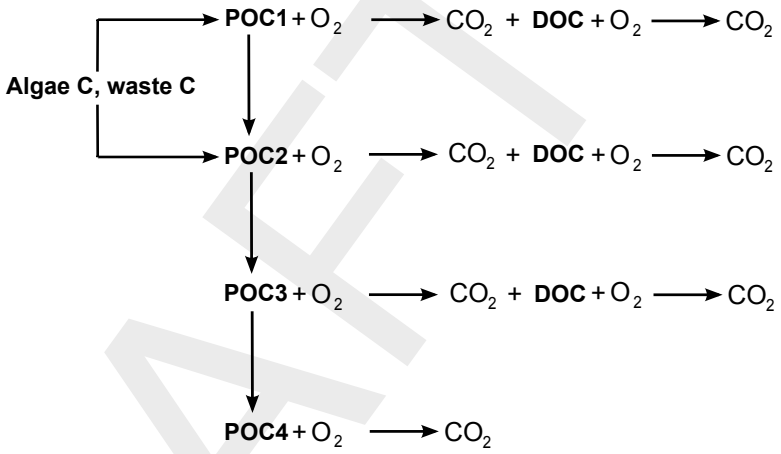

Figure 8.1: *When an algae module is included.*

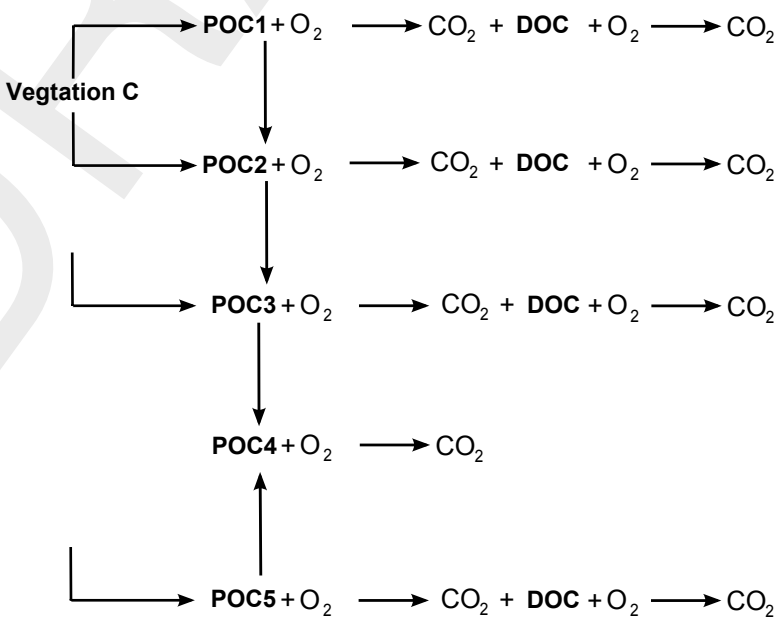

Figure 8.2: *When the terrestrial vegetation module is included.*

The first scheme (Figure 8.1) applies when an algae module is included in a model. The second scheme (Figure 8.2) concerns the situation when the terrestrial vegetation module is included. Both schemes apply when both algae and vegetation are in the model.

POC1 is the fast decomposing detritus fraction, POC2 the medium slow decomposing fraction POC3 the slow decomposing fraction, and POC4 the particulate refractory fraction. DOC represents dissolved refractory organic matter. POC5 contains the organic matter in stems

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and roots that may be subjected to (very) slow decomposition. POC5 should only be included in a model when the vegetation module is used.

At the absence of (sufficient) oxygen, nitrate and sulfate, not only CO2 (carbon dioxide) but also CH4 (methane) will be produced. The consumption fluxes of the electron-acceptors OXY, NO3 and SO4, and the production fluxes of CO2 and CH4 are generated by another process, called CONSELAC

The schemes represent carbon, but is similarly applicable to nitrogen, phosphorus and sulfur, for which the mineralization products are ammonium (NH4), phosphate (PO4) and sulfide (SUD).

Mineralization
Mineralization has been formulated as a first-order kinetic process. The first-order mineralization rate is a function of limiting factors related to the electron acceptor used, the preferential stripping of nutrients, and the nutrient availability for bacteria. Two options are available. One option concerns a comprehensive approach with nutrient stripping. The other option does not explicitly consider nutrient stripping (Smits and Beek (2013)). However, a difference in the mineralization of the nutrients relative to carbon can be established by using different rate constants for C, N and P.

For the comprehensive approach the formulations are as follows ($SWOMDec$=0.0):

$$Rmin_{j,i} = fel \times facc_{j,i} \times kmin_i \times Cx_{j,i}$$
$$kmin_i = kmin_{i,20} \times ktmin^{(T-20)}$$

where:

Cx	organic carbon, nitrogen, phosphorus or sulfur concentration ([gC/N/P/S m^{-3}]; x is oc, on, op or os)
$facc$	acceleration factor for nutrient stripping [-]
fel	limiting factor for electron acceptors [-]
$kmin$	first-order mineralization rate [d^{-1}]
$kmin_{20}$	first-order mineralization rate at 20 °C [d^{-1}]
$ktmin$	temperature coefficient for mineralization [-]
$Rmin$	mineral. rate for organic carbon, nitrogen, phosphorus or sulfur [gC/N/P/S m^{-3}.d^{-1}]
T	temperature [°C]
i	index for the organic matter fraction (1–5; see scheme above)
j	index for the nutrient (1–4, that is C, N, P and S)

The mineralization rate of a specific detritus fraction has a maximal and a minimal value. The first-order rate is a linear function of the nutrient (N, P) availability according to:

if $Coni/Coci > an_{i,\max}$ and $Copi/Coci > ap_{i,\max}$

$$kmin_{i,20} = kmin_{i,\max,20}$$

if $Coni/Coci < an_{i,\min}$ or $Copi/Coci < ap_{i,\min}$

$$kmin_{i,20} = kmin_{i,\min,20}$$

else

$$kmin_{i,20} = kmin_{i,\min,20} + fnut_i \times (kmin_{i,\max,20} - kmin_{i,\min,20})$$

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$$fnut_i = \min\left\{\frac{((Con_i/Coc_i) - an_{i,\min})}{an_{i,\max} - an_{i,\min}}, \frac{((Cop_i/Coc_i) - ap_{i,\min})}{ap_{i,\max} - ap_{i,\min}}\right\}$$

(if $an_{i,max}$ = $an_{i,min}$ or $ap_{i,max}$ = $ap_{i,min}$ then $fnut_i$ = 0.5!)

where:

an	stochiometric constant of nitrogen in organic matter [gN gC^{-1}]
ap	stochiometric constant of phosphorus in organic matter [gP gC^{-1}]
Coc	organic carbon concentration [gC m^{-3}]
Con	organic nitrogen concentration [gN m^{-3}]
Cop	organic phosphorus concentration [gP m^{-3}]
$fnut$	limiting factor for nutrient availability [-]
i	index for the organic matter fraction (1–5; see scheme above)
$\max$	index for the maximal value, the upper limit
$\min$	index for the minimal value, the lower limit

The limiting factor for electron acceptors is simply a constant, the value of which depends on the presence of dissolved oxygen and nitrate:

$$fel = \begin{cases} 1.0 & \text{if } Cox > 0.0 \\ bni & \text{if } Cox < 0.0 \text{ and } Cni > 0.1 \\ bsu & \text{if } Cox < 0.0 \text{ and } Cni < 0.1 \end{cases}$$

where:

bni	attenuation constant in case nitrate is the prevailing electron acceptor [-]
bsu	attenuation constant in case sulfate or carbon monoxide is the prevailing electron acceptor [-]

The acceleration factor for nutrient stripping is proportional to the relative difference of the actual nutrient composition and the stochiometric constant of refractory detritus:

$$facc_{j,i} = 1.0 + \frac{((Cx_{j,i}/Coc_i) - ar_j)}{ar_j}$$

with:

ar	stochiometric constant of nitrogen, phosphorus or sulfur in refractory [gN/P/S gC^{-1}]

Notice that the acceleration factor is 1.0 for the carbon detritus components.

In principal, the above formulations concern each of the 24 organic carbon, nitrogen, phosphorus and sulfur detritus components. However, in the model the acceleration factor *facc* and the nutrient related variability of the first-order mineralization rate are ignored for the refractory fractions POC/N/P/S4 and DOC/N/P/S. Consequently, the processes DECREFR and DECDOC do not contain the process parameters connected with these aspects.

The decomposition of POC5 continues in above-ground grid cells when these run dry. The decomposition rate is a function of the temperature of the air and the sediment, an additional input parameter *NatTemp*, different from the temperature of water. All decomposition products except CO2 accumulate in these cells during a dry period. The production of CO2 as well as the consumption of oxygen (OXY) continue in process DECPOC5 (in stead of in process CONSELAC), and pertinent fluxes are calculated in order to maintain full mass balances for

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these substances. However, oxygen (OXY) is obtained from the atmosphere, and carbon dioxide is released into it. Therefore, additional inverse fluxes of CO2 and OXY are generated by process DECPOC5 to prevent the change of concentrations during a dry period as well as the impacts of such concentration changes on water quality when the water returns.

The alternative approach ($SWOMDec$=1.0) uses the same formulations for the dependencies of nutrient availability, electron acceptor dominance and temperature. The acceleration factors for nutrient stripping are set equal to 1.0. The first-order mineralization rates for fast, medium and slow decomposing organic carbon (POC1-3), nitrogen (PON1-3) and phosphorus (POP1-3) are different. This requires two additional sets of input parameters. The maximal and minimal rates for organic sulfur are the same as for organic carbon.

Conversion

The production of a less readily degradable detritus fraction from a more readily degradable fraction is supposed to be proportional to the mineralization rate. The rationale behind this hypothesis is that bacterial activity is driving the conversion process. Chemical reactions are highly dependent on the presence of all kinds of intermediate decomposition products. Consequently, the conversion rate has been linked to the mineralization rate according to the following formulation, which is the same for both mineralization options: :

$$Rcon_{j,i} = b_i \times Rmin_{j,i}/facc_{j,i}$$

where:

b	constant fraction of detritus C component i converted into detritus C component $i+1$ relative to and in addition to mineralization [-]
$Rcon$	conversion rate for particulate organic carbon, nitrogen, phosphorus or sulfur to slower particulate or dissolved fractions [gC/N/P/S m^{-3}.d^{-1}]

Notice that the fractions b are equal for organic carbon, nitrogen, phosphorus and sulfur. The mineralization rate of organic carbon is taken as the reference rate, which implies the need for correction of the mineralization rate for nitrogen, phosphorus and sulfur for acceleration (nutrient stripping).

For POC5, just like decomposition, conversion continues when a grid cell runs dry.

Directives for use

- ◇ The simulation of the consumption of dissolved oxygen (substance OXY) resulting from the decomposition of organic matter requires that process CONSELAC (Consumption of electron-acceptors) is included in the model! This also holds for taking into account denitrification, sulfate reduction, iron(III) reduction and methanogenesis. As an alternative when sediment-water interaction is simulated according to the S1/2 option, denitrification can be taken into account by means of processes DENSED_NO3 and/or DENWAT_NO3.
- ◇ Option $SWOMDec$=0.0 (default) for the comprehensive approach with nutrient stripping based on the input mineralization rate for organic carbon. Option $SWOMDec$=1.0 does not use the formulation for nutrient stripping but has different mineralization rates for POC1/2, PON1/2 and POP1/2. Consequently, two additional sets of input decomposition rates are required for N and P. The names of the mineralization rates of POC1-5 and DOC have changed after the introduction of separate mineralization rates of PON1-5, DON, POP1-5 and DOP. When using the new names for the mineralization rates of POC1-5 and DOC (as in the tables below), for option $SWOMDec$=1.0 it is necessary to also allocate input values to the mineralization rates of PON1-5, DON, POP1-5 and DOP. The rates for POC1-5 and DOC will also be used for POS1-5 and DOS.
- ◇ For a start, the first-order mineralisation rates *ky_YdcX20* for POX_{1-5} and DOX can be set to 0.15, 0.05, 0.005, 0.00001, 0,00001 and 0.001 d^{-1} respectively, the maximal and

minimal values being the same. The attenuation constants for electron acceptors b_{ni} and b_{su} can be set at 1.0. When using option $SWOMDec$=0.0, the stochiometric constants for refractory detritus *a_dNpr*, *a_dPpr* and *a_dSpr* can be set at 0.05 gN.gC^{-1}, 0.005 gP.gC^{-1} and 0.005 gS.gC^{-1}. The conversion fractions *b_poc1poc2*, *b_poc2poc3* and *b_poc3poc4* can be set at 1.0, conversion fractions *b_poc1doc*, *b_poc2doc* and *b_poc3doc* at 0.025, and the additional conversion fractions for POC5 *b_poc5poc4* and *b_poc5doc* at 0.0. Redfield ratios ($C_{106}N_{16}P_1S_1$) and 40 % lower values may be used for the maximal and minimal values of the remaining stochiometric constants.

- ◇ Not all POX1-5 and DOX substances need to be included in a model, but the substances need to form a logical coherent decomposition scheme. The most simple scheme contains POX1 only. Extensions subsequently add POX2 and/or DOC, POX3 and POX4. POX5 can be added independently. The default values of *b_poc1poc2*, *b_poc2poc3* and *b_poc3poc4* are 1.0, and the default value of *b_poc5poc4* is 0.4. The default value of *b_poc1doc* is 0.0, the default values of *b_poc2doc* and *b_poc3doc* are 0.025, and the default value of *b_poc5doc* is 0.04. If some of the POX2-4 and DOC substances are not included in the model, the conversion fractions that would deliver a production flux for one of the missing substances need to be allocated the value 0.0.
- ◇ In case an upper limit of a stochiometric constant is set equal to its lower limit (for instance au_dNf = al_dNf or au_dPf = al_dPf.), then the process routine might set the pertinent mineralization rate at the average of the maximal and minimal rates to prevent dividing by zero. In this case it is recommended to also allocate the same value to the maximal rate and the minimal rate in order to avoid misinterpretation.
- ◇ Loads of organic matter may be allocated to each of the detritus fractions. The user must make a choice on the basis of the origin and the history of the organic loads. For instance, dead algae biomass and raw domestic waste may be allocated to the fast (mainly) and medium slow decomposing detritus fractions. Treated domestic waste to the medium slow and slow decomposing fractions, terrestrial organic matter to the slow decomposing fraction, and dissolved organic (humic) matter to the dissolved refractory fraction.
- ◇ When the terrestrial vegetation module is included in a model, detritus fractions for vegetation biomass can be specified by the user. Stem and root biomass will be allocated to POC/N/P/S5. In connection with the vegetation module these substances must be defined as inactive substances. When the vegetation module is not used, there is no need to include POC/N/P/S5 in the model.
- ◇ The algae module and/or the terrestrial vegetation module can be used with or without POS1-5 and DOS.

Additional references

DiToro (2001), Smits and Molen (1993), Westrich and Berner (1984), WL | Delft Hydraulics (1997), WL | Delft Hydraulics (1980a)

Table 8.1: *Definitions of the input parameters in the above equations for DECFAST, DECMEDIUM and DECSLOW. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas[1]	**Name in input**	**Definition**	**Units**
$an_{i,max}$	au_dNf	max. st. constant N in fast dec. detritus	gN.gC^{-1}
„	au_dNm	max. st. const. N in medium slow detr.	gN.gC^{-1}
„	au_dNs	max. st. constant N in slow dec. detritus	gN.gC^{-1}
$an_{i,min}$	al_dNf	min. st. constant N in fast dec. detritus	gN.gC^{-1}
„	al_dNm	min. st. const. N in medium slow detr.	gN.gC^{-1}

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Table 8.1: *Definitions of the input parameters in the above equations for DECFAST, DECMEDIUM and DECSLOW. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas[1]	**Name in input**	**Definition**	**Units**
„	al_dNs	min. st. constant N in slow dec. detritus	gN.gC^{-1}
ap$_{i,max}$	au_dPf	max. st. constant P in fast dec. detritus	gP.gC^{-1}
„	au_dPm	max. st. const. P in medium slow detr.	gP.gC^{-1}
„	au_dPs	max. st. constant P in slow dec. detritus	gP.gC^{-1}
ap$_{i,min}$	al_dPf	min. st. const. P in fast dec. detritus	gP.gC^{-1}
„	al_dPm	min. st. const. P in medium slow detr.	gP.gC^{-1}
„	al_dPs	min. st. constant P in slow dec. detritus	gP.gC^{-1}
ar$_j$	a_dNpr	stoch. constant N in refractory detritus	gN.gC^{-1}
„	a_dPpr	stoch. constant P in refractory detritus	gP.gC^{-1}
„	a_dSpr	stoch. constant S in refractory detritusitus	gS.gC^{-1}
b$_i$	$b_poc1poc2$	conv. fraction fast detr. into medium detr.	-
„	$b_poc2poc3$	conv. fraction medium detr. into slow detr.	-
„	$b_poc2doc$	conv. fr. medium detr. into diss. refr. detr.	-
„	$b_poc3poc4$	conv. fr. slow detr. into part. refr. detr.	-
„	$b_poc3doc$	conv. fr. slow detr. into diss. refr. detr.	-
b_{ni}	b_ni	atten. const. for nitrate as el. acceptor	-
b_{su}	b_su	atten. const. for sulfate as el. acceptor	-
Coc$_i$	$POC1$	conc. organic carbon in fast detritus	gC.m$^{-3}\mathscr{b}$
„	$POC2$	conc. organic carbon in medium detritus	gC.m$^{-3}\mathscr{b}$
„	$POC3$	conc. organic carbon in slow detritus	gC.m$^{-3}\mathscr{b}$
Con$_i$	$PON1$	conc. organic nitrogen in fast detritus	gN.m$^{-3}\mathscr{b}$
„	$PON2$	conc. organic nitrogen in medium detritus	gN.m$^{-3}\mathscr{b}$
„	$PON3$	conc. organic nitrogen in slow detritus	gN.m$^{-3}\mathscr{b}$
Cop$_i$	$POP1$	conc. organic phosphorus in fast detritus	gP.m$^{-3}\mathscr{b}$
„	$POP2$	conc. organic phosphorus in medium detritus	gP.m$^{-3}\mathscr{b}$
„	$POP3$	conc. organic phosphorus in slow detritus	gP.m$^{-3}\mathscr{b}$
Cos$_i$	$POP1$	conc. organic sulfur in fast detritus	gS.m$^{-3}\mathscr{b}$
„	$POP2$	conc. organic sulfur in medium detritus	gS.m$^{-3}\mathscr{b}$
„	$POP3$	conc. organic sulfur in slow detritus	gS.m$^{-3}\mathscr{b}$
Cox	OXY	concentration of dissolved oxygen	gO$_2$ m$^{-3}\mathscr{b}$
Cni	$NO3$	concentration of nitrate	gN m$^{-3}\mathscr{b}$
$facc_{j,i}$	–	accel. factors nutrient strip. for six detritus components	-
fel	–	limiting factor for electron acceptors	-

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Table 8.1: *Definitions of the input parameters in the above equations for DECFAST, DECMEDIUM and DECSLOW. Volume units refer to bulk (b) or to water (w).*

Name in formulas[1]	**Name in input**	**Definition**	**Units**
$fnut_i$	–	limiting factors for nutrient availability	-
$kmin_{i,max,20}$	$ku_dFdcC20$	max. min. rate fast detr-C at 20 °C	d^{-1}
„	$ku_dMdcC20$	max. min. rate medium detr-C detr. at 20 °C	d^{-1}
„	$ku_dSdcC20$	max. min. rate slow detr-C at 20 °C	d^{-1}
$kmin_{i,min,20}$	$kl_dFdcC20$	min. min. rate fast detr-C at 20 °C	d^{-1}
„	$kl_dMdcC20$	min. min. rate medium detr-C at 20 °C	d^{-1}
„	$kl_dSdcC20$	min. min. rate slow detr-C at 20 °C	d^{-1}
ktmin	kT_dec	temperature coefficient for mineralization	-
$kmin_{i,max,20}$	$ku_dFdcN20$	max. min. rate fast detr-N at 20 °C	d^{-1}
„	$ku_dMdcN20$	max. min. rate medium detr-N at 20 °C	d^{-1}
„	$ku_dSdcN20$	max. min. rate slow detr-N at 20 °C	d^{-1}
$kmin_{i,min,20}$	$kl_dFdcN20$	min. min. rate fast detr-N at 20 °C	d^{-1}
„	$kl_dMdcN20$	min. min. rate medium detr-N at 20 °C	d^{-1}
„	$kl_dSdcN20$	min. min. rate slow detr-N at 20 °C	d^{-1}
$kmin_{i,max,20}$	$ku_dFdcP20$	max. min. rate fast detr-P at 20 °C	d^{-1}
„	$ku_dMdcP20$	max. min. rate medium detr-P at 20 °C	d^{-1}
„	$ku_dSdcP20$	max. min. rate slow detr-P at 20 °C	d^{-1}
$kmin_{i,min,20}$	$kl_dFdcP20$	min. min. rate fast detr-P at 20 °C	d^{-1}
„	$kl_dMdcP20$	min. min. rate medium detr-P at 20 °C	d^{-1}
„	$kl_dSdcP20$	min. min. rate slow detr-P at 20 °C	d^{-1}
$SWOMDec$	$SWOMDec$	option (0.0 = nutrient stripping; 1.0 = different rates)	-
T	$Temp$	temperature of water	°C
T	$NatTemp$	temperature of air and sediment when ran dry	°C

[1] j = C, N, P or S; i = POC1, POC2 or POC3.

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Table 8.2: *Definitions of the input parameters in the above equations for DECREFR, DECDOC and DECPOC5. Volume units refer to bulk (ℓ) or to water (w).*

Name in formulas[1]	**Name in input**	**Definition**	**Units**
$an_{i,max}$	au_dNPOC5	max. stoch. constant N in stem/root POC5	gN.gC^{-1}
$an_{i,min}$	al_dNPOC5	min. stoch. constant N in stem/root POC5	gN.gC^{-1}
$ap_{i,max}$	au_dPPOC5	max. stoch. constant P in stem/root POC5	gP.gC^{-1}
$ap_{i,min}$	al_dPPOC5	min. stoch. constant P in stem/root POC5	gP.gC^{-1}
ar_j	a_dNpr	stoch. constant N in refr. detritus	gN.gC^{-1}
„	a_dPpr	stoch. constant P in refr. detritus	gP.gC^{-1}
„	a_dSpr	stoch. constant S in refr. detritus	gS.gC^{-1}
b_i	$b_poc5poc4$	conv. fraction stem/root POC5 into part. refr. detr.	-
„	$b_poc5doc$	conv. fraction stem/root POC5 into diss. refr. detr.	-
bni	b_ni	attenuation constant for nitrate as electron acceptor	-
bsu	b_su	attenuation constant for sulfate as electron acceptor	-
Coc_i	$POC4$	conc. organic C in part. refr. detritus	gC.m$^{-3}\ell$
„	$POC5$	conc. organic C in stems and roots	gC.m$^{-3}\ell$
„	DOC	conc. organic C in diss. refr. detritus	gC.m$^{-3}\ell$
Con_i	$PON4$	conc. organic N in part. refr. detritus	gN.m$^{-3}\ell$
„	$PON5$	conc. organic N in stems and roots	gN.m$^{-3}\ell$
„	DON	conc. organic N in diss. refr. detritus	gN.m$^{-3}\ell$
Cop_i	$POP4$	conc. organic P in part. refr. detritus	gP.m$^{-3}\ell$
„	$POP5$	conc. organic P in stems and roots	gP.m$^{-3}\ell$
„	DOP	conc. organic P in diss. refr. detritus	gP.m$^{-3}\ell$
Cos_i	$POP4$	conc. organic S in part. refr. detritus	gS.m$^{-3}\ell$
„	$POP5$	conc. organic S in stems and roots	gS.m$^{-3}\ell$
„	DOP	conc. organic S in diss. refr. detritus	gS.m$^{-3}\ell$
Cox	OXY	concentration of dissolved oxygen	gO_2.m$^{-3}\ell$
Cni	$NO3$	concentration of nitrate	gN.m$^{-3}\ell$
fel	-	limiting factor for electron acceptors	-
$kmin_{i,20}$	$k_dprdcC20$	min. rate part. refractory detr. at 20 °C	d^{-1}
„	$ku_P5dcC20$	max. min. rate stem/root POC5 at 20 °C	-
„	$kl_P5dcC20$	min. min. rate stem/root POC5 at 20 °C	d^{-1}
„	$k_DOCdcC20$	min. rate diss. refractory detr. at 20 °C	d^{-1}

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Table 8.2: *Definitions of the input parameters in the above equations for DECREFR, DECDOC and DECPOC5. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas[1]	**Name in input**	**Definition**	**Units**
$ktmin$	kT_dec	temperature coefficient for mineralisation	-
T	$Temp$	temperature	°C
T	$NatTemp$	temperature of air and sediment when ran dry	°C

[1] j = C, N, P or S; i = POC4, POC5 or DOC.

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8.2 Consumption of electron-acceptors

PROCESS: CONSELAC

The microbial decomposition (mineralisation, oxidation) of organic matter into carbon dioxide involves the consumption (reduction) of electron acceptors. These substances are used by different species of bacteria in a specific order in agreement with the thermodynamic potentials of the reduction processes (Santschi et al., 1990; DiToro, 2001). The electron acceptors are used in the following sequence: dissolved oxygen, nitrate, manganese(IV), iron(III), sulfate and carbon monoxide. The last substance as well as the electron donor hydrogen are derived from organic matter itself as intermediate products in methanogenesis, whereas the final products are more or less equal amounts of carbon dioxide and methane. The subsequent redox processes are indicated as:

- ◇ oxygen consumption;
- ◇ denitrification;
- ◇ manganese reduction;
- ◇ iron reduction;
- ◇ sulfate reduction; and
- ◇ methanogenesis.

In principal the thermodynamically more favourable reduction process excludes the less favourable process, provided that the more favourable electron acceptor is available. When an electron acceptor is not sufficiently supplied from an external source it will eventually become depleted. Therefore, oxygen consumption, denitrification and sulfate reduction are mutually exclusive to a large extent. However, denitrification may also be carried out in the water column at aerobic conditions by highly specialised bacteria (aerobic denitrification). After depletion of the respective electron acceptors methanogenesis takes over as a final possibility for bacteria to utilise organic matter for energy and growth. The reduction of manganese and iron are excluded by oxygen consumption and denitrification, but may concur with sulfate reduction and methanogenesis due to slow kinetics. Consequently, one would expect the occurrence of the various reduction processes in distinct stages in time, or in distinct water or sediment layers. However, due to spatial heterogeneity various processes may be active at the same time in the same compartment. In other words: Compartments may show substantial overlap with respect to the reduction processes.

The electron acceptors that can be considered in DELWAQ currently are dissolved oxygen, nitrate, iron(III), sulfate and organic matter, which replaces carbon monoxide as the actual electron acceptor. Methane as the product of organic matter decomposition by means of methanogenesis included in DELWAQ too. The production of reducing iron(II), sulfide, methane has implications for the dissolved oxygen budget. It is possible to exclude nitrate, iron(III), sulfate or methane from simulations. The reduction of manganese is ignored, as it can be considered implicit in sulfate and iron reduction.

Denitrification, iron reduction, sulfate reduction and methanogenesis are relatively sensitive to low temperature. In contrast with the aerobic decomposition of detritus, which may proceed at a slow but measurable rate below 4 $^{\circ}$C, the other processes nearly come to a halt below this temperature. This may be connected with the fact that only a rather small number of specialised bacteria species are capable of one of these processes. As contrasted with this the decomposition of organic matter is performed by a very large number of species, including species that are adapted to low temperature environments.

Denitrifiers, iron reducers, sulfate reducers and methanogens are predominantly sessile bac-

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teria, that need readily available organic substrates and that can only actively survive in an anoxic environment. This implies that denitrification usually only proceeds in the lower part of the oxidising top sediment layer. The reducing substance may be organic matter but also ammonium (anaerobic ammonium oxidation; annamox). Denitrification may also be carried out in the water column at aerobic conditions by highly specialised bacteria or in anoxic pockets of suspended particles. Sulfate and iron reduction and even more so methanogenesis usually only occur in the deeper parts of sediment. However, all these may proceed in completely anoxic water layers in deep stratified water systems.

The consumption (reduction) rates depend on electron acceptor availability (limitation) as well as on inhibition by the next more favourable process. The overall consumption of electron acceptors is dependent of the organic matter decomposition flux. The fractional contributions of the electron acceptors are deduced on the basis of the relative abundance of electron acceptors, taking into account both limitation and inhibition. These fractions add up to one, and are used to calculate the organic matter mineralisation fluxes connected with dissolved oxygen consumption, denitrification, iron reduction, sulfate reduction and methanogenesis. DELWAQ converts these fluxes into the concurrent consumption fluxes for DO, nitrate, iron(III) and sulfate, and into the concurrent methane production flux.

Dead organic matter in natural water, also called detritus, is a complicated mixture of substances that vary greatly with respect to chemical structure. Therefore, the microbial decomposition (oxidation) of detritus is described considering various fractions of organic matter, each having its own decomposition rate. The decomposition of the organic fractions is described elsewhere for processes DECFAST, DECMEDIUM, DECSLOW, DECREFR, DECPOC5 and DECDOC. These processes are based on first-order kinetics regarding the concentration of organic matter. The total organic matter decomposition flux is calculated in CONSELAC as the sum of the fluxes for the four organic matter fractions.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process CONSELAC is generic in the sense that it is applied to both water layers and sediment layers, when sediment layers are simulated as compartments. However, it can also be used for the water column only in combination with one of the other options for mineralisation in the sediment (BMS1/2_i).

Process DENSED_NO3 is to be used in addition to CONSELAC only when the sediment is simulated according to the S1/S2 option. When sediment layers are not simulated explicitly, this process takes care that denitrification in the sediment proceeds anyhow, and ultimately causes the removal of nitrate from the water column.

Process CONSELAC has been implemented for the following substances:

◇ OXY, NO3, FeIIIpa, FeIId, SO4, SUD and CH4,

in connection with the following organic substances:

◇ POC1, POC2, POC3, POC4, POC5 and DOC.

The oxygen consumed is stored in TIC or CO2. The nitrate reduced is removed from the model as elementary nitrogen is not simulated. The iron reduced is withdrawn from the amorphous fraction of the particulate oxidizing iron FeIIIp, and added to the dissolved reducing iron FeIId.

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The sulfate reduced is added to dissolved sulfide SUD. Table 8.3 provides the definitions of the parameters occurring in the formulations.

Formulation

The relative contributions of the electron acceptors in the microbial decomposition of organic matter are formulated on the basis of limitation and inhibition terms according to Michaelis-Menten kinetics (Smits and Beek (2013)).

Consumption of oxygen

The consumption of oxygen at the aerobic decomposition of organic matter can be described with the following simplified reaction equation:

$$O_2 + CH_2O \Longrightarrow CO_2 + H_2O$$

For simplicity it is assumed that organic matter is represented by the molecular stochiometry of glucose, whereas in reality organic matter may be richer in hydrogen. In this example 2.667 gram of oxygen is consumed for every gram of carbon oxidised. The consumption of oxygen is limited by the availability of dissolved oxygen. This process is not inhibited by any other electron acceptor. However, the decomposition of organic matter is temperature dependent. Since the temperature dependency of the consumption of the electron acceptors is different to a certain extent for each of the electron acceptors, it is necessary to consider this in the contributions of the electron-acceptors. The contribution of dissolved oxygen in the mineralisation of organic matter is proportional to:

$$fox_{20} = \left(\frac{Cox}{Ksox \times \phi + Cox} \right)$$

where:

Cox	dissolved oxygen concentration [g.m$^{-3}_{\ell}$]
fox_{20}	unscaled relative contr. of oxygen consumption in mineralisation at 20 °C [-]
$Ksox$	half saturation constant for dissolved oxygen limitation [gO_2 m$^{-3}_{w}$]
ϕ	porosity [-]

The relative contribution is the following function of temperature:

$$fox = fox_{20} \times ktoxc^{(T-20)}$$

where:

fox	unscaled relative contribution of oxygen consumption in mineralisation [-]
$ktoxc$	temperature coefficient for oxygen consumption [-]
T	temperature [°C]

Denitrification

Denitrification can be described as a number of consecutive chemical reactions in which oxygen is made available for the oxidation of organic matter. Several intermediate reduction products are formed, but the first step from nitrate to a nitrite is rate limiting. The accumulation of the intermediate products including toxic nitrite and various toxic nitrogen oxides is generally negligible. The overall reaction equation is:

$$4NO_3^- + 4H_3O^+ + 5CH_2O \Longrightarrow 2N_2 + 5CO_2 + 11H_2O$$

Denitrification ultimately removes nitrate from the water phase and produces elemental nitrogen that may escape into the atmosphere. The process delivers 2.86 gO_2 gN^{-1}, instantly consumed for the oxidation of organic matter. Consequently, the process consumes 0.933 gram N

per gram C. Denitrification is limited by the availability of nitrate. It is inhibited by dissolved oxygen. The contribution of nitrate in the mineralisation of organic matter is proportional to:

$$fni_{20} = \left(\frac{Cni}{Ksni \times \phi + Cni}\right) \times \left(1 - \frac{Cox}{Ksoxi \times \phi + Cox}\right)$$

where:

Cni	nitrate concentration [gN m_{ℓ}^{-3}]
fni_{20}	unscaled relative contribution of denitrification in mineralisation at 20 °C [-]
$Ksni$	half saturation constant for nitrate limitation [gN m_{w}^{-3}]
$Ksoxi$	half saturation constant for dissolved oxygen inhibition [$gO_2.m_{w}^{-3}$]

The relative contribution of denitrification needs to be adjusted for (low) temperature:

$$fni = fct \times fni_{20} \times ktden^{(T-20)}$$
$$fct = 1.0 \qquad \text{if} \quad T \geq T_c$$
$$fct = fden \qquad \text{if} \quad T < T_c$$

where:

fct	reduction factor for temperatures below critical temperature [-]
$fden$	reduction factor for denitrification below critical temperature [-]
fni	unscaled relative contribution of denitrification in mineralisation [-]
$ktden$	temperature coefficient for denitrification [-]
T	temperature [°C]
T_c	critically low temperature for specific bacterial activity [°C]

Imposing of a higher temperature coefficient than the coefficient for aerobic detritus composition leads to reduction of the relative contribution of denitrification. Below the critical temperature, the contribution of denitrification may be reduced further to a low background level, when $fden$ receives a value smaller than 1.0. The second reduction implies a discontinuity at the critical temperature.

Because denitrification is not to occur when dissolved oxygen is present in significant quantity, it is necessary to exclude denitrification if DO exceeds a certain critical level:

$$fni = 0.0 \qquad \text{if} \quad Cox \geq Coxc_1 \times \phi$$

where:

$Coxc_1$	critical dissolved oxygen conc. for inhibition of denitrification [g m_{ℓ}^{-3}]

Iron reduction

Iron reduction is assumed to take place on the surface of iron minerals, the amorphous fraction $Fe(OH)_3$ or FeOOH, which leads to the following reaction equation:

$$4Fe(OH)_3a + CH_2O \Rightarrow 4FeIId + CO_2 + 3H_2O + 8OH^-$$

The resulting dissolved reducing iron may largely precipitate with sulfide. The process delivers 0.143 $gO_2.gFe^{-1}$, instantly consumed for the oxidation of organic matter. Consequently, the process consumes 18.67 gram Fe per gram C. Iron reduction is limited by the availability of the amorphous fraction of particulate oxidizing iron. It is inhibited by both nitrate and dissolved oxygen. However, it is reasonable to assume that nitrate is present in substantial quantities at

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the significant presence of dissolved oxygen. Therefore, the relative contribution of iron in the mineralisation of organic matter is proportional to:

$$ffe_{20} = \left(\frac{Cfea}{Ksfe \times \phi + Cfea}\right) \times \left(1 - \frac{Cni}{Ksnifei \times \phi + Cni}\right)$$

where:

$Cfea$	amorphous oxidizing iron concentration [gFe.m$^{-3}_{b}$]
ffe_{20}	unscaled relative contrib. of iron reduction in mineralisation at 20 °C [-]
$Ksfe$	half saturation constant for iron limitation [gFe.m$^{-3}_{w}$]
$Ksnifei$	half saturation constant for nitrate inhibition of iron reduction [gN.m$^{-3}_{w}$]

The relative contribution of iron reduction is adjusted for (low) temperatures in the same way as in the case of denitrification:

$$ffe = fct \times ffe_{20} \times ktird^{(T-20)}$$
$$fct = 1.0 \quad \text{if } T \geq Tc$$
$$fct = fird \quad \text{if } T < Tc$$

where:

$fird$	reduction factor for iron reduction below critical temperature [-]
ffe	unscaled relative contribution of iron reduction in mineralisation [-]
$ktird$	temperature coefficient for iron reduction [-]

Because iron reduction is not to occur when dissolved oxygen is present in significant quantity, it is necessary to exclude iron reduction if DO exceeds a certain critical level:

$$ffe = 0.0 \quad \text{if } Cox \geq Coxc_2 \times \phi$$

where:

$Coxc_2$	= critical dissolved oxygen conc. for inhibition of iron reduction (g.m^{-3}b)

Sulfate reduction

Sulfate reduction is also carried out in a number of consecutive steps in which oxygen is made available for the oxidation of organic matter. The overall reaction equation is:

$$SO_4^{-2} + 2CH_2O \Longrightarrow S^{-2} + 2CO_2 + 2H_2O$$

Sulfate reduction removes sulfate and ultimately produces sulfide, which may largely precipitate with iron(II). The process delivers 2 gO_2 gS^{-1}, instantly consumed for the oxidation of organic matter. Consequently, the process consumes 1.333 gram S per gram C. Sulfate reduction is limited by the availability of sulfate. It is inhibited by both nitrate and dissolved oxygen, but not by oxidizing iron due to the slow kinetics of iron reduction. However, it is reasonable to assume that nitrate is present in substantial quantities at the significant presence of dissolved oxygen. Therefore, the relative contribution of sulfate in the mineralisation of organic matter is proportional to:

$$fsu_{20} = \left(\frac{Csu}{Kssu \times \phi + Csu}\right) \times \left(1 - \frac{Cni}{Ksnisui \times \phi + Cni}\right)$$

with:

Csu	sulfate concentration [gS m^{-3}_{ℓ}]
fsu_{20}	unscaled relative contrib. of sulfate reduction in mineralisation at 20 °C [-]
$Kssu$	half saturation constant for sulfate limitation [gS m^{-3}_{w}]
$Ksnisui$	half saturation constant for nitrate inhibition of sulfate reduction [gN m^{-3}_{w}]

The relative contribution of sulfate reduction is adjusted for (low) temperatures in the same way as in the case of denitrification:

$$fsu = fct \times fsu_{20} \times ktsrd^{(T-20)}$$
$$fct = 1.0 \quad \text{if} \quad T \geq T_c$$
$$fct = fsrd \quad \text{if} \quad T < T_c$$

where:

$fsrd$	reduction factor for sulfate reduction below critical temperature [-]
fsu	unscaled relative contribution of sulfate reduction in mineralisation [-]
$ktsrd$	temperature coefficient for sulfate reduction [-]

Because sulfate reduction is not to occur when dissolved oxygen is present in significant quantity, it is necessary to exclude sulfate reduction if DO exceeds a certain critical level:

$$fsu = 0.0 \quad \text{if} \quad Cox \geq Coxc_3 \times \phi$$

where:

$Coxc_3$	critical dissolved oxygen conc. for inhibition of sulfate reduction [g.m^{-3}_{ℓ}]

Methanogenesis

Organic matter will be decomposed by bacteria into carbon dioxide and methane when all other electron acceptors have been depleted. The production of these substances takes place in several intermediate steps, in which carbon monoxide and hydrogen feature. Assuming the glucose molecular stochiometry for organic matter the overall reaction equation is:

$$2CH_2O \Longrightarrow CO_2 + CH_4$$

Methane dissolves until saturation, after which methane may be stored and removed as gass bubbles (ebullition). Methanogenesis does not deliver dissolved oxygen, and is only limited by the availability of organic matter. The process is inhibited by the availability of sulfate, nitrate and dissolved oxygen, but not by oxidizing iron due to the slow kinetics of iron reduction. However, it is reasonable to assume that sulfate is present in substantial quantities at the significant presence of dissolved oxygen or nitrate. Therefore, the relative contribution of sulfate in the mineralisation of organic matter is proportional to:

$$fch4_{20} = \left(1 - \frac{Csu}{Kssui \times \phi + Csu}\right)$$

where:

$fch4_{20}$	unscaled relative contribution of methanogenesis in mineralisation at 20 °C [-]
$Kssui$	half saturation constant for sulfate inhibition [gS m^{-3}_{w}]

The relative contribution of methanogenesis is adjusted for low temperatures in the same way as in the case of denitrification:

$$fch4 = fct \times fch4_{20} \times ktmet^{(T-20)}$$
$$fct = 1.0 \quad \text{if} \quad T \geq T_c$$
$$fct = fmet \quad \text{if} \quad T < T_c$$

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where:

$fch4$	unscaled relative contribution of methanogenesis in mineralisation [-]
$fmet$	reduction factor for methanogenesis below critical temperature [-]
$ktmet$	temperature coefficient for methanogenesis [-]

Because methanogenesis is not to occur when dissolved oxygen or nitrate are present in significant quantities, it is necessary to exclude methanogenesis if DO or nitrate exceeds a certain critical level:

$$fch4 = 0.0 \qquad \text{if} \quad Cox \geq Coxc_4 \times \phi \quad \text{or} \quad Cni \geq Cnic \times \phi$$

where:

$Coxc_4$	critical dissolved oxygen conc. for inhibition of methanogenesis [g m_w^{-3}]
$Cnic$	critical nitrate conc. for inhibition of methanogenesis [gN m_w^{-3}]

Corrections for negative concentrations

Notice that negative concentrations would cause incorrect relative contributions. DELWAQ checks on negative concentrations anyway and equals them effectively to zero, but only locally in process CONSELAC.

The scaled relative contributions

The scaled contributions of the five reduction processes to the decomposition of organic matter now follow from the requirement that the sum of these contributions equals one:

$$\begin{aligned}
frox &= \frac{fox}{fox + fni + ffe + fsu + fch4} \\
frni &= \frac{fni}{fox + fni + ffe + fsu + fch4} \\
frfe &= \frac{ffe}{fox + fni + ffe + fsu + fch4} \\
frsu &= \frac{fsu}{fox + fni + ffe + fsu + fch4} \\
frch4 &= 1 - frox - frni - ffe - frsu
\end{aligned}$$

where:

$frox$	scaled contribution of dissolved oxygen consumption [-]
$frni$	scaled contribution of denitrification [-]
$frfe$	scaled contribution of iron reduction [-]
$frsu$	scaled contribution of sulfate reduction [-]
$frch4$	scaled contribution of methanogenesis [-]

The total mineralisation flux

The total flux of the decomposition (mineralisation) of organic matter $Rtmin$ is equal to the sum of the mineralisation fluxes of the six fractions:

$$Rtmin = Rmin_1 + Rmin_2 + Rmin_3 + Rmin_4 + Rmin_5 + Rmin_6$$

where:

$Rmin_1$	mineralisation flux for organic carbon in the fast decomposing detritus fraction POC1 [gC m_ℓ^{-3} d^{-1}]
$Rmin_2$	mineralisation flux for organic carbon in the slowly decomposing detritus fraction POC2 [gC m_ℓ^{-3} d^{-1}]

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$Rmin_3$	mineralisation flux for organic carbon in the very slowly decomposing detritus fraction POC3 [gC m_{ℓ}^{-3} d^{-1}]
$Rmin_4$	mineralisation flux for organic carbon in the particulate refractory detritus fraction POC4 [gC m_{ℓ}^{-3} d^{-1}]
$Rmin_5$	mineralisation flux for organic carbon in dead stems and roots of vegetation detritus fraction POC5 [gC m_{ℓ}^{-3} d^{-1}]
$Rmin_6$	mineralisation flux for organic carbon in the dissolved refractory detritus fraction DOC [gC m_{ℓ}^{-3} d^{-1}]
$Rtmin$	total mineralisation flux for organic carbon [gC m_{ℓ}^{-3} d^{-1}]

Oxygen consumption

The mineralisation flux connected to oxygen consumption follows from:

$$Rcns = \min\left(frox \times Rtmin, 0.5 \times \frac{Cox}{2.67 \times \Delta t}\right)$$

$$frox' = \frac{0.5 \times Cox}{frox \times Rtmin \times 2.67 \times \Delta t}$$

where:

$frox'$	corrected scaled relative contribution of oxygen consumption [-]
$Rcns$	mineralisation flux connected to oxygen consumption [gC m_{ℓ}^{-3} d^{-1}]
Δt	the timestep of DELWAQ [days]

Since the oxygen consumption rate is only proportional to the concentration of organic matter and not to the concentration of dissolved oxygen, it is possible that negative dissolved oxygen concentrations arise. This happens when the stock of dissolved oxygen is too small to satisfy the demand. A negative concentration leads to $frox = 0.0$ as described before. Negative oxygen concentrations will therefore remain small and they will soon be eliminated by means of diffusion of oxygen. Negative oxygen concentrations are acceptable in DELWAQ, because they can be perceived as the negative oxygen equivalents of reduced substances such as iron(II) and manganese(II). However, in order to reduce negative concentrations as much as possible, a correction is carried out by means of limiting the oxygen consumption rate to 50 % of the stock of oxygen divided by the timestep, when the stock is too small to satisfy the demand.

Denitrification

The mineralisation flux connected to denitrification cannot be coupled to the total mineralisation flux in the same straightforward way as in the case of oxygen consumption. As explained above negative nitrate concentrations might arise. A negative concentration leads to $frni = 0.0$ as described above. However, negative nitrate concentrations are conceptually unacceptable. A correction is therefore carried out by means of limiting the denitrification rate to 90 % of the stock of nitrate divided by the timestep, when the stock is too small to satisfy the demand. The mineralisation flux and the corrected contribution are calculated as follows:

$$Rden = \min\left(frni \times Rtmin, 0.9 \times \frac{Cni}{0.933 \times \Delta t}\right)$$

$$frni' = \frac{0.9 \times Cni}{frni \times Rtmin \times 0.933 \times \Delta t}$$

where:

Cni	nitrate concentration [gN.m_{ℓ}^{-3}]

$frni'$	corrected scaled relative contribution of denitrification [-]
$Rden$	mineralisation flux connected to denitrification [gC.m$^{-3}_{\ell}$ d^{-1}]
Δt	the timestep of DELWAQ [days]

Iron reduction

The mineralisation flux connected to iron reduction needs a similar correction as made for denitrification, when the stock of oxidizing iron is too small to satisfy the demand. The mineralisation flux and the corrected contribution are calculated as follows:

$$Rird = min\left(frfe \times Rtmin\ ,\ 0.9 \times \frac{Cfea}{18.67 \times \Delta t}\right)$$

$$frfe' = \frac{0.9 \times Cfea}{frfe\ \times Rtmin \times 18.67 \times \Delta t}$$

where:

$Cfea$	amorphous oxidizing iron concentration [gFem-3ℓ]
$frfe'$	corrected scaled relative contribution of iron reduction [-]
$Rird$	mineralisation flux connected to iron reduction [gC m-3ℓd-1]

Sulfate reduction

The mineralisation flux connected to sulfate reduction needs a similar correction as made for denitrification, when the stock of sulfate is too small to satisfy the demand. The mineralisation flux and the corrected contribution are calculated as follows:

$$Rsrd = \min\left(frsu \times Rtmin, 0.9 \times \frac{Csu}{1.33 \times \Delta t}\right)$$

$$frsu' = \frac{0.9 \times Csu}{frsu \times Rtmin \times 1.33 \times \Delta t}$$

where:

Csu	sulfate concentration [gS m$^{-3}_{\ell}$]
$frsu'$	corrected scaled relative contribution of sulfate reduction [-]
$Rsrd$	mineralisation flux connected to sulfate reduction [gC m$^{-3}_{\ell}$ d^{-1}]

Methanogenesis

A limitation of the methanogenesis flux is not needed because the stock of electron acceptor (organic matter) is always large enough. The mineralisation flux connected to methanogenesis follows from:

$$Rmet = am \times frch4 \times Rtmin$$

where:

am	fraction of organic C actually turned into methane [-]
$Rmet$	mineralisation flux connected to methanogenesis [gC m$^{-3}_{\ell}$ d^{-1}]

The coefficient am is in fact a stochiometric constant of the decomposition reaction. By default this constant has a value of 0.5, assuming that the composition of organic matter is CH2O on average. Half of carbon ends up in methane, the other half in carbon dioxide.

Correction of oxygen consumption and methanogenesis

When one or more of the contributions of oxygen consumption, denitrification, iron reduction and sulfate reduction have changed due to limited stocks, the contribution of the other processes need to be corrected too. This is achieved by

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- ◇ shifting the required decrease of the fraction of denitrification to the fraction of oxygen consumption
- ◇ if also necessary, the required decrease of the fraction of oxygen consumption to the fraction of sulfate reduction
- ◇ if also necessary, the required decrease of the fraction of iron consumption to the fraction of sulfate reduction
- ◇ and if also necessary, the required decrease of the fraction of sulfate reduction to the fraction of methanogenesis.

The corrected contribution of methanogenesis follows from:

$$frch4' = 1 - frox' - frni' - frfe' - frsu'$$

where:

$frch4'$ corrected scaled relative contribution of methanogenesis [-]

Directives for use

- ◇ Indicative values for the limitation constants are: $KsOxCon = 1.0$ gO_2 $m^{-3}{}_w$, $KsNiDen = 0.25$ gN $m^{-3}{}_w$, $KsFeRed = 100\,000.0$ gFe $m^3{}_w$, $KsSuRed = 2.0$ gS $m^{-3}{}_w$.
  Indicative values for the inhibition constants are: $KsOxDenInh = 1.0$ gO_2 $m^{-3}{}_w$, $KsNiIReInh = 0.2$ gN $m^{-3}{}_w$, $KsNiSReInh = 0.2$ gN $m^3{}_w$, $KsSuMetInh = 1.0$ gS $m^{-3}{}_w$.
- ◇ The half saturation constants may have different values for the sediment and the water column, reflecting differences as to the abundance and activity of specific bacteria species. Raising a limitation constant leads to a smaller contribution of the specific process. Raising an inhibition constant leads to a larger contribution.
- ◇ The half saturation constants in the limitation and inhibition functions determine the actually occurring spatial overlap of processes. Denitrification, iron reduction, sulfate reduction and methanogenesis are virtually excluded from the water column when the values of the inhibition constants of these processes are decreased to 10% of the indicative values.
- ◇ The half saturation constants for inhibition in the water column may also be used to account for the consequences of inhomogeneity in the water column. Denitrification, iron reduction, sulfate reduction and even methanogenesis may occur in the lower part of the water column due to oxygen depletion near the sediment. The average dissolved oxygen concentration can still be clearly positive, which may lead to the underestimation of three of the reduction processes. The user could then decide to schematise the water column with several layers (compartments). As an alternative he may decide to raise the values of the half saturation constants for inhibition.
- ◇ A similar reasoning goes for the concentration gradients that may occur in organic matter rich suspended particles. Denitrification in the particles can be accounted for by raising the oxygen inhibition constant to about 2 gO_2 m^{-3}_w, which is an appropriate value for physical reasons.
- ◇ The temperature coefficients are connected to the temperature coefficient of the decomposition of organic matter. Default values are: $TcOxCon = 1.07$, $TcDen = 1.07$, $TcIRed = 1.07$, $TcSRed = 1.07$, $TcMet = 1.07$.
- ◇ The adjustment of the relative contributions of denitrification, iron reduction, sulfate reduction and methanogenesis for (low) temperature is based on retardation of consumption of the respective electron acceptors compared to the aerobic decomposition of detritus (retardation factors < 1.0). The critically low temperature $CTBactAc$ is 2–4 °C. In case sediment temperature is set equal to water temperature, one wants some enhancement in stead of retardation because generally sediment temperature is higher than water temperature in winter time. Enhancement factors $RedFacDen$, $RedFacIRed$, $RedFacSRed$, $RedFacMet$ can be 1.25.

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- ◇ The critical concentrations for inhibition of denitrification, iron reduction, sulfate reduction and methanogenesis should have low values. Recommended values are: $CoxDenInh = 1.0$ in water column, and = 5.0 in sediment, $CoxIRedInh = 0.05$, $CoxSRedInh = 0.05$, $CoxMetInh = 0.02$, $CniMetInb = 0.05$.
- ◇ Assuming CH2O as a measure for the chemical structure of organic matter the default stochiometric coefficients in the processes matrix of DELWAQ are:

  The amount of oxygen consumed per amount of carbon is 2.667 gO_2 gC^{-1}.
  The amount of nitrate consumed per amount of carbon is 0.932 gN gC^{-1}.
  The amount of iron consumed per amount of carbon is 18.67 gFe.gC^{-1}.
  The amount of sulfate consumed per amount of carbon is 1.333 gS gC^{-1}.
  The amount of methane produced per amount of carbon is 0.5 gC gC^{-1}.

- ◇ The corrected scaled relative contributions of dissolved oxygen consumption, denitrification, iron reduction, sulfate reduction and methanogenesis are available as the following output parameters: $FrOxCon$, $FrNitDen$, $FrFeRed$, $FrSulRed$, $FrMetGen$.
- ◇ Coeffcient $FrMetGeCH4$ is 0.5 by default. If the user would modify its value, he should realize that all oxygen and carbon dioxide fluxes have been quantified assuming that the basic composition of organic matter is CH_2O. He should modify these fluxes too.

Additional references

Boudreau (1996), DiToro (2001), Luff and Moll (2004), Santschi et al. (1990), Smits and Molen (1993), Soetaert et al. (1996), Vanderborght et al. (1977), Wang and Cappellen (1996), WL | Delft Hydraulics (2002), Wijsman et al. (2001)

Table 8.3: *Definitions of the parameters in the above equations for CONSELAC. Volume units refer to bulk ($\mathcal{b}$) or to water ($\mathcal{w}$).*

Name in formulas	Name in input	Definition	Units
Cox	OXY	dissolved oxygen concentration	gO_2 $m^{-3}_{\mathcal{b}}$
Cni	$NO3$	nitrate concentration	gN $m^{-3}_{\mathcal{b}}$
$Cfea$	$FeIIIpa$	particulate amorphous oxidizing iron concentration	gFe $m^{-3}_{\mathcal{b}}$
Csu	$SO4$	sulfate concentration	gS $m^{-3}_{\mathcal{b}}$
$Coxc_1$	$CoxDenInh$	critical diss. oxygen conc. inhibition of denitrific.	gO_2 $m^{-3}_{\mathcal{w}}$
$Coxc_2$	$CoxIRedInh$	critical diss. oxygen conc. inhibition of iron red.	gO_2 $m^{-3}_{\mathcal{w}}$
$Coxc_3$	$CoxSRedInh$	critical diss. oxygen conc. inhibition of sulfate red.	gO_2 $m^{-3}_{\mathcal{w}}$
$Coxc_4$	$CoxMetInh$	critical diss. oxygen conc. inhib. of methanogenesis	gO_2 $m^{-3}_{\mathcal{w}}$
$Cnic$	$CniMetInb$	critical nitrate conc. inhibition of methanogenesis	gN $m^{-3}_{\mathcal{w}}$
fox	-	unscaled rel. contr. of oxygen cons. in mineralisation	-

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Table 8.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
fni	-	unscaled rel. contr. of denitrif. in mineralisation	-
ffe	-	unscaled rel. contr. of iron red in mineralisation	-
fsu	-	unscaled rel. contr. of sulfate red. in mineralisation	-
$fch4$	-	unscaled rel. contr. of methanog. in mineralisation	-
$frox$	-	scaled rel. contr. of dissolved oxygen consumption	-
$frni$	-	scaled rel. contribution of denitrification	-
$frfe$	-	scaled rel. contribution of iron reduction	-
$frsu$	-	scaled rel. contribution of sulfate reduction	-
$frch4c$	-	scaled rel. contribution of methanogenesis	-
fct	-	reduction factor for temp. below critical temperature	-
$fden$	$RedFacDen$	reduction factor for denitr. below critical temperature	-
$fird$	$RedFacIRed$	reduction factor for iron red. below critical temperature	-
$fsrd$	$RedFacSRed$	reduction factor for sulfate red. below critical temperature	-
$fmet$	$RedFacMet$	reduction factor for methanog. below critical temperature	-
$ktoxc$	$TcOxCon$	temperature coefficient for oxygen consumption	-
$ktden$	$TcDen$	temperature coefficient for denitrification	-
$ktird$	$TcIred$	temperature coefficient for iron reduction	-
$ktsrd$	$TcSRed$	temperature coefficient for sulfate reduction	-
$ktmet$	$TcMet$	temperature coefficient for methanogenesis	-
$Ksox$	$KsOxCon$	half saturation constant for oxygen limitation	$gO_2\ m_w^{-3}$
$Ksni$	$KsNiDen$	half saturation constant for nitrate limitation	$gN\ m_w^{-3}$
$Ksfe$	$KsFiRed$	half saturation constant for iron limitation	$gFe\ m_w^{-3}$

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Table 8.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
$Kssu$	$KsSuRed$	half saturation constant for sulfate limitation	gS m_w^{-3}
$Ksoxi$	$KsOxDenInh$	half sat. const. for DO inhibition of denitrification	gO_2 m_w^{-3}
$Ksnifei$	$KsNiIRdInh$	half sat. const. for nitrate inhib. of iron reduction	gN m_w^{-3}
$Ksnisui$	$KsNiSRdInh$	half sat. const. for nitrate inhib. of sulfate reduction	gN m_w^{-3}
$Kssui$	$KsSuMetInh$	half sat. const. for sulfate inhib. of methanogenesis	gS m_w^{-3}
$Rcns$	-	mineralisation flux connected to oxygen consumption	gC m_b^{-3} d^{-1}
$Rden$	-	mineralisation flux connected to denitrification	gC m_b^{-3} d^{-1}
$Rird$	-	mineralisation flux connected to iron red	gC m_b^{-3} d^{-1}
$Rsrd$	-	mineralisation flux connected to sulfate reduction	gC m_b^{-3} d^{-1}
$Rmet$	-	mineralisation flux connected to methanogenesis	gC m_b^{-3} d^{-1}
$Rmin_1$	$f_MinPOC1$	mineralisation flux for organic carbon in the fast decomposing detritus fraction POC1	gC m_b^{-3} d^{-1}
$Rmin_2$	$f_MinPOC2$	mineralisation flux for organic carbon in the slowly decomposing detritus fraction POC2	gC m_b^{-3} d^{-1}
$Rmin_3$	$f_MinPOC3$	mineralisation flux for organic carbon in the very slowly decomposing detritus fraction POC3	gC m_b^{-3} d^{-1}
$Rmin_4$	$f_MinPOC4$	mineralisation flux for organic carbon in the particulate refractory detritus fraction POC4	gC m_b^{-3} d^{-1}
$Rmin_5$	$f_MinPOC5$	mineralisation flux for organic carbon in dead stems and roots, detritus fraction POC5	gC m_b^{-3} d^{-1}
$Rmin_6$	f_MinDOC	mineralisation flux for organic carbon in the dissolved refractory detritus fraction DOC	gC m_b^{-3} d^{-1}
am	$FrMetGeCH4$	fraction of organic C converted into methane (CH4)	-
T	$Temp$	temperature	°C

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Table 8.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
T_c	$CTBactAc$	critically low temp. for specific bacterial activity	°C
Δt	$Delt$	computational time-step	d
ϕ	$POROS$	porosity	$m^3_w\ m^{-3}_b$

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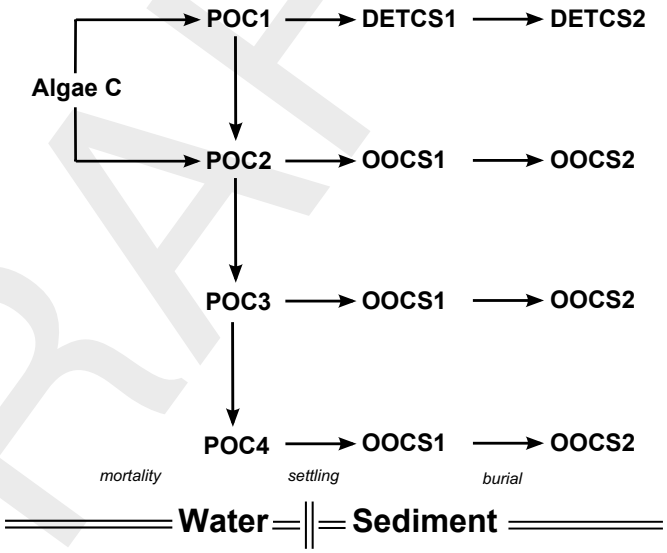
8.3 Settling of detritus

PROCESSES: SED_(I), SEDN(I), SED_CAAP, CALVS(I), COMPOS

The particulate organic matter components also indicated as detritus settle on the sediment. After settling these substances become part of the sediment detritus pools, depending on the way of modelling the detritus and the sediment. The detritus pools in the sediment are:

1 DET(C,N,P)S1/2 and OO(C,N,P)S1/2 for the S1/S2 approach
2 POC/N/P/S1-4, the same substances when sediment layers are simulated explicitly

For POX combined with the S1/2 approach the organic matter fractions are allocated to the sediment detritus pools as follows:



The decomposition rate constants of DETCS1/2 and OOCS1/2 should be lower than those for POC1 and POC2 taking into account that the sediment contains more refractory detritus.

Similar schemes apply to organic nitrogen (PON) and organic phosphorus (POP). For organic sulfur (POS) no provision has been made for option S1/2. The inorganic nutrients adsorbed phosphate (AAP), vivianite phosphate (VIVP), apatite phosphate (APATP) and opal silicate (OPAL) settle respectively into AAPS1 and DETSiS1 for S1/2.

Implementation

Processes SED_(i) have been implemented for the following substances:

◇ POC1, POC2, POC3, POC4, AAP, VIVP, APATP, OPAL, DETCS1, OOCS1, AAPS1 and DETSIS1

Processes SED_CAAP (independent settling) and SED_AAP (settling coupled to IM1/2/3) can be selected for AAP.

Process SEDN(i = POC1, POC2, POC3, POC4) has been implemented for the following substances:

◇ PON1, PON2, PON3, PON4, POP1, POP2, POP3, POP4, POS1, POS2, POS3, POS4, DETNS1, DETPS1, OONS1, and OOPS1.

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Processes SEDN(i) deliver the settling rates of organic nutrients (i) relative to organic carbon components (i). Process COMPOS provides the current local stoichiometric ratios fs of the organic nutrients (N,P,S) for this. in other words: the nutrients bound in the organic material settle proportionally to the organic matter as a whole. There can be no faster or slower settling, as that would lead to a separation of nutrients in a "physical" way instead of a biochemical.

Process SED_AAP is used for settling coupled to IM1/2/3. Alternative process SED_CAAP can be selected for independent settling.

Processes CALVS(i) may be used to modify the input settling velocity for shear stress and/or flocculation, which requires alternative input parameters $V0Sed(i)$.

Table 8.4 provides the definitions of the input parameters occurring in the formulations.

Formulation

The settling rates of the organic carbon components and the particulate inorganic nutrient components are described as the sum of zero-order and first-order kinetics. The rates are zero, when the shear stress exceeds a certain critical value, or when the water depth is smaller than a certain critical depth Krone (1962). The rates are calculated according to:

$$R_{set_i} = f_{\tau_i} \times \frac{F_{set_i}}{H}$$

$$\begin{aligned} if H < H_{min} \\ F_{set_i} &= 0.0 \\ else \\ F_{set_i} &= \min\left(F_{set'_i}, \frac{Cx_i \times H}{\Delta t}\right) \\ F_{set'_i} &= F_{set0_i} + s_i \times Cx_i \end{aligned}$$

$$\begin{aligned} if \tau = -1.0 \\ f_{\tau_i} &= 1.0 \\ else \\ f_{\tau_i} &= \max\left(f_{\tau_{min_i}}, \left(1 - \frac{\tau}{\tau_{c_i}}\right)\right) \end{aligned}$$

where:

C_x	concentration of a substance [gC/P/Si m^{-3}]
F_{set0}	zero-order settling flux of a substance [gC/P/Si m^{-2} d^{-1}]
F_{set}	settling flux of a substance [gC/P/Si m^{-2} d^{-1}]
f_τ	shear stress limitation function [-]
$f_{\tau_{min}}$	user-supplied minimum value for shear stress limitation function [-]
H	depth of the water column [m]
H_{min}	minimal depth of the water column for resuspension [m]

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R_{set}	settling rate of a substance [gC/P/Si m^{-3} d^{-1}]
s	settling velocity of a substance [m d^{-1}]
τ	shear stress [Pa]
τ_c	critical shear stress for settling of a substance [Pa]
Δt	timestep in DELWAQ [d]
i	index for substance (i), POC1, POC2, POC3, POC4, AAP, VIVP, APATP, OPAL.

For use in combination with the "buffer" model by (Kessel et al., 2011), the settling flux may be distributed over S1 and S2:

$$R_{set_{i,S1}} = (1 - \alpha_i) R_{set_i}$$
$$R_{set_{i,S2}} = \alpha_i R_{set_i}$$

where:

$R_{set_{i,S1}}$	settling rate to S1 [g m^{-3} d^{-1}]
$R_{set_{i,S2}}$	settling rate to S2 [g m^{-3} d^{-1}]
α_i	fraction of settling to S2 [-]

The settling of organic nutrients is coupled to the settling of organic carbon as follows:

$$R_{sn_{j,i}} = \frac{R_{set_i}}{f_{s_{j,i}}}$$

where:

$f_{s_{j,i}}$	stochiometric ratios carbon over nutrient j in detritus component i [gC gX^{-1}]
$R_{sn_{j,i}}$	settling rate of nutrient j in organic detritus component i [gX m^{-3} d^{-1}]
i	index for organic carbon component (i); POC1, POC2, POC3, POC4
j	index for organic nutrient (j); PON1/2/3/4, POP1/2/3/4 and POS1/2/3/4

Directives for use

- ◇ τ can be simulated with process CALTAU. If not simulated or imposed τ will have the default value -1.0, which implies that settling is not affected by the shear stress. For specific input parameters, see the process description of CALTAU.
- ◇ Settling does not occur, when $Depth$ (actually the water layer thickness) is smaller than the minimum thickness $MinDepth$ for settling, which has a default value of 0.1 m. When desired $MinDepth$ may be given a different value.
- ◇ The primary settling fluxes $fSed(i)$ delivered by processes SED_(i), and the additional settling fluxes $fSed(j)$ delivered by processes SEDNPOC1, SEDNPOC2, SEDNPOC3 and SEDNPOC4 are available as additional output parameters.
- ◇ The option to distribute the settling flux over layers S1 and S2 and the option to use a user-supplied minimum value for the shear stress limitation function have only been implemented for POC1-5 and Opal, not for the other state variables mentioned in this Section.

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Table 8.4: *Definitions of the input parameters in the above equations for SED_(i), SEDN(i) and SED_CAAP.*

Name in formulas	Name in input	Definition	Units
Cx_i^1	$(i)^1$	concentration of substance (i)	gC/P/Si m^{-3}
F_{set0_i}	$ZSed(i)$	zero-order settling flux of substance (i)	gC/P/Si m^{-2} d^{-1}
$f_{s_{j,i}}$	$C-NPOC1^2$	actual ratio C and N in POC1	gC gN^{-1}
	$C-NPOC2$	actual ratio C and N in POC2	gC gN^{-1}
	$C-NPOC3$	actual ratio C and N in POC3	gC gN^{-1}
	$C-NPOC4$	actual ratio C and N in POC4	gC gN^{-1}
	$C-PPOC1$	actual ratio C and P in POC1	gC gN^{-1}
	$C-PPOC2$	actual ratio C and P in POC2	gC gP^{-1}
	$C-PPOC3$	actual ratio C and P in POC3	gC gP^{-1}
	$C-PPOC4$	actual ratio C and P in POC4	gC gP^{-1}
	$C-SPOC1$	actual ratio C and S in POC1	gC gS^{-1}
	$C-SPOC2$	actual ratio C and S in POC2	gC gS^{-1}
	$C-SPOC3$	actual ratio C and S in POC3	gC gS^{-1}
	$C-SPOC4$	actual ratio C and S in POC4	gC gS^{-1}
$f_{s2,TIM}$	$FrTIMS2$	actual fraction of TIM in S2	[-]
$f_{max_{s2,TIM}}$	$FrTIMS2-MAX$	maximum allowed fraction of TIM in S2	[-]
$f_{\tau_{min_i}}$	$PSedMin(i)$	minimum value for shear stress limitation function for (i)	[-]
H	$Depth$	depth of the water column, thickness of water layer	m
H_{min}	$MinDepth$	minimum layer thickness for settling and resuspension	m
s_i	$VSedPOC$	settling velocity of POC	m d^{-1}
	$VSedIM$	settling velocity of inorg. matter	m d^{-1}
	$VSedAAP$	settling velocity of AAP	m d^{-1}
	$VSedVIVP$	settling velocity of VIVP	m d^{-1}
	$VSedAPATP$	settling velocity of APATP	m d^{-1}
	$VSedOPAL$	settling velocity of OPAL	m d^{-1}
α_i	$Fr(i)SedS2$	fraction of settling to S2 for (i)	[-]
τ	Tau	shear stress	Pa

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Table 8.4 – continued from previous page

Name in formulas	Name in input	Definition	Units
τ_{c_i}	$TaucS(i)$	critical shear stress for settling of substance (I)	Pa
Δt	$Delt$	timestep in DELWAQ	d

[1]) Substances are POC1, POC2, POC3, POC4, AAP, VIVP, APATP and OPAL. Additional substances (j) for output are PON1, PON2, PON3, PON4, POP1, POP2, POP3, POP4, POS1, POS2, POS3 and POS4.
[2]) All stochiometric ratios are delivered by process COMPOS.

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8.4 Mineralization of detritus in the sediment (S1/2)

PROCESS: BMS1/2_i

Detritus is produced when algae and higher plants die off. The microbial decomposition of detritus into its basic inorganic components such as carbon dioxide, ammonium and phosphate is called mineralization. The mineralization starts in the water column, where (most of) the detritus is produced. The process continues at and in the sediment after settling of detritus particles at the sediment. This process specifically deals with the mineralization in the sediment according to simplified formulations. Various factors that limit the mineralization rates are ignored here. The decomposition in the water column, formulated with much more process detail is described elsewhere in this manual.

During the decomposition process the organic matter is gradually converted into material that is more resistant to microbial breakdown. This phenomenon is ignored in the simplified approach of mineralization in the sediment. Two detritus fractions are considered, the slow decomposing detritus fraction ($DETC/N/P/SiS1/2$) and the refractory detritus fraction ($OOC/N/PS1/2$). In the sediment the latter pool is not produced from the former pool. Both settle from the water column. The fast decomposing detritus fraction ($POC/N/P1$) and OPAL settle into the former pool, whereas the other fractions ($POC/N/P2$, $POC/N/P3$, $POC/N/P3$) settle into the latter pool. Carbon, nitrogen, phosphorus and silicate in detritus are considered as separate state variables in the model. Opal silicate in the sediment is dealt with as a detritus component. For the water column a specific dissolution process has been implemented.

In addition to mineralization the desorption of phosphate can be taken into account. The adsorbed phosphate in the water column AAP settles into $AAPS1$ The sorption in water and sediment formulated with much more process detail is described elsewhere in this manual.

The rates of mineralization and desorption are also a function of the temperature. The rates tend to decrease progressively at temperatures below 4 °C. Since the decomposition of organic matter is performed by a very large number of species, including species that are adapted to low temperature environments, the effect is not nearly as strong as in the case of nitrification. This ”near-freezing” effect can be taken into account in the sediment by means of imposing a discontinuity at a critically low temperature.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Processes BMS1_i , BMS2_i , DESO_AAPS1 and DESO_AAPS2 deal with so-called ”inactive substances”. (i) refers to the name of one of the detrital substances mentioned below. In the model these substances are as if present in the water column, but they are not subjected to transport by advection and dispersion. The resulting mineralization fluxes are input to the water column.

Processes BMS1_i and BMS2_i have been implemented for the following substances:

- ◇ OXY, NH4, PO4 and Si
- ◇ DETCS1, DETNS1, DETPS1, DETSiS1, DETCS2, DETNS2, DETPS2, DETSiS2, OOCS1, OONS1, OOPS1, OOSiS1, OOCS2, OONS2, OOPS2 and OOSiS2.

Processes DESO_AAPS1 and DESO_AAPS2 have been implemented for the following sub-

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stances:

◇ PO4, AAPS1 and AAPS2

Table 8.5 provides the definitions of the parameters occurring in the formulations.

Formulation

The mineralization of all detritus components and the desorption of phosphate has been formulated as the sum of a first-order kinetic process and a zero-order kinetic process. The first-order process is only active when the temperature exceeds a critical temperature. Consequently, the formulations are as follows:

$$Rmin_{i,k} = \begin{cases} \frac{k0min_{i,k}}{H} + \frac{kmin_{i,k} \times Mx_{i,k}}{V} & \text{if} \quad T \geq Tc \\ \frac{k0min_{i,k}}{H} & \text{if} \quad T < Tc \end{cases}$$

$$kmin_{i,k} = kmin_{i,k,20} \times ktmin_i^{(T-20)}$$

where:

Mx	quantity of organic carbon, nitrogen, phosphorus or silicate ([gC/N/P/Si]; x is oc, on, op, osi or aap)
$k0min$	zero-order mineralization or desorption rate [gC/N/P/Si m^{-2} d^{-1}]
$kmin$	first-order mineralization or desorption rate [d^{-1}]
$kmin_{20}$	first-order mineralization or desorption rate at 20 °C [d^{-1}]
$ktmin$	temperature coefficient for mineralization or desorption [-]
$Rmin$	mineral. rate org. carbon, nitrogen, phosphorus or silicate, or desorption rate of phosphate [gC/N/P/Si m_{ℓ}^{-3} d^{-1}]
T	temperature [°C]
T_c	critical temperature [°C]
i	index for the detritus component
k	index for sediment layers S1 and S2

Directives for use

◇ For a start, the first-order mineralization rates $RcDetXS1$ and $RcOOXS1$ can be set to 0.01 and 0.001 d^{-1}, the zero-order mineralization rates $ZMinDetXS1$ and $ZminOOXS1$ to 0.0 gX m^{-2} d^{-1} and the critical temperature $CTMin$ to 0.0 °C. If used at all, 4 °C seems an appropriate choice for the critical temperature. It is possible (and very much justifiable) to provide lower mineralization rates to the S2 sediment layer than to the S1 layer.

◇ Calibration of the rates should lead to a more or less stable amount of detritus in the sediment, provided that the input of detritus into the sediment does not substantially change from one year to the next. That is to say, the amounts of detritus at the end of a simulated year should be more or less equal to the initial amounts.

Additional references

Smits and Molen (1993), Westrich and Berner (1984), WL | Delft Hydraulics (1980a)

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Table 8.5: *Definitions of the parameters in the above equations for BMS1_i, BMS2_i, DESO_AAPS1 and DESO_AAPS2.) (i) is one of the names of the 7 detritus components or AAP. (k) indicates sediment layer 1 or 2. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas[1]	**Name in input**	**Definition**	**Units**
Mx_i	$(i)S(k)$	quantity of slow decomposing detritus carbon, nitrogen, phosphorus, silicate, or refractory detritus carbon, nitrogen, phosphorus, silicate, or desorbing phosphate	gC/N/P/Si
H	$Depth$	depth of overlying water segment	m
$kmin_{i,20}$	$Rc(i)S(k)$	first-order mineralisation or desorption rate	d^{-1}
$ktmin_i$	$TcBM(i)$	temperature coefficient for mineralization	-
$ktmin_i$	$TcAAPS(k)$	temperature coefficient for desorption	-
$k0min_i$	$ZMin(i)S(k)$	zero-order mineralization or desorption rate	gX $m^{-2}_{\mathscr{b}}$
T	$Temp$	temperature	°C
T_c	$CTMin$	critical temperature for mineralization	°C
T_c	$CTMinAAPS$	critical temperature for desorption	°C
V	$Volume$	volume of overlying water segment	m^3

[1]) i = one of the 7 detritus components or AAP.

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9 Inorganic substances and pH

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9.1 Air-water exchange of CO2

PROCESS: REARCO2

Carbon dioxide (CO_2) in surface water tends to saturate with respect to the atmospheric carbon dioxide concentration. However, carbon dioxide production and consumption processes in the water column counteract saturation, causing a CO_2-excess or CO_2-deficit. Furthermore, the CO_2 concentration is dependent on the pH:

$$CO_2 + H_2O \quad \Leftrightarrow \quad H_2CO_3 + H_2O \quad \Leftrightarrow \quad HCO_3^- + H_3O^+ + H_2O \quad \Leftrightarrow \quad CO_3^{2-} + 2H_3O^+$$

The resulting super- or undersaturation leads to reaeration, the exchange of carbon dioxide between the atmosphere and the water. Reaeration may cause a carbon dioxide flux either way, to the atmosphere or to the water. The process is enhanced by the difference of the saturation and actual CO_2 concentrations, and by the difference of the flow velocities of the water and the overlying air. Since lakes are rather stagnant, only the windspeed is important as a driving force for lakes. The reaeration rate tends to saturate for low windspeeds (< 3 m s^{-1}). On the other hand, the stream velocity may deliver the dominant driving force for rivers. Both forces may be important in estuaries.

Extensive research has been carried out all over the world to describe and quantify reaeration processes for dissolved oxygen (DO), including the reaeration of natural surface water. Quite a number of models have been developed. The most generally accepted model is the "film layer" model. This model assumes the existence of a thin water surface layer, in which a concentration gradient exists bounded by the saturation concentration at the air-water interface and the water column average CO_2 concentration. The reaeration rate is characterised by a water transfer coefficient, which can be considered as the reciprocal of a mass transfer resistance. The resistance in the overlying gas phase is assumed to be negligibly small.

Many formulations have been developed and reported for the water transfer coefficient, mostly in connection with the reaeration of DO (WL | Delft Hydraulics, 1980b). These formulations are often empirical, but most have a deterministic background. They contain the stream velocity or the windspeed or both. Most of the relations are only different with respect to the coefficients, the powers of the stream velocity and the windspeed in particular. Reaeration has been implemented in DELWAQ with four different formulations for the transfer coefficient. The first two options are pragmatic simplifications to accommodate preferences of the individual modeller. The other two relations have been copied or derived from scientific publications. All reaeration rates are also dependent on the temperature according to the same temperature function.

Implementation

Process REARCO2 has been implemented in such a way, that it only affects the CO_2-budget of the top water layer. An option for the transfer coefficient can be selected by means of input parameter $SWRearCO2$ (= 0, 1, 4, 11, 13). The other options concern DO. The saturation concentration required for the process REARCO2 is calculated by an additional process SATURCO2.

The process has been implemented for substance CO_2.

Table 9.4 provides the definitions of the parameters occurring in the formulations.

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Formulation

The reaeration rate has been formulated as a linear function of the temperature dependent mass transfer coefficient in water and the difference between the saturation and actual concentrations of CO_2 as follows:

$$Rrear = klrear \times [Cco2s - \max(Cco2, 0.0)] / H$$
$$klrear = klrear_{20} \times ktrear^{(T-20)}$$
$$klrear_{20} = \left(\frac{a \times v^b}{H^c}\right) + \left(d \times W^2\right)$$
$$Cco2s = f\,(T, Ccl \text{ or } SAL) \qquad \text{(delivered by SATURCO2)}$$
$$fsat = 100 \times \frac{\max(Cco2, 0.0)}{Cco2s}$$

with:

a, b, c, d	coefficients with different values for eleven reaeration options
Ccl	chloride concentration [gCl m^{-3}]
$Cco2$	actual carbon dioxide concentration [gCO_2 m^{-3}]
$Cco2s$	saturation carbon dioxide concentration [gCO_2 m^{-3}]
$fsat$	percentage of saturation [%]
H	depth of the water column [m]
$klrear$	reaeration transfer coefficient in water [d^{-1}]
$klrear_{20}$	reaeration transfer coefficient at reference temperature 20 °C [d^{-1}]
$ktrear$	temperature coefficient of the transfer coefficient [-]
$Rrear$	reaeration rate [gCO_2 m^{-3} d^{-1}]
SAL	salinity [kg m^{-3}, ppt]
T	temperature [°C]
v	stream velocity [m s^{-1}]
W	windspeed at 10 m height [m s^{-1}]

Notice that the reaeration rate is always calculated on the basis of a positive carbon dioxide concentration. Although not realistic, CO_2 may have negative values in the model due to the consumption of CO_2 by phytoplankton. This may happen only at exceptional conditions.

Depending on the reaeration option, the transfer coefficient is only dependent on the stream velocity or the windspeed. With respect to temperature dependency option $SWRear = 11$ is an exception. The respective formulation is not dependent on temperature according the above equations, but has its own temperature dependency on the basis of the Schmidt number. Information on the coefficients $a - d$ and the applicability is provided below for each of the options.

$\underline{SWRearCO2 = 0}$
The transfer coefficient is simplified to a constant, multiplied with the water depth H, using the transfer coefficient as input parameter. **So *klrear*$_{20}$ is to be provided as a value in d^{-1} in stead of in m d^{-1}** Consequently, the coefficients are:

$$a = klrear_{20} \times H, \qquad b = 0.969, \qquad c = 0.5, \qquad d = 0.0$$

$\underline{SWRearCO2 = 1}$
The transfer coefficient is simplified to a constant, using the transfer coefficient as input parameter. Consequently, the coefficients are:

$$a = klrear_{20}, \qquad b = 0.969, \qquad c = 0.5, \qquad d = 0.0$$

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$\underline{SWRearCO2 = 4}$

The coefficients are according to (O' Connor and Dobbins, 1956) for DO, but coefficient a can be scaled for CO_2 using the transfer coefficient as input parameter. Consequently, the coefficients are:

$$a = klrear_{20} \times 3.863, \qquad b = 0.5, \qquad c = 0.5, \qquad d = 0.0$$

The relation is valid for rivers, and therefore independent of windspeed.

$\underline{SWRearCO2 = 11}$

The relation according to Wanninkhof (1992) deviates from the previous relations with respect to temperature dependency, that is not included according to the above Arrhenius equation for $klrear$. The temperature dependency enters the relation in a scaling factor on the basis of the Schmidt number. Coefficient d had to be scaled from cm h^{-1} to m d^{-1}. Consequently, the coefficients are:

$$a = F(T), \qquad b = 0.0, \qquad c = 0.0, \qquad d = 0.0744 \times fsc$$

$$F(T) = 2.5 \times (0.5246 + 0.016256 \times T + 0.00049946 \times T^2)$$

$$fsc = \left(\frac{Sc}{Sc_{20}} \right)^{-0.5}$$

$$Sc = d_1 - d_2 \times T + d_3 \times T^2 - d_4 \times T^3$$

with:

d_{1-4}	coefficients
fsc	scaling factor for the Schmidt number [-]
Sc	Schmidt number at the ambient temperature [m d^{-1}]
Sc_{20}	Schmidt number at reference temperature 20 °C [m d^{-1}]
T	temperature [°C]

The relation is valid for lakes and seas, and therefore independent of stream velocity.
The Schmidt number is the ratio of the kinematic viscosity of water (ν) and the molecular diffusion coefficient of oxygen in water (D). The appropriate constants to compute the Schmidt number in both seawater and fresh water are given in the table below.

Water system	d_1	d_2	d_3	d_4
Sea water, Salinity > 1 kg m^{-3}	2073.1	125.62	3.6276	0.043219
Fresh water, Salinity ≤ 1 kg m^{-3}	1911.1	118.11	3.4527	0.041320

$\underline{SWRearCO2 = 13}$

The relation according to Guérin (2006) and Guérin et al. (2007) deviates strongly from the previous relations, with respect to wind dependency, with respect to an additional forcing parameter, namely rainfall, and with respect to temperature dependency. The latter is not included according to the above Arrhenius equation for *klrear*. Like the relation described for option 10, the temperature dependency enters the relation in a scaling factor on the basis of the Schmidt number. The relation for transfer coefficient is:

$$klrear = \left(a \times \exp\left(b_1 \times W^{b2}\right) \; + \; \left(c_1 \times P^{c2}\right)\right) \times fsc \tag{9.1}$$

$$fsc = \left(\frac{Sc}{Sc_{20}} \right)^{-0.67} \tag{9.2}$$

$$Sc = d_1 - d_2 \times T + d_3 \times T^2 - d_4 \times T^3 \tag{9.3}$$

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with:

a, b, c, d	coefficients
$klrear$	transfer coefficient in water [m.d^{-1}]
P	precipitation, e.g. rainfall [mm.h^{-1}]
Sc	Schmidt number at the ambient temperature [g.m^{-3}]
Sc^{20}	Schmidt number at reference temperature 20 °C [d^{-1}]
T	temperature [°C]
W	windspeed at 10 m height [m.s^{-1}]

The relation is valid for (tropical) lakes and therefore independent of stream velocity. The general coefficients have the following input names and values:

a	b_1	b_2	c_1	c_2
CoefACO2	*CoefB1CO2*	*CoefB2 CO2*	*CoefC1CO2*	*CoefC2CO2*
1.660	0.26	1.0	0.66	1.0

The Schmidt number is the ratio of the kinematic viscosity of water (ν) and the molecular diffusion coefficient of oxygen in water. The appropriate constants to compute the Schmidt number for fresh water are given in the table below (Guérin, 2006):

d_1	d_2	d_3	d_4
CoefD1CO2	*CoefD2 CO2*	*CoefD3 CO2*	*CoefD4 CO2*
1911.1	118.11	3.4527	0.04132

Directives for use

- ◇ Options $SWRearCO2 = 0, 1, 4$ provide the user with the possibility to scale the mass transfer coefficient $KLRearCO2$. The options contain fixed coefficients.
- ◇ When using option $SWRearCO2 = 0$ the user should be aware that the mass transfer coefficient $KLRearCO2$ has the unusual dimension d^{-1}. Since high values of $KLRear$ may cause numerical instabilities, the maximum $KLRearCO2$ value is limited to 1.0 d^{-1}.
- ◇ When using option $SWRearCO2 = 4$ the user should be aware that the input parameter $KLRearCO2$ is used as a dimensionless scaling factor. The default value of $KLRearCO2$ is 1.0 in order to guarantee that scaling is not carried out when not explicitly wanted.
- ◇ The coefficients a–c_2 are input parameters for option $SWRearCO2 = 13$ only. The default values are those for option 13.
- ◇ The coefficients $d_{1–4}$ are input parameters for options $SWRearCO2 = 11, 13$. The default values are the freshwater values, which are the same for both options.

Table 9.4: *Definitions of the parameters in the above equations for REARCO2.*

Name in formulas[1]	**Name in input**	**Definition**	**Units**
$Cco2$	$DisCO2$	concentration of carbon dioxide	gCO_2 m^{-3}

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Table 9.4: *Definitions of the parameters in the above equations for REARCO2.*

Name in formulas[1]	**Name in input**	**Definition**	**Units**
$Cco2s$	$SaturCO2$	saturation conc. of carbon dioxide from SATURCO2	$gCO_2\ m^{-3}$
a	$CoefACO2$	coefficients for option 13 only	-
b_1	$CoefB1CO2$		-
b_2	$CoefB2CO2$		-
c_1	$CoefC1CO2$		-
c_2	$CoefC2CO2$		-
d_1	$CoefD1CO2$	coefficients for option 11 and 13	-
d_2	$CoefD2CO2$		-
d_3	$CoefD3CO2$		-
d_4	$CoefD4CO2$		-
fcs	–	scaling factor for the Schmidt number	-
$fsat$	–	percentage carbon dioxide saturation	%
H	$Depth$	depth of the top water layer	m
$klrear_{20}$	$KLRearCO2$	water transfer coefficient for carbon dioxide[1]	$m\ d^{-1}$
$kltemp$	$TCRearCO2$	temperature coefficient for reaeration	-
P	$rain$	Rainfall	$mm\ h^{-1}$
$Rrear$	–	reaeration rate for carbon dioxide	$gCO_2\ m^{-3}\ d^{-1}$
SAL	$Salinity$	salinity	$kg\ m^{-3}$
Sc	–	Schmidt number for carbon dioxide in water	-
$SWRearCO2$	$SWRearCO2$	switch for selection of options for transfer coefficient	-
T	$Temp$	temperature	°C
v	$Velocity$	stream velocity	$m\ s^{-1}$
W	$VWind$	windspeed at 10 m height	$m\ s^{-1}$

[1] $KLRearCO2$ is a dimensionless scaling factor for option 4.

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9.2 Saturation concentration of CO2

PROCESS: SATURCO2

The reaeration of carbon dioxide proceeds proportional to the difference of the saturation CO_2 concentration and the actual dissolved CO_2 concentration. The saturation concentration of CO_2 is primarily a function of the partial atmospheric CO_2 pressure, the water temperature and the salinity. However, the partial atmospheric CO_2 pressure is assumed to be constant.

The calculation of the saturation concentration in DELWAQ is performed as a separate process, which has been implemented with two alternative formulations. Such formulations have been described by Weiss (1974) and Stumm and Morgan (1981).

Implementation

Process SATURCO2 delivers the CO_2 saturation concentration in water required for the process REARCO2. The process has been implemented with two options for the formulations of the saturation concentration, which can be selected by means of input parameter $SWSatCO2$ $(= 1 - 2)$.

The process has been implemented in connection with substance CO_2. Table 9.5 provides the definitions of the parameters occurring in the formulations.

Formulation

The saturation concentration ($SaturCO2$) has been formulated as the following functions of the temperature and the salinity.

For $SWSatCO2 = 1$ (Stumm and Morgan, 1981):

$$fac = 10^{-ftemp}$$

$$ftemp = a - \frac{b}{(T + 273)} - c \times (T + 273) + fcl \times (d - m \times (T + 273))$$

$$fcl = n + o \times Ccl + p \times Ccl^2$$

For $SWSatCO2 = 2$ (Weiss, 1974):

$$fac = \exp\left(a + \frac{b}{Tf} + c \times \ln(Tf) + SAL \times \left(m + n \times Tf + o \times Tf^2\right)\right)$$

$$Tf = \left(\frac{T + 273}{100}\right)$$

For both options:

$$Cco2s = Pco2 \times fac \times 44 \times 1000$$

with:

a, b, c, d coefficients with different values for the two formulations

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m, n, o, p	
Ccl	chloride concentration [gCl m^{-3}]
$Cco2s$	saturation carbon dioxide concentration in water [gCO_2 m^{-3}]
fac	factor for temperature and salinity dependency
fcl	function for chloride concentration dependency
$ftemp$	function for temperature dependency
$Pco2$	atmospheric carbon dioxide pressure [atm]
T	temperature [°C]
Tf	temperature function [°C]
SAL	salinity [kg m^{-3}, ppt]

The coefficients in both formulations are fixed. The values are presented in the table below.

Option	**a**	**b**	**c**	**d**
$SWSatOxy = 1$	14.0184	2385.73	0.015264	0.28569
$SWSatOxy = 2$	-58.0931	90.5069	22.2940	-
Option	**m**	**n**	**o**	**p**
$SWSatOxy = 1$	0.6167×10^{-5}	0.00147	0.3592×10^{-4}	0.68×10^{-10}
$SWSatOxy = 2$	0.027766	-0.025888	0.0050578	-

Directives for use

◇ The chloride concentration Cl can either be imposed by the user or simulated with the model. The salinity can be estimated from the chloride concentration with:

$$SAL = 1.805 \times Cl/1000$$

◇ A representative value for the atmospheric carbon dioxide pressure $PAPCO2$ is 3.162×10^{-4} atm.

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Table 9.5: *Definitions of the parameters in the above equations for SATURCO2.*

Name in formulas	Name in input	Definition	Units
$Cco2s$	–	saturation concentration of carbon dioxide in water	$gCO_2\ m^{-3}$
Ccl	Cl	chloride concentration	$gCl\ m^{-3}$
fac	–	factor for temperature and salinity dependency	-
fcl	–	unction for chloride concentration dependency	-
$ftemp$	–	function for temperature dependency	-
$Pco2$	$PAPCO2$	atmospheric carbon dioxide pressure	atm
SAL	$Salinity$	salinity	$kg\ m^{-3}$
$SWSatCO2$	$SWSatCO2$	switch for selection options for saturation equation	-
T	$Temp$	temperature	$^\circ C$
Tf	–	temperature function	-

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9.3 Calculation of the pH and the carbonate speciation

PROCESSES: PH_SIMP, SPECCARB, PH_CARB

The pH, the carbonate speciation (CO_2, pCO_2, H_2CO_3, HCO_3^- and CO_3^{2-}) and the saturation states of calcium carbonate (calcite and aragonite) in the water column and the sediment bed can be calculated from the alkalinity (Alka; gHCO3 m^{-3}) and the total dissolved inorganic carbon concentration (TIC; gC m^{-3}). Salinity (g kg^{-1}) and temperature (°C) are necessary inputs.

The dissolved [CO_2] concentration is more than two orders of magnitude higher than the concentration of carbonic acid [H_2CO_3]. Consequently, the concentration of carbonic acid can be ignored and the sum of the concentrations of these species, [CO_2^*], is practically identical to the concentration of [CO_2], and thus TIC is defined as:

TIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]

The equilibrium in the carbonate system is dependent of temperature, salinity and pressure. The relative proportions of inorganic carbon species control the pH in natural waters.

Alkalinity is defined as carbonate, borate and water alkalinity, the dissociation constants of which are calculated from salinity and temperature. The [H^+] concentration is derived from the alkalinity equation and is used to calculate pH:

ALKA =[HCO_3^-] + 2[CO_3^{2-}] +[$B(OH)_4^-$] + [OH^-] - [H^+]

In process pH_carb two sets of equilibrium constants are used, one for fresh water and one for saline water. The sets only differ in the way to calculate the first (K_1) and the second dissociation constant of carbonic acid (K_2). The appropriate set is selected by the model depending on salinity.

The acidity or pH is defined as:

$$pH_T = -\,^{10}\log([H^+])$$

A number of processes influence the pH of the water. For example, mineralisation of organic carbon produces CO_2 (an acid) and thus lowers the pH. On the other hand denitrification consumes H^+, raising the pH. Table 9.6 gives a general summary of all processes within D-Water Quality that have a pH effect.

Table 9.6: *Processes in D-Water Quality with effects on pH*

process description	**equivalent chemical reaction**	**stoichiometry**
reaeration of CO_2	$CO_2(g) + H_2O \leftrightarrow H_2CO_{3(aq)}^*$	TIC +0.273 [a])
		continued on next page

Table 9.6 – continued from previous page

process description	**equivalent chemical reaction**	**stoichiometry**
primary production	$CO_2 + H_2O \rightarrow CH_2O + O_2$	TIC -1.000 H2O -1.500 C_{org} +1.000 OXY +2.670
mineralisation of organic C	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	TIC +1.000 H2O +1.500 C_{org} -1.000 OXY -2.670
denitrification	$NO_3^- + H^+ \rightarrow \frac{1}{2} N_2 + 1\frac{1}{4} O_2 + \frac{1}{2} H_2O$	NO3 -1.000 [b]) ALKA +4.357 OXY +2.857 H2O +0.643
nitrification	$NH_4^+ + 2\ O_2 \leftrightarrow NO_3^- + 2\ H^+ + H_2O$	NH4 -1.000 OXY -4.571 NO3 +1.000 ALKA -8.714 H2O +1.286
Uptake of ammonia [c])	$NH_4^+ \rightarrow (NH_3)_{org} + H^+$	NH4 -1.000 N_{org} +1.000 ALKA -4.357
Uptake of phosphate [c])	$H_2PO_4^- + H^+ \rightarrow (H_3PO_4)_{org}$	PO4 -1.000 P_{org} +1.000 ALKA 1.968
Uptake of nitrate	$NO_3^- + H^+ + H_2O \rightarrow (NH_3)_{org} + 2\ O_2$	NO3 -1.000 ALKA +4.357 H2O -1.286 N_{org} +1.000 OXY -4.571
Atmospheric deposition of nitrate	$HNO_3 \rightarrow H^+ + NO_3^-$	NO3 +1.000 H+ +0.071 ALKA -4.357
Atmospheric deposition of ammonium	$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$	NH4 +1.000 ALKA +4.357
Atmospheric deposition of sulfate	$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$	SO4 +1.000 H+ +0.143 ALKA -8.714

[a]The CO_2 flux in D-Water Quality has units $gCO_2\ m^{-3}\ d^{-1}$ and is converted to $gC\ m^{-3}\ d^{-1}$.

continued on next page

Table 9.6 – continued from previous page

process description	equivalent chemical reaction	stoichiometry

[b]Denitrification in the sediment is thought to be a sink for nitrate. No alkalinity, oxygen and water are added to the water column.

[c]Mineralisation reactions are the reverse of the uptake reactions.

Implementation

Processes pH_simp and pH_carb have been implemented for the following substances:

◇ TIC, Alka and Salinity

The process SpecCarb takes the output from the process pH_simp to determine the concentrations of carbon dioxide, carbon hydroxide and other related ions, whereas most of these are automatically available via the process pH_carb.

Although the processes have been formulated in a generic way, the calculation of the pH should be preferably applied to water layers. Concentrations are corrected for porosity (input parameter POROS) to allow for application to sediment layers, but buffering of the pH by solid phase minerals like calcite is not considered. Processes pH_simp and pH_carb can both be used for a model with ”layered sediment” and with the S1/S2 approach, but pH_carb does not take porosity into account.

Instead of simulating the pH using the processes pH_simp or pH_carb, it can also be imposed on a model. The carbonate speciation computed by pH_simp in combination with SpecCarb can be used by process PRIRON for the formation of iron(II) carbonate (note that currently ph_carb does not provide all required species). The dissolved carbon dioxide concentration $DisCO2$ computed by pH_simp or pH_carb can be used for process REARCO2 to calculate the CO_2 exchange flux between atmosphere and water.

Table 9.7 provides the definitions of the input parameters in the formulations and Table 9.8 provides the output parameters.

Formulation

Process pH_carb

The hydrolysis reactions of carbonate and borate and the self-ionization of water proceed according to the following reaction equations:

$$
\begin{aligned}
CO_2(g) &\Leftrightarrow CO_2(aq)\\
CO_2(aq) + H_2O &\Leftrightarrow H_2CO_3\\
CO_2(aq) + H_2O &\Leftrightarrow HCO_3^- + H^+\\
HCO_3^- &\Leftrightarrow CO_3^{2-} + H^+\\
B(OH)_3 + H_2O &\Leftrightarrow B(OH)_4^- + H^+\\
H_2O &\Leftrightarrow OH^- + H^+
\end{aligned}
$$

As the concentration of H_2CO_3 is negligible compared to CO_2(aq), and therefore the dissociation constants for carbonic acid do not differentiate between these substances, it is common to combine the second and the third reaction, and to allocate an acidity constant to the combined reaction based on CO_2, which is the sum of H_2CO_3 and CO_2(aq). Consequently, the chemical equilibria are described with:

$$K_0 = \frac{[CO_2]}{pCO_2}$$
$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]}$$
$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$
$$K_B = \frac{[H^+][B(OH)_4^-]}{[B(OH)_3]}$$
$$K_W = [H^+][OH^-]$$

where:

K_0	solubility constant of carbon dioxide in water [mol kg^{-1} atm^{-1}]
K_1	first dissociation constant of carbonic acid [mol kg^{-1} solution]
K_2	second dissociation constant of carbonic acid [mol kg^{-1} solution]
K_B	dissociation constant of boric acid [mol kg^{-1} solution]
K_W	dissociation constant of water [mol^2 kg^{-2} solution]

The equilibrium constants are functions of the absolute temperature and the salinity. The absolute temperature is defined as:

$$T_{abs} = T + 273.15$$

where:

T	ambient water temperature [°C]
T_{abs}	absolute temperature [K]

Because the model calculates bulk salinity, it is corrected for porosity as follows:

$$S = Salinity/\phi$$

where:

S	salinity of the water phase [g kg^{-1} water]
ϕ	porosity [-]

The following K_1 and K_2 formulations from Roy (1993) were determined in artificial water and for total pH scale.

For Salinity (S) $<$ 5 g kg^{-1} (psu):

$$\begin{aligned}\ln K_1 = {} & 290.9097 - 14554.21/T_{abs} - 45.0575 \times \ln(T_{abs}) + \\ & (-228.39774 + 9714.36839/T_{abs} + 34.485796 \times \ln(T_{abs})) \times S^{0.5} + \\ & (54.20871 - 2310.48919/T_{abs} - 8.19515 \times \ln(T_{abs})) \times S + \\ & (-3.969101 + 170.22169/T_{abs} + 0.603627 \times \ln(T_{abs})) \times S^{1.5} - \\ & 0.00258768 \times S^2 + \ln(1 - S \times 0.001005)\end{aligned}$$

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$$K_1 = \mathrm{e}^{\ln K_1}$$

$$\begin{aligned}\ln K_2 = {} & 207.6548 - 11843.79/T_{abs} - 33.6485 \times \ln(T_{abs}) + \\ & (-167.69908 + 6551.35253/T_{abs} + 25.928788 \times \ln(T_{abs})) \times S^{0.5} \\ & (39.75854 - 1566.13883/T_{abs} - 6.171951 \times \ln(T_{abs})) \times S + \\ & (-2.892532 + 116.270079/T_{abs} + 0.45788501 \times \ln(T_{abs})) \times S^{1.5} - \\ & 0.00613142 \times S^2 + ln(1 - S \times 0.001005)\end{aligned}$$

$$K_2 = \mathrm{e}^{\ln K_2}$$

For Salinity (S) $<$ 45 and $\geq$ 5 g kg^{-1} (psu):

$$\begin{aligned}\ln K_1 = {} & 2.83655 - 2307.1266/T_{abs} - 1.5529413 \times \ln(T_{abs}) + \\ & (-0.20760841 - 4.0484/T_{abs}) \times S^{0.5} + 0.08468345 \times S \\ & - 0.00654208 \times S^{1.5} + \ln(1 - 0.001005 \times S)\end{aligned}$$

$$K_1 = \mathrm{e}^{\ln K_1}$$

$$\begin{aligned}\ln K_2 = {} & -9.226508 - 3351.6106/T_{abs} - 0.2005743 \times \ln(T_{abs}) + \\ & (-0.106901773 - 23.9722/T_{abs}) \times S^{0.5} + 0.1130822 \times S \\ & - 0.00846934 \times S^{1.5} + \ln(1 - 0.001005 \times S)\end{aligned}$$

$$K_2 = \mathrm{e}^{\ln K_2}$$

For all values of salinity:

$$\begin{aligned}\ln K_0 = {} & -60.2409 + 93.4517/(T_{abs}/100) - 23.3585 \times \ln(T_{abs}/100) + \\ & S \times (0.023517 - 0.023656 \times (T_{abs}/100) + 0.000447036 \times (T_{abs}/100)^2)\end{aligned}$$

$$K_0 = \mathrm{e}^{\ln K_0}$$

$$\begin{aligned}\ln K_B = {} & (-8966.90 - 2890.53 \times S^{0.5} - 77.942 \times S + 1.728 \times S^{1.5} - 0.0996 \times S^2)/T_{abs} \\ & + 148.0248 + 137.1942 \times S^2 + 1.62142 \times S + \\ & (-24.4344 - 25.085 \times S^{0.5} - 0.2474 \times S) \times \ln(T_{abs}) + 0.053105 \times S^{0.5} \times T_{abs}\end{aligned}$$

$$K_B = \mathrm{e}^{\ln K_B}$$

$$\begin{aligned}\ln K_W = {} & 148.96502 - 13847.26/T_{abs} - 23.6521 \times \ln(T_{abs}) + \\ & (118.67/T_{abs} - 5.977 + 1.0495 \times \ln(T_{abs})) \times S^{0.5} - 0.01615 \times S\end{aligned}$$

$$K_W = \mathrm{e}^{\ln K_W}$$

$$\begin{aligned}\ln K_{Cal} = {} & -171.9065 - 0.077993 \times T_{abs} + 2839.319/T_{abs} + 71.595 \times \ln(T_{abs}) + \\ & (-0.77712 + 0.0028426 \times T_{abs} + 178.34/T_{abs}) \times S^{0.5} - \\ & 0.07711 \times S + 0.0041249 \times S^{1.5}\end{aligned}$$

$$K_{Cal} = \mathrm{e}^{\ln K_{Cal}}$$

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$$\ln K_{Arg} = -171.9065 - 0.077993 \times T_{abs} + 2903.293/T_{abs} + 71.595 \times \ln(T_{abs}) + (-0.068393 + 0.0017276 \times T_{abs} + 88.135/T_{abs}) \times S^{0.5} - 0.10018 \times S + 0.0059415 \times S^{1.5}$$

$$K_{Arg} = \mathrm{e}^{\ln K_{Arg}}$$

where:

S	salinity in the water phase [g kg^{-1} water or psu]
K_{Cal}	solubility constant of calcite [mol^2 kg^{-2} solution]
K_{Arg}	solubility constant of aragonite [mol^2 kg^{-2} solution]

Apart from the definition of total dissolved inorganic carbon (TIC) and alkalinity (Alka) as the sums of their components, the following formulations are needed to solve the above equilibrium and to calculate the saturation states of calcite and aragonite:

$$\begin{aligned}
\rho_w &= \left(1000. + 0.7 \times S/(1 - S/1000.) - 0.0061 \times (T - 4.0)^2\right)/1000 \\
TICM &= mtmm \times (TIC/(MWC \times \rho_w \times m3tl \times \phi)) \\
AlkaM &= mtmm \times (Alka/(MWHCO3 \times \rho_w \times m3tl \times \phi)) \\
B &= mtmm \times 0.000416 \times (S/35) \\
[Ca^{2+}] &= mtmm \times 0.01028 \times (S/35)
\end{aligned}$$

where:

$mtmm$	conversion factor for mol to mmol (10^3) [mmol mol^{-1}]
$m3tl$	conversion factor for m^3 to litre (10^3) [l m^{-3}]
MWC	molar weight of carbon (12) [g mol^{-1}]
$MWHCO3$	molar weight of the bicarbonate ion (61) [g mol^{-1}]
ρ_w	density of water [kg l^{-1}]
TIC	total dissolved inorganic carbon concentration [gC m^{-3}]
$TICM$	molar total dissolved inorganic carbon concentration [mmolC kg^{-1}]
$Alka$	alkalinity [gHCO$_3$ m^{-3}]
$AlkaM$	molar alkalinity [mmolHCO$_3$ kg^{-1}]
B	molar total boric acid concentration [mmol kg^{-1}]
Ca^{2+}	molar calcium ion concentration [mmol kg^{-1}]
ϕ	porosity [-]

The equilibrium equations can now be substituted in the component sums resulting in:

$$TICM \times (K_1 \times [H^+] + 2 \times K_1 \times K_2)/([H^+]^2 + K_1 \times [H^+] + K_1 \times K_2) + B \times K_B/([H^+] + K_B) + K_W/[H^+] - [H^+] - AlkaM = 0$$

From this quintic polynomial equation in $[H^+]$ the following outputs are generated:

$$\begin{aligned}
pH &= -\,{}^{10}\log[H^+] \\
CO2 &= mtmm \times m3tl \times MWCO2 \times \rho_w \times TICM \times \\
&\qquad [H^+]^2/([H^+]^2 + K_1 \times [H^+] + K_1 \times K_2) \\
pCO2_w &= FCO2/(\exp(atpa \times (BV + 2 \times D)/(R \times T_{abs}))) \\
FCO2 &= atma \times CO2M/K_0 \\
BV &= (-1636.75 + 12.0408 \times T_{abs} - 0.0327957 \times T_{abs}^2 + 3.16528 \times 10^{-5} \times T_{abs}^3)/m3tcm3 \\
D &= (57.7 - 0.118 \times T_{abs})/m3tcm3
\end{aligned}$$

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$$HCO3 = MWC \times \rho_w \times m3tl \times \phi \times (TICM \times K_1 \times [H^+])/(([H^+]^2 + K_1 \times [H^+] + K_1 \times K_2) \times mtmm)$$
$$CO3 = MWC \times \rho_w \times m3tl \times \phi \times (TICM \times K_1 \times K_2)/(([H^+]^2 + K_1 \times [H^+] + K_1 \times K_2) \times mtmm)$$
$$BOH4 = MWB \times \rho_w \times m3tl \times \phi \times B/(([H^+] + K_B) \times mtmm)$$

$$\Omega_{Cal} = Ca^{2+} \times CO3/(K_{Cal} \times MWC \times \rho_w \times m3tl \times mmtm \times \phi)$$
$$\Omega_{Arg} = Ca^{2+} \times CO3/(K_{Arg} \times MWC \times \rho_w \times m3tl \times mmtm \times \phi)$$

where:

$atma$	conversion factor for atmosphere to microatmosphere (10^6) [μatm atm^{-1}]
$atpa$	conversion factor for atmosphere to pascal (101325) [Pa atm^{-1}]
$m3tcm3$	conversion factor for m^3 to cm^3 (10^6) [m^{-3} m^3]
BV	virial coefficient of carbon dioxide in air [m^3 mol^{-1}]
D	virial coefficient of pure carbon dioxide [m^3 mol^{-1}]
H^+	proton activity [mol kg^{-1} solution]
MWB	molar weight of boron (10.8) [g mol^{-1}]
$MWCO2$	molar weight of carbon dioxide (44) [g mol^{-1}]
R	ideal gas constant [m^3 Pa K^{-1} mol^{-1}]
$CO2$	dissolved carbon dioxide concentration [gCO$_2$ m^{-3}]
$CO2M$	molar dissolved carbon dioxide concentration [mmolCO$_2$ kg^{-1}]
$FCO2$	fugacity of carbon dioxide concentration [μatm^{-1}]
$pCO2_w$	partial pressure of carbon dioxide in water [μatm^{-1}]
$CO3$	dissolved carbonate CO_3^{2-} concentration [gC m^{-3}]
$HCO3$	dissolved bicarbonate HCO_3^- concentration [gC m^{-3}]
$BOH4$	dissolved borate $B(OH)_4^-$ concentration [gB m^{-3}]
Ω_{Cal}	saturation state of calcite [-]
Ω_{Arg}	saturation state of aragonite [-]

If the pH is larger than pH_max, it is set to pH_max. If the pH is smaller than pH_min, it is set to pH_min.

Processes pH_simp and SpecCarb

The simplified process pH_simp uses only the formulations for K_1 and K_2 valid for salinity smaller than 5 psu. Boric acid is not considered. The equilibrium equations substituted in the component sums result in:

$$Alka \times [H^+]^2/K_1 + (Alka - TIC) \times [H^+] + K_2 \times (Alka - 2 \times TIC) = 0$$

This quadratic equation in $[H^+]^2$ delivers two roots, the feasible one of which is used to calculate the pH.

The carbonate species are calculated slightly differently. The hydrolysis reactions of carbonate proceed according to the following reaction equations:

$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3$$
$$H_2CO_3 + H_2O \Leftrightarrow HCO_3^- + H_3O^+$$
$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$$

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It is common to combine the first and the second reaction, and to allocate an acidity constant to the combined reaction based on $H_2CO_3{}^*$, the sum of true H_2CO_3 and CO_2(aq). Consequently, the chemical equilibria are described with:

$$Kc_0 = \frac{Ccd_0}{Ccd_1}$$
$$Kc_1 = \frac{Ccd_2 \times H^+}{(Ccd_0 + Ccd_1)}$$
$$Kc_2 = \frac{Ccd_3 \times H^+}{Ccd_2}$$
$$Ccdt = Ccd_0 + Ccd_1 + Ccd_2 + Ccd_3$$

where:

Ccd_0	dissolved carbon dioxide [mol.l^{-1}]
Ccd_1	dissolved H_2CO_3 [mol.l^{-1}]
Ccd_2	dissolved $HCO_3{}^-$ [mol.l^{-1}]
Ccd_3	dissolved $CO_3{}^{2-}$ [mol.l^{-1}]
$Ccdt$	total dissolved inorganic carbon [mol.l^{-1}]
H^+	proton concentration [mol.l^{-1}]
Kc_0	hydrolysis (equilibrium,) constant for CO_2 [-]
Kc_1	acidity (equilibrium, hydrolysis) constant for $H_2CO_3{}^*$ [mol.l^{-1}]
Kc_2	acidity (equilibrium, hydrolysis) constant for $HCO_3{}^-$ [mol.l^{-1}]

The proton concentration H^+ and the stability constants follow from:

$$H^+ = 10^{-pH}$$
$$Kc_0 = 650.0$$
$$Kc_1 = 10^{lKc_1}$$
$$Kc_2 = 10^{lKc_2}$$
$$lKc_1 = -3404.71/Tabs - 0.032786 \times Tabs + 14.712 + 0.19178 \times (0.543 \times S)^{0.333}$$
$$lKc_2 = -2902.39/Tabs - 0.02379 \times Tabs + 6.471 + 0.4693 \times (0.543 \times S)^{0.333}$$
$$Tabs = T + 273.15$$

where:

pH	acidity [-]
S	salinity [psu]
T	temperature [°C]
$Tabs$	absolute temperature [K]

Salinity replaces chlorinity in the above formulations derived from Stumm and Morgan (1981) based on 19 ‰ chlorinity agreeing with 35 psu (‰) salinity.

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The concentration of the relevant carbonate species in solution can now be calculated from:

$$Ccdt = \frac{Ctic}{12\,000 \times \phi}$$
$$Ccd_1 = \frac{Ccdt}{(1 + Kc_1/H^+ + (Kc_1 \times Kc_2)/(H^+)^2)} \times \frac{1}{(1 + Kc_0)}$$
$$Ccd_0 = Kc_0 \times Ccd_1$$
$$Ccd_2 = \frac{Kc_1 \times (Kc_0 + 1) \times Ccd_1}{H^+}$$
$$Ccd_3 = Ccdt - Ccd_0 - Ccd_1 - Ccd_2$$

if due to rounding off the resulting $Ccd_3 \leq 0.0$

$$Ccd_3 = \frac{Kc_2 \times Ccd_2}{H^+}$$

where:

$Ctic$	total dissolved inorganic carbon (gC.m$^{-3}_{\ell}$)
ϕ	porosity

The constant 12 000 concerns the conversion from gC.m^{-3} to mol.l^{-1}. This constant is also used to convert the above molar concentrations back into gC.m^{-3} for the carbonate species. A constant 44 000 is used to convert the molar concentration of dissolved carbon dioxide into gCO_2.m^{-3}.

The pertinent carbonate fractions (mol mol^{-1} or g g^{-1}) follow from:

$$fc_0 = \frac{Ccd_0}{Ccdt}$$
$$fc_1 = \frac{Ccd_1}{Ccdt}$$
$$fc_2 = \frac{Ccd_2}{Ccdt}$$
$$fc_3 = 1 - fc_0 - fc_1 - fc_2$$

if due to rounding off the resulting $fc_3 \leq 0.0$

$$fc_3 = \frac{Ccd_3}{Ccdt}$$

where:

fc_0	fraction CO_2 of TIC [$-$]
fc_1	fraction H_2CO_3 of TIC [$-$]
fc_2	fraction $HCO_3{}^-$ of TIC [$-$]
fc_3	fraction $CO_3{}^{2^-}$ of TIC [$-$]

The saturation states of calcite and aragonite are *not* calculated.

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Directives for use

◇ The pH is actually measured on the 'total pH scale' (pH_T):

$$pH_T = -\,^{10}\log([H^+] + [HSO_4^-]) \quad > \quad -\,^{10}\log([H^+]) = pH$$

So, not the free [H^+] is measured but [H^+]$_T$ (=[H^+] + [HSO_4^-]). In fresh water [HSO_4^-] is negligible, but through the abundance of sulfate it is significant in seawater. Because in this model the pH is calculated from [H^+] only, the calculated pH slightly underestimates the pH measured in seawater.

◇ The process pH_carb is also suitable for water with a salinity $>$ 5 psu, the process pH_simp should be used for fresh water only.

◇ With the input parameters for process pH_simp, pH_min and pH_max, the pH can be constrained within a certain user defined range. This is required for the sediment bed in the "layered sediment" approach, because the pH calculation does not account for buffering of the pH by minerals like calcite. Reasonable values for the lower and upper pH for the bed sediment are 6.5 and 7.5.

◇ The process pH_simp in combination with SpecCarb calculates $DisH2CO3$ and $FrH2CO3d$, whereas this is not done by the other process, pH_carb, because this species is assumed included in $DisCO2$.

◇ Dissociation constants are calculated internally and cannot be modified through input parameters.

◇ The CO_2 concentration in water needed for the exchange of carbon dioxide between water and atmosphere (process REARCO2) is delivered by pH_simp as $DisCO2$.

◇ The fraction of carbonate CO_3^{2-} concentration in water needed for the formation of Fe(II)CO_3 (process PRIRON) is delivered by pH_simp as $FrCO3dis$.

Additional references

Millero (1995), Roy (1993), Millero (1982), Mucci (1983), Dickson (1990), Dickson and Goyet (1994), Zeebe and Wolf-Gladrow (2001)

Table 9.7: *Definitions of the input parameters in the above equations for pH_simp, pH_carb and SpecCarb. Volume units refer to bulk (ℓ) or to water (w).*

Name in formulas	Name in Input	Definition	Units
$Alka$	$Alka$	alkalinity	gHCO$_3$ m$^{-3}_{\ell}$
TIC	TIC	total dissolved inorganic carbon concentration	gC.m$^{-3}_{\ell}$
pH_max	pH_max	maximum pH	-
pH_min	pH_min	minimum pH	-
S	$Salinity$	salinity	psu$_{\ell}$
T	$TEMP$	ambient water temperature	°C
ϕ	$POROS$	porosity (for SpecCarb only)	-

Table 9.8: *Definitions of the output parameters of pH_simp and pH_carb. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in Input	Definition	Units
pH	pH	simulated pH, acidity	-
$CO2$ or Ccd_0	$DisCO2$	concentration of dissolved CO_2	$gCO_2.m^{-3}_{\mathscr{b}}$
$HCO3$ or Ccd_1	$DisHCO3$	concentration of dissolved HCO_3^-	$gC.m^{-3}_{\mathscr{b}}$
$CO3$ or Ccd_2	$DisCO3$	concentration of dissolved CO_3^{2-}	$gC.m^{-3}_{\mathscr{b}}$
$H2CO3$ or Ccd_3	$DisH2CO3$	concentration of dissolved H_2CO_3	$gC.m^{-3}_{\mathscr{b}}$
	(Output from process Spec-Carb only)		
fc_0	$FrCO2dis$	fraction of dissolved carbon dioxide	gC gC^{-1}
fc_1	$FrH2CO3d$	fraction of dissolved H_2CO_3	gC gC^{-1}
fc_2	$FrHCO3dis$	fraction of dissolved HCO_3^-	gC gC^{-1}
fc_3	$FrCO3dis$	fraction of dissolved CO_3^{2-}	gC gC^{-1}
	(Output from process pH_carb only)		
$BOH4$	$BOH4$	dissolved borate $B(OH)_4^-$ concentration	$gB\ m^{-3}_{\mathscr{b}}$
$pCO2_w$	$pCO2water$	partial pressure of carbon dioxide in water	μatm^{-1}
Ω_{Cal}	$SatCal$	saturation state of calcite	-
Ω_{Arg}	$SatArg$	saturation state of aragonite	-

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9.4 Volatilisation of methane

PROCESS: VOLATCH4

Methane (CH_4) in surface water tends to escape to the atmosphere, because its partial atmospheric pressure is extremely low. Volatisation is enhanced by the difference of the CH_4 saturation concentration and the actual CH_4 concentration, and by the difference of the velocities of the water and the overlying air. The saturation concentration is approximately zero.

Since lakes are rather stagnant, only the windspeed is important as a driving force for lakes. The volatilisation rate tends to saturate for low windspeeds (< 3 m s^{-1}). On the other hand, the stream velocity may deliver the dominant driving force for rivers. Both forces may be important in estuaries.

The rate of methane volatilisation is described in the same way as the reaeration of dissolved oxygen (DO). Only those formulations can be applied that may be valid for methane too. A scaling factor is available to scale methane volatilisation relation relative to reaeration.

Extensive research has been carried out all over the world to describe and quantify reaeration processes for DO, including the reaeration of natural surface water. Quite a few different models have been developed. The most generally accepted model is the 'film layer' model. This model assumes the existence of a thin water surface layer, in which a concentration gradient exists bounded by the saturation concentration at the air-water interface and the water column average DO concentration. The reaeration rate is characterised by a water transfer coefficient, which can be considered as the reciprocal of a mass transfer resistance. The resistance in the overlying gas phase is assumed to be negligibly small.

Many formulations have been developed and reported for the water transfer coefficient, mostly in connection with the reaeration of DO, WL | Delft Hydraulics (1980b). These formulations are often empirical, but most have a deterministic background. They contain the stream velocity or the windspeed or both. Most of the relations are only different with respect to the coefficients, the powers of the stream velocity and the windspeed in particular. Volatisation has been implemented in DELWAQ with four different formulations for the transfer coefficient. The first two options are pragmatic simplications to accommodate preferences of the individual modeller. The other two relations have been copied or derived from scientific publications. All reaeration rates are also dependent on the temperature according to the same temperature function.

Implementation

Process VOLATCH4 has been implemented in such a way, that it only affects the CH_4-budget of the top water layer. An option for the transfer coefficient can be selected by means of input parameter $SWVolCH4$ (= 0, 1, 4, 9, 13). The other options concern only DO or CO2. The saturation concentration required for the process VOLATCH4 is calculated by an additional process SATURCH4.

The process has been implemented for substance CH_4.

Table 9.9 provides the definitions of the parameters occurring in the formulations.

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Formulation

The volatilisation rate has been formulated as a reaeration rate. This rate is a linear function of the temperature dependent mass transfer coefficient in water and the difference between the saturation and actual concentrations of CH_4 as follows:

$$Rvol = klvol \times [Cch4s - \max(Cch4, 0.0)] / H$$
$$klvol = klvol_{20} \times ktvol^{(T-20)}$$
$$klvol_{20} = \left(\frac{a \times v^b}{H^c}\right) + \left(d \times W^2\right)$$
$$Cch4s = f(T, Pch4) \qquad \text{(delivered by SATURCH4)}$$
$$fsat = 100 \times \frac{\max(Cch4, 0.0)}{Cch4s}$$

with:

a, b, c, d	coefficients with different values for eleven reaeration options
$Cch4$	actual dissolved methane concentration [gC m^{-3}]
$Cch4s$	saturation methane concentration [gC m^{-3}]
$fsat$	percentage of saturation [%]
H	depth of the water column [m]
$klvol$	transfer coefficient in water [m d^{-1}]
$klvol_{20}$	transfer coefficient at reference temperature 20 °C [m d^{-1}]
$ktvol$	temperature coefficient of the transfer coefficient [-]
$Pch4$	partial atmospheric methane pressure [gC m^{-3}]
$Rvol$	volatilisation rate [gC m^{-3} d^{-1}]
T	temperature [°C]
v	stream velocity [m.s^{-1}]
W	windspeed at 10 m height [m.s^{-1}]

Notice that the volatilisation rate is always calculated on the basis of a positive methane concentration. Allthough technically possible, negative concentrations of methane should not occur in the model.

Depending on the volatilisation option, the transfer coefficient is only dependent on the stream velocity or the windspeed. Information on the coefficients $a-d$ and the applicability is provided below for each of the options.

SWVolCH4 = 0

The transfer coefficient is simplified to a constant, multiplied with the water depth H, using the transfer coefficient as input parameter. **So *klvol*$_{20}$ is to be provided as a value in [d^{-1}] instead of [m d^{-1}]** Consequently, the coefficients are:

$$a = klvol_{20} \times H, \quad b = 0.0, \quad c = 0.0, \quad d = 0.0$$

SWVolCH4 = 1

The transfer coefficient is simplified to a constant, using the transfer coefficient as input parameter. Consequently, the coefficients are:

$$a = klvol_{20}, \quad b = 0.0, \quad c = 0.0, \quad d = 0.0$$

SWVolCH4 = 4

The coefficients are according to O' Connor and Dobbins 1956 for DO, but coefficient a can be scaled for CH_4 using the transfer coefficient as input parameter. Consequently, the coefficients are:

$$a = klvol_{20} \times 3.863, \quad b = 0.5, \quad c = 0.5, \quad d = 0.0$$

The relation is valid for rivers, and therefore independent of windspeed.

SWVolCH4 = 9

The relation for DO is according to Banks and Herrera (1977) as reported by WL | Delft Hydraulics (1980b), but the coefficients have been modified according to WL | Delft Hydraulics (1978); ($d = 0.03 - 0.06$) and later modelling studies for Dutch lakes (WL | Delft Hydraulics, 1992c). Coefficient d can be scaled for CH_4 using the transfer coefficient as input parameter. Consequently, the coefficients are:

$$a = 0.3, \quad b = 0.0, \quad c = 0.0, \quad d = klvol_{20} \times 0.028$$

The relation is valid for lakes and seas, and therefore independent of stream velocity. The relation takes into account that the mass transfer coefficient saturates at a lower boundary for low wind velocities ($W < 3$ m s^{-1}).

SWVolCH4 = 13

The relation according to Guérin (2006) and Guérin et al. (2007) deviates strongly from the previous relations, with respect to wind dependency, with respect to an additional forcing parameter, namely rainfall, and with respect to temperature dependency. The latter is not included according to the above Arrhenius equation for *klrear*. The temperature dependency enters the relation in a scaling factor on the basis of the Schmidt number. The relation for transfer coefficient is:

$$klrear = \left(a \times \exp\left(b_1 \times W^{b2}\right) + \left(c_1 \times P^{c2}\right)\right) \times fsc$$
$$fsc = \left(\frac{Sc}{Sc_{20}}\right)^{-0.67}$$
$$Sc = d_1 - d_2 \times T + d_3 \times T^2 - d_4 \times T^3$$

with:

a, b, c, d	coefficients
$klrear$	transfer coefficient in water [m.d^{-1}]
P	precipitation, e.g. rainfall [mm.h^{-1}]
Sc	Schmidt number at the ambient temperature [g.m^{-3}]
Sc^{20}	Schmidt number at reference temperature 20 °C [d^{-1}]
T	temperature [°C]
W	windspeed at 10 m height [m.s^{-1}]

The relation is valid for (tropical) lakes and therefore independent of stream velocity. The general coefficients have the following input names and values:

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a	b_1	b_2	c_1	c_2
CoefACH4	*CoefB1CH4*	*CoefB2CH4*	*CoefC1CH4*	*CoefC2CH4*
1.660	0.26	1.0	0.66	1.0

The Schmidt number is the ratio of the kinematic viscosity of water (ν) and the molecular diffusion coefficient of oxygen in water. The appropriate constants to compute the Schmidt number for fresh water are given in the table below (Guérin, 2006):

d_1	d_2	d_3	d_4
CoefD1 CH4	*CoefD2 CH4*	*CoefD3 CH4*	*CoefD4 CH4*
1897.8	114.28	3.2902	0.039061

Directives for use

- ◇ Options $SWVolCH4 = 0, 1, 4, 9$ provide the user with the possibility to scale the mass transfer coefficient $KLVolCH4$. Other options contain fixed coefficients.
- ◇ When using option $SWVolCH4 = 0$ the user should be aware that the mass transfer coefficient $KLVolCH4$ has the unusual dimension d^{-1}. Since high values of $KLVolCH4$ may cause numerical instabilities, the maximum $KLVolCH4$ value is limited to 1.0 day^{-1}.
- ◇ When using option $SWVolCH4 = 1$ the user should be aware that the mass transfer coefficient $KLVolCH4$ has the standard dimension m d^{-1}.
- ◇ When using options $SWVolCH4 = 4$ or 9 the user should be aware that the input parameter $KLVolCH4$ is used as a dimensionless scaling factor. The default value of $KLVolCH4$ is 1.0 in order to guarantee that scaling is not carried out when not explicitly wanted.
- ◇ The coefficients a–d4 are input parameters for option $SWVolCH4 = 13$ only. The default values are those for option 13.

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Table 9.9: *Definitions of the parameters in the above equations for VOLATCH4.*

Name in formulas[1]	Name in input	Definition	Units
$Cch4$	$CH4$	concentration of methane	gC m^{-3}
$Cch4s$	$SaturCH4$	saturation conc. of methane from SATURCH4	gC m^{-3}
a	$CoefACH4$	coefficients for option 13 only	-
b_1	$CoefB1CH4$		-
b_2	$CoefB2CH4$		-
c_1	$CoefC1CH4$		-
c_2	$CoefC2CH4$		-
d_1	$CoefD1CH4$	coefficients for option 13 only	-
d_2	$CoefD2CH4$		-
d_3	$CoefD3CH4$		-
d_4	$CoefD4CH4$		-
fcs	–	scaling factor for the Schmidt number	-
$fsat$	–	percentage methane saturation	%
H	$Depth$	depth of the top water layer	m
$klvol_{20}$	$KLVolCH4$	water transfer coefficient for methane[1]	d^{-1}
$ktvol$	$TCVolCH4$	temperature coefficient for methane volatilisation	-
P	$Rain$	rainfall	mm h^{-1}
$Rvol$	–	methane volatilisation rate	gC m^{-3} d^{-1}
$SWVolCH4$	$SWVolCH4$	switch for selection of options for transfer coefficient	-
T	$Temp$	temperature	°C
v	$Velocity$	stream velocity	m s^{-1}
W	$VWind$	windspeed at 10 m height	m s^{-1}

[1] See directives for use concerning the dimension of $KLVolCH4$

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9.5 Saturation concentration of methane

PROCESS: SATURCH4

The volatilization of methane proceeds proportional to the difference of the saturation CH_4 concentration and the actual dissolved CH_4 concentration. The saturation concentration of CH_4 is primarily a function of water temperature, allthough salinity affects the saturation concentration too.

The saturation concentration at the water surface is also proportional to the partial atmospheric CH_4 pressure. This pressure is so low that is reasonable to assume that this pressure is equal to zero. This means that the saturation concentration at the water surface is also approximately equal to zero.

The calculation of the saturation concentration in DELWAQ is performed as a separate process, the formulation of which has been described by DiToro (2001).

Implementation

Process SATURCH4 delivers the CH_4 saturation concentration in water required for the process REARCH4, referring to the loss of methane to the atmosphere by means of the transfer of dissolved methane transfer at the water surface.

The process has been implemented for substance CH_4. Table 9.10 provides the definitions of the parameters occurring in the formulations.

Formulation

The saturation concentration is:

$$Cch4s = 18.76 \times Pch4 \times (1.024)^{(20-T)}$$

where:

$Cch4s$	methane saturation concentration at the water surface [gC m^{-3}]
$Pch4$	atmospheric methane pressure [atm]
T	temperature [°C]

Directives for use

- ◇ A representative value for the atmospheric methane pressure $AtmPrCH4$ is 10$^{-}5$ atm.
- ◇ The name of the output parameter for the saturation concentration of methane is $SaturCH4$.

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Table 9.10: *The efinitions of the parameters in the above equations for SATURCH4.*

Name in formulas	**Name in input**	**Definition**	**Units**
$Cch4s$	–	saturation concentration of methane in water	gC m^{-3}
$Pch4$	$AtmPrCH4$	atmospheric methane pressure	atm
T	$Temp$	temperature	°C

9.6 Ebullition of methane

PROCESS: EBULCH4

The ebullition of methane from sediment or deep water layers concerns the loss of methane that escapes to the atmosphere via gas bubbles. It is assumed that supersaturation does not occur and that all methane produced in excess of the dissolved saturation concentration is immediately transferred to gas bubbles. Gas bubbles accumulate in sediment until a certain maximal part of the volume is taken up by bubbles. Continuation of the methane gas production results in ebullition from this point on. However, the initial phase of gas accumulation can be ignored. In most cases it is reasonable to assume that the maximal amount of gas is already present at the start of a simulation. This means that all methane produced after establishment of the dissolved saturation concentration is lost to the atmosphere.

The saturation concentration of CH_4 in sediment pore water or in deep water layers concerns the equilibrium of water with a more or less pure methane gas phase. The saturation concentration is primarily a function of water pressure (depth) and water temperature, although salinity will affect the saturation concentration too. This function has been described by DiToro (2001).

Implementation

Process EBULCH4 delivers the flux of methane escaping to the atmosphere as gas bubbles.

The process has been implemented for substance CH4.

Table 9.11 provides the definitions of the parameters occurring in the formulations.

Formulation

The methane ebullition flux follows from:

$$Rebu = f \times \left(\frac{Cch4/\phi - Cch4s}{\Delta t} \right) \qquad \text{if} \quad Cch4/\phi \geq Cch4s$$

$$Cch4s = 18.76 \times \left(1 + \frac{H}{10} \right) \times (1.024)^{(20-T)}$$

with:

$Cch4$	dissolved methane concentration [gC m^{-3}]
$Cch4s$	methane saturation concentration [gC m^{-3}]
f	scaling factor [-]
H	water depth [m]
T	temperature [°C]
ΔT	timestep in DELWAQ [day]
ϕ	porosity [-]

It is obvious that $Rebu = 0.0$ at undersaturation.

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Directives for use

◇ The scaling factor $fScEbul$ can be used to scale the ebullition flux in order to established the required degree of supersaturation. This factor should not be larger than the default value 1.0. A value zero will result in no methane escaping at all.

Table 9.11: *Definitions of the parameters in the above equations for EBULCH4.*

Name in formulas	**Name in input**	**Definition**	**Units**
$Cch4$	$CH4$	dissolved methane concentration	gC m^{-3}
$Cch4s$	–	saturation concentration of methane in water	gC m^{-3}
f	$fScEbul$	scaling factor for methane ebullition	-
H	$TotalDepth$	total depth of the water column	m
$Rebu$	–	methane ebullition rate	gC m^{-3} d^{-1}
T	$Temp$	temperature	°C
Δt	$Delt$	computational time-step	d
ϕ	$POROS$	porosity	-

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9.7 Oxidation of methane

PROCESS: OXIDCH4

Dissolved methane does not react in a purely chemical way with dissolved oxygen. However, methane is oxidised by several families of bacteria species. The microbial oxidation with oxygen has been confirmed extensively. The oxidation with sulfate has not been so extensively investigated. For the model, however, it is assumed that both oxidations may proceed, but not to full extent at the same time because of thermodynamic reasons. Sulfate reduction does not deliver energy at the (substantial) presence of dissolved oxygen. Therefore, the oxidation with sulfate only occurs when sulfate is abundant and oxygen is present in very low concentrations. Such conditions occur in sediment.

The microbial oxidation of methane is a function of the concentrations of dissolved methane and the electron-acceptor. It is also a relatively steep function of the temperature, because only a rather small number of specialised bacteria species are capable of methane oxidation. The process may effectively take place at a rather constant, small rate at low temporatures. It may even come to a halt.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process METHOX has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers.

The process has been implemented for the following substances:

- CH4, OXY and SO4.

Table 9.12 provides the definitions of the parameters occurring in the formulations.

Formulation

Methane oxidation can be described with the following overall reaction equations:

$$\begin{aligned} CH_4 + 2O_2 &\Longrightarrow CO_2 + 2H_2O \\ CH_4 + SO_4^{2-} &\Longrightarrow CO_2 + 2H_2S + 2OH^- \end{aligned}$$

These processes require 5.33 gO_2 gC^{-1} or 2.67 gS gC^{-1}.

Methane oxidation is modelled as the sum of a zero-order process and a process according to Michaelis-Menten kinetics. The rate of the MM-contribution is limited by the availability of methane and dissolved oxygen or sulfate. It is also a function of the temperature. When the water temperature drops below a critical value, the zero-order rate takes over. The oxidation with dissolved oxygen excludes the oxidation with sulfate at DO concentrations exceeding a certain critical concentration.

Methane oxidation is formulated as follows to accommodate the above features (Smits and

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Beek (2013)):

$$Roxi_1 = k0oxi_1 + koxi_1 \times \left(\frac{Cch4}{Ksch4 \times \phi + Cch4}\right) \times \left(\frac{Cox}{Ksox \times \phi + Cox}\right)$$

$$koxi_1 = koxi_{1,20} \times ktoxi_1^{(T-20)}$$

$$\begin{aligned} koxi_1 = 0.0 \quad & \text{if} \quad T < Tc \\ & \text{or} \quad Cox \leq 0.0 \\ & \text{or} \quad Cox \leq Coxc \times \phi \\ k0oxi_1 = 0.0 \quad & \text{if} \quad Cox > Coxc \times \phi \\ & \text{or} \quad Cox \leq 0.0 \end{aligned}$$

$$Roxi_2 = k0oxi_2 + koxi_2 \times \left(\frac{Cch4}{Ksch4 \times \phi + Cch4}\right) \times \left(\frac{Csu}{Kssu \times \phi + Csu}\right)$$

$$koxi_2 = koxi_{2,20} \times ktoxi_2^{(T-20)}$$

$$\begin{aligned} koxi_2 = 0.0 \quad & \text{if} \quad T < Tc \\ & \text{or} \quad Csu \leq 0.0 \\ & \text{or} \quad Csu \leq Csuc \times \phi \\ & \text{or} \quad Cox > Coxc \times \phi \\ k0oxi_2 = 0.0 \quad & \text{if} \quad Csu > Csuc \times \phi \\ & \text{or} \quad Csu \leq 0.0 \\ & \text{or} \quad Cox > Coxc \times \phi \end{aligned}$$

with:

$Cch4$	dissolved methane concentration [gC m_ℓ^{-3}]
Cox	dissolved oxygen concentration [gO_2 m_ℓ^{-3}]
$Coxc$	critical dissolved oxygen concentration for oxidation with sulfate [gO_2 m_w^{-3}]
Csu	sulfate concentration [gS m_ℓ^{-3}]
$Csuc$	critical sulfate concentration for oxidation with sulfate [gS m_w^{-3}]
$k0oxi_1$	zero-order methane oxidation rate for diss. oxygen consumption [gC m_ℓ^{-3} d^{-1}]
$k0oxi_2$	zero-order methane oxidation rate for sulfate consumption [gC m_ℓ^{-3} d^{-1}]
$koxi1$	Michaelis-Menten rate for oxidation with dissolved oxygen [gC m_ℓ^{-3} d^{-1}]
$ktoxi1$	temperature coefficient for oxidation with dissolved oxygen [-]
$Ksch4$	half saturation constant for methane consumption [gC m_w^{-3}]
$Ksox$	half saturation constant for dissolved oxygen consumption [gO_2 m_w^{-3}]
$koxi_2$	Michaelis-Menten rate for oxidation with sulfate [gC m_ℓ^{-3} d^{-1}]
$ktoxi_2$	temperature coefficient for oxidation with sulfate [-]
$Kssu$	half saturation constant for sulfate consumption [gS m_w^{-3}]
$Roxi_1$	methane oxidation rate with DO [gC m_ℓ^{-3} d^{-1}]
$Roxi_2$	methane oxidation rate with sulfate [gC m_ℓ^{-3} d^{-1}]
T	temperature [°C]
Tc	critical temperature for methane oxidation [°C]
ϕ	porosity [-]

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Directives for use

- ◇ For a start, the zero-order rates $Rc0MetOx$ and $Rc0MetSu$ and the critical concentrations $CoxMet$ and $CsuMet$ can be set to zero. In a next step the zero-order rates for low temperatures can be quantified in establishing a good balance between summer and winter oxidation rates.
- ◇ Care must be taken that the zero-order reaction rates are given values, that are in proportion with the first-order kinetics. They should not deliver more than 20 % of the total rate at $T = 20$ °C, and average methane, DO and sulfate concentrations. Using zero-order kinetics may cause negative methane concentrations, when the time-step is too large!
- ◇ The critical temperature for methane oxidation $CTMetOx$ is approximately 3–4 °C.
- ◇ An indicative value for the critical DO concentration $CoxMet$ is 2 gO_2 m_w^{-3}.
- ◇ An indicative value for the temperature coefficients $TcMetOx$ and $TcMetSu$ is 1.07.
- ◇ The oxidation with sulfate can simply be excluded from the simulation by setting rates $Rc0MetSu$ and $RcMetSu20$ equal to 0.0.

Additional references

DiToro (2001), WL | Delft Hydraulics (2002), Wijsman et al. (2001)

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Table 9.12: *Definitions of the parameters in the above equations for OXIDCH4. Volume units refer to bulk (b) or to water (w).*

Name in formulas	Name in input	Definition	Units
$Cch4$	$CH4$	methane concentration	gC m_b^{-3}
Cox	OXY	dissolved oxygen concentration	gO_2 m_b^{-3}
$Coxc$	$CoxMet$	critical DO concentration for methane oxidation	gO_2 m_w^{-3}
$Csuc$	$CsuMet$	critical sulfate concentration for methane oxidation	gS m_w^{-3}
Csu	$SO4$	sulfate concentration	gS m_b^{-3}
$koxi_{1,20}$	$RcMetOx20$	MM-rate for methane oxidation with DO at 20 °C	gC m_b^{-3} d^{-1}
$ktoxi_1$	$TcMetOx$	temp. coefficient for methane oxidation with DO	-
$koxi_{2,20}$	$RcMetSu20$	MM-rate for methane oxid. with sulfate at 20 °C	gC m_b^{-3} d^{-1}
$ktoxi_2$	$TcMetSu$	temp. coefficient for methane oxidation with sulfate	-
$Ksch4$	$KsMet$	half saturation constant for methane consumption	gC m_w^{-3}
$Ksox$	$KsOxMet$	half saturation constant for DO consumption	gO_2 m_w^{-3}
$Kssu$	$KsSuMet$	half saturation constant for sulfate consumption	gS m_w^{-3}
$k0oxi_1$	$Rc0MetOx$	zero-order methane oxid. rate for DO consumption	gC m_b^{-3} d^{-1}
$k0oxi_2$	$Rc0MetSu$	zero-order methane oxid. rate for sulfate cons.	gC m_b^{-3} d^{-1}
$Roxi_1$	–	rate of oxidation of methane with DO	gC m_b^{-3} d^{-1}
$Roxi_2$	–	rate of oxidation of methane with sulfate	gC m_b^{-3} d^{-1}
T	$Temp$	temperature	°C
Tc	$CTMetOx$	critical temperature for methane oxidation	°C
ϕ	$POROS$	porosity	m_w^3 m_b^{-3}

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9.8 Oxidation of sulfide

PROCESS: OXIDSUD

Sulfide oxidation is established by both a purely chemical reaction and a microbially mediated process. Both processes are temperature dependent. However, the chemical oxidation is usually dominant at the significant presence of dissolved oxygen, because it proceeds very fast. The oxidation can be complete within an hour. The microbial oxidation of sulfide can be important at low dissolved oxygen concentrations. Specific autotrophic bacteria species are capable of oxidising sulfide when solar radiation is available as a source of energy. Given the specific features of sulfide oxidation, this process usually takes place in regions with steep concentration gradients. Examples are the sediment-water interface and water layers near the thermocline in a water column.

The chemical oxidation of sulfide is taken as a starting point for the formulation of the oxidation rate. Although oxidation occurs both in solution as well as on the surface of sulfide minerals, it is assumed that only dissolved sulfide is available to quick oxidation.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process SULFOX has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers.

The process has been implemented for the following substances:

- ◇ SUD, SO4 and OXY.

Table 9.13 provides the definitions of the parameters occurring in the formulations.

Formulation

Sulfide oxidation can be described with following overall reaction equation:

$$H_2S + 2O_2 + 2OH^- \quad \Longrightarrow \quad SO_4^{2-} + 2H_2O$$

The process requires 2.0 gO_2 gS^{-1}.

Sulfide oxidation is modelled as the sum of a zero order process and a second-order kinetic process, involving the concentrations of both total dissolved sulfide and dissolved oxygen. The rate is also a function of the temperature.

The zero-order rate should generally be equal to zero, but it can be used for two different purposes. One purpose is to add a contribution of microbial sulfide oxidation when the dissolved oxygen concentration falls below a critical level. The other purpose is to have sulfide oxidation in a water column, in which the average dissolved oxygen concentration is zero or even negative. In this way it can be taken into account that the water column may not be homogeneously mixed in reality, and a surface layer with positive oxygen concentrations persists. The zero-order rate is set to zero, when the dissolved oxygen concentration is above the critical concentration, the second-order rate is set to zero when the dissolved oxygen concentration is negative.

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The sulfate oxidation rate is formulated as follows to accommodate the above features (Smits and Beek (2013)):

$$Roxi = k0oxi + koxi \times \left(\frac{Csud}{\phi}\right) \times \left(\frac{Cox}{\phi}\right) \times \phi$$

$$koxi = koxi_{20} \times ktoxi^{(T-20)}$$

$$koxi = 0.0 \quad \text{if} \quad Cox \leq 0.0$$

$$k0oxi = 0.0 \quad \text{if} \quad Cox > Coxc \times \phi$$

with:

Cox	dissolved oxygen concentration [$gO_2\ m_{\ell}^{-3}$]
$Coxc$	critical dissolved oxygen concentration [$gO_2\ m_w^{-3}$]
$Csud$	total dissolved sulfide concentration [$gS\ m_{\ell}^{-3}$]
$koxi$	pseudo second-order sulfide oxidation rate [$gO_2^{-1}\ m_w^3\ d$]
$ktoxi$	temperature coefficient for sulfide oxidation [-]
$k0oxi$	zero-order sulfide oxidation rate [$gS\ m_{\ell}^{-3}\ d^{-1}$]
T	temperature [°C]
ϕ	porosity [-]

Notice that the porosity occurs three times in the rate equation, whereas only once would suffice. However, a systematic formulation is preferred in order to make clear how the porosity affects the rate.

The oxidation process must stop at the depletion of dissolved sulfide. Therefore, the oxidation flux is made equal to half the concentration of dissolved sulfide SUD divided with timestep Δt, when the flux as calculated with the above formulation is larger than $SUD/\Delta t$.

Directives for use

- ◇ The zero-order rate $Rc0Sox$ should always be equal to its default value 0.0, unless it is really required to have sulfide oxidation going on when the water column average oxygen concentration is negative.
- ◇ Care must be taken that the zero-order reaction rates is given a value, that is in proportion with the second-order kinetics. They should not deliver more than 20 % of the total rate at $T = 20$ °C, and average DO concentrations. Using zero-order kinetics may cause negative sulfide concentrations, when the time-step is too large!
- ◇ The critical dissolved oxygen concentration CoxSUD needs to be 0.0 to accommodate the use of $Rc0Sox$ for sulfide oxidation in a water column with negative oxygen concentrations.

Additional references

DiToro (2001), Wang and Cappellen (1996), WL | Delft Hydraulics (2002), Wijsman et al. (2001)

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Table 9.13: *Definitions of the parameters in the above equations for OXIDSUD. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	**Name in input**	**Definition**	**Units**
Cox	OXY	dissolved oxygen concentration	$gO_2\ m^{-3}_{\mathscr{b}}$
$Coxc$	$CoxSUD$	critical dissolved oxygen concentration	$gO_2\ m^{-3}_{\mathscr{w}}$
$Csud$	SUD	total dissolved sulfide concentration	$gS\ m^{-3}_{\mathscr{b}}$
Δt	$Delt$	timestep	d
$koxi_{20}$	$RcSox20$	pseudo second-order sulfide oxidation rate at 20 °C	$gO_2^{-1}\ m^3_{\mathscr{w}}\ d^{-1}$
$ktoxi$	$TcSox$	temperature coefficient for sulfide oxidation	-
$k0oxi$	$Rc0Sox$	zero-order sulfide oxidation rate	$gS\ m^{-3}_{\mathscr{b}}\ d^{-1}$
$Roxi$	–	sulfide oxidation rate	$gS\ m^{-3}_{\mathscr{b}}\ d^{-1}$
T	$Temp$	temperature	°C
ϕ	$POROS$	porosity	$m^3_{\mathscr{w}}\ m^{-3}_{\mathscr{b}}$

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9.9 Precipitation and dissolution of sulfide

PROCESS: PRECSUL

At reducing conditions sulfide resulting from sulfate reduction may precipitate with iron(II) as rather amorphous iron(II) sulfide. This mineral is thermodynamically unstable at oxidising conditions. At the presence of dissolved oxygen iron(II) in sulfides is oxidised into iron(III), sulfide into sulfate, resulting in the subsequent dissolution of the mineral.

Not only sulfide but also elementary sulfur is produced at sulfate reduction. Crystalline pyrite (FeS_2) is formed from iron(II) sulfide and sulfur, a mineral which can be very stable under oxidising conditions. However, the formation of pyrite is not considered in the model. It can be argued that the formation of pyrite being a slow process does not play an important part is the oxygen budget and sediment diagenesis in the short term. It should nevertheless be noticed, that ignoring pyrite may cause some overestimation of the sediment oxygen demand.

The precipitation of iron(II) sulfide only occurs at the absence of dissolved oxygen in a solution supersaturated with respect to free sulfide and iron(II) ions. These conditions usually occur in the reducing sediment, just below an oxidising top layer. However, sulfide may also precipitate in the lower part of the water column at lasting stratification. Precipitation is not only temperature dependent, but also pH dependent among other things due to the acid-base equilibria to which sulfide is subjected. The pH-dependency is taken into account via the calculation of a pH dependent free sulfide concentration with process SPECSUD.

The dissolution of iron(II) sulfide occurs when the solution is undersaturated with respect to sulfide and iron(II). Since the oxidation of these ions with dissolved oxygen proceeds rapid, it is assumed in the model that oxidation entirely occurs in the solution. This is described elsewhere for process SULPHOX. Rapid oxidation implies that the dissolved concentrations of sulfide and iron(II) will be very small at the presence of dissolved oxygen. In other words, the solution will be strongly undersaturated with respect to iron(II) sulfide. However, in reality oxidation will also take place at the mineral surface to a certain extent.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process PRECSUL has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. The precipitation of sulfide in sediment is not considered, when substances in the sediment are modeled as a ‘inactive’ substances (the S1/2 approach).

The process has been implemented for the following substances:

- ◇ total dissolved sulfide SUD and particulate sulfide SUP.

The process should only be applied when iron (7 substances) is not simulated. When iron is simulated, SUP should not be simulated. Process PRIRON will take care of the precipitation and dissolution of sulfide as iron sulfide in stead of process PRECSUL.

Table 9.14 provides the definitions of the parameters occurring in the formulations. The actual dissolved free sulfide concentration (Csd) can be delivered by process SPECSUD or imposed to DELWAQ via the input.

Formulation

The precipitation and dissolution equilibrium of iron(II) sulfide can be described with the following simplified reaction equation:

$$Fe^{2+} + S^{2-} \quad \Leftrightarrow \quad FeS$$

The precipitation and dissolution rates are formulated with first-order kinetics, with the difference between the actual dissolved free sulfide concentration and the equilibrium dissolved concentration as driving force (Smits and Beek (2013)):

$$Rprc = 32\,000 \times kprc \times (Csd - Csde) \times \phi \qquad \text{if } Csd \geq Cdse$$

$$Rdis = 32\,000 \times kdis \times (Csde - Csd) \times \phi \qquad \text{if } Csd < Cdse$$

$$kprc = kprc_{20} \times ktprc^{(T-20)}$$

$$kdis = kdis_{20} \times ktdis^{(T-20)}$$

with:

Csd	dissolved free sulfide concentration [mol l^{-1}]
$Csde$	equilibrium dissolved free sulfide concentration [mol l^{-1}]
$kdis$	dissolution reaction rate [d^{-1}]
$kprc$	precipitation rate [d^{-1}]
$ktdis$	temperature coefficient for dissolution [-]
$ktprc$	temperature coefficient for precipitation [-]
$Rdis$	rate of dissolution [gS m_{ℓ}^{-3} d^{-1}]
$Rprc$	rate of precipitation [gS m_{ℓ}^{-3} d^{-1}]
T	temperature [°C]
ϕ	porosity [-]

The constant of 32,000 concerns the conversion of [mol/l] to [gS/m^{-3}].

The dissolution process must stop at the depletion of precipitated sulfide. Therefore, the dissolution flux is made equal to half the concentration of precipitated sulfide SUP divided with timestep Δt, when the flux as calculated with the above formulation is larger than $SUP/\Delta t$.

Notice that the effect of the dissolved iron(II) concentration is ignored. In case iron is simulated too, the driving force can be formulated on the basis of the solubility product of the dissolved free sulfide and iron(II) concentrations. However, iron is currently not included in DELWAQ.

Directives for use

- ◇ The equilibrium dissolved free sulfide concentration can be calculated with process SULFID using an imposed total dissolved sulfide concentration. However, it is also possible to impose fixed dissolved free sulfide concentrations by assigning values to $DisSWK$ as input parameter.
- ◇ The equilibrium dissolved free sulfide concentration $DisSEqFeS$ is an input parameter. Its value can be deduced from the solubility product of iron(II) sulfide and an estimated dissolved free iron(II) concentration.
- ◇ As a start the precipitation and dissolution reaction rates can be given the same value. The rates must be high enough to establish a near equilibrium at the absence of oxidation. The dissolution rate should be consistent with the sulfide oxidation rate $RcSox20$ for process OXIDSUD.

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◇ When simulating the substances in the sediment as “inactive” substances (the S1/2 approach) process SULFPR only affects SUD and SUP in the water column. Settled SUP is then permanently removed from the simulated system.

Additional references

DiToro (2001),
Stumm and Morgan (1996),
Wang and Cappellen (1996),
WL | Delft Hydraulics (2002),
Wijsman et al. (2001)

Table 9.14: *Definitions of the parameters in the above equations for PRECSUL. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
Csd	$DisSWK$	dissolved free sulfide concentration	mol l^{-l}
$Csde$	$DisSEqFeS$	equilibrium dissolved free sulfide concentration for amorphous iron sulfide	mol l^{-1}
$Csup$	SUP	precipitated sulfide concentration	gS $m^{-3}_{\mathscr{b}}$
Δt	$Delt$	timestep	d
$kdis_{20}$	$RcDisS20$	dissolution reaction rate	d^{-1}
$ktdis$	$TcDisS$	temperature coefficient for dissolution	-
$kprc_{20}$	$RcPrcS20$	precipitation reaction rate	d^{-1}
$ktprc$	$TcPrcS$	temperature coefficient for precipitation	-
$Rdis$	–	dissolution rate	gS $m^{-3}_{\mathscr{b}}$ d^{-1}
$Rprc$	–	precipitation rate	gS $m^{-3}_{\mathscr{b}}$ d^{-1}
T	$Temp$	temperature	°C
ϕ	$POROS$	porosity	$m^3_{\mathscr{w}}$ $m^{-3}_{\mathscr{b}}$

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9.10 Speciation of dissolved sulfide

PROCESS: SPECSUD AND SPECSUDS1/2

Sulfide can only persist in anoxic environment, the reducing enviroment which usually occurs in the sediment. Being a weak acid sulfide forms two protonised species in solution. These equilibrium processes are temperature dependent. The pH-dependent speciation affects dissolved metal concentrations as well as total dissolved sulfide concentrations in the reducing environment. Metal sulfide complexes are formed and only the concentrations of the free metal ion and the free sulfide ion affect the precipitation and the dissolution of a solid metal sulfide.

The computed sulfide speciation is used in processes PARTWK_(i) and PARTS1/S2_(i) to determine the precipitated and dissolved heavy metal fractions. It is also used for the generic process PRECSUL to compute the precipitation and dissolution rates concerning iron sulfide.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process SPECSUD is fully generic, meaning that it can be applied both to water layers and sediment layers. However, in case the sediment is modeled as a number of 'inactive' substances, the processes SPECSUDS1/2 have to be applied next to SPECSUD. In stead of using these processes, it is also possible to provide the dissolved sulfide species as model input

The processes have been implemented for the following substances:

- ◇ dissolved sulfide species SUD and SUDS1/2.

Table 9.15 and Table 9.16 provide the definitions of the parameters occurring in the formulations. Table 9.17 provides the output parameters.

Formulation

The hydrolysis of hydrogen sulfide proceeds according to the following reaction equations:

$$\begin{aligned} H_2S + H_2O &\Leftrightarrow HS^- + H_3O^+ \\ HS^- + H_2O &\Leftrightarrow S^{2-} + H_3O^+ \end{aligned}$$

The chemical equilibria are described with:

$$Ks_1 = \frac{Csd_2 \times H^+}{Csd_1} \tag{9.4}$$

$$Ks_2 = \frac{Csd_3 \times H^+}{Csd_2} \tag{9.5}$$

$$Csdt = Csd_1 + Csd_2 + Csd_3 \tag{9.6}$$

with:

Csd_1	concentration of dissolved hydrogen sulfide [mol l^{-1}]
Csd_2	concentration of hydrogen sulfide anion [mol l^{-1}]

Csd_3	concentration of free dissolved sulfide [mole l^{-1}]
$Csdt$	concentration of total dissolved sulfide [mol l^{-1}]
H^+	proton concentration [mol l^{-1}]
Ks_1	acidity (dissociation, equilibrium) constant for H_2S [mol l^{-1}]
Ks_2	acidity (dissociation, equilibrium) constant for HS^- [mol l^{-1}]

The proton concentration H^+ and the temperature dependent equilibrium constants follow from:

$$H^+ = 10^{-pH}$$
$$Ks_1 = 10^{-lK1_1} \times kth2s^{(T-20)}$$
$$Ks_2 = 10^{-lKs_2} \times kths^{(T-20)}$$

where:

$kths$	temperature coefficient for HS^{-1} equilibrium [-]
$kth2s$	temperature coefficient for H_2S equilibrium [-]
pH	acidity [-]
T	temperature [°C]

The concentration of the relevant sulfide species in solution can now be calculated from:

$$Csdt = \frac{Csud}{32\,000 \times \phi}$$
$$Csd_1 = \frac{Csdt}{(1 + Ks_1/H^+ + (Ks_1 \times Ks_2)/(H^+)^2)}$$
$$Csd_2 = \frac{Ks_1 \times Csd_1}{H^+}$$
$$Csd_3 = Csdt - Csd_1 - Csd_2$$

if due to round off the resulting $Csd_3 \leq 0.0$

$$Csd_3 = \frac{Ks_2 \times Csd_2}{H^+}$$

where:

$Csud$	concentration of total dissolved sulfide [gS m^{-3}_{ℓ}]
ϕ	porosity [-]

The constant 32 000.0 concerns the conversion from gS m^{-3} to mol l^{-1}.

The pertinent fractions follow from:

$$fs_1 = \frac{Csd_1}{Csdt}$$
$$fs_2 = \frac{Csd_2}{Csdt}$$
$$fs_3 = 1 - fs_1 - fs_2$$

if due to rounding off the resulting $fs_3 = 0.0$

$$fs_3 = \frac{Csd_3}{Csdt}$$

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Directives for use

- ◇ The acidity constants for the hydrogen sulfides have to be provided in the input of the model as logarithmic values ($^{10}\log$)!
- ◇ The negative logarithms of the equilibrium constants at 20 °C are:
  - ▫ $lKstH2S = -7.1$ and $lKstHS = -14.0$.
  - ▫ An indicative value for total sulfide concentration SUD is 32 mg/l or 10^{-3} mol l^{-1}.
- ◇ The temperature dependencies are ignored by default temperature coefficients of the acidity constants equal to 1.0. Temperature dependency can be established by modification of the values of *TcKstHS* and *TcKstH2S*.
- ◇ Different pH's and total sulfide concentrations apply to the water column and the various sediment layers.

Additional references

Stumm and Morgan (1996)

Table 9.15: *Definitions of the input parameters in the above equations for SPECSUD.*

Name in formulas	Name in input	Definition	Units
Csdt	-	concentration of total dissolved sulfide	mol l^{-1}
Csud	SUD	concentration of total dissolved sulfide	gS.m^{-3}_{ℓ}
lKs_1	lKstH2S	log acidity constant for H_2S (mol l^{-1})	log(-)
lKs_2	lKstHS	log acidity constant for HS^- (mol l^{-1})	log(-)
kth2s	TcKstH2S	temperature coefficient for KstH2S	-
kths	TcKstHS	temperature coefficient for KstHS	-
H^+	–	proton concentration	mol l^{-1}
pH	pH	acidity	-
T	TEMP	ambient temperature	°C
ϕ	POROS	porosity	m^3w.m^{-3}_{ℓ}

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Table 9.16: *Definitions of the input parameters in the above equations for SPECSUDS1/2.*

Name in formulas	Name in input	Definition	Units
Csdt	–	concentration of total dissolved sulfide	mol l^{-1}
Csud	SUDS1/2	concentration of total dissolved sulfide	gS.m^{-3}_{ℓ}
lKhs	lKstHS	log acidity constant for HS^- (mol l^{-1})	log(-)
lKh_2s	lKstH2S	log acidity constant for H_2S (mol l^{-1})	log(-)
kth2s	TcKstH2S	temperature coefficient for KstH2S	-
kths	TcKstHS	temperature coefficient for KstHS	-
H^+	–	proton concentration	mol l^{-1}
pH	pH	acidity	-
T	TEMP	ambient temperature (currently not used)	°C
ϕ	PORS1/2	porosity	m^3w.m^{-3}_{ℓ}

Table 9.17: *Definitions of the output parameters of SPECSUD and SPECSUDS1/2.*

Name in formulas	Name in input	Definition	Units
Csd_1	DisH2SWK	of dissolved hydrogen sulfide	mol l^{-1}
Csd_2	DisHSWK	concentration of hydrogen sulfide anion	mol l^{-1}
Csd_3	DisSWK	concentration of free dissolved sulfide	mol l^{-1}
fs_1	FrH2Sdis	fraction of dissolved hydrogen sulfide	-
fs_2	FrHSdis	fraction of hydrogen sulfide anion	-
fs_3	FrS2dis	fraction of free dissolved sulfide	-
Csd_1	DisH2SS1	concentration of dissolved hydrogen sulfide in S1	mol l^{-1}
Csd_2	DisHSS1	concentration of hydrogen sulfide anion in S1	mol l^{-1}
Csd_3	DisSS1	concentration of free dissolved sulfide in S1	mol l^{-1}
Csd_1	DisH2SS2	concentration of dissolved hydrogen sulfide in S2	mol l^{-1}
Csd_2	DisHSS2	concentration of hydrogen sulfide anion in S2	mol l^{-1}
Csd_3	DisSS2	concentration of free dissolved sulfide in S2	mol l^{-1}

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9.11 Precipitation, dissolution and conversion of iron

PROCESS: PRIRON

This process considers the precipitation dissolution and conversion of oxidizing and reducing iron minerals.

Particulate oxidizing iron in the model consists of iron(III) oxyhydroxide chemically indicated with $Fe(OH)_3$ or FeOOH. In the model an amorphous fraction and a crystalline fraction (goethite) are distinguished respectively substances FeIIIpa and FeIIIpc. The latter fraction reacts much more slowly due to the additional activation energies needed to add ions to or to detach ions from its crystal lattice. Due to "aging" the amorphous fraction slowly turns into the crystalline fraction. The precipitation of Fe^{3+} adds to the amorphous fraction. Precipitation occurs at oxidizing conditions when the solution is supersaturated that is when the ion activity product with regard to OH^- overrides the solubility product. Dissolution occurs when the solubility product overrides the ion activity product usually at reducing conditions (Luff and Moll, 2004; Wang and Cappellen, 1996; Boudreau, 1996).

Particulate reducing iron in the model consists of rather amorphous iron(II) sulfide rather crystalline pyrite and rather crystalline iron(II) carbonate (siderite) chemically indicated with FeS FeS_2 and $FeCO_3$. In the model these substances are indicated with Fes FeS2 and FeCO3. Pyrite reacts much more slowly than iron(II) sulfide due to the additional activation energies needed to add ions to or to detach ions from its crystal lattice. Siderite is usually also less reactive than iron(II) sulfide. Precipitation of Fe^{2+} adds to the FeS whereas FeS_2 is formed from FeS and S. Elementary sulfur is produced at sulfate reduction but is not considered in the model. For the model it is assumed that FeS reacts with H_2S. Precipitation occurs at reducing conditions when the solution is supersaturated either with regard to S^{2-} or ${CO_3}^{2-}$ that is when the at least one of the ion activity products overrides the pertinent solubility product. Dissolution occurs when the solubility product overrides the ion activity product usually at oxidizing conditions (Luff and Moll, 2004; Wang and Cappellen, 1996; Boudreau, 1996).

Iron(II) sulfide and pyrite are thermodynamically unstable at oxidizing conditions. At the presence of dissolved oxygen the sulfide is oxidized into sulfate upon which the dissolved iron(II) gets oxidized too. The oxidation of the iron(II) in siderite proceeds after dissolution of this mineral. See process SULPHOX for the oxidation of FeS and FeS_2.

The precipitation of iron(II) sulfide only occurs at the absence of dissolved oxygen which is usually only the case in reducing sediment just below an oxidizing top layer. However iron(II) sulfide may also precipitate in the lower part of the water column at lasting stratification.

The precipitation of the iron minerals is not only temperature dependent but also pH dependent. The pH dependency is due to the concentrations of the co-precipitating ions OH^- S^{2-} and ${CO_3}^{2-}$ are ruled by acid-base equilibria. The pH-dependency with regard to sulfide can be taken into account via the calculation of the pH dependent concentration of S^{2-}. The pH-dependency with regard to carbonate can be taken into account via the calculation of the pH dependent concentration of ${CO_3}^{2-}$.

Implementation

Process PRIRON has been implemented in a generic way meaning that it can be applied both to water layers and sediment layers. If PRIRON is applied the process PRESUL must not be used. The precipitation dissolution and conversion of iron in sediment is not considered when substances in the sediment are modeled as a 'inactive' substances (the S1/2 approach).

The process has been implemented for the following substances:

◇ FeIIIpa FeIIIpc FeIIId FeS FeS2 FeCO3 FeIId and SUD.

Tables 9.18 and 9.19 provide the definitions of the parameters occurring in the formulations. The dissolved free iron(III) and iron(II) fractions can be delivered by auxiliary process SPECIRON or imposed on the model as an input parameter. The fraction dissolved free sulfide can be delivered by auxiliary process SPECSUD or imposed on the model as an input parameter. The fraction of dissolved free carbonate can be delivered by auxiliary process SPECCARB or imposed on the model as an input parameter. Either TIC or CO2 must be simulated or imposed for computation of the free carbonate fraction. Option parameter *SWTICCO2* indicates which substance is used.

Formulation

Precipitation and dissolution of iron(III)

The precipitation and dissolution equilibrium of amorphous iron(III) oxyhydroxide (*FeIIIpa*) can be described with the following simplified reaction equation:

Fe^{3+} + 3 OH^- $\Leftrightarrow$ $Fe(OH)_3$

The precipitation and dissolution rates are formulated with approximate kinetics with the difference of the ion activity and solubility products as driving force:

$$Rpfe3 = kpfe3 \times \left(\frac{IAP_1}{Ksp_1} - 1\right) \times \phi \qquad \text{if } IAP_1 \geq Ksp_1$$

$$Rdfe3 = kdfe3 \times Cfea \times \left(1 - \frac{IAP_1}{Ksp_1}\right) \qquad \text{if } IAP_1 < Ksp_1$$

$$IAP_1 = Cfe3d \times (OH^-)^3$$

$$Cfe3d = ffe3_1 \times Cfe3dt \times \frac{1}{56\,000 \times \phi}$$

$$OH^- = 10^{-(14-pH)}$$

$$Ksp_1 = 10^{lKsp_1}$$

$$Kfe_1 = 10^{lKfe_1}$$

$$kpfe3 = kpfe3_{20} \times ktpfe3^{(T-20)}$$

$$kdfe3 = kdfe3_{20} \times ktdfe3^{(T-20)}$$

where:

$Cfea$	particulate amorphous oxidizing iron concentration [gFe.m$^{-3}_{\ell}$]
$Cfe3dt$	dissolved oxidizing iron concentration [gFe.m$^{-3}_{\ell}$]
$Cfe3d$	equilibrium dissolved free iron(III) concentration [mol.l^{-1}]
$ffe3_1$	fraction dissolved free iron(III) [-]
IAP_1	ion activity product for $Fe(OH)_3$ [(mol.l^{-1})^4]
Ksp_1	solubility product for $Fe(OH)_3$ [(mol.l^{-1})^4]
$kdfe3$	specific iron(III) dissolution rate [d^{-1}]
$kpfe3$	specific iron(III) precipitation rate [gFe.m$^{-3}_{\ell}$.d^{-1}]
$ktdfe3$	temperature coefficient for iron(III) dissolution [-]

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$ktpfe3$	temperature coefficient for iron(III) precipitation [-]
OH^-	hydroxyl concentration [mol.l^{-1}]
pH	acidity [-]
$Rdfe3$	rate of amorphous iron(III) dissolution [gFe.m$^{-3}_{\ell}$.d^{-1}]
$Rpfe3$	rate of amorphous iron(III) precipitation [gFe.m$^{-3}_{\ell}$.d^{-1}]
T	temperature [°C]
ϕ	porosity [-]

The constant of 56 000 concerns the conversion of gFe.m^{-3} to mol.l^{-1}.

The dissolution process must stop at the depletion of precipitated iron(III). Therefore the dissolution flux is made equal to half the concentration of amorphous precipitated iron(III) *Cfea* divided with timestep Δt when the flux as calculated with the above formulation is larger than *Cfea*/Δt.

Aging of iron(III)

The coversion of amorphous iron(III) oxyhydroxide (*FeIIIpa*) into crystalline iron(III) oxyhydroxide (*FeIIIpc*) can be described with the following simplified reaction equation:

$Fe(OH)_3 \Rightarrow FeOOH + H_2O$

The rate of aging is equal to:

$$Rafe3 = kafe3 \times Cfea$$
$$kafe3 = kafe3_{20} \times ktafe3^{(T-20)}$$

where:

$Cfea$	particulate amorphous oxidizing iron concentration [gFe.m$^{-3}_{\ell}$]
$kafe3$	specific iron(III) aging rate [d^{-1}]
$ktafe3$	temperature coefficient for iron(III) aging [-]
$Rafe3$	rate of amorphous iron(III) aging [gFe.m$^{-3}_{\ell}$.d^{-1}]
T	temperature [°C]

Precipitation and dissolution of iron(II)

The precipitation of iron(II) minerals in the model includes iron(II) sulfide (FeS) and siderite ($FeCO_3$). The precipitation and dissolution equilibria can be described with the following simplified reaction equations:

$Fe^{2+} + S^{2-} \Leftrightarrow FeS$

$Fe^{2+} + {CO_3}^{2-} \Leftrightarrow FeCO_3$

The precipitation and dissolution rates are formulated with approximate kinetics with the difference of the ion activity and solubility products as driving force. The formulations for iron

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sulfide formation are:

$$Rpfes = kpfes \times \left(\frac{IAP_2}{Ksp_2} - 1\right) \times \phi \qquad \text{if } IAP_2 \geq Ksp_2$$

$$Rdfes = kdfes \times Cfes \times \left(1 - \frac{IAP_2}{Ksp_2}\right) \qquad \text{if } IAP_2 < Ksp_2$$

$$IAP_2 = Cfe2d \times Csd_3$$

$$Cfe2d = ffe2_1 \times Cfe2dt \times \frac{1}{56\,000 \times \phi}$$

$$Csd_3 = fs_3 \times Csdt \times \frac{1}{32\,000 \times \phi}$$

$$Ksp_2 = 10^{lKsp_2}$$

$$kpfes = kpfes_{20} \times ktpfes^{(T-20)}$$

$$kdfes = kdfes_{20} \times ktdfes^{(T-20)}$$

where:

$Cfes$	iron(II) sulfide concentration [gFe.m$^{-3}_{\ell}$]
$Cfe2dt$	dissolved reducing iron concentration [gFe.m$^{-3}_{\ell}$]
$Cfe2d$	equilibrium dissolved free iron(II) concentration [mol.l^{-1}]
$Csdt$	total dissolved sulfide concentration [gS.m$^{-3}_{\ell}$]
Csd_3	dissolved free sulfide concentration [mol.l^{-l}]
fs_3	fraction dissolved free sulfide [-]
IAP_2	ion activity product for Fes [mol.l^{-12}]
Ksp_2	solubility product for Fes [mol.l^{-12}]
$kdfes$	specific FeS dissolution rate [d^{-1}]
$kpfes$	specific Fes precipitation rate [gFe.m$^{-3}_{\ell}$.d^{-1}]
$ktdfes$	temperature coefficient for FeS dissolution [-]
$ktpfes$	temperature coefficient for FeS precipitation [-]
$Rdfes$	rate of Fes dissolution [gFe.m$^{-3}_{\ell}$.d^{-1}]
$Rpfes$	rate of Fes precipitation [gFe.m$^{-3}_{\ell}$.d^{-1}]
T	temperature [°C]
ϕ	porosity [-]

The constant of 56 000 concerns the conversion of gFe.m^{-3} to mol.l^{-1}.

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The formulations for iron carbonate formation are:

$$Rpfeco3 = kpfeco3 \times \left(\frac{IAP_3}{Ksp_3} - 1\right) \times \phi \qquad \text{if } IAP_3 \geq Ksp_3$$

$$Rdfeco3 = kdfeco3 \times Cfeco3 \times \left(1 - \frac{IAP_3}{Ksp_3}\right) \qquad \text{if } IAP_3 < Ksp_3$$

$$IAP_3 = Cfe2d \times Cco3d$$

$$Cfe2d = ffe2_1 \times Cfe2td \times \frac{1}{56\,000 \times \phi}$$

$$Cco3d = fc_3 \times Ctic \times \frac{1}{12\,000 \times \phi}$$

$$Ksp_3 = 10^{lKsp_3}$$

$$kpfeco3 = kpfeco3_{20} \times ktpfeco3^{(T-20)}$$

$$kdfeco3 = kdfeco3_{20} \times ktdfeco3^{(T-20)}$$

where:

$Cfeco3$	iron(II) carbonate concentration [gFe.m$^{-3}_{\ell}$]
$Cfe2td$	dissolved reducing iron concentration [gFe.m$^{-3}_{\ell}$]
$Cfe2d$	equilibrium dissolved free iron(II) concentration [mol.l^{-1}]
$Ctic$	total dissolved inorganic carbon concentration [gC.m$^{-3}_{\ell}$]
$Cco3d$	total dissolved free carbonate concentration [mol.l^{-l}]
fc_3	fraction dissolved free carbonate [-]
IAP_3	ion activity product for FeCO3 [mol.l^{-12}]
Ksp_3	solubility product for FeCO3 ([mol.l^{-12}])
$kdfeco3$	specific FeCO3 dissolution rate [d^{-1}]
$kpfeco3$	specific FeCO3 precipitation rate [gFe.m$^{-3}_{\ell}$.d^{-1}]
$ktdfeco3$	temperature coefficient for FeCO3 dissolution [-]
$ktpfeco3$	temperature coefficient for FeCO3 precipitation [-]
$Rdfeco3$	rate of FeCO3 dissolution [gFe.m$^{-3}_{\ell}$.d^{-1}]
$Rpfeco3$	rate of FeCO3 precipitation [gFe.m$^{-3}_{\ell}$.d^{-1}]
T	temperature [°C]
ϕ	porosity [-]

The constant of 12 000 concerns the conversion of gC.m^{-3} to mol.l^{-1}.

The dissolution process must stop at the depletion of precipitated FeS or $FeCO_3$. Therefore the dissolution fluxes are made equal to half the concentration of mineral concerned *Cfes* or *Cfeco3* divided with timestep Δt when the flux as calculated with the above formulation is larger than *Cfes*/Δt or *Cfeco3*/Δt.

The total inorganic carbonate concentration is derived from *TIC* when *SWTICCO2* = 0.0 (default) or from CO2*12/44 when *SWTICCO2* = 1.0.

Formation of pyrite

The formation of pyrite (*FeS2*) can be described with the following simplified reaction equations:

FeS + S $\Rightarrow$ FeS_2

or

$FeS + H_2S \Rightarrow FeS_2 + H_2$

Nor elemental sulfide nor elemental hydrogen is included in the model consequently the electrons transferred cannot be accounted for. Pragmatically the formation rate is formulated as follows:

$$Rpyr = kpyr \times Cfes \times fs_1 \times Csdt/\phi$$
$$kpyr = kpyr_{20} \times ktpyr^{(T-20)}$$

where:

$Cfes$	iron(II) sulfide concentration [gFe.m$^{-3}_{\ell}$]
$Csdt$	total dissolved sulfide concentration [gS.m$^{-3}_{\ell}$]
fs_1	fraction dissolved hydrogen sulfide [-]
$kpyr$	specific pyrite formation rate (gS^{-1}.m^3.d^{-1})
$ktpyr$	temperature coefficient for iron(III) aging [-]
$Rpyr$	rate of pyrite formation [gFe.m$^{-3}_{\ell}$.d^{-1}]
T	temperature [°C]
ϕ	porosity [-]

Directives for use

- ◇ The fractions dissolved free iron(II) and iron(III) *FrFe2dis* and *FrFe2dis* can be calculated with process SPECIRON using an imposed or simulated total dissolved iron(II) and iron(III) concentrations.
- ◇ The fraction dissolved free sulfide *FrS2dis* can be calculated with process SPECSUD using an imposed or simulated total dissolved sulfide concentration.
- ◇ The fraction dissolved free carbonate *FrCO3dis* can be calculated with process SPECCARB using an imposed or simulated total carbonate concentration. This may be *TIC* or *CO2*. The model will choose the substance according to option parameter *SWTICCO2* (0.0 = use *TIC;* 1.0 = use *CO2*).
- ◇ As a start the precipitation and dissolution reaction rates of a mineral can be given the same value.
- ◇ The solubility products have to be provided in the input of the model as logarithmic values ($^{10}\log$)!!!
- ◇ The logarithms of the solubility products at 25 °C and I=0.0 are:
  lKspFeOH3 = -38.7 *lKspFeS* = -18.1 and *lKspFeCO3* = -10.7 .
- ◇ The temperature dependency of the solubilities is ignored in the model but can be taken into account by modification of the default solubility products as constants or as time series.

References

DiToro (2001),
Stumm and Morgan (1996),
Wang and Cappellen (1996),
WL | Delft Hydraulics (2002),
Wijsman et al. (2001)

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Table 9.18: *Definitions of the parameters in the above equations for PRIRON concerning oxidizing iron. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in Input	Definition	Units
Cfea	FeIIIpa	particulate amorphous oxidizing iron concentration	gFe.m$^{-3}_{\mathscr{b}}$
Cfe3dt	FeIIId	dissolved oxidizing iron concentration	gFe.m$^{-3}_{\mathscr{b}}$
Cfe3d	–	equilibrium dissolved free iron(III) concentration	mol.l^{-l}
ffe3$_1$	FrFe3dis	fraction dissolved free iron(III)	
lAP$_1$	–	ion activity product for Fe(OH)$_3$	mol.l^{-14}
lKsp$_1$	lKspFeOH3	log solubility product for Fe(OH)$_3$ [mol.l^{-14}]	log(-)
kafe3$_{20}$	RcAgFe320	specific iron(III) aging rate at 20 °C	d^{-1}
kdfe3$_{20}$	RcDisFe320	specific iron(III) dissolution rate at 20 °C	d^{-1}
kpfe3$_{20}$	RcPrcFe320	specific iron(III) precipitation rate at 20 °C	gFe.m$^{-3}_{\mathscr{b}}$.d^{-1}
ktafe3	TcAgFe3	temperature coefficient for iron(III) aging	-
ktdfe3	TcDisFe3	temperature coefficient for iron(III) dissolution	-
ktpfe3	TcPrcFe3	temperature coefficient for iron(III) precipitation	-
OH$^-$	–	hydroxyl concentration	mol.l^{-1}
pH	pH	acidity	-
Rafe3	–	rate of amorphous iron(III) aging	gFe.m$^{-3}_{\mathscr{b}}$.d^{-1}
Rdfe3	–	rate of amorphous iron(III) dissolution	gFe.m$^{-3}_{\mathscr{b}}$.d^{-1}
Rpfe3	–	rate of amorphous iron(III) precipitation	gFe.m$^{-3}_{\mathscr{b}}$.d^{-1}
T	Temp	temperature	°C
Δt	Delt	timestep	d
ϕ	POROS	porosity	m$^3_{\mathscr{w}}$.m$^{-3}_{\mathscr{b}}$

Table 9.19: *Definitions of the parameters in the above equations for PRIRON concerning reducing iron. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in Input	Definition	Units
Cfes	FeS	iron(II) sulfide concentration	gFe.m$^{-3}_{\mathscr{b}}$

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Table 9.19: *Definitions of the parameters in the above equations for PRIRON concerning reducing iron. Volume units refer to bulk (ℓ) or to water (w).*

Name in formulas	Name in Input	Definition	Units
Cfe2dt	FeIId	total dissolved reducing iron concentration	gFe.m$^{-3}_{\ell}$
Cfe2d	–	equilibrium dissolved free iron(II) concentration	mol.l^{-l}
ffe2$_1$	FrFe2dis	fraction dissolved free iron(II)	$^-$
Csdt	SUD	total dissolved sulfide concentration	gS.m$^{-3}_{\ell}$
Csd$_3$	–	dissolved free sulfide concentration	mol.l^{-l}
fs$_1$	FrH2Sdis	fraction dissolved hydrogen sulfide	-
fs$_3$	FrS2dis	fraction dissolved free sulfide	-
Cfeco3	FeCO3	iron(II) carbonate concentration	gFe.m$^{-3}_{\ell}$
Ctic	TIC or CO2	total dissolved inorganic carbon concentration	gC.m$^{-3}_{\ell}$
Cco3d	–	total dissolved sulfide concentration	gCO$_2$.m$^{-3}_{\ell}$
fc$_3$	FrCO3dis	fraction dissolved free carbonate	mol.l^{-l}
IAP$_2$	–	ion activity product for FeS	[mol.l^{-12}]
lKsp$_2$	lKspFeS	log solubility product for FeS [mol.l^{-12}]	log(-)
IAP$_3$	–	ion activity product for FeCO$_3$	[mol.l^{-12}]
Ksp$_3$	lKspFeCO3	log solubility product for FeCO$_3$ [mol.l^{-12}]	log(-)
kpyr$_{20}$	RcPyrite20	specific pyrite formation rate at 20 °C	gS^{-1}.m^3.d^{-1}
kdfes$_{20}$	RcDisFeS20	specific iron(II) sulfide dissolution rate at 20 °C	d^{-1}
kpfes$_{20}$	RcPrcFeS20	specific iron(II) sulfide precipitation rate at 20 °C	gFe.m$^{-3}_{\ell}$.d^{-1}
kdfeco3$_{20}$	RcDisFeC20	specific iron(II) carbonate dissolution rate at 20 °C	d^{-1}
kpfeco3$_{20}$	RcPrcFeC20	specific iron(II) carbonate precipitation rate at 20 °C	gFe.m$^{-3}_{\ell}$.d^{-1}
ktpyr	TcPyrite	temperature coefficient for pyrite formation	-
ktdfes	TcDisFeS	temperature coefficient for iron(II) sulfide diss.	-
ktpfes	TcPrcFeS	temperature coefficient for iron(II) sulfide prec.	-
ktdfeco3	TcDisFeCO3	temperature coefficient for iron(II) carbonate diss.	-
ktpfeco3	TcPrcFeCO3	temperature coefficient for iron(II) carbonate prec.	-

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Table 9.19: *Definitions of the parameters in the above equations for PRIRON concerning reducing iron. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	**Name in Input**	**Definition**	**Units**
Rpyr	–	rate of pyrite formation	gFe.m$^{-3}_{\mathscr{b}}$.d^{-1}
Rdfes	–	rate of iron(II) sulfide dissolution	gFe.m$^{-3}_{\mathscr{b}}$.d^{-1}
Rpfes	–	rate of iron(II) sulfide precipitation	gFe.m$^{-3}_{\mathscr{b}}$.d^{-1}
Rdfeco3	–	rate of iron(II) carbonate dissolution	gFe.m$^{-3}_{\mathscr{b}}$.d^{-1}
Rpfeco3	–	rate of iron(II) carbonate precipitation	gFe.m$^{-3}_{\mathscr{b}}$.d^{-1}
SWTICCO2	SWTICCO2	option parameter (0.0 = use *TIC;* 1.0 = use *CO2*)	-
T	Temp	temperature	$^{\circ}$C
Δt	Delt	timestep	d
ϕ	POROS	porosity	m$^{3}_{\mathscr{w}}$.m$^{-3}_{\mathscr{b}}$

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9.12 Reduction of iron by sulfides

PROCESS: IRONRED

Particulate oxidizing iron in the model consists of iron(III) oxyhydroxide, chemically indicated with $Fe(OH)_3$ or FeOOH. Particulate oxidizing iron can be reduced abiotically by dissolved sulfides and particulate iron sulfides (Luff and Moll, 2004; Wang and Cappellen, 1996; Boudreau, 1996). The latter reaction is very slow compared to the former reaction. Both reactions produce reducing iron Fe^{2+} and sulfate. See process CONSELAC for the biotic reduction of iron.

For particulate oxidizing iron two fractions are distinguished in the model, an amorphous fraction and a crystalline fraction (goethite). The amorphous reactive fraction is indicated as substance FeIIIpa. The less reactive crystalline fraction is indicated as substance FeIIIpc. The latter fraction reacts much more slowly due to the additional activation energy needed to detach ions from its crystal lattice.

Implementation

Process IRONRED has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. It covers all simulated abiotic particulate oxidizing iron reduction processes and has been implemented for the following substances:

- ◇ FeIIIpa, FeIIIpc, FeS, FeIId, SUD and SO4

The reducing iron produced is added to FeIId, the sulfate produced is added to SO4. Table I provides the definitions of the parameters occurring in the formulations.

Formulation

The following reduction reactions are included in the model:

$$H_2S + 8\ Fe(OH)_3 \Rightarrow 8\ Fe^{2+} + SO_4^{2-} + 6\ H_2O + 14\ OH^-$$

$$FeS + 8\ Fe(OH)_3 \Rightarrow 9\ Fe^{2+} + SO_4^{2-} + 4\ H_2O + 16\ OH^-$$

The reduction of iron oxyhydroxide requires 0.0714 gS.gFe^{-1} in the cases of H_2S and FeS, and 0.125 gFe.gFe^{-1} in the case of FeS.

The reduction reactions are formulated according to double first-order kinetics:

$$\begin{aligned} Rire_1 &= kire_1 \times Cfea \times \left(\frac{fs_1 \times Csdt}{\phi}\right) \times \phi \\ Rire_2 &= kire_2 \times Cfec \times \left(\frac{fs_1 \times Csdt}{\phi}\right) \times \phi \\ Rire_3 &= kire_3 \times Cfes \times Cfea \\ Rire_4 &= kire_4 \times Cfes \times Cfec \end{aligned}$$

where:

$Cfes$	particulate iron sulfide concentration [gFe.m$^{-3}_{\ell}$]
$Cfea$	particulate amorphous oxidizing iron concentration [gFe.m$^{-3}_{\ell}$]

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$Cfec$	particulate crystalline oxidizing iron concentration [gFe.m$^{-3}_{\ell}$]
$Csdt$	total dissolved sulfide [gS.m$^{-3}_{\ell}$]
fs_1	fraction hydrogen sulfide [-]
$kire_1$	specific rate of amorphous iron reduction with H_2S [1/(gS.m^{-3}.d)]
$kire_2$	specific rate of crystalline iron reduction with H_2S [1/(gS.m^{-3}.d)]
$kire_3$	specific rate of amorphous iron reduction with FeS [1/(gFe.m^{-3}.d)]
$kire_4$	specific rate of crystalline iron reduction with FeS [1/(gFe.m^{-3}.d)]
$Rire_1$	rate of amorphous iron reduction with H_2S [gFe.m^{-3}.d^{-1}]
$Rire_2$	rate of crystalline iron reduction with H_2S [gFe.m^{-3}.d^{-1}]
$Rire_3$	rate of amorphous iron reduction with FeS [gFe.m^{-3}.d]
$Rire_4$	rate of crystalline iron reduction with FeS [gFe.m^{-3}.d]
ϕ	porosity [-]

Notice that the porosity occurs two times in some of the rate equations, whereas it does not affect the rates. However, a systematic formulation is preferred in order to make clear how the porosity affects kinetics.

The specific reduction rates are temperature dependent according to:

$$kire_i = kire_{i,20} \times ktire^{(T-20)}$$

where:

$kire_{i,20}$	specific rate of abiotic particulate iron reduction i at 20 °C [1/(gS.m^{-3}.d)]
$ktire$	temperature coefficient for abiotic particulate iron reduction [-]
T	temperature [°C]

The reduction process must stop at the depletion of particulate oxidizing iron or hydrogen sulfide or particulate iron sulfide. Therefore, each of the reduction fluxes is made equal to half the concentration of amorphous oxidizing iron or crystalline oxidizing iron or hydrogen sulfide or iron sulfide divided with timestep Δt, when a flux as calculated with the above formulations is larger.

Directives for use

- ◇ The specific rates for the reduction of amorphous oxidizing iron should have much higher value than the specific rates for the oxidation of crystalline oxidizing iron.
- ◇ The specific rates of reduction with H_2S should be higher than the specific rates of reduction with FeS.

References

Boudreau (1996),
DiToro (2001),
Luff and Moll (2004),
Soetaert et al. (1996),
Wang and Cappellen (1996)

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Table 9.20: *Definitions of the parameters in the above equations for IRONRED. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in Input	Definition	Units
Cfes	FeS	particulate iron sulfide concentration	$gFe.m^{-3}_{\mathscr{b}}$
Cfea	FeIIIpa	particulate amorphous oxidizing iron concentration	$gFe.m^{-3}_{\mathscr{b}}$
Cfec	FeIIIpc	particulate crystalline oxidizing iron concentration	$gFe.m^{-3}_{\mathscr{b}}$
Csdt	SUD	total dissolved sulfide concentration	$gS.m^{-3}_{\mathscr{b}}$
fs_1	FrH2Sdis	fraction dissolved hydrogen sulfide (H_2S)	-
$kire_{1,20}$	RcFeaH2S20	spec. rate of amorphous iron red. with H_2S at 20 °C	$gS^{-1}.m^3_{\mathscr{w}}.d^{-1}$
$kire_{2,20}$	RcFecH2S20	spec. rate of crystalline iron red. with H_2S at 20 °C	$gS^{-1}.m^3_{\mathscr{w}}.d^{-1}$
$kire_{3,20}$	RcFeaFeS20	spec. rate of amorphous iron red. with FeS at 20 °C	$gFe^{-1}.m^3_{\mathscr{w}}.d^{-1}$
$kire_{4,20}$	RcFecFeS20	spec. rate of crystalline iron red. with FeS at 20 °C	$gFe^{-1}.m^3_{\mathscr{w}}.d^{-1}$
ktire	TcFeRed	temperature coeff. for abiotic iron reduction at 20 °C	-
$Rire_1$	-	rate of amorphous iron reduction with H_2S	$gFe.m^{-3}_{\mathscr{b}}.d^{-1}$
$Rire_2$	-	rate of crystalline iron reduction with H_2S	$gFe.m^{-3}_{\mathscr{b}}.d^{-1}$
$Rire_3$	-	rate of amorphous iron reduction with FeS	$gFe.m^{-3}_{\mathscr{b}}.d^{-1}$
$Rire_4$	-	rate of crystalline iron reduction with FeS	$gFe.m^{-3}_{\mathscr{b}}.d^{-1}$
T	Temp	temperature	°C
Δt	Delt	timestep	d
ϕ	POROS	porosity	$m^3_{\mathscr{w}}.m^{-3}_{\mathscr{b}}$

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9.13 Oxidation of iron sulfides

PROCESS: SULPHOX

Particulate components FeS and FeS_2 are oxidized chemically as well as by microbs using dissolved oxygen (Luff and Moll (2004), Wang and Cappellen (1996), Wijsman et al. (2001), Boudreau (1996)). The oxidation of iron sulfides proceeds in two steps. First the sulfide part is oxidized into sulfate. Secondly, the iron released as Fe^{2+} is oxidized. The latter process is taken care of in process IRONOX.

The particulate component $FeCO_3$ is assumed not to be oxidized directly. The iron in this component is oxidized after dissolution.

The oxidation of dissolved sulfide is taken care of in process OXIDSUD.

Implementation

Process SULPHOX has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. It covers all simulated iron sulfide oxidation processes and has been implemented for the following substances:

- ◇ place FeS, FeS2, FeIId, OXY and SO4

The iron from FeS and FeS2 is added to the dissolved reducing iron FeIId. The oxygen consumed is removed from the model as water, which is not simulated. The sulfide oxidized is added to sulfate. Table I provides the definitions of the parameters occurring in the formulations.

Formulation

The following oxidation reactions are included in the model:

$$FeS + 2\ O_2 \Rightarrow Fe^{2+} + {SO_4}^{2-}$$

$$2\ FeS_2 + 7\ O_2 + 4\ OH^- \Rightarrow 2\ Fe^{2+} + 4\ {SO_4}^{2-} + 2\ H_2O$$

The oxidation of iron sulfide requires 1.143 $gO_2.gFe^{-1}$ or 2.0 $gO_2.gS^{-1}$. The oxidation of pyrite requires 2.0 $gO_2.gFe^{-1}$ or 1.75 $gO_2.gS^{-1}$.

The oxidation reactions are formulated according to double first-order kinetics:

$$Rsox_1 = ksox_1 \times Cfes \times \left(\frac{Cox}{\phi}\right) \times \phi$$

$$Rsox_2 = ksox_2 \times Cfes2 \times \left(\frac{Cox}{\phi}\right) \times \phi$$

where:

$Cfes$	iron sulfide concentration [$gFe.m_{\ell}^{-3}$]
$Cfes2$	pyrite concentration [$gFe.m_{\ell}^{-3}$]
Cox	dissolved oxygen concentration [$gO_2.m_{\ell}^{-3}$]
$ksox_1$	specific rate of iron sulfide oxidation [$1/(gO_2.m^{-3}.d)$]

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$ksox_1$	specific rate of pyrite oxidation [1/(gO_2.m^{-3}.d)]
$Rsox_2$	rate of iron sulfide oxidation [gFe.m^{-3}.d^{-1}]
$Rsox_2$	rate of pyrite oxidation [gFe.m^{-3}.d^{-1}]
ϕ	porosity [-]

Notice that the porosity occurs two times in the rate equation, whereas it does not affect the rate. However, a systematic formulation is preferred in order to make clear how the porosity affects kinetics.

The specific oxidation rates are temperature dependent according to:

$$ksox_i = ksox_{i,20} \times ktsox^{(T-20)}$$
$$ksox_i = 0.0 \qquad \text{if } Cox \leq 0.0$$

where:

$ksox_{i,20}$	specific rate of iron sulfide or pyrite oxidation at 20 °C [1/(gO_2.m^{-3}.d)]
$ktsox$	temperature coefficient for iron sulfide oxidation [-]
T	temperature [°C]

The oxidation process must stop at the depletion of iron sulfide. Therefore, each of the oxidation fluxes is made equal to half the concentration of the iron sulfide concerned divided with timestep Δt, when this flux as calculated with the above formulations is larger than *CfeS* /Δt or *CfeS2* /Δt.

Directives for use

◇ The specific rate for the oxidation of pyrite should have a much lower value than the specific rate for the oxidation of iron sulfide.

References

Boudreau (1996)
DiToro (2001)
Luff and Moll (2004)
Santschi et al. (1990)
Soetaert et al. (1996)
Wang and Cappellen (1996)
WL | Delft Hydraulics (2002)
Wijsman et al. (2001)

Table 9.21: *Definitions of the parameters in the above equations for SULPHOX. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$)*

Name in formulas	Name in Input	Definition	Units
Cfes	FeS	particulate iron sulfide concentration	gFe.$m^{-3}_{\mathscr{b}}$
Cfes2	FeS2	pyrite concentration	gFe.$m^{-3}_{\mathscr{b}}$
Cox	OXY	dissolved oxygen concentration	gO_2.$m^{-3}_{\mathscr{b}}$
$ksox_{1,20}$	RcFeSox20	specific rate of iron sulfide oxidation at 20 °C	$gO_2{}^{-1}$.$m^3_{\mathscr{w}}$.d^{-1}

Table 9.21: *Definitions of the parameters in the above equations for SULPHOX. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$)*

Name in formulas	**Name in Input**	**Definition**	**Units**
$ksox_{2,20}$	RcFeS2ox20	specific rate of pyrite oxidation at 20 °C	$gO_2{}^{-1}.m^3_{\mathscr{w}}.d^{-1}$
ktsox	TcFeSox	temperature coefficient for iron sulfide oxidation	-
$Rioo_1$	–	rate of iron sulfide oxidation	$gFe.m^{-3}_{\mathscr{b}}.d^{-1}$
$Rioo_2$	–	rate of pyrite oxidation	$gFe.m^{-3}_{\mathscr{b}}.d^{-1}$
T	Temp	temperature	°C
Δt	Delt	timestep	d
ϕ	POROS	porosity	$m^3_{\mathscr{w}}.m^{-3}_{\mathscr{b}}$

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9.14 Oxidation of dissolved iron

PROCESS: IRONOX

The oxidation of reducing iron components can be abiotic as well as biotic. The dissolved species Fe^{2+}, $Fe(OH)^{+}$ and $Fe(OH)_2$ are primarily oxidized by dissolved oxygen and nitrate in abiotic chemical processes. Although all three oxidation processes can be described with the same kinetics, the oxidation rate constants are different (Luff and Moll, 2004; Wang and Cappellen, 1996; Wijsman et al., 2001; Boudreau, 1996).

Particulate components FeS and FeS_2 are oxidized chemically as well as by microbs using dissolved oxygen. The oxidation of iron sulfides proceeds in two steps. First the sulfide part is oxidized into sulfate, which is a separate process and is described for process SULPHOX. Secondly, the iron released as Fe^{2+} is oxidized. The particulate component $FeCO_3$is assumed not to be oxidized directly. The iron in this component is only oxidized after dissolution.

Implementation

Process IRONOX has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. It covers all simulated iron oxidation processes and has been implemented for the following substances:

- ◇ FeIId, FeIIId, OXY and NO3

The dissolved reducing iron FeIId oxidized is added to the dissolved oxidizing iron FeIIId. The dissolved iron fractions can be provided by auxiliary process SPECIRON or imposed on the model as input parameters. The oxygen and nitrate consumed are removed from the model as water and elementary nitrogen, which are not simulated. Table I provides the definitions of the parameters occurring in the formulations.

Formulation

The following oxidation reactions are included in the model:

$$4\ Fe^{2+} + O_2 + 4\ H^{+} \Rightarrow 4\ Fe^{3+} + 2\ H_2O$$

$$4\ Fe(OH)^{+} + O_2 + 4\ H^{+} \Rightarrow 4\ Fe^{3+} + 2\ H_2O + OH^{-}$$

$$4\ Fe(OH)_2 + O_2 + 4\ H^{+} \Rightarrow 4\ Fe^{3+} + 2\ H_2O + 2\ OH^{-}$$

$$10\ Fe^{2+} + 2\ NO_3^{-} + 12\ H^{+} \Rightarrow 10\ Fe^{3+} + N_2 + 6\ H_2O$$

$$10\ Fe(OH)^{+} + 2\ NO_3^{-} + 12\ H^{+} \Rightarrow 10\ Fe^{3+} + N_2 + 6\ H_2O + 10\ OH^{-}$$

$$10\ Fe(OH)_2 + 2\ NO_3^{-} + 12\ H^{+} \Rightarrow 10\ Fe^{3+} + N_2 + 6\ H_2O + 20\ OH^{-}$$

The processes require 0.143 $gO_2.gFe^{-1}$ or 0.05 $gN.gFe^{-1}$.

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The oxidation reactions are formulated according to double first-order kinetics:

$$Rioo = (kioo_1 \times ffe_1 + kioo_2 \times ffe_2 + kioo_3 \times ffe_3) \times \left(\frac{CfeIId}{\phi}\right) \times \left(\frac{Cox}{\phi}\right) \times \phi$$

$$Rion = (kion_1 \times ffe_1 + kion_2 \times ffe_2 + kion_3 \times ffe_3) \times \left(\frac{CfeIId}{\phi}\right) \times \left(\frac{Cni}{\phi}\right) \times \phi$$

where:

$CfeIId$	total dissolved reducing iron concentration [gFe.m$^{-3}_{\ell}$]
Cox	dissolved oxygen concentration [gO_2.m$^{-3}_{\ell}$]
Cni	nitrate concentration [gN.m$^{-3}_{\ell}$]
ffe_i	fraction Fe^{2+} (i=1), $Fe(OH)^{+}$ (i=2) or $Fe(OH)_2$ (i=3) in FeIId [-]
$kioo_i$	specific rate of iron i oxidation with dissolved oxygen [1/(gO_2.m^{-3}.d)]
$kion_i$	specific rate of iron i oxidation with nitrate [1/(gN.m^{-3}.d)]
$Rioo$	total rate of iron oxidation with oxygen [gFe.m^{-3}.d^{-1}]
$Rion$	total rate of iron oxidation with nitrate [gFe.m^{-3}.d^{-1}]
ϕ	porosity [-]

Notice that the porosity occurs three times in the rate equation, whereas only once would suffice. However, a systematic formulation is preferred in order to make clear how the porosity affects kinetics.

The specific oxidation rates are temperature dependent according to:

$$kioo_i = kioo_{i,20} \times ktiox^{(T-20)}$$
$$kioo_i = 0.0 \qquad \textit{if Cox} \leq \textit{0.0}$$
$$kion_i = kion_{i,20} \times ktiox^{(T-20)}$$
$$kion_i = 0.0 \qquad \textit{if Cox} \leq \textit{0.0}$$

where:

$kioo_{i,20}$	specific rate of iron i oxidation with oxygen at 20 °C [1/(gO_2.m^{-3}.d)]
$kion_{i,20}$	specific rate of iron i oxidation with nitrate at 20 °C [1/(gO_2.m^{-3}.d)]
$ktiox$	temperature coefficient for iron oxidation [-]
T	temperature [°C]

The oxidation process must stop at the depletion of dissolved iron. Therefore, the total oxidation flux (*Rioo+Rion*) is made equal to half the concentration of dissolved iron divided with timestep Δt, when the flux as calculated with the above formulations is larger than *FeIId*/Δt.

Directives for use

- ◇ The specific rates for the oxidation of iron species with oxygen can be given the same average value.
- ◇ The specific rates for the oxidation of iron species with nitrate can be given the same average value.

References

Boudreau (1996),
DiToro (2001),
Santschi et al. (1990),

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Soetaert et al. (1996),
Wang and Cappellen (1996),
WL | Delft Hydraulics (2002),
Wijsman et al. (2001)

Table 9.22: *Definitions of the parameters in the above equations for IRONOX. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	**Name in Input**	**Definition**	**Units**
CfeIId	FeIId	dissolved reducing iron concentration	$gFe.m_{\mathscr{b}}^{-3}$
Cox	OXY	dissolved oxygen concentration	$gO_2.m_{\mathscr{b}}^{-3}$
Cni	NO3	nitrate concentration	$gN.m_{\mathscr{b}}^{-3}$
ffe_1	FrFe2dis	fraction of Fe2+ in FeIId	-
ffe_2	FrFe2OHd	fraction of $FeOH^+$ in FeIId	-
ffe_3	FrFe2OH2d	fraction of $Fe(OH)_2$ in FeIId	-
$kioo_{120}$	RcI1oxox20	specific rate of Fe^{2+} oxidation with oxygen at 20 °C	$gO_2{}^{-1}.m_{\mathscr{w}}^3.d^{-1}$
$kioo_{220}$	RcI2oxox20	specific rate of $FeOH^+$ oxid. with oxygen at 20 °C	$gO_2{}^{-1}.m_{\mathscr{w}}^3.d^{-1}$
$kioo_{320}$	RcI3oxox20	specific rate of $Fe(OH)_2$ oxid. with oxygen at 20 °C	$gO_2{}^{-1}.m_{\mathscr{w}}^3.d^{-1}$
$kion_{120}$	RcI1oxni20	specific rate of Fe^{2+} oxidation with nitrate at 20 °C	$gN^{-1}.m_{\mathscr{w}}^3.d^{-1}$
$kion_{220}$	RcI2oxni20	specific rate of $FeOH^+$ oxidation with nitrate at 20 °C	$gN^{-1}.m_{\mathscr{w}}^3.d^{-1}$
$kion_{320}$	RcI3oxni20	specific rate of $Fe(OH)_2$ oxid. with nitrate at 20 °C	$gN^{-1}.m_{\mathscr{w}}^3.d^{-1}$
ktiox	TcIox	temperature coefficient for iron oxidation	
Rioo	-	rate of iron oxidation with dissolved oxygen	$gFe.m_{\mathscr{b}}^{-3}.d^{-1}$
Rion	-	rate of iron oxidation with nitrate	$gFe.m_{\mathscr{b}}^{-3}.d^{-1}$
T	Temp	temperature	°C
Δt	Delt	timestep	d
ϕ	POROS	porosity	$m_{\mathscr{w}}^3.m_{\mathscr{b}}^{-3}$

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9.15 Speciation of dissolved iron

PROCESS: SPECIRON

Iron ions in solution associate with numerous anions, but under oxidizing conditions the dominant ligand is the hydroxyl ion. Under reducing conditions the sulfide ion may play a role too. Dissolved organic matter may be important as a ligand when high concentrations of humic and fulvic acids are present. In the model we only consider the hydrolysis of dissolved iron as a useful approximation of the free dissolved iron concentration.

The computed iron speciation is used in processes PRIRON and IRONOX to calculate precipitation/dissolution rates of iron minerals and oxidation rates of dissolved iron(II).

Implementation

Process SPECIRON is fully generic, meaning that it can be applied both to water layers and sediment layers. However, this process cannot be used for speciation in the sediment, when substances are modeled as a number of 'inactive' substances according to the S1/2 approach. The pH needed as input can be either imposed or simulated with process pH_SIMP.

The processes have been implemented for the following substances:

- ◇ FeIIId and FeIId.

The process calculates equilibrium speciation, not the associated mass fluxes. Table I provides the definitions of the parameters occurring in the formulations. Table II provides the output parameters.

Formulation

Iron(III)

The hydrolysis of dissolved oxidizing iron proceeds according to the following reaction equations:

$Fe^{3+} + 2\,H_2O \Leftrightarrow FeOH^{2+} + H_3O^+$

$Fe^{3+} + 4\,H_2O \Leftrightarrow Fe(OH)_2{}^+ + 2\,H_3O^+$

The chemical equilibria are described with:

$$Kfe3_1 = \frac{Cfe3d_2 \times H^+}{Cfe3d_1}$$
$$Kfe3_2 = \frac{Cfe3d_3 \times (H^+)^2}{Cfe3d_1}$$
$$Cfe3dt = (Cfe3d_1 + Cfe3d_2 + Cfe3d_3) \times 56\,000 \times \phi$$

where

$Cfe3d_1$	concentration of free dissolved Fe^{3+} [mol.l^{-1}]
$Cfe3d_2$	concentration of dissolved $FeOH^{2+}$ [mol.l^{-1}]
$Cfe3d_3$	concentration of dissolved $Fe(OH)_2{}^+$ [mol.l^{-1}]
$Cfe3dt$	concentration of total dissolved oxidizing iron [gFe.m^{-3}_{ℓ}]

H^+	proton concentration [mol.l^{-1}]
$Kfe3_1$	stability (equilibrium, hydrolysis) constant for $FeOH^{2+}$ [mol.l^{-1}]
$Kfe3_2$	stability (equilibrium, hydrolysis) constant for $Fe(OH)_2{}^+$ [mol.l^{-1}]
ϕ	porosity

The constant 56 000 concerns the conversion from gFe.m^{-3} to mol.l^{-1}.

The proton concentration H^+ and the temperature dependent stability constants follow from:

$$H^+ = 10^{-pH}$$
$$Kfe3_1 = 10^{lKfe3_1} \times ktfe3_1^{(T-20)}$$
$$Kfe3_2 = 10^{lKfe3_2} \times ktfe3_2^{(T-20)}$$

where

$ktfe3_1$	temperature coefficient for $FeOH^{2+}$ equilibrium [-]
$ktfe3_2$	temperature coefficient for $Fe(OH)_2{}^+$ equilibrium [-]
pH	acidity [-]
T	temperature [°C]

The concentration of the relevant iron(III) species in solution can now be calculated from:

$$Cfe3d_1 = \frac{Cfe3dt}{(1 + Kfe3_1/H^+ + Kfe3_2/(H^+)^2)} \times \frac{1}{56\,000 \times \phi}$$
$$Cfe3d_2 = \frac{Kfe3_1 \times Cfe3d_1}{H^+}$$
$$Cfe3d_3 = \frac{Cfe3dt}{56\,000 \times \phi} - Cfe3d_1 - Cfe3d_2$$

if due to rounding off the resulting $Cfe3d_3 < 0.0$

$$Cfe3d_3 = \frac{Kfe3_2 \times Cfe3d_1}{(H^+)^2}$$

The pertinent fractions follow from:

$$ffe3_1 = \frac{Cfe3d_1}{Cfe3dt} \times 56\,000 \times \phi$$
$$ffe3_2 = \frac{Cfe3d_2}{Cfe3dt} \times 56\,000 \times \phi$$
$$ffe3_3 = 1 - ffe3_1 - ffe3_2$$

if due to rounding off the resulting $ffe_3 < 0.0$

$$ffe3_3 = \frac{Cfe3d_3}{Cfe3dt} \times 56\,000 \times \phi$$

Iron(II)

The hydrolysis of dissolved reducing iron proceeds according to the following reaction equations:

$Fe^{2+} + 2\ H_2O \Leftrightarrow FeOH^+ + H_3O^+$

Fe^{2+} + 4 $H_2O \Leftrightarrow Fe(OH)_2$ + 2 H_3O^+

The chemical equilibria are described with:

$$Kfe2_1 = \frac{Cfe2d_2 \times H^+}{Cfe2d_1}$$
$$Kfe2_2 = \frac{Cfe2d_3 \times (H^+)^2}{Cfe2d_1}$$
$$Cfe2dt = (Cfe2d_1 + Cfe2d_2 + Cfe2d_3) \times 56\,000 \times \phi$$

where

$Cfe2d_1$	concentration of free dissolved Fe^{2+} [mol.l^{-1}]
$Cfe2d_2$	concentration of dissolved $FeOH^+$ [mol.l^{-1}]
$Cfe2d_3$	concentration of dissolved $Fe(OH)_2$ [mol.l^{-1}]
$Cfe2dt$	concentration of total dissolved reducing iron [gFe.m$^{-3}_{\ell}$]
H^+	proton concentration [mol.l^{-1}]
$Kfe2_1$	stability (equilibrium, hydrolysis) constant for $FeOH^+$ [mol.l^{-1}]
$Kfe2_2$	stability (equilibrium, hydrolysis) constant for $Fe(OH)_2{}^+$ [mol.l^{-1}]
ϕ	porosity

The constant 56 000 concerns the conversion from gFe.m^{-3} to mol.l^{-1}.

The proton concentration H^+ and the temperature dependent stability constants follow from:

$$H^+ = 10^{-pH}$$
$$Kfe2_1 = 10^{lKfe2_1} \times ktfe2_1^{(T-20)}$$
$$Kfe2_2 = 10^{lKfe2_2} \times ktfe2_2^{(T-20)}$$

where

$ktfe2_1$	temperature coefficient for $FeOH^+$ equilibrium [-]
$ktfe2_2$	temperature coefficient for $Fe(OH)_2$ equilibrium [-]
pH	acidity [-]
T	temperature [°C]

The concentration of the relevant iron(II) species in solution can now be calculated from:

$$Cfe2d_1 = \frac{Cfe2dt}{(1 + Kfe2_1/H^+ + Kfe2_2/(H^+)^2)} \times \frac{1}{56\,000 \times \phi}$$
$$Cfe2d_2 = \frac{Kfe2_1 \times Cfe2d_1}{H^+}$$
$$Cfe3d_2 = \frac{Cfe2dt}{56\,000 \times \phi} - Cfe2d_1 - Cfe2d_2$$

if due to rounding off the resulting $Cfe2d_3$ = 0.0

$$Cfe2d_3 = \frac{Kfe2_2 \times Cfe2d_1}{(H^+)^2}$$

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The pertinent fractions follow from:

$$ffe2_1 = \frac{Cfe2d_1}{Cfe2dt} \times 56\,000 \times \phi$$
$$ffe2_2 = \frac{Cfe2d_2}{Cfe2dt} \times 56\,000 \times \phi$$
$$ffe2_3 = 1 - ffe2_1 - ffe2_2$$

if due to rounding off the resulting *ffe*$_2$ = 0.0

$$ffe2_3 = \frac{Cfe2d_3}{Cfe2dt} \times 56\,000 \times \phi$$

Directives for use

- ◇ The stability constants have to be provided in the input of the model as logarithmic values ($^{10}\log$)!
- ◇ The logarithms of the stability constants at 20 °C are:
  lKstFe3OH = -3.05 and *lKstFe3OH2* = -6.31.
  lKstFe2OH = -9.50 and *lKstFe2OH2* = -17.0 (?).
- ◇ The temperature dependencies are ignored by default temperature coefficients of the stability constants equal to 1.0. Temperature dependency can be established by modification of the values of *TcKFe2OH* and *TcKFe2OH2*.
- ◇ The total dissolved oxidizing iron(III) and dissolved reducing iron(II) concentrations are dependent on pH. An indicative value of iron(III) for pH = 7 is 5.6 10^{-4} mg/l or 10^{-8} mol.l^{-1}. For pH 8 the concentration is five times lower. An indicative value of iron(II) under reducing conditions is 56 mg/l or 10^{-3} mole.l^{-1}.
- ◇ Different pH's and total dissolved iron concentrations apply to the water column and the various sediment layers.

References

Stumm and Morgan (1996)

Table 9.23: *Definitions of the input parameters in the above equations for SPECIRON.*

Name in formulas	Name in Input	Definition	Units
Cfe3dt	FeIIId	concentration of total dissolved oxidizing iron(III)	gFe.m$^{-3}_{\ell}$
Cfe2dt	FeIId	concentration of total dissolved reducing iron(II)	gFe.m$^{-3}_{\ell}$
lKfe3$_1$	lKstFe3OH	log stability constant for $Fe3OH^{2+}$ (l.mol^{-1})	log(-)
lKfe3$_2$	lKstFe3OH2	log stability constant for $Fe3OH_2{}^{+}$ (l.mol^{-1})	log(-)
ktfe3$_1$	TcKFe3OH	temperature coefficient for KstFe3OH	-
ktfe3$_2$	TcKFe3OH2	temperature coefficient for KstFe3OH2	-

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Table 9.23: *Definitions of the input parameters in the above equations for SPECIRON.*

Name in formulas	**Name in Input**	**Definition**	**Units**
$lKfe2_1$	lKstFe2OH	log stability constant for $Fe2OH^+$ ($l.mol^{-1}$)	log(-)
$lKfe2_2$	lKstFe2OH2	log stability constant for $Fe2OH_2$ ($l.mol^{-1}$)	log(-)
$ktfe2_1$	TcKFe2OH	temperature coefficient for KstFe2OH	-
$ktfe2_2$	TcKFe2OH2	temperature coefficient for KstFe2OH2	-
H^+	–	proton concentration	$mol.l^{-1}$
pH	pH	acidity	-
T	Temp	temperature	°C
ϕ	POROS	porosity	$m^3_w.m^{-3}_\ell$

Table 9.24: *Definitions of the output parameters of SPECIRON.*

Name in formulas	Name in output	Definition	Units
$Cfe3d_1$	DisFe3	concentration of free dissolved iron(III)	$mol.l^{-1}$
$Cfe3d_2$	DisFe3OH	concentration of dissolved $FeOH^{2+}$	$mol.l^{-1}$
$Cfe3d_3$	DisFe3OH2	concentration of dissolved $Fe(OH)_2{}^+$	$mol.l^{-1}$
$ffe3_1$	FrFe3dis	fraction of free dissolved iron(III)	-
$ffe3_2$	FrFe3OHd	fraction of dissolved $FeOH^{2+}$	-
$ffe3_3$	FrFe3OH2d	fraction of dissolved $Fe(OH)_2{}^+$	-
$Cfe2d_1$	DisFe2	concentration of free dissolved iron(II)	$mol.l^{-1}$
$Cfe2d_2$	DisFe2OH	concentration of dissolved $FeOH^+$	$mol.l^{-1}$
$Cfe2d_3$	DisFe2OH2	concentration of dissolved $Fe(OH)_2$	$mol.l^{-1}$
$ffe2_1$	FrFe2dis	fraction of free dissolved iron(II)	-
$ffe2_2$	FrFe2OHd	fraction of dissolved $FeOH^+$	-
$ffe2_3$	FrFe2OH2d	fraction of dissolved $Fe(OH)_2$	-

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9.16 Conversion salinity and chloride process

PROCESSES: SALINCHLOR

Salinity is defined as the total solids content of water that results after all carbonates have been converted to oxides, all bromide and iodide has been replaced by chloride, and all organic matter has been removed by oxidation. It is usually reported as practical salinity units (psu) which is equivalent to grams per kilogram and parts per thousand (ppt, ‰). Associated terms are chlorinity and chlorosity. Chlorinity includes chloride, bromide and iodide, and is reported as grams Cl per kilogram. Chlorosity is chlorinity multiplied by the water density at 20°C, and is assumed to be equal to the chloride concentration ($gCl.L^{-1}$). This concentration can be calculated from salinity and vice versa as described below.

The empirical relation between salinity and the chloride concentration (chlorosity) used is:

$$S = 0.03 + \frac{1.805 \times Cl}{\rho_w}$$

The chloride concentration is expressed as $gCl.m^{-3}$ when density is expressed as $kg.m^{-3}$.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Auxiliary process SALINCHLOR has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. The process does not deliver mass fluxes.

The process has been implemented for the following substances:

- ◇ Salinity and Cl.

If Salinity is simulated the process will generate Cl from it. If Cl is simulated the process will generate Salinity from it. Table 9.25 provides the definitions of the parameters occurring in the formulations.

Formulation

The conversion of chloride into salinity follows from (*SWSalCl* = 0.0):

$$\rho_w = 1000 + \frac{0.7 \times Cl}{1000} \times r_{scl} - 0.0061 \times (T - 4.0)^2$$
$$S = S_0 + \frac{r_{scl} \times Cl}{\rho_w}$$

The conversion of salinity into chloride follows from (*SWSalCl* = 1.0):

$$\rho_w = 1000 + \frac{700 \times S}{(1000 - S)} \times r_{scl} - 0.0061 \times (T - 4.0)^2$$
$$Cl = \frac{(S - S_0) \times \rho_w}{r_{scl}}$$

where:

Cl	chloride concentration ($g.m^{-3}$ $\mathscr{b}$)
r_{scl}	ratio of salinity and chloride in water ($g.g^{-1}$)
S	salinity ($g.kg^{-1}$; psu; ppt; ‰)
S_0	minimal salinity at zero Cl ($g.kg^{-1}$; psu; ppt; ‰)
T	temperature (°C)
ρ_w	density of water with dissolved salts ($kg.m^{-3}$ $\mathscr{b}$)

Directives for use

1 The relations described here are best applicable for marine and brackish water. They may be very inaccurate when applied to fresh water.
2 Option *SWSalCl* set to be set at 0.0 when *Salinity* is simulated, *SWSalCl* needs to be set at 1.0 when *Cl* is simulated (default value = 0.0).

References

Greenberg et al. (1980)

Table 9.25: *Definitions of the parameters in the above equations for SALINCHLOR. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
Cl	*Cl*	chloride concentration	g.m^{-3} $\mathscr{b}$
S	*Salinity*	salinity	g.kg^{-1}
S_0	–	salinity at zero Cl	g.kg^{-1}
r_{scl}	*GtCl*	ratio of salinity and chloride in water	g.g^{-1}
$SWSalCl$	*SWSalCl*	option parameter for simulated substance	–
T	*Temp*	temperature	°C
ρ_w	–	density of water with dissolved salt	kg.m^{-3} $\mathscr{b}$

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10 Organic micropollutants

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10.1 Partitioning of organic micropollutants

PROCESS: PARTWK_i AND PARTS1/2_i

Partitioning is the process in which a substance is distributed among various dissolved and adsorbed species. Organic micropollutants adsorb to organic matter components, that is detritus (POC, dead particulate organic matter), dissolved organic matter (DOC) and phytoplankton (PHYT). The partitioning of micropollutants is usually described as an equilibrium process by means of a linear partition coefficient, based on amounts of organic carbon. The partition coefficients for the various organic matter components may be different, although the coefficient for DOC is usually considered proportional to the coefficient for POC.

Slow diffusion in solid matter has been acknowledged to take place after fast equilibrium adsorption or prior to fast equilibrium desorption. Therefore, the sorption flux can be calculated according to equilibrium partitioning or slow sorption by choosing one of the available options.

The model only actually simulates the total concentration (or the total particulate and total dissolved concentrations) of a micro-pollutant. The partitioning process delivers the dissolved and adsorbed species as fractions of the total concentration, as well as the sorption flux.

Volume units refer to bulk (b) or to water (w).

Implementation

Processes PARTWK_(i) are generic and can be used for water and sediment compartments. For the S1/2 option for the sediment processes PARTS1_(i) and PARTS2_(i) can be used.

The substances in the sediment are modeled as 'inactive' substances. Whereas PARTWK_(i) needs concentrations (g m^{-3}) as input, PARTS1_(i) and PARTS2_(i) require total quantities per sediment layer (g) as input with only one exception (DOC in g $m^{-3}w$). The formulations are identical for PARTWK_(i) and PARTS1/2_(i) with two exceptions:

- ◇ the correction of DOC for porosity is not carried out in PARTWK; and
- ◇ PARTS1/2 carries out a conversion from concentration units into quantity units and vice versa, and therefore needs the input of layer thickness and surface area.

The processes have been implemented for the following substances:

- ◇ OMP, unspecified organic micropollutant
- ◇ HCH, lindane or hexachlorohexane
- ◇ HCB, hexachlorobenzene
- ◇ 153, polychlorinated biphenyl (or PCB) 153
- ◇ BaP, benzo[a]pyrene
- ◇ Flu, fluoranthene
- ◇ Diu, diuron
- ◇ Atr, atrazine
- ◇ Mef, mefinphos

OMP can be any micro-pollutant. The default values of the input parameters for OMP should be replaced by values suitable for the particular compound. For instance, PCB52 can be simulated as OMP (but also as PCB153) by replacing the values of the input parameters by those for PCB52.

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The above substance names concern the situation, where equilibrium partitioning is simulated. The simulation of slow sorption requires the use of two simulated substances for each micro-pollutant in stead of the one simulated substance (total concentration). The names of these substances are OMP(or other name)-dis and OMP-par. OMP-dis is the total dissolved concentration, the sum of free dissolved and DOC-adsorbed micro-pollutant. OMP-par is the total particulate micro-pollutant concentration. The two methods cannot be combined, so either use OMP or a combination of OMP-dis and OMP-par.

The process formulations are the same for all substances, but default values for properties are substance specific. The organic micro-pollutants belong to the group 4 substances. The input parameter $OMPGroup$ identifies the group to which a substance belongs, in order to distinguish them from other groups of substances such as heavy metals, for which other partitioning formulations are used.

The concentrations of detritus ($Cpoc$), dissolved organic matter ($Cdoc$) and phytoplankton ($Calg$) can either be calculated by the model or be imposed on the model via its input. In case of the former $Cpoc$ is generated by processes COMPOS, S1_COMP and S2_COMP. $Calg$ is generated by processes PHY_BLO (BLOOM) or PHY_DYN (DYNAMO), S1_COMP and S2_COMP.

Tables 10.1 and 10.2 provide the definitions of the input parameters occurring in the formulations. Tables 10.3 and 10.4 contain the definitions of the output parameters.

Formulation

The fractions of the dissolved and adsorbed species add up to one. Consequently these fractions as resulting from equilibrium are computed with:

$$fdf = \frac{\phi}{\phi + Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

$$fdoc = (1 - fdf) \times \frac{Kppoc' \times Xdoc \times Cdoc}{Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

$$fpoc = (1 - fdf) \times \frac{Kppoc' \times Cpoc}{Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

$$falg = (1 - fdf - fdoc - fpoc)$$

where:

$Calg/poc/doc$	concentration of algae biomass, dead particulate organic matter matter, and dissolved organic matter [gC m^{-3} 🖉]
$falg/poc/doc$	fraction of a micropollutant adsorbed to algae, dissolved organic matter, dead particulate organic matter [-]
fdf	freely dissolved fraction of a micropollutant [-]
$Kpalg/poc'$	partition coefficient for algae and dead particulate organic matter [m^3 🌊 gC^{-1}]
$Xdoc$	adsorption efficiency of DOC relative to POC [-]
ϕ	porosity ([m^3 🌊 m^{-3} 🖉]; equal to 1.0 for the water column)

For PARTS1_(i) and PARTS2_(i), $Cdoc$ is corrected for porosity considering the fact that DOC input only in this case is specified as concentrations in pore water:

$$Cdoc = DOC \times \phi$$

All substance quantities in the above partitioning equations are converted in case of PARTS1/2 into bulk concentrations by dividing with the volume of the layer ($V = Z \cdot A$).

The partition coefficients in the above equations expressed in [$m^3 w.gC^{-1}$] are derived from the input parameters expressed in [$^{10}\log$(l.kgC^{-1})], corrected for temperature:

$$logKppoc = logKppoc_{20} + a \times (\frac{1}{(T + 273.15)} - \frac{1}{293.15})$$

$$logKpalg = logKpalg_{20} + a \times (\frac{1}{(T + 273.15)} - \frac{1}{293.15})$$

$$Kppoc' = 10^{logKppoc} \times 10^{-6}$$

$$Kpalg' = 10^{logKpalg} \times 10^{-6}$$

where:

a	temperature coefficient [K]
$Kpalg/poc_{20}$	partition coefficient for algae and dead particulate organic matter at a temperature of 20 °C [L kgC^{-1}]
T	temperature [°C]

The simulation of slow partitioning is optional. Equilibrium partitioning (option 0) occurs when the half-life-time of the adsorption process or the desorption process is equal to or smaller than 0.0. Slow partitioning (option 1) is applied when one of these half-life-times is bigger than 0.0.

Option 0

When $tads$ and $tdes \leq 0.0$, the above equations are applied to calculate the fractions in equilibrium.

Option 1

When $tads$ or $tdes > 0.0$, the above equations are also applied to calculate the fractions in equilibrium. In addition the various micropollutant fractions are corrected for slow sorption proportional to the difference between the equilibrium fractions and the fractions in the previous time step. No distinction is made regarding the various particulate adsorbents. Average sorption rates are used for POC and phytoplankton. The calculation using first-order sorption reaction rates derived from half-life-times proceeds as follows:

$$fp' = fpoc' + falg' = \frac{Cmpp'}{Cmpt'}$$

$$fpe = fpoc + falg$$

if $fp < fpe$ then

$$ksorp = \frac{\ln(2)}{tads}$$

else

$$ksorp = \frac{\ln(2)}{tdes}$$

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and

$$fp = fpe - (fpe - fp') \times \exp(-ksorp \times \Delta t)$$
$$fdf = fdfe \times \frac{(1 - fp)}{(1 - fpe)}$$
$$fdoc = fdoce \times \frac{(1 - fp)}{(1 - fpe)}$$
$$fpoc = fpoce \times \frac{fp}{fpe}$$
$$falg = falge \times \frac{fp}{fpe}$$

where:

$Cmpt/mpp'$	total and particulate concentration of micropollutant after the previous time-step [g m^{-3}]
$falg/poc'$	fractions of micropollutant adsorbed to algae and dead particulate organic matter after the previous time step [-]
$fp'/p/pe$	total particulate micropollutant fraction after the previous time-step, at the end of the present timestep, and in equilibrium [-]
$ksorp$	sorption rate [d^{-1}]

For both options the sorption rate is calculated as:

$$Rsorp = \frac{fp \times Cmpt' - Cmpp'}{\Delta t}$$

where:

$Rsorp$	sorption rate [g m$^{-3}_{\ell}$ d^{-1}]
Δt	timestep of DELWAQ [d^{-1}]

The calculation of the rate requires division with the volume of the overlying water segment ($V = Z \cdot A$) in case of PARTS1_(i) and PARTS2_(i).

The dissolved and particulate micropollutant concentrations and the quality of the particulate organic fractions follow from:

$$Cmpdf = \frac{fdf \times Cmpt'}{\phi}$$
$$Cmpdoc = \frac{fdoc \times Cmpt'}{\phi}$$
$$Cmpd = Cmpdf + Cmpdoc$$
$$Cmpp = (fpoc + falg) \times Cmpt'$$
$$Cmppoc = \frac{fpoc \times Cmpt'}{Cpoc}$$
$$Cmpalg = \frac{falg \times Cmpt'}{Calg}$$

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For PARTS1_(i) and PARTS2_(i) the calculation of the dissolved concentrations also requires division with the volume of the layer (V).

Output
The process generates output for:

- ◇ the various particulate and dissolved micropollutant fractions;
- ◇ the total micropollutant concentration, the freely dissolved concentration, the concentration adsorbed to DOC;
- ◇ the apparent overall partition coefficient; and
- ◇ the micropollutant contents of total suspended solids, detritus and phytoplankton.

The micro-pollutant content of total suspended solids and the apparent partition coefficient follow from:

$$Cmppt = \frac{Cmpp \times 10^6}{Css}$$

$$Kpt = \frac{Cmppt \times 10^{-3}}{Cmpd + Cmpdoc}$$

where:

Css	the total suspended solids concentration [g m^{-3}].
$Cmppt$	the micropollutant content of total suspended solids [mg kg^{-1}].
Kpt	the apparent overall parttion coefficient [m^3 kg^{-1}].

The contents of the individual particulate fractions are calculated in a similar way.

Directives for use

- ◇ The partition coefficients for phytoplankton and POC have to be provided in the input of the model as logarithmic values ($^{10}\log$) of [L kgC^{-1}] or [L $kgDW^{-1}$]. If the partition coefficient is to be temperature dependent its input value concerns reference temperature 20 °C. When temperature coefficient $TcKp(i)$ = 0.0 (default value), this implies a partition coefficient that is not dependent on temperature.
- ◇ The concentrations of $DOCS1/2$ for the S1/S2 sediment option have to be provided as pore water concentrations. In all other cases DOC needs to be provided as bulk concentrations. DOC is calculated as bulk concentration, when simulated with the model.
- ◇ The process of aging (internal diffusion in particles) may cause the apparent partition coefficient to increase over time. The partitioning in the sediment may therefore require a substantially higher partition coefficient than the partitioning in the water column.
- ◇ The formulations do not allow for an irreversibly adsorbed fraction. Such a fraction can be taken into account implicitly by reducing the load proportionally, or by increasing the partition coefficients and slowing down of the sorption process, which may be relevant for sediment compartments in particular.
- ◇ Field partition coefficients may not (readily) be available. For many substances the field partition coefficient can be estimated from the octanol-water partition coefficient according to $\log(Kppoc) = a\log(Kow) + b$ ($a = 0.8 - 1.0$ and $b = 0.0 - 0.3$; these coefficients are different for the various types of micropollutants).
- ◇ The input parameters $SWSedYes/No$ and $OMPGroup$ always have the same default value, respectively 1.0/0.0 and 4.0, which must not be changed by the user!
- ◇ Slow sorption requires the use of two simulated substances (total particulate and total dissolved) in stead of the one substance (total concentration), see above! All other input parameters and output parameters remain the same.

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Additional references

WL | Delft Hydraulics (1992b), DiToro and Horzempa (1982), Karickhoff et al. (1979), O' Connor and Connolly (1980), Connolly et al. (2000)

Table 10.1: *Definitions of the input parameters in the above equations for PARTWK_(i). (i) is a substance name. Volume units refer to bulk (b) or to water (w).*

Name in formulas	Name in input	Definition	Units
-	$OMPGroup$	identifier of group 4 substances (organic micropollutants)	-
$Calg$	$PHYT$[1]	phytoplankton concentration	gC m^{-3}_b
$Cdoc$	DOC	dissolved organic matter concentration	gC m^{-3}_b
Cim_i	IMi	conc. inorg. particulate fractions i=1,2,3	gDW m^{-3}_b
$Cpoc$	$POCnoa$[2]	particulate organic matter concentration without algae	gC m^{-3}_b
$Cmpt$	(i)	total micropollutant concentration	g m^{-3}_b
$Cmpd$	$(i)-dis$	total dissolved micropollutant conc.	g m^{-3}_w
$Cmpp$	$(i)-par$	totsl particulate micropollutant conc.	g m^{-3}_b
Css	SS	total suspended matter concentration	gDW m^{-3}_b
$logKpalg$	$lKphy(i)$	10 logarithm of part. coeff. for phytoplankton	$^{10}\log$ (L kgC^{-1})
$logKppoc$	$lKpoc(i)$	10 logarithm of part. coeff. for POC	$^{10}\log$ (L kgC^{-1})
a	$TcKp(i)$	temperature coefficient of partition coefficient	K
$-$	$WSedNo$[3]	option for process in water column (default = 0.0)	-
$tads$	$HLTAds(i)$	half-life-time adsorption process	d
$tdes$	$HLTDes(i)$	half-life-time desorption process	d
T	$Temp$	temperature	K
V	$Volume$	volume	K
$Xdoc$	$XDOC(i)$	adsorption efficiency of DOC relative to POC	-
ϕ	$POROS$	porosity	m^3_w m^{-3}_b
Δt	$Delt$	timestep	d^{-1}

[1]) Delivered by processes PHY_BLO (BLOOM) or PHY_DYN (DYNAMO).

continued on next page

Table 10.1 – continued from previous page

Name in formulas	Name in input	Definition	Units

[2]) Delivered by process COMPOS.

[3]) Default value must not be changed.

Table 10.2: *Definitions of the input parameters in the above equations for PARTS1_(i) and PARTS2_(i). (i) is a substance name. (k) indicates sediment layer 1 or 2. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
A	$Surf$	surface area	m^2
$Calg$	$PHYTS(k)$[1]	phytoplankton quantity	gC
$Cdoc$	$DOCS(k)$	dissolved organic matter concentration	gC $m^{-3}_{\mathscr{w}}$
Cim_i	$IMiS(k)$	quantity inorg. particulate fractions i=1,2,3	gDW
$Cpoc$	$POCS(k)$[1]	part. organic matter without algae	gC
$Cmpt$	$(i)S(k)$	quantity of total micropollutant	g
$Cmpd$	$(i)S(k) - dis$	quantity of total diss. org. micro-poll.	g
$Cmpp$	$(i)S(k) - par$	quantity of total part. org. micro-poll.	g
Css	$DMS(k)$[1]	total quantity of total sediment	gDW
$logKpalg$	$lKphy(i)S(k)$	10 logarithm of part. coeff. for phyt.	log(L kgC^{-1})
$logKppoc$	$lKpoc(i)S(k)$	10 logarithm of part. coeff. for POC	log(L kgC^{-1})
a	$TcKp(i)S(k)$	temperature coefficient of partition coefficient	K
-	$SWSedYes$[2]	identifier for processes PARTS1/2	-
$tads$	$HLTAds(i)S(k)$	half-life-time adsorption process	d
$tdes$	$HLTDes(i)S(k)$	half-life-time desorption process	d
$Xdoc$	$XDOC(i)$	adsorption efficiency of DOC relative to POC	-
T	$Temp$	temperature	K
V	$Volume$	volume	$m^{-3}_{\mathscr{b}}$
Z	$ActThS(k)$	thickness of sediment layer	m
ϕ	$PORS(k)$	porosity	$m^3_{\mathscr{w}}$ $m^{-3}_{\mathscr{b}}$

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Table 10.2 – continued from previous page

Name in formulas	Name in input	Definition	Units
Δt	$Delt$	timestep	d^{-1}

[1]) Delivered by processes S1_COMP and S1_COMP.

[2]) Default value must not be changed.

Table 10.3: *Definitions of the output parameters for PARTWK_(i). (i) is a substance name. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
$Cmpt$	$(i)tot$	total micropollutant concentration	g m$^{-3}_{\mathscr{b}}$
$Cmpd$	$Dis(i)$	freely dissolved micropollutant conc.	g m$^{-3}_{\mathscr{w}}$
$Cmpdoc$	$Doc(i)$	DOC adsorbed micropollutant conc.	g m$^{-3}_{\mathscr{w}}$
fdf	$Fr(i)Dis$	freely diss. micropoll. fraction (not bound to DOC!)	-
$fdoc$	$Fr(i)DOC$	fraction micropollutant adsorbed to DOC	-
$fpoc$	$Fr(i)POC$	fraction micropollutant adsorbed to POC	-
$falg$	$Fr(i)PHYT$	fraction micropollutant adsorbed to phytoplankton	-
Kpt	$Kd(i)SS$	apparent overall partition coefficient for susp. solids	m^3 kgDW^{-1}
-	$Q(i)POC$	micropoll. content of particulate detritus	g gC^{-1}
-	$Q(i)PHYT$	micropoll. content of phyt. biomass	g gC^{-1}
$Cmppt$	$Q(i)SS$	micropollutant content of total suspended solids	mg kgDW^{-1}

Table 10.4: *Definitions of the output parameters for PARTS1_(i) and PARTS2_(i). (i) is a substance name. (k) indicates sediment layer 1 or 2. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input[1]	Definition	Units
Name in formulas	**Name in input**	**Definition**	**Units**
$Cmpt$	$(i)S(k)tot$	total mass of the micropollutant	g
$Cmpd$	$Dis(i)S(k)$	freely dissolved micropollutant conc.	g m$^{-3}_{\mathscr{w}}$
$Cmpdoc$	$Doc(i)S(k)$	DOC adsorbed micropollutant conc.	g m$^{-3}_{\mathscr{w}}$

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Table 10.4: *Definitions of the output parameters for PARTS1_(i) and PARTS2_(i). (i) is a substance name. (k) indicates sediment layer 1 or 2. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	**Name in input**[1]	**Definition**	**Units**
Name in formulas	**Name in input**	**Definition**	**Units**
fdf	$Fr(i)DisS(k)$	freely diss. micropoll. fraction (not bound to DOC!)	-
$fdoc$	$Fr(i)DOCS(k)$	fraction micropollutant adsorbed to DOC	-
$fpoc$	$Fr(i)POCS(k)$	fraction micropollutant adsorbed to POC	-
$falg$	$Fr(i)PHYTS(k)$	fraction micropollutant adsorbed to phytoplankton	-
Kpt	$Kd(i)DMS(k)$	apparent overall partition coefficient for susp. solids	m^3 kgDW^{-1}
-	$Q(i)POCS(k)$	micropollutant content of part. detritus	g gC^{-1}
-	$Q(i)PHYTS(k)$	micropollutant content of phyt. biomass	g gC^{-1}
$Cmppt$	$Q(i)DMS(k)$	micropollutant content of total suspended solids	mg kgDW^{-1}

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10.2 Calculation of organic matter

PROCESS: MAKOOC AND MAKOOCS1/2

When organic matter components are actually simulated or imposed as POC1-4, total POC is made available as the sum of these components by process COMPOS. In that case processes MAKOOC, MAKOOCS1 and MAKOOCS2 are not needed.

However, when modelling organic micropollutants or heavy metals, organic matter might not be simulated. The particulate organic matter concentration POC can then be derived from (suspended) inorganic sediment using processes MAKOOC, MAKOOCS1 and MAKOOCS2. Inorganic sediment may be simulated, or may be imposed as forcing function.

Implementation

Process MAKOOC has been implemented for the following substances:

◇ IM1, IM2 and IM3

Processes MAKOOCS1 and MAKOOCS2 have been implemented for the following substances:

◇ IM1S1, IM2S1, IM3S1, IM1S2, IM2S2 and IM3S2

Process MAKOOC is generic and can be used for water and sediment layers. Whereas MAKOOC needs concentrations as input, MAKOOCS1 and MAKOOCS2 require total quantities per sediment layer as input. The formulations for the processes are identical.

Table 10.5 and Table 10.6 provide the definitions of the input and output parameters.

Formulation

The total POC concentration is the sum of the contribution of the three sediment fractions:

$$Cpoc = \sum_{i=1}^{3} (focsed_i \times \frac{Cim_i}{1 - focsed_i \times fctr})$$

where:

Cim	the concentration or quantity of inorganic matter [gDM m$^{-3}_{\ell}$ or gDM]
$Cpoc$	the concentration or quantity of particulate organic carbon [gC m$^{-3}_{\ell}$ or gOC]
$fctr$	weight conversion factor [gDM gOC^{-1}]
$focsed$	content organic carbon in total of sediment fraction [gOC gDM^{-1}]
i	index for sediment component

The conversion factor $fctr$ enters the equation because the content of organic matter $focsed$ is provided as organic carbon per dry matter total sediment for each fraction. From the converted organic content, the inorganic fraction and the total weight of the sediment in dry weight is calculated. Then, using the content of organic matter $focsed$ again, the $Cpoc$ is calculated from the total sediment dry weight for each fraction, and summed.

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Table 10.5: *Definitions of the input parameters in the above equations for MAKOOC, MAKOOCS1 and MAKOOCS2.*

Name in formulas	Name in input	Definition	Units
Cim_i	$IM(i)S(k)$	concentration of inorganic particulate fractions i = 1,2,3	DW m^{-3}
$fctr$	$DMCFOOC$	weight conversion factor for water column	gDW gC^{-1}
	$DMCFOOCS$	weight conversion factor for sediment layers	gDW gC^{-1}
$focsed_i$	$FCSEDIM(i)S(k)$	content organic carbon in total of sediment fractions	gOC gDM^{-1}

[1]) (i) is 1, 2 or 3 for IM1, IM2 or IM3. (k) is 1 or 2 for sediment layer S1 or S2.

Table 10.6: *Definitions of the ouput parameters in the above equations for MAKOOC, MAKOOCS1 and MAKOOCS2.*

Name in formulas	Name in input	Definition	Units
$Cpoc$	$POCnoa$	conc. of total particulate organic carbon in water (with or without algae biomass!)	gC m^{-3}_{ℓ}
$Cpoc$	$POCS(k)$	quantity of total part. organic carbon in sediment (with or without algae biomass!)	gC

[1]) (i) is 1, 2 or 3 for IM1, IM2 or IM3. (k) is 1 or 2 for sediment layer S1 or S2.

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10.3 Dissolution of organic micropollutants

PROCESS: DISOMP_(I)

Organic micropollutants may be discharged into a water system contained in an organic solvent. This applies to for instance PCB containing oil. If not already dispersed into droplets prior to discharge, dispersion proceeds in the receiving water system. The micropollutant in the solvent as well as the solvent in the droplets slowly dissolve into water. Dissolution may be slow compared to the transport of substances, implying that the fate of the micropollutant is dependent on the slow dissolution.

The dissolution of the micropollutant can also be understood as the desorption from organic matter. In the case that the solvent dissolves much slower in water than the micropollutant desorption eventually leads to equilibrium concentrations in water and organic solvent. When the initial concentration of the micropollutant in the solvent is much higher than the equilibrium concentration, practically all micropollutant dissolves. In the case that the organic solvent dissolves at a similar or higher rate than the micropollutant, the adsorbent disappears eventually also leading to the dissolution of all micropollutant. For the formulation of the dissolution process it is assumed that conditions for the eventual dissolution of all micropollutant are fulfilled. Equilibrium sorption with respect to the solvent is ignored.

In order to take slow dissolution from an organic solvent into account an additional substance was defined for the micropollutant contained in an organic solvent. After dissolution the micropollutant repartitions among various organic phases also defined in the model.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process DISOMP_(i) has been implemented for the following substances:

- ◇ OMP-dis, OMP, OMP-dis (any micropollutant); and
- ◇ 153-dis, 153, 153-dis (PCB153).

Substance (i)-ios concerns the micropollutant in organic solvent. Substance (i) concerns the micropollutant in the other dissolved and particulate phases in the model. The process formulations in the model are generic, as they are similar for all substances. Default values for process coefficients are substance specific. Consequently, the name (i) has to be added in the names of pertinent process coefficients.

For the substance name (i) equilibrium partitioning is simulated as based on the total concentration of this substance. For the substance name (i)-dis slow sorption is simulated in combination with equilibrium partitioning. In that case the micropollutant is simulated with two substance names, (i)-dis for the total dissolved concentration which is the sum of free dissolved and DOC-adsorbed micropollutant, and (i)-par for the total particulate micropollutant concentration which is the sum of PHYT-adsorbed and POC-adsorbed micropollutant.

Table 10.7 provides the definitions of the input parameters occurring in the formulations.

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Formulation

Assuming the eventual dissolution of all micropollutant in a solvent the dissolution is formulated as a first order kinetic process:

$$Rdis = -kdis \times Cios$$
$$kdis = kdis_{20} \times ktdis^{(T-20)}$$

where:

$Cios$	concentration of micropollutant in organic solvent in water [$g.m_{\ell}^{-3}$]
$kdis_{20}$	dissolution rate constant at 20 °C [d^{-1}]
$ktdis$	temperature constant for dissolution [-]
$Rdis$	dissolution rate [$g.m^{-3}.d^{-1}$]

The micropollutant dissolved from the organic solvent is allocated to the total micropollutant (i) or to the dissolved micropollutant (i)-dis.

Directives for use

The dissolution rate constant *RcDis(i)* should ideally be quantified on the basis of experimental data. An indicative range for the dissolution rate of PCBs is $0.3 - 1.5\ d^{-1}$. An indicative value for the dissolution rate of PCB153 is $0.7\ d^{-1}$ (measured for the desorption from natural organic detritus by means of tenax-extraction keeping a near zero dissolved concentration).

References

None.

Table 10.7: *Definitions of the parameters in the above equations for DISOMP_(i). (i) is a substance name. Volume units refer to bulk (ℓ) or to water (w).*

Name in formulas	Name in input	Definition	Units
$Cios$	(i)-ios	micropollutant in organic solvent concentration	$g.m_{\ell}^{-3}$
$kdis_{20}$ $ktdis$	RcDis(i) $TcDis(i)$	dissolution rate constant at 20 °C temperature constant of dissolution	d^{-1} $-$
$Rdis$	$-$	dissolution rate	$g.m_{\ell}^{-3}.d^{-1}$

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10.4 Overall degradation

PROCESS: LOS_WK_i AND LOS_S1/2_i

Organic micropollutants may be decomposed in various ways, either chemical or biochemical in nature. The rates of degradation processes in water systems are complex functions of numerous local conditions. Often the individual degradation processes are not well known or can not be quantified exactly for a given substance. Overall degradation rates, usually calibrated on concentration data for the water system concerned, are applied in models in stead.

Degradation rates are different for water column, oxidising sediment and reducing sediment (WL | Delft Hydraulics, 1992b). This module calculates the overall degradation fluxes for each compartment, taking these differences into account. When formulation option $SWVnDegMP$ = 1.0 different values can be provided for the rate constants for oxidising and reducing conditions, which are assigned according to the value of the dissolved oxygen concentration. The appropriate degradation rate is selected using a switch.

The degradation rate is described according to temperature dependent first order kinetics. Below a critical temperature the flux is set equal to a constant value (zero order constant). By means of a switch ($SWDeg$) the degradation can be made proportional to dissolved fractions or the total concentration of the micropollutant.

Implementation

Process LOS_WK_(i) is generic and can be used for water and sediment compartments. However, when substances in the sediment are modeled as 'inactive' substances, processes LOS_S1/2_(i) are to be used in stead for these 'inactive' substances. These processes calculate the overall degradation fluxes for sediment layers S1 and S2. In order to account for different rates at oxidising and reducing conditions, different values can be provided for the rate constants for S1 and S2. Whereas LOS_WK_(i) needs concentrations as input, processes LOS_S1/2_(i) require total quantities per sediment layer as input. Moreover, the zeroth-order degradation rate in LOS_S1/2_(i) is expressed in [g m^{-2} d^{-1}] in stead of [g m^{-3} d^{-1}].

Two options are available with respect to the formulation of the rate of degradation. An option can be selected with parameter $SWVnDegMP$. The processes have been implemented for the following substances:

- ◇ OMP (unspecified organic micropollutant);
- ◇ HCH (hexachlorohexane),
- ◇ HCB (hexachlorobenzene),
- ◇ 153 (PCB 153);
- ◇ BaP (Benzo[a]pyrene),
- ◇ Flu (fluoranthene);
- ◇ Diu (diuron);
- ◇ Atr (atrazine); and
- ◇ Mef (mevinphos).

The names (i) of these substances are known to the model, and have to be part of the relevant input parameters (see tables Table 10.8 and Table 10.9 with parameter definitions). The processes in the model are generic. They are similar for all substances. Default values for the properties of the above substances are substance specific.

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OMP can be any micropollutant. The default values of the input parameters for OMP are meaningless. For instance, PCB 52 can be simulated as OMP (but also as PCB 153) by replacing the values of the input parameters by those for PCB 52.

The switch for oxizing or reducing conditions can be delivered by auxiliary process SWOXY-PARWK as based on the dissolved oxygen concentration, which can be simulated or imposed in the input of DELWAQ.

The (freely) dissolved and DOC-bound fractions of a micropollutant are also input to LOS_WK_(i) and LOS_S1/2_(i). These parameters are calculated with partitioning processes PARTWK_(i) and PARTS1/2_(i).

Formulation

Two different sets of formulations are available. These sets differ with respect to the distinction of oxidising and reducing conditions and the pollutant fractions that are subjected to degradation.

Formulation with distinction of oxidising and reducing conditions (SWVnDegMP = 1.0)
The degradation rate for a specific compartment is equal to:

$$Rdeg = k0deg \qquad \text{if} \quad T < T_c$$

and else equal to:

$$Rdeg = k0deg + \left(k1deg_{20} \times ktdeg^{(T-20)} \times frdeg \times Cmpt\right)$$

where:

$Cmpt$	total micropollutant concentration [g.m^{-3}]
$frdeg$	fraction subjected to degradation [-]
$k0deg$	zeroth order degradation rate [g.m^{-3}.d^{-1}]
$k1deg$	first order degradation rate [d^{-1}]
$ktdeg$	temperature coefficient of degradation [-]
$Rdeg$	degradation rate [g.m^{-3}.d^{-1}]
T	temperature [°C]
T_c	critical temperature for degradation [°C]

The first order degradation rate at 20 °C $k1deg_{20}$ [d^{-1}] depends on the redox conditions according to:

$$k1deg_{20} = \begin{cases} kdego_{20} & \text{if} \quad SWOXY = 1 \\ kdegr_{20} & \text{if} \quad SWOXY = 0 \end{cases}$$

where:

$k1dego$	first order degradation rate at oxidising conditions [d^{-1}]
$k1degr$	first order degradation rate at reducing conditions [d^{-1}]

The switch is determined as function of the dissolved oxygen concentration in process SWOXY-PARWK.

In case of LOS_S1/2_(i), the zeroth-order degradation rate and the quantity of micropollutant are divided with the depth of the overlying water segment (H) and the volume of this segment respectively ($V = H \cdot A$), in order to change units into [g m^{-3} d^{-1}] and [g m^{-3}]. (After all

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fluxes have been quantified, they are multiplied with the water volume in order to obtain fluxes in terms of [g d^{-1}]!)

Factor $frdeg$ is different for various options imposed with $SWDeg$ with respect to the concentration fraction that is subjected to degradation.

Option 0

$$frdeg = 1.0 \qquad \text{(default)}$$

Option 1

$$frdeg = fdf$$

Option 2

$$frdeg = fdf + fdoc$$

where:

fdf	freely dissolved fraction of the micropollutant [-]
$fdoc$	DOC-bound fraction of the micropollutant [-]

A situation in which only the particulate fraction is subjected to degradation is very unlikely. Consequently, such an option has not been implemented.

Formulation without distinction of oxidising and reducing conditions (SWVnDegMP = 0.0)

The degradation rate for a specific compartment is equal to:

$$Rdeg = k0deg \qquad \text{if} \quad T < T_c$$

and else equal to:

$$Rdeg = k0deg + \left(k1deg_{20} \times ktdeg^{(T-20)} \times fdf \times Cmpt\right)$$

where:

$Cmpt$	total micropollutant concentration [g.m^{-3}]
fdf	freely dissolved fraction of the micropollutant [-]
$k0deg$	zeroth order degradation rate [g.m^{-3}.d^{-1}]
$k1deg$	first order degradation rate [d^{-1}]
$ktdeg$	temperature coefficient of degradation [-]
$Rdeg$	degradation rate [g.m^{-3}.d^{-1}]
T	temperature [°C]
T_c	critical temperature for degradation [°C]

In case of LOS_S1/2_(i), the zeroth-order degradation rate and the quantity of micropollutant are divided with the depth of the overlying water segment (H) and the volume of this segment respectively ($V = H \cdot A$), in order to change units into [g.m^{-3}.d^{-1}] and [g.m^{-3}]. (After all fluxes have been quantified, they are multiplied with the water volume in order to obtain fluxes in terms of [g.d^{-1}]!)

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Directives for use

- ◇ Formulation option $SWVnDegMP = 0.0$ is the default option for historical reasons.
- ◇ Overall degradation may be connected with biodegradation, photolysis and/or hydrolysis. When photolysis is the dominant process, the degradation rate should reflect either the time average effects of solar radiation at the water surface and light extinction in the water column. When hydrolysis is the main degradation process, the rate should be based on the time average effect of the pH.
- ◇ The rates for degradation in sediment are usually much higher than the rates in water, when mainly biodegradation occurs. The rates for degradation in water are usually much higher when mainly photolysis occurs.
- ◇ The rates for degradation at oxidising conditions can be given equal values to the rates for degradation at reducing conditions, when degradation of a micropollutant is not sensitive to the presence of oxygen.
- ◇ The default values for all kinetic parameters and option parameters are equal to zero with two exceptions. The default values of temperature constants $Tc(i)$ and $Tc(i)Sed$ are equal to 1.07. The default value of the option parameters $SWDeg(i)$ and $SWDeg(i)S1/2$ are equal to 1.0.

Additional references

WL | Delft Hydraulics (1993b), Burns (1982)

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Table 10.8: *Definitions of the parameters in the above equations for LOS_WK_(i). (i) is a substance name.*

Name in formulas	Name in input	Definition	Units
$Cmpt$	(i)	total micropollutant concentration	g m^{-3}
$frdeg$	-	fraction subjected to degradation	-
fdf	$Fr(i)Dis$	freely dissolved micropollutant fraction	-
$fdoc$	$Fr(i)Doc$	DOC-bound dissolved micropollutant fraction	-
$SWDeg$	$SWDeg(i)$	switch for selection of one of the options	-
$SWOXY$	$SWWaterCh$	switch for oxidising and reducing conditions, computed with SWOXYPARWK	-
-	$SWVnDegMP$	switch for selection of formulations (no redox dependency = 0.0, with redox dependency = 1.0)	-
$k0deg$	$ZLoss(i)$	zeroth-order degradation rate	g m^{-3} d^{-1}
$kdego_{20}$	$RcDegO(i)$	first-order degr. rate at oxid. cond. and at 20 °C	d^{-1}
$kdegr_{20}$	$RcDegR(i)$	first-order degr. rate at red. cond. and at 20 °C	d^{-1}
$k1deg_{20}$	$Rc(i)$	first-order degradation rate at 20 °C	d^{-1}
$ktdeg$	$Tc(i)$	temperature constant of degradation	-
$Rdeg$	-	overall degradation rate	g m^{-3} d^{-1}
T	$Temp$	ambient temperature	°C
T_c	$CTLoss$	critical temperature for degradation	°C

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Table 10.9: *Definitions of the parameters in the above equations for LOS_S1/2_(i). (i) is a substance name.*

Name in formulas	Name in input	Definition	Units
H	$Depth$	depth of overlying water segment	m
$Cmtt$	$(i)S1/2$	total micropollutant concentration	g
$frdeg$	-	factor for conc. fraction subjected to degradation	-
fdf	$Fr(i)DisS1/2$	freely dissolved micropollutant fraction	-
$fdoc$	$Fr(i)DocS1/2$	DOC-bound dissolved micropollutant fraction	-
$SWDeg$	$SWDeg(i)S1/2$	switch that allows selection of one of the options	-
$SWOXY$	$SWPoreChS1/2$	switch for oxidising and reducing conditions computed with SWOXYPARWK	-
-	$SWVnDegMP$	switch for selection of formulations (no redox dependency = 0.0, with redox dependency = 1.0)	-
$k0deg$	$ZLoss(i)S1/2$	zeroth-order degradation rate	g m^{-2} d^{-1}
$kdego_{20}$	$RcDgO(I)S1/2$	first-order degr. rate at oxid. cond. and at 20 °C	d^{-1}
$kdegr_{20}$	$RcDgR(i)S1/2$	first-order degr. rate at red. cond. and at 20 °C	d^{-1}
$k1deg_{20}$	$Rc(i)S1/2$	first-order degradation rate at 20 °C	d^{-1}
$ktdeg$	$Tc(i)Sed$	temperature constant of degradation	-
$Rdeg$	-	overall degradation rate	g.d^{-1}
T	$Temp$	ambient temperature	°C
T_c	$CTLoss$	critical temperature for degradation	°C
V	$Volume$	volume	m^3

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10.5 Redox status

PROCESS: SWOXYPARWK

The partitioning of heavy metals and the degradation rate of organic micropollutants depend on the presence of oxidising or reducing conditions. The dissolved oxygen concentration is an indicator for the prevailing conditions. Because the conditions in (suspended) particles may be different from those in the surrounding water, anaerobic reduction of adsorbing components and anaerobic degradation may already occur in these particles at a small but positive ambient dissolved oxygen concentration. The specific consequences of spatial heterogeneity within segments are not considered in the present model. It is assumed that the prevailing conditions are decisive with respect to the dissolved concentrations.

This module determines the value of a switch ($SWWaterKCh$) for oxidising or reducing conditions, depending on the local dissolved oxygen concentration. The latter maybe simulated or provided as input. The switch is used in processes PARTWK_(i) and DEGMP_(i). The switch is used for the water phase and the sedment layers if the layered sediment option is used (Section 1.6). If the S1/S2 approach is used, then two other switches are important as well: $SwPoreChS1$ and $SWPoreChS2$ for respectively the upper, S1, layer and the lower, S2, layer. It is assumed for this approach that the oxygen concentration in layer S1 is the same as that for the overlying water and that the oxygen concentration in layer S2 is zero.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

Process SWOXYPARWK is generic and can be used for water and sediment compartments. When substances in the sediment are modeled as 'inactive' substances, SWOXYPARWK affects both the water compartments and the S1/2 partitioning processes. See Table 10.10 below for definition of the parameters.

Formulation

The prevailing chemical conditions are determined on the basis of a critical dissolved oxygen concentration. The switch may have one of two values as follows:

$$SWOXY = 1 \quad \text{if} \quad Cox/\phi > Coxc$$
$$SWOXY = 0 \quad \text{if} \quad Cox/\phi \leq Coxc$$

with:

Cox	actual dissolved oxygen concentration [g $m^{-3}_{\mathscr{b}}$]
$Coxc$	critical dissolved oxygen concentration [g $m^{-3}_{\mathscr{w}}$]
ϕ	porosity (Section 1.6.1) [-]

The critical concentration $Coxc$ maybe different for water and sediment compartments, when this parameter is provided in the input as a segment function. In case of the S1/2 sediment option, the critical concentration for S1 is the same as for the overlying water compartment. The value of $SWOXY$ is always 0 for S2, assuming that this layer is a reducing layer by definition.

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Directives for use

◇ The critical dissolved oxygen concentration $CoxPart$ is generally below 2 g m^{-3}, as can be learned from growth experiments with fungal pellets with a diameter of about a few millimetres in a very well mixed medium. Such a value seems applicable to sediment layers. A substantially smaller value could be applied for the water column, but 0.25 g m^{-3} seems appropriate considering that such an average concentration may imply the presence of rather large anaerobic water masses within a compartment.

Table 10.10: *Definitions of the parameters in the above equations for SWOXYPARWK. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input/output	Definition	Units
Cox	OXY	dissolved oxygen concentration	g $m^{-3}_{\mathscr{b}}$
$Coxc$	$CoxPart$	critical dissolved oxygen concentration	g $m^{-3}_{\mathscr{w}}$
ϕ	$POROS$	porosity (Section 1.6.1)	-
$SWOXY$	$SWWaterKch$	switch for oxidising or reducing cond. water column	-
$SWOXY$	$SWPoreChS1$	switch for oxidising or reducing cond. sediment S1	-
$SWOXY$	$SWPoreChS2$	switch for oxidising or reducing cond. sediment S2	-

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10.6 Volatilisation

PROCESS: VOLAT_i

Transfer of dissolved organic micropollutants from the water column to the atmosphere is called volatilization. Transfer in the opposite direction is called intake. Both processes may occur in the model, depending on the direction of the concentration gradient. However, intake is usually not relevant as the concentration of a micropollutant in the atmosphere is almost always negligibly small. For this reason the overall process is given the generally accepted name 'volatilization'. This process only applies to water segments that are in contact with the atmosphere. The volatilization rate equals 0 in all other segments.

The model formulations for both processes are based on the double film theory for diffusive transport of a substance across gas-liquid interfaces as described by Liss and Slater (1974). Further background and literature references can be found in Lyman et al. (1990). According to the double film theory, the air-water interface consists of two stagnant layers: a gas film and a liquid film. In steady-state, the flux across the gas film equals the flux across the liquid film. Both fluxes can be calculated according to a finite difference approximation of Fick's Law.

Equilibrium is assumed between the concentrations of the micropollutant at the interface of the gas film and the liquid film according to Henry's Law. The concentration of a micropollutant in the atmosphere is not modelled but can be supplied by the user as boundary condition.

Implementation

The process VOLAT is implemented for the following substances:

- ◇ OMP (unspecified organic micropollutant),
- ◇ HCH (hexachlorohexane),
- ◇ HCB (hexachlorobenzene),
- ◇ 153 (PCB 153),
- ◇ BaP (Benzo[a]pyrene),
- ◇ Flu (fluoranthene),
- ◇ Diu (diuron),
- ◇ Atr (atrazine) and
- ◇ Mef (mevinphos).

The names (i) of these substances are known to the model, and have to be part of the relevant input parameters (see Table 10.11 with parameter definitions). The processes in the model are generic. They are similar for all substances. Default values for the properties of the above substances are substance specific.

OMP can be any micropollutant. The default values of the input parameters for OMP are meaningless. For instance, PCB 52 can be simulated as OMP (but also as PCB153) by replacing the values of the input parameters by those for PCB 52.

The transfer coefficients k_l and k_g are inputs to VOLAT. These parameters are calculated with 'process' TRCOEF_(i) . The (freely) dissolved fraction of a micropollutant fdf concentration is also input to VOLAT_(i) . This parameter is calculated with partitioning process PARTWK_(i) .

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Formulation

The volatilization rate for a specific water segment is equal to:

$$Rvol = \frac{kvol \times (Cd - Cde)}{H}$$

with:

Cd	freely dissolved micropollutant concentration [g m^{-3}]
Cde	freely dissolved micropollutant concentration in equilibrium [g m^{-3}]
H	water depth [m]
$kvol$	overall transfer coefficient for volatilization [m d^{-1}]
$Rvol$	volatilization rate [g m^{-3} d^{-1}]

The dissolved concentrations follow from:

$$Cd = fdf \times Ct$$
$$Cde = \frac{Cg}{He}$$

with:

Ct	total micropollutant concentration [g m^{-3}]
Cg	micropollutant concentration in the atmosphere [g m^{-3}]
fdf	freely dissolved micropollutant fraction [-]
He	dimensionless Henry's constant at ambient temperature [(mol m^{-3}) (mol m^{-3})$^{-1}$]

The overall transfer coefficient k_{vol} consists of contributions for the gas film and the liquid film. The reciprocals can be interpreted as resistances. Adding these resistances results in:

$$k_{vol} = 1/\left(\frac{1}{k_l} + \frac{1}{(He \times k_g)}\right)$$

with:

k_l	transfer coefficient for the liquid film [m d^{-1}]
k_g	transfer coefficient for the gas film [m d^{-1}]

The dimensionless Henry's constant He at ambient temperature is derived from Henry's constant on the basis of partial vapour pressure (He_{pr} in Pa.m^3.mol^{-1}) at reference temperature. In literature this constant is usually given for reference temperature 20 °C. The following formula is used to calculate the dimensionless Henry's constant He at ambient temperature:

$$He = \frac{Ng}{Nl} \times \mathrm{e}^{(a_1 + a_2/(T+273.15))}$$
$$Ng = \frac{P}{Rg \times (T_{ref} + 273.15)}$$
$$a_2 = (T_{ref} + 273.15) \times (\ln(He_{mr}) - a_1)$$
$$He_{mr} = He_{pr} \times \frac{Nl}{P}$$

with:

a_1	temperature coefficient for volatization entropy [-]
a_2	temperature coefficient for volatilization enthalpy [K^{-1}]

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He_{mr}	ref. Henry's constant on the basis of mole fraction [(molefr gas) (molefr water)$^{-1}$]
He_{pr}	ref. Henry's constant on the basis of vapour pressure [Pa m^3 mol^{-1}]
Ng	number of moles in a m^3 gas [m^{-3}]
Nl	number of moles in a m^3 water (55510 m^{-3})
P	atmospheric pressure (1.01×10^5 Pa)
Rg	the gas constant (8.314 Pa m^3 mol^{-1} K^{-1})
T	ambient temperature [°C]
T_{ref}	reference temperature [°C]

Coefficient a_2 represents the specific enthalpy of volatilization for the micropollutant, divided by the gas constant ($\Delta H^\circ / Rg$). The coefficient a_1 is an input, which can be derived from the specific entropy of volatilization for the micropollutant, divided by the gas constant ($\Delta S^\circ / Rg$). Literature sometimes reports data on the thermodynamic property ΔS°(in [kJ mol^{-1} K^{-1}]), that can be used to calculate Henry's constant at ambient temperature T. The reference temperature T_{ref} and the He_{pr} are also inputs.

The various constants of Henry at a specific temperature are related in the following way:

$$He_p = \frac{Pm}{Cd} = He \times R \times (T_{ref} + 273.15)$$

$$He_p = He_m \times R \times (T_{ref} + 273.15) \times \frac{Ng}{Nl} = He_m \times \frac{P}{Nl}$$

$$He_m = \mathrm{e}^{\frac{-\Delta H^o}{Rg \times (T+273.15)} + \frac{\Delta S^o}{Rg}}$$

with:

He	dimensionless Henry's constant on the basis of concentration [(mol m^{-3}) (mol m^{-3})$^{-1}$]
He_m	Henry's constant on the basis of mole fraction [(molefr gas).(molefr water)$^{-1}$]
He_p	Henry's constant on the basis of vapour pressure [Pa.m^3 mol^{-1}]
Pm	partial vapour pressure of a micropollutant [Pa]
R	universal gas constant [Pa.m^3 mol^{-1} K^{-1}]
ΔH°	enthalpy of volatilization for a micropollutant [kJ mol^{-1}]
ΔS°	entropy of volatilization for a micropollutant [kJ mol^{-1} K^{-1}]

Directives for use

- ◇ If no information on the input for a_1 ($= TFHe$) is available, a reasonable value is 20. This value implies a temperature dependence comparable to a Q_{10} of 5, a five-fold increase of He if the temperature rises with 10 degrees.
- ◇ Henry's constant He_{pr} ($= HeTref$) gives some insight into the controlling rate processes. This parameter may range from less than 10^{-2} to up to 10^3 Pa m^3 mol^{-1}:
  - ▫ In the range of 10^{-2} to 1.0 Pa m^3 mol^{-1} the micropollutant volatilizes slowly at a rate dependent on He_{pr}. The gas-phase resistance dominates the liquid-phase resistance by a factor of at least 10. The rate is controlled by slow molecular diffusion through air.
  - ▫ In the range of 1.0 to 10^2 Pa m^3 mol^{-1} the liquid-phase and the gas-phase resistance are both important. Volatilization for pollutants in this range is less rapid than for pollutants in a higher range of He_{pr}, but is still a significant transfer mechanism. Polycyclic aromatic hydrocarbons (PAH's) are in this range.
  - ▫ When He_{pr} is higher than 102 Pa m^3 mol^{-1}, the resistance of the water film dominates by a factor of at least 10. The transfer is liquid-phase controlled. Most hydrocarbons are in this range.

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◇ Note that the temperature at which a Henry's constant is measured in the literature T_{ref} should be used as model input.

Additional references

Mackay et al. (1980), Ten Hulscher et al. (1992)

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Table 10.11: *Definitions of the parameters in the above equations. (i) is a substance name.*

Name in formulas	Name in input	Definition	Units
a_1	$TFHe(i)$	temperature coefficient for volatization entropy	-
a_2	-	temperature coefficient for volatilization enthalpy	K^{-1}
Cd	-	dissolved micropollutant concentration	$g.m^{-3}$
Cde	-	freely dissolved micropollutant concentration in equilibrium with the atmosphere	$g.m^{-3}$
Cg	$Atm(i)$	micropollutant concentration in the atmosphere	$g.m^{-3}$
Ct	(i)	total micropollutant concentration in the water	$g.m^{-3}$
fdf	-	freely dissolved micropollutant fraction	-
H	$Depth$	depth of the upper water segment	m
He	-	dimensionless Henry's constant of micropollutant (i) at ambient temperature [$(mol.m^{-3}).(mol.m^{-3})^{-1}$]	-
He_{mr}	-	Henry's constant of micropoll. (i) on the basis of mole fractions at ref. Temp.[(mfr.Gas).$(mfr.water)^{-1}$]	-
He_{pr}	$HeTref(i)$	Henry's constant of micropollutant (i) on the basis of vapour pressure at reference temperature	$Pa.m^3.mol^{-1}$
k_l	-	transfer coefficient for a micropollutant for the liquid film	$m.d^{-1}$
k_g	-	transfer coefficient for a micropollutant for the gas film	$m.d^{-1}$
N_g	-	number of moles in a m^3 gas	m^{-3}
N_l	-	number of moles in a m^3 water	m^{-3}
P	-	atmospheric pressure	Pa
R	-	universal gas constant	$Pa.m^3.mol^{-1}.K^{-1}$
$Rvol$	-	volatilization rate	$g.m^{-3}.d^{-1}$
T	$Temp$	ambient water temperature	°C
T_{ref}	$Tref(i)$	reference temperature	°C

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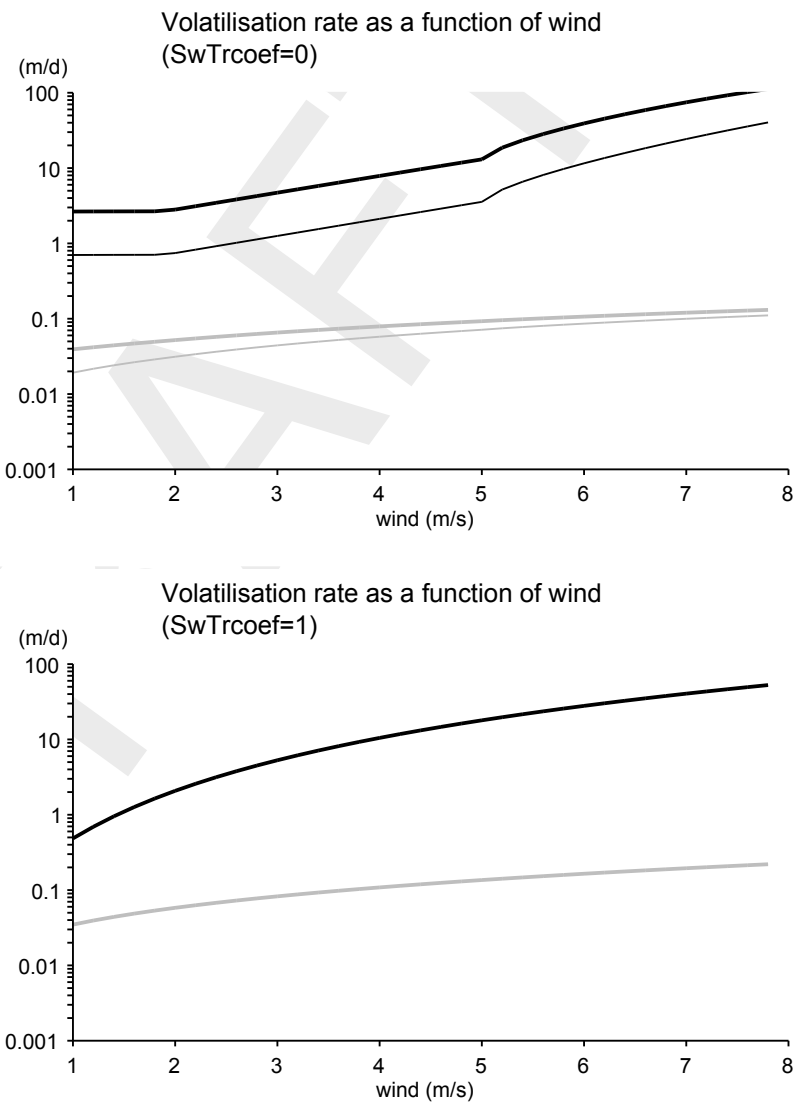

Figure 10.1: *Liquid-air exchange rate ($kvol$) for a very volatile pollutant: toluene (dashed lines: $He_{pr} = 660$) and a non-volatile pollutant lindane (solid lines: $He_{pr} = 0.48$ Pa.m^3.mole^{-1}). Values of kl and kg for $kvol$ were calculated using the two options implemented in process TRCOEF (1: Water flow velocity = 0.5 m s^{-1}, 2: Water flow velocity = 2.0 m s^{-1}).*

10.7 Transport coefficients

PROCESS: TRCOEF_i

The transfer coefficients k_l and k_g are used to quantify the exchange of organic micropollutants between water and atmosphere in process VOLAT_i. The process of mass exchange is also indicated as volatilization. The coefficients relate to the double film theory, according to which this process has been formulated by Liss and Slater (1974). Two transfer coefficients have to be determined, k_l for the liquid film and k_g for the gas film bordering the interface between water and atmosphere. These coefficients are in fact mass transfer velocities.

Numerous empirical relations exist, that describe the transfer coefficients as functions of the wind speed and/or the water flow velocity (Lyman et al., 1990). Two options have been implemented, for flowing water systems and for stagnant water systems respectively:

- ◇ Option 0 is based on the water flow velocity, the wind velocity and the molecular weight of the pollutant. This method was developed for Henry's constants ranging from 1 to 102 Pa m^3 mol^{-1} and for molecular weights exceeding 65 g mol^{-1}, but will hold for a broader range as well. The formulations are suitable for water systems, in which flow is caused by the force of gravity, such as rivers and estuaries.
- ◇ Option 1 is based on formulations of O' Connor (1983) (as used in IMPAQT; IMPAQT UM (1996)), using wind velocity and the molecular diffusion coefficients of the micropollutant in gas and water. The formulations were originally developed for stagnant systems, such as lakes, and therefore do not include the influence of water flow velocity.

Implementation

The micropollutant specific transfer coefficients k_g and k_l are input parameters to process VOLAT_(i). Process TRCOEF_(i) has been implemented for the same substances (i) as process VOLAT. The names of these substances are known to the model, and have to be part of the names of the relevant input parameters (see Table 10.11 with parameter definitions below). Default values for the properties of the above substances are available.

An option can be selected by giving input parameter $SWTrCoef$ value 0 (option 0) or value 1 (option 1).

Formulation

Option 0

This method is suitable for flowing water systems, such as rivers and estuaries. The transfer coefficients are formulated as the following functions of both the water flow velocity and the wind speed:

$$k_g = 273.15 \times (W + v) \times \sqrt{\frac{18}{Mw}}$$

for $W < 1.9$ m s^{-1}:

$$k_l = 5.64 \times \left(\frac{v^{0.969}}{H^{0.673}} \right) \times \sqrt{\frac{32}{Mw}}$$

for 1.9 m s$^{-1} \leq W < 5$ m s^{-1}:

$$k_l = 5.64 \times \left(\frac{v^{0.969}}{H^{0.673}} \right) \times \sqrt{\frac{32}{Mw}} \times e^{(0.526 \times (W - 1.9))}$$

for $W \geq 5$ m s^{-1}:

$$k_l = 5.64 \times \left(\frac{v^{0.969}}{H^{0.673}} \right) \times \sqrt{\frac{32}{Mw}} \times e^{(0.526 \times (5.0 - 1.9))} \times \left(1 + (W - 5.0)^{0.7}\right)$$

with:

Mw	molecular weight of the micropollutant [g mol^{-1}]
v	water flow velocity [m s^{-1}]
W	windspeed at 10 meters above water level [m s^{-1}]

The water flow velocity v has to be larger than a critical small value (0.001 m s^{-1}). When smaller than the critical value, v is set equal to this value.

Option 1

This method is suitable for stagnant water systems, such as lakes. The transfer coefficients are formulated as the following functions of the friction velocity and the Schmidt numbers for air and water:

$$k_g = 86\,400 \times \left(0.001 + 0.0463 \times \frac{u}{Sc_g^{0.67}} \right)$$

for $u < 0.3$ m s^{-1}:

$$k_l = 86\,400 \times \left(10^{-6} + 0.0144 \times \frac{u^{2.2}}{\sqrt{Sc_l}} \right)$$

for $u \geq 0.3$ m s^{-1}:

$$k_l = 86\,400 \times \left(10^{-6} + 0.00341 \times \frac{u}{\sqrt{Sc_l}} \right)$$

with:

Sc_g	Schmidt number for the micropollutant in the atmosphere [-]
Sc_l	Schmidt number for the micropollutant in the water [-]
u	friction velocity [m.s^{-1}]

The friction velocity at the water surface u is a function of the wind speed. The Schmidt numbers are derived from the viscosity, density and the molecular diffusion coefficient in water and air, and are corrected for temperature.

$$u = 0.01 \times W \times \sqrt{(6.1 + 0.63 \times W)}$$

$$Sc_g = 86\,400 \times \frac{\eta_g}{\rho_g \times D_g}$$

$$Sc_l = 86\,400 \times \frac{\eta_l}{\rho_l \times D_l}$$

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$$\rho_g = \frac{1.293}{1 + 0.00367 \times T}$$
$$\rho_l = 1\,000 - 0.088 \times T$$
$$\eta_g = 10^{-5} \times (1.32 + 0.009 \times T)$$
$$\eta_l = 0.001$$

with:

D_g	molecular diffusion coeff. of micropollutant in air [m^2 d^{-1}]
D_l	molecular diffusion coeff. of micropollutant in water [m^2 d^{-1}]
T	ambient temperature [°C]
ρ_g	density of air [kg m^{-3}]
ρ_l	density of water [kg m^{-3}]
η_g	dynamic viscosity of air [Pa s^{-1}]
η_l	dynamic viscosity of water [Pa s^{-1}]

Directives for use

- ◇ Wind speed and water flow velocity are provided in [m s^{-1}], whereas the transfer coefficients are calculated in [m day^{-1}]. Differences in time units between the various (input) parameters have been taken into account in the equations by means of the conversion number 86 400, the number of seconds in a day.
- ◇ Figure 10.1 of process VOLAT_(i) shows the dependency of the windspeed and the water flow velocity for the overall transfer coefficient for both calculation methods.

Additional references

O' Connor and St. John (1982)

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Table 10.12: *Definitions of the parameters in the above equations for TRCOEF_(i). (i) is a substance name.*

Name in formulas	Name in input	Definition	Units
D_g	$GDif(i)$	molecular diffusion coeff. of micropol. (i) in air	$m^2\ d^{-1}$
D_l	$LDif(i)$	molecular diffusion coeff. of micropol. (i) in water	$m^2\ d^{-1}$
H	$Depth$	depth of the upper water segment	m
k_l	$Kl(i)$	transfer coefficient for micropollutant (i) for the liquid film	$m\ d^{-1}$
k_g	$Kg(i)$	transfer coefficient for micropollutant (i) for the gas film	$m\ d^{-1}$
Mw	$Mol(i)$	molecular weight of micropollutant (i)	$g\ mol^{-1}$
$option$	$SWTrCoef$	switch that allows selection of one of the options	-
Sc_g	-	Schmidt number for a micropollutant in the atmosphere	-
Sc_l	-	Schmidt number for a micropollutant in the water	-
u	-	friction velocity at the water surface	$m\ s^{-1}$
v	$Velocity$	water flow velocity	$m\ s^{-1}$
W	$VWind$	wind speed at 10 meter above water level	$m\ s^{-1}$
T	$Temp$	ambient water temperature	°C
η_g	-	dynamic viscosity of air [Pa s^{-1}]	$kg\ m^{-1}.s^{-1}$
η_l	-	dynamic viscosity of water [Pa s^{-1}]	$kg\ m^{-1}.s^{-1}$
ρ_g	-	density of air	$kg\ m^{-3}$
ρ_l	-	density of water	$kg\ m^{-3}$

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10.8 Settling of micropollutants

PROCESS: SED_(i)

Organic micro-pollutants adsorb to detritus and algae. Heavy metals also adsorb to suspended inorganic matter. The micro-pollutants settle on the sediment together with these substances. After settling the micro-pollutants become part of the sediment micro-pollutant pools, depending on the way of modelling the sediment. The micro-pollutant pools in the sediment are:

1 the same substances (i) when sediment layers are simulated in a generic way; or
2 the connected (i)S1/2 substances for the S1/S2 approach.

When the S1/S2 approach is followed, the micropollutants are allocated to the sediment micropollutant pools as follows:

$$\begin{array}{ccccc} \mathbf{MP} & \Longrightarrow & \mathbf{MPS1} & \Longrightarrow & \mathbf{MPS2} \\ settling & & burial & & \\ ====== Water = || = Sediment ====== & & & & \end{array}$$

Process SED_(j) delivers the settling rates of the carrier substances (j). Process SED_(i) delivers the settling rates of the micropollutants (i). The rates are zero, when the shear stress exceeds a certain critical value, or when the water depth is smaller than a certain critical depth. The rates are calculated according to Krone (1962).

Implementation

Process SED_(i) has been implemented for the following substances:

heavy metals,

- Cd, Cu, Zn, Ni, Hg and Pb (group 1; sulfide forming heavy metals)
- Cr (group 2; hydroxide forming metal)
- As and Va (group 3; anion forming “metals”)

organic micropollutants,

- OMP (unspecified organic micropollutant)
- HCH (hexachlorohexane), HCB (hexachlorobenzene)
- 153 (PCB 153)
- BaP (Benzo[a]pyrene), Flu (fluoranthene);
- Diu (diuron)
- Atr (atrazine)
- Mef (mevinphos)
- (i)S1 with (i) one of the above names

Processes SED_(i) deliver the settling rates of the above mentioned micro-pollutants (i), for which processes SED_(j) (IM1-3, POC1-4, ALG01-30, Green, Diat), SUM_SEDIM (POC), and SEDPHBLO (PHYT; BLOOM) or SEDPHDYN (PHYT; DYNAMO) deliver the settling fluxes of the carrier substances (j). The individual substances (j) and the pertinent settling parameters are the additional input parameters required.

Processes PARTWK_(i) provide the concentrations of the micro-pollutants in the carrier substances (IM1, IM2, IM3, POC, PHYT) for this.

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Table 10.13 provides the definitions of the input parameters occurring in the formulations.

Formulation

The settling of the heavy metals is coupled to the settling of inorganic matter ($IM1/2/3$), particulate particulate organic detritus (POC) and algae biomass ($PHYT$). The settling of the organic micro-pollutants is coupled to the settling of particulate organic detritus (POC) and algae biomass ($PHYT$). The settling rates of all individual carrier substances are generated by process SED_(j) as the sum of zero-order and first-order kinetics. The rates are zero, when the shear stress exceeds a certain critical value, or when the water depth is smaller than a certain critical depth Krone (1962). The rates are calculated according to:

$$Rset_j = ftau_j \times \frac{Fset_j}{H}$$

$$\begin{aligned} if H < Hmin \\ Fset_j = 0.0 \\ else \\ Fset_j = \min\left(Fset'_j, \frac{Cx_j \times H}{\Delta t}\right) \\ Fset'_j = Fset0_j + s_j \times Cx_j \end{aligned}$$

$$\begin{aligned} if \tau = -1.0 \\ ftau = 1.0 \\ else \\ ftau_j = \max\left(0.0, \left(1 - \frac{\tau}{\tau c_j}\right)\right) \end{aligned}$$

where:

Cx	concentration of a carrier substance ([gDM m^{-3}] or [gC m^{-3}])
$Fset0$	zero-order settling flux of a carrier substance ([gDM m^{-2} d^{-1}] or [gC m^{-2} d^{-1}])
$Fset$	settling flux of a carrier substance ([gDMm^{-2} d^{-1}] or [gC m^{-2} d^{-1}])
$ftau$	shear stress limitation function [-]
H	depth of the water column [m]
$Hmin$	minimum depth of the water column for settling and resuspension [m]
$Rset$	settling rate of a carrier substance ([gDM m^{-3} d^{-1}] or [gC m^{-3} d^{-1}])
s	settling velocity of a carrier substance [m d^{-1}]
τ	shear stress [Pa]
τc	critical shear stress for the settling of a carrier substance [Pa]
Δt	timestep in DELWAQ (d)
j	index for carrier substance (j), IM1, IM2, IM3, POC1, POC2, POC3, POC4, ALG01-30 (BLOOM) or Green and Diat (DYNAMO)

The settling fluxes of the aggregated carrier substances POC and PHYT are computed as the sum of the fluxes of the individual detritus components (POC1-4) or the individual algae species.

The settling of micro-pollutants is coupled to the settling of carrier substances as follows:

$$Rsmp_{i,j} = fs_{i,j} \times Rset_j$$

where:

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$fs_{i,j}$	conc. of micro-pollutant i in carrier substance j ([gX gDM^{-1}] or [gX gC^{-1}])
$Rset_j$	settling rate carrier substance j ([gDW m^{-3} d^{-1}] or [C m^{-3} d^{-1}])
$Rsmp_{i,j}$	settling rate of micro-pollutant i in carrier substance j [gX m^{-3} d^{-1}]
i	index for micro-pollutant (i)
j	index for carrier substance (j), IM1, IM2, IM3, POC or PHYT

Directives for use

- ◇ Tau can be simulated with process TAU. If not simulated or imposed Tau will have the default value -1.0, which implies that settling is not affected by the shear stress.
- ◇ Settling does not occur, when $Depth$ (acutally the water layer thickness) is smaller than the minimum thickness $MinDepth$ for settling, which has a default value of 0.1 [m]. When desired $MinDepth$ may be given a different value.
- ◇ The settling fluxes $fSed(i)$ and $fSed(j)$ are available as additional output parameters.

Table 10.13: *Definitions of the input parameters in the above equations for SED_(i).*

Name in formulas	Name in input	Definition	Units
Cx_j^1	(j^1)	concentration of carrier substance (j)	gC/DM m^{-3}
$Fset0_j$	$ZSed(j)$	zero-order sett. flux of carrier subst. (j)	gC/DM.m^{-2}d^{-1}
$Fset_j$	$fSedIM1^2$	settling flux of carrier substance IM1	gDM m^{-2} d^{-1}
	$fSedIM2^2$	settling flux of carrier substance IM2	gDM m^{-2} d^{-1}
	$fSedIM3^2$	settling flux of carrier substance IM3	gDM m^{-2} d^{-1}
	$fSedPHYT^2$	settling flux of carrier substance PHYT	gC m^{-2} d^{-1}
	$fSedPOCnoa^2$	settling flux of carrier substance POC without algae biomass	gC m^{-2} d^{-1}
$fs_{i,j}$	$Q(i)IM1^3$	metal conc. in inorg. part. fraction IM1	g gDW^{-1}
	$Q(i)IM2$	metal conc. in inorg. part. fraction IM2	g gDW^{-1}
	$Q(i)IM3$	metal conc. in inorg. part. fraction IM3	g gDW^{-1}
	$Q(i)PHYT$	micro-pollutant conc. in algae PHYT	g gC^{-1}
	$Q(i)POC$	micro-pollutant conc. in POC	g gC^{-1}
–	$Fr(i)IM1^3$	fraction metal ads. to inorg. IM1	-
–	$Fr(i)IM2$	fraction metal ads. to inorg. IM2	-
–	$Fr(i)IM3$	fraction metal ads. to inorg. IM3	-
–	$Fr(i)PHYT$	fraction micro-pollutant ads. to phyto-plankton	-
–	$Fr(i)POC$	fraction micro-pollutant ads. to POC	-
H	$Depth$	depth of the overlying water compartment	m
$Hmin$	$MinDepth$	minimum layer thickness for settling and resuspension	m
s_j	$VSed(j)$	settling velocity of carrier substance (j)	m d^{-1}

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Table 10.13: *Definitions of the input parameters in the above equations for SED_(i).*

Name in formulas	Name in input	Definition	Units
τ	Tau	shear stress	Pa
τc_j	$TaucS(j)$	crit. shear stress for settling of carrier substance (j)	Pa
Δt	$Delt$	timestep in DELWAQ	d

[1]) Carrier substances (j) are IM1, IM2, IM3, POC (POC1-4) and PHYT (ALG01-30 for BLOOM, or Green and Diat for DYNAMO).

[2]) Settling fluxes are delivered by processes SED_(j), SUM_SEDIM (POCnoa), and SEDPHBLO (PHYT – BLOOM) or SEDPHDYN (PHYT – DYNAMO).

[3]) Organic micro-pollutants and heavy metals are indicated with (i). All qualities and fractions are delivered by processes PARTWK_(i). The fractions are needed for the calculation of vertical mass transport in the water column.

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10.9 Sediment-water exchange of dissolved micropollutants

PROCESSES: SWEOMP_(I)

Dissolved organic micropollutants may be exchanged between sediment and overlying water by means of a number of advective and dispersive processes. Advective transport arises from seepage (upwelling or downwelling), that is calcuted from a seepage flow velocity. Dispersive transport arises from diffusion, bio-irrigation and flow induced dispersion. The overall dispersion coefficient is applied to calculate a dispersion flux proportional to a concentration gradient across the sediment-water interface.

The concentration gradient across the sediment-water interface is affected by sorption in the top sediment layer. If sorption is slow, dissolved and adsorbed concentrations are not in equilibrium in this top layer. For organic micropollutants it can be assumed that adsorption is always fast enough to establish equilibrium. Desorption will generally be much slower though, meaning that dissolved concentrations are often not in equilibrium.

Seepage, dispersion and sorption interact. Ideally, these processes should be modelled in a way that takes the effects of interaction into account. However, in the present transport formulations sorption is ignored, and only the dominant transport process is active.

Volume units refer to bulk (b) or to water (w).

Implementation

Process SWEOMP_(i) has been implemented for the following substances:

- ◇ OMP, OMP-dis, OMPS1, OMPS2 (any micropollutant); and
- ◇ 153, 153-dis, 153S1, 153S2 (PCB153).

Substance (i) concerns the micropollutant in the various dissolved and particulate phases in the model. The process formulations in the model are generic, as they are similar for all substances. Default values for process coefficients are substance specific. Consequently, the name (i) has to be added in the names of pertinent process coefficients.

For the substance name (i) equilibrium partitioning is simulated as based on the total concentration of this substance. For the substance name (i)-dis slow sorption is simulated in combination with equilibrium partitioning. In that case the micropollutant is simulated with two substance names, (i)-dis for the total dissolved concentration which is the sum of free dissolved and DOC-adsorbed micropollutant, and (i)-par for the total particulate micropollutant concentration which is the sum of POC-adsorbed and PHYT-adsorbed micropollutant.

Table 10.14 provides the definitions of the input parameters occurring in the formulations. A part of the input parameters, namely the dissolved concentrations, is calculated by processes PARTWK_(i), PARTS1_(i) and PARTS2_(i)

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Formulation

The advective transport flux at the sediment-water interface due to seepage is formulated as follows:

$$Rseep = \ vseep \times Cmpd$$
$$Cmpd = \begin{cases} Cmpd_{s1} = \ Cmpdf_{s1} + Cmpdoc_{s1} & \text{if } vseep \geq 0.0 \\ Cmpd_{w} = \ Cmpdf_{w} + Cmpdoc_{w} & \text{if } vseep < 0.0 \end{cases}$$

where:

$Cmpd$	total dissolved micropollutant concentration [$g.m^{-3}$]
$Cmpdoc$	DOC-bound dissolved micropollutant concentration [$g.m^{-3}$]
$Cmpdf$	freely dissolved micropollutant concentration [$g.m^{-3}$]
$Rseep$	seepage transport flux [$g.m^{-2}.d^{-1}$]
$vseep$	volumetric seepage velocity [$m.d^{-1}$]
$s1$	index for the top sediment S1
w	index for water

The advective transport flux between the two sediment layers S1 and S2 due to seepage is formulated similarly, but the dissolved concentrations apply to the sediment pools:

$$Cmpd = \begin{cases} Cmpd_{s2} = Cmpdf_{s2} + Cmpdoc_{s2} & \text{if } vseep \geq = 0.0 \\ Cmpd_{s1} = Cmpdf_{s1} + Cmpdoc_{s1} & \text{if } vseep < 0.0 \end{cases}$$

where:

$s1$	index for the top sediment S1
$s2$	index for the deep sediment S2

$Vseep$ has a positive value for upwelling, a negative value for downwelling. In the case of upwelling the dissolved micropollutants concentrations concern the sediment (S1 or S2). For downwelling the dissolved micropollutants concentrations concern the concentrations in the overlying water or in the top sediment (S1). These concentrations are delivered by processes PARTWK_(i), PARTS1_(i) and PARTS2_(i).

The dispersive transport flux at the sediment-water interface due bio-irrigation, flow induced dispersion and molecular diffusion is formulated as follows:

$$Rdisp = \phi_{s1} \times D_{sw} \times \frac{(Cmpd_{s1} - Cmpd_{w})}{L_{sw}}$$

where:

D	dispersion coefficient ($m^2.d^{-1}$)
L	mixing length (m)
$Rdisp$	dispersive transport flux ($g.m^{-2}.d^{-1}$)
ϕ	porosity of the sediment (-)
sw	index for the sediment-water interface
$s1$	index for the top sediment S1
w	index for water

A positive flux results in the transport of micropollutant from the sediment to the overlying water, a negative flux in the transport of micropollutant from the overlying water to the sediment.

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The dispersive transport flux between the top and deep sediment S1 and S2 is formulated as follows:

$$Rdisp = \phi_{s2} \times D_{ss} \times \frac{(Cmpd_{s2} - Cmpd_{s1})}{L_{ss}}$$

where:

ss	index for the interface of sediment S1 and S2
$s1$	index for the deep sediment S1
$s2$	index for the deep sediment S2

A positive flux results in the transport of micropollutant from sediment S1 to sediment S2, a negative flux in the transport of micropollutant from sediment S2 to sediment S1.

For the sediment-water interface only the dominant transport process is active in any time step as follows from:

Rseep = 0.0, if $|vseep| < \phi.s1.D_{sw}/L_{sw}$

Rdisp = 0.0, if $|vseep| \geq \phi.s1.D_{sw}/L_{sw}$

Both processes are always active for the interface between the two sediment layers.

The seepage and dispersion fluxes are truncated at half the mass of micropollutant stored in S1 when they are larger than this quantity in order guarantee numerical stability. The fluxes are larger are converted into rates (g.d-1) by multiplication with the area of the sediment-water interface. The seepage and dispersion rates are deducted from or added to total micropollutant (i)S1 and (i)S2 in the sediment and total micropollutant (i) in the overlying water. When a micropollutant is simulated with substances (i)-dis and (i)-par, the fluxes are abstracted from or allocated to dissolved micropollutant (i)-dis in the overlying water and abstracted from or allocated to total micropollutant (i)S1 and (i)S2 in the sediment.

Directives for use

1 $VSeep$ has a positive value for upwelling, a negative value for downwelling. It is defined as the flow velocity of water in sediment multiplied with the porosity.
2 *DisCoefSW* and *DisCoefSS* always have positive values. The minimal value of the dispersion coefficients is the molecular diffusion coefficient adjusted for tortuosity. This adjustment can be made by multiplication with $\phi 2$ (ϕ = porosity).
3 An indicative value for*MixLsw*and *MixLss* is 0.02 m.

References

None.

Table 10.14: *Definitions of the parameters in the above equations for SWEOMP_(i). (i) is a substance name. Volume units refer to bulk (b) or to water (w).*

Name in formulas	Name in input	Definition	Units
Cmpdfw	*Dis(i)*	freely dissolved micropollutant concentration water	$g.m^{-3}{}_w$

Table 10.14: *Definitions of the parameters in the above equations for SWEOMP_(i). (i) is a substance name. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
$Cmpdf_{s1}$	*Dis(i)S1*	freely dissolved micropollutant conc. in sediment S1	$g.m^{-3}\mathscr{w}$
$Cmpdf_{s2}$	*Dis(i)S2*	freely dissolved micropollutant conc. in sediment S2	$g.m^{-3}\mathscr{w}$
$Cmpdoc_{w}$	*Doc(i)*	DOC-bound micropollutant concentration in water	$g.m^{-3}\mathscr{w}$
$Cmpdoc_{s1}$	*Doc(i)S1*	DOC-bound micropollutant conc. in sediment S1	$g.m^{-3}\mathscr{w}$
$Cmpdoc_{s2}$	*Doc(i)S2*	DOC-bound micropollutant conc. in sediment S2	$g.m^{-3}\mathscr{w}$
Cmpd	*(i)-dis*	total dissolved micropollutant concentration in water	$g.m^{-3}\mathscr{w}$
D_{sw}	*DisCoefSW*	dispersion coefficient at the sediment-water interface	$m^2.d^{-1}$
D_{ss}	*DisCoefSS*	dispersion coefficient at the sediment S1/2 interface	$m^2.d^{-1}$
L_{sw}	*MixLsw*	mixing length across the sediment-water interface	m
L_{ss}	*MixLss*	mixing length across the sediment S1/2 interface	m
vseep	*VSeep*	volumetric seepage velocity	$m.d^{-1}$
Rdisp	-	dispersive transport rate	$g.m^{-2}.d^{-1}$
Rseep	-	seepage transport rate	$g.m^{-2}.d^{-1}$
ϕ_{s1}	*PORS1*	porosity of the top sediment S1	$m^3\mathscr{w}.m^{-3}\mathscr{b}$
ϕ_{s2}	*PORS2*	porosity of the deep sediment S2	$m^3\mathscr{w}.m^{-3}\mathscr{b}$

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10.10 General contaminants

PROCESS: CASCADE

The process CASCADE allows the user to model a small set of non-specific contaminants. Currently two types of processes are implemented for these contaminants: first-order decay and first-order transformation, that is:

- ◇ Substance 1, called *cascade1*, may be subject to decay and may be transformed into any of the four other substances, *cascade2*, *cascade3*, *cascade4* and *cascade5*.
- ◇ Similarly, substance *cascade2*, may be subject to decay and may be transformed into any of the three substances *cascade3*, *cascade4* and *cascade5*.
- ◇ Substance *cascade3*, may be subject to decay and may be transformed into *cascade4* and *cascade5*.
- ◇ Substance *cascade4*, may be subject to decay and may be transformed into *cascade5*.
- ◇ Substance *cascade5*, may be subject to decay only.

Thus you can define a *cascade* of transformation products, such as may be pertinent for metabolites of pharmaceuticals or a chain of radioactive elements.

Implementation

Process CASCADE has been implemented for these substances. At a minimum you must include *cascade1*, but all others are optional, as are the processes.

Table 10.15 provides the definitions of the input parameters occurring in the formulations.

Formulation

Decay is assumed to be first-order:

$$\frac{dC_i}{dt} = -d_i C_i$$

The transformation process of *cascade(i)* into *cascade(j)* (index j larger than index i) is also assumed to be of first-order:

$$\frac{dC_i}{dt} = -t_{ij} C_i$$
$$\frac{dC_j}{dt} = +t_{ij} C_i$$

where:

C_i	concentration of contaminant *cascade(i)* [$g.m^{-3}$]
C_j	concentration of contaminant *cascade(j)* [$g.m^{-3}$]
d_i	decay rate of contaminant *cascade(i)* [d^{-1}]
t_{ij}	transformation rate of contaminant *cascade(i)* into *cascade(j)*[d^{-1}]

The transformations are restricted to substances with a higher index (so *cascade2* cannot be formed from *cascade2*) to prevent "circular" transformations, but otherwise there are no restrictions. Substance *cascade2* may therefore simultaneously be transformed into *cascade3*, *cascade4* as well as *cascade5*, similarly for all others.

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Directives for use

At least *cascade1* must be present in the simulation.

As the actual contaminants that are to be modelled using this set of substances may be very diverse, there is not much guidance possible as to rate coefficients or the actual set of transformations.

References

This process was inspired by a similar capability in the WASP model from the US EPA.

Table 10.15: *Definitions of the specific parameters in the above equations for* cascade(i) .

Name in formulas	Name in input	Definition	Units
C_1	cascade1	Generic contaminant *cascade1*	$g.m^{-3}$
C_2	cascade2	Generic contaminant *cascade2*	$g.m^{-3}$
C_3	cascade3	Generic contaminant *cascade3*	$g.m^{-3}$
C_4	cascade4	Generic contaminant *cascade4*	$g.m^{-3}$
C_5	cascade5	Generic contaminant *cascade5*	$g.m^{-3}$
d_1	decay1	Decay rate constant for *cascade1*	d^{-1}
d_2	decay2	Decay rate constant for *cascade2*	d^{-1}
d_3	decay3	Decay rate constant for *cascade3*	d^{-1}
d_4	decay4	Decay rate constant for *cascade4*	d^{-1}
d_5	decay5	Decay rate constant for *cascade1*	d^{-1}
t_{12}	trans1to2	Transformation rate constant for *cascade1* to *cascade2*	d^{-1}
t_{13}	trans1to3	Transformation rate constant for *cascade1* to *cascade3*	d^{-1}
t_{14}	trans1to4	Transformation rate constant for *cascade1* to *cascade4*	d^{-1}
t_{15}	trans1to5	Transformation rate constant for *cascade1* to *cascade5*	d^{-1}
t_{23}	trans2to3	Transformation rate constant for *cascade2* to *cascade3*	d^{-1}
t_{24}	trans2to4	Transformation rate constant for *cascade2* to *cascade4*	d^{-1}
t_{25}	trans2to5	Transformation rate constant for *cascade2* to *cascade5*	d^{-1}
t_{34}	trans3to4	Transformation rate constant for *cascade3* to *cascade4*	d^{-1}
t_{35}	trans3to5	Transformation rate constant for *cascade3* to *cascade5*	d^{-1}

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t_{45}	trans4to5	Transformation rate constant for *cascade4* to *cascade5*	d^{-1}

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11 Heavy metals and radio-active isotopes

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11.1 Partitioning of heavy metals

PROCESS: PARTWK_i AND PARTS1/2_i

Partitioning is the process in which a substance is distributed among various dissolved, adsorbed and precipitated species. Heavy metals adsorb to inorganic matter components (IM1–3, dead organic matter components (particulate detritus POC and dissolved organic matter DOC) and phytoplankton (PHYT).

The partitioning of heavy metals caused by sorption is usually described as an equilibrium process by means of a linear partition coefficient, based on amounts of dry weight (inorganic particulate matter) or on amounts of organic carbon. The partition coefficients for the various inorganic and organic matter components may be different, although the coefficient for DOC is usually considered proportional to the coefficient for POC. Copper for instance adsorbs rather strongly to organic components compared to other metals. Arsenic is predominantly adsorbed on organic components.

The adsorption capacity of inorganic matter mainly depends on the contents of iron oxyhydroxides, aluminium hydroxides, manganese oxide and clays such as illite. Moreover, the adsorption is strongly dependent on the pH, the redox-potential and complexation, and weakly dependent on temperature. The dependency on redox potential is connected with the reduction of iron and manganese at low redox potential, implying the loss of adsorption capacity especially in sediments. The complexation in solution is metal specific and depends on the abundance of ligands such as hydroxyl (OH^-), bicarbonate, chloride, sulfide and sulfate. Complexation is therefore much stronger in the sediment than in the water column. However, the effects of pH and complexation on sorption can be taken into account, when using so-called repro-functions for the partition coefficient.

Vanadium and arsenic (not truly one of the heavy metals) show basically different sorption behaviour compared to the sulfide forming heavy metals like zinc and copper, since they are present in anionic forms in stead of in cationic form. Arsenic occurs in arsenate, that is As(V), in an oxidising environment and as dissolved arsenic hydroxide, that is As(III), in a reducing environment. Chromium is predominantly present as cationic Cr(III) forms, but chromium may also be present partially in anionic Cr(VI) form, that is as chromate. The adsorption of anions becomes stronger with decreasing pH, the adsorption of metal cations becomes weaker with decreasing pH.

Whereas chromium may precipitate as hydroxide both at oxidising and reducing conditions, arsenic and vanadium do not precipitate due to high solubility. The sulfide forming heavy metals may precipitate as sulfides at reducing conditions, especially in sediments. The co-precipitation with iron(II) sulfides is likely to occur.

Slow diffusion in solid matter has been acknowledged to take place after fast equilibrium adsorption or prior to fast equilibrium desorption. Therefore, the sorption flux can be calculated according to equilibrium partitioning or slow sorption by choosing one of the available options.

DELWAQ only actually simulates the total concentration (or the total particulate and total dissolved concentrations) of a heavy metal. The partitioning process delivers the dissolved, the adsorbed and the precipitated species as fractions of the total concentration, as well as the aggregate sorption/precipitation flux.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

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Implementation

Processes PARTWK_(i) are generic and can be used for water and sediment compartments. For the S1/2 option for the sediment processes PARTS1_(i) and PARTS2_(i) can be used.

The substances in the sediment are modeled as 'inactive' substances. Whereas PARTWK_(i) needs concentrations g m^{-3} as input, PARTS1_(i) and PARTS2_(i) require total quantities per sediment layer (g) as input with only one exception (DOC in g $m^{-3}w$). The formulations are identical for PARTWK_(i), PARTS1_(i), PARTS2_(i) with two exceptions: The substances in the sediment are modeled as 'inactive' substances. Whereas PARTWK_(i) needs concentrations g m^{-3} as input, PARTS1_(i) and PARTS2_(i) require total quantities per sediment layer (g) as input with only one exception (DOC in g $m^{-3}w$). The formulations are identical for PARTWK_(i), PARTS1_(i), PARTS2_(i) with two exceptions:

- ◇ the correction of DOC for porosity is not carried out in PARTWK_(i); and
- ◇ PARTS1_(i) and PARTS2_(i) carry out a conversion from concentration units into quantity units and vice versa, and therefore need the input of layer thickness and surface area.

The processes have been implemented for the following substances:

- ◇ Cd, Cu, Zn„ Ni, Hg, Pb (group 1, sulfide forming heavy metals)
- ◇ Cr (group 2, hydroxide forming metals)
- ◇ As and Va (group 3, anion forming "metals")
- ◇ (i)S1 and (i)S2 with (i) each of the above names

The above substance names concern the situation, where equilibrium partitioning is simulated. The simulation of slow sorption requires the use of two simulated substances for heavy metal in stead of the one simulated substance (i). The names of these substances are (i)-dis and (i)-par. (i)-dis is the total dissolved concentration, the sum of free dissolved and DOC-adsorbed heavy metal. (i)-par is the total particulate heavy metal concentration.

The process formulations depend on the group that a heavy metals belongs to, and default values for properties are substance specific. The private parameters $HMGroup1/2/3$ identify the group to which a heavy metal belongs.

The concentrations of inorganic matter ($Cim1$–3), detritus ($Cpoc$), dissolved organic matter ($Cdoc$) and phytoplankton ($Calg$) can either be calculated by the model or be imposed on the model via its input. In case of the former Cpoc is generated by processes COMPOS, S1_COMP and S2_COMP. $Calg$ is generated by processes PHY_BLO (BLOOM) or PHY_DYN (DYNAMO), S1_COMP and S2_COMP.

Precipitation is dependent on the oxygen concentration. The required dissolved sulfide concentrations can be generated by processes SPECSUD, SPECSUDS1 and SPECSUDS2. Process SWOXYPARWK generates the input parameter $SWWaterKCh$, that indicates the oxidising (oxic) or reducing (anoxic) conditions.

Tables 11.1, 11.2 and 11.3 provide the definitions of the input parameters occurring in the formulations. Tables 11.4 and 11.5 contain the definitions of the output parameters.

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Formulation

The partitioning of group 1 heavy metals is different for oxidising conditions and for reducing conditions. The prevailing conditions are defined with switch $SWOXY$, the value of which depends on the dissolved oxygen concentration. The value of the switch is determined by process SWOXYPARWK or can be provided as input parameter.

Oxidising conditions (SWOXY = 1), without precipitation

The fractions of the dissolved and adsorbed species add up to one. Consequently these fractions as resulting from an equilibrium are computed with:

$$fdf = \frac{\phi}{\phi + \sum_{i=1}^{3}(Kpim'_i \times Cim_i) + Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

for i = 1, 2 and 3:

$$fim_i = \frac{(1 - fdf) \times Kpim'_i \times Cim_i}{\sum_{i=1}^{3}(Kpim'_i \times Cim_i) + Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

$$fdoc = \frac{(1 - fdf) \times Kppoc' \times Xdoc \times Cdoc}{\sum_{i=1}^{3}(Kpim'_i \times Cim_i) + Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

$$fpoc = \frac{(1 - fdf) \times Kppoc' \times Cpoc}{\sum_{i=1}^{3}(Kpim'_i \times Cim_i) + Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

$$falg = (1 - fdf - fim_1 - fim_2 - fim_3 - fdoc - fpoc)$$

where:

$Calg/poc/doc$	concentration of algae biomass, dead particulate organic matter matter, and dissolved organic matter [gC m^{-3}]
Cim_i	concentration of inorganic matter fractions i = 1, 2 and 3 [gDW m^{-3}]
$falg/poc/doc$	fraction of micropollutant adsorbed to algae, dead particulate organic matter dissolved organic matter, [-]
fim_i	fraction of micropollutant adsorbed to inorganic matter fractions i = 1, 2 and 3 [-]
fdf	freely dissolved fraction of a micropollutant [-]
$Kpalg/poc'$	partition coefficient for algae and dead particulate organic matter [m^3_w gC^{-1}]
$Kpim'_i$	partition coefficient for inorganic matter fractions i = 1, 2 and 3 [m^3_w gDW^{-1}]
$Xdoc$	adsorption efficiency of DOC relative to POC [-]
ϕ	porosity ([m^3_w m^{-3}]; equal to 1.0 for the water column)

In case of PARTS1_(i) and PARTS2_(i), $Cdoc$ is corrected for porosity considering the fact that DOC input only in this case is specified as concentrations in pore water:

$$Cdoc = DOC \times \phi$$

All substance quantities in the above partitioning equations are converted in case of PARTS1_(i) and PARTS2_(i) into bulk concentrations by dividing with the volume of the layer ($V = Z \cdot A$).

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The partition coefficients in the above equations expressed in [m^3_w gC^{-1}] or in [m^3_w gDW^{-1}] are derived from the input parameters expressed in [m^3_w kgC^{-1}] or [m^3_w $kgDW^{-1}$]:

$$Kpim'_i = \frac{Kpim_i}{1000} \quad \text{for} \quad i = 1, 2 \text{ and } 3$$

$$Kppoc' = \frac{Kppoc}{1000}$$

$$Kppoc' = \frac{Kppoc}{1000}$$

The simulation of slow partitioning is optional. Equilibrium partitioning (option 0) occurs when the half-life-time of the adsorption process or the desorption process is equal to or smaller than 0.0. Slow partitioning (option 1) is applied when one of these half-life-times is bigger than 0.0.

Option 0

When $tads$ and $tdes \leq 0.0$, the above equations are applied to calculate the fractions in equilibrium.

Option 1

When $tads$ or $tdes > 0.0$, the above equations are also applied to calculate the fractions in equilibrium. In addition the various metal fractions are corrected for slow sorption proportional to the difference between the equilibrium fractions and the fractions in the previous time step. No distinction is made regarding the various particulate adsorbents. Average sorption rates are used for inorganic matter, POC and phytoplankton. The calculation using first-order sorption reaction rates derived from half-life-times proceeds as follows:

$$fp' = fim'_1 + fim'_2 + fim'_3 + fpoc' + falg' = \frac{Chmp'}{Chmt'}$$

$$fpe = fim_1 + fim_2 + fim_3 + fpoc + falg$$

and

$$ksorp = \begin{cases} \frac{\ln(2)}{tads} & \text{if } fp < fpe \\ \frac{\ln(2)}{tdes} & \text{if } fp \geq fpe \end{cases}$$

with

$$fp = fpe - (fpe - fp') \times \exp(-ksorp \times \Delta t)$$

$$fdf = fdfe \times \frac{(1 - fp)}{(1 - fpe)}$$

$$fdoc = fdoce \times \frac{(1 - fp)}{(1 - fpe)}$$

$$fim_i = fime_i \times \frac{fp}{fpe} \quad \text{for} \quad i = 1, 2 \text{ and } 3$$

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$$fpoc = fpoce \times \frac{fp}{fpe}$$

$$falg = falge \times \frac{fp}{fpe}$$

where:

$Chmt/hmp'$	total and particulate conc. of metal after the previous time-step [g m^{-3} ℓ]
$fimi'$	fractions of metal adsorbed to inorganic matter fractions I = 1, 2 or 3 after the previous time step [-]
$falg/poc'$	fractions of metal adsorbed to algae and dead particulate organic matter after the previous time step [-]
$fp'/p/pe$	total particulate metal fraction after the previous time-step, at the end of the present timestep, and in equilibrium [-]
$ksorp$	sorption reaction rate [d^{-1}]

For both options the sorption rate is calculated as:

$$Rsorp = \frac{fp \times Chmt' - Chmp'}{\Delta t}$$

where:

$Rsorp$	sorption rate [g m^{-3} ℓd^{-1}]
Δt	timestep of DELWAQ [d^{-1}]

The calculation of the rate also requires division with the volume of the volume of the sediment layer (V= Z.A) in case of PARTS1_(i) and PARTS2_(i).

The dissolved and particulate metal concentrations and the quality of the particulate organic fractions follow from:

$$Chmdf = \frac{fdf \times Chmt'}{\phi}$$

$$Chmdoc = \frac{fdoc \times Chmt'}{\phi}$$

$$Chmd = Chmdf + Chmdoc$$

$$Chmp = (fim_1 + fim_2 + fim_3 + fpoc + falg) \times Chmt'$$

$$Chmim_i = \frac{fim_i \times Chmt'}{Cpoc} \quad \text{for} \quad i = 1, 2 \quad \text{or} \quad 3$$

$$Chmpoc = \frac{fpoc \times Chmt'}{Cpoc}$$

$$Chmalg = \frac{falg \times Chmt'}{Calg}$$

For PARTS1_(i) and PARTS2_(i) the calculation of the dissolved concentrations also requires division with the volume of the layer ($V = Z \cdot A$).

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Oxidising conditions (SWOXY = 1), with precipitation

The above equations need a modification for group 2 metals such as chromium. These metals may precipitate as hydroxide. Consequently the metal fractions have to be corrected for a precipitated fraction, when the molar ion activity product calculated using the above formulations exceeds the solubility product. A correction factor for precipitation to be applied on the various sorbed metal fractions can be derived from the ratio of the dissolved concentration in equilibrium with the metal hydroxide and the dissolved concentration estimated on the basis of sorption only. The initial estimate of the freely dissolved chromium concentration resulting form the above equations is indicated with $Crdf'$. The molar freely dissolved concentration follows from:

$$Crdf' = Chmdf$$

$$Crdf'_m = \frac{Crdf'}{Mw \times 10^{+3}}$$

with:

$Crdf'_m$	molar freely dissolved chromium concentration [mol l^{-1}]
Mw	molecular weight of chromium [g mol^{-1}]

The solubility of metal hydroxide is proportional to the free metal ion concentration, which is derived from equilibrium equations for the three hydroxyl complexes that are formed by the metal. The equilibrium molar free chromium ion concentration in case of sorption only follows from:

$$OH = 10^{-(14-pH)}$$

$$Crfr'_m = \frac{Crdf'_m}{1 + 10^{logKCr_1} \times OH + 10^{logKCr_2} \times OH^2 + 10^{logKCr_3} \times OH^3}$$

where:

$Crfr'_m$	molar free chromium ion concentration [mol l^{-1}]
$logKCr1/2/3$	the three equilibrium constants for hydroxyl complexation of chromium [$^{10}\log((\text{l mol}^{-1})^{1,2or3})$]
OH	the hydroxyl concentration [mol l^{-1}]
pH	acidity [-]

The ion activity product based on this concentration and the solubility product are:

$$IAP = Crfr'_m \times OH^3$$

$$SOL = 10^{logKCrS}$$

where:

$logKCrS$	solubility equilibrium constant for chromium hydroxide [$^{10}\log(\text{mol l}^{-1})^4$]

Precipitation occurs only when $IAP > SOL$. Consequently a correction of the various chromium fractions is only carried when this condition is met. The correction factor for precipitation is derived from the equilibrium free chromium ion concentration:

$$Crfr_m = \frac{10^{logKCrS}}{OH^3}$$

$$Crdf_m = Crfr_m \times \left(1 + 10^{logKCr_1} \times OH + 10^{logKCr_2} \times OH^2 + 10^{logKCr_3} \times OH^3\right)$$

$$Crdf = Crdf_m \times Mw \times 10^{+3}$$

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$$fcor = \frac{Crdf}{Crdf'}$$

Multiplying this correction factor (< 1) with the initially estimated sorbed fractions delivers the actual fractions. Keeping in mind that all fractions add up to one, the precipated fraction fpr must be equal to:

$$fpr = 1 - fcor$$

The corrected sorbed fractions and concentrations for chromium are:

$$fdf = fdf' \times (1 - fpr)$$
$$fdoc = fdoc' \times (1 - fpr)$$
$$fim_i = fim_i' \times (1 - fpr) \quad \text{for} \quad i = 1, 2 \text{ or } 3$$
$$fpoc = fpoc' \times (1 - fpr)$$
$$falg = falg' \times (1 - fpr)$$
$$Chmdf = Crdf \times (1 - fpr)$$
$$Chmdoc = Chmdoc' \times (1 - fpr)$$
$$Chmd = Chmd' \times (1 - fpr)$$
$$Chmp = (fim_1 + fim_2 + fim_3 + fpoc + falg + fpr) \times Chmt'$$
$$Chmim_i = Chmim_i' \times (1 - fpr) \quad \text{for} \quad i = 1, 2 \text{ or } 3$$
$$Chmpoc = Chmpoc' \times (1 - fpr)$$
$$Chmalg = Chmalg' \times (1 - fpr)$$

The group 2 metals such as chromium have been excluded from slow sorption as a consequence of the correction for precipitation!

Reducing conditions (SWOXY = 0), without precipitation

Group 3 metals do not precipitate at all. Therefore no modification of the partitioning formulations is needed.

Reducing conditions (SWOXY = 0), with precipitation

Group 1 and group 2 metals may precipitate in reducing conditions. The required modification of the partitioning formulations has already been dealt with above in the case of group 2 metals, as there is no difference regarding the kind of precipitate formed between oxidising and reducing conditions. Group 1 metals however, the sulfide forming metals, precipitate as sulfides at reducing conditions and form two sulfide complexes at the same time (MeS^0 and $MeHS^+$). The solubility of the metal sulfides is so low, that sorption can be ignored. The computation starts with calculation of the molar total dissolved metal concentration from the equilibrium equations for solubility and complexation:

$$Chmdf_m = \frac{1 + 10^{logKhm_1} \times Csd + 10^{logKhm_2} \times Chsd}{10^{logKhmS} \times Csd}$$

$$Chmdf = Chmdf_m \times Mw \times 10^{+3}$$

where:

$Chmdf_m$	molar total dissolved metal concentration [mol l^{-1}]
Csd	molar dissolved sulfide S^{2-} concentration [mol l^{-1}]
$Chsd$	molar dissolved hydrogen sulfide HS^- concentration [mol l^{-1}]
$logKhm1/2$	the two equilibrium constants for sulfide complexation of a metal [$^{10}\log$(l mol^{-1})]
$logKhmS$	solubility equilibrium constant for metal sulfide [$^{10}\log((l\ mol^{-1})^2)$]
Mw	molecular weight of the metal [g mol^{-1}]

The molar dissolved sulfide and hydrogen sulfide concentrations are computed in processes SPECSUD(S1/2), using the pH, the total dissolved sulfide concentration and two equilibrium constants as input.

The fractions of the dissolved and precipitated species add up to one. Consequently the various concentrations and fractions are:

$$fdf = \frac{Chmdf_m \times \phi}{Chmt'}$$

$$fpr = 1 - fdf$$

$$fdoc = fim_1 = fim_2 = fim_3 = fpoc = falg = 0.0$$

$$Chmdoc = Chmim_1 = Chmim_2 = Chmim_3 = Chmpoc = Chmalg = 0.0$$

$$Chmd = Chmdf$$

$$Chmp = fpr \times Chmt'$$

Output

The process generates output for:

- ◇ the various particulate and dissolved heavy metals fractions;
- ◇ the total metal concentration, the freely dissolved concentration, the concentration adsorbed to DOC;
- ◇ the apparent overall partition coefficient; and
- ◇ the metal contents of total suspendid solids, particulate inorganic matter fractions, detritus and phytoplankton.

The metal content of total suspended solids and the apparent partition coefficient follow from:

$$Chmpt = \frac{Chmp \times 10^{+6}}{Css}$$

$$Kpt = \frac{Chmpt \times 10^{-3}}{Chmd + Chmdoc}$$

where:

Css	the total suspended solids concentration [g m^{-3}].
$Chmpt$	the metal content of total suspended solids [mg kg^{-1}].
Kpt	the apparent overall partition coefficient [m^3 kg^{-1}].

The contents of the individual particulate fractions are calculated in a similar way.

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Directives for use

- ◇ The partition coefficients for inorganic matter fractions, phytoplankton and POC have to be provided in the input of DELWAQ on the basis of [$m^{-3}_{\mathscr{w}}$ kgC^{-1}] or [$m^{-3}_{\mathscr{w}}$ kgDW^{-1}].
- ◇ The concentrations of $DOCS1/2$ for the S1/S2 sediment option have to be provided as pore water concentrations. In all other cases DOC needs to be provided as bulk concentrations. DOC is calculated as bulk concentration, when simulated with the model.
- ◇ The process of aging (internal diffusion in particles) may cause the apparent partition coefficient to increase over time. The partitioning in the sediment may therefore require a substantially higher partition coefficient than the partitioning in the water column.
- ◇ The formulations do not allow for an irreversibly adsorbed fraction. Such a fraction can be taken into account implicitly by reducing the load proportionally, or by increasing the partition coefficients and slowing down of the sorption process, which may be relevant for sediment compartments in particular.
- ◇ The partition coefficients for inorganic matter should be based on field partition coefficients, since the sorption capacity of sediments may vary substantially among water systems. In case three inorganic sediment fractions are considered one could take the partition coefficient for the finest fraction and derive the coefficient for the other two fractions by multiplication with the relative clay or iron content.
- ◇ The implementation uses several private parameters to indicate the metal group and the occurrence or absence of precipitation. These parameters should never be changed to ensure correct operation.
- ◇ Slow sorption requires the use of two simulated substances (total particulate and total dissolved) in stead of the one substance (total concentration), see above! All other input parameters and output parameters remain the same.

Additional references

WL | Delft Hydraulics (1992b), DiToro and Horzempa (1982), O' Connor and Connolly (1980), Rai et al. (1989), Schnoor et al. (1987)

Table 11.1: *Definitions of the input parameters in the above equations for PARTWK_(i) in relation to sorption. (i) is a substance name. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in input	Definition	Units
$Calg$	$PHYT^1$	phytoplankton concentration	gC $m^{-3}_{\mathscr{b}}$
$Cdoc$	DOC	dissolved organic matter conc.	gC $m^{-3}_{\mathscr{b}}$
Cim_i	IMi	conc. inorg. part. fractions i = 1,2,3	gDW $m^{-3}_{\mathscr{b}}$
$Cpoc$	$POCnoa^2$	particulate organic matter concentration without algae	gC $m^{-3}_{\mathscr{b}}$
$Chmt$	(i)	total metal concentration	g $m^{-3}_{\mathscr{b}}$
$Chmd$	$(i)-dis$	total dissolved metal concentration	g $m^{-3}_{\mathscr{b}}$
$Chmp$	$(i)-par$	total particulate metal concentration	g $m^{-3}_{\mathscr{b}}$
Css	SS^2	total suspended matter concentration	gDW $m^{-3}_{\mathscr{b}}$
$Kpalg$	$Kd(i)PHYT$	partition coefficient for phytoplankton (see directives!)	m^{-3} kgC^{-1}

continued on next page

Table 11.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
$Kpim_i$	$Kd(i)IMi$	part. coeff. for inorg. fractions i = 1,2,3	m^{-3} $kgDW^{-1}$
$Kppoc$	$Kd(i)POC$	partition coefficient for POC	m^{-3} kgC^{-1}
$SWOXY$	$SWWaterKCh$[3]	switch for oxidising or reducing conditions	-
$tads$	$HLTAds(i)$	half-life-time adsorption process	d
$tdes$	$HLTDes(i)$	half-life-time desorption process	d
$Xdoc$	$XDOC(i)$	ads. efficiency of DOC relative to POC	-
V	$Volume$	volume	m^{-3} b
ϕ	$POROS$	porosity	$m^3 w$ $m^{-3} b$
Δt	$Delt$	timestep	d

[1] Delivered by processes PHY_BLO (BLOOM) or PHY_DYN (DYNAMO).
[2] Delivered by process COMPOS.
[3] Can be computed by process SWOXYPARWK.
[4] Default value must not be changed.

Table 11.2: *Definitions of the input parameters in the above equations for PARTS1_(i) and PARTS2_(i) in relation to sorption. (i) is a substance name. (k) indicates sediment layer 1 or 2. Volume units refer to bulk (b) or to water (w).*

Name in formulas	Name in input	Definition	Units
A	$Surf$	surface area	m^2
$Calg$	$PHYTS(k)$[1]	phytoplankton quantity	gC
$Cdoc$	$DOCS(k)$	dissolved organic matter concentration	gC $m^{-3} w$
Cim_i	$IMiS(k)$	quantity of inorganic particulate fractions i = 1,2,3	gDW
$Cpoc$	$POCS(k)$[1]	particulate organic matter quantity	gC
$Chmt$	$(i)S(k)$	quantity total heavy metal	g
$Chmd$	$(i)S(k) - dis$	quantity total dissolved heavy metal	g
$Chmp$	$(i)S(k) - par$	quantity total particulate heavy metal	g
Css	$DMS(k)$[1]	quantity of total sediment	gDW
$Kpalg$	$Kd(i)PHYTS(k)$	partition coeff. for phytoplankton (see directives!)	m^{-3} kgC^{-1}

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Table 11.2 – continued from previous page

Name in formulas	Name in input	Definition	Units
$Kpimi$	$Kd(i)IMiS(k)$	part. coeff. for inorg. fractions i = 1,2,3	m^{-3} kgDW^{-1}
$Kppoc$	$Kd(i)POCS(k)$	part. coeff. for POC (see directives!)	m^{-3} kgC^{-1}
$SWOXY$	$SWPoreChS(k)$[2]	switch for oxidising or reducing conditions	-
$tads$	$HLTAds(i)S(k)$	half-life-time adsorption process	d
$tdes$	$HLTDes(i)S(k)$	half-life-time desorption process	d
$Xdoc$	$XDOC(i)$	ads. efficiency of DOC relative to POC	-
V	-	volume	$m^{-3}\ell$
Z	$ActThS(k)$	thickness of sediment layer	m
ϕ	$PORS(k)$	porosity	$m^3 w\, m^{-3}\ell$
Δt	$Delt$	timestep	d

[1] Delivered by processes S1_COMP and S1_COMP.
[2] Can be computed by process SWOXYPARWK.
[3] Default value must not be changed.

Table 11.3: *Definitions of the input parameters in the above equations for PARTWK_(i), PARTS1_(i) and PARTS2_(i) in relation to precipitation. (i) is a substance name. (k) indicates sediment layer 1 or 2.*

Name in formulas	Name in input	Definition	Units
$Chsd$	$DisHSWK$[1)] or $DisHSS(k)$	molar diss. hydrogen sulfide HS^- concentration	mol l^{-1}
Csd	$DisSWK$ or $DisSS(k)$	molar dissolved sulfide S^{2-} concentration	mol l^{-1}
$logKCr1$	$logK(i)OH1$	metal hydroxyl compl. constant (1xOH; group 2)	$^{10}\log$(l mol^{-1})
$logKCr2$	$logK(i)OH2$	metal hydroxyl compl. constant (2xOH; group 2)	$^{10}\log$((l mol^{-1})^2)
$logKCr3$	$logK(i)OH3$	metal hydroxyl compl. constant (3xOH; group 2)	$^{10}\log$((l mol^{-1})^3)
$logKCrS$	$logK(i)Sol$	metal hydroxide solubility constant (group 2)	$^{10}\log$((l mol^{-1})^4)
$logKhm1$	$logK(i)Saq$	metal sulfide S^{2-} complexation constant (group 1)	$^{10}\log$(l mol^{-1})

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Table 11.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
$logKhm2$	$logK(i)HSaq$	metal hydr. sulfide HS^- compl. constant (group 1)	$^{10}\log$(l mol^{-1})
$logKhmS$	$logK(i)Ss$	metal sulfide solubility const. (group 1)	$^{10}\log$((l mol^{-1})^2)
Mw_i	$MolWt(i)$	molecular weight of a metal	g mol^{-1}
pH	pH or $pHS(k)$	acidity	-

1) The sulfide concentrations can be generated by processes SPECSUD, SPESUDS1 and SPECSUDS2.

Table 11.4: *Definitions of the output parameters for PARTWK_(i). (i) is a substance name. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in output	Definition	Units
$Chmt$	$(i)tot$	total metal concentration	g m$^{-3}\mathscr{b}$
$Chmd$	$Dis(i)$	freely dissolved metal concentration	g m$^{-3}\mathscr{w}$
$Chmdoc$	$Doc(i)$	DOC adsorbed metal concentration	g m$^{-3}\mathscr{w}$
fdf	$Fr(i)Dis$	freely dissolved metal fraction (not bound to DOC!)	-
$fdoc$	$Fr(i)DOC$	fraction metal adsorbed to DOC	-
fim_1	$Fr(i)IM1$	fraction metal ads. to inorg. fraction IM1	-
fim_2	$Fr(i)IM2$	fraction metal ads. to inorg. fraction IM2	-
fim_3	$Fr(i)IM3$	fraction metal ads. to inorg. fraction IM3	-
$fpoc$	$Fr(i)POC$	fraction metal adsorbed to POC	-
$falg$	$Fr(i)PHYT$	fraction metal ads. to phytoplankton	-
fpr	$Fr(i)Sulf$	fraction metal precipitated	-
Kpt	$Kd(i)SS$	apparent overall partition coefficient for susp. solids	m^3 kgDW^{-1}
-	$Q(i)IM1$	metal content of inorg. matter fr. IM1	g gDW^{-1}
-	$Q(i)IM2$	metal content of inorg. matter fr. IM2	g gDW^{-1}
-	$Q(i)IM3$	metal content of inorg. matter fr. IM3	g gDW^{-1}
-	$Q(i)POC$	metal content of particulate detritus	g gC^{-1}
-	$Q(i)PHYT$	metal content of phytoplankton biomass	g gC^{-1}
$Chmpt$	$Q(i)SS$	metal content of total suspended solids	mg kgDW^{-1}

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Table 11.5: *Definitions of the output parameters for PARTS1_(i) and PARTS2_(i). (i) is a substance name. (k) indicates sediment layer 1 or 2. Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).*

Name in formulas	Name in output	Definition	Units
$Chmt$	$(i)S(k)tot$	total metal concentration	g m$^{-3}\mathscr{b}$
$Chmd$	$Dis(i)S(k)$	freely dissolved metal concentration	g m$^{-3}\mathscr{w}$
$Chmdoc$	$Doc(i)S(k)$	DOC adsorbed metal concentration	g m$^{-3}\mathscr{w}$
fdf	$Fr(i)DisS(k)$	freely dissolved metal fraction (not bound to DOC!)	-
$fdoc$	$Fr(i)DOCS(k)$	fraction metal adsorbed to DOC	-
fim_1	$Fr(i)IM1S(k)$	fraction metal ads. to inorg. fraction IM1	-
fim_2	$Fr(i)IM2S(k)$	fraction metal ads. to inorg. fraction IM2	-
fim_3	$Fr(i)IM3S(k)$	fraction metal ads. to inorg. fraction IM3	-
$fpoc$	$Fr(i)POCS(k)$	fraction metal adsorbed to POC	-
$falg$	$Fr(i)PHYTS(k)$	fraction metal ads. to phytoplankton	-
fpr	$Fr(i)SulfS(k)$	fraction metal precipitated	-
Kpt	$Kd(i)DMS(k)$	apparent overall partition coefficient for susp. solids	m^3 kgDW^{-1}
-	$Q(i)IM1S(k)1$	metal content of inorg. matter fr. IM1	g gDW^{-1}
-	$Q(i)IM1S(k)$	metal content of inorg. matter fr. IM2	g gDW^{-1}
-	$Q(i)IM1S(k)$	metal content of inorg. matter fr. IM3	g gDW^{-1}
-	$Q(i)POCS(k)$	metal content of part. detritus	g gC^{-1}
-	$Q(i)PHYTS(k)$	metal content of phytopl. biomass	g gC^{-1}
$Chmpt$	$Q(i)DMS(k)$	metal content of total suspended solids	mg kgDW^{-1}

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11.2 Reprofunctions for partition coefficients

PROCESS: RFPART_(i)

The partition coefficient for (heavy) metals is a function of the composition of particulate matter, and therefore varies substantially among surface water systems. Strongly adsorbing components of suspended sediment are iron(III) oxyhydroxides, manganese oxides, aluminium hydroxide, clays and organic matter. The overall adsorption capacity can be quantified using the so-called cation exchange capacity (CEC), which can be measured. (These remarks do not apply to anion forming metals like As!)

The partition coefficient is a function of the pH, the alkalinity, the chlorinity (or salinity) and the concentrations of various anions and macrochemical metal ions. In case of sulfide forming heavy metals, this is caused by the fact that the dominant adsorbing metal species is the free metal ion. The concentration of the free metal ion depends on the extent of pH dependent complexation of this ion by a number of ligands such as OH^-, HCO_3^-, SO_4^{2-} and Cl^- (at oxidising conditions). The pH also directly influences adsorption via the competition of a free metal ion with H_3O^+ or a metal anion with OH^- at the sorption sites of particulate matter. Competition of heavy metals and macrochemical metals (Ca^{2+}, K^+, Na^+, etc.) regarding sorption plays a role too, but the concentrations of these metals in surface water are rather constant over time.

In order to allow the variation over time due to the pH and to take into account the dependency of particulate matter composition, so-called repro-functions have been developed for the partition coefficient on the basis of multivariate (log)linear regression. These functions quantify the partition coefficient as a function of the chemical composition of surface water and or the CEC of suspended sediment in this surface water. Process RFPART_i calculates the partition coefficient using such repro-functions.

The dependency of partitioning on the redox potential (the dissolved oxygen concentration) and on the supersaturation of heavy metal minerals is not considered here. These aspects are taken into account in the process of partitioning itself.

Implementation

Process RFPART_(i) delivers partition coefficients for three inorganic matter fractions $IM1-3$, and has been implemented for the following heavy metals:

a. the sulfide forming metals Cd, Cu, Zn, Ni, Hg, Pb;
b. the hydroxide forming metal Cr: and
c. the anion forming “metal” As.

See Table 11.6 for the definition of input and output parameters.

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Formulation

Two forms of repro-functions have been implemented. A rather simplified function, that was found to give satisfying results for cadmium in the North Sea (WL | Delft Hydraulics, 1993c) is based on pH, salinity and CEC. A more complicated function was derived for several heavy metals in the river Rhine (WL | Delft Hydraulics, 1993a). A selection can be made from these 2 options by means of switch $SWRepro$.

SWRepro = 1

The River Rhine repro-function is applied. This function reads:

$$Kp_0 = 10^a \times 10^{(b \times pH)} \times 10^{c \times pH^2} \times ALK^d \times Ccl^g \times DOC^l \times ALK^{m \times pH} \times ALK^{n \times pH \times \log(ALK)} \times ALK^{o \times pH^2}$$

$$Kpim_i = Kp_0 \times \frac{(10^3 \times CEC_i)}{0.2} \quad \text{for i = 1, 2 and 3}$$

with:

Kp_0	reference partition coefficient [m^3 kgDW^{-1}]
$Kpim_i$	partition coefficient with respect to sediment fraction i [m^3 kgDW^{-1}]
ALK	alkalinity [mole HCO_3^- m^{-3}]
Ccl	chloride concentration [g m^{-3}]
CEC_i	cation exchange capacity of sediment fraction i [eq gDW^{-1}]
DOC	dissolved organic carbon concentration [gC m^{-3}]
pH	acidity [-]
a, b, c	metal specific coefficients
d, g, l	metal specific coefficients
m, n, o	metal specific coefficients

Sediment ($IM1-3$) basically includes inorganic matter and detritus (POC). However, the model only applies the partition coefficient to concentrations of IM1-3, assuming that it contains a certain percentage organic matter. Like other sediment components organic matter contributes to the CEC. River Rhine suspended matter has an average CEC of 0.2 eq kg^{-1}. The metal specific coefficients established for the River Rhine are (WL | Delft Hydraulics, 1993a):

Metal	a	b	c	d	l	g	m	n	o
cadmium	-7.680	1.894	-0.0604	-0.0583	-0.715	0	0	0	0
copper	-10.351	2.826	-0.159	0.994	-0.101	-0.138	-0.209	-0.0255	0
lead	-2.265	1.270	-0.0705	0	-0.141	0	-0.112	-0.0141	0
zinc	-25.811	6.719	-0.394	1.337	-0.201	0	0	-0.0590	-0.0270
mercury	-33.411	9.633	-0.616	0	-0.936	0	0	0	0
nickel	-22.654	5.702	-0.329	0	-0.171	0	0.289	-0.0388	-0.0492
chromium	-40.123	11.121	-0.709	0	-0.110	-0.244	0	0	0
arsenic	3.555	-0.164	0.0098	-0.0159	-0.196	0	0	0	0

From a theoretical point of view, the CEC-approach is incorrect for the anion forming metals like arsenic and chromium. For pragmatic reasons no distinction has been made in the formulations between cation and anion forming metals. This seems acceptable because the CEC is more or less proportional to the AEC (anion exchange capacity).

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SWRepro = 2

The North Sea repro-function is applied. This function reads:

$$Kp_0 = 10^a \times 10^{b \times pH} \times (1.8 \times 10^{+3} \times Ccl + c)^d$$

$$Kpim_i = Kp_0 \times 10^3 \times CEC_i \quad \text{for i = 1, 2 and 3}$$

with:

Kp_0	reference partition coefficient per unit CEC [m^3 eq^{-1}]
$Kpim_i$	partition coefficient with respect to sediment fraction i [m^3 $kgDW^{-1}$]
Ccl	chloride concentration [g m^{-3}]
CEC_i	cation exchange capacity of sediment fraction i [eq gDW^{-1}]
pH	acidity [-]
a, b, c, d	metal specific coefficients

North Sea suspended sediment was estimated to have an average CEC of 0.2 eq kg^{-1}. The values of the coefficients established for cadmium in the North Sea are (WL | Delft Hydraulics, 1993c): $a = 4.27$, $b = 0.347$, $c = 5.0$ and $d = -1.9$.

Directives for use

- ◇ Coefficients a–o are specific for a water system and/or for a metal. Obtained values for one particular water system may not be suitable for other water systems. The user should verify the validity of the coefficients used in the repro-functions. It is strongly advised to check whether the calculated value of the partitioning coefficient is within the expected range during the simulation (create output for $Kpim_1$).
- ◇ Typical CEC values for some substances are: (i) kaolinite 0.3 eq kg^{-1}, (ii) illite 0.4 eq kg^{-1}, (iii) montmorillonite 0.7 eq kg^{-1} and (iv) humic matter 2.0-3.0 eq kg^{-1}. The CEC of suspended sediment can be estimated with:

  $$CEC = CECpoc \times foc + CECsilt \times fsilt$$

  The CEC of POC and the CEC of silt (fraction $< 2\mu$ = "silt") are both about 0.01 eq kg^{-1}. The percentage organic carbon in sediment foc can be estimated from the percentage organic matter by dividing with a factor 1.7 (humic material) to 2.5 (fresh detritus). Both foc and the percentage silt $fsilt$ are to be provided as percentage dry weight. Notice that the input for the CEC must be specified in eq g^{-1}!
- ◇ In the above approach of the partition coefficient it is assumed that the detritus (POC) contribution is included in the adorption capacity. The effect of DOC is taken into account as well. Algae are not included. Only $Kppoc$ should therefore be made equal to 0.0. However, it is possible to take the POC contribution from the CEC and to define $Kppoc$ separately.

Additional references

WL | Delft Hydraulics (1991)

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Table 11.6: *Definitions of input parameters in RFPART_(i), (i) is a substance name.*

Name in formulas	Name in input	Definition	Units
ALK	ALK	alkalinity*	mol m^{-3}
Ccl	Cl	chloride concentration	g m^{-3}
CEC_i	$CECIMi$	cation exchange capacity of sediment fractions $i = 1, 2, 3$	eq gDW^{-1}
DOC	DOC	dissolved organic carbon concentration	gC m^{-3}
$Kpim_i$	$Kd(i)IMi$	partition coefficient for sediment fractions $i = 1, 2, 3$	m^3 $kgDW^{-1}$
a	$CaRFKp(i)$	metal specific coefficients in the repro-functions	various
b	$CbRFKp(i)$		(formula
c	$CcRFKp(i)$		defined)
d	$CdRFKp(i)$		
g	$CgRFKp(i)$		
l	$ClRFKp(i)$		
m	$CmRFKp(i)$		
n	$CnRFKp(i)$		
o	$CoRFKp(i)$		
pH	pH	acidity	-
$SWRepro$	$SWRepro$	switch for selection of partition coefficient function (1 = Rhine repro, default; 2 = North Sea repro)	-

* mol m^{-3} = meq L^{-1}

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Isotope	*Atomic mass* (g/mol)	*Half-life* (year)
Tritium	3.0	12.32
Caesium-137	137.0	30.17
Uranium-235	235.0	703.8·10^6
Uranium-238	238.0	4.468·10^9
Plutonium-238	238.0	87.74
Strontium-90	90.0	28.90

11.3 Radio-active isotopes and radio-active decay

PROCESS: RADIOU, RADIOCS, RADIOSUB1, RADIOSUB2, RADIOSUB3

Pollution by radio-active isotopes is characterised by both the concentration of the isotopes and the intensity of the associated radiation. This process calculates the concentration based on the half-life (first-order decay) and optionally the radiation intensity.

Note: There is no provision as yet to model possible adsorption to particulate matter and subsequent sedimentation.

Implementation

Processes RADIOU, RADIOCS, RADIOSUB1, RADIOSUB2, RADIOSUB3 have been implemented respectively for uranium-238, caesium-137 and three generic isotopes. Modelling specific radio-isotopes is possible via two parameters, the half-life period and the atomic mass. The latter is of importance to estimate the radiation intensity, which is expressed in Bq, the number of decaying atoms per second.

There is information on the half-life periods and the atom masses for all known isotopes, but for convenience, here is a short table of commonly encoutered isotopes.

More information can be found at https://en.wikipedia.org/wiki/List_of_radioactive_nuclides_by_half-life

For units concerning radio-activity see https://www.remm.nlm.gov/radmeasurement.htm for instance.

Formulation

For radio-active isotopes the decay is a first-order process:

$$\begin{aligned} \frac{dC}{dt} &= -kC \\ k &= ln(2)/(365 \cdot T_{half}) \end{aligned}$$

where:

C	concentration of the isotope in [mg.m^{-3}] (or, equivalently, [μ g.L^{-1}])
k	decay rate coefficient for the isotope in [d^{-1}]
T_{half}	half-life in years, for convenience [y]

From the decay rate kC the radiation in [Bq.m^{-3}] is calculated (conversion factor from day to second omitted):

$$R = kC \cdot N_A / M_{iso}$$

where:

R	radiation in [Bq.m^{-3}] (number of disintegrating atoms per second per cubic meter)
N_A	Avogradro's number
M_{iso}	atomic mass of the isotope

Table 11.7: *Definitions of the parameters and substances*

Name in formulas	**Name in Input**	**Definition**	**Units**
C		Concentration of the isotope, in particular:	mg.m^{-3}
	Uranium	Uranium-238	
	Caesium137	Caesium-137	
	Radio1	Radio-isotope 1	
	Radio2	Radio-isotope 2	
	Radio3	Radio-isotope 3	
k		Decay rate for the isotope (calculated from the half-life)	d^{-1}
T_{half}		Half-life for the isotope, in particular:	y
	HalflifeU	For uranium-238	
	HalflifeCs	For caesium-137	
	HalflifeR1	For radio-isotope 1	
	HalflifeR2	For radio-isotope 2	
	HalflifeR3	For radio-isotope 3	
M_{iso}		Atomic mass of the isotope, in particular:	g/mol
	AtommassU	For uranium-238	
	AtommassCs	For caesium-137	
	AtommassR1	For radio-isotope 1	
	AtommassR2	For radio-isotope 2	
	AtommassR3	For radio-isotope 3	
R		Radiation, in particular:	Bq.m^{-3}
	RadiatU	For uranium-238	
	RadiatCs	For caesium-137	
	RadiatR1	For radio-isotope 1	

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Table 11.7: *Definitions of the parameters and substances*

Name in formulas	**Name in Input**	**Definition**	**Units**
	RadiatR2 RadiatR3	For radio-isotope 2 For radio-isotope 3	

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12 Bacteria and viruses

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12.1 Mortality of coliform bacteria

PROCESS: (I)MRT

Coliform bacteria originate from human and animal faeces and are often used as indicator for the presence of disease vectors. The mortality of coliform bacteria is enhanced by temperature, salinity and solar radiation.

However, little or no mortality may occur at low temperatures. Distinction is made between *Escherichia Coli*, faecal coli, total coliforms and Enterococci. Available formulations for the mortality of coliforms are mainly empirical. The formulations as reported by Mancini (1978) have been implemented. For a more recent publication, see Chan et al. (2015). Equal formulations are used for all coliform species, the coefficients can be specified by the user.

Note: In previous versions ultraviolet radiation was incorrectly used as the light component responsible for bacterial mortality. Also the day length was used in combination with the daily averaged irradiation. This has been corrected, as the literature clearly states that instantaneous visible light should be considered.

Implementation

Process (i)MORT has been implemented for four "substances" (i), namely:

- ECOLI, FCOLI, TCOLI and ENCOC.

Process CALCRADDAY can be used to deliver the intensity of visible light at the top and the bottom of the water layers in the model. Process Extinc_VLG can be used to provide the total extinction coefficient of visible light.

Table 12.2 provides the definitions of the parameters occurring in the formulations.

Formulation

The mortality rate of coliform bacteria can be quantified with the following empirical function of temperature, chlorinity and solar radiation (as derived from visible light):

For $T > Tc_i$:

$$Rmrt_i = kmrt_i \times Cx_i \tag{12.1}$$

$$kmrt_i = (kmb_i + kmcl_i) \times ktmrt_i^{(T-20)} + kmrd \tag{12.2}$$

$$kmcl_i = kcl_i \times Ccl \tag{12.3}$$

$$kmrd = krd \times I_0 \times \frac{\left(1 - e^{-\varepsilon \times H}\right)}{\varepsilon \times H} \tag{12.4}$$

For $T \leq Tc_i$:

$$Rmrt_i = 0.0 \tag{12.5}$$

where:

Cx_i	concentration of coliform bacteria species i [MPN.m^{-3}]
ε	extinction of visible light [m^{-1}]

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H	water depth [m]
I_0	instantaneous solar radiation as visible light at the water surface [W.m^{-2}]
kcl	chloride related mortality constant [m^3.g^{-1}.d^{-1}]
kmb	basic mortality rate [d^{-1}]
$kmcl$	chloride dependent mortality rate [d^{-1}]
$kmrd$	radiation dependent mortality rate [d^{-1}]
$kmrt$	first order mortality rate [d^{-1}]
krd	radiation related mortality constant [m^2.W^{-1}.d^{-1}]
$ktmrt$	temperature coefficient of the mortality rate [-]
$Rmrt$	mortality rate of coliform bacteria [MPN.m^{-3}.d^{-1}]
T	temperature [°C]
Tc	critical temperature for mortality [°C]
Ccl	chloride concentration [g.m^{-3}]
i	index for coliform species, ECOLI, FCOLI, TCOLI and ENCOC

Notice that solar radiation has been defined as the energy in visible light, the intensity of which is to be corrected for reflection at the water surface.

Directives for use

- ◇ In clear water, for instance seawater, and at high radiation intensity, mortality rates up to and over 50 d^{-1} have been observed (Mancini, 1978).
- ◇ The process uses $RADDAY$ as input parameter, but this is derived from RadSurf when process CalcRadDay is active. This process must be active for models with more than one water layer.
- ◇ Average solar radiation (visible light) at the surface yields 160 W m^{-2}, but can be as high as 250 W m^{-2} in sunny places.
- ◇ The value of the radiation dependent mortality constant krd depends on the units in which $RadDay$ ($RadSurf$) is specified. A value of 1.0 h langley^{-1} d^{-1} was found by Mancini (1978), when the radiation was expressed in [langley h^{-1}]. An indicative value of krd for radiation in W m^{-2} is 0.0862 (m^2 W^{-1} d^{-1}).
- ◇ For other units of $RadDay$ ($RadSurf$) the conversion constants listed in Table 12.1 can be helpful.

Table 12.1: *Conversion constants*

1 langley	1 cal cm^{-2}	4.18 J cm^{-2}
1 einstein m^{-2} s^{-1}	12.1 W m^{-2}	$370 < l < 540$ nm
1 kLux	3.75 W m^{-2}	
1 ergs m^{-2} s^{-1}	10^{-7} W m^{-2}	
1 lumen	0.005 W	White light

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Table 12.2: *Definitions of the parameters in the above equations for (i)MORT.*

Name in formulas[1]	**Name in input**	**Definition**	**Units**
Cx_i	(i)	concentration of coliform bacteria species i[1]	MPN.m^{-3}
Ccl	Cl	chloride concentration	gCl.m^{-3}
DL	$DAYL$	daylength, fraction of a day	-
ε	$ExtVL$	extinction of visible light	m^{-1}
H	$Depth$	water depth (layer thickness)	m
I_0	$RADDAY$	solar radiation varying over the day	W.m^{-2}
kcl_i	$SpMrt(i)$	chloride dependent mortality constant	m^3.g^{-1}.d^{-1}
kmb_i	$RcMrt(i)$	basic mortality rate	d^{-1}
$kmcl_i$	–	chloride dependent mortality rate	d^{-1}
$kmrd_i$	–	radiation dependent mortality rate	d^{-1}
$kmrt_i$	–	first order mortality rate	d^{-1}
krd	$CFRAD$	radiation dependent mortality constant	m^2.W^{-1}.d^{-1}
$ktmrt$	$TcMrt(i)$	temperature coefficient of the mortality rate	-
$Rmrt_i$	–	mortality rate of coliform bacteria	MPN.m^{-3}.d^{-1}
T	$Temp$	temperature	°C
Tc_i	$CTMrt(i)$	critical temperature for mortality	°C

[1]substances (i) are ECOLI, FCOLI,TCOLI and ENCOC

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12.2 Mortality, adsorption to sediment and sedimentation of viruses

PROCESSES: (I)MRT, (I)S1MRT, PARTWK(I), PARTS1(I), SED_(I)

Human viruses multiply within humans and spread via air (aerosols) or water (via sewer system). Different viruses have different routes. Once in the (sewer) water, human pathogenic viruses can not multiply, but will be transported, possibly subject to adsorption, inactivation, to surface and ground water bodies. Research questions associated with this transport and fate are:

- ◇ What is the inactivation rate of viruses under different conditions (temperature, UV, light, salinity)
- ◇ Given a concentration of viruses in a water body or sewer system, can the prevalence in the human population be predicted?

To answer such questions, it is helpful to model transport and fate (survival) of viruses. The processes library provides the basic tools for this, but does not provide a comprehensive set of process parameters for the simple reason that literature data are scarce and ambiguous.

To help setting the process parameters, here is a description of the current general knowledge:

Waterborne viruses, like other pathogens, enter surface waters via raw and treated sewage inputs, open defecation, land-based runoff, and bather shedding. Once they enter surface waters, they are advected and dispersed by ambient currents, and subject to non-conservative processes including settling, predation, and inactivation. Inactivation is generally modelled as first-order decay with respect to pathogen concentration, although biphasic or delayed decay profiles have been observed under certain conditions (cited from Boehm et al. (2019)).

Enveloped viruses (to which influenza, HIV, SARS, MERS, and Ebola belong) remained viable on the timescale of days in wastewater (Gundy et al. (2009) and Ye et al. (2016)), but longer in tap water (Gundy et al. (2009)). Non-enveloped viruses remained viable for much longer times. Enveloped viruses adsorbed more (up to 26 %) to particles in wastewater than non-enveloped viruses (6 %). MHV, a coronavirus, showed higher first-order decay rates at 25 °C than at 10 °C (T_{90} of 13h and 36h respectively). The authors present a model for partitioning and decay of viruses suitable for wastewater (not including the effect of temperature, light and chlorinity).

Recent communication displayed higher survival rates of SARS CoV-2 as compared to SARS CoV-1, being in aerosols for hours, and on surfaces for days (Doremalen et al. (2020)). It is yet unknown how these results translate to virus decay in water.

Quantitative information on the survival rates of virus is limited. Also, rate determinations are sensitive to the virus enumeration methods. A review collected over 500 first-order decay rates (k) of mammalian viruses (SARS was not included in this study) in water at temperatures between 4 and 29 °C, and average k values varied from 0.07 to 0.9 day^{-1}. In this study, first-order decay constant (k) of mammalian viruses were in general higher for experiments performed at higher temperatures, in sunlight, estuarine waters, and where culture enumeration was used as the quantification method. There were statistical differences between different types of viruses. However, there was not enough consistent data to parameterize the relationships with temperature and light (Boehm et al. (2019)).

The implementation of the processes that gouvern the transport and fate of viruses in the aquatic environment has been entirely based on existing process routines. For in-depth details

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you can look up the relevant sections.

Implementation

The substances representing viruses are called *Virus1*, *Virus2* and *Virus3*. By means of the process parameters that are specific for each virus you can model specific viruses. (Note that the abbreviation *Vir1* is used for several of the processes, in view of the restricted length of the process names).

The following processes have been implemented for three different viruses:

- ◇ Mortality under the influence of solar radiation (cf. the mortality of bacteria, section 12.1). This can occur in both the water phase and the sediment. Since viruses require a host to multiply, there can be no growth.
- ◇ Adsorption of virus particles to sediment – it is assumed that the partitioning is an equilibrium process in much the same way as for metals and organic micropollutants (cf. section 11.1). This is implemented for both the water phase and the sediment and in principle separate partitioning coefficients can be used.
- ◇ Sedimentation of virus particles as adsorbed to suspended particulate matter (inorganic and organic) (cf. section 10.8).

Formulations

As the processes for viruses are all based on processes that are described elsewhere, this section contains only information specific for the configuration specific to viruses. As a general guideline: because there is very little quantitative information, coefficients should be chosen conservatively. For instance: the temperature dependency of the mortality rate should probably be set to 1 in the absence of more concrete evidence that the mortality increases with increasing temperature.

The formulation for the mortality rate is based on that of bacteria:

For $T > Tc_i$:

$$Rmrt_i = kmrt_i \times Cx_i \tag{12.6}$$

$$kmrt_i = (kmb_i + kmcl_i) \times ktmrt_i^{(T-20)} + kmrd \tag{12.7}$$

$$kmcl_i = kcl_i \times Ccl \tag{12.8}$$

$$kmrd = krd \times I_0 \times \frac{\left(1 - e^{-\varepsilon \times H}\right)}{\varepsilon \times H} \tag{12.9}$$

For $T \leq Tc_i$:

$$Rmrt_i = 0.0 \tag{12.10}$$

where:

Cx_i	concentration of virus particles i [fpu.m^{-3}]
ε	extinction of visible light [m^{-1}]
H	water depth [m]
I_0	instantaneous solar radiation as visible light at the water surface [W.m^{-2}]
kcl	chloride related mortality constant (*by default set to zero*) [m^3.g^{-1}.d^{-1}]
kmb	basic mortality rate [d^{-1}]
$kmcl$	chloride dependent mortality rate [d^{-1}]
$kmrd$	radiation dependent mortality rate [d^{-1}]

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$kmrt$	first order mortality rate [d^{-1}]
krd	radiation related mortality constant (*by default set to zero*) [$m^2.W^{-1}.d^{-1}$]
$ktmrt$	temperature coefficient of the mortality rate [-]
$Rmrt$	mortality rate of coliform bacteria [$MPN.m^{-3}.d^{-1}$]
T	temperature [°C]
Tc	critical temperature for mortality (*by default set to zero*) [°C]
Ccl	chloride concentration [$g.m^{-3}$]
i	index for coliform species, ECOLI, FCOLI, TCOLI and ENCOC

Taking the simplifications into account, the formulation becomes:

$$Rmrt_i = kmrt_i \times Cx_i \tag{12.11}$$

$$kmrt_i = kmb_i \times ktmrt_i^{(T-20)} \tag{12.12}$$

Note: as a consequence some of the input and output parameters have no practical meaning and instead suggest a more comprehensive modelling than is actually available. They are documented here for reasons of completeness.

The sedimentation of viruses as adsorbed to particulate matter (inorganic and organic) is completely determined by the sedimentation of the particulate matter and the partitioning. Hence there are no process coefficients regarding sedimentation that are specific to viruses.

Table 12.3: *Definitions of the parameters for mortality of virus 1 in water (similar parameters are available for the other two*

Name in input	**Definition**	**Units**
Virus1	Concentration of Virus 1	$pfu.m^{-3}$
RcMrtVir1	First-order mortality rate Virus 1	d^{-1}
TcMrtVir1	Temperature coefficient for mortality Virus 1	[-]
CTMrtVir1	Critical temperature for mortality Virus 1	°C
RadDay	Actual irradiation at the upper-boundary	$W.m^{-2}$
CFRADVir1	Conversion factor RAD to mortality rate	$m^2.W^{-1}.d^{-1}$
SpMrtVir1	Chloride enhanced mortality rate Virus 1	$m^3.g^{-1}.d^{-1}$
	Output parameters	
MrtToVir1	Overall mortality rate Virus 1	d^{-1}
MrtRaVir1	Mortality rate due to by radiation Virus 1	d^{-1}

For viruses in the sediment layer it is assumed that the same mortality process holds with the same process coefficients. The concentration of the viruses (name: Virus1S1) is expressed in $number.m^{-2}$ instead of $number.m^{-3}$.

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Table 12.4: *Definitions of the parameters for the partitioning of virus 1 in water (similar parameters are available for the other two*

Name in input	Definition	Units
Virus1	Concentration of Virus 1	pfu.m^{-3}
XDOCVirus1	Efficiency DOC relative to POC for Virus 1	[-]
KdVir1IM1	Partition coefficient Virus 1-IM1	m^3.kgDM^{-1}
KdVir1IM2	Partition coefficient Virus 1-IM2	m^3.kgDM^{-1}
KdVir1IM3	Partition coefficient Virus 1-IM3	m^3.kgDM^{-1}
KdVir1poc	Partition coefficient Virus 1-POC	m^3.kgDM^{-1}
KdVir1phy	Partition coefficient Virus 1-PHYT	m^3.kgDM^{-1}
HLTAdsVir1	Half-life time non-eq. adsorption Virus 1	d
HLTDesVir1	Half-life time non-eq. desorption Virus 1	d
	Output parameters	
FrVir1Dis	Fraction free dissolved Virus 1 in water column	[-]
FrVir1DOC	Fraction Virus 1 adsorbed to DOC	[-]
FrVir1IM1	Fraction Virus 1 adsorbed to IM1	[-]
FrVir1IM2	Fraction Virus 1 adsorbed to IM2	[-]
FrVir1IM3	Fraction Virus 1 adsorbed to IM3	[-]
FrVir1POC	Fraction Virus 1 adsorbed to POC	[-]
FrVir1PHYT	Fraction Virus 1 adsorbed to phytoplankton	[-]
DisVirus1	Free (non-adsorbed) Virus 1 in water column	pfu.m^{-3}
DOCVirus1	Virus 1 adsorbed to DOC	pfu.m^{-3}
QVir1IM1	Quality IM1 for Virus 1	pfu.gDM^{-1}
QVir1IM2	Quality IM2 for Virus 1	pfu.gDM^{-1}
QVir1IM3	Quality IM3 for Virus 1	pfu.gDM^{-1}
QVir1POC	Quality POC for Virus 1 in water column	pfu.gC^{-1}
QVir1PHYT	Quality phytoplankton for Virus 1 in water column	pfu.gC^{-1}
Virus1tot	Concentration Virus 1 in water column	pfu.m^{-3}
QVirus1SS	Overall quality suspended solid for Virus 1	pfu.gDM^{-1}
KdVirus1SS	Overall partition coefficient Virus 1 in SS	m^3.kgDM^{-1}

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Table 12.5: *Definitions of the parameters for the partitioning of virus 1 in sediment layer S1 (similar parameters are available for the other two*

Name in input	Definition	Units
Virus1S1	Concentration of Virus 1 in sediment layer S1	pfu.m^{-2}
KdVi1IM1S1	Partition coefficient Virus 1-IM1 (layer S1)	m^3.kgDM^{-1}
KdVi1IM2S1	Partition coefficient Virus 1-IM2 (layer S1)	m^3.kgDM^{-1}
KdVi1IM3S1	Partition coefficient Virus 1-IM3 (layer S1)	m^3.kgDM^{-1}
KdVi1pocS1	Partition coefficient Virus 1-POC (layer S1)	m^3.kgDM^{-1}
KdVi1phyS1	Partition coefficient Virus 1-PHYT (layer S1)	m^3.kgDM^{-1}
	Output parameters	
FrVir1DS1	Fraction free (non-adsorbed) Virus 1 in layer S1	[-]
FrVir1DOS1	Fraction Virus 1 adsorbed to DOC (layer S1)	[-]
FrVir1IM1S	Fraction Virus 1 adsorbed to IM1 (layer S1)	[-]
FrVir1IM2S	Fraction Virus 1 adsorbed to IM2 (layer S1)	[-]
FrVir1IM3S	Fraction Virus 1 adsorbed to IM3 (layer S1)	[-]
FrVir1POS1	Fraction Virus 1 adsorbed to POC (layer S1)	[-]
FrVir1PHS1	Fraction Virus 1 adsorbed to phytoplankton (S1)	[-]
DisVir1S1	Free (non-adsorbed) Virus 1 in pore water layer S1	pfu.m^{-2}
DOCVir1S1	Virus 1 adsorbed to DOC in pore water (S1)	pfu.m^{-2}
QVir1IM1S1	Quality IM1 for Virus 1 (layer S1)	pfu.gDM^{-1}
QVir1IM2S1	Quality IM2 for Virus 1 (layer S1)	pfu.gDM^{-1}
QVir1IM3S1	Quality IM3 for Virus 1 (layer S1)	pfu.gDM^{-1}
QVir1POCS1	Quality POC for Virus 1 (layer S1)	pfu.gC^{-1}
QVir1PHYS1	Quality phytoplankton for Virus 1 (layer S1)	pfu.gC^{-1}
Vir1S1tot	Concentration Virus 1 (layer S1)	pfu.m^{-2}
QVir1DMS1	Overall sediment quality for Virus 1 (layer S1)	pfu.gDM^{-1}
KdVir1DM1S	Overall partition coefficient Virus 1 (layer S1)	m^3.kgDM^{-1}

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13 Sediment and mass transport

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13.1 Settling of sediment

PROCESS: SED_(I), S_(I), CALVS_(I)

The inorganic sediment components settle on the bed sediment. After settling these substances become part of the sediment inorganic matter pools, depending on the way of modelling the bed sediment. The inorganic sediment components in the bed sediment are:

1 IMS1/2, IM2S1/2 and IM3S1/2 for the S1/2 approach
2 IM1-3, the same substances when sediment layers are simulated explicitly

After settling BOD and COD components become part of SOD (Sediment oxygen demand, see also section 12.2), which is an "'inoactive"' substance.

Implementation

Process SED_(i) is implemented for the following substances (i):

◇ IM1, IM2 and IM3

This process is also used for the settling of algae biomass and organic detritus (POC1-4), which is dealt with by the relevant sections of Chapters 4 and 7. Process CALVS_(i) delivers the settling velocities as modified from the settling velocities supplied by the user (implemented for inorganic sediment IM1-3, and for algae biomass). The total suspended sediment concentration for this is delivered by process COMPOS.

Process S_(i) is implemented for the following substances (i):

◇ CBOD5, CBOD5_2, CBOD5_3, CBODu, CBODu_2, NBOD5, NBODu, COD_Cr and COD_Mn

Table 13.1 provides the definitions of the input parameters occurring in the formulations.

Formulations

The settling rates of the inorganic matter components and the BOD and COD substances are described as the sum of zero-order and first-order kinetics. The rates are zero, when the shear stress exceeds a certain critical value, or when the water depth is smaller than a certain critical depth. The settling probability is calculated according to the formulation of Krone (1962). The settling velocity is calculated from a user-supplied settling velocity and the flocculation effect, as determined from salinity, total suspended solid concentration and water temperature (density effect). The rates are calculated according to:

$$R_{set_i} = f_{\tau_i} \times \frac{F_{set_i}}{H}$$

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$$
\begin{aligned}
if H < H_{min} \\
&F_{set_i} = 0.0 \\
else \\
&F_{set_i} = \min\left(F_{set'_i}, \frac{Cx_i \times H}{\Delta t}\right) \\
&F_{set'_i} = F_{set0_i} + s_i \times Cx_i
\end{aligned}
$$

$$
\begin{aligned}
if \tau = -1.0 \\
&f_{\tau_i} = 1.0 \\
else \\
&f_{\tau_i} = \max\left(f_{\tau_{min_i}}, \left(1 - \frac{\tau}{\tau_{c_i}}\right)\right)
\end{aligned}
$$

where:

C_x	concentration of a substance [gDM/O_2 m^{-3}]
F_{set0}	zero-order settling flux of a substance [gDM/O_2 m^{-2} d^{-1}]
F_{set}	settling flux of a substance [gDM/O_2 m^{-2} d^{-1}]
f_τ	shear stress limitation function [-]
$f_{\tau_{min}}$	user-supplied minimum value for shear stress limitation function [-]
H	depth of the water column [m]
H_{min}	minimal depth of the water column for resuspension [m]
R_{set}	settling rate of a substance [gDM/O_2 m^{-3} d^{-1}]
s	settling velocity of a substance [m d^{-1}]
τ	shear stress [Pa]
τ_c	critical shear stress for settling of a substance [Pa]
Δt	timestep in DELWAQ [d]
i	index for substance (i)

For use in combination with the "buffer" model by (Kessel et al., 2011), the settling flux may be distributed over S1 and S2:

$$
\begin{aligned}
if\ f_{S2,TIM} < f_{maxS2,TIM} \\
&R_{set_{i,S1}} = (1 - \alpha_i) R_{set_i} \\
&R_{set_{i,S2}} = \alpha_i R_{set_i} \\
else \\
&R_{set_{i,S1}} = R_{set_i} \\
&R_{set_{i,S2}} = 0
\end{aligned}
$$

where:

$f_{S2,TIM}$	actual fraction of TIM in S2 [-]
$f_{max_{S2,TIM}}$	maximum allowed fraction of TIM in S2 [-]
$R_{set_{i,S1}}$	settling rate to S1 [g m-3 d^{-1}]
$R_{set_{i,S2}}$	settling rate to S2 [g m-3 d^{-1}]

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α_i	fraction of settling to S2 [-]

The settling velocity as dependent on flocculation is formulated as follows:

$$
\begin{aligned}
s_i &= f_{temp} \times f_{sal} \times f_{con} \times s_{0_i} \\
f_{temp} &= kt^{(T-20)} \\
f_{sal} &= (\frac{a_i + 1}{2}) - (\frac{a_i - 1}{2}) \times cos(\frac{\pi \times S}{S_{max}}) \\
f_{con} &= (\frac{Cs}{Cs_c})^{n_i}
\end{aligned}
$$

where:

a	coefficient for the enhancement of flocculation [-]
Cs	concentration of total suspended solids [gDM m^{-3}]
Cs_c	critical concentration of total susp. solids above which flocc. occurs [gDM m^{-3}]
f_{con}	function for the concentration dependency of flocculation, see Figure 13.1A [-]
f_{sal}	function for the salinity function dependency of flocculation, range [0,EnhSedi), see Figure 13.1B [-]
f_{temp}	function for temperature dependency of settling [-]
kt	temperature coefficient for settling (water density correction) [-]
n_i	constant for concentration effect on flocculation [-]
S	salinity [psu, g/kg]
S_{max}	salinity at which the salinity function is at its maximum [g/kg]
T	water temperature [°C]
i	index for substance (i)

Remarks:

- ◇ No more than the available amount of substance in the water column can settle in one model time step.
- ◇ The parameter H_{min} is purely a numerical parameter - it was introduced to avoid having to use very small time steps in very shallow grid cells.

Directives for use

- ◇ In three-dimensional applications the settling flux in all segments above the bottom layer is calculated as a transport flux instead of a process flux. Settling in the upper layers is not related to the bottom shear stress. The settling velocity in each layer is equal to the settling velocity in the bottom layer. The process flux for settling F_{set} (ouput parameter $fSed(i)$) is zero for the upper layers. Also τ is set to zero in the output for all water layers except the bottom layer.
- ◇ Note that if the bottom shear stress, τ, equals -1, the settling limitation function (settling probability) equals one.
- ◇ Note that DELWAQ can reduce the settling flux of a component, if the available amount in the water column is too small to fulfil the calculated flux within one time step. Reduce the settling rate or the DELWAQ time step if this is not wanted.
- ◇ The calculation of settling velocity by process CALVS_i is triggered when you supply a value for $V0Sed(i)$. By default, all three functions (temperature, flocculation and salinity) are equal to unity.
- ◇ A reasonable value for kt ($TCSed$), the temperature influence on the sedimentation) is 1.01.
- ◇ The values of the critical suspended solid concentration C_sc ($CrSS$) and the coefficient $n(i)$ determine the increase of the settling velocity at concentrations above the critical

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concentrations, see Figure 13.1, WL | Delft Hydraulics (1989), finds the following range for n: $1 < n < 2$.

- ◇ The effect of salinity on the flocculation and therefore on the settling velocity is presented in Figure 13.2.
- ◇ The option to distribute the settling flux over layers S1 and S2 and the option to use a user-supplied minimum value for the shear stress limitation function have only been implemented for IM1-3, not for the BOD and COD related state variables.

Table 13.1: *Definitions of the input parameters in the above equations for SED_(i), S_(i) and CALVS_(i). (i) is the name of a substance.*

Name in formulas	Name in input	Definition	Units
Cx_i^1	$(i)^1$	concentration of substance (i)	gDM m^{-3}
a_i	$EnhSed(i)$	coefficient for the enhancement of flocculation of substance (i)	-
F_{set0_i}	$ZSed(i)$	zero-order settling flux of substance (i)	gDM m^{-2} d^{-1}
$f_{\tau_{min_i}}$	$PSedMin(i)$	minimum value for shear stress limitation function for (i)	[-]
H	$Depth$	depth of the water column, thickness of water layer	m
H_{min}	$MinDepth$	minimum layer thickness for settling and resuspension	m
s_i	$VSed(i)$	settling velocity of substance (i) for SED_(i)	m d^{-1}
$s0_i$	$V0Sed(i)$	settling velocity of substance (i) for CALVS_(i)	m d^{-1}
Sal	$Salinity$	salinity	psu
Sal_{max}	$SMax$	salinity at which the salinity function is at its maximum	psu
Cs	SS	concentration of total suspended solids	gDM m^{-3}
Cs_c	$CrSS$	critical concentration of total suspended solids for flocculation	gDM m^{-3}
n_i	$N(i)$	constant for concentration effect on flocculation	-
T	$Temp$	temperature	°C
kt	$TcSed$	temperature coefficient for settlingy	-
τ	Tau	shear stress	Pa

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Table 13.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
τ_{c_i}	$TaucS(i)$	critical shear stress for settling of substance (I)	Pa
α_i	$Fr(i)SedS2$	fraction of settling to S2 for (i)	[-]
$f_{S2,TIM}$	$FrTIMS2$	actual fraction of TIM in S2	[-]
$f_{max_{S2,TIM}}$	$FrTIMS2 - Max$	maximum allowed fraction TIM in S2	[-]
Δt	$Delt$	timestep in DELWAQ	d

[1]) Substances are IM1, IM2 and IM3, or the BOD and COD substances. The latter only apply for S_(i) input parameters.

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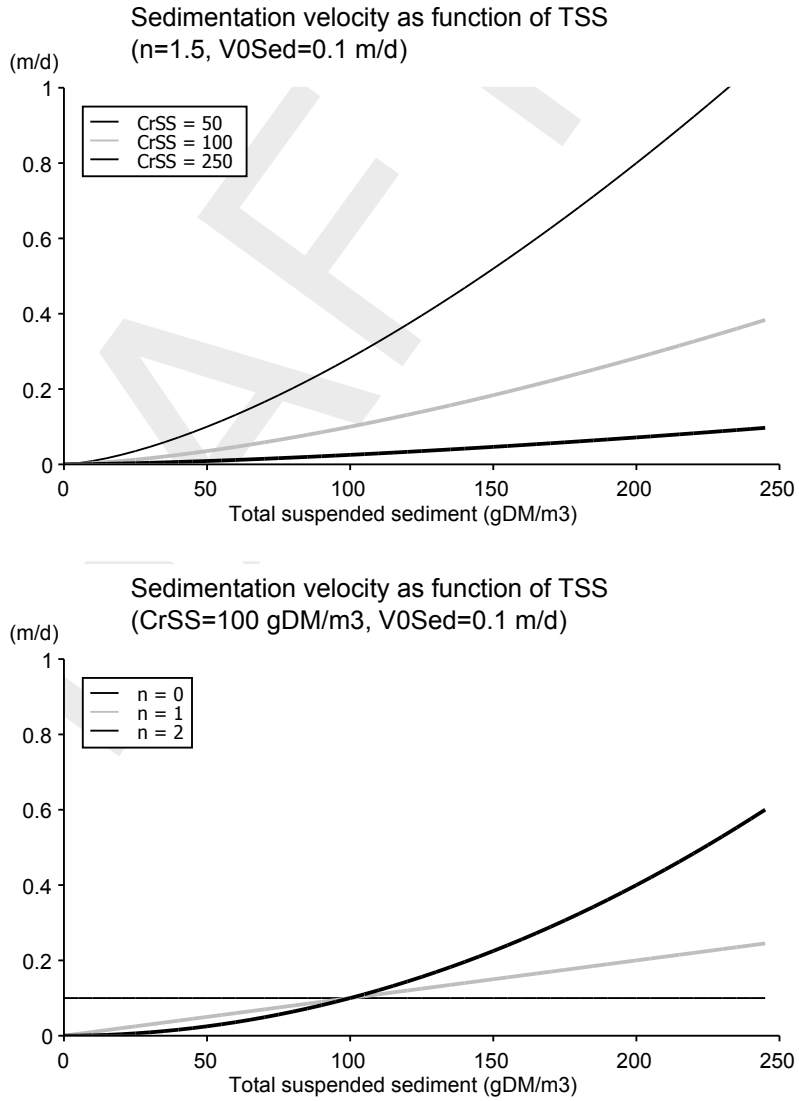

Figure 13.1: *Sedimentation velocity (Vsed) as a function of total suspended solid concentration (SS) solely (no effect of salinity and density included) at A):a critical suspended solid concentration and B) at one value of n (constant in the sedimentation formulation)*

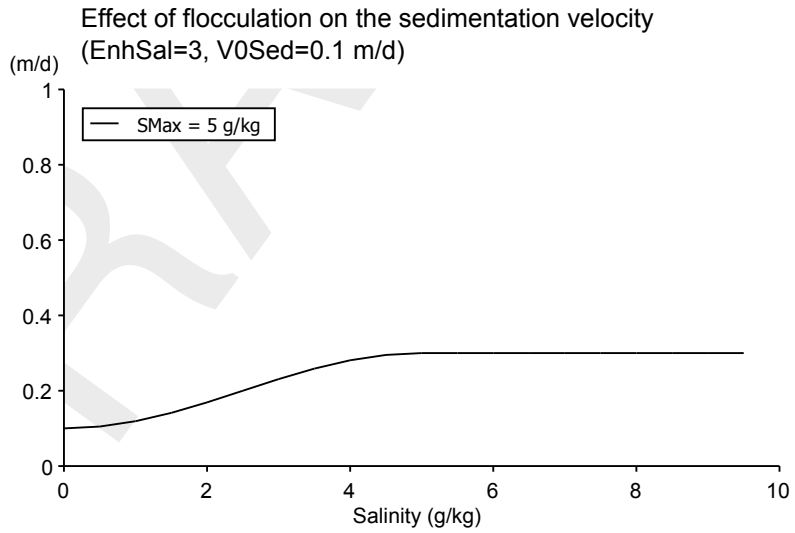

Figure 13.2: *Sedimentation velocity (VSed) as a function of salinity solely (effect of flocculation and density not included).*

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13.2 Calculation of settling fluxes of suspended matter

PROCESSES: SUM_SEDIM, SEDPHBLO_P, SEDPHBLO, SEDPHDYN, SED_(I), SED_SOD, S_(I)

The settling fluxes of total dry matter, total inorganic matter (TIM), total organic matter (POC with and without algae biomass) and total BOD (SOD) are derived from the settling fluxes of the individual substances and phytoplankton (PHYT).

Implementation

Process SUM_SEDIM is implemented for the following substances:

- ◇ IM1, IM2, IM3, POC1, POC2, POC3, POC4, BLOOMALG1-30, Green and Diat

Processes SED_(i) deliver the settling fluxes of the individual inorganic matter and detritus components. Process SEDPHBLO_P (or SEDPHBLO) delivers the algae biomass settling flux $fSedAlgDM$ for BLOOM. Process SEDPHDYN delivers the algae biomass settling flux $fSedAlgDM$ for DYNAMO.

The output parameters $fSedTIM$ and $fSedPOCnoa$ are used to calculate the settling fluxes of organic micro-pollutants and heavy metals. Table 13.2 provides the definitions of the input parameters.

Process SED_SOD is implemented for the following substance:

- ◇ SOD, CBOD5, CBOD5_2, CBOD5_3, CBODu, CBODu_2, NBOD5, NBODu, COD_Cr and COD_Mn

Processes $S_(i)$ deliver the settling fluxes of the individual BOD or COD components. The process delivers an additional output parameter $fSedSOD$, the settling flux of total BOD and or COD. Table 13.3 provides the definitions of the input parameters.

Formulation

The formulations for Sum_Sedim are:

$$f_{Sed_{TIM}} = \sum_{i=1}^{3} f_{Sed_{IM_i}}$$

$$f_{Sed_{POMnoa}} = \sum_{j=1}^{4} f_{Sed_{POC_j}} \times DMcfPOC_j$$

$$f_{Sed_{DM}} = \sum_{i=1}^{3} f_{Sed_{IM_i}} \times DMcfIM_i + f_{Sed_{POMnoa}} + f_{Sed_{AlgDM}}$$

$$f_{Sed_{POCnoa}} = \sum_{j=1}^{4} f_{Sed_{POC_j}}$$

$$f_{Sed_{POC}} = f_{Sed_{POCnoa}} + f_{Sed_{Phyt}}$$

where:

$f_{Sed_{PHYT}}$	settling flux of total phytoplankton [gC $m^{-2}d^{-1}$]
$f_{Sed_{AlgDM}}$	settling flux of total phytoplankton [gDM m^{-2} d^{-1}]
$f_{Sed_{POC}}$	settling flux of total particulate organic carbon [gC $m^{-2}d^{-1}$]
$f_{Sed_{POC_j}}$	settling flux of detritus fraction j [gC $m^{-2}d^{-1}$]
$f_{Sed_{POCnoa}}$	settling flux of POC excluding algae [gC $m^{-2}d^{-1}$]
$f_{Sed_{POMnoa}}$	settling flux of POC excluding algae [gDM m^{-2} d^{-1}]
$f_{Sed_{TIM}}$	settling flux of total inorganic matter [gDM m^{-2} d^{-1}]
$f_{Sed_{IM_i}}$	settling flux of inorganic matter fraction i [gDM m^{-2} d^{-1}]
$f_{Sed_{DM}}$	settling flux of dry matter [gDM m^{-2} d^{-1}]
$DMcfIM_i$	dry matter conversion factor for inorganic matter fraction i (1-3) [gDM/gX]
$DMcfPOC_j$	dry matter conversion factor for detritus fraction j (1-4) [gDM/gX]

The formulations for SED_SOD are:

if $SWOxyDem = 0$;

$$f_{Sed_{SOD}} = f_{Sed_{BOD5}} + f_{Sed_{BOD5_2}} + f_{Sed_{BOD5_3}} + f_{Sed_{BODu}} + \\ + f_{Sed_{BODu_2}} + f_{Sed_{NBOD5}} + f_{Sed_{NBODu}}$$

if $SWOxyDem = 1$;

$$f_{Sed_{SOD}} = f_{Sed_{CODCr}} + f_{Sed_{CODMn}} \tag{13.1}$$

if $SWOxyDem = 2$;

$$f_{Sed_{SOD}} = f_{Sed_{CODCr}} + f_{Sed_{CODMn}} + f_{Sed_{BOD5}} + f_{Sed_{BOD5_2}} + f_{Sed_{BOD5_3}} + \\ + f_{Sed_{BODu}} + f_{Sed_{BODu_2}} + f_{Sed_{NBOD5}} + f_{Sed_{NBODu}}$$

where:

$f_{Sed_{SOD}}$	settling flux of sediment oxygen demand [gO $m^{-2}d^{-1}$]
$f_{Sed(i)}$	settling flux of the individual component (i) [gO $m^{-2}d^{-1}$]
$SwOxyDem$	option parameter for substance definition (0=BOD, 1=COD, 2=BOD+COD) [-]

Directives for use

◇ Because you are free to select any combination of sediment components, the defaults for the calculation of fSedTIM, fSedPHYT and fSedPOC are zero.

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Table 13.2: *Definitions of the input parameters in the formulations for SUM_SEDIM. (i) is IM1, IM2 or IM3. (j) is POC1, POC2, POC3 or POC4.*

Name in formulas	Name in input	Definition	Units
$DMcfIM_i$	$DMCF(i)$	dry matter conversion factor for inorganic matter (i)	gDW/gX
$DMcfPOC_j$	$DMCF(j)$	dry matter conversion factor for detritus fraction (j)	gC/gX
$f_{Sed_{IM_i}}$	$fSed(i)$	settling flux of inorganic matter fraction (i)	gDM $m^{-2}d^{-1}$
$f_{Sed_{POC_j}}$	$fSed(j)$	settling flux of detritus fraction (j)	gC $m^{-2}d^{-1}$
$f_{Sed_{AlgDM}}$	$fSedAlgDM$	settling flux of total phytoplankton	gDM $m^{-2}d^{-1}$
$f_{Sed_{PHYT}}$	$fSedPHYT$	settling flux of total phytoplankton	gC $m^{-2}d^{-1}$

Table 13.3: *Definitions of the input parameters in the formulations for SED_SOD.*

Name in formulas	Name in input	Definition	Units
$SwOXYDem$	$SwOXYDem$	option parameter for substance definition (0=BOD, 1=COD, 2=BOD+COD)	-
$f_{Sed_{BOD5}}$	$fSedBOD5$	settling flux of $CBOD5$	gO_2 $m^{-2}d^{-1}$
$f_{Sed_{BOD5_2}}$	$fSedBOD5_2$	settling flux of $CBOD5_2$	gO_2 $m^{-2}d^{-1}$
$f_{Sed_{BOD5_3}}$	$fSedBOD5_3$	settling flux of $CBOD5_3$	gO_2 $m^{-2}d^{-1}$
$f_{Sed_{BODu}}$	$fSedBODu$	settling flux of $CBODu$	gO_2 $m^{-2}d^{-1}$
$f_{Sed_{BODu_2}}$	$fSedBODu$	settling flux of $CBODu_2$	gO_2 $m^{-2}d^{-1}$
$f_{Sed_{NBOD5}}$	$fSedNBOD5$	settling flux of $NBOD5$	gO_2 $m^{-2}d^{-1}$
$f_{Sed_{NBODu}}$	$fSedNBODu$	settling flux of $NBODu_2$	gO_2 $m^{-2}d^{-1}$
$f_{Sed_{CODCr}}$	$fSedCODCr$	settling flux of COD_Cr	gO_2 $m^{-2}d^{-1}$
$f_{Sed_{CODMn}}$	$fSedCODMn$	settling flux of COD_Mn	gO_2 $m^{-2}d^{-1}$

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13.3 Transport in sediment for layered sediment

PROCESSES: ADVTRA, DSPTRA, TRASE2_(I) (OR TRSE2_(I), TRSE2(I))

The substances simulated for the water column and the sediment are the same. A particulate substance in the water column can settle to or resuspend from the same substance in the sediment, and vice versa. A dissolved substance in the water column disperses to the same substance in the pore water of the sediment, and vice versa.

Apart from settling (sedimentation) and resuspension (erosion), particulate substances present in the sediment layers can be subject to burial, digging, seepage and dispersion. Burial results from net settling and leads to the transport of substances from layer to layer in a downward direction. Digging results from net resuspension and leads to the transport of substances from layer to layer in an upward direction. The magnitude of a burial flux or a digging flux between sediment layers depends also on whether layer thickness and porosity are fixed or transient. Apart from the above advective processes, particulate substances or particulate components of substances are also subject to dispersive transport between sediment layers due to bioturbation.

Dissolved substances or dissolved components of substances in the sediment are subject to advective transport resulting from downward or upward water flow, downwelling or upwelling, both indicated as seepage. Dissolved components disperse between water column and top sediment layer, and between sediment layers due to bio-irrigation, flow induced dispersion and molecular diffusion. All dispersion processes can be formulated as diffusion.

The transport of substances across the lower sediment boundary in a model requires imposing the concentrations of substances below the “deep” sediment boundary.

The layered sediment formulations are generic, implying that all possible combinations of settling fluxes, resuspension fluxes and fixed or transient layer thickness and porosity should be covered. However, the formulations have been tested extensively for cases with (net) settling only, in which sediment layer thickness and sediment porosity are constant over time. Further testing needs to be done for resuspension, transient layer thickness and transient porosity. A process for sediment consolidation that would be needed for transient porosity is not available in the present processes library.

Volume units refer to bulk ($\mathscr{b}$), water ($\mathscr{w}$) or solids ($\mathscr{s}$).

Implementation

Processes ADVTRA, DSPTRA and TRASE2_(i) (or TRSE2_(i) or TRSE2(i)) with (i) equal to a name of a substance have been implemented for the following substances:

- IM1, IM2, IM3
- BLOOMALG01 - BLOOMALG30 (BLOOM), Diat, Green (DYNAMO)
- POC1, PON1, POP1, POS1, POC2, PON2, POP2, POS2, POC3, PON3, POP3, POS3, POC4, PON4, POP4, POS4, DOC, DON, DOP, DOS
- NH4, NO3, PO4, AAP, APATP, VIVP, Si, Opal
- OXY, SO4, SUD, SUP, CH4
- FeIIIpa, FeIIIpc, FeIIId, FeS, FeS2, FeCO3, FeIId
- OMP, 153, Atr, BaP, Diu, Flu, HCB, HCH, Mef
- As, Cd, Cr, Hg, Ni, Pb, Va, Zn
- Cl, Salinity

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◇ TIC, Alka

Processes ADVTRA and DSPTRA deliver the velocities for advection and dispersion for processes TRASE2_(i) (or TRSE2_(i) or TRSE2(i)). The latter processes deliver total transport velocities to be used by Delwaq for the calculation of fluxes by multiplication with concentrations. Process ADVTRA uses the settling flux of sediment dry matter from process SUM_SEDIM. Processes TRASE2_(i) use the dissolved fractions of organic micropollutants and heavy metals generated by processes PARTWK_(i). Porosity is delivered by auxiliary process DMVOLUME. Shear stress can be provided by process CALTAU.

Table 13.4 provides the definitions of the input parameters occurring in the formulations.

Formulation

Resuspension

The resuspension flux of sediment dry matter is described as zero-order kinetics according to Partheniades-Krone ($SwErosion = 0.0$):

$$Fres' \;=\; ftau \;\times\; Fres0$$

if $H < Hmin$ $Fres' = 0.0$ *else*

$$Fres \;= \min\left(Fres', \frac{Cdm}{A \times \Delta t}\right)$$

if $\tau = -1.0$ $ftau = 1.0$ *else*

$$ftau = \max\left(0.0, \left(\frac{\tau}{\tau c} - 1.0\right)\right)$$

where:

A	surface area of overlying water compartment [m^2]
Cdm	amount of sediment dry matter in the top sediment layer [gDM]
$Fres0$	zero-order resuspension flux of sediment [$gDM.m^{-2}.d^{-1}$]
$Fres$	resuspension flux of sediment [$gDM.m^{-2}.d^{-1}$]
$ftau$	shear stress limitation function [$-$]
H	depth of the water column, thickness overlying water layer [m]
$Hmin$	minimal depth of the water column for resuspension [m]
τ	shear stress [Pa]
τc	critical shear stress for resuspension [Pa]
Δt	timestep in DELWAQ [d]

Cdm and H are calculated by the model.

Advection

The burial of particulate substances results from (net) settling at the sediment-water interface, digging results from (net) resuspension at this interface. The advection of particulate substances by burial or digging follows from:

$$Fadv_p = \frac{vp \times fp \times Cx}{(1 - \phi)}$$

where:

Cx	concentration of a substance [$g.m^{-3}$]
$Fadv_p$	particulate advection flux [$g.m^{-2}.d^{-1}$]
fp	particulate fraction of a substance [$-$]
vp	volumetric burial or digging velocity [$m.d^{-1}$]
j	porosity [$-$]

Fraction fp is equal to 1.0 for all particulate substances, except for organic micro-pollutants and heavy metals. The model calculates fp for these substances as depending on adsorption.

For fixed porosities and fixed layer thickness burial and digging imply transport fluxes across all the interfaces of the sediment layers. This includes the interface of the lower sediment layer in the model and the deeper inactive sediment (boundary condition). The burial and digging velocities vp are calculated in the model from the settling and resuspension fluxes in such a way that constant porosity in and constant thickness (volume) of each sediment layer is maintained. This uses the following definition of porosity:

$$\phi = 1 - \sum_{i=1}^{i=n} \left(\frac{fp_i \times Cx_i}{\rho_i} \right)$$

where:

Cx	concentration of a substance, a sediment component [$g.m^{-3}$]
$Fadv_p$	particulate advection flux [$g.m^{-2}.d^{-1}$]
f_p	particulate fraction of a substance [$-$]
ρ	density of a solid matter component [$g.m^{-2}.d^{-1}$]
i	index of a solid matter component [$-$]
n	number of solid matter components [$-$]

For transient layer thickness or for transient porosity the volumetric burial or digging velocity vp is the sum of an imposed velocity and an additional velocity to maintain maximal layer thickness or minimal layer thickness. In the case of fixed porosity the additional velocity also serves to maintain porosity at its imposed value. The additional velocity is calculated within the model.

Seepage can be upwelling or downwelling (infiltration). It affects only the dissolved substances. Seepage implies transport fluxes across the sediment-water interface, the interfaces of the sediment layers, and the interface of the lower sediment layer and the deeper inactive sediment. The seepage advection flux is:

$$Fadv_d \; = \; \frac{vd \times fd \times Cx}{\phi}$$

where:

Cx	concentration of a substance [$g.m^{-3}$]
$Fadv_d$	dissolved advection flux [$g.m^{-2}.d^{-1}$]
fd	dissolved fraction of a substance [$-$]
vd	volumetric seepage velocity [$m.d^{-1}$]
j	porosity [$-$]

The fraction $fd = 1 - fp$ is equal to 1.0 for all dissolved substances, except for organic micro-pollutants and heavy metals.

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Dispersion

Bioturbation by benthic organisms causes the dispersion of particulate substances. The pertinent dispersion flux is approximated with:

$$Fdis_p = \max(1-\phi_1, 1-\phi_2) \times Dp \times \frac{(fp_1 \times Cx_1/(1-\phi_1) - fp_2 \times Cx_2/(1-\phi_2))}{(L_1+L_2)}$$

where:

Cx	bulk concentration of a substance [$g.m^{-3}$]
Dp	particulate dispersion coefficient [$m^2.d^{-1}$]
$Fdis_p$	particulate dispersion flux [$g.m^{-2}.d^{-1}$]
f_p	particulate fraction of a substance [$-$]
L	dispersion length [m]
ϕ	porosity [$-$]
indexes	1 and 2 refer to two adjacent sediment layers (grid cells)

Each dispersion length L is the half thickness of the sediment layer concerned. The bioturbation flux is zero at the sediment-water interface.

Benthic organisms also cause bio-irrigation, the dispersion of dissolved substances. Water flow across the sediment causes micro-turbulence in the upper pore water, which is another source of dispersion. The overall dispersion coefficient includes the effects of bio-irrigation, flow and molecular diffusion. The dispersion of dissolved substances implies transport fluxes across the sediment-water interface. These fluxes include the so-called return fluxes of nutrients to the water column and the sediment oxygen consumption flux. The dispersion flux of a solute follows from:

$$Fdis_d = \min(\phi_1, \phi_2) \times Dd \times \frac{(fd_1 \times Cx_1/\phi_1 - fd_2 \times Cx_2/\phi_2)}{(L_1+L_2)}$$

where:

Cx	concentration of a substance [$g.m^{-3}$]
Dd	diffusion or dispersion coefficient [$m^2.d^{-1}$]
$Fdis_d$	dissolved dispersion flux [$g.m^{-2}.d^{-1}$]
fd	dissolved fraction of a substance [$-$]
L	dispersion length [m]
ϕ	porosity [$-$]
indexes	1 and 2 refer to two adjacent sediment layers (grid cells)

Each dispersion length L is the half thickness of the sediment layer concerned. For the sediment-water interface L_1 in the lower water layer is an input parameter. The bio-irrigation flux is zero at the interface of the lower sediment layer and the deeper sediment (lower boundary).

Directives for use

1 Porosity ϕ is the input parameter *Porinp* which can be used for fixed porosity (constant) as well as transient porosity (time series). The porosity is "fixed", equal to the input value, if *Porinp* is larger than 10^{-4}. If smaller, porosity is variable. Representative values of the porosity are 0.4 for sandy sediment, 0.7 for silty sediment and 0.9 for peaty sediment (partially consolidated top sediment in a water system!).
2 *Poros* is an output parameter that can be used to verify the imposed porosity. It is calculated by auxiliary process DMVolume that needs densities *RhoIM* and *RhoOM* as input parameters.

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3 Input option parameter *SwErosion* can be used to choose the resuspension formulations. The Partheniades-Krone formulations (*SwErosion* = 0.0) are given above. The De Boer formulations (*SwErosion* $= 1.0$) have been documented elsewhere.
4 Input option parameter *SwSediment* can be used to choose fixed or variable layer thickness. *SwSediment* $= 0.0$ for fixed thickness, and *SwSediment* $= 1.0$ for variable thickness. These input parameters are also used to calculate initial volumes and quantities of substances in all sediment grid cells.
5 With regard to layer thickness three parameters can be defined for each layer. *FixTh* is used to quantify fixed layer thicknesses. *MaxTh* and *MinTh* specify the maximal and minimal layer thickness in the case of transient layer thickness.
6 The seepage velocity is the input parameter *Vseep*, which has a negative value in the case of downwelling.
7 Only in the case of transient layer thickness the volumetric burial and digging velocity needs to be provided as input parameter *VburDM*. A positive value implies burial, a negative value digging
8 *DifCoef* affects mass transport of dissolved substances across all sediment interfaces, except for the lower sediment boundary. Any value given for this interface will be ignored. The first given value concerns the sediment-water interface. A representative summer value for *DifCoef* near the sediment-water interface for a shallow freshwater system is 5.0×10^{-4} $m^2\,d^{-1}$. This value is the sum of bio-irrigation, flow induced dispersion and molecular diffusion. The winter value can be $20\ \%$ of the summer value. Bio-irrigation can be significantly faster in marine sediments. *DifCoef* decreases exponentially with depth, and is practically equal to the molecular diffusion coefficient corrected for tortuosity (ϕ^2) at depths below $0.1\ m$ in freshwater systems, and below $0.4\ m$ in marine water systems. A representative value for the corrected molecular diffusion coefficient is 0.25×10^{-4} $m^2\,d^{-1}$.
9 *TurCoef* affects mass transport of particulate substances across all sediment interfaces, except for the sediment-water interface. The first given value concerns the interface between the top sediment layer and the second layer. A representative summer value for *TurCoef* near the sediment-water interface for a shallow freshwater system is 2.0×10^{-6} $m^2\,d^{-1}$. The winter value can be $10\ \%$ of the summer value. Bioturbation can be significantly faster in marine sediments. *TurCoef* decreases exponentially with depth, and is practically equal to zero at depths below $0.1\ m$ in freshwater systems, and below $0.4\ m$ in marine water systems.
10 The dispersion length at the water side of the sediment-water interface *Diflen* can usually be provided as a constant value between 0.0005 and $0.001\ m$.

References

Smits and Beek (2013)

Table 13.4: *Definitions of the input parameters in the above equations for ADVTRA, DSPTRA and TRASE2_(i) (or TRSE2_(i) or TRSE2(i)). Volume units refer to bulk ($\mathcal{b}$), water ($\mathcal{w}$) or solids ($\mathcal{s}$).*

Name in formulas	Name in input	Definition	Units
A	*Surf*	surface area of overlying water compartment	m^2
Dd	$DifCoef^{1)}$	dispersion coefficient for solutes	$m^2.d^{-1}$
Dp	$TurCoef^{1)}$	dispersion coefficient for particulates	$m^2.d^{-1}$

$Fres0$	*ZResDM*	zero order resuspension flux	$gDM.m^{-2}.d^{-1}$
$Hmin$	*MinDepth*	minimum layer thickness for resuspension	m
L_1	*Diflen*	dispersion length in the overlying water	m
$-$	$FixTh$ [2)]	fixed layer thickness	m
$-$	$MaxTh$ [2)]	maximal layer thickness for variable thickness	m
$-$	$MinTh$ [2)]	minimal layer thickness for variable thickness	m
SwErosion	*SwErosion*	option (0= Part-Krone; 1= De Boer)	$-$
SwSediment	*SwSediment*	option (0= fixed layers; 1= variable)	$-$
vp	*VburDM*	burial and digging velocity	$m.d^{-1}$
vd	*Vseep*	seepage velocity	$m.d^{-1}$
Δt	*Delt*	timestep	d^{-1}
ρ_i	*RhoIM*	density of inorganic matter	$g.m^{-3}$
	RhoOM	density of organic matter	$g.m^{-3}$
j	$Porinp$ [2)]	input porosity	$-$
τ	*Tau*	shear stress	Pa
τc	*TauCrDM*	critical shear stress for resuspension	Pa

[1)] Needs to be specified for each interface in a sediment column.

[2)] Needs to be specified for each layer in a sediment column.

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13.4 Transport in sediment and resuspension (S1/2)

PROCESSES: S12TRA(I), RES_DM, BUR_DM, DIG_DM, S1_COMP, S2_COMP, PARTS1_(I), PARTS2_(I), RES_BUFFER

Sediment components as present in the model for sediment layers S1 and S2 are subject to resuspension (erosion) and burial or digging. Components are released into the water column due to resuspension (erosion). Burial leads to the transport of components from layer S1 to layer S2, and to the removal of components from the layer S2 to deeper sediment (boundary). Digging is the opposite of burial, and may transport components from deeper sediment to layer 2 (boundary), and from layer S2 to layer S1. The “deep” sediment boundary for S2 is defined by means of the concentrations of the components in the boundary layer. The fluxes of these processes are proportional to the fluxes of total sediment (dry matter) for all sediment components. These components may include inorganic sediment, microphytobenthos biomass, particulate detritus (C, N, P, Si), organic micropollutants and heavy metals.

The destination of the resuspension fluxes to the water column is as follows:

- ◇ the inorganic sediment components are allocated to similar substances in the water column;
- ◇ the biomass of microphytobenthos (DiatS1) is allocated to the particulate detritus pools (POC/N/P1) and OPAL;
- ◇ the particulate detritus fractions DET(C,N,P,Si) and OO(C,N,P,Si) are allocated to the particulate detritus pools (POC/N/P1) and OPAL, and to the particulate detritus pools (POC/N/P2) and OPAL, respectively;
- ◇ inorganic adsorbed phosporus, organic micropollutants and heavy metals are allocated to to similar substances in the water column .

Resuspension is shear stress dependent according to Partheniades-Krone (Partheniades, 1962; Krone, 1962) formulations. The resuspension rate is zero, when the shear stress exceeds a certain critical value, or when the water depth is smaller than a certain critical depth.

Volume units refer to bulk (b), water (w) or solids (s).

Implementation

Processes S12TRA(i) with (i) equal to a name of a substance in the water column have been implemented for the following substances:

- ◇ IM1, IM1S1, IM1S2, IM2, IM2S1, IM2S2, IM3, IM3S1 and IM3S2.

Process S12TRADiat has been implemented for the following substances:

- ◇ Diat, DiatS1, DiatS2 (DYNAMO), POC1, PON1, POP1 and Opal.

Processes S12TRA(i) with (i) equal to a name of a substance in the water column and S12TRADetS have been implemented for the following substances:

- ◇ POC1, DetCS1, DetCS2, PON1, DetNS1, DetNS2, POP1, DetPS1, DetPS2, Opal, DetSiS1 and DetSiS2.

Processes S12TRA(i) with (i) equal to a name of a substance in the water column have been implemented for the following substances:

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◇ POC2, OOCS1, OOCS2, PON2, OONS1, OONS2, POP2, OOPS1, OOPS2, Opal, OOSiS1 and OOSiS2.

Process S12TRAAAP has been implemented for the following substances:

◇ AAP, AAPS1 and AAPS2.

Processes S12TRA(i) with (i) equal to a name of a substance in the water column have been implemented for the following substances:

◇ OMP, OMPS1, OMPS2, 153, 153S1, 153S2, Atr, AtrS1, AtrS2, BaP, BaPS1, BaPS2, Diu, DiuS1, DiuS2, Flu, FluS1, FluS2, HCB, HCBS1, HCBS2, HCH, HCHS1, HCHS2, Mef, MefS1 and MefS2.

Processes S12TRA(i) with (i) equal to a name of a substance in the water column have been implemented for the following substances:

◇ As, AsS1, AsS2, Cd, CdS1, CdS2, Cr, CrS1, CrS2, Hg, HgS1, HgS2, Ni, NiS1, NiS2, Pb, PbS1, PbS2, Va, VaS1, VaS2, Zn, ZnS1 and ZnS2.

Processes S12TRA(i) use the resuspension fluxes of sediment dry matter from process RES_DM, the burial fluxes of sediment dry matter from process BUR_DM, and the digging fluxes of sediment dry matter from process DIG_DM. These processes derive the quantities of dry matter in layers S1 and S2 from processes S1_COMP and S2_COMP, and the dry matter settling flux from process SUM_SEDIM.

The processes for organic nutrients in detritus use input from processes S1_COMP and S2_COMP with regard to stochiometric ratios for nutrients N, P and Si, the actual layer thicknesses and the densities of the sediment in the layers.

The processes for organic micropollutants and heavy metals use input from processes PARTS1_(i) and PARTS1_(i) with regard to particulate concentrations.

Table 13.5 to 13.9 provide the definitions of the input parameters occurring in the formulations.

Formulation

Resuspension

There are two options to calculate the resuspension flux of sediment dry matter. In option 1 (process Res_DM), the resuspension flux of sediment dry matter is described as the sum of zero-order and first-order kinetics according to:

$$Fres_j{}' = ftau_j \times (Fres0 + r \times Cdm_j/A)$$

if $H < Hmin \quad Fres_j{}' = 1.0 \quad else$

$$Fres_j = min\left(Fres_j{}', \frac{Cdm}{A \times \Delta t}\right)$$

if $DMS1 > 0.0 \quad FresS2 = 0.0$

if $\tau = -1.0 \quad f_\tau = 1.0 \quad else$

$$ftau_j = \max(0.0, (\frac{\tau}{\tau c_j} - 1.0))$$

where:

A	surface area of overlying water compartment [m^2]
Cdm	amount of sediment dry matter [gDM]
$Fres0$	zero-order resuspension flux of sediment [$gDM.m^{-2}.d^{-1}$]
$Fres$	resuspension flux of sediment [$gDM.m^{-2}.d^{-1}$]
$ftau$	shear stress limitation function [$-$]
H	depth of the water column, thickness overlying water layer [m]
$Hmin$	minimal depth of the water column for resuspension [m]
r	first-order resuspension rate [d^{-1}]
τ	shear stress [Pa]
τc	critical shear stress for resuspension [Pa]
Δt	timestep in DELWAQ [d]
j	index for sediment layer S1 or S2.

Option 2 entails the "buffer" layer concept by (Kessel et al., 2011). The resuspension of each fraction of inorganic matter out of the fluff layer (S1) is calculated as follows:

$$E_1 = min\big(Z_{res}, V_{res} f_{IMiS1} M\big) \left(\frac{\tau_b}{\tau_\alpha, S1} - 1 \right)$$

For the resuspensiopn flux from the buffer layer (S2):

$$E_2 = f_{IMiS2} F_{resPUp} \rho_s \big((s-1) g D_{50}\big)^{0.5} D_*^{0.3} \left(\frac{\tau_b}{\tau_{Sh}} - 1 \right)$$

$$D_* = D_{50} \big(\frac{()s-1)g}{\nu^2} \big)^{1/3}$$

$$s = \frac{\rho_s}{\rho_w}$$

with:

D_{50}	median grain size (diameter) [m]
D_*	reduced grain size [-]
E_1	resuspension flux of the i'th SPM fraction (IMiS1) from layer S1 [g m^{-2} d^{-1}]
E_2	resuspension flux of the i'th SPM fraction (IMiS2) from layer S2 [g m^{-2} d^{-1}]
F_{resPUp}	Van Rijn (1993) pickup factor from buffer layer [-]
f_{IMiS1}	the i'th fraction of SPM in layer S1 [-]
f_{IMiS2}	the i'th fraction of SPM in layer S2 [-]
Z_{res}	zeroth-order resuspension rate from layer S1 [g m^{-2} d^{-1}]
ρ_s	density of the sediment [kg m^{-3}]
ρ_w	density of water [kg m^{-3}]
$\tau_{\alpha,S1}$	critical bed shear stress for layer S1 [Pa]
τ_{Sh}	Shields shear stress for layer S2 [Pa]

The total dry matter resuspension flux from S1 and S2 respectively is calculated as follows:

$$Fres_{S1} = (E_{1,IM1} + E_{1,IM2} + E_{1,IM3}) \times \frac{DMS1}{TIMS1}$$

$$Fres_{S2} = (E_{2,IM1} + E_{2,IM2} + E_{2,IM3}) \times \frac{DMS2}{TIMS2}$$

Where

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DM	total inorganic plus organic dry matter content [g m^{-2}]
TIM	total inorganic dry matter content [g m^{-2}]

Resuspension from both layers is de-activated when the layer thickness is below a certain threshold (MinDepth). The total resuspension from layer S2 is maximized to a value MaxResPup.

The resuspension of inorganic sediment components, organic carbon, nitrogen, phosphorus and silicate components, adsorbed phosphate, micro-pollutants and heavy metals in the sediment follows from:

$$Rres_{i,j} = fs_{i,j} \times fr_{i,j} \times Fres_j / H$$

where:

fr	fraction of a component in sediment dry matter [$gX.gDM^{-1}$]
fs	scaling factor [$-$] or [$gX.gY^{-1}$]
$Rres$	resuspension rate of a component [$gX.m^{-3}\ell.d^{-1}$]
i	index for component i
j	index for sediment layer S1 or S2.

The ratio fs is a scaling factor that is equal to 1.0 for most substances. It is component specific for the organic nutrients, in fact the stochiometric ratio of N, P or Si in organic detritus.

Burial

The burial fluxes can be calculated on the basis of sediment layers with fixed thicknesses or on the basis of imposed burial rates.

For option *SWSediment=0.0* layer thicknesses are kept constant. The burial fluxes of sediment dry matter follows from:

$$Fbur_j = \begin{cases} Fin_j + \frac{(Z_j - Zfix_j) \times \rho_j \times (1-\phi_j)}{\Delta t} & \text{if } Z_j \geq Zfix_j \\ 0.0 \end{cases}$$

$$Fin_1 = Fset$$
$$Fin_2 = Fbur_1$$

where:

Fbur	burial flux of sediment [$gDM.m^{-2}.d^{-1}$]
Fin	influx of sediment [$gDM.m^{-2}.d^{-1}$]
Fset	settling flux of sediment [$gDM.m^{-2}.d^{-1}$]
Z	actual thickness of sediment layer [m]
Zfix	fixed thickness of sediment layer [m]
ϕ	porosity [$-$]
ρ	density of sediment dry matter ($g.m^{-3}_{\ell}$)
Δt	timestep in DELWAQ [d]
j	index for sediment layer S1 or S2.

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For option *SWSediment=1.0* layer the burial fluxes of sediment dry matter are described as the sum of zero-order and first-order kinetics according to:

$$Fbur_j = \min\left((Fbin_j + Fbad_j), Fbmax_j\right)$$
$$Fbin_j = Fbur0_j + rb_j \times Cdm_j / A$$
$$Fbad_j = \max\left(0, \frac{(Z_j - Zmax_j) \times \rho_j \times (1 - \phi_j)}{\Delta t}\right)$$
$$Fbmax_j = Fin_j - Fout_j + \frac{Cdm_j}{A \times \Delta t}$$

$$Cdm_j = A \times Z_j \times \rho_j \times (1 - \phi_j)$$

$$Fin_1 = Fset$$
$$Fin_2 = Fbur_1$$

$$Fout_1 = Fres_1$$
$$Fout_2 = Fdig_1$$

where:

A	surface area of overlying water compartment [m^2]
Cdm	amount of sediment dry matter [gDM]
$Fbad$	additional burial flux to obey maximal layer thickness [$gDM.m^{-2}.d^{-1}$]
$Fbin$	burial flux of sediment based on input parameters [$gDM.m^{-2}.d^{-1}$]
$Fbmax$	maximal possible burial based on available sediment [$gDM.m^{-2}.d^{-1}$]
$Fbur0$	zero-order burial flux of sediment [$gDM.m^{-2}.d^{-1}$]
$Fbur$	burial flux of sediment [$gDM.m^{-2}.d^{-1}$]
$Fdig$	digging flux of sediment [$gDM.m^{-2}.d^{-1}$]
Fin	influx of sediment [$gDM.m^{-2}.d^{-1}$]
$Fout$	outflux of sediment [$gDM.m^{-2}.d^{-1}$]
$Fres$	resuspension flux of sediment [$gDM.m^{-2}.d^{-1}$]
$Fset$	settling flux of sediment [$gDM.m^{-2}.d^{-1}$]
rb	first-order burial rate [d^{-1}]
Z	actual thickness of sediment layer [m]
$Zfix$	fixed thickness of sediment layer [m]
$Zmax$	maximal thickness of sediment layer [m]
ϕ	porosity [$-$]
ρ	density of sediment dry matter [$g.m_{\ell}^{-3}$]
Δt	timestep in DELWAQ [d]
j	index for sediment layer S1 or S2.

The burial of inorganic sediment components, organic carbon, nitrogen, phosphorus and silicate components, adsorbed phosphate, micro-pollutants and heavy metals in the sediment follows from:

$$Fbur_{i,j} = fs_{i,j} \times fr_{i,j} \times Fbur_j$$
$$Rbur_{i,j} = Fbur_{i,j} / H$$

where:

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fr	fraction of a component in sediment dry matter [$gX.gDM^{-1}$]
fs	scaling factor [$-$] or [$gX.gY^{-1}$]
H	depth of the water column, thickness overlying water layer [m]
$Fbur$	burial flux of a component [$gX.m^{-2}.d^{-1}$]
$Rbur$	burial rate of a component [$gX.m^{-3}\ell.d^{-1}$]
i	index for component i
j	index for sediment layer S1 or S2.

The ratio fs is a scaling factor that is equal to 1.0 for most substances. It is component specific for the organic nutrients, in fact the stochiometric ratio of N, P or Si in organic detritus.

Digging

As for burial the digging fluxes can be calculated on the basis of sediment layers with fixed thicknesses or on the basis of imposed digging rates.

For option *SWSediment=0.0* layer thicknesses are kept constant. The burial fluxes of sediment dry matter follows from:

if $Z_j < Zfix_j$ *then*

$$Fdig_j = Fout_j + \frac{(Zfix_j - Z_j) \times \rho_j \times (1 - \phi_j)}{\Delta t}$$

if $Z_j = Zfix_j$ *then*

$$Fdig_j = Fout_j$$

and

$$Fout_1 = Fres_1$$
$$Fout_2 = Fdig_1$$

where:

$Fdig$	digging flux of sediment [$gDM.m^{-2}.d^{-1}$]
$Fout$	outflux of sediment [$gDM.m^{-2}.d^{-1}$]
$Fres$	resuspension flux of sediment [$gDM.m^{-2}.d^{-1}$]
Z	actual thickness of sediment layer [m]
$Zfix$	fixed thickness of sediment layer [m]
ϕ	porosity [$-$]
ρ	density of sediment dry matter [$g.m^{-3}_{\ell}$]
Δt	timestep in DELWAQ [d]
j	index for sediment layer S1 or S2.

For option *SWSediment=1.0* layer the digging fluxes of sediment dry matter are described with zero-order kinetics according to:

$$Fdig_j = \min(Fdig0_j, Fdmax_j)$$
$$Fdmax_1 = \frac{C_{dm_2}}{A \times \Delta t}$$
$$Fdmax_2 = \infty$$
$$C_{dm_2} = A \times Z_2 \times \rho_2 \times (1 - \phi_2)$$

where:

A	surface area of overlying water compartment [m^2]
Cdm	amount of sediment dry matter [gDM]
$Fdig$	digging flux of sediment based on input parameters [$gDM.m^{-2}.d^{-1}$]
Fdig0	zero-order digging flux of sediment [$gDM.m^{-2}.d^{-1}$]
Fdmax	maximal possible digging based on available sediment [$gDM.m^{-2}.d^{-1}$]
Z	actual thickness of sediment layer [m]
ϕ	porosity [$-$]
ρ	density of sediment dry matter ($g.m^{-3}$)
Δt	timestep in DELWAQ [d]
j	index for sediment layer S1 or S2.

The digging of inorganic sediment components, organic carbon, nitrogen, phosphorus and silicate components, adsorbed phosphate, micro-pollutants and heavy metals in the sediment is dependent on the quality of an underlying sediment layer. Using an option parameter it is possible to allocate the quality of the layer itself or the quality of the underlying layer. Digging follows from:

if $SWDig_j$ = 0.0 (quality of the layer itself)

$$Fdig_{i,j} = fs_{i,j} \times fr_{i,j} \times Fdig_j$$

if $SWDig_j$ = 1.0 (quality of underlying layer)

$$Fdig_{i,j} = fs_{i,j+1} \times fr_{i,j+1} \times Fdig_j$$

and

$$Rdig_{i,j} = Fdig_{i,j}/H$$

where:

fr	fraction of a component in sediment dry matter [$gX.gDM^{-1}$]
fs	scaling factor [$-$] or [$gX.gY^{-1}$]
H	depth of the water column, thickness overlying water layer [m]
$Fdig$	digging flux of a component [$gX.m^{-2}.d^{-1}$]
$Rdig$	digging rate of a component [$gX.m^{-3}.d^{-1}$]
i	index for component i
j	index for sediment layer S1 or S2.

The ratio fs is a scaling factor that is equal to 1.0 for most substances. It is component specific for the organic nutrients, in fact the stochiometric ratio of N, P or Si in organic detritus.

Directives for use

1 This transport process requires a lower boundary condition as to the composition of dry matter and the nutrient stoichiometry of detrital organic matter. However, this lower boundary condition only comes into effect when digging is included in the model. If only S1 substances are simulated, it is required to include process S2_COMP that provides the parameters for the boundary of S1, including *FrDetCS2, FrOOCS2, N-CDETCS2, N-COOCS2, P-CDETCS2, P-COOCS2, S-CDETCS2, S-COOCS2* for organic matter. A realistic boundary requires that all relevant input parameters of S2_COMP are allocated an input value. If both S1 and S2 substances are simulated, the transport process uses its additional input parameters that define an S3 boundary. For organic matter this concerns *FrDetCS3, FrOOCS3, FrDetNS3, FrOONS3, FrDetPS3, FrOOPS3, FrDetSiS3, FrOOSiS3*, the weight fractions of the various components in dry matter of boundary S3.

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2 Tau can be simulated with process TAU. If not simulated or imposed *Tau* will have the default value -1.0, which implies that resuspension is not affected by the shear stress.
3 Resuspension does not occur, when the layer thickness is smaller than the minimum thickness *MinDepth* for settling, which has a default value of 0.1 m. When desired *MinDepth* may be given a different value.
4 The *Res_DM* resuspension module checks from which layer resuspension should take place: only if no mass is available in the uppermost layer (S1), resuspension can take place from the second layer (S2). It is assumed that mass in layer S1 protects layer S2 against resuspension in that timestep, even if the actual bottom shear stress exceeds the critical shear stress for bottom layer S2 ($Tau > TauCrS2DM$).
5 Dry matter as such is not a DELWAQ substance. Dry matter is calculated from all the substances which contributes to dry mass and are modelled.
6 In the *Res_DM* resuspension module, usually only the zeroth-order part of the resuspension formulation is used.
7 If the *Res_Buffer* module is used to calculate resuspension, the resuspension fluxes of IM1-3 from S1/2 are automatically accounted for. The use of S12TraIM1-3 is not required (as it would be if *Res_DM* had been used).
8 The buffer layer concept has been set up and implemented without burial and digging for IM1-3.
9 Previous undocumented versions of the buffer layer concept in Delft3D relied on the process *Res_Pickup* and special versions of S12TraIM1-3. This functionality is now integrally available in *Res_Buffer* in a way that provides an alternative for *Res_DM*.
10 The scaling factor *ScalCar* is equal to 10^{-6} for organic micro-pollutants and heavy metals for the conversion from mgX.kgDM^{-1} to gX.gDM. By default *ScalCar* is equal to 1.0 for all other substances.
11 For both burial options, the user may want to define the fixed or maximum thickness of the layers as a function of time. This means that some burial can occur even if the settling rate and the user-defined burial rate are zero. This happens if the user-defined thickness decreases.
12 The option parameter *SWDigS1 = 0.0 (default)* leads to the allocation of the quality of layer S1 ($fr_{i,1}$, $fs_{i,1}$) to the digging flux for layer S1. This option should only be used if only S1 is simulated. The option parameter *SWDigS2 = 0.0 (default)* leads to the allocation of the quality of layer S2 ($fr_{i,2}$, $fs_{i,2}$) to the digging flux for layer S2.
13 The option parameter *SWDigS1 = 1.0* leads to the allocation of the quality of underlying boundary layer S2 ($fr_{i,2}$, $fs_{i,2}$) to the digging flux for layer S1, which is logical when S1 and S2 are simulated both. The option parameter *SWDigS2 = 1.0* leads to the allocation of the quality of underlying boundary layer S3 ($fr_{i,3}$, $fs_{i,3}$) to the digging flux for layer S2. Boundary S3 is not simulated but imposed.
14 The fluxes *fResS1(i), fResS2(i), fBurS1(i), fBurS2(i), fDigS1(i), fDigS2(i)* are available as additional output parameters [$gX.m^{-2}.d^{-1}$].

References

Krone (1962), Partheniades (1962)

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Table 13.5: *Definitions of the input parameters in the above equations for S12TRA(i).*

Name in formulas	Name in input	Definition	Units
$Fbur_j$	*fBur(i)DM3*	burial flux of sediment from layer j	$gDM.m^{-2}.d^{-1}$
$Fdig_j$	*fDig(i)DM3*	digging flux of sediment to layer j	$gDM.m^{-2}.d^{-1}$
$Fres_j$	*fRes(i)DM3*	resuspension flux of sediment from layer j	$gDM.m^{-2}.d^{-1}$
$fr_{i,j}$	*Fr(i)(j)*	fraction of a component in sediment layer j for inorganic sediment components, microphytobenthos, detritus components, and AAP	$gX.gDM^{-1}$
$fr_{i,j}$	*Q(i)DM(j)*	content in sediment layer j for organic micropollutants and heavy metals	$mgX.kgDM^{-1}$
$fs_{i,j}$	N-CDetC(j)	ratio of DetN and DetC in sediment layer j	$gN.gC^{-1}$
	P-CDetC(j)	ratio of DetP and DetC in sediment layer j	$gP.gC^{-1}$
	S-CDetC(j)	ratio of DetSi and DetC in sediment layer j	$gSi.gC^{-1}$
	or		
	N-COOC(j)	ratio of OON and OOC in sediment layer j	$gN.gC^{-1}$
	P-COOC(j)	ratio of OOP and OOC in sediment layer j	$gP.gC^{-1}$
	S-COOC(j)	ratio of OOSi and OOC in sediment layer j	$gSi.gC^{-1}$
$fs_{i,j}$	*ScalCar*	scaling factor for all other components	-
H	*Depth*	depth of the overlying water compartment	m
$SWDig_j$	*SWDig(j)*	option parameter, =0.0 quality of layer itself, =1.0 quality from underlying layer	-

1) *(i)* is equal to one of the components in sediment.

2) *(j)* is generally equal to S1 or S2, that represent the pertinent sediment layer. For $fr_{i,j}$ and $fs_{i,j}$ (j) also concerns underlying boundary layer S3.

3) These fluxes are calculated by processes SUM_SEDIM, RES_DM, BUR_DM and DIG_DM.

Table 13.6: *Definitions of the input parameters in the above equations for RES_DM.*

Name in formulas	Name in input	Definition	Units
Cdm_j	*DM(j)*	amount of sediment dry matter in sediment layer j	gDM
$Fres0$	*ZResDM*	zero-order resuspension flux of sediment	$gDM.m^{-2}.d^{-1}$

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Table 13.6: *Definitions of the input parameters in the above equations for RES_DM.*

Name in formulas	Name in input	Definition	Units
A	Surf	surface area of overlying water comp.	m^2
H	Depth	depth of the overlying water compartment	m
$Hmin$	MinDepth	minimal layer thickness for resusp. and settling	m
r	*VResDM*	first-order resuspension rate of sediment	d^{-1}
τ	*Tau*	shear stress	Pa
τc_j	*TaucR(j)DM*	critical shear stress for resusp. from sediment layer j	Pa
Δt	*Delt*	timestep in DELWAQ	d

1)*(j)* is equal to S1 or S2, which represents the pertinent sediment layer

Table 13.7: *Definitions of the input parameters in the above equations for RES_Buffer.*

Name in formulas	Name in input	Definition	Units
	IM(i)S2	IM fraction in layer S2	$gDMm^{-2}$
τ_b	*Tau*	total bottom shear stress	Nm^{-2}
τ_{Sh}	*TauShields*	Shields shear stress for resusp. pick-up	Nm^{-2}
D_{50}	*Grain50*	Grain size (D50)	m
g	*Grav*	Gravitational acceleration	ms^{-2}
ν	*KinViscos*	kinematic viscosity	$m2s^{-1}$
ρ_s	*RhoSand*	bulk density sand	$gDMm^{-3}$
ρ_w	*RhoWater*	density of water	kgm^{-3}
	PorS2	porosity of sediment layer S2	m^3pores $m^{-3}bulk$
	ThickS2	thickness of layer S2	m
	Surf	horizontal surface area	m^2
	Depth	depth of segment	m
	Delt	timestep for processes	d

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Table 13.7: *Definitions of the input parameters in the above equations for RES_Buffer.*

Name in formulas	Name in input	Definition	Units
	MinDepth	minimum layer thickness for sedimentation/resuspension	m
	MaxResPup	maximum resuspension pick-up	$gm^{-2}d^{-1}$
$FresPUp$	*FactResPup*	factor resuspension pick-up	$-$
	IM(i)S1	IM fraction in layer S1	$gDMm^{-2}$
$Zres$	*ZResIM(i)*	zeroth-order resuspension flux IM fraction	$gDMm^{-2}d^{-1}$
$Vres$	*VResIM(i)*	first order resuspension velocity IM fraction	d^{-1}
$\tau_{a,S1}$	*TaucRS1IM(i)*	critical shear stress for resuspension IM fraction from S1	Nm^{-2}
	DMS1	total amount of dry matter in layer S1	$gDMm^{-2}$
	DMS2	total amount of dry matter in layer S2	$gDMm^{-2}$

1)*(j)* is equal to S1 or S2, which represents the pertinent sediment layer

Table 13.8: *Definitions of the input parameters in the above equations for BUR_DM.*

Name in formulas	Name in input	Definition	Units
$Fbur0_j$	*ZBurDM(j)*	zero-order burial flux of sediment in layer j	$gDM.m^{-2}.d^{-1}$
$Fset$	$fSedDM^{2)}$	settling flux of sediment	$gDM.m^{-2}.d^{-1}$
$Fres_j$	*fRes(j)DM*	resuspension flux of sediment	$gDM.m^{-2}.d^{-1}$
A	*Surf*	surface area of overlying water compartment	m^2
Z_j	*ActTh(j)*	actual thickness of sediment layer j fixed thickness of sediment layer j maximal thickness of sediment layer j	m
$Zfix_j$	*FixTh(j)*	fixed thickness of sediment layer j maximal thickness of sediment layer j	m
$Zmax_j$	*MaxTh(j)*	maximal thickness of sediment layer j	m
rb_j	*VBurDM(j)*	first-order burial rate of sediment in layer j	d^{-1}

continued on next page

Table 13.8 – continued from previous page

Name in formulas	Name in input	Definition	Units
$SWSediment$	*SWSediment*	option parameter, =0.0 apply fixed layer thickness, =1.0 apply burial kinetics	-
ϕ_j	*Por(j)*	shear stress	Pa
ρ_j	*Rho(j)*	critical shear stress for resusp. from sediment layer j	Pa
Δt	*Delt*	timestep in DELWAQ	d

[1] *(j)* is equal to S1 or S2, which represents the pertinent sediment layer

[2] fSedDM is calculated by process SUM_SEDIM

Table 13.9: *Definitions of the input parameters in the above equations for DIG_DM.*

Name in formulas	Name in input	Definition	Units
$Fdig0_j$	*ZDigDM(j)*	zero-order digging flux of sediment in layer j	$gDM.m^{-2}.d^{-1}$
$Fres_1$	*fResS1DM2*	resuspension flux of sediment in layer 1	$gDM.m^{-2}.d^{-1}$
A	*Surf*	surface area of overlying water comp.	m^2
Z_j	*ActTh(j)*	actual thickness of sediment layer j	m
$Zfix_j$	*FixTh(j)*	fixed thickness of sediment layer j	m
$SWSediment$	*SWSediment*	option parameter, =0.0 apply fixed layer thickness, =1.0 apply burial kinetics	-
ϕ_j	*Por(j)*	shear stress	Pa
ρ_j	*Rho(j)*	critical shear stress for resusp. from sediment layer j	Pa
Δt	*Delt*	timestep in DELWAQ	d

[1] *(j)* is equal to S1 or S2, which represents the pertinent sediment layer

[2] fResS1DM is calculated by process RES_DM.

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13.5 Empirical model for flocculation equilibrium

PROCESS: IM_FLOCEQ

Flocculation is a complex process where individual sediment particles may interact and form larger flocs with different size and shape, density and settling properties. The process IM_FLOCEQ is an implementation of the empirical model formulated by Manning and Dyer (Manning and Dyer, 2007). As such it defines an equilibrium distribution between two fractions of inorganic material (two of IM1, IM2, IM3, where one represents the macro-flocs and the other the micro-flocs. The distribution is treated such that there is a relatively fast exchange of material between the two fractions.

Implementation

The process is implemented for the three fractions of inorganic material IM1, IM2 and IM3. Only two of them play a role and the choice is made via an input parameter (SwFloceq).

Formulation

The ratio of macro-flocs and micro-flocs depends on the total concentration of particulate matter (including organic material) according to the formula:

$$SPM_{ratioEM} = 0.815 + 3.18 \cdot 10^{-3}\, TPM - 1.4 \cdot 10^{-7}\, TPM^2$$

$$M_{eq} = (M_{macro} + M_{micro}) \frac{SPM_{ratioEM}}{1 + SPM_{ratioEM}}$$

$$dfloc = Rc(M_{eq} - M_{macro})$$

$$Rc = \begin{cases} Rc_{Floc} & \text{if} \quad M_{macro} < M_{eq} \\ Rc_{Breakup} & \text{if} \quad M_{macro} \geq M_{eq} \end{cases}$$

where

$SPM_{ratioEM}$	mass ratio between macro and micro flocs [-]
TPM	total concentration of particulate matter (inorganic and organic) [g m^{-3}]
$dfloc$	flux of material from either macro-flocs to micro-flocs or vice versa [g m^{-3} d^{-1}]
M_{eq}	equilibrium concentration for the macro flocs [g m^{-3}]
M_{macro}	instantaneous concentration of the macro-flocs [g m^{-3}]
M_{micro}	instantaneous concentration of the micro-flocs [g m^{-3}]
Rc	rate constant for the exchange of the material [d^{-1}]
Rc_{Floc}	rate constant for floc formation ($M_{macro} < M_{eq}$) [d^{-1}]
$Rc_{Breakup}$	rate constant for floc breakup ($M_{macro} \geq M_{eq}$) [d^{-1}]

The total concentration TPM is determined in general by the process Compos.

Note: This presumes that the total concentration TPM is below 11000 g $m-3$. Such high sediment concentrations are beyond the usual range for D-Water Quality though.

Directives for use

- ◇ Only two fractions of inorganic material are involved, the third can therefore be used for other purposes. Which two fractions is determined by the constant SwFloceq:
  - □ SwFloceq = 0 (default): IM1 represents the macro-flocs and IM2 represents the micro-flocs.

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- SwFloceq = 1: IM2 represents the macro-flocs and IM1 represents the micro-flocs.
- SwFloceq = 2: IM2 represents the macro-flocs and IM3 represents the micro-flocs.
- SwFloceq = 3: IM3 represents the macro-flocs and IM2 represents the micro-flocs.

◇ The process does not calculate the settling velocities for the macro and micro-flocs. This is left to the user instead, either by specifying the settling velocity directly or having them calculated via the process CALVS_i (i = IM1, IM2 or IM3).

Table 13.10: *Definitions of the input parameters in the above equations*

Name in formulas	**Name in input**	**Definition**	**Units**
M_{macro}	$IM(i)$	concentration of fraction IM1, IM2 or IM3	g m^{-3}
M_{micro}	$IM(j)$	concentration of companion fraction	g m^{-3}
TPM	TPM	total concentration of particulate matter	g m^{-3}
Rc_{Floc}	$RcFloc$	rate constant for floc formation ($M_{macro} < M_{eq}$)	d^{-1}
$Rc_{Breakup}$	$RcBreakup$	rate constant for floc breakup ($M_{macro} > M_{eq}$)	d^{-1}
$SWFloceq$	$SWFloceq$	switch for selecting the two fractions IM1, IM2 or IM3	-

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13.6 Dynamic model for flocculation

PROCESS: IM_FLOCDYN

Flocculation is a complex process where sediment particles form larger flocs which have different properties than the individual particles. The process IM_FLOCDYN is an implementation of two empirical models, one formulated by Manning and Dyer (Manning and Dyer, 2007) and the other by Chassagne and Safar (Chassagne and Safar, 2020). Instead of an equilibrium distribution between two fractions of inorganic material (section 13.5), this process uses a dynamic approach. In addition it calculates the settling velocities of the two fractions.

Note: The settling velocity should not be specified as a process parameter in the input (VSedIM1 or VSedIM2) or calculated via the CALVS_i process.

The substances IM1 and IM2 are used to represent respectively macro-flocs and micro-flocs. The total concentration of particulate matter (so including organic material) is required for the calculation (see the process COMPOS in section 16.1 for this parameter).

Implementation

The process is implemented for two fractions of inorganic material IM1, IM2.

Formulation

Two options have been implemented in the process routine:

- ◇ *SWFloForm = 1*: Use the formulations by Manning and Dyer (Manning and Dyer, 2007). The floc ratio is calculated in a manner identical to the process IM_FLOCEQ, but in addition the settling velocities are calculated.
- ◇ *SWFloForm = 2*: Use the formulations by Chassagne and Safar (Chassagne and Safar, 2020).

Formulations by Manning and Dyer

The ratio of macro-flocs and micro-flocs depends on the total concentration of particulate matter (including organic material) according to the formula:

$$SPM_{ratioEM} = 0.815 + 3.18 \cdot 10^{-3}\, TPM - 1.4 \cdot 10^{-7}\, TPM^2$$

$$M_{eq} = (M_{macro} + M_{micro}) \frac{SPM_{ratioEM}}{1 + SPM_{ratioEM}}$$

$$dfloc = Rc(M_{eq} - M_{macro})$$

$$Rc = \begin{cases} Rc_{Floc} & \text{if} \quad M_{macro} < M_{eq} \\ Rc_{Breakup} & \text{if} \quad M_{macro} \geq M_{eq} \end{cases}$$

where

$SPM_{ratioEM}$	mass ratio between macro and micro flocs [-]
TPM	total concentration of particulate matter (inorganic and organic) [g m^{-3}]
$dfloc$	flux of material from either macro-flocs to micro-flocs or vice versa [g m^{-3} d^{-1}]
M_{eq}	equilibrium concentration for the macro flocs [g m^{-3}]
M_{macro}	instantaneous concentration of the macro-flocs [g m^{-3}]
M_{micro}	instantaneous concentration of the micro-flocs [g m^{-3}]

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Rc	rate constant for the exchange of the material [d^{-1}]
Rc_{Floc}	rate constant for floc formation ($M_{macro} < M_{eq}$) [d^{-1}]
$Rc_{Breakup}$	rate constant for floc breakup ($M_{macro} \geq M_{eq}$) [d^{-1}]

The total concentration TPM is determined in general by the process COMPOS.

The settling velocity for macro-flocs is calculated as follows:

Shear stress $\tau < 0.65$ Pa:

$$w_{s,macro} = 0.644 - 0.000471 \cdot TPM + 9.36\tau - 13.1\tau^2$$

Shear stress $0.65 \leq \tau < 1.45$ Pa:

$$w_{s,macro} = 3.96 + 0.000346 \cdot TPM - 4.38\tau + 1.33\tau^2$$

Shear stress $\tau \geq 1.45$ Pa:

$$w_{s,macro} = 1.18 + 0.000302 \cdot TPM - 0.491\tau + 0.057\tau^2$$

The settling velocity for micro-flocs is calculated as follows:

Shear stress $\tau < 0.52$ Pa:

$$w_{s,micro} = 0.244 + 3.25\tau - 3.71\tau^2$$

Shear stress $\tau \geq 0.52$Pa:

$$w_{s,micro} = 0.65\tau^{-0.541}$$

Note: The shear stress (in [Pa]) is taken to be proportional to the turbulent kinetic energy (TKE, in [J m^{-3}]) according to the relationship by Soulsby (Manning and Dyer, 2007):

$$\tau = TKE/3.0$$

(using the above units).

where

$w_{s,macro}$	settling velocity of macro-flocs [mm s^{-1}]
$w_{s,micro}$	settling velocity of micro-flocs [mm s^{-1}]
TPM	total concentration of particulate matter (inorganic and organic) [g m^{-3}]
τ	shear stress in the water phase [Pa]

Formulations by Chassagne and Safar

The ratio of macro-flocs and micro-flocs depends on the total concentration of particulate matter (including organic material) according to the following formulae:

Total concentration of suspended solids $TPM < 0.1$ g m^{-3}:

$$SPM_{ratioEM} = 0.1$$

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Total concentration of suspended solids $0.1 \leq TPM < 1174$ g m^{-3}:

$$SPM_{ratioEM} = 0.1 + 0.221 * \log_{10} TPM$$

Total concentration of suspended solids $TPM \geq 1174$ g m^{-3}:

$$SPM_{ratioEM} = 1.0$$

The dynamic transformation of macro-flocs into micro-flocs and vice versa is handled in the same way as in the Manning-Dyer option.

The settling velocity of macro-flocs is calculated using the following formula:

$$w_{s,macro} = 0.095 \cdot g \cdot \phi_1 \cdot \phi_2 \cdot \phi_3 \cdot e^{-\phi_4^{0.463}}$$

The settling velocity of micro-flocs is calculated using the following formulae:

$$w_{s,micro} = 0.5372 \cdot g \cdot \phi_1 \cdot \phi_3 \cdot e^{-\phi_4^{0.66}}$$

The auxiliary quantities in both sets of formulae are:

$$\phi_1 = \left(\frac{u_*^3 D}{z\mu^3}\right)^{0.166}$$
$$\phi_2 = \left(\frac{TPM}{\rho_{water}}\right)^{0.22044}$$
$$\phi_3 = \sqrt{\frac{z\mu}{u_*^3}}$$
$$\phi_4 = \frac{u_{*,macro}}{u_*} \cdot \sqrt{\frac{z}{z_{local}}}$$
$$\mu = \nu_{water} \cdot \rho_{water}$$
$$u_* = \sqrt{\frac{\tau}{\rho_{water}}}$$
$$u_{*,macro} = 0.067 \text{ m s}^{-1}$$
$$u_{*,micro} = 0.025 \text{ m s}^{-1}$$
$$z = \frac{z_{local}}{1 - z_{local}/H}$$

In these formulae:

g	gravitational acceleration (set to 9.81 [m s^{-2}])
z_{local}	height above the bottom [m]
H	total depth [m]
ν_{water}	kinematic viscosity of the water (converted to the dynamic viscosity, μ) [m^2 s^{-1}]
ρ_{water}	density of the water [kg m^{-3}]
D	diameter, in the above formulae either $10 \cdot 10^{-6}$ m for micro-flocs or $100 \cdot 10^{-6}$ m for macro-flocs.

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Directives for use

◇ Only two fractions of inorganic material are involved, the third can therefore be used for other purposes. IM1 represents the macro-flocs and IM2 represents the micro-flocs.

Table 13.11: *Definitions of the input parameters in the above equations*

Name in formulas	Name in input	Definition	Units
M_{macro}	$IM1$	concentration of fraction IM1 (macro-flocs)	g m^{-3}
M_{micro}	$IM2$	concentration of fraction IM2 (micro-flocs)	g m^{-3}
TPM	TPM	total concentration of particulate matter	g m^{-3}
Rc_{Floc}	$RcFloc$	rate constant for floc formation ($M_{macro} < M_{eq}$)	d^{-1}
$Rc_{Breakup}$	$RcBreakup$	rate constant for floc breakup ($M_{macro} > M_{eq}$)	d^{-1}
$SWFloForm$	$SWFloForm$	switch for selecting the actual formulation	-
H	$TotalDepth$	total depth at the location of the segment	m
z_{local}	$LocalDepth$	local depth of the segment	m
ν_{water}	$KinViscos$	kinematic viscosity of water	m^2 s^{-1}
ρ_{water}	$RhoWater$	density of the water	kg m^{-3}
τ	Tau	shear stress due to flow, waves, etc.	Pa

Table 13.12: *Output parameters for IM_FLOCDYN*

Name in formulas	Name in output	Definition	Units
$w_{s,macro}$	$VSedIM1$	sedimentation velocity IM1 (macro-flocs)	m s-1
$w_{s,micro}$	$VSedIM2$	sedimentation velocity IM2 (micro-flocs)	m s-1
$SPM_{ratioEM}$	$SPMratioEM$	flocculation ratio macro:micro empirical model	-

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13.7 Calculation of horizontal flow velocity

PROCESS: VELOC

This process calculates the horizontal flow velocity in a segment. It is assumed that per segment in at most two horizontal directions mass-flows of water are known. These directions are assumed to be perpendicular to each other. In each direction the two flow velocities are averaged. Next the horizontal flow velocity is calculated using Pythagoras' theorem, the minimum or the maximum from the two directions.

To account for model grids that are not aligned to the coordinate system, two parameters for the grid orientation are available (see the table). Also the contributions in each directions may be weighed differently – as the arithmetic mean of the velocities per exchange, weighed by the flow rate or the area or using the maximum velocity value.

Note 1: If the grid is actually curved strongly, then the orientation will differ per segment and you will have to use an orientation *parameter* instead of a constant if you want to have the velocity vector.

Note 2: Because the process as implemented assumes that the underlying grid is a *curvilinear* or *rectangular* structured grid, *it is unsuited for unstructured grids*, in particular for the grids used by D-Flow FM– even if the grid cells are quandragular. No check is made whether the grid is structured or not, so it is the responsibility of the user to apply this process correctly.

Formulation

$$VelocAvg_1 = \frac{\frac{Flow_{1,1}}{Area_{1,1}} + \frac{Flow_{1,2}}{Area_{1,2}}}{2}$$

$$VelocAvg_2 = \frac{\frac{Flow_{2,1}}{Area_{2,1}} + \frac{Flow_{2,2}}{Area_{2,2}}}{2}$$

$$Veloc = \sqrt{VelocAvg_1^2 + VelocAvg_2^2}$$

where

$Flow_{1,1}$	horizontal "from"-flow direction 1 [m^3 s^{-1}]
$Flow_{1,2}$	horizontal "to"-flow direction 1 [m^3 s^{-1}]
$Flow_{2,1}$	horizontal "from"-flow direction 2 [m^3 s^{-1}]
$Flow_{2,2}$	horizontal "to"-flow direction 2 [m^3 s^{-1}]
$Area_{1,1}$	horizontal "from"-area direction 1 [m^2]
$Area_{1,2}$	horizontal "to"-area direction 1 [m^2]
$Area_{2,1}$	horizontal "from"-area direction 2 [m^2]
$Area_{2,2}$	horizontal "to"-area direction 2 [m^2]
$VelocAvg_1$	average horizontal flow velocity direction 1 [m s^{-1}]
$VelocAvg_2$	average horizontal flow velocity direction 2 [m s^{-1}]
$Veloc$	average horizontal flow velocity [m s^{-1}]

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Directives for use

The process VELOC uses flows in the horizontal direction and therefore is only applicable if one of both of the horizontal (1st and 2nd) directions are available (1DH, 2DH, 2DV, 3D).

Note: The computed flow velocity is not identical to the one that would have been computed by Delft3D-FLOW. As a result, artificial peaks may occur near shallow areas. If you use this velocity to estimate the shear stress for sediment transport, this causes large erosion fluxes. It is better, if possible, to rely on the shear stresses as computed by the hydrodynamic model.

Table 13.13: *Definitions of the input and output parameters for VELOC*

Name in formulas	Name in output	Definition	Units
–	$Orient_1$	Angle of the main positive flow direction with the x-axis	°
–	$Orient_2$	Angle of the secondary positive flow direction (both optional)	°
$Veloc_{max}$	$MaxVeloc$	Maximum velocity (useful to "clip" spurious results)	ms^{-1}
–	$SWCalcVelo$	Weighing method: 1 – linear average, 2 – weighed by flow rate	[-]
		3 – weighed by area, 4 – maximum contribution	[-]
–	$SWAvgVelo$	Method for determining the velocity magnitude: 1 – Pythagoras,	[-]
		2 – maximum, 3 – minimum	[-]
$Veloc$	$Velocity$	Velocity magnitude	ms^{-1}
–	$FlowDir$	Direction of the flow velocity	°
$VelocAvg_1$	$Veloc1$	Velocity component in main direction	ms^{-1}
$VelocAvg_2$	$Veloc2$	Velocity component in secondary direction	ms^{-1}

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13.8 Calculation of the Chézy coefficient

PROCESS: CHEZY

Implementation

This process calculates the Chézy coefficient based on the Manning coefficient or Nikuradse roughness length. For 3D calculations a corrected coefficient is calculated.

Formulation

Depth-averaged Velocities

Two methods have been implemented to calculate the Chézy coefficient for depth averaged velocities.

1. White-Colebrook

$$C_{2D} = 18\ {}^{10}\log\left(12\frac{H}{k_s}\right) \tag{13.2}$$

C_{2D}	Chézy coefficient for depth averaged conditions [m$^{1/2}$ s^{-1}]
H	water depth [m]
k_s	Nikuradse roughness length scale [m]

2. Manning (default)

$$C_{2D} = \frac{\sqrt[6]{H}}{n}$$

C_{2D}	Chézy coefficient [m$^{1/2}$ s^{-1}]
H	total depth of water column (segment depth) [m]
n	Manning coefficient [m$^{-1/3}$ s]

Three-dimensional Velocity

Under the requirement that the depth-averaged velocity of 3D computations equals the velocities obtained with the 2DH model the Chézy coefficient can de derived as follows:

Roughness height z_0 of the bed:

$$z_0 = H\ e^{-\left(1+\frac{\kappa\ C_{2D}}{\sqrt{g}}\right)} \tag{13.3}$$

with

z_0	roughness height of the bed [m]
H	depth of the entire water column [m]
κ	0.41 - Von Kármán coefficient [-]
g	9.811 - gravity constant [m s^{-2}]
C_{2D}	Chézy coefficient for 2D using the segment depth [m$^{1/2}$ s^{-1}]

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Chézy coefficient for three-dimensional velocities

$$C_{3D} = \frac{\sqrt{g}}{\kappa} \ln\left(1 + \frac{h_b/2}{z_0}\right)$$

C_{3D}	Chézy coefficient in case of 3D velocities [m$^{1/2}$ s^{-1}]
h_b	depth of the computational layer at the bed [m]
κ	0.41 - Von Kármán coefficient [-]
g	9.811 - gravity constant [m s^{-2}]
z_0	roughness height of the bed [m]

Directives for use

- ◇ Chézy is sometimes available from hydrodynamical models (e.g. from Delft3D-FLOW Deltares (2024)).
- ◇ For the three-dimensional case, the conversion from C_{2D} to C_{3D} is done within the CALTAU process, not the CHEZY process. This parameter is not output from the process.

Additional references

Deltares (2024)

Table 13.14: *Definitions of the input and output parameters for CHEZY*

Name in formulas	Name in output	Definition	Units
k_s	$Rough$	Nikuradse roughness length	m
n	$Manncoef$	Manning coefficient	m$^{-1/3}s$
h_b	$Depth$	Thickness of the segment (near the bed)	m
H	$TotalDepth$	Depth of the entire water column	m
$SwChezy$	$SwChezy$	Choice for White-Colebrook or Manning	[-]
C_{2D}	$CHEZY$	Two-dimensional Chézy coefficient	m$^{1/2}$s^{-1}

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13.9 Waves

PROCESS: WAVE

Formulations

The computation of the shear stress from wind generated waves uses three wave parameters: the wave height H, the wave period T and the wave length L. They are calculated as follows (Groen and Dorrestein, 1976; Holthuijsen, 1980):

$$g = 9.8$$
$$\rho_l = 1000$$

if InitDepth ≤ 0 : InitDepth = TotalDepth

$$F_S = \frac{g \times Fetch}{vWind^2}$$
$$d_S = \frac{g \times InitDepth}{vWind^2}$$
$$H_S = 0.24 \times \tanh(0.71 \times {d_S}^{0.763}) \times \tanh\left(\frac{0.015 \times {F_S}^{0.45}}{\tanh(0.71 \times {d_S}^{0.763})}\right)$$
$$H = \frac{H_S \times vWind^2}{g}$$
$$T_S = 2\pi \times \tanh(0.855 \times {d_S}^{0.365}) \tanh\left(\frac{0.0345 \times {F_S}^{0.37}}{\tanh(0.855 \times {d_S}^{0.365})}\right)$$
$$T = \frac{T_S \times vWind}{g}$$

with

F_S	standardized fetch [-]
TotalDepth	total water depth [m]
InitDepth	water depth were waves are generated [m]
d_S	significant depth [-]
H_S	significant wave height [-]
T_S	significant wave period [-]

The wave length L is then approximated via a straightforward iteration:

$$L_0 = \frac{gT^2}{2\pi}$$
$$L_{k+1} = L_0 \tanh\left(\frac{2\pi InitDepth}{L_k}\right)$$

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The wave length L, wave period T and water depth h satisfy the dispersion relation:

$$\omega = \frac{2\pi}{T}$$
$$k = \frac{2\pi}{L}$$
$$\omega^2 = gk \tanh(k \times TotalDepth)$$

with

ω	radial frequency [1/s]
k	wave number [1/m]

Directives for use

- ◇ By default the depth at the origin of the wave (InitDepth) equals the actual depth (TotalDepth), because the default value for InitDepth is -1. InitDepth and Fetch can be determined from the wind direction by the processes WDepth and WFetch.
- ◇ This process can be active for non-layered and multi-layer models. The fact that the water column is modelled in layers does not affect the result.

Table 13.15: *Definitions of the input and output parameters for WAVE*

Name in formulas	Name in output	Definition	Units
$vWind$	$VWind$	Wind velocity	ms[1]
$Fetch$	$Fetch$	Fetch length	m
$InitDepth$	$InitDepth$	Depth where the waves originate	m
$TotalDepth$	$TotalDepth$	Depth of the entire water column (if InitDepth = -1)	m
H	$WaveHeight$	Significant wave height	m
L	$WaveLength$	Significant wave length	m
T	$WavePeriod$	Significant wave period	s

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13.10 Calculation of wind fetch and wave initial depth

PROCESS: WDEPTH, WFETCH

The wind fetch ($Fetch$) and the wave initial depth ($InitDepth$) at which the waves have been created can be provided by you as a (block) function of the wind direction.

Implementation

This process is implemented for the characteristics $Fetch$ and $InitDepth$, determining the forming of waves.

Formulations

Assume $WinDir_0 = 0°$

For $WinDir_{i-1} < WindDir \leq WinDir_i$

$$Fetch = WFetch_i$$
$$InitDepth = WDepth_i$$

with

$WindDir$ actual wind direction [degr]
$WinDir_i$ wind direction of data pair i [degr]
$WFetch_i$ fetch of data pair i [m]
$WDepth_i$ wave initial depth of data pair i [m]

Directives for use

- ◇ A minimum of two data pairs and a maximum of eigth data pairs should be provided. The first data pair applies to wind directions between 0°and $WinDir_1$, the second between $WinDir_1$ and $WinDir_2$, etc. The last data pair provided by you applies to all wind direction ranging from the one but last provided $WinDir_{i-1}$ to 360°.
- ◇ The wind direction is defined as the angle relative to north of the direction where the wind is *coming from*, while the flow direction is defined as the angle of the direction where the water is *going to*.

Table 13.16: *Definitions of the input and output parameters for WDEPTH. (i) runs from 1 to 8. Only the input parameters for (i) is 1 and 2 are required.*

Name in formulas	Name in output	Definition	Units
$WindDir$	$WindDir$	Actual direction of the wind	°
$WDepth_(i)$	$WDepth_(i)$	Depth for wind from direction (i)	m
$WinDir_(i)$	$WinDir_(i)$	Direction (i) for wind	°
$InitDepth$	$InitDepth$	Depth to be used for wave parameters	m

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Table 13.17: *Definitions of the input and output parameters for WFETCH. (i) runs from 1 to 8. Only the input parameters for (i) is 1 and 2 are required.*

Name in formulas	Name in output	Definition	Units
$WindDir$	$WindDir$	Actual direction of the wind	°
$WFetch_(i)$	$WFetch_(i)$	Fetch length for wind from direction (i)	m
$WinDir_(i)$	$WinDir_(i)$	Direction (i) for wind	°
$Fetch$	$Fetch$	Fetch length used for wave parameters	m

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13.11 Calculation of bottom shear stress

PROCESS: CALTAU

Implementation

The bottom shear stress is calculated as the sum of the shear stress caused by waves, flow and ship movements. If the directions of the flow (FlowDir) and the wind (WindDir) are supplied the wind and flow stresses are summed as vectors, otherwise as scalars. The stress by ship movements is always added as a scalar as it is assumed to be independent of direction.

$$\tau = \tau_{wind} + \tau_{flow} + \tau_{ship}$$

Formulations

Bed shear stress due to flow (used if the switch $SWTauVeloc$ is set to 1, the default – see below):

$$\tau_{flow} = \frac{\rho_l \times g \times Velocity^2}{Chezy^2}$$

The Chézy coefficients is either user input or can be calculated by the process CHEZY.

Bed shear stress due to wave friction, time averaged over half a wave period:

$$\tau_{wind} = F \rho_l f_w U_{bg,\max}^2$$

$$U_{bg,\max} = \frac{\pi H}{T \sinh\left(\frac{2\pi \times TotalDepth}{L}\right)}$$

$$\omega = \frac{2\pi}{T}$$

$$A_g = \frac{U_{bg,\max}}{\omega}$$

A_g [m] is the peak value of the horizontal displacement at the bottom.

$$CalVelTau = \sqrt{\left(\frac{\tau \times Chezy^2}{\rho_l \times g}\right)}$$

The factor F is taken to be $\frac{1}{4}$ if the shear stress is to be *averaged* over the wave period or $\frac{1}{2}$ if the maximum shear stress over the wave period is chosen as the representative stress. This is controlled by the switch $SWTauMax$ – 0 means that the average is used, 1 that the maximum is used.

The wave parameters H, T and L are input items, which can be calculated by process WAVE.

The wave height H is limited according to (Nelson, 1983):

$$H = \min(M_{Nelson} \times TotalDepth, H)$$

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(M_{Nelson} is the maximum fraction for the wave height, by default 0.55)

In some cases it is useful to be able to use the "HRMS" value (root mean square of the wave heights) instead of the significant wave height. The relation between the two is:

$$H_s = \frac{1}{\sqrt{2}} H_{RMS}$$

The option $SWHrms$ controls which interpretation is used. By default, the wave parameter H is interpreted as the significant wave height ($SWHrms = 1$). With $SWHrms = 2$ it is interpreted as "HRMS".

The wave friction factor f_w can be calculated according to Tamminga (1987) and Swart (1974) or Soulsby (1997).

SWTau = 1 (Tamminga, 1987):

$$f_w = 0.16 \sqrt{\frac{Rough}{U_{bg,max} \times T/2\pi}}$$

SWTau = 2 (Swart, 1974):

$$r = \frac{H}{2 \times Rough \times \sinh(\frac{2\pi \times TotalDepth}{L})}$$

if $r > \pi/2$ then

$$f_w = 0.00251 \exp(5.213 r^{-0.19})$$

else

$$f_w = 0.32$$

SWTau = 3 (Soulsby, 1997):

$$r = \frac{H}{2 \times Rough \times \sinh(\frac{2\pi \times TotalDepth}{L})}$$
$$f_w = 0.237 r^{-0.52}$$

$SWTau$	switch to calculate the wave fraction factor [-]
$SWTauVeloc$	switch to calculate the bottom shear stress due to flow from the flow velocity or rely on $TauFlow$ instead [-]
$SWHrms$	switch to interpret the wave height as "H-significant" (1) or "HRMS" (2) [-]
τ	bottom shear stress [N m^{-2}]=[Pa]
τ_{wind}	part of bottom shear stress caused by wind [Pa]
τ_{flow}	part of bottom shear stress caused by flow velocity [Pa]

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τ_{ship}	part of bottom shear stress defined by you, e.g. to describe the effect of ships [Pa]
$Veloc$	flow velocity [m s^{-1}]
$U_{bg,max}$	amplitude of the wave orbital velocity [m s^{-1}]
$Rough$	Nikuradse bottom roughness length scale, calculated from the Chézy coefficient via the inverse of Eq. 13.2 [m]
g	acceleration of gravity [m s^{-2}]
ρ_l	density of water [kg m^{-3}]
H	wave height [m]
T	wave period [s]
L	wave length [m]
Fw	wave (friction) factor [-]
$TauFlow$	bottom shear stress due to flow (used only if $SWTauVeloc$ is set to 2) [-]

Directives for use

- ◇ The bottom shear stress is sometimes available from hydrodynamic models. If so, you can set the switch $SWTauVeloc$ to 2. The component of the shear stress due to the flow velocity is then taken from the input parameter TauFlow.
- ◇ The process is meant to combine the contributions to the bottom shear stress from various sources. If a hydrodynamic model provides a bottom shear stress that incorporates the contribution from surface waves already, then you should take care not to add the wave component via this process. (For instance you could put the shear stress as available from the hydrodynamic model into the input parameter Tau directly and not use this process at all.)

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Table 13.18: *Definitions of the input and output parameters for CALTAU*

Name in formulas	Name in output	Definition	Units
$Chezy$	$Chezy$	Chezy coefficient	$m^{-1/2}s-1$
$Depth$	$Depth$	Thickness of the segment (near the bed)	m
$TotalDepth$	$TotalDepth$	Total water depth	m
$Velocity$	$Velocity$	Flow velocity	ms^1
H	$WaveHeight$	Significant wave height	m
L	$WaveLength$	Significant wave length	m
T	$WavePeriod$	Significant wave period	s
τ_{flow}	$TauFlow$	Shear stress due to flow	Pa
τ_{ship}	$TauShip$	Shear stress due to ships	Pa
$SWTau$	$SWTau$	Switch for determining the wave roughness	[-]
$SWTauVeloc$	$SWTauVeloc$	Switch for using flow velocity or given flow shear stress	[-]
$SWTauMax$	$SWTauMax$	Switch for using the maximum stress (1) or the mean stress (0) for the contribution by wind waves	[-]
$SWHrms$		SWitch to interpret the wave height: "H-significant" (1) or "HRMS" (2)	[-]
M_{Nelson}	$MaxNelson$	Maximum fraction of the total depth for the wave height	[-]
τ	Tau	Total shear stress	Pa
τ_{veloc}	$TauVeloc$	Shear stress due to flow velocity	Pa
τ_{wind}	$TauWind$	Shear stress due to wind	Pa
$CalVelTau$	$CalVelTau$	Velocity as derived from the total shear stress	ms^{-1}
τ	Tau	Total shear stress	[-]

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13.12 Computation of horizontal dispersion

PROCESS: HDISPERVEL

Sometimes it is convenient to relate the horizontal dispersion to the flow velocity, for instance in river systems or if the horizontal grid cells are too large to resolve important variations in the flow field.

The process *HDisperVel* estimates a horizontal dispersion coefficient to the flow velocity via the following basic formula:

$$D_H = aV^b H^c + D_{H,background}$$

Formulations

The actual formulation is more versatile than shown above:

- ◇ The horizontal dispersion coefficient is limited to a range $(D_{H,min}, D_{H,max})$.
- ◇ The flow velocity is determined from the available flow rate and the area per exchange.

The formulation used is:

$$velocity = \begin{cases} |flow/area|, & \text{if } area > 10^{-10} \\ 0 & \text{otherwise} \end{cases}$$

$$horzdisp = \begin{cases} Dfact_a \times velocity^{Dfact_b} \times TotalDepth^{Dfact_c} + D_{back} \\ \max(\min(horzdisp, D_{max}), D_{min}) \end{cases}$$

Table 13.19: *Definitions of the input and output parameters for HDISPERVEL*

Name in formulas	Name in output	Definition	Units
$flow$	$flow$	Flow rate at exchange (automatically available)	m^3s^{-1}
$area$	$area$	Area at exchange (automatically available)	m^2
$Dfact_a$	$Dfact_a$	Factor a in dispersion calculation	[-]
$Dfact_b$	$Dfact_b$	Factor b in dispersion calculation	[-]
$Dfact_c$	$Dfact_c$	Factor c in dispersion calculation	[-]
D_{back}	D_{back}	Background dispersion coefficient	m^2s^{-1}
D_{min}	D_{min}	Minimum dispersion coefficient to be used	m^2s^{-1}
D_{max}	D_{max}	Maximum dispersion coefficient to be used	m^2s^{-1}
$TotalDepth$	$TotalDepth$	Mean total depth at the segments on either side of the exchange	m
$horzdisp$	$horzdisp$	Computed horizontal dispersion coefficient at exchange	m^2s^{-1}

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13.13 Computation of horizontal dispersion (one-dimension)

PROCESS: HORZDISPER

Sometimes it is convenient to relate the horizontal dispersion to the flow velocity, for instance in network systems. Because the representative flow velocity may not be simply related to the flow rate and the wet area per exchange, you have to specify the velocity explicitly. Furthermore the width and the bottom roughness of the channel are taken into account.

The process *HorzDisper* estimates a horizontal dispersion coefficient from the given flow velocity, width and roughness via the following basic formula:

$$D_H = \frac{\alpha V W^2}{H\sqrt{g/C^2}}$$

Formulations

The formulation using the names of the coefficients is:

$$D_H = DispConst \times \frac{Velocity \times Width^2 \times Chezy}{TotalDepth \times \sqrt{g}}$$

$Velocity$	mean of the specified flow velocity at the *segments* on both sides of the exchange [m/s]
$Width$	mean of the specified width at the *segments* on both sides of the exchange [m]
$TotalDepth$	mean of the total depth at the *segments* on both sides of the exchange [m]
$Chezy$	mean of the Chézy coefficients *segments* on both sides of the exchange [$m^{1/2}/s$]
$DispConst$	horizontal dispersion coefficient (again specified at the segments and averaged) [-]
g	gravitational acceleration (fixed at 9.81) [m/s^2]

Table 13.20: *Definitions of the input and output parameters for HORZDISP*

Name in formulas	Name in output	Definition	Units
$Velocity$	$Velocity$	Magnitude of the flow velocity	m^{-1}
$Width$	$Width$	Width of the segments	m
$Chezy$	$Chezy$	Chezy coefficient	$m^{-1/2}s{-}1$
$TotalDepth$	$TotalDepth$	Total water depth	m^2s^{-1}
$DispConst$	$DispConst$	Coefficient for the horizontal dispersion	ms^1
–	$HorzDispMx$	Maximum value for the dispersion coefficient	m^2s^{-1}
D_H	$HorzDisp$	Calculated value for the dispersion coefficient	m^2s^{-1}

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13.14 Allocation of dispersion from segment to exchange

PROCESS: VERTDISP

This process converts values available within the computational segments to values on the exchanges (contact surfaces) between two computational segments, *in the third vertical direction only.*

Implementation

The process is implemented for Vertical Dispersion.

Formulation

The process copies the value in the *from segment* of every exchange to the value at the exchange area. In the current version **no checks** are implemented to verify whether the from segment is indeed a real segment and not a boundary. This is not a problem if the process is used in Delft3D.

Directives for use

◇ Be aware of the fact that this process only acts in the *third direction*, and that it does not check for boundary segments.

Table 13.21: *Definitions of the input and output parameters for VERTDISP*

Name in formulas	Name in output	Definition	Units
–	$VertDisper$	Vertical dispersion at segment level	m^2s^{-1}
–	$ScaleVdisp$	Scale factor that is applied (defaults to 1)	[-]
–	$VertDisp$	Computed vertical dispersion at exchanges	m^2s^{-1}

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13.15 Conversion of segment variable to exchange variable

PROCESS: S2X_RHO

This process calculates the value of segment related variables at an exchange area by linear interpolation.

Implementation

This process is implemented for the variable RhoWater.

Formulation

$$VarExc = VarFrom + \frac{VarTo - VarFrom}{XLenTo + XLenFrom} \times XLenFrom$$

where

VarExc	value of a segment-related variable at the exchange area RhoExc : density of water [kg m^{-3}]
XLenFrom	DELWAQ "from"-length [m]
XLenTo	DELWAQ "to"-length [m]
VarFrom	value of segment-related variable in "from"-segment RhoWater density of water [kg m^{-3}]
VarTo	value of segment-related variable in "to"-segment RhoWater density of water [kg m^{-3}]

Directives for use

◇ This process can be active if the third direction is defined.

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13.16 Conversion of exchange variable to segment variable

PROCESS: RHOEXTOS, RHOGRTOS, VDISPTOS, VGRDTOS

This process converts values available on the exchanges (contact surfaces) between two computational segments to values within the computational segments *in the third vertical direction only!*

Implementation

The process is implemented for the Density, for the Density Gradient, for the Vertical Dispersion and for the Velocity Gradient.

Formulation

The process copies the value at the exchange area between two segments to both the *from segment* and the *to segment* of the exchange, if they do not represent a boundary. This is done for the third (vertical) direction only.

Directives for use

◇ The results of the current version depend on the order of the exchanges in the pointer table. Every segment gets **two times** a value: from the exchange where it is the *from segment* and from the exchange where it is the *to segment*. The one that occurs last in the pointer table determines the outcome. No averaging is performed.

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14 Temperature

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14.1 Calculation of water temperature

PROCESS: TEMPERATUR

The water temperature can be modelled in two ways, one representing the absolute water temperature and the other representing the excess water temperature (surplus above an ambient background temperature).

The water temperature process regulates the heat gain and loss of the water phase to the atmosphere. The process takes into account evaporation, re-aeration and the influence of wind on this process. The process is based on a relation for the heat exchange coefficient by Sweers (1976) The natural water temperature in the formulation refers to the equilibrium temperature that the water body would obtain in equilibrium circumstances, in practice, the temperature far away from sources of thermal pollution.

Implementation

This process is implemented for TEMPERATURE only.

Formulation

If $SwitchTemp = 0$ the modelled temperature is the absolute temperature, in this case:

$$\begin{aligned} T &= ModTemp \\ SurTemp &= T - NatTemp \end{aligned}$$

If $SwitchTemp = 1$ the modelled temperature is the surplus temperature, in this case:

$$\begin{aligned} SurTemp &= ModTemp \\ T &= SurTemp + NatTemp \end{aligned}$$

The calculation of the heat exchange is in both cases:

$$\begin{aligned} dModTemp &= -RcHeat \times FactRcHeat \times Surtemp + ZHeatExch \\ RcHeat &= \frac{4.48 + 0.049 \times T + F_{wind} \times (1.12 + 0.018 \times T + 0.00158 \times T^2) \times 86400}{C_p \times \rho_w \times Depth} \\ \rho_w &= 1000.0 - 0.088 \times T \\ F_{wind} &= 0.75 \times (3.5 + 2.05 \times V_{wind}) \end{aligned}$$

where

$ModTemp$	modelled temperature [°C]
$SwitchTemp$	switch: modelled temperature is absolute (0) or surplus (1) [-]
$SurTemp$	surplus temperature [°C]
T	ambient water temperature [°C]
$NatTemp$	ambient natural background water temperature [°C]
$Depth$	depth of a DELWAQ segment [m]
V_{wind}	wind velocity at 10 m height above the surface [m s^{-1}]
C_p	specific heat of water [J kg^{-1} $°C^{-1}$]
$RcHeat$	rate constant for surplus temperature exchange [d^{-1}]

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$FactRcHeat$	factor on rate constant for surplus temperature exchange (usually set to 1) [-]
ρ_w	density of water at ambient water temperature [kg m^{-3}]
$ZHeatExch$	zeroth order temperature exchange flux [°C d^{-1}]
$dModTemp$	temperature exchange flux [°C d^{-1}]

Directives for use

◇ The maximum value the temperature exchange flux can reach is limited to the amount of surplus temperature present ($-SurTemp/\Delta t$).

If surplus temperature is modelled the ambient natural background temperature must be supplied as a constant value in time and place. Variable background temperature would lead to an error in the energy balance of the system.

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14.2 Calculation of temperature for flats run dry

PROCESS: TEMPERATUR

The temperature of mud- and sandflats in intertidal water systems can deviate strongly from the water temperature during periods of emersion. The temperature increase on the flats can be over 10 °C. The rate of temperature increase can be as high as 3 °C per hour. The difference in temperature is to be accounted for in the rates of various biological processes, the processes to which microphytobenthos is subjected in particular. The current simulation of the temperature on flats is based on strongly simplified formulations, reflecting an pragmatic estimation method that does not involve energy budget calculations.

In principle, the temperature on a “run-dry” flat is a function of:

- ◇ water temperature;
- ◇ air temperature;
- ◇ solar radiation;
- ◇ back radiation;
- ◇ windspeed and relative air humidity;
- ◇ quantity and temperature of precipitation; and
- ◇ duration of the emersion period.

The following simplications are applied to the formulations in the model in order to incorporate the various contributions to the temperature on the dry flat.

The temperature in the upper layer of a flat attains the air temperature within a short period. Therefore, the air temperature is assigned to the top of a flat from the onset of a run-dry period. Relative to the air temperature a further adjustment of the temperature is made according to a gradual increase due to solar radiation and an instantaneous constant decrease due to evaporation. Using the actual solar radiation intensity the temperature increase is scaled on the basis of a maximal increase. The effect of reflection dependent on sediment properties is implicit. The additional effects of back radiation and precipitation are generally small and incidental. These effects are ignored. Water temperature is restored at the submersion of the flat.

The actual solar radiation intensity is derived from the daily radiation and the daylength in an auxiliary process DAYRAD. The water and air temperatures are input into the model.

Implementation

The “temperature at dry flats” process has been implemented as an additional, optional process in the generic process TEMPERATUR, that calculates the temperature of segments on the basis of the selected option. Several options are available. The additional process can be applied to the toplayer(s) of the sediment. The process can be made inactive using the option parameter $SWTempDF$ (default 0.0 = inactive; 1.0 = active).

The process modifies the input parameter $Temp$. Table 14.1 provides the definitions of the parameters occurring in the formulations.

Formulation

In a first step the model checks whether emersion has taken place. The switch parameter $SWemersion$ is set (0.0 = submersion, 1.0 = emersion) according to auxiliary process

EMERSION. In a second step the model identifies segments as water, top sediment layers and deeper sediment layers. The top sediment layers belong to the upper sediment layer in which the temperature adjusts to emersion. The thickness of this layer is Hst.

In the case of submersion of a certain segment the water temperature $Temp$ is not modified. This temperature is assigned to both the water segment concerned and all underlying sediment segments.

In the case of emersion of a certain segment the water temperature $Temp$ is modified for the top sediment layers above Hst. The water segments and the deeper sediment layers are assigned water temperature $Temp$. The temperature of the top sediment layers is adjusted as follows:

$$
\begin{aligned}
Tts &= Ta + \Delta Trad - \Delta Tev \\
\Delta Trad &= \Delta t \times RTrad + \Delta Trad_0 \quad \text{and} \quad \Delta Trad = \Delta Treq \\
RTrad &= RTrmax \times \frac{I}{Imax} \\
\Delta Treq &= \Delta Trmax \times \frac{I}{Imax} \\
T &= Tts
\end{aligned}
\tag{14.1}
$$

with:

I	solar radiation intensity [W m^{-2}]
$Imax$	maximal solar radiation intensity [W m^{-2}]
T	temperature [°C]
Ta	air temperature [°C]
Tts	top sediment temperature in run-dry segments [°C]
$RTrad$	rate of temperature increase due to solar radiation [°C d^{-1}]
$RTrmax$	maximal rate of temperature increase due to solar radiation [°C d^{-1}]
Δt	timestep [d]
ΔTev	temperature decrease due to evaporation [°C]
$\Delta Trad$	temperature increase due to solar radiation [°C]
$\Delta Trad0$	temperature increase due to solar radiation in the previous timestep [°C]
$\Delta Treq$	equilibrium temperature increase due to solar radiation [°C]
$\Delta Trmax$	maximal temperature increase due to solar radiation [°C]

Directives for use

◇ The formulations have been designed in such a way, that all contributions to the temperature can be manipulated by the user. The shortcomings of the strongly simplified formulations can be compensated as much as possible by appropriate quantification of the input parameters.

Additional references

Guarini et al. (2000)

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Table 14.1: *Definitions of the parameters in the above equations for TEMPERATUR.*

Name in formulas	Name in input/output	Definition	Units
Hst	$ThSedDT$	thickness top sediment layer subjected to temperature change	m
I	$DayRadSurf$	solar radiation intensity	W m^{-2}
$Imax$	$RadMax$	maximal solar radiation intensity	W m^{-2}
$RTrmax$	$RTradMax$	maximal rate of temperature increase due to solar radiation	°C d^{-1}
$SWemersion$	$SWemersion$	switch that determines emersion or submersion	-
$SWTempDF$	$SWTempDF$	switch that (de)activates modification of temperature (default 0 = inactive; 1 = active)	-
T	$Temp$	actual temperature	°C
Ta	$NatTemp$	air temperature	°C
Tst	$ModTemp$	top sediment temperature	°C
Δt	$Delt$	timestep	d
ΔTev	$DelTev$	temperature decrease due to evaporation	°C
$\Delta Trmax$	$DelRadMax$	maximal temperature increase due to solar radiation	°C

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15 Microplastics associated with tyre abrasion (TRWP)

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DRAFT

15.1 Introduction

Tyre and road wear particles (TRWP) are formed at the frictional interface of the tyre and road surface, and consist of polymer-containing tread with pavement mineral and binder encrustations. This chapter describes some processes that can be used to represent the fate of TRWP in 3D models of aquatic systems.

The formulations have been derived from the first integral model-based catchment-scale TRWP mass balance model published for the Seine watershed by Unice et al. 2019. Where applicable, references to underlying scientific publications are provided. The formulations have been adapted for use in a water column that is discretised in layers.

The processes are implemented for variable numbers of TRWP fractions (n) and natural particles (m) fractions.

The processes include the hetero-aggregation between TRWP and natural particles (IM1, IM2, IM3 in the Delft3D Processes Library), and the settling of single TRWP and aggregates. Aggregates consist of one TRWP and one natural particle ($n \times m$ possible combinations). Supportive processes are provided that estimate settling properties and calculate cumulative concentrations over all fractions.

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15.2 Properties of aggregated and unaggregated TRWP and natural particles

PROCESS: PROPSING, PROPTAGG

The processes in this section characterize the aggregated and unaggregated TRWP and natural particles in terms of their settling velocity and critical shear stress.

Implementation

The processes are implemented for 4 fractions of TRWP and 3 fractions of natural particles. Indicative properties of these particles are compiled in Table 15.1.

Table 15.1: *Indicative properties of TRWP and natural particles.*

Particle type	Fraction	Diameter (μm)	Density (g/cm^3)	Shape Factor (-)
TRWP	1	30	1.8	0.8
	2	75	1.8	0.8
	3	125	1.8	0.8
	4	200	1.8	0.8
natural	1	2	2.65	0.7
	2	16	2.65	0.7
	3	63	2.65	0.7

Formulation

The settling velocity of a particle is estimated according to Waldschläger and Schüttrumpf 2019. This formulation reads:

$$w_s = C_{ws} D^*$$

where

$$D^* = \left[\frac{g\left(\rho - \rho_w\right)}{\nu^2 \rho_w} \right]^{1/3} D$$

with:

w_s	settling velocity [mm/s]
C_{ws}	empirical factor equal to 2.5 [-]
g	gravitational acceleration [m/s^2]
ρ	density of particle [kg/m^3]
ρ_w	density of water [kg/m^3]
ν	kinematic viscosity of water [m^2 s^{-1}]
D	particle diameter [m]

The critical shear stress for sedimentation is calculated as follows:

$$\tau_{cr} = \phi \left(\rho - \rho_w\right) g D$$

with:

ϕ	Shields number [-]

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The Shields number is defined after Wu 2007 based on the non-dimensional particle size D^*:

$\phi = 0.126D^{*-0.44}$ for $D^* < 1.5$
$\phi = 0.131D^{*-0.55}$ for $1.5 \leq D^* < 10$
$\phi = 0.0685D^{*-0.27}$ for $10 \leq D^* < 20$
$\phi = 0.0173D^{*0.19}$ for $20 \leq D^* < 40$
$\phi = 0.0115D^{*0.30}$ for $40 \leq D^* < 150$
$\phi = 0.052$ for $150 \leq D^*$

For hetero-aggregates consisting of a TRWP fraction (i) and a natural particle fraction (j), the properties are derived from those of the parent particles:

$$M = \frac{\pi}{6}D_i^3\rho_i + \frac{\pi}{6}D_j^3\rho_j$$

$$V = \frac{\pi}{6}D_i^3 + \frac{\pi}{6}D_j^3$$

$$D = \left(\frac{6V}{\pi}\right)^{1/3}$$

$$\rho = \frac{M}{v}$$

$$S_f = \sqrt{\frac{\max\left(D_i, D_j\right)}{D_i + D_j}}$$

with:

M	mass [kg]
V	volume [m^3]
S_f	shape factor [-]

A biofilm (BF) is added to a single particle or to an aggregate (x):

$$M = \frac{\pi}{6}D_x^3\rho_x + \frac{\pi}{6}\left(\left(D_x + 2\delta_{BF}\right)^3 - D_x^3\right)\rho_{BF}$$

$$D = D_x + 2\delta_{BF}$$

$$\rho = \frac{M}{\frac{\pi}{6}D^3}$$

with:

δ_{BF}	biofilm thickness [μm]
ρ_{BF}	biofilm density [kg/m^3]

Remarks

The formulations account for the shape factor of the particles, though this is no longer used for calculating the settling velocity.

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Directives for use

Table 15.2: *Definitions of the input parameters in the above equations for processes PropSing and PropTAgg. (i) is a single digit number representing the TRWP fraction. (j) is a single digit number representing the natural sediment fraction.*

Name in formulas	Name in input	Definition	Units
D_i	$DiamTyre(i)$	Diameter of the TRWP, fraction (i)	μm
D_j	$Diam_Susp(j)$	Diameter of the natural sediment particles, fraction (j)	μm
ρ_i	$Dens_Tyre(i)$	Density of the TRWP, fraction (i)	kg/m^3
ρ_j	$Dens_Susp(j)$	Density of the natural sediment particles, fraction (j)	kg/m^3
S_f	$ShapeFac(i)$	Shape factor of the TRWP, fraction (i)	[-]
S_f	$ShapeFacSu$	Shape factor of the natural sediment particles	[-]
δ_{BF}	$BioFilmThk$	Thickness of a biofilm around the particles	[-]
ρ_{BF}	$BioFilmDen$	Density of a biofilm around the particles particles	[-]

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15.3 Hetero-aggregation of TRWP and SPM particles

PROCESS: HTRAGG

This process describes the formation of hetero-aggregates consisting of a single TRWP and a single natural particle.

Implementation

The processes are implemented for 4 fractions of TRWP and 3 fractions of natural particles, forming 4×3 different aggregate fractions.

Formulation

The hetero-aggregation process is formulated following the approach of Besseling et al. 2017 for microplastics. The rate of hetero-aggregation between fraction (i) of TRWP and fraction (j) of natural particles is approximated by a first-order process, assuming that the concentration of free natural particles is not significantly affected by the process:

$$\frac{\mathrm{d}TyreAgg_{i,j}}{\mathrm{d}t} = -\frac{\mathrm{d}Tyre_j}{\mathrm{d}t} = ECF_{i,j}N_jTyre_i$$

with:

$TyreAgg_{i,j}$	concentration of aggregate of TRWP fraction (i) and natural particle fraction (j) [g/m^3]
$Tyre_j$	concentration of TRWP fraction (i) [g/m^3]
t	time [s]
E	attachment efficiency [-]
$CF_{i,j}$	collision frequency of TRWP fraction (i) and natural particle fraction (j) [1/s]
N_j	number of natural particles fraction (j) [-]

The collision frequency is estimated as the sum of terms representing Brownian motion, shear and differential settling:

$$CF_{i,j} = \frac{2k_bT\left(D_i + D_j\right)^2}{3\mu D_iD_j} + \frac{G}{6}\left(D_i + D_j\right)^3 + \frac{\pi}{4}\left(D_i + D_j\right)^2\left|w_{s,i} - w_{s,j}\right|$$

with:

μ	dynamic viscosity of water [kg m^{-1} s^{-1}]
k_b	Boltzmann constant ([J/K]
G	shear rate [1/s]
D_i	diameter of TRWP fraction (i) [μm]
D_j	diameter of natural particle fraction (j) [μm]
T	temperature [K]
$w_{s,i}$	settling velocity of TRWP fraction (i) [m/s]
$w_{s,j}$	settling velocity of natural particle fraction (j) [m/s]

The calculation of the shear rate G (s^{-1}) is based on general theory for turbulence models (Rijn 2011). First, we can relate the turbulent energy dissipation (ϵ) to the shear (G) as follows:

$$\epsilon = 15\nu G^2 = 15\nu\left|\frac{\partial u_i}{\partial x_j}\right|^2$$

with:

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ν	kinematic viscosity of water [m^2 s^{-1}]
ϵ	turbulent energy dissipation [m^2 s^{-3}]

We can describe the turbulent energy dissipation in channels and rivers via a hyperbolic profile:

$$\epsilon = \frac{u_*^3}{\kappa\left(z + z_0\right)}$$

with:

κ	von Kármán constant [-]
u_*	friction velocity [m/s]
z	vertical coordinate ($z = 0$ at bottom) [m]

The vertical coordinate z in the hyperbolic profile is set off by a parameter z_0, which is usually chosen to be the roughness length, and is much smaller than the water depth. The friction velocity u_* is defined as:

$$\tau_{bottom} = \rho u_*^2$$

Using the Chézy approach we can write this as:

$$\tau_{bottom} = \frac{\rho g U^2}{C^2}$$

with:

τ_{bottom}	bottom shear [Pa]
ρ	water density [kg/m^3]
g	acceleration of gravity [m/s^2]
U	vertically averaged velocity [m/s]
C	Chézy coefficient [m$^{1/2}$/s]

Combining these formulae gives us an expression for the shear stress G as a function of the distance to the bottom z:

$$G = \sqrt{\frac{\epsilon}{15\nu}} = \sqrt{\frac{1}{15\nu}\left(\frac{\sqrt{g}U}{C}\right)^3} \cdot \sqrt{\frac{1}{\kappa\left(z + z_0\right)}}$$

NOTE: THIS PART NEEDS TO BE MODIFIED (3-dimensionalized) As we are interested in the average shear, we should integrate this over the depth (setting z_0 to 0, as it is small with respect to the depth anyway):

$$\overline{G} = \sqrt{\frac{4}{15\nu\kappa H}\left(\frac{\sqrt{g}U}{C}\right)^3}$$

To get some feeling for the resulting expression, Table 15.3 gives the shear as function of the flow velocity at a depth of 5 and 10 m and a typical roughness ($C = 50$ m$^{1/2}$/s).

Table 15.3: *Numeric examples of the shear, calculated as a function of the flow velocity and the water depth.*

Depth (m)	Flow velocity (m/s)	Shear (1/s)
5	0.1 - 0.2 - 0.5 - 1.0	0.18 - 0.51 - 2.0 - 5.7
10	0.1 - 0.2 - 0.5 - 1.0	0.13 - 0.36 - 1.4 - 4.0

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Particle concentrations expressed as numbers are derived from the mass-based concentrations as follows:

$$N_i = \frac{Tyre_i}{\frac{\pi}{6} D_i^3 \rho_i}$$

$$N_j = \frac{IM_j}{\frac{\pi}{6} D_j^3 \rho_j}$$

Remarks

- ◇ In the model implementation only a single aggregation between natural particles and TRWP can take place.
- ◇ In the code, a limiter is applied. As each tyre fraction can aggregate to several sediment fractions, the maximum aggregation rate is limited to $1/10$ of the available mass per timestep.

Directives for use

Table 15.4: *Definitions of the input parameters in the above equations for process HtrAgg. (i) is a single digit number representing the TRWP fraction. (j) is a single digit number representing the natural sediment fraction.*

Name in formulas	Name in input	Definition	Units
$Tyre_i$	$Tyre(i)$	Concentration of the TRWP, fraction (i)	g/m^3
IM_j	$IM(j)$	Concentration of the natural sediment particles, fraction (j)	g/m^3
D_i	$DiamTyre(i)$	Diameter of the TRWP, fraction (i)	μm
D_j	$Diam_Susp(j)$	Diameter of the natural sediment particles, fraction (j)	μm
ρ_i	$Dens_Tyre(i)$	Density of the TRWP, fraction (i)	kg/m^3
ρ_j	$Dens_Susp(j)$	Density of the natural sediment particles, fraction (j)	kg/m^3
$w_{s,i}$	$VSedTRWP(i)$	Settling velocity of the TRWP, fraction (i)	m/d
$w_{s,i}$	$VSedIM(j)$	Settling velocity of the natural sediment particles	m/d
E	$Efficiency$	Aggregation efficiency	[-]
	$Temp$	Temperature	°C
	$Velocity$	Flow velocity	m/s
	$Chezy$	Chézy coefficient	m$^{1/2}$/s
	$Delt$	Time step	d
	$Depth$ or $TotalDepth$		

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15.4 Settling of aggregated and unaggregated TRWP

PROCESS: SEDTYRE, SEDTAGG

These processes arrange the settling of aggregated (with natural particles) and unaggregated TRWP.

Implementation

The processes are implemented for 4 fractions of TRWP and 3 fractions of natural particles, as well as for the 12 (4×3) possible hetero-aggregate fractions.

Formulation

The settling process is implemented just as for all other components (see for example process Sed_IM1). Single TRWP are assumed to aggregate after settling, to the different fractions of natural particles in proportion to their presence in the top sediment layer:

$$\frac{\mathrm{d}Tyre_i}{\mathrm{d}t} = -\frac{F_{set,i}}{H}$$

$$\frac{\mathrm{d}TAggSed_{i,j}}{\mathrm{d}t} = +F_{set,i}\frac{IM_{j,S1}}{\sum_j IM_{j,S1}}$$

with:

$Tyre_i$	concentration of TRWP, fraction (i) [g/m^3]
t	time [s]
$F_{set,i}$	settling flux of TRWP, fraction (i) [g m^{-2} s^{-1}]
H	water depth [m]
$TAggSed_{i,j}$	mass of aggregate (i)(j) in sediment (g m^{-2})
$IM_{j,S1}$	mass of natural particles fraction (j) in the top sediment layer [g/m^2]

Remarks

◇ In the code, a limiter is applied that deviates from the limiter used in other parts of the Processes Library. The maximum settling is limited to a fraction $SafeFactor$ of the available mass.

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Directives for use

Table 15.5: *Definitions of the input parameters in the above equations for processes $SedTyre$, $SedTAgg$. (i) is a single digit number representing the TRWP fraction. (j) is a single digit number representing the natural sediment fraction.*

Name in formulas	Name in input	Definition	Units
$Tyre_i$	$Tyre(i)$	Concentration of the TRWP, fraction (i)	g/m^3
	$TyreAgg(i)(j)$	Concentration of aggregates of TRWP fraction (i) and natural particles fraction (j)	g/m^3
	$VSedTRWP(i)$	Settling velocity of the TRWP, fraction (i)	m/d
	$VSedTagg(i)(j)$	Settling velocity of aggregates of TRWP fraction (i) and natural particles fraction (j)	m/d
	$TcrsTyre(i)$	Critical shear stress for the TRWP, fraction (i)	Pa
	$TcrsTagg(i)(j)$	Critical shear stress of aggregates of TRWP fraction (i) and natural particles fraction (j)	Pa
$IM_{S1,j}$	$IM(j)S1$	Concentration of the natural sediment particles in the sediment top layer $(S1)$, fraction (j)	g/m^2
	Tau	Bottom shear stress	Pa
	$Delt$	Time step	d
H	$Depth$	Depth of segment	m
	$SafeFactor$	Safety factor for sedimentation delimiter	[-]

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15.5 Sum of concentrations of unaggregated and aggregated TRWP fractions

PROCESS: SUMTRWP

This process provides the sum of the concentrations of all TRWP fractions in the water column and (if applicable) in the top sediment layer.

Implementation

The processes are implemented for 4 fractions of TRWP, 3 fractions of natural particles and 4×3-aggregate fractions.

Formulation

The sum of TRWP in the water column:

$$TyreNN = \sum_{i} Tyre_i + \sum_{i,j} TyreAgg_{i,j}$$

The sum of TRWP in the top sediment layer:

$$TaggSedNN = \sum_{i,j} TAggSed_{i,j}$$

The sum of natural particles in the water column:

$$SuspNN = \sum_{j} IM_j$$

Remarks

◇ The formula for the total of the natural particles concentrations duplicates functionality in the process Compos.

Directives for use

Table 15.6: *Definitions of the input parameters in the above equations for process SumTRWP. (i) is a single digit number representing the TRWP fraction. (j) is a single digit number representing the natural sediment fraction.*

Name in formulas	Name in input	Definition	Units
$Tyre_i$	$Tyre(i)$	Concentration of the TRWP, fraction (i)	g/m^3
$TyreAgg_{i,j}$	$TyreAgg(i)(j)$	Concentration of aggregates of TRWP fraction (i) and natural particles fraction (j)	g/m^3
$TAggSed_{i,j}$	$TAggSed(i)(j)$	Concentration of aggregates of TRWP fraction (i) and natural particles fraction (j) in the sediment top layer $(S1)$	g/m^2
IM_j	$IM(j)$	Concentration of the natural sediment particles, fraction (j)	g/m^2

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16 Various auxiliary processes

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16.1 Computation of aggregate substances

PROCESS: COMPOS

The simulated substances for detrital organic matter and algae biomass do not provide all essential information to interprete and assess simulation output. The auxiliary process COMPOS provides the additional parameters needed. This concerns the nutrient composition of particulate detritus and parameters that represent organic matter and total matter as measured.

The nutrient composition of particulate detritus is used in the model to simulate the settling of organic nutrients (N, P, S) in particulate detritus, since these fluxes are computed relative to the detritus carbon settling flux. Process COMPOS computes the stochiometric ratios of nitrogen, phosphorus, sulfur and silicon in the individual detritus fractions for this purpose.

Process COMPOS also delivers the total particulate matter, carbon, nitrogen, phosphorus, silicon and sulfur concentrations, the Kjeldahl-N concentration, and the concentrations of a number of other aggregate substances. The total particulate concentrations are computed with and without algae biomass.

Volume units refer to bulk ($\mathscr{b}$) or to water ($\mathscr{w}$).

Implementation

The process has been implemented for the following substances:

- ◇ simulated substances NO3, NH4, PO4, AAP, VIVP, APATP, Si, OPAL, SO4, SUD, SUP, POC1, PON1, POP1, POS1, POC2, PON2, POP2, POS2, POC3, PON3, POP3, POS3, POC4, PON4, POP4, POS4, DOC, DON, DOP, DOS, IM1, IM2 and IM3
- ◇ auxiliary substances Phyt, AlgN, AlgP, AlgSi, AlgS and AlgDM

The process does not directly influence state variables, since they do not generate mass fluxes. It is generic, so that it applies to water as well sediment layers.

Table 16.1 provides the definitions of the output parameters as related to the formulations.

Formulation

The individual stochiometric nutrient ratios follow from:

$$an_i = \frac{Coc_i}{Con_i}$$
$$ap_i = \frac{Coc_i}{Cop_i}$$
$$as_i = \frac{Coc_i}{Cos_i}$$

where:

an	stochiometric ratio of carbon and nitrogen in organic matter [gC gN^{-1}]
ap	stochiometric ratio of carbon and phosphorus in organic matter [gC gP^{-1}]
as	stochiometric ratio of carbon and sulfur in organic matter [gC gS^{-1}]
Coc	concentration of detritus carbon [gC m$^{-3}\mathscr{b}$]

Con	concentration of detritus nitrogen [gN m^{-3}]
Cop	concentration of detritus phosphorus [gP m^{-3}]
Cos	concentration of detritus sulfur [gS m^{-3}]
i	index for the particulate detritus fraction [-]

The total particulate detritus pools follow from:

$$Cpoc = \sum_{i=1}^{4} Coc_i$$

$$Cpon = \sum_{i=1}^{4} Con_i$$

$$Cpop = \sum_{i=1}^{4} Cop_i$$

$$Cpos = \sum_{i=1}^{4} Cos_i$$

$$Cpom = \sum_{i=1}^{4} (fdm_i \times Coc_i)$$

where:

$Cpoc$	concentration of total particulate detritus carbon [gC m^{-3}]
$Cpon$	concentration of total particulate detritus nitrogen [gN m^{-3}]
$Cpop$	concentration of total particulate detritus phosphorus [gP m^{-3}]
$Cpos$	concentration of total particulate detritus sulfur [gS m^{-3}]
$Cpom$	concentration of total particulate detritus dry matter [gC m^{-3}]
fdm	dry matter conversion factor [gDM gC^{-1}]
i	index for the particulate detritus fraction [-]

The concentration of total inorganic sediment follows from:

$$Ctim = \sum_{j=1}^{3} (fidm_j \times Cim_j)$$

where:

Cim	concentration of inorganic sediment fraction [gDM m^{-3}]
$Ctim$	concentration of total inorganic dry matter [gDM m^{-3}]
$fidm$	dry matter ratio of inorganic sediment fraction [gDM gDM^{-1}]
j	index for the inorganic sediment fraction [-]

The other ”total” concentrations arise from summing the various simulated substances as follows:

$$POC = Cpoc + Phyt$$
$$TOC = POC + DOC$$

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$$
\begin{aligned}
PON &= Cpon + AlgN \\
TON &= PON + DON \\
KjelN &= TON + NH4 \\
DIN &= NH4 + NO3 \\
TOTN &= TON + DIN
\end{aligned}
$$

$$
\begin{aligned}
POP &= Cpop + AlgP \\
TOP &= POP + DOP \\
PIP &= AAP + VIVP + APATP \\
TOTP &= TOP + PO4 + PIP
\end{aligned}
$$

$$
\begin{aligned}
POS &= Cpos + AlgS \\
TOS &= POS + DOS \\
TOTS &= TOS + SO4 + SUD + SUP
\end{aligned}
$$

$$TOTSi = AlgSi + Opal + Si$$

$$
\begin{aligned}
TPMnoa &= Ctim + Cpom \\
TPM = SS &= TPMnoa + AlgDM
\end{aligned}
$$

Directives for use

- ◇ The input parameters are the concentrations of the modelled substances and auxiliary substances mentioned under section ”Implementation”, plus the dry matter carbon ratios (fdm) of the particulate detritus fractions ($DmCfPOC1$, $DmCfPOC2$, $DmCfPOC3$, $DmCfPOC4$, default = 2.5) and the dry matter ratio (fidm) of the inorganic sediment fractions ($DMCFIM1$, $DMCFIM2$, $DMCFIM3$, default = 1.0).
- ◇ Sulfur in algae biomass is not taken into account in the case of DYNAMO.
- ◇ $TOTS$ is not defined for the modelling of substances FeS and FeS2.

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Table 16.1: *Definitions of the output parameters for COMPOS. (i) is POC1, POC2, POC3 or POC4.*

Name in formulas	Name in output	Definition	Units
an_i	$C-N(i)$	stoch. ratio of carbon and nitrogen detr. fraction i	gC gN^{-1}
ap_i	$C-P(i)$	stoch. ratio of carbon and phosphorus in detritus fraction i	gC gP^{-1}
as_i	$C-S(i)$	stoch. ratio of carbon and sulfur in detritus fraction i	gC gS^{-1}
TOC	TOC	concentration total organic carbon	gC $m^{-3}\ell$
POC	POC	conc. total part. organic carbon	gC $m^{-3}\ell$
POM	POM	conc. total part. dry matter	gDM $m^{-3}\ell$
$Cpoc$	$POCnoa$	conc. total total part. org. carbon without algae	gC $m^{-3}\ell$
$Cpom$	$POMnoa$	conc. total part. dry matter without algae	gDM $m^{-3}\ell$
$TOTN$	$TOTN$	concentration total nitrogen	gN $m^{-3}\ell$
TON	TON	conc. total organic nitrogen	gN $m^{-3}\ell$
PON	PON	conc. total part. organic nitrogen	gN $m^{-3}\ell$
$Cpon$	$PONnoa$	conc. total part. org. nitrogen without algae	gN $m^{-3}\ell$
DIN	DIN	conc. total diss. inorganic nitrogen	gN $m^{-3}\ell$
$KjelN$	$KjelN$	conc. total Kjeldahl nitrogen	gN $m^{-3}\ell$
$TOTP$	$TOTP$	concentration total phosphorus	gP $m^{-3}\ell$
TOP	TOP	conc. total organic phosphorus	gP $m^{-3}\ell$
POP	POP	conc. total part. org. phosphorus	gP $m^{-3}\ell$
$Cpop$	$POPnoa$	conc. total part. org. phosphorus without algae	gP $m^{-3}\ell$
PIP	PIP	conc. total part. inorg. phosphorus	gP $m^{-3}\ell$
$TOTS$	$TOTS$	conc. total sulfur	gS $m^{-3}\ell$
TOS	TOS	conc. total organic sulfur	gS $m^{-3}\ell$
POS	POS	conc. total part. organic sulfur	gS $m^{-3}\ell$
$Cpos$	$POSnoa$	conc. total part. org. sulfur without algae	gS $m^{-3}\ell$
$TOTSi$	$TOTSi$	concentration total silicon	gSi $m^{-3}\ell$
TMP	SS	conc. total (susp.) sediment (solids)	gDM $m^{-3}\ell$
$Ctim$	TIM	conc. total inorganic sediment	gDM $m^{-3}\ell$
TMP	TMP	conc. total part. matter with algae	gDM $m^{-3}\ell$
$TMPnoa$	$TMPnoa$	conc. total part. matter without algae	gDM $m^{-3}\ell$

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16.2 Computation of the sediment composition (S1/2)

PROCESS: S1/2_COMP

The composition of the sediment is important information for evaluation of the results of water quality simulations. The composition of sediment layers S1 is also used in the model to simulate the burial of organic matter and nutrients (N, P, Si), since these fluxes are computed relative to the sediment dry matter resuspension, burial and digging fluxes. For this purpose the quantities of simulated substances, the fractions of major compo¬nents of dry matter and the carbon-nutrient ratios for detritus are calculated.

Processes S1_COMP and S2_COMP calculate the total amount of dry matter in a sediment layer and some major components, the thickness of the sediment layer, and the overall dry matter density. The dry matter composition is expressed in fractions of total inorganic matter, total particulate organic carbon in detritus and total carbon in phyto-plankton biomass. Additionally the processes deliver the amounts of all simulated substances on the basis of g m^{-2}.

Implementation

In principle processes S1_COMP and S2_COMP can be combined with all phytoplankton and microphytobenthos modules. The processes have been implemented for the following substances:

- ◇ IM1S1, IM2S1, IM3S1, DETCS1, DETNS1, DETPS1, DETSiS1, OOCS1, OONS1, OOPS1, OOSiS1, AAPS1, DiatS1; and
- ◇ IM1S2, IM2S2, IM3S2, DETCS2, DETNS2, DETPS2, DETSiS2, OOCS2, OONS2, OOPS2, OOSiS2, AAPS2, DiatS2.

The processes do not directly influence state variables, since they do not generate mass fluxes. Tables 16.2 and 16.3 provide the definitions of the input and output parameters occurring in the formulations.

Formulation

The total amount of dry matter and the fractions of its major components in the sediment layer S1 or S2 follow from:

$$Mdm_k = \sum_{l=1}^{n} (fdm_{i,k} \times Mx_{i,k})$$

$$frx_{i,k} = \frac{Mx_{i,k}}{Mdm_k}$$

$$frpha_k = \frac{Mpha_k}{Mdm_k}$$

where:

Mdm	total amount of dry matter in a layer [gDM]
$Mpha$	amount of adsorbed phophate in a layer [gP]
Mx	amount of substance x in a layer [gX]
fdm	dry matter conversion factor [gDM gDM^{-1}, gDM gC^{-1}]
$frpha$	weight fraction of adsorbed phosphate in dry matter [gP gDM^{-1}]

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frx	weight fractions of major components in dry matter [gX gDM^{-1}]
i	index for major components in the sediment [-]
k	index for sediment layer S1 or S2 [-]
n	number of major components that contribute to dry matter [-], $n = 6$, including IM1S1/2, IM2S1/2, IM3S1/2, DETCS1/2, OOCS1/2 and DiatS1/2

The individual stochiometric nutrient ratios are computed according to:

$$an_{i,k} = \frac{Moc_{i,k}}{Mon_{i,k}}$$

$$ap_{i,k} = \frac{Moc_{i,k}}{Mop_{i,k}}$$

$$asi_{i,k} = \frac{Moc_{i,k}}{Mosi_{i,k}}$$

where:

an	stochiometric ratio of carbon over nitrogen in detritus fraction k [gC gN^{-1}]
ap	stochiometric ratio of carbon over phosphorus in detritus fraction k [gC gP^{-1}]
asi	stochiometric ratio of carbon over silicon in detritus fraction k [gC gSi^{-1}]
Moc	amount of carbon in particulate detritus fraction k [gC]
Mon	amount of nitrogen in particulate detritus fraction k [gN m^{-3}]
Mop	amount of phosphorus in particulate detritus fraction k [gP m^{-3}]
$Mosi$	amount of silicon in particulate detritus fraction k [gSi m^{-3}]
i	index for particulate detritus fractions [-]
k	index for sediment layer S1 or S2 [-]

The total amounts of major components in the sediment layer S1 or S2 are:

$$Mimt_k = \sum_{j=1}^{3} (Mim_{j,k})$$

$$Moct_k = \sum_{i=1}^{2} (Moc_{i,k})$$

$$Malgt_k = \sum_{l=1}^{n} (Malg_{l,k})$$

$$Mpom_k = \sum_{l=1}^{n} (fdm_l \times Malg_l) + \sum_{i=1}^{2} (fdm_i \times Moc_{i,k})$$

where:

fdm	dry matter conversion factor [gDM gC^{-1}]
$Malg$	amount of biomass of algae species [gC]
$Malgt$	total amount of algae biomass [gC]
Mim	amount of a sediment inorganic matter fraction [gDW]
$Mimt$	total amount of sediment inorganic matter [gDW]
$Moct$	total amount of carbon in particulate detritus [gC]
$Mpom$	total amount of organic matter in the sediment [gDM gDM^{-1}]
i	index for particulate detritus fractions [-]
j	index for sediment inorganic matter fractions [-]

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k	index for sediment layer S1 or S2 [-]
l	index for algae / microphytobenthos species [-]
n	number of algae / microphytobenthos species, n=1 currently [-]

The comprehensive composition of the sediment layers S1 and S2 is calculated with:

$$Cx_{i,k} = \frac{Mx_{i,k}}{A}$$

where:

A	surface area of the water overlying water compartment [m^2]
Cx	surface concentration of substance x in a layer [gX m^{-2}]
Mx	amount of substance x in a layer [gX]
i	index for all sediment components including the nutrients in detritus [-]
k	index for sediment layer S1 or S2 [-]

The relevant physical properties of the sediment layers S1 and S2 follow from:

$$Vdm_k = \sum_{i=1}^{n} (fdm_{i,k} \times Cx_{i,k}/\rho_i)$$

$$\rho dm_k = \frac{Cdm_k}{Vdm_k}$$

$$Z_k = \frac{Vdm_k}{(1-\phi_k) \times A}$$

where:

A	surface area of the water overlying water compartment [m^2]
Cdm	surface concentration of dry matter [gDM m$^-2$]
fdm	dry matter conversion factor [gDM gDM^{-1}, gDM gC^{-1}]
Vdm	sediment dry matter volume [m^3]
Z	thickness of the sediment layer [m]
ϕ	porosity of the sediment [-]
ρ	solid matter density of a major sediment component k [gDM m^{-3}DM]
ρdm	density of sediment dry matter [gDM m^{-3}DM]
i	index for major components in the sediment [-]
k	index for sediment layer S1 or S2 [-]
n	number of major components that contribute to dry matter (-), n = 6 [-]

Directives for use

◇ Organic nutrients and adsorbed inorganic phosphorus do not contribute to the dry matter and the volume of the sediment! Notice that because of this the sum of all fractions in the sediment ($frx_{i,k}$; see the table with output parameters) may not equal 1.

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Table 16.2: *Definitions of the input parameters in the above equations for S1_COMP and S2_COMP.*

Name in formulas	Name in input	Definition	Units
A	$Surf$	surface area of the overlying water compartment	m^2
$fdm_{j,k}$	$DMCFIM1$	dry matter conv. factor sed. inorg. matter fraction 1	gDM gDM^{-1}
or	$DMCFIM2$	dry matter conv. factor sed. inorg. matter fraction 2	gDM gDM^{-1}
	$DMCFIM3$	dry matter conv. factor sed. inorg. matter fraction 3	gDM gDM^{-1}
$fdm_{i,k}$	$DMCFDetCS$	dry matter conv. factor detr. fraction 1	gDM gC^{-1}
	$DMCFOOCS$	dry matter conv. factor detr. fraction 2	gDM gC^{-1}
$fdm_{l,k}$	$DMCFDiatS$	dry matter conv. factor algae species 1	gDM gC^{-1}
$Malg_{l,k}$	$DiatS(k)$	amount of biomass of algae species 1	gC
$Mim_{j,k}$	$IM1S(k)$	amount of sed. inorg. matter fraction 1	gDW
	$IM2S(k)$	amount of sed. inorg. matter fraction 2	gDW
	$IM3S(k)$	amount of sed. inorg. matter fraction 3	gDW
$Moc_{i,k}$	$DetCS(k)$	amount of detr. C in part. fraction 1	gC
	$OOCS(k)$	amount of detr. C in part. fraction 2	gC
$Mon_{i,k}$	$DetNS(k)$	amount of detr. N in part. fraction 1	gN
	$OONS(k)$	amount of detr. N in part. fraction 2	gN
$Mop_{i,k}$	$DetPS(k)$	amount of detr. P in part. fraction 1	gP
	$OOPS(k)$	amount of detr. P in part. fraction 2	gP
$Mosi_{i,k}$	$DetSiS1(k)$	amount of detr. Si in part. fraction 1	gSi
	$OOSiS1(k)$	amount of detr. Si in part. fraction 2	gSi
$Mpha$	$AAPS(k)$	amount of adsorbed phosphate	gP
ϕ	$PORS(k)$	sediment porosity	-
ρ_i	$RHOIM1$	density of sed. inorg. matter fr. 1	gDM m^{-3}
	$RHOIM2$	density of sed. inorg. matter fr. 2	gDM m^{-3}
	$RHOIM3$	density of sed. inorg. matter fr. 3	gDM m^{-3}
	$RHODetC$	density of detritus fraction 1	gDM m^{-3}
	$RHOOOC$	density of detritus fraction 2	gDM m^{-3}
	$RHODiat$	density of biomass of algae species 1	gDM m^{-3}

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Table 16.2 – continued from previous page

Name in formulas	Name in input	Definition	Units

[1](k) is sediment layer 1 or 2.

Table 16.3: *Definitions of the output parameters in the above equations for S1_COMP and S2_COMP .*

Name in formulas	Name in output	Definition	Units
$an_{i,k}1$	$C - NDetCS(k)$	stoch. ratio C over N in detr. fraction 1	gC gN^{-1}
or	$C - NOOC(k)$	stoch. ratio C over N in detr. fraction 2	gC gN^{-1}
$ap_{i,k}$	$C - PDetCS(k)$	stoch. ratio C over P in detr. fraction 1	gC gP^{-1}
or	$C-POOCS(k)$	stoch. ratio C over P in detr. fraction 2	gC gP^{-1}
$asi_{i,k}$	$C-SDetCS(k)$	stoch. ratio C over Si in detr. fraction 1	gC gSi^{-1}
	$C-SOOCS(k)$	stoch. ratio C over Si in detr. fraction 2	gC gSi^{-1}
$Calg_{l,k}$	$DiatS(k)M2$	surface conc. of algae species 1	gC m^{-2}
$Cim_{j,k}$	$IM1S(k)M2$	surf. conc. of sed. inorg. matter fr. 1	gDW m^{-2}
	$IM2S(k)M2$	surf. conc. of sed. inorg. matter fr. 2	gDW m^{-2}
	$IM3S(k)M2$	surf. conc. of sed. inorg. matter fr. 3	gDW m^{-2}
$Coc_{i,k}$	$DetCS(k)M2$	surf. conc. of detr. C in part. fr. 1	gC m^{-2}
or	$OOCS(k)M2$	surf. conc. of detr. C in part. fr. 2	gC m^{-2}
$Con_{i,k}$	$DetNS(k)M2$	surf. conc. of detr. N in part. fr. 1	gN m^{-2}
or	$OONS(k)M2$	surf. conc. of detr. N in part. fr. 1	gN m^{-2}
$Cop_{i,k}$	$DetPS(k)M2$	surf. conc. of detr. P in part. fr. 1	gP m^{-2}
or	$OOPS(k)M2$	surf. conc. of detr. P in part. fr. 1	gP m^{-2}
$Cosi_{i,k}$	$DetSiS1(k)M2$	surf. conc. of detr. Si in part. fr. 1	gSi m^{-2}
	$OOSiS1(k)M2$	surf. conc. of detr. Si in part. fr. 1	gSi m^{-2}
Cxi,k	$AAPS(k)M2$	surface conc. of adsorbed phosphate	gP m^{-2}
Zk	$ActThS(k)$	thikness of sediment layer	m
$frx_{i,k}$	$FrIM1S(k)$	fraction inorg. matter 1 in sediment	gDM gDM^{-1}
	$FrIM2S(k)$	fraction inorg. matter 2 in sediment	gDM gDM^{-1}
	$FrIM3S(k)$	fraction inorg. matter 3 in sediment	gDM gDM^{-1}

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Table 16.3 – continued from previous page

Name in formulas	Name in output	Definition	Units
	$FrDetCS(k)$	fraction detritus 1 in sediment	gC gDM^{-1}
	$FrOOCS(k)$	fraction detritus 2 in sediment	gC gDM^{-1}
	$FrCFDiatS(k)$	fraction algae species 1 in sediment	gC gDM^{-1}
Mdm_k	$DMS(k)$	total amount of dry matter	gDM
$Mimt_k$	$TIMS(k)$	total amount of sed. inorganic matter	gDM
$Moct_k$	$POCS(k)$	total amount of part. organic carbon	gC
$Malgt_k$	$PHYTS(k)$	total amount of algae biomass	gC
$Mpom_k$	$POMS(k)$	total amount of organic matter	gDM
ρdm_k	$RHOS(k)$	density of sediment dry matter	gDM m^{-3}

[1](k) is sediment layer 1 or 2.

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16.3 Allocation of diffusive and atmospheric loads

PROCESS: DFWAST_I, ATMDEP_I

Both processes calculate diffusive fluxes. The processes convert user input in [g m^{-2} d^{-1}] to DELWAQ required units of [g m^{-3} d^{-1}].

Implementation

These processes are implemented for IM1, IM2, IM3, NO3, NH4, PO4, all heavy metals and all organic micro-pollutants.

Formulation

Diffusive waste load:

$$\text{dDfwast}_i = \frac{\text{fDfwast}_i}{depth} \tag{16.1}$$

Atmospheric deposition:

$$\text{dAtmDep}_i = \frac{\text{fAtmDep}_i}{depth} \tag{16.2}$$

where

dDfwast_i	diffusive waste load [g m^{-3} d^{-1}]
dAtmDep_i	atmospheric waste load [g m^{-3} d^{-1}]
fDfwast_i	diffusive waste load [g m^{-2} d^{-1}]
fAtmDep_i	atmospheric waste load [g m^{-2} d^{-1}]
depth	depth of a DELWAQ segment [m]

Directives for use

◇ Waste loads are normally not considered processes and are provided separately by you. This method is inconvenient when large amounts of segments are involved as is the case with diffusive wastes. In this case it is advised to use one of the two processes described in this section.

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16.4 Calculation of the depth of water column or water layer

PROCESS: DEPTH

Depth of a segment (computational element of DELWAQ) is calculated from the horizontal surface area (user-defined) and the volume. TOTDEPTH calculates the total depth of a multi-layer water column.

Implementation

Not relevant in this context.

Formulation

$$Depth = \frac{Volume}{Surf}$$

$$TotalDepth = \sum_{i=1}^{n} Depth_i$$

$$LocalDepth_m = \sum_{j=1}^{m} Depth_j$$

where

$Depth$	depth of a DELWAQ segment [m]
$Volume$	volume of a DELWAQ segment [m^3]
$Surf$	horizontal surface area of a DELWAQ segment [m^2]
$Totaldepth$	depth of entire water column [m]
$Localdepth_m$	depth from the surface to bottom of DELWAQ segment m [m]
m	index of the layer
n	total number of layers

Directives for use

◇ Either $Depth$ or $Surf$ must be supplied by you (or a water quantity model)!

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16.5 Calculation of horizontal surface area

PROCESS: DYNSURF

The horizontal surface area (SURF) of a segment (computational element of DELWAQ) is calculated from the depth (user defined) and the volume (DELWAQ).

Implementation

Not relevant in this context.

Formulation

$$Surf = \frac{Volume}{Depth}$$

where

$Depth$	depth of a DELWAQ segment [m]
$Volume$	volume of a DELWAQ segment [m^3]
$Surf$	horizontal surface area of a DELWAQ segment [m^2]

Directives for use

◇ Either $Depth$ or $Surf$ must be supplied by you (or a water quantity model)!

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16.6 Calculation of gradients

PROCESS: GRD_RHO, GRD_VE

This process calculates the gradient in space of segment-related variables at an exchange area.

Implementation

This process is implemented for the variables Veloc and RhoWater.

Formulation

$$VarGrd = \frac{VarTo - VarFrom}{XLenTo + XLenFrom}$$

VarGrd	gradient in space of segment-related variable (a) VelocGrd gradient in horizontal flow velocity [m s^{-1} m^{-1}] (b) RhoGrd gradient in density of water [kg m^{-3} m^{-1}]
XLenFrom	DELWAQ "from"-length [m]
XLenTo	DELWAQ "to"-length [m]
VarFrom	value of segment related variable in "from"-segment (a) Veloc horizontal flow velocity [m s^{-1}] (b) RhoWater density of water [kg m^{-3}]
VarTo	value of segment related variable in "to"-segment (a) Veloc horizontal flow velocity [m s^{-1}] (b) RhoWater density of water [kg m^{-3}]

Directives for use

◇ This process can be active if the third direction is defined.

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16.7 Calculation of residence time

PROCESS: RESTIM

This process calculates the residence time of water in a computational cell. The process only takes into account the advective transport — i.e. flows in [$m^3\ s^{-1}$] — as derived from D-Flow FM, D-Flow 1D or another hydrodynamic model. *Dispersion* is not taken into account.

Formulation

$$ResTim = \frac{Volume}{\sum_{exchanges} |Flow| \, /2} \tag{16.3}$$

where

$ResTim$	residence time [s]
$Volume$	DELWAQ water volume of a segment [m^3]
$Flow$	DELWAQ water flow over an exchange [$m^3\ s^{-1}$]

Directives for use

The process RESTIM can be used in all schematisations.

- ◇ No user input is required.
- ◇ You can access the RESTIM process in the PLCT through the state variable ‘Continuity’.

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16.8 Calculation of age of water

PROCESS: AGE

The 'age' of water from a specific source in a computational cell is defined as the difference in time between the actual time and the time at which the water entered the model area through the source and is thus equal to the travel time from the source to the computational cell. Common sources are boundaries and discharges (for example rivers).

Evaluation of the travel time ('age') of water from several sources may be valuable in the early stages of a water quality study as an indicator for the importance of water quality processes.

Implementation

In a single water quality simulation a maximum of five sources can be distinguished:

$i = 1, 2, 3, 4$ and 5

Formulation

$$ageTr_i = \frac{\ln\left(\frac{dTr_i}{cTr_i}\right)}{RcDecTr_i}$$
$$dDecTr_i = RcDecTr_i \times dTr_i$$

where

$ageTr_i$	age of tracer i [d]
cTr_i	concentration of conservative tracer i [g m^{-3}]
dTr_i	concentration of decayable tracer i [g m^{-3}]
$RcDecTr_i$	first order decay rate constant for decayable tracer i [d^{-1}]
$dDecTr_i$	flux for decayable tracer i [g m^{-3} d^{-1}]

Directives for use

- ◇ Two substances have to be defined for every source that has to be distinguished. The first of these substances is conservative (cTr_i), the other is decayable (dTr_i). For a correct calculation of the age, both substances must have the same concentration at all the source: it is advised to specify a concentration of 1.0 at the source that has to be distinguished and a concentration of 0.0 at all the other sources.
- ◇ Do not combine the 'age' proces with a 'decay' process for the same tracer. The 'decay' process will interfere with the age calculation, and lead to incorrect results.

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16.9 First order decay of decayable tracer

PROCESS: DECAY

First order decay of decable tracers without using the 'age' calculation.

Implementation

In a single water quality simulation a maximum of five decayable tracers can be distinguished:

$i = 1, 2, 3, 4$ and 5

Formulation

$$dDecaydTR_i = dDecdTR_i \times dTr_i$$

where

dTr_i concentration of decayable tracer i [g m^{-3}]
$dDecdTR_i$ first order decay rate constant for decayable tracer i [d^{-1}]
$dDecaydTR_i$ flux for decayable tracer i [g m^{-3} d^{-1}]

Directives for use

- ◇ Do not combine the 'age' proces with a 'decay' process for the same tracer. The 'decay' process will interfere with the age calculation, and lead to incorrect results.
- ◇ You can combine 'age' using a tracer and decable tracer (e.g. cTR1 with dTR1), and 'decay' for another decable tracer (dTR2).

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16.10 Inspecting the attributes

PROCESS: ATTRIBOUT

Within D-Water Quality each segment has two or more attributes:

- ◇ Attribute 1 is used to determine if the segment should participate in the calculation. It is in fact a dynamic attribute: if the segment becomes dry during the calculation, its first attribute is set to 0, indicating it is not active at that moment. Other segments may be set inactive permanently.
- ◇ Attribute 2 indicates the position of the segment in the water column:
  - □ A value of 1 means the segment is in middle of the water column, that is, not adjacent to the surface or the bottom.
  - □ A value of 2 means the segment is at the surface and should therefore be involved in processes like reaeration.
  - □ A value of 3 means the segment is at the bottom and should therefore be involved in processes like sedimentation oxygen demand or settling of suspended matter.
  - □ A value of 0 means the segment is adjacent to the surface and the bottom and should therefore be involved in all processes. This type of segment is typical for 1D and 2D applications.
- ◇ It is also possible to define your own attributes, even attributes that change in time. Their meaning is determined by the process routines that actually use them.
- ◇ To output all attributes, in an "aggregated" form, specify an attribute "0". For instance for an active segment at the surface (and only the standard attributes defined) the result will be: 21, where the digit 2 is the value of the second attribute and the digit 1 is the value of the first.

To make inspection of an attribute possible, you can use this process: it fills the output parameter *Attribute* with the value of the selected attribute for each segment. When you set AttribIdx to zero, you will retrieve all attributes in one number where the last digit is the first attribute, the before last digit is the second attribute, etcetera.

Table 16.4: *Definitions of the input and output parameters*

Name in input/output	**Definition**	**Units**
AttribIdx	Index of the attribute to output	[-]
Attribute	Output parameter	[-]

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17 Deprecated processes descriptions

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17.1 Growth and mortality of algae (MONALG)

PROCESS: MND1DIAT-M, MND2FLAG-M, MND3DIAT-F, MND4FLAG-F, MND(I)TEMP, MND(I)LLIM, MND(I)NLIM

Algae are subject to gross primary production, respiration, excretion, mortality, grazing, resuspension and settling. Net growth is the result. Net primary production is defined as the difference of gross primary production and respiration. The algae module MONALG includes specific formulations for these processes with the exception of grazing, resuspension and settling. These processes are equally valid for other algae modules, and are therefore dealt with in separate process descriptions.

MONALG considers four different algae species groups: marine diatoms, marine flagellates, fresh water diatoms and fresh water flagellates. Diatoms differ from flagellates among other things by their dependency on dissolved silicon for growth. Separate processes have been implemented for each of these groups (i), which allows the application of group average or species specific process coefficients. Other fresh water species discharged by rivers into estuaries should be allocated to the detritus pool.

The distinction between fresh water and marine species groups refers to conditions typical for estuaries, that may contain both fresh water and marine algae species. Fresh water algae die when entering the saline water body of an estuary, whereas marine species die when entering the upstream fresh water body.

MONALG contains a combination of formulations for phytoplankton derived from various ecosystem models (Klepper et al., 1994; Scholten and Tol, 1994; NIOO/CEMO, 1993; WL | Delft Hydraulics, 1988; Rijkswaterstaat/DGW, 1993). The module uses a mechanistic approach to describe algae dynamics. The primary production in MONALG is formulated according to Monod kinetics. A general feature of this type of kinetics is that the production rate is multiplicatively limited by environmental factors like nutrient availability, light availability, and temperature. The chlorophyll content dependency of the production rate is ignored (Klepper, 1989). The remaining processes are based on first-order kinetics with respect to algae biomass.

The total extinction coefficient and the available light averaged over the water column are calculated with separate processes described elsewhere. These processes are similar for other algae modules.

The algae processes affect a number of other model substances apart from the biomass concentrations [gC m^{-3}]. Primary production involves the uptake of inorganic nutrients [gN/P/Si m^{-3}] and the production of dissolved oxygen [gO_2 m^{-3}]. Preferential uptake of ammonium over nitrate is included in the model (McCarthy et al., 1977). Respiration consumes dissolved oxygen. Excretion and mortality produce detritus [gC/N/P m^{-3}] and opal silicate [gSi m^{-3}]. The process fluxes concerning these substances are derived from the algae process fluxes by means of multiplication with stochiometric constants. These ratios reflect the chemical composition of the algae biomass, which is assumed to be invariable over time.

All fluxes are daily averaged in connection with the way light limitation is integrated over a day. Consequently, nutrient uptake is assumed to be a continuous process over a day, whereas in reality it is a discontinuous process.

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Implementation

The algae module MONALG has been implemented as four processes for each of the four algae groups:

- ◇ the main process, where all process rates are calculated: MND(i), with different process names for the different species groups (i) to be modelled: MND1Diat-m, MND2Flag-m, MND3Diat-f, MND4-Flag-f;
- ◇ extra process: MND(i)Temp, calculating the limitation function for temperature;
- ◇ extra process: MND(i)LLim, calculating the limitation function for light; and
- ◇ extra process: MND(i)NLim, calculating the limitation function for nutrients.

The processes have been implemented in a generic way, which means that they are applicable both to water and sediment compartments. Live algae that settle eventually end up in the top sediment layer. Mortality and resuspension are the only active processes for sediment compartments, meaning that algae in sediment do not grow but are slowly converted into detritus. The current implementation of MONALG does not allow using any of the sediment options S1/2 and GEMSED!

MONALG calculates process rates for the following substances:

- ◇ MND1Diat-m, MND2Flag-m, MND3Diat-f, MND4Flag-f, POC1, PON1, POP1, Opal, NH4, NO3, PO4, Si and OXY.

Table 17.1 provide the definitions of the parameters occurring in the user-defined input and output.

Formulation

Formulations are subsequently presented for primary production, respiration, excretion and mortality. The rates and additional output are presented in the final sections.

The rate formulation for primary production is composed of limiting factors for temperature, nutrients and light. The rates of the other processes are dependent on the temperature, and in the case of mortality also on the chloride concentration. The processes lead to the consumption and production of nutrients and dissolved oxygen, or to the production of detritus components.

Primary production
Gross primary production is formulated as a temperature dependent first order process limited by light and nutrient availability:

$$Rgp_i = fnut_i \times flt_i \times kgp_i \times Calg_i$$

$$kgp_i = kpg_i^{10} \times ftmp_i$$

$$ftmp_i = ktpg_i^{(T-10)}$$

with:

$Calg$	algal biomass concentration [gC m^{-3}]
flt	light limitation factor [-]
$fnut$	Monod nutrient limitation factor [-]
$ftmp$	temperature limitation factor for production [-]
kgp	potential gross primary production rate [d^{-1}]
kgp^{10}	potential gross primary production rate at 10 °C [d^{-1}]

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$ktgp$	temperature coefficient for primary production [-]
Rgp	gross primary production rate [gC m^{-3} d^{-1}]
T	water temperature [°C]
i	index for species group 1-4 [-]

The nutrient limitation factor has been described in various ways. In most models Liebig's law of the minimum is applied to calculate the overall nutrient limitation. Here the additive model described by O' Neill et al. (1989) was selected. This additive model assumes that more than one nutrient can be limiting at the same time, and that the limitations add up according to multiplication of the Michaelis-Menten functions for individual nutrients.

The model must deal with several complications. Firstly, the limitation factors for diatoms and flagellates are slightly different, because only diatoms need silicate. Secondly, algae can use two inorganic sources of nitrogen, although they prefer ammonium. Consequently, the limitation factor must consider both the availability of and affinity for ammonium and nitrate. The following nutrient limitation factor takes all this into account:

$$fnut_i = fam_i + (1 - fam_i) \times fni_i$$

$$fam_i = \frac{Cam \times Cph \times Csi}{(Ksam_i \times Cph \times Csi + Cam \times Ksph_i \times Csi + Cam \times Cph \times Kssi_i + Cam \times Cph \times Csi}$$

$$fni_i = \frac{Cni \times Cph \times Csi}{(Ksni_i \times Cph \times Csi + Cni \times Ksph_i \times Csi + Cni \times Cph \times Kssi_i + Cni \times Cph \times Csi)}$$

with:

fam	ammonium specific nutrient limitation factor [-]
fni	nitrate specific nutrient limitation factor [-]
Cam	ammonium concentration [gN m^{-3}]
Cni	nitrate concentration [gN m^{-3}]
Cph	phosphate concentration [gP m^{-3}]
Csi	dissolved inorganic silicate concentration [gSi m^{-3}]
$Ksam$	half saturation constant for ammonium [gN m^{-3}]
$Ksni$	half saturation constant for nitrate [gN m^{-3}]
$Ksph$	half saturation constant for phosphate [gP m^{-3}]
$Kssi$	half saturation constant for silicate [gSi m^{-3}]

Phytoplankton production is limited, if the light availability in the water column is less than the temperature dependent optimal radiation for a phytoplankton species. Below this optimal radiation light limitation is a saturating function of light availability. There is inhibition if light availability exceeds the optimum.

Light limitation depends on a functional relationship between in situ light intensity and primary production. This function must be integrated over time and depth to obtain the daily and depth averaged light limitation factor. The integration by discretisation is done according to Eilers and Peeters (1988):

$$flt_i = \frac{\left(\sum_{k=1}^{n}\sum_{j=1}^{m}\left(Rrgp_{i,j,k} \times \Delta z \times \Delta t\right)\right)}{(86400 \times H)}$$

$$Rrgp_{i,j,k} = \frac{Ir_{i,j,k} \times (c_i + 2)}{\left(Ir_{i,j,k}^2 + c_i \times Ir_{i,j,k} + 1\right)}$$

$$Ir_{i,j,k} = \frac{I_{j,k}}{Io_i}$$

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$$c_i = \frac{Io_i}{(kgp_i/d_i)} - 2$$
$$Io_i = Io_i^{10} \times ktpg_i^{(T-10)}$$
$$I_{j,k} = Itop_k \times e^{(-et \times z_j)}$$

with:

c	shape coefficient of the production factor [-]
d	initial slope of the light-production curve [gC d^{-1}.W m^{-2})$^{-1}$]
et	total extinction coefficient of visible light [m^{-1}]
flt	light limitation factor [-]
H	depth of a water compartment or water layer [m]
I	light intensity at depth z_j and time t_k [W m^{-2}]
Io	optimal light intensity [W m^{-2}]
Ir	light intensity at depth z_j and time t_k, relative to optimal intensity [-]
$Itop$	light intensity at depth z_o (top of layer or compartment) and time t [W m^{-2}]
kgp	potential gross primary production rate [d^{-1}]
$ktgp$	temperature coefficient for primary production [-]
$Rrgp$	gross production at depth z_j and time t_k, relative to maximal production [-]
z	depth [m]
Δt	time interval for light limitation integration, that is the DELWAQ timestep [s]
Δz	depth interval for light limitation integration ([m]; = H/m)
i	index for species group 1–4 [-]
j	index for depth interval 1–m [-]
k	index for time interval 1–n [-]
n	number of time intervals in a day ([-]; $= 86\,400/\Delta t$)
m	number of depth intervals in a water compartment or water layer [-]

The $Rrgp_{i,j,k}$ factor has a sinusoidal shape within the daylength period (light hours), and is equal to zero outside this period.

Respiration

Algal respiration is simulated as of maintenance respiration and growth respiration. Maintenance respiration is temperature dependent. Growth respiration depends on the primary production rate. The total respiration rate is given by:

$$Rrsp_i = krsp_i \times Calg_i + frsp_i \times Rgp_i$$
$$krsp_i = krsp_i^{10} \times ktrsp_i^{(T-10)}$$

with:

$frsp$	fraction of gross production respired [-]
$krsp$	maintenance respiration rate [d^{-1}]
$krsp^{10}$	maintenance respiration rate at 10 °C [d^{-1}]
$ktrsp$	temperature coefficient for maintenance respiration [-]
$Rrsp$	total respiration rate [gC m^{-3} d^{-1}]

Excretion

Excretion is a function of nutrient stress (Klepper, 1989). Excretion decreases with increasing nutrient limitation. It is modelled as a fraction of the gross primary production as follows:

$$Rexc_i = fexc_i \times (1 - fnut_i) \times Rgp_i$$

with:

$fexc$	fraction of gross production excreted at the absence of nutrient limitation [-]
$Rexc$	excretion rate [gC m^{-3} d^{-1}]

Mortality

Algal mortality is caused by temperature dependent natural mortality, salinity stress mortality, and grazing by consumers. The latter process is described elsewhere in relation to the modelling of grazers. Salinity driven mortality is described with a sigmoidal function of chlorinity (NIOO/CEMO, 1993), leading to the following formulations:

$$Rmrt_i = kmrt_i \times Calg_i$$

$$kmrt_i = kmrt_i^{10} \times ktmrt_i^{(T-10)}$$

$$kmrt_i^{10} = \frac{m1_i - m2_i}{1 + e^{(b1_i \times (Ccl - b2_i))}} + m2_i \qquad \text{for fresh water algae,} \quad MND(i)Type = 2.0$$

$$kmrt_i^{10} = \frac{m2_i - m1_i}{1 + e^{(b1_i \times (Ccl - b2_i))}} + m1_i \qquad \text{for marine algae,} \quad MND(i)Type = 1.0$$

with:

$b1$	coefficient 1 of salinity stress function [g^{-1} m^3]
$b2$	coefficient 2 of salinity stress function [g m^{-3}]
$m1$	rate coefficient 1 of salinity stress function [d^{-1}]
$m2$	rate coefficient 2 of salinity stress function [d^{-1}]
Ccl	chloride concentration [g m^{-3}]
$kmrt$	total mortality process rate [d^{-1}]
$kmrt^{10}$	total mortality process rate at 10 °C [d^{-1}]
$ktmrt$	temperature coefficient for mortality [-]
$Rmrt$	total mortality rate [gC m^{-3} d^{-1}]

$m1$ and $m2$ are the end members of the above function, meaning that the function obtains the value $m1$ at high Ccl, and the value $m2$ for low Ccl. The mortality rate increases with decreasing chloride concentration, when $m2$ is larger than $m1$. This situation which applies to marine algae is depicted in the example of figure 17.1. The mortality rate increases with increasing chloride concentration, when $m1$ is larger than $m2$. This situation applies to fresh water algae.

In case DELWAQ-G is applied the mortality is the only process that is active with respect to algae biomass. The first-order mortality rate in the sediment has a specific temperature independent mortality process rate $kmrts, i$ [d^{-1}].

Resulting process rates affecting model substances

The consumption and production rates for nutrients and dissolved oxygen are derived from the production rate as follows:

$$Rprd_{ox,i} = (Rgp_i - Rrsp_i) \times aox_i$$

$$Rcns_{am,i} = (Rgp_i - Rrsp_i) \times an_i \times fam_i / fnut_i$$

$$Rcns_{ni,i} = (Rgp_i - Rrsp_i) \times an_i \times (1 - fam_i / fnut_i)$$

$$Rcns_{ph,i} = (Rgp_i - Rrsp_i) \times aph_i$$

$$Rcns_{si,i} = (Rgp_i - Rrsp_i) \times asi_i$$

$$Rprd_{oc,i} = (Rmrt_i + Rexc_i)$$

$$Rprd_{on,i} = (Rmrt_i + Rexc_i) \times an_i$$

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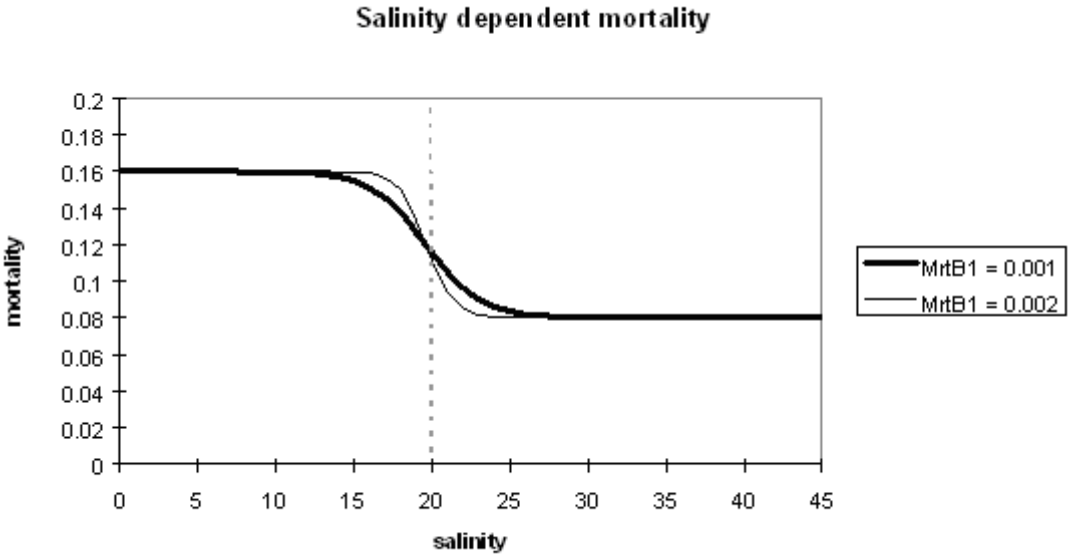

Figure 17.1: *Example of the salinity dependent mortality function. m1 = 0.08 d^{-1}; m2 = 0.16 d^{-1}; b2 = 11000 (equivalent with 20 ppt salinity) [gCl m^{-3}]; b1 = 0.001 and 0.002 $m^3.gCl^{-1}$.*

$$Rprd_{op,i} = (Rmrt_i + Rexc_i) \times aph_i$$
$$Rprd_{osi,i} = (Rmrt_i + Rexc_i) \times asi_i$$

with:

an	stochiometric constant for nitrogen over carbon in algae biomass [gN.gC^{-1}]
aph	stochiometric constant for phosphorus over carbon in algae biomass [gP.gC^{-1}]
aox	stochiometric constant for oxygen over carbon in algae biomass [gO_2.gC^{-1}]
asi	stochiometric constant for silicon over carbon in algae biomass [gSi.gC^{-1}]
$Rcns_{am}$	net consumption rate for ammonium [gN m^{-3} d^{-1}]
$Rcns_{ni}$	net consumption rate for nitrate [gN m^{-3} d^{-1}]
$Rcns_{ph}$	net consumption rate for phosphate [gP m^{-3} d^{-1}]
$Rcns_{si}$	net consumption rate for silicate [gSi m^{-3} d^{-1}]
$Rprd_{ox}$	net production rate for dissolved oxygen [gO_2 m^{-3} d^{-1}]
$Rprd_{oc}$	net production rate for detritus organic carbon [gC m^{-3} d^{-1}]
$Rprd_{on}$	net production rate for detritus organic nitrogen [gN m^{-3} d^{-1}]
$Rprd_{op}$	net production rate for detritus organic phosphorus [gP m^{-3} d^{-1}]
$Rprd_{osi}$	net production rate for opal silicate [gSi m^{-3} d^{-1}]

The immediate release of inorganic nutrients due to mortality (autolysis) of algae is simulated in GEM as the fast decay of the labile detritus fraction (POC1, PON1, POP1).

fam and $fnut$ are used to calculate the preference for ammonium uptake. The ratio of the ammonium specific limitation factor and the overall nutrient limitation factor defines the fraction of nitrogen obtained from ammonium.

Chlorophyll to carbon ratio

MONALG delivers some additional output parameters, such as the chlorophyll content of the algae, expressed as the carbon to chlorophyll ratio, and the chlorophyll concentration. The carbon to chlorophyll ratio depends on the availability of light and nutrients. The ratio is mod-

elled with an empirical function of the light and nutrient limitation factors (Klepper, 1989). The chlorophyll concentration for each algae group is calculated according to:

$$Cchf_i = \frac{Calg_i}{achf_i}$$

$$achf_i = \frac{achf_{min,i}}{(fnut_i \times (1 - flt_i \times fnut_i))^{g_i}}$$

with:

$achf$	stoch. constant for carbon over chlorophyll in algae biomass [gC gChf^{-1}]
$achfmin$	minimal stoch. const. for carbon over chlorophyll in algae biomass [gC gChf^{-1}]
$Cchf$	chlorophyll concentration connected with an algae group [gChf m^{-3}]
g	scaling coefficient for growth limitation factor [-]

The total concentration of chlorophyll is calculated by a separate process PHY_GEM, which is described elsewhere in this manual.

Directives for use

- ◇ The process rates of gross primary production and maintenance respiration have a temperature basis of 10 °C. That means that input values have to be corrected when provided for a more common temperature basis of 20 °C.
- ◇ The growth limitation for a specific nutrient can be made inactive by allocating value zero to the half saturation constant for this nutrient.
- ◇ The salinity effect on mortality can be inactivated by allocating the same value to coefficients $MND(i)m1$ and $MND(i)m2$.
- ◇ Always make sure that the light input (observed solar radiation) is consistent with the light related parameters of MONALG. This concerns the use of either visible light or the photosynthetic fraction of visible light (approximately 45 %). The input incident light time series should have been corrected for cloudiness and reflection (approximately 10 %).

Additional references

WL | Delft Hydraulics (1997)

Table 17.1: *Definitions of the input parameters in the formulations for MONALG.*

Name in formulas	Name in input	Definition	Units
Cam	$NH4$	ammonium concentration	gN m^{-3}
Ccl	Cl	chloride concentration	gCl m^{-3}
Cni	$NO3$	nitrate concentration	gN m^{-3}
Cph	$PO4$	phosphate concentration	gP m^{-3}

continued on next page

[1](i) indicates species groups 1-4.

[2]This parameter is only used for initialisation during the first timestep.

[3]This parameter is calculated by processes ExtPhGVL and Extinc_VL.

[4]This parameter is not part of the input.

Table 17.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
Csi	Si	dissolved inorganic silicate concentration	gSi m^{-3}
$Calg_1$	$MND1Diat-m$	biomass concentration of marine diatoms	gC m^{-3}
$Calg_2$	$MND2Flag-m$	biomass concentration of marine flagellates	gC m^{-3}
$Calg_3$	$MND3Diat-f$	biomass concentration of fresh water diatoms	gC m^{-3}
$Calg_4$	$MND4Flag-f$	biomass concentration of fresh water flagellates	gC m^{-3}
-	$MND(i)Type$	type of algae group (1 = brackish/marine, 2 = fresh)	-
$achf_i$	$MND(i)AChl_0$[2]	group specific stoch. const. carbon over chlorophyll	gC.gChf^{-1}
$achf_{\min,i}$	$MND(i)amchl$	group spec. min. stoch. const. carbon over chlorophyll	gC.gChf^{-1}
an_i	$MND(i)NCrat$	group specific stoch. const. for nitrogen over carbon	gN.gC^{-1}
aox_i	-[4]	group specific stoch. const. for oxygen over carbon	gO_2.gC^{-1}
aph_i	$MND(i)PCrat$	group spec. stoch. const. for phosphorus over carbon	gP.gC^{-1}
asi_i	$MND(i)SiCrat$	group specific stoch. const. for silicon over carbon	gSi.gC^{-1}
$m1_i$	$MND(i)m1$	group spec. rate coefficient 1 of salinity stress function	d^{-1}
$m2_i$	$MND(i)m2$	group spec. rate coefficient 2 of salinity stress function	d^{-1}
$b1_i$	$MND(i)b1$	group specific coefficient 1 of salinity stress function	g^{-1} m^3
$b2_i$	$MND(i)b2$	group specific coefficient 2 of salinity stress function	g m^{-3}
d_i	$MND(i)schl$	group specinitial slope of the light-production curve	gC d^{-1}.(W m^{-2})$^{-1}$
et	$ExtVl$[3]	total extinction coefficient of visible light	m^{-1}

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[1](i) indicates species groups 1-4.

[2]This parameter is only used for initialisation during the first timestep.

[3]This parameter is calculated by processes ExtPhGVL and Extinc_VL.

[4]This parameter is not part of the input.

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Table 17.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
g_i	$MND(i)b$	group spec. scaling coef. for growth limitation factor	-
$Ksam_i$	$MND(i)Kam$	group specific half saturation constant for ammonium	gN m^{-3}
$Ksni_i$	$MND(i)Kni$	group specific half saturation constant for nitrate	gN m^{-3}
$Ksph_i$	$MND(i)Kph$	group specific half saturation constant for phosphate	gP m^{-3}
$Kssi_i$	$MND(i)Ksi$	group specific half saturation constant for silicate	gSi m^{-3}
$fexc_i$	$MND(i)b_ex$	group spec. frac. gross prod. excrát abs. of nutr. lim.	-
$frsp_i$	$MND(i)r_pr$	group specific fraction of gross production respired	-
H	$Depth$	depth of a water compartment or water layer	m
Io_i	$MND(i)Iopt$	group specific optimal light intensity	W m^{-2}
$Itop$	Rad	light intensity at top of layer or compartment	W m^{-2}
kgp_i^{10}	$MND(I)Pm10$	group spec. potential gross primary prod. rate at 10 °C	d^{-1}
$krsp_i^{10}$	$MND(i)r_mt10$	group spec. maintenance respiration rate at 10 °C	d^{-1}
$ktgp_i$	$MND(i)ktgp$	group spec. temperature coefficient for primary prod.	-
$ktmrt_i$	$MND(i)mt$	group spec. temperature coefficient for mortality	-
$ktrsp_i$	$MND(i)rt$	group spec. temperature coef. for maintenance resp.	-
$kmrt_{s,i}$	$MND(i)MorSed$	group spec. mortality process rate in sediment	d^{-1}
T	$Temp$	water temperature	°C
-	$ITIME$	time	s

continued on next page

[1](i) indicates species groups 1-4.

[2]This parameter is only used for initialisation during the first timestep.

[3]This parameter is calculated by processes ExtPhGVL and Extinc_VL.

[4]This parameter is not part of the input.

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Table 17.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
Δt	IDT	time interval, that is the DELWAQ timestep	s
m	Nr_dz	number of depth intervals in a water comp. or layer	-

[1](i) indicates species groups 1-4.

[2]This parameter is only used for initialisation during the first timestep.

[3]This parameter is calculated by processes ExtPhGVL and Extinc_VL.

[4]This parameter is not part of the input.

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Rijkswaterstaat
Ministry of Infrastructure and Water Management

Deltares
Enabling Delta Life

PO Box 177
2600 MH Delft
Boussinesqweg 1
2629 HV Delft
The Netherlands

+31 (0)88 335 81 88

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