

Simulation packages for rivers, estuaries and seas

D-HYDRO SUITE

Dutch Delta Systems



D-Water Quality Processes Library Description

Technical Reference Manual

Processes Library Description

Detailed description of Processes

Technical Reference Manual

D-Water Quality

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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 process 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 Library used for Sobek still uses its own set of substances and processes,

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 â€“S1-S2â€ approach, for which additional substances represent two sediment layers. This manual includes the S1-S2 specific substances and processes. The comprehensive â€“layered sedimentâ€ approach involves adding a sediment grid to the computational grid and including a sediment specific transport process. This is described in the addition manual â€“Sediment Water Interactionâ€. 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 â€“layered sedimentâ€ 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 \(chapter 5\)](#)
- ◊ [Primary consumers \(chapter 6\)](#)
- ◊ [Organic matter \(detritus\) \(chapter 7\)](#)
- ◊ [Inorganic substances and pH \(chapter 8\)](#)
- ◊ [Organic micropollutants \(chapter 9\)](#)
- ◊ [Heavy metals \(chapter 10\)](#)
- ◊ [Bacterial pollutants \(chapter 11\)](#)
- ◊ [Sediment and mass transport \(chapter 12\)](#)
- ◊ [Temperature \(chapter 13\)](#)
- ◊ [Various auxiliary processes \(chapter 14\)](#)
- ◊ [Deprecated processes descriptions \(chapter 15\)](#)

Generic mass transport processes are dealt with together with the substances group â€“IJs-sedimentâ€ ([chapter 12](#)).



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

- (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 ([D-WAQ Processes Library Tables, 2013](#)).

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.

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 14) 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 1.1 to 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, insofar 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) *GreenS1* 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 (micro-phytobenthos), 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) and ultraviolet light (UV) have been integrated in two overall processes *Extinc_VLG* and *Extinc_UVG*.
- ◊ 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* (sulphate), *SUD*, *SUP* (dissolved and particulate sulphide), *POC5*, *PON5*, *POP5* (non-transportable detritus, see below), *POS1*, *POS2*, *POS3*, *POS4*, *POS5*, *DOS* (particulate and dissolved organic sulphur), *FelliPa*, *FelliPc*, *FelliId*, *FeS*, *FeS2*, *FeCO3*, *Felld* (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 sulphate, and the production of methane in the mineralization of organic matter), *SPECSUD*, *OXIDSUD*, *SULPHOX*, *SPECSUDS1*, *SPECSUDS2*, *PRECSUL* (speciation, oxidation and precipitation of sulphide), *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

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

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 IJS_3) 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 IJS_3) 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 IJS_3) 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 IJS_3) is now specified directly as a solid phase concentration (e.g. QAtRDRMS3 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 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.

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 ($< 3 \text{ m.s}^{-1}$). 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, 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* (= 0–10, 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.

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:

$$R_{rear} = klrear \times (Coxs - \max(Cox, 0.0)) / H$$

$$klrear = klrear^{20} \times ktrear^{(T-20)}$$

$$klrear^{20} = \left(\frac{a \times v^b}{H^c} \right) + (d \times W^2)$$

$$Coxs = f(T, Ccl \text{ or } SAL) \quad (\text{delivered by SATUROXY})$$

$$fsat = 100 \times \frac{\max(Cox, 0.0)}{Coxs}$$

with:

a, b, c, d	coefficients with different values for each reaeration options
Ccl	chloride concentration [gCl m^{-3}]
Cox	actual dissolved oxygen concentration [$\text{gO}_2 \text{ m}^{-3}$]
$Coxs$	saturation dissolved oxygen concentration [$\text{gO}_2 \text{ m}^{-3}$]
$fsat$	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}]
$ktrear$	temperature coefficient of the transfer coefficient [-]
R_{rear}	reaeration rate [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
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

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.

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 \(1978\)](#); $d = 0.3\text{--}0.6$ and later [WL | Delft Hydraulics](#) modelling studies for Dutch lakes. Consequently, the coefficients are:

$$a = 3.863, \quad b = 0.5, \quad c = 0.5, \quad d = 0.065 \times k_{lrear}^{20}$$

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 \(1978\)](#); $d = 0.03\text{--}0.06$ and later modelling studies for Dutch lakes [WL | Delft Hydraulics \(1992c\)](#). Consequently, the coefficients are:

$$a = 0.3, \quad b = 0.0, \quad c = 0.0, \quad d = 0.028 \times k_{lrear}^{20}$$

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 ($W < 3 \text{ m s}^{-1}$).

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 k_{lrear} . 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:

$$a = 0.0, \quad b = 0.0, \quad c = 0.0, \quad d = 0.0744 \times f_{sc}$$

$$f_{sc} = \left(\frac{Sc}{Sc^{20}} \right)^{-0.5}$$

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

with:

$d_{1\text{--}4}$	coefficients
f_{sc}	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]

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	d_1	d_2	d_3	d_4
Sea water Salinity $> 5 \text{ kg m}^{-3}$	1953.4	128.0	3.9918	0.050091
Fresh water Salinity $\leq 5 \text{ kg m}^{-3}$	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 hybrid 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](#)):

$$a = 3.93, b = 0.5, c = 0.5, d = 0.0 \text{ if}$$

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

([Owens et al., 1964](#)):

$$a = 5.32, b = 0.67, c = 0.85, d = 0.0 \text{ if}$$

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

$$klrear^{20} = \max(klrear_{\min}, klrear^{20}) \quad (2.3)$$

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 \(2006\)](#); [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:

$$klrear = (a \times \exp(b_1 \times W^{b2}) + (c_1 \times P^{c2})) \times fsc$$

$$fsc = \left(\frac{Sc}{Sc^{20}} \right)^{-0.67}$$

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

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
<i>CoefAOXY</i>	<i>CoefB1OXY</i>	<i>CoefB2OXY</i>	<i>CoefC1OXY</i>	<i>CoefC2OXY</i>
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
<i>CoefD1OXY</i>	<i>CoefD2OXY</i>	<i>CoefD3OXY</i>	<i>CoefD4OXY</i>
1800.06	120.10	3.7818	0.047608

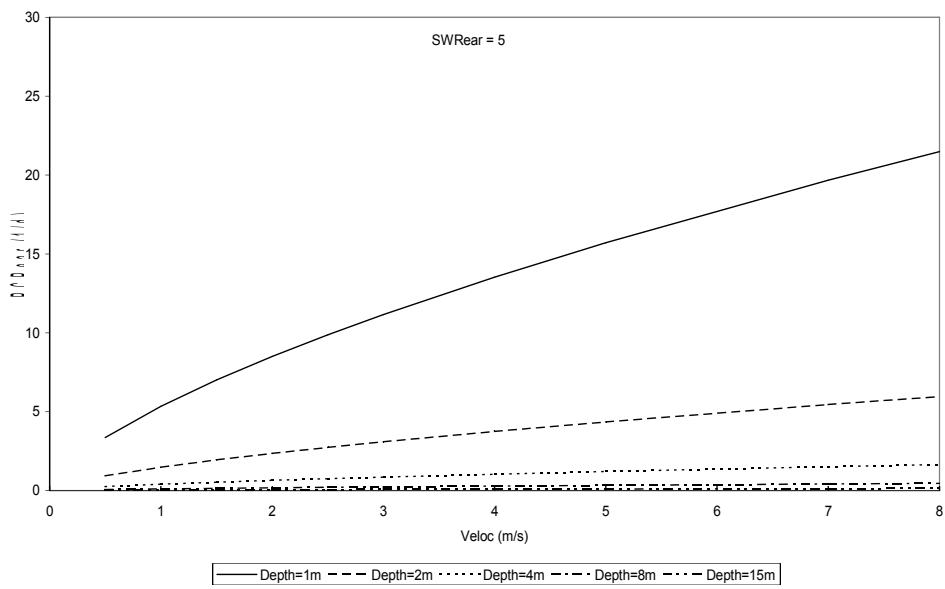
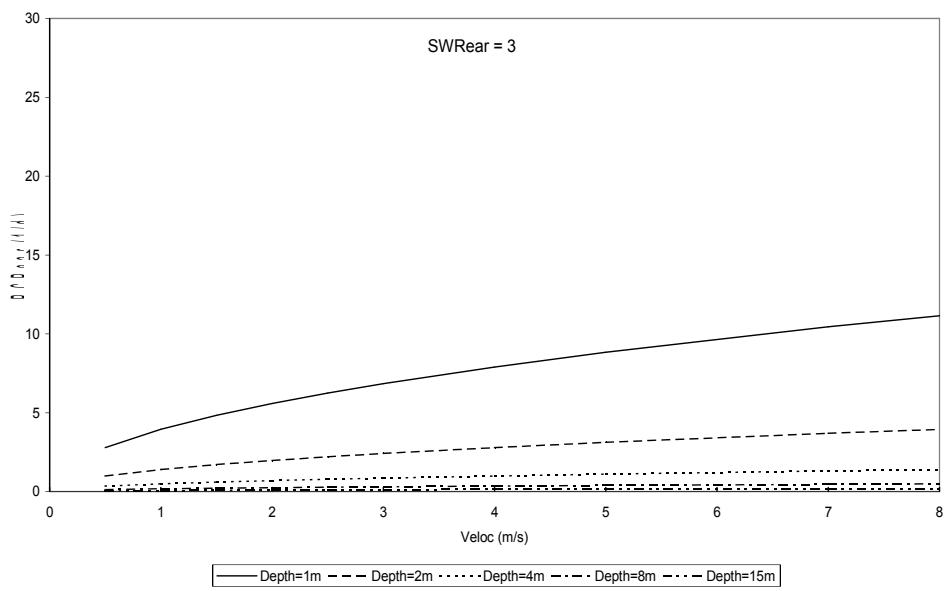
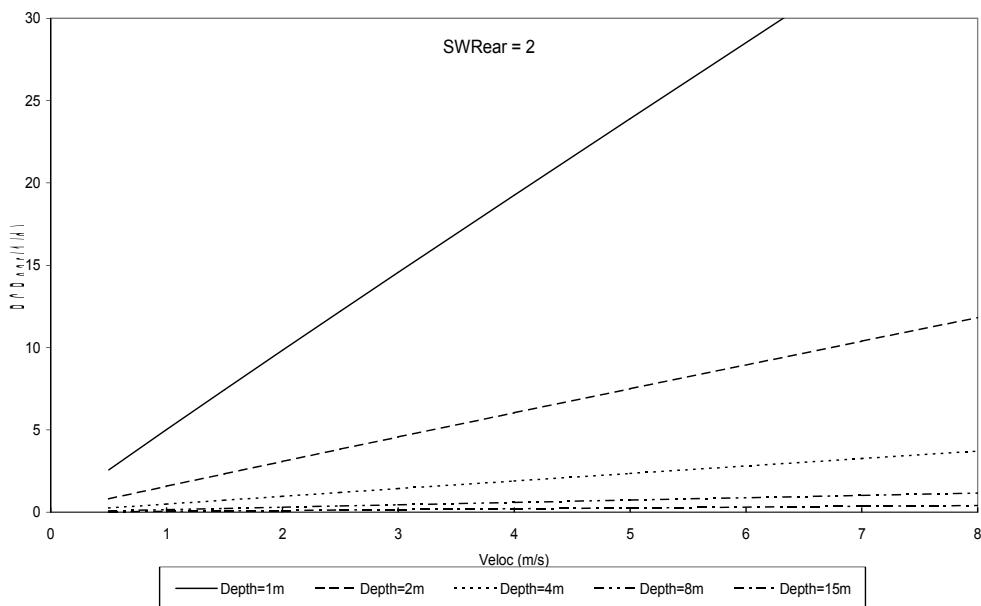
Directives for use

- ◊ 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* is used as a dimensionless scaling factor. The default value of *KLRear* 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](#).
- ◊ 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 $Coxs$	OXY $SaturOXY$	concentration of dissolved oxygen saturation concentration dissolved oxygen from SATUROXY	$gO_2\ m^{-3}$ $gO_2\ m^{-3}$
a b_1 b_2 c_1 c_2	$CoefAOXY$ $CoefB1OXY$ $CoefB2OXY$ $CoefC1OXY$ $CoefC2OXY$	coefficients for option 13 only	- - - - -
d_1 d_2 d_3 d_4	$CoefD1OXY$ $CoefD2OXY$ $CoefD3OXY$ $CoefD4OXY$	coefficients for options 10 and 13	- - - -
fcs $fsat$	- -	scaling factor for the Schmidt number percentage oxygen saturation	- %
H	<i>Depth</i>	depth of the water layer	m
$klrear^{20}$ $klttemp$	$KLRear$ $TCRear$	water transfer coefficient for oxygen ¹⁾ temperature coefficient for reaeration	$m\ d^{-1}$ -
P	rain	rainfall	mm^{-1}
$Rrear$	-	reaeration rate	$gO_2\ m^{-3}\ d^{-1}$
SAL	<i>Salinity</i>	salinity	$kg\ m^{-3}$
Sc	-	Schmidt number for dissolved oxygen in water	-
$SWRear$	$SWRear$	switch for selection of options for transfer coefficient	-
T	<i>Temp</i>	temperature	$^{\circ}C$
v W	<i>Velocity</i> $VWind$	flow velocity wind speed at 10 m height	$m\ s^{-1}$ $m\ s^{-1}$

¹⁾ See directives for use concerning the dimension of $KLRear$.



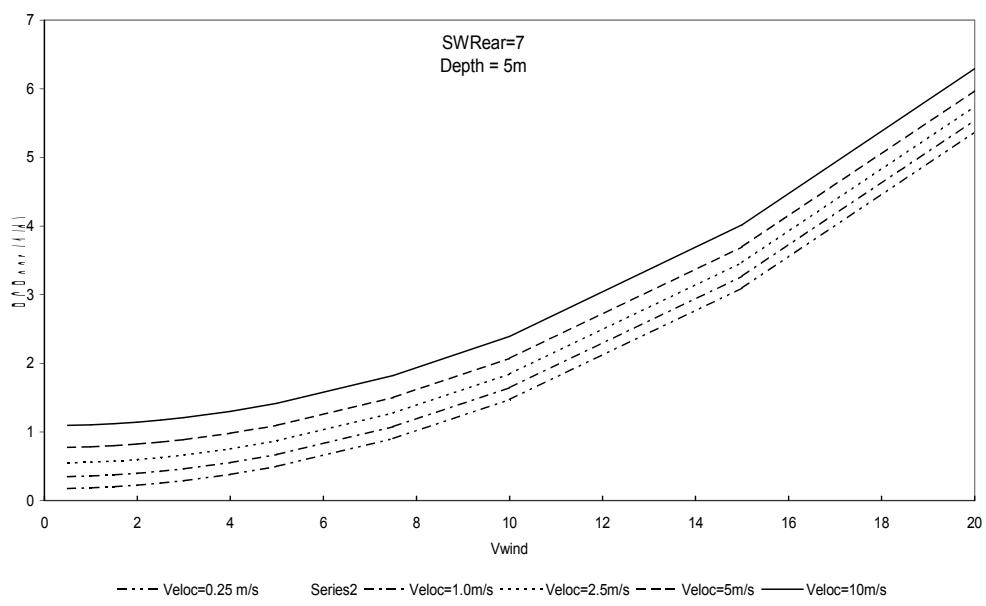
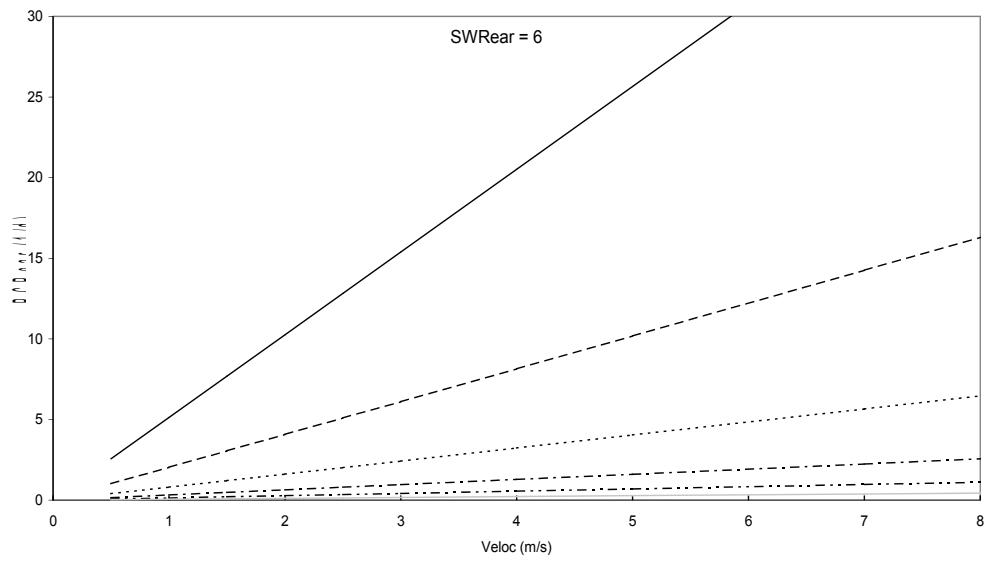


Figure 2.1: The reaeration rate RC_{Rear} ($=k_{lrear}^{20} 20/H$) as a function of water depth, flow velocity and/or wind velocity for various options $SWRear$ for the mass transfer coefficient k_{lrear}

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:

$$Rdrear = \frac{Cox - Cox_{t-1}}{\Delta t} \quad (2.4)$$

with:

<i>Rdrear</i>	oxygen reaeration rate as a result of dam reaeration [$\text{gO}_2 \cdot \text{m}^{-3} \cdot \text{d}^{-1}$]
<i>Cox</i>	oxygen concentration [$\text{gO}_2 \cdot \text{m}^{-3}$]
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:

$$Cox = \frac{1}{fdrear} \times (Coxs(fdrear - 1) + Coxup) \quad (2.5)$$

with:

<i>fdraer</i>	oxygen deficit ratio [-]
<i>Coxs</i>	oxygen saturation concentration [$\text{gO}_2 \cdot \text{m}^{-3}$]
<i>Coxup</i>	oxygen concentration upstream of weir [$\text{gO}_2 \cdot \text{m}^{-3}$]

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.

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

$$fdrear = 1.0 + 0.38 \times a \times b \times \Delta h \times (1 - 0.11 \times \Delta h) \times (1 + 0.046 \times T) \quad (2.6)$$

with:

<i>a</i>	water quality factor [—]
<i>b</i>	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]
<i>T</i>	water temperature [$^{\circ}\text{C}$]

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.

$$fdrear = 1 + (fdrearn - 1) \times a \times b \times (1 + 0.02(T - 20)) \quad (2.7)$$

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

with:

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

The water quality factor is related to the BOD concentration:

$$a = \min \left(1.80, \frac{1.90}{C_{bod}^{0.44}} \right) \quad (2.9)$$

with:

<i>C_{bod}</i>	biological oxygen demand [$\text{gO}_2 \text{ m}^{-3}$]
------------------------	---

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 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 C_e 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	$\text{gO}_2 \cdot \text{m}^{-3}$
Cox $Coxs$ $Coxup$	OXY $SaturOXY$ OXY	concentration of dissolved oxygen saturation conc. dissolved oxygen from saturoxy oxygen concentration upstream of weir	$\text{gO}_2 \cdot \text{m}^{-3}$ $\text{gO}_2 \cdot \text{m}^{-3}$ $\text{gO}_2 \text{ m}^{-3}$
$fdrear$ $fdrearn$	- -	oxygen deficit ratio oxygen deficit ratio according to Nakasone	- -
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

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

Name in formulas ¹⁾	Name in input	Definition	Units
H	<i>Depth</i>	depth of the top water layer	m
L	<i>Widthsti</i>	width of crest of structure i	m
Q	<i>DischSti</i>	discharge over structure i	$\text{m}^3 \text{ s}^{-1}$
$Rdrear$	-	oxygen reaeration rate as a result of dam aeration	$\text{gO}_2 \cdot \text{m}^{-3} \text{ d}^{-1}$
Δt	<i>Delt</i>	timestep	d
T	<i>Temp</i>	temperature	°C

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); 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:

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

For SWSatOxy = 2:

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

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

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 [$\text{gO}_2 \text{ m}^{-3}$]

T water temperature [$^\circ\text{C}$]

T_f temperature function [-]

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 $C\text{l}$ can either be imposed by you or simulated with the model.
The salinity can be estimated from the chloride concentration with:

$$SAL = 1.805 \times C\text{l} / 1\,000.$$

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
C_{oxs} $C\text{Cl}$	<i>SaturOXY</i> $C\text{l}$	saturation concentration of oxygen in water chloride concentration	$\text{gO}_2 \text{ m}^{-3}$ gCl m^{-3}
SAL <i>SWSatOxy</i>	<i>Salinity</i> <i>SWSatOxy</i>	salinity switch for selection options for saturation equation	kg m^{-3} -
T T_f	<i>Temp</i> –	water temperature temperature function	$^{\circ}\text{C}$ -

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:

<i>Fnp</i>	net primary production flux [gC m ⁻² d ⁻¹]
<i>Frsp</i>	respiration flux [gC m ⁻² d ⁻¹]
<i>H</i>	depth of the water column [m]
<i>Rgp_a</i>	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 *t₁* and *t₂* 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:

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

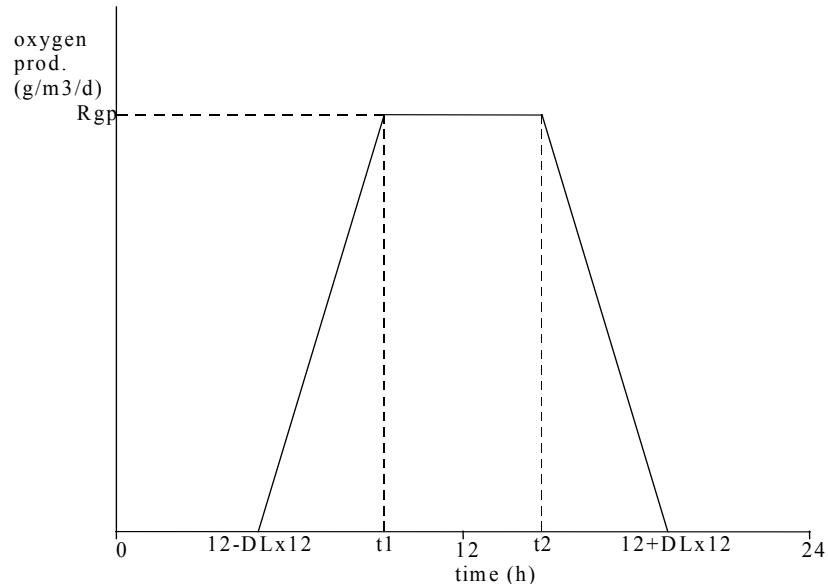


Figure 2.2: The distribution of gross primary production over a day

with:

DL	day length, fraction of a day [-]
Rgp_{max}	maximal gross primary production rate during a day [$\text{gC m}^{-3} \text{ d}^{-1}$]
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:

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

with:

Rnp	net primary production (or respiration) rate during a day [$\text{gC m}^{-3} \text{ d}^{-1}$]
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 $Frsp$	$fPPtot$ $fResptot$	net primary production flux respiration flux	$\text{gC m}^{-2} \text{ d}^{-1}$ $\text{gC m}^{-2} \text{ d}^{-1}$
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	$\text{gC m}^{-3} \text{ d}^{-1}$
Rgp_a	-	average gross primary production rate during a day	$\text{gC m}^{-3} \text{ d}^{-1}$
Rgp_{max}	-	maximal gross primary production rate during a day	$\text{gC m}^{-3} \text{ d}^{-1}$
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}
-	$Reffhour$	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: $t_2 < (12 + DL \times 12)$ and $t_1 > (12 - DL \times 12)$.
- ◊ The actual time in a day is available as output parameter *ActualTime*.

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 [$\text{gO}_2 \text{ m}^{-3}$]
Cox_{min1}	minimal dissolved oxygen concentration in a day for estimation method 1 [$\text{gO}_2 \text{ m}^{-3}$]
DL	day length, fraction of a day [-]
$krsp$	algae respiration rate constant [d^{-1}]
$Rrsp$	total algae respiration rate [$\text{gC m}^{-3} \text{ d}^{-1}$]

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
$Calg_1$	<i>Green</i>	biomass of Green algae	gC m^{-3}
$Calg_2$	<i>Diat</i>	biomass of Diatoms	gC m^{-3}
Cox	<i>OXY</i>	average dissolved oxygen concentration	$\text{gO}_2 \text{ m}^{-3}$
Cox_{min}	<i>OXYMIN</i>	minimal dissolved oxygen concentration in a day	$\text{gO}_2 \text{ m}^{-3}$
DL	<i>DayL</i>	day length, fraction of a day	-
kgp_1	<i>RcGroGreen</i>	gross primary prod. rate constant of Green algae	d^{-1}
kgp_2	<i>RcGroDiat</i>	gross primary prod. rate constant of Diatoms	d^{-1}
$krsp_1$	<i>RcRespGreen</i>	algae respiration rate constant of Green algae	d^{-1}
$krsp_2$	<i>RcRespDiat</i>	algae respiration rate constant of Diatoms	d^{-1}
Rgp	-	total gross primary production rate	gC m^{-3}
$Rrsp$	-	total algae respiration rate	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:

$$Cox_{min2} \quad \text{minimal dissolved oxygen concentration in a day for estimation method 2 [gO}_2 \text{ m}^{-3}]$$

$$kgp \quad \text{gross primary production rate constant [d}^{-1}]$$

$$Rgp \quad \text{total net primary production rate [gC m}^{-3} \text{ d}^{-1}]$$

In order to avoid overestimation of the DO-minimum, the minimal value 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.

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

Name in formulas	Name in in/output	Definition	Units
C_{ox}	OXY	equivalent dissolved oxygen concentration	$\text{gO}_2 \text{ m}^{-3}$
DO	–	positive dissolved oxygen concentration	$\text{gO}_2 \text{ m}^{-3}$

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 sulphate 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 sulphate) are included in DELWAQ, the reduced substances are included 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:

$$DO = \max(C_{ox}, 0.0)$$

with:

DO	actual dissolved oxygen concentration [$\text{gO}_2 \text{ m}^{-3}$]
C_{ox}	equivalent dissolved oxygen concentration [$\text{gO}_2 \text{ m}^{-3}$]

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.

Table 2.8: Typical values for oxygen demanding waste waters (values in [mgO₂/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.

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 CO₂ and H₂O. 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 O₂ are used to oxidize 1 mg of carbon. The ratio between CBOD₅ and CBOD_u depends on the decay rate of the organic material: $BOD_5/BOD_u = (1 - \exp(-5 \times R_{CBOD}C))$. The higher the decay rate the more the ratio will reach unity. From the BOD_5/BOD_u 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 \(1987\)](#)). BOD_5/BOD_u 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:

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

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:

$$\begin{aligned}
 BODu &= CBODu + CBODu_2 + CBOD5 \times (1 - e^{-5 \times R_{cBOD}})^{-1} + \\
 &\quad + CBOD5_2 \times (1 - e^{-5 \times R_{cBOD_2}})^{-1} \\
 BOD5 &= CBODu \times (1 - e^{-5 \times R_{cBOD}}) + CBODu_2 \times (1 - e^{-5 \times R_{cBOD_2}}) + \\
 &\quad + CBOD5 + CBOD5_2 \\
 COD &= \frac{COD_Cr}{EffCOD_Cr} + \frac{COD_Mn}{EffCOD_Mn} \\
 NBOD &= NBODu + NBOD5 \times (1 - e^{-5 \times R_{cBODN}})^{-1} \\
 BODu_PHYT &= PHYT \times AlgFrBOD \times OXCCF \\
 BOD5_PHYT &= BODu - PHYT \times BOD5/uPHYT \\
 BODu - POC &= POC \times POCFrBOD \times OXCCF \\
 BOD5 - POC &= BODu - POC \times BOD5/inf PO \\
 BOD5 &= BOD5 + BOD5 - POC + BOD5 - PHYT \\
 BODu &= BODu + BODu - POC + BODu - PHYT
 \end{aligned}$$

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'):

$$AgeIndx = \frac{COD}{BOD5} \quad (2.13)$$

for $AgeIndx \leq LAgeIndx$:

$$AgeFun = UAgeFun \quad (2.14)$$

for $LAge < AgeIndx < LAgeIndx$:

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

for $AgeIndx \geq LAgeIndx$:

$$AgeFun = LAgeFun \quad (2.16)$$

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:

<i>AgeFun</i>	scaling function for decay rates [-]
<i>AgeIndx</i>	ratio of CBOD5 and COD [-]
<i>AlgFrBOD</i>	fraction of algae that contribute to BOD [-]
<i>BOD5</i>	calculated carbonaceous BOD at 5 days [$\text{gO}_2 \text{ m}^{-3}$]
<i>BOD5/uPhyt</i>	ratio BOD5_BOD_ultimate for PHYT [-]
<i>BOD5/infPO</i>	ratio BOD5_BOD_ultimate for POC [-]
<i>CBOD5</i>	carbonaceous BOD (first pool) at 5 days [$\text{gO}_2 \text{ m}^{-3}$]
<i>CBOD5_2</i>	carbonaceous BOD (second pool) at 5 days [$\text{gO}_2 \text{ m}^{-3}$]
<i>BODu</i>	calculated carbonaceous BOD at ultimate [$\text{gO}_2 \text{ m}^{-3}$]
<i>CBODu</i>	carbonaceous BOD (first pool) ultimate [$\text{gO}_2 \text{ m}^{-3}$]
<i>CBODu_2</i>	carbonaceous BOD (second pool) ultimate [$\text{gO}_2 \text{ m}^{-3}$]
<i>COD</i>	calculated chemical oxygen demand days [$\text{gO}_2 \text{ m}^{-3}$]
<i>COD_Cr</i>	COD concentration by the Cr-method [$\text{gO}_2 \text{ m}^{-3}$]
<i>COD_Mn</i>	COD concentration by the Mn-method [$\text{gO}_2 \text{ m}^{-3}$]
<i>COXBOD</i>	critical oxygen concentration: [g m^{-3}]
<i>CFLBOD</i>	value of the oxygen function for oxygen levels below the critical oxygen concentration [-]
<i>CurvBOD</i>	factor that determines the curvature [-] between COXBOD and OOX-BOD ($-1 < \text{CurvBOD} < 0$)
<i>dCBOD5</i>	decay flux of CBOD5 [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
<i>dCBOD5_2</i>	decay flux of CBOD5_2 [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
<i>dCOD_Cr</i>	decay flux of COD_Cr [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
<i>dCBODu</i>	decay flux of CBODu [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
<i>dCBODu_2</i>	decay flux of CBODu_2 [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
<i>dCOD_Mn</i>	decay flux of COD_Mn [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
<i>dBOD5</i>	decay flux of NBOD5 [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
<i>dBODu</i>	decay flux of NBODu [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
<i>dOxyBODCOD</i>	oxygen consumption flux of BOD and COD species [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
<i>EffCOD_Cr</i>	efficiency of the Cr_method [-]
<i>EffCOD_Mn</i>	efficiency of the Mn_method [-]
<i>LAgeFun</i>	lower value of age function [-]
<i>LAgeIndx</i>	lower value of age index [-]
<i>NBOD</i>	calculated nitrogenous BOD at ultimate [$\text{gO}_2 \text{ m}^{-3}$]
<i>NBOD5</i>	nitrogenous BOD after 5 days [$\text{gO}_2 \text{ m}^{-3}$]
<i>NBODu</i>	nitrogenous BOD ultimate [$\text{gO}_2 \text{ m}^{-3}$]
<i>O2Func</i>	oxygen function for decay of CBOD [-]
<i>OXCCF</i>	oxygen to carbon ratio
<i>OOXBOD</i>	optimum oxygen concentration: above this value the oxygen function becomes 1.0 [$\text{gO}_2 \text{ m}^{-3}$]
<i>OXY</i>	oxygen concentration [$\text{gO}_2 \text{ m}^{-3}$]
<i>PHYT</i>	total phytoplankton concentration [$\text{gC m}^{-3} \text{ d}^{-1}$]
<i>POC</i>	total particulate organic carbon concentration [$\text{gC m}^{-3} \text{ d}^{-1}$]
<i>POCFrBOD</i>	fraction of POC that contribute to BOD [-]
<i>RcBOD</i>	reaction rate BOD (first pool) at 20 °C [d^{-1}]
<i>RcBOD_2</i>	reaction rate BOD_2 (second pool) at 20 °C [d^{-1}]
<i>RcBODN</i>	reaction rate BODN (second pool) at 20 °C [d^{-1}]
<i>RcCOD</i>	reaction rate COD (first pool) at 20 °C [d^{-1}]
<i>SWOxyDem</i>	switch that determines the oxygen consuming substance (0: BOD; 1: COD; 2: COD+BOD) [-]
<i>TcBOD</i>	temperature coefficient BOD [-]
<i>TcBOD_2</i>	temperature coefficient BOD (second pool)[-]
<i>TcCOD</i>	temperature coefficient COD [-]
<i>Temp</i>	water temperature [°C]
<i>UAgeFun</i>	upper value of age function [-]

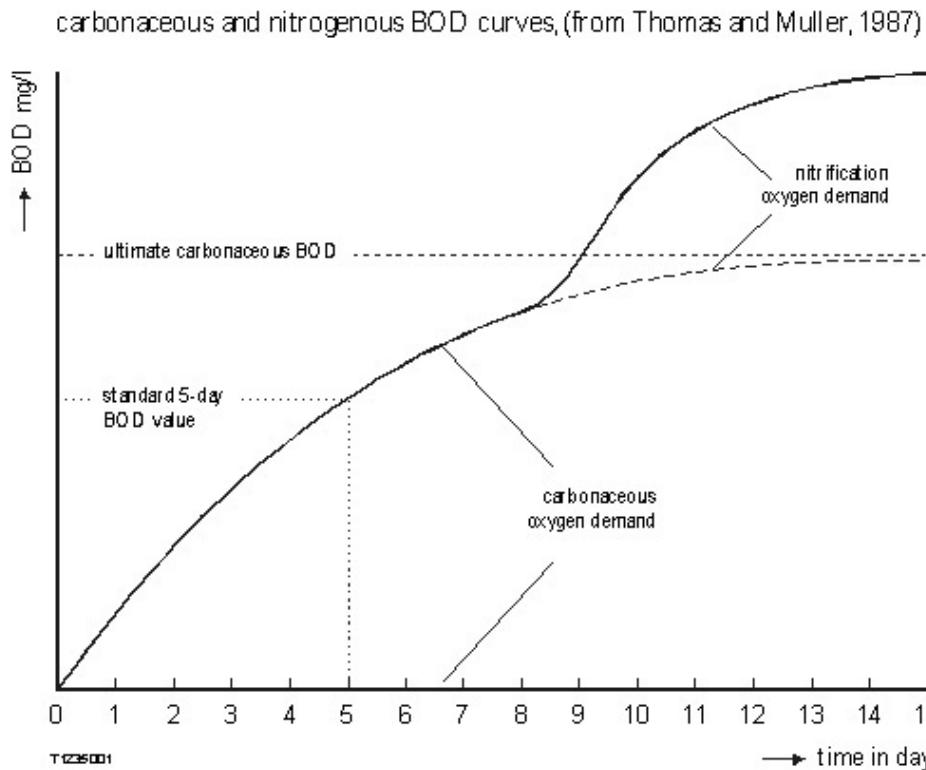


Figure 2.3: A typical oxygen demand curve

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 \(1987\)](#)

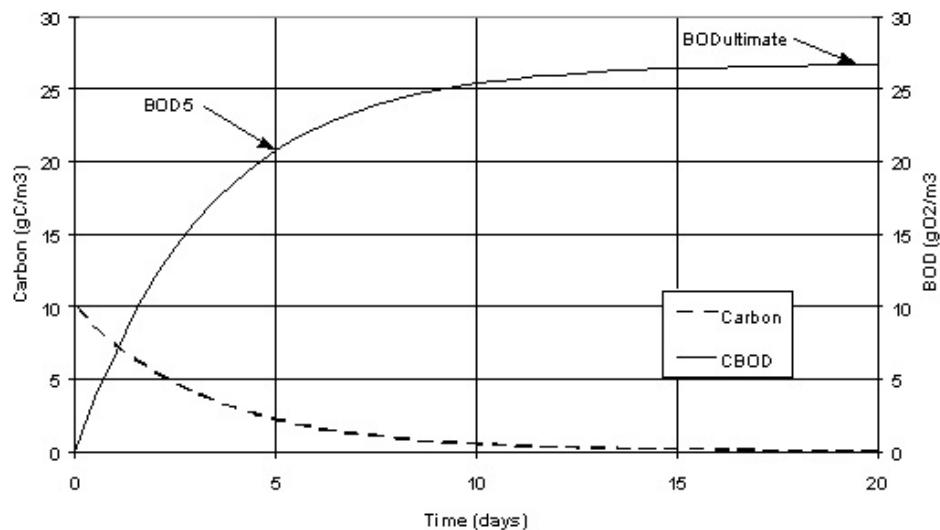


Figure 2.4: The relation between the amount of oxidizable carbonaceous material [mgC/l], the amount of oxygen consumed in the stabilisation of this organic material after 5 days and after ultimate time

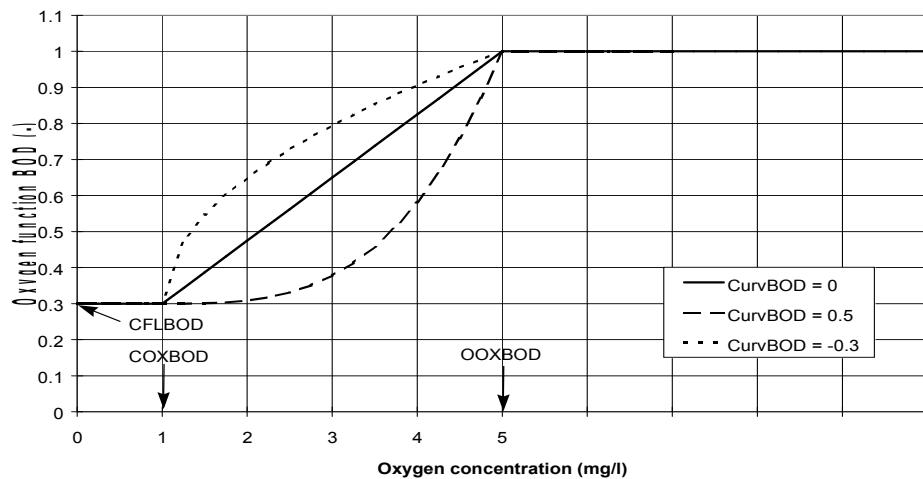


Figure 2.5: Default and optional oxygen functions for decay of CBOD ($O2FuncBOD$)

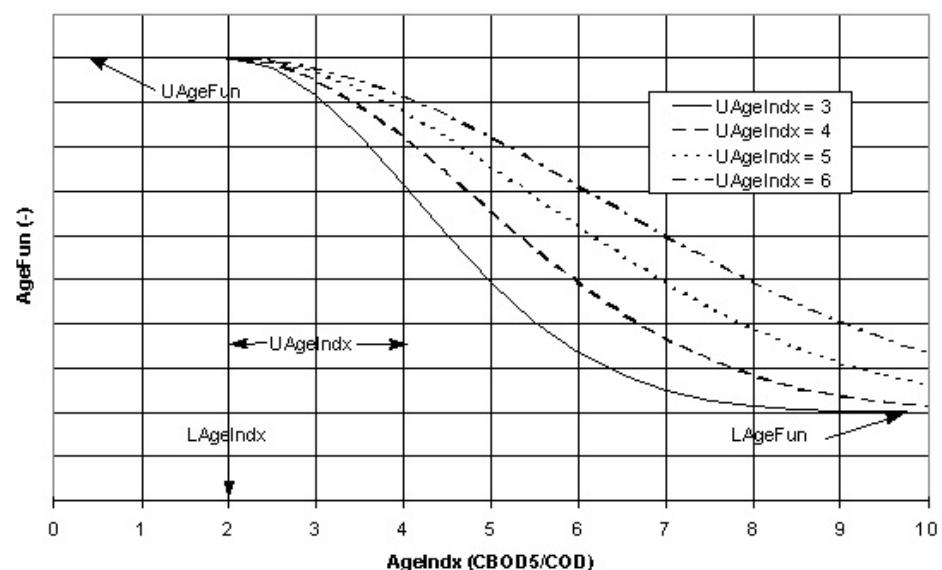


Figure 2.6: Optional function for the calculation of the first order rate constant for BOD and NBOD

2.8 Sediment oxygen demand

PROCESS: SEDOXYDEM

This process scales a user-defined sediment oxygen demand flux fSOD [$\text{gO}_2 \text{ m}^{-2} \text{ d}^{-1}$] 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 [DiToro et al. \(1990\)](#).

Implementation

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

Formulations

If $SwCH4bub \neq 1$:

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

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

$$dOxSOD = dSOD$$

where

$fSOD$	user-specified sediment oxygen demand [$\text{gO}_2 \text{ m}^{-2} \text{ d}^{-1}$]
SOD	BOD/COD components, accumulated in sediment [gO_2]

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

$$dOxMinSed = 2.67 \times (dMinDetCS1 + dMinDetCS2 + dMinOOCSS1 + dMinOOCSS2)$$

where:

<i>dOxMinSed</i>	oxygen consumption by mineralisation of DetC and OOC in sediment [$gO_2 m^{-3} d^{-1}$]
<i>dMinDetCS1</i>	mineralisation of DetC in sediment layer 1 [$gC m^{-3} d^{-1}$]
<i>dMinDetCS2</i>	mineralisation of DetC in sediment layer 2 [$gC m^{-3} d^{-1}$]
<i>dMinOOCSS1</i>	mineralisation of OOC in sediment layer 1 [$gC m^{-3} d^{-1}$]
<i>dMinOOCSS2</i>	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 $dSOD + dOxMinSed$.

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

Additional output parameter:

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

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 subtracted 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:

<i>fSOD*</i>	calculated total oxygen consumption in sediment [$gO_2 m^{-2} d^{-1}$]
<i>DifCH4bub</i>	oxygen consumption by CH_4 dissolving from bubbles [$gO_2 m^{-2} d^{-1}$]

DifCH4dis oxygen consumption by CH₄ diffusing from sediment towards water column [gO₂ m⁻² d⁻¹]

**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, *FICH4* 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 Van der Molen \(1993\)](#), [DiToro \(1986\)](#)

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) ∈ {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.

$$R_{tewor_i} = f_{tewor_i} \quad (2.17)$$

with:

$$\begin{aligned} R_{tewor_i} & \text{ TEWOR production flux (g i.m}^{-3}\text{)} \\ f_{tewor_i} & \text{ TEWOR production flux (g i.m}^{-3}\text{)} \end{aligned}$$

Directives for use

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

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

Name in formulas	Name in input	Definition	Units
R_{tewor_i}	$dTEWOR_i$	TEWOR production flux	g.m^{-3}
f_{tewor_i}	$fTEWOR_i$	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.

$$Rmin_i = kmin_i \times C5_i \times \frac{Cox}{Ksox + Cox} \quad (2.18)$$

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.

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

with:

- $C5_i$ carbonaceous BOD (pool i) at 5 days [$\text{g O}_2 \text{ m}^{-3}$]
- Cox dissolved oxygen [$\text{g O}_2 \text{ m}^{-3}$]
- $kmin_i$ oxidation reaction rate BOD (pool i) [d^{-1}]
- $Ksox$ half saturation constant for oxygen limitation on oxidation of BOD [$\text{g O}_2 \text{ m}^{-3}$]

Directives for use

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

[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	$\text{g O}_2 \text{ m}^{-3}$
Cox	OXY	dissolved oxygen	$\text{g O}_2 \text{ m}^{-3}$
Cu_i	$CBODu_i$	carbonaceous BOD (pool i) ultimate	$\text{g O}_2 \text{ m}^{-3}$
$kmin_i$	$RCBOD_i$	oxidation reaction rate BOD (pool i)	d^{-1}
$Ksox$	$KMOX$	half saturation constant for oxygen limitation on oxidation of BOD	$\text{g O}_2 \text{ m}^{-3}$

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 (b) or to water (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*.

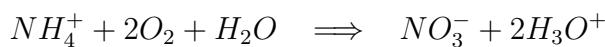
The process has been implemented for the following substances:

- ◊ 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:



Nitrification ultimately removes ammonium (ammonia) and oxygen from the water phase and produces nitrate. The process requires $4.57 \text{ gO}_2 \text{ gN}^{-1}$.

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 Van 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:

$$R_{nit} = k_{0nit} + knit \times \left(\frac{Cam}{K_{sam} \times \phi + Cam} \right) \times \left(\frac{Cox}{K_{sox} \times \phi + Cox} \right)$$

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

$$\begin{aligned} knit &= 0.0 && \text{if } T < T_c \text{ or } Cox \leq 0.0 \\ k_{0nit} &= 0.0 \\ k_{0nit} &= k_{0temp} && \text{if } T < T_c \text{ and } Cox > 0.0 \\ k_{0nit} &= k_{0ox} && \text{if } T \geq T_c \text{ and } Cox \leq 0.0 \\ k_{0nit} &= 0.0 && \text{if } Cox \leq Cox_c \times \phi \end{aligned}$$

with:

Cam	ammonium concentration [gN.m^{-3}_ℓ]
Cox	dissolved oxygen concentration ≥ 0.0 [g.m^{-3}_ℓ]
Cox_c	critical dissolved oxygen concentration [g.m^{-3}_w]
$knit$	Michaelis-Menten nitrification rate [$\text{gN.m}^{-3}_\ell \text{d}^{-1}$]
$ktnit$	temperature coefficient for nitrification [-]
k_{0nit}	zeroth order nitrification rate [$\text{gN.m}^{-3}_\ell \text{d}^{-1}$]
k_{0ox}	zeroth order nitrif. rate at negative average DO concentrations [$\text{gN.m}^{-3}_\ell \text{d}^{-1}$]
k_{0temp}	zeroth order nitrification rate at low temperatures [$\text{gN.m}^{-3}_\ell \text{d}^{-1}$]
K_{sox}	half saturation constant for dissolved oxygen limitation [g.m^{-3}_w]
K_{sam}	half saturation constant for ammonium limitation [gN.m^{-3}_w]
T	temperature [$^\circ\text{C}$]
T_c	critical temperature for nitrification [$^\circ\text{C}$]
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), 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:

$$R_{nit} = k0_{nit} + fox \times k1_{nit} \times Cam$$

$$k1_{nit} = \begin{cases} k1_{nit}^{20} \times ktnit^{(T-20)} & \text{if } T < T_c \\ 0.0 & \text{if } T \geq T_c \end{cases}$$

with:

Cam	ammonium concentration [gN m^{-3}]
fox	the oxygen limitation function [-]
$k1_{nit}$	first order nitrification rate [d^{-1}]
$ktnit$	temperature coefficient for nitrification [-]
$k0_{nit}$	zeroth order nitrification rate [$\text{gN m}^{-3} \text{d}^{-1}$]
T	temperature [$^{\circ}\text{C}$]
T_c	critical temperature for nitrification [$^{\circ}\text{C}$]

The oxygen limitation function reads:

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

with:

a	curvature coefficient [-]
Cox	dissolved oxygen concentration ≥ 0.0 [g m^{-3}]
Cox_o	optimal dissolved oxygen concentration [g m^{-3}]
Cox_c	critical dissolved oxygen concentration [g m^{-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 (SWVNit = 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:

$$R_{nit} = knit \times Cam \times \left(\frac{Cox}{K_{sox} + Cox} \right) \quad (3.1)$$

with:

Cam	ammonium concentration [$\text{gN.m}^{-3}\text{b}$]
Cox	dissolved oxygen concentration ≥ 0.0 [$\text{g.m}^{-3}\text{b}$]
$knit$	First order nitrification rate [$\text{gN.m}^{-3}\text{b.d}^{-1}$]
K_{sox}	half saturation constant for dissolved oxygen limitation [$\text{g.m}^{-3}\text{w}$]

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.

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 $T = 20^\circ\text{C}$, 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 $OONit$ occurs, when $CurvNit$ is equal to 0.0, whereas the value -1 establishes maximal curvature.
- ◊ The optimal oxygen concentration $OONit$ 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 $OONit$ (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 Van der Molen \(1993\)](#), [WL | Delft Hydraulics \(1997c\)](#), [Vanderborght et al. \(1977\)](#)

Table 3.1: Definitions of the parameters in the above equations for NITRIF_NH4. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
a	$CurvNit$	curvature coefficient for the oxygen lim. function	-
Cam	$NH4$	ammonium concentration	$gN\ m_\ell^{-3}$
Cox	OXY	dissolved oxygen concentration	$g\ m_\ell^{-3}$
$Coxc$	$CoxNit$	critical DO concentration for nitrification	$g\ m_w^{-3}$
$Coxo$	$OoxNit$	optimal DO concentration for nitrification	$g\ m_w^{-3}$
$foxmin$	$CFLNit$	minimal value of the oxygen limitation function	-
$knit20$	$RcNit20$	MM- nitrification reaction rate at 20 °C	$gN\ m_\ell^{-3}\ d^{-1}$
$k1nit20$	$RcNit$	first order nitrification rate at 20 °C	d^{-1}
$ktnit$	$TcNit$	temperature coefficient for nitrification	-
$k0ox$	$Rc0NitOx$	zeroth order nitrification rate at negative DO	$gN\ m_\ell^{-3}\ d^{-1}$
$k0temp$	$Rc0NitT$	zeroth order nitrification rate at low temperatures	$gN\ m_\ell^{-3}\ d^{-1}$
$k0nit$	$Znit$	zeroth order nitrification rate	$gN\ m_\ell^{-3}\ d^{-1}$
$Ksam$	$KsAmNit$	half saturation constant for ammonium limitation	$gN\ m_w^{-3}$
$Ksox$	$KsOxNit$	half saturation constant for DO limitation	$g\ m_w^{-3}$
$Rnit$	-	nitrification rate	$gN\ m_\ell^{-3}\ d^{-1}$
-	$SWVnNit$	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	$m_w^3\ m_\ell^{-3}$

Nitrification as function of oxygen concentration

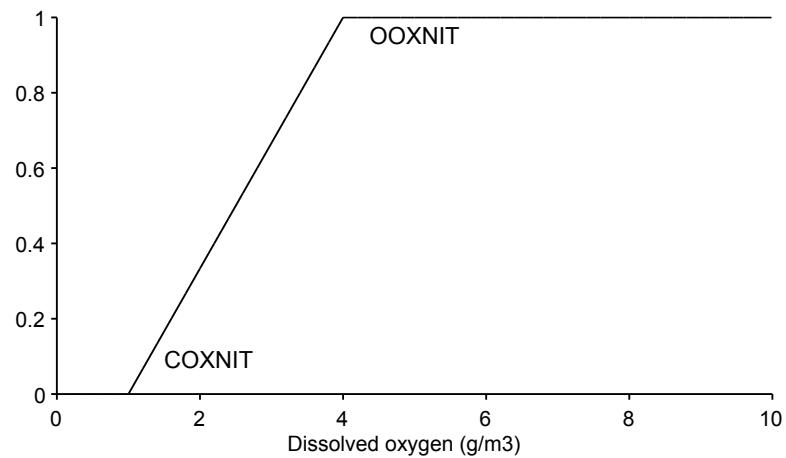


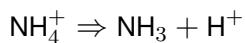
Figure 3.1: Figure 1 Default pragmatic oxygen limitation function for nitrification (O2FuncNit, option 0).

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 (NH₃) is toxic to fish.

NH₃ is the product of the dissociation of the ammonium (NH₄⁺) ion:



The reaction is characterised by the equilibrium constant K :

$$K' = \frac{a_{\text{NH}_3} a_{\text{H}^+}}{a_{\text{NH}_4^+}}$$

where:

$$a_i \quad \text{activity of species } i [\text{mol l}^{-1}]$$

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

$$\log \left(\frac{a_{\text{NH}_3}}{a_{\text{NH}_4^+}} \right) = \log K' + pH$$

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

$$K = K' \frac{\gamma_{\text{NH}_4^+}}{\gamma_{\text{NH}_3}}$$

where:

$$\begin{aligned} \gamma_i &\quad \text{activity coefficient of species } i [-] \\ K &\quad \text{equilibrium constant } [\text{mol l}^{-1}], \text{ after correction for activities} \end{aligned}$$

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

$$\log \frac{(\text{NH}_3)}{(\text{NH}_4^+)} = \log K + pH$$

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 NH₄⁺ ([Millero, 1995](#)).

In DELWAQ, *totalNH₄* is modelled as substance NH4, which is the sum of NH₄⁺ and NH₃. The concentration of NH₃ is derived from the above equation and total NH₄ according to:

$$(\text{NH}_3) = \frac{\frac{(\text{NH}_3)}{(\text{NH}_4^+)}}{1 + \frac{(\text{NH}_3)}{(\text{NH}_4^+)}} \times (\text{totalNH}_4)$$

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 reprofuntion for the dissociation constant, based upon the Netherlands' water quality standards which tabulate the maximum allowed total NH₄ 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 reprofuntion 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.m³), and is active in all types of computational elements.

Tabel 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

$$\begin{aligned} (\text{totalNH}_4) &= \text{NH4} \times \frac{m^3}{l} \times \frac{1}{M} \\ \log K &= a + b \times T \\ (\text{NH}_3) &= \frac{10^{\log K + pH}}{1 + 10^{\log K + pH}} \times (\text{totalNH}_4) \\ \text{NH3} &= (\text{NH}_3) \times M \times \frac{l}{m^3} \\ fr\text{NH3} &= \frac{(\text{NH}_3)}{(\text{totalNH}_4)} \end{aligned}$$

If NH3_Sw = 2 then

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

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

$$\begin{aligned} (\text{NH}_4) &= \text{NH4} \times \frac{m^3}{l} \times \frac{1}{M \times \rho} \\ (\text{NH}_3) &= (\text{NH}_4) / (1 + \frac{10^{-pH}}{K}) \\ \text{NH3} &= (\text{NH}_3) \times M \times \rho \times \frac{l}{m^3} \end{aligned}$$

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 ₂ O]
NH4	concentration of ammonium (DELWAQ substance) [gN m^{-3}]
(NH ₄)	molar concentration of ammonium [mol l ⁻¹ or mol kg ⁻¹ H ₂ O]
a	coefficient a of reprofuction 1 [-]
b	coefficient b of reprofuction 1 [°K ⁻¹]
frNH3	fraction NH3 of NH4 [-]
K	dissociation constant [mol l ⁻¹ or mol kg ⁻¹ H ₂ O]
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]

[m³] 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 *KNH3rf1b*.

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

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

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 °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 (ℓ) or to water (ω).

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_NO3 and 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*.

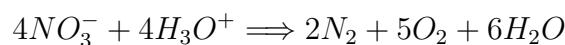
The processes have been implemented for the following substances:

- ◊ 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:



Denitrification ultimately removes nitrate from the water phase and produces elemental nitrogen. The process delivers $2.86 \text{ gO}_2 \text{ gN}^{-1}$. The oxygen in nitrate used to oxidise organic matter is accounted for in the model using this stoichiometric 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^{-3}]
Cox	dissolved oxygen concentration $\geq 0.0 \text{ [g m}^{-3}\text{]}$

C_{oxc}	critical dissolved oxygen concentration [g m^{-3}_w]
f_{ox}	oxygen inhibition function [-]
k_{den}	Michaelis-Menten denitrification rate [$\text{gN m}^{-3} \text{d}^{-1}$]
k_{tden}	temperature coefficient for denitrification [-]
k_{0den}	zeroth order denitrification rate [$\text{gN m}^{-3} \text{d}^{-1}$]
k_{0ox}	zeroth order denitrification rate at moderate DO concentrations [$\text{gN m}^{-3} \text{d}^{-1}$]
k_{0temp}	zeroth order denitrification rate at low temperatures [$\text{gN m}^{-3} \text{d}^{-1}$]
K_{sni}	half saturation constant for nitrate limitation [gN m^{-3}_w]
K_{sox}	half saturation constant for dissolved oxygen inhibition [g m^{-3}_w]
T	temperature [$^{\circ}\text{C}$]
T_c	critical temperature for denitrification [$^{\circ}\text{C}$]
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:

$$R_{den} = k_{0den} + f_{ox} \times k_{1den} \times C_{ni}$$

$$k_{1den} = \begin{cases} 0.0 & \text{if } T < T_c \\ k_{1den}^{20} \times k_{tden}^{(T-20)} & \text{else} \end{cases}$$

with:

C_{ni}	nitrate concentration [gN m^{-3}_w]
f_{ox}	the oxygen inhibition function [-]
k_{1den}	first order denitrification rate [d^{-1}]
k_{tden}	temperature coefficient for denitrification [-]
k_{0den}	zeroth order denitrification rate [$\text{gN m}^{-3} \text{d}^{-1}$]
T	temperature [$^{\circ}\text{C}$]
T_c	critical temperature for denitrification [$^{\circ}\text{C}$]

The oxygen inhibition function reads:

$$f_{ox} = \begin{cases} 1.0 & \text{if } Cox \leq Cox_0 \\ \frac{Cox_c - Cox}{Cox_c - Cox_0 + (e^a - e)(Cox - Cox_0)} & \text{if } Cox_0 < Cox < Cox_c \\ 0.0 & \text{if } Cox \geq Cox_c \end{cases}$$

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}]

The pragmatic oxygen inhibition 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 [$\text{g.m}^{-2} \text{d}^{-1}$]. The resulting denitrification rate is divided by the depth of the water column H in order to obtain the rate in [$\text{g.m}^{-3} \text{d}^{-1}$].

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 $T=20^\circ\text{C}$, 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 $OXDEN$, when curvature coefficient $Curvat$ is equal to 1.0. Maximal curvature is established, when $Curvat$ is equal to 4.0
- ◊ The optimal oxygen concentration $OXDEN$ 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 $OXDEN$.

Additional references

[DiToro \(2001\)](#), [Smits and Van der Molen \(1993\)](#), [WL | Delft Hydraulics \(1997c\)](#), [Vanderborgh et al. \(1977\)](#)

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

Name in formulas	Name in input	Definition	Units
a	<i>Curvat</i>	curvature coefficient for the oxygen inhib. function	-
Cni	<i>NO3</i>	nitrate concentration	gN m^{-3}
Cox	<i>OXY</i>	dissolved oxygen concentration	g m^{-3}
$Coxc$	<i>CoxDen</i>	optimal DO concentration for denitrification	g m_w^{-3}
$Coxo$	<i>OoxDen</i>	critical DO concentration for denitrification	g m_w^{-3}
$kden^{20}$	<i>RcDen20</i>	MM- denitrification reaction rate at 20 °C	$\text{gN m}^{-3} \text{ d}^{-1}$
$k1den^{20}$	<i>RcDenWat</i>	first order denitrification reaction rate at 20 °C	d^{-1}
$ktden$	<i>TcDenWat</i>	temperature coefficient for denitrification	-
$k0ox$	<i>Rc0DenOx</i>	zeroth order denitrification rate at moderate DO	$\text{gN m}^{-3} \text{ d}^{-1}$
$k0temp$	<i>Rc0DenT</i>	zeroth order denitrification rate at low temperatures	$\text{gN m}^{-3} \text{ d}^{-1}$
$k0den$	<i>ZDenWat</i>	zeroth order denitrification rate	$\text{gN m}^{-3} \text{ d}^{-1}$
$Ksni$	<i>KsNiDen</i>	half saturation constant for nitrate limitation	gN m^{-3}
$Ksox$	<i>KsOxDen</i>	half saturation constant for DO inhibition	g m_w^{-3}
$Rden$	-	denitrification rate	$\text{gN m}^{-3} \text{ d}^{-1}$
-	<i>SWVnDen</i>	switch for selection of the process formulations (pragmatic kinetics = 0.0, MM-kinetics = 1.0)	-
T	<i>Temp</i>	temperature	°C
T_c	<i>CTDen</i>	critical temperature for denitrification	°C
ϕ	<i>POROS</i>	porosity	$\text{m}_w^3 \text{ m}^{-3}$

Table 3.4: Definitions of the parameters in the above equations for DENSED_NO3. Volume units refer to bulk (ℓ) or to water (ω).

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

Denitrification as function of oxygen concentration

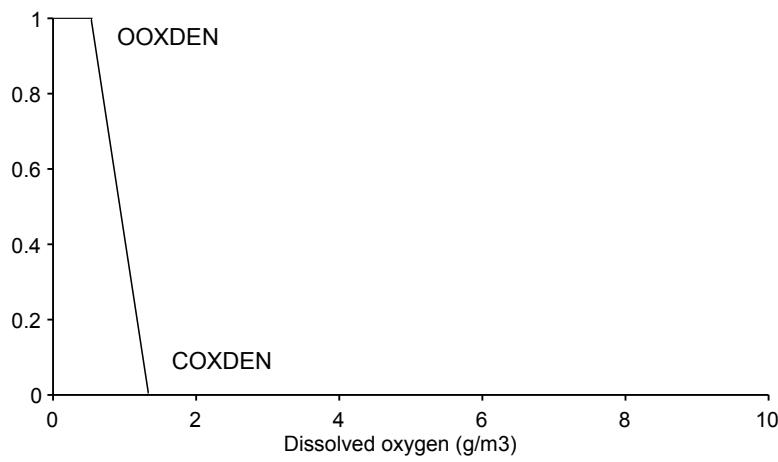


Figure 3.2: Default pragmatic oxygen inhibition function for denitrification (O2Func, option 0).

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 ($< 0.63 \mu m$), 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 sulphide 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 (β) or to water (ω).

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 7.4, 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 $^{-3}$]
$Cphd_e$	equilibrium dissolved phosphate concentration [gP m $^{-3}$]
$Kdph$	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 $^{-3}$]
$Cphd$	the dissolved phosphate concentration after the previous time-step [gP m $^{-3}$]

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:



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

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

where:

$Cadse_e$	equilibrium concentration of free adsorption sites in P equivalents [gP m^{-3}]
$Cpha_e$	equilibrium adsorbed phosphate concentration [gP m^{-3}]
$Cphd_e$	equilibrium dissolved phosphate concentration [gP m^{-3}]
$Kads$	adsorption equilibrium constant [$\text{m}^3 \text{ gP}^{-1}$]
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}]
Cim_i	concentration of inorganic matter fractions $i=1, 2, 3$ [gDW.m^{-3}]
fim_i	fraction of adsorbed phosphate bound to inorganic matter fractions $i=1, 2, 3$ [-]
$fcap$	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:

$$Cpha_e + Cphd_e = Cpha + Cphd \quad (3.2)$$

$$Cads_e = Cads = Cadst - Cpha \quad (3.3)$$

where:

$Cads$ the concentration of free ads. sites after the previous time-step [gP m $^{-3}$]

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

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

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:

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

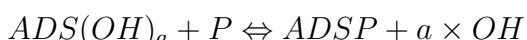
where:

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

$Rsorp$ adsorption or desorption rate [gP m $^{-3}$ 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 Van Beek \(2013\)](#)):



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

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

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

where:

a stoichiometric reaction constant [-]

$Cads_e$ equilibrium concentration of free adsorption sites [molFe l $^{-1}$]

$Cpha_e$ equilibrium adsorbed phosphate concentration [molP l $^{-1}$]

$Cphd_e$ equilibrium dissolved phosphate concentration [molP l $^{-1}$]

$Kads$ adsorption equilibrium constant [(mol l $^{-1}$) $^{a-1}$]

$ktads$ temperature coefficient for adsorption [-]

OH molar hydroxyl concentration [mol l $^{-1}$]

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:

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

$$\begin{aligned} fcor &= 1.0 && \text{if } Cox \geq Coxc \times \phi \\ fcor &= ffeox && \text{if } Cox < Coxc \times \phi \end{aligned}$$

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

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 _f ⁻³]
Cox	dissolved oxygen concentration [g m _f ⁻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 _f ⁻³]
$Cphd$	the dissolved phosphate concentration after the previous time-step [gP m _f ⁻³]
e	index for chemical equilibrium value

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:

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

A positive value of the adsorption flux $Rsorp$ represents adsorption of PO_4 , a negative value represents desorption of PO_4 .

Directives for use

- ◊ Version $SWVnAdsP = 0.0$ uses $RcAdsPg_{em}$ 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 $KdPO_4AAP$ is 0.5.
- ◊ Using data of [Stumm and Morgan \(1996\)](#), it can be deduced that $KadsP_{-20}$ and $a_{OH-} - PO_4$ may be approximately equal to respectively $3.8 \text{ (mole l}^{-1}\text{)}^{a-1}$ 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 $FPIM3$ ($= f_{im_i}$) 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 \(1997c\)](#)

Table 3.5: Definitions of the parameters in the above equations for ADSPO4AAP. Volume units refer to bulk (ℓ) or to water (ω).

Name in formulas	Name in input	Definition	Units
a	$a_OH - PO4$	stoichiometric reaction constant for pH-dependency	-
Cim_i	IMi	conc. of inorg. matter fractions $i = 1,2,3$	$gDW \text{ m}^{-3}$
Cox	OXY	dissolved oxygen concentration	$g \text{ m}^{-3}$
$Coxc$	Cc_oxPsor	critical DO concentration for iron reduction	$g \text{ m}^{-3}$
$Cpha$	AAP	adsorbed phosphate concentration	$gP \text{ m}^{-3}$
$Cphd$	$PO4$	dissolved phosphate concentration	$gP \text{ m}^{-3}$
$fcap$	$MaxPO4AAP$	phosphate adsorp. capacity of inorg. matter	$gP \text{ gFe}^{-1}$
fim_i	-	fraction ads. phosphate in inorg. matter fr. $i = 1,2,3$	-
ffe_i	fr_FeIMi	fraction react. iron in inorg. fr. $i=1,2,3$ ($SWVnAdsP=1$)	$gFe \text{ gDW}^{-1}$
"	fr_Fe	fraction reactive iron in inorg. matter ($SWVnAdsP=0$)	$gFe \text{ gDW}$
$ffeox$	fr_Feox	fraction oxidised iron(III) in the reactive iron fraction	-
$Kdph$	$KdPO4AAP$	distribution coefficient ($SWAdsP = 0$; see directives!)	-
$Kpads$	$KdPO4AAP$	adsorption eq. constant ($SWAdsP = 1$)	$\text{m}^3 \text{ gP}^{-1}$
$Kads^{20}$	$KadsP_20$	molar adsorption equil. const. ($SWAdsP = 2$; see directives!)	$(\text{mol l}^{-1})^{a-1}$
$ksorp$	$RCAdPO4AAP$	sorption reaction rate ($SWVnAdsP = 1$)	d^{-1}
"	$RcAdsPgем$	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	$\text{g m}^{-3} \text{ d}^{-1}$
$SWAdsP$	$SWAdsP$	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	$^{\circ}\text{C}$
ϕ	$POROS$	porosity	$\text{m}_w^3 \text{ m}_{\ell}^{-3}$
Δt	$Delt$	computational time-step	d

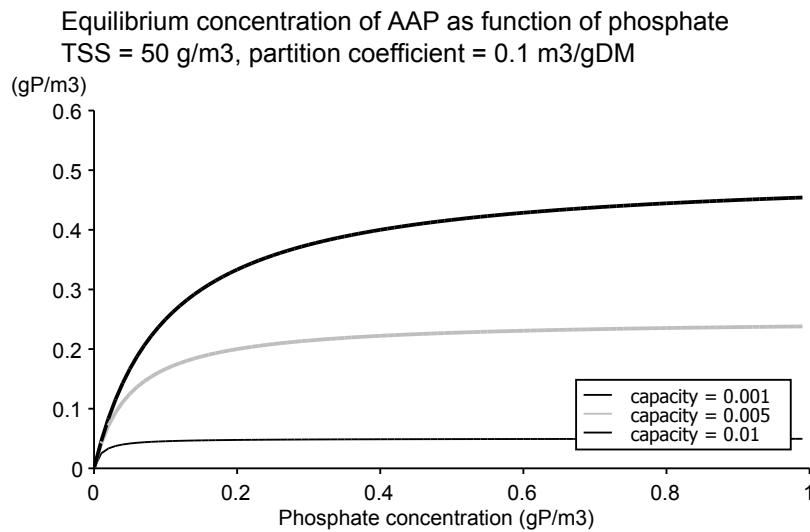


Figure 3.3: Variation of the equilibrium concentration AAP (eqAAP) as a function of PO₄ and the maximum adsorption capacity (MaxPO₄AAP).

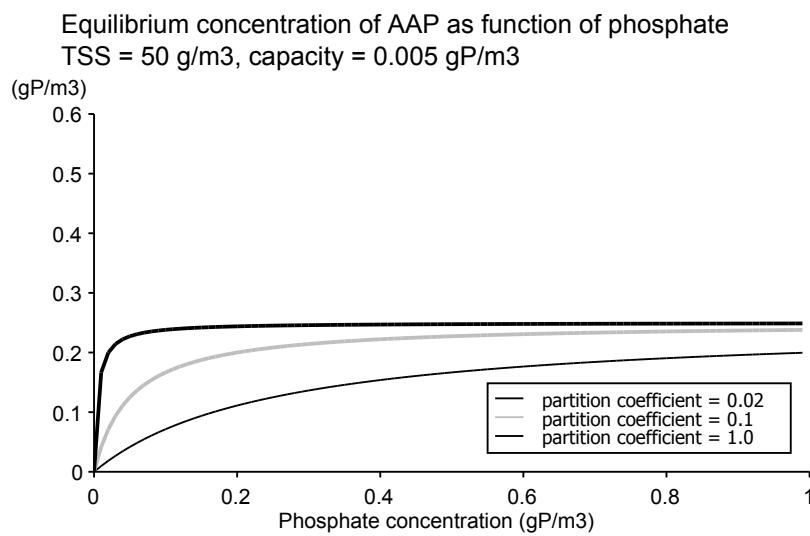


Figure 3.4: Variation of the equilibrium concentration of AAP (eqAAP) as a function of PO₄ and the partition coefficient of PO₄ (K_dPO₄AAP).

3.5 Formation of vivianite

PROCESS: VIVIANITE

At reducing conditions phosphate may precipitate with iron(II) as vivianite (iron(II) phosphate: $\text{Fe}_3[\text{PO}_4]_2$). 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 (b) or to water (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 PO_4 and VIVP.

[Table 3.6](#) provides the definitions of the parameters occurring in the formulations. The dissolved oxygen concentration (C_{ox}) can be either calculated by DELWAQ or imposed to DELWAQ via the input.

Formulation

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



The precipitation rate is formulated with first-order kinetics, with the difference between the ac-

tual dissolved phosphate concentration and the equilibrium dissolved concentration as driving force ([Smits and Van Beek \(2013\)](#)):

$$Rprc = \begin{cases} frp \times kprc \times \left(\frac{Cphd}{\phi} - Cphde \right) \times \phi & \text{if } Rprc < 0.0 \\ 0.0 & \text{if } Rprc \geq 0.0 \end{cases}$$

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

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

with:

Cox	dissolved oxygen concentration [g m^{-3}]
$Coxc$	critical dissolved oxygen concentration [g m^{-3}]
$Cphd$	dissolved phosphate concentration [gP m^{-3}]
$Cphde$	equilibrium dissolved phosphate concentration [gP m^{-3}]
frp	switch concerning the redox conditions for precipitation [-]
$kprc$	precipitation reaction rate [d^{-1}]
$ktprc$	temperature coefficient for precipitation [-]
$Rprc$	rate of precipitation [$\text{g m}^{-3} \text{ d}^{-1}$]
T	temperature [$^{\circ}\text{C}$]
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:

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

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

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

with:

$Cphpr$	precipitated phosphate concentration [gP m^{-3}]
frd	switch concerning the redox conditions for dissolution [-]
$ksol$	dissolution reaction rate [$\text{m}_w^3 \text{ gO}_2^{-1} \text{ d}^{-1}$]
$ktsol$	temperature coefficient for dissolution [-]
$Rsol$	rate of dissolution [$\text{g m}^{-3} \text{ d}^{-1}$]

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: $EqVIVDisP = 0.05 \text{ gP m}_w^{-3}$, $RcPrecP20 = 0.8 \text{ d}^{-1}$, $RcDissP20 = 0.005 \text{ m}^3 \text{ gO}_2^{-1} \text{ d}^{-1}$.
- ◊ 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 Van der Molen \(1993\)](#), [Stumm and Morgan \(1996\)](#), [WL | Delft Hydraulics \(1997c\)](#)

Table 3.6: Definitions of the parameters in the above equations for VIVIANITE. Volume units refer to bulk (ℓ) or to water (ω).

Name in formulas	Name in input	Definition	Units
Cox	OXY	dissolved oxygen concentration	g m^{-3}_ℓ
$Coxc$	Cc_oxPsor	critical DO concentration for iron reduction	g m^{-3}_ω
$Cphd$	$PO4$	dissolved phosphate concentration	gP m^{-3}_ℓ
$Cphde$	$EqVIVDisP$	equilibrium dissolved phosphate concentration	gP m^{-3}_ω
$Cphpr$	$VIVP$	precipitated vivianite phosphate concentration	gP m^{-3}_ℓ
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	$\text{m}^3_\omega \text{ gO}_2^{-1} \text{ d}^{-1}$
$ktsol$	$TcDissolP$	temperature coefficient for dissolution	-
$Rprc$	—	vivianite precipitation rate	$\text{g m}^{-3}_\ell \text{ d}^{-1}$
$Rsol$	—	vivianite dissolution rate	$\text{g m}^{-3}_\ell \text{ d}^{-1}$
T	$Temp$	temperature	$^\circ\text{C}$
Δt	$Delt$	timestep	d
ϕ	$POROS$	porosity	$\text{m}^3_\omega \text{ m}^{-3}_\ell$

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: $\text{Ca}_3[\text{PO}_4]_2$; stable at $\text{pH} > 8.5$). However, the co-precipitation of phosphate with several carbonates and sulphides 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 (ℓ) or to water (ω).

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.

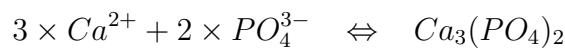
The process has been implemented for the following substances:

- ◊ dissolved PO_4 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:



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 Van Beek \(2013\)](#)):

$$R_{prc} = f_{rr} \times k_{prc} \times \left(\frac{C_{phd}}{\phi} - C_{phde} \right) \times \phi$$

$$R_{prc} = 0.0 \quad \text{if } R_{prc} < 0.0$$

$$k_{prc} = k_{prc}^{20} \times k_{tprc}^{(T-20)}$$

with:

C_{phd}	dissolved phosphate concentration [gP m^{-3}_ℓ]
C_{phde}	equilibrium dissolved phosphate concentration [gP m^{-3}_w]
f_{rr}	ratio of the apatite and vivianite precipitation reaction rates [-]
k_{prc}	precipitation reaction rate [d^{-1}]
k_{tprc}	temperature coefficient for precipitation [-]
R_{prc}	rate of precipitation [$\text{g m}^{-3}_\ell \text{d}^{-1}$]
T	temperature [$^\circ\text{C}$]
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:

$$R_{sol} = k_{sol} \times C_{phpr} \times \left(C_{phde} - \frac{C_{phd}}{\phi} \right)$$

$$R_{sol} = 0.0 \quad \text{if } R_{sol} < 0.0$$

$$k_{sol} = k_{sol}^{20} \times k_{tsol}^{(T-20)}$$

with:

C_{phpr}	precipitated phosphate concentration [gP m^{-3}_ℓ]
k_{sol}	dissolution reaction rate [$\text{m}^3_w \text{gP}^{-1} \text{d}^{-1}$]
k_{tsol}	temperature coefficient for dissolution [-]
R_{sol}	rate of dissolution [$\text{g m}^{-3}_\ell \text{d}^{-1}$]

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 $R_{atAP} and VP = 1.0$. For a start the dissolution rate may be set at zero.

- ◇ 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 (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
$Cphd$	$PO4$	dissolved phosphate concentration	$gP m_\ell^{-3}$
$Cphde$	$EqAPATDisP$	equilibrium dissolved phosphate concentration	$gP m_w^{-3}$
$Cphpr$	$APATP$	precipitated “apatite” phosphate concentration	$gP m_\ell^{-3}$
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	$m_w^3 gP^{-1} d^{-1}$
$ktsol$	$TcDissolP$	temperature coefficient for dissolution	-
$Rprc$	-	apatite precipitation rate	$g m_\ell^{-3} d^{-1}$
$Rsol$	-	apatite dissolution rate	$g m_\ell^{-3} d^{-1}$
T	$Temp$	temperature	$^\circ C$
Δt	$Delt$	timestep	d
ϕ	$POROS$	porosity	$m_w^3 \cdot m_\ell^{-3}$

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 (ℓ) or to water (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 Van Beek \(2013\)](#)):

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

where:

$Csid$	dissolved silicate concentration [gSi m^{-3}_ℓ]
$Cside$	equilibrium dissolved silicate concentration [gSi m^{-3}_w]
$Csip$	opal silicate concentration [gSi m^{-3}_ℓ]
$ksol$	dissolution reaction rate [$\text{m}^3_w \text{ gSi}^{-1} \text{ d}^{-1}$]
ϕ	porosity [-]

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

$$Rsol = ksol \times C_{sip}$$

where:

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

In both cases the rate is dependent on temperature:

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

where:

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

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: $EqDisSi = 10 \text{ gSi m}_w^{-3}$, $RcDisSi20 = 0.09 \text{ d}^{-1}$.
- ◊ 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 Van der Molen (1993), Stumm and Morgan (1996), Vanderborgh *et al.* (1977), WL | Delft Hydraulics (1997c)

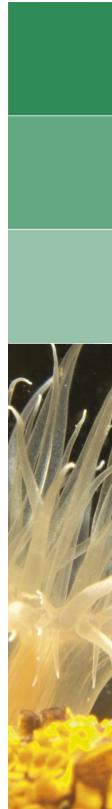
Table 3.8: Definitions of the parameters in the above equations for DISSI. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
C_{sid}	Si	dissolved silicate concentration	gSi m^{-3}_ℓ
C_{side}	Ceq_DisSi	equilibrium dissolved silicate concentration	gSi m^{-3}_w
C_{sip}	$Opal$	opal silicate concentration	gSi m^{-3}_ℓ
k_{sol}^{20}	$RcDisSi20$	second order dissolution reaction rate, or first order dissolution rate	$\text{m}^3_w \text{ gSi}^{-1} \text{ d}^{-1}$
$ktsol$	$TcDisSi$	temperature coefficient for dissolution	-
$Rsol$	-	dissolution rate	$\text{g m}^{-3}_\ell \text{ d}^{-1}$
$SWDissi$	$SWDissi$	option (=0.0 for second order, =1.0 for first order)	-
T	$Temp$	temperature	$^\circ\text{C}$
ϕ	$POROS$	porosity	$\text{m}^3_w \text{ m}^{-3}_\ell$

4 Primary producers

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4.1 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 net 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 \(1991\)](#); [BLOOM \(1985\)](#). 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 N₂) 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.

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 [$\text{gN/P/Si/S/C m}^{-3}$] and the production of dissolved oxygen [$\text{gO}_2 \text{ m}^{-3}$], 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 UIVAFIX (plus ULVAFIX_P), PHY_BLO (plus PHY_BLO_P), DEPAVE, VTRANS and DAYLENGTH. UIVAFIX 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.

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

and output. BLOOM requires an additional input file <bloominp.frm> containing tabulated data describing the relation between the daily averaged light intensity in the water column and the production efficiency for the species groups in the model. This file can be automatically generated with the PLCT. For simulations with BLOOM also the files: <bloominp.d09> and <bloominp.spe> need to be available in the work directory.

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], <i>an</i> , <i>aph</i> or <i>asi</i>
$Calg_i$	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

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 stoichiometric 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.

Sulphur is not a constraint, because it has been included in BLOOM only in the form of the sulphur stored in biomass, assuming that sulphate is always amply available. Sulphate 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.

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 $eatmax_i$ 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 concentration. 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:

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

$$eamin_i \leq eat \leq eatmax_i$$

$$eamin_i = eatmin_i - eb$$

$$eatmax_i = eatmax_I - eb$$

$$eb = et - eat$$

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}]
$eatmax_i$	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:

$$Ef_{ci} = \frac{(krsp_i + kmrt_i)}{kgp_i}$$

with:

Ef	light efficiency factor [-]
Ef_{ci}	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 photosynthetic 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 (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:

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

$$Ia_i = f(Efc_i)$$

with:

fpa	fraction of photosynthetically 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:

$$kgp_i = kpg_i^0 \times ktgpg_i^T \quad \text{for } TFP MxAlg(i) = 1.0$$

$$kgp_i = kpg_i^0 \times (T - ktgpg_i) \quad \text{for } TFP MxAlg(i) = 0.0$$

$$kgp_i \geq 0.0$$

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

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

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

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

with:

kgp^0	growth rate at 0 °C [d^{-1}], or per degree centigrade [${}^\circ\text{C}^{-1} \text{d}^{-1}$]
$ktgpg$	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 [${}^\circ\text{C}^{-1} \text{d}^{-1}$]
$ktmrt$	temperature coefficient for mortality [-]
$krsp^0$	specific maintenance respiration rate at 0 °C [d^{-1}]
$ktrsp$	temperature coefficient for maintenance respiration [-]
T	water temperature [${}^\circ\text{C}$]

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](#))

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

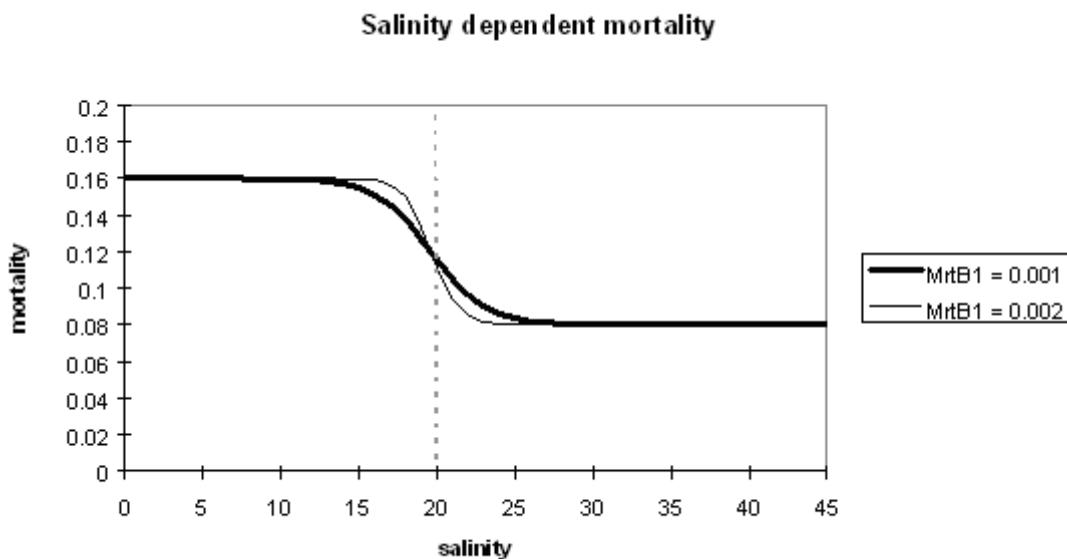


Figure 4.1: Example of the salinity dependent mortality function. $m1 = 0.08 \text{ d}^{-1}$; $m2 = 0.16 \text{ d}^{-1}$; $b2 = 11000$ (equivalent with 20 ppt salinity) [gCl m^{-3}]; $b1 = 0.001$ and $0.002 \text{ m}^3 \text{ gCl}^{-1}$.

with:

- $b1_i$ coefficient 1 of salinity stress function [$\text{g}^{-1} \cdot \text{m}^3$]
- $b2_i$ coefficient 2 of salinity stress function [$\text{g} \cdot \text{m}^{-3}$]
- $m1_i$ 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:

$$Calgmax_i = Calg1_i \times e^{((kgpi \times Ef_i - krsp_i) \times \Delta tb)}$$

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

```
If   Calgmax_j ≥ Calgc_j  Then
    Calgmax_j = Calgmax_j
If   Calgmax_j < Calgc_j  Then
    Calgmax_j = 0
Endif
```

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

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

with:

<i>Calgmax</i>	maximum concentration of an algae species or type at time t_2 , the end of a timestep [gC m ⁻³]
<i>Calgc</i>	threshold biomass concentration of an algae species at time t_1 , the beginning of a timestep [gC m ⁻³]
<i>Calg₁</i>	biomass concentration of algae species j at time t_1 [gC m ⁻³]
<i>Calg₂</i>	biomass concentration of algae species j at time t_2 [gC m ⁻³]
<i>ft</i>	ratio of the BLOOM timestep and the DELWAQ timestep ≥ 1.0 [-]
<i>Ef</i>	light efficiency factor [-]
<i>kgp</i>	potential specific growth rate of the fastest growing type of an algae species [d ⁻¹]
<i>krsp</i>	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.

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:

$$\begin{aligned} Calgmin_i &= Calg1_i \times e^{(-kmrt_i \times \Delta tb)} \\ Calgmin_j &= \sum_{i=l}^m (CAlgmin_i) \\ \text{if } Calgmin_j \geq Calgc_j &\quad \text{then } Calgmin_j = Calgmin_j \\ \text{if } Calgmin_j < Calgc_j &\quad \text{then } Calgmin_j = 0 \\ \sum_{i=l}^m (CAlg2_i) &\geq Calgmin_j \end{aligned}$$

with:

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

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 [$\text{gC.m}^{-3} \text{d}^{-1}$]
Rgr	growth rate for organic carbon [$\text{gC.m}^{-3} \text{d}^{-1}$]
Rgr_{on}	growth rate for organic nitrogen [$\text{gN m}^{-3} \cdot \text{d}^{-1}$]
Rgr_{op}	growth rate for organic phosphorus [$\text{gP m}^{-3} \text{d}^{-1}$]
Rgr_{osi}	growth rate for "organic" silicate [$\text{gSi m}^{-3} \text{d}^{-1}$]
$Rmrt$	mortality rate [$\text{gC m}^{-3} \text{d}^{-1}$]
Rnp	net primary production rate [$\text{gC m}^{-3} \text{d}^{-1}$]
$Rrsp$	respiration rate [$\text{gC m}^{-3} \text{d}^{-1}$]
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:

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

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

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

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

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

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

$$Rfix_i = Rnp_i \times aen_i$$

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

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

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

$$Raut_i = faut_i \times Rmrt_i$$

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned}
 Rprd_{on2,i} &= Rmrt_i \times an_i \times (1 - faut_i) \times (1 - fdet_i) \\
 Rprd_{op2,i} &= Rmrt_i \times aph_i \times (1 - faut_i) \times (1 - fdet_i) \\
 Rprd_{osi2,i} &= Rmrt_i \times asi_i \times (1 - faut_i) \times (1 - fdet_i) \\
 Rprd_{os2,i} &= Rmrt_i \times as_i \times (1 - faut_i) \times (1 - fdet_i)
 \end{aligned}$$

with:

<i>aen</i>	stoichiometric constant of nitrogen originating from elementary nitrogen in algae biomass [gN gC ⁻¹]
<i>an</i>	stoichiometric constant for ammonium/nitrate over carbon in algae biomass [gN gC ⁻¹]
<i>adn</i>	stoichiometric constant for detritus nitrogen over carbon in algae biomass [gN gC ⁻¹]
<i>aph</i>	stoichiometric constant for phosphate over carbon in algae biomass [gP gC ⁻¹]
<i>adph</i>	stoichiometric constant for detritus phosphorus over carbon in algae biomass [gP gC ⁻¹]
<i>aox</i>	stoichiometric constant for oxygen over carbon in algae biomass [gO ₂ gC ⁻¹]
<i>asi</i>	stoichiometric constant for silicon over carbon in algae biomass [gSi gC ⁻¹]
<i>as</i>	stoichiometric constant for sulphur over carbon in algae biomass [gS.gC ⁻¹]
<i>fam</i>	fraction of ammonium in the consumed nitrogen nutrients [-]
<i>fdet</i>	fraction of dead algae biomass allocated to fast decomposing detritus [-]
<i>faut</i>	fraction of dead algae biomass autolysed [-]
<i>Raut</i>	autolysis rate for dead algae biomass (organic carbon) [gC m ⁻³ d ⁻¹]
<i>Raut_{am}</i>	autolysis rate for ammonium [gN m ⁻³ d ⁻¹]
<i>Raut_{ph}</i>	autolysis rate for phosphate [gP m ⁻³ d ⁻¹]
<i>Raut_{si}</i>	autolysis rate for silicate [gSi m ⁻³ d ⁻¹]
<i>Raut_s</i>	autolysis rate for sulphide [gS m ⁻³ d ⁻¹]
<i>Rcns_{am}</i>	consumption rate for ammonium [gN m ⁻³ d ⁻¹]
<i>Rcns_{ni}</i>	consumption rate for nitrate [gN m ⁻³ d ⁻¹]
<i>Rcns_{ph}</i>	consumption rate for phosphate [gP m ⁻³ d ⁻¹]
<i>Rcns_{si}</i>	consumption rate for silicate [gSi m ⁻³ d ⁻¹]
<i>Rcns_s</i>	consumption rate for sulphate [gS m ⁻³ d ⁻¹]
<i>Rcns_{oc1}</i>	consumption rate for detritus carbon [gC m ⁻³ d ⁻¹]
<i>Rcns_{on1}</i>	consumption rate for detritus nitrogen [gN m ⁻³ d ⁻¹]
<i>Rcns_{oph1}</i>	consumption rate for detritus phosphorus [gP m ⁻³ d ⁻¹]
<i>Rfix</i>	nitrogen fixation (consumption) rate [gN m ⁻³ d ⁻¹]
<i>Rprd_{ox}</i>	net production rate for dissolved oxygen [gO ₂ m ⁻³ d ⁻¹]
<i>Rprd_{oc1}</i>	production rate for fast decomposing detritus carbon POC1 [gC m ⁻³ d ⁻¹]
<i>Rprd_{on1}</i>	production rate for fast decomposing detritus nitrogen PON1 [gN m ⁻³ d ⁻¹]
<i>Rprd_{op1}</i>	production rate for fast decomposing detritus phosphorus POP1 [gP m ⁻³ d ⁻¹]
<i>Rprd_{osi1}</i>	production rate for particulate soluble silicate OPAL [gSi m ⁻³ d ⁻¹]
<i>Rprd_{os1}</i>	production rate for fast decomposing detritus sulphur POS1 [gS m ⁻³ d ⁻¹]
<i>Rprd_{oc2}</i>	production rate for slowly decomposing detritus carbon POC2 [gC m ⁻³ d ⁻¹]
<i>Rprd_{on2}</i>	production rate for slowly decomposing detritus nitrogen PON2 [gN m ⁻³ d ⁻¹]
<i>Rprd_{op2}</i>	production rate for slowly decomposing detritus phosphorus POP2 [gP m ⁻³ d ⁻¹]
<i>Rprd_{osi2}</i>	production rate for particulate soluble silicate OPAL [gSi m ⁻³ d ⁻¹]
<i>Rprd_{os2}</i>	production rate for slowly decomposing detritus sulphur POS2 [gS m ⁻³ d ⁻¹]

The stoichiometric constants for oxygen and sulphur 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 f_{am} 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:

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

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

$$Cchf = 1000 \times \sum_{i=1}^n (achfi \times Calgi)$$

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

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

$$Cas = \sum_{i=1}^n (asi_i \times Calgi)$$

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:

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

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

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

with:

$Rfixt$ total nitrogen fixation rate [$\text{gN m}^{-2} \text{d}^{-1}$]

$Rrspt$ total algal maintenance respiration rate [$\text{gC m}^{-2} \text{d}^{-1}$]

$Rnptt$ total algal primary production rate [$\text{gC m}^{-2} \text{d}^{-1}$]

If the option parameter $SwBloomOut$ is set to 1.0, and the option ‘DUMP’ is selected in the file bloomip.d09, the model writes information on the bloom-calculations to the additional output file “bloominp.dbg”.

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 vice 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]
τ_c	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:

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

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 than the transport. With the process decomposition method also for the other water quality processes a larger time step than the transport 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 steps 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 *XNCRAAlg(i)* and *XPCRAAlg(i)* respectively. These coefficients must be equal to 0.0 for autotrophic algae. The sum of the stoichiometric constants *NCRAAlg(i)* and *XNCRAAlg(i)*, or *PCRAAlg(i)* and *XPCRAAlg(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 (*XNCRAAlg(i)* and *XPCRAAlg(i)*).
- ◊ It is possible to describe nitrogen fixation by algae types by providing a positive value for the coefficient *FNCRAAlg(i)*. These coefficients must be equal to 0.0 for autotrophic and mixotrophic algae. Again the sum of the stoichiometric constants *NCRAAlg(i)* and *FNCRAAlg(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 *FNCRAAlg(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 $25 \text{ kgN ha}^{-1} \text{ y}^{-1} \sim 0.0068 \text{ gN m}^{-2} \text{ d}^{-1}$ (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 *FNCRAAlg(i)* can be calculated as $0.0068 / (10 \times 0.1 \times 2) = 0.0034 \text{ gN gC}^{-1}$.
- ◊ 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 or 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 equal to 0.0 when *Tau* is more than two times *TauCrUlva*. This can be modified by changing the value of *FixGrad*.
- ◊ 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 [$\text{J cm}^{-2} \text{ week}^{-1}$]. 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 sulphur content of algae will only be taken into account automatically, when *SO4*, *SUD*, *POS1* and *POS2* are actually modelled.

Additional references

[Van der Molen et al. \(1994a\)](#), [WL | Delft Hydraulics \(1992c\)](#), [BLOOM \(1985\)](#), [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}
$Cnutc_2$	$ThrAlgNO3$	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}

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Table 4.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
–	$PON1$ 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	$DMCFAAlg(i)$	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	$\text{g}^{-1} \cdot \text{m}^3$
$b2_i$	$MrtB2Alg(i)$	algae type spec. coefficient 2 of salinity stress function	g m^{-3}
ea_i	$ExtVlAlg(i)$	algae species type specific extinction coefficient	$\text{m}^2 \text{ gC}^{-1}$
$KCO2$	$KCO2$	limitation constant for carbon	gC m^3
$faut_i$ $fdet_i$	$FrAutAlg(i)$ $FrAutAlg(i)$	fraction of dead algae biomass autolised 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)	-
–	$SwBloomOut$	option for specific BLOOM output (0 = no, 1 = yes)	-

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Table 4.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
-	<i>SWOxyProd</i> ²	option for calc. oxygen conc. (0 = daily av., 1 = daily var.)	-
-	<i>SWDepAve</i>	option depth aver. over BLOOM timestep (0 = off, 1 = on)	-
<i>H</i> <i>Ha</i> <i>V</i>	<i>Depth</i> <i>BloomDepth</i> <i>Volume</i>	depth of a water compartment or water layer average depth during a BLOOM timestep volume of a water compartment or water layer	m m m ³
<i>DL</i> <i>et</i> <i>eat</i> <i>Itop</i>	<i>DayL</i> <i>ExtVl</i> ⁴ <i>ExtVlPhyt</i> ⁴ <i>Rad</i>	daylength, fraction of a day total extinction coefficient of visible light extinction coefficient of all algae species types light intensity at top of layer or compartment	- m ⁻¹ m ⁻¹ W m ⁻²
<i>kgp</i> ⁰ <i>ktgp</i> -	<i>PPMaxAlg(i)</i> <i>TcPMxAlg(i)</i> <i>TFPMxAlg(i)</i>	algae type spec. pot. gross primary prod. rate at 0 °C algae type spec. temperature coeff. for primary prod. option temperature dep. of prod. (0 = linear, 1 = exp.)	d ⁻¹ - or °C -
<i>krsp</i> ⁰ -	<i>MRespAlg(i)</i> <i>MrtExAlg(i)</i> <i>TcMrtAlg(i)</i>	algae type spec. maintenance respiration rate at 0 °C algae type spec. extra rapid mortality rate algae type spec. temperature coefficient for mortality	d ⁻¹ d ⁻¹ °C ⁻¹ -
<i>ktrsp</i> _i	<i>TcRspAlg(i)</i>	algae type spec. temperature coef. for maint. resp.	-
<i>T</i>	<i>Temp</i>	water temperature	°C
<i>af</i> <i>τ</i> <i>τc</i>	<i>FixGrad</i> <i>Tau</i> <i>TauCrUlva</i>	attachment affinity coefficient shear stress at the sediment water interface critical shear stress for resuspension	- Pa Pa
<i>ft</i>	<i>TimMultBl</i>	ratio of the BLOOM timestep and the DELWAQ timestep	-
<i>Δt</i>	<i>Delt</i>	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].

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

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

⁴These parameters are calculated by processes ExtinaBVL and Extinc_VL.

Table 4.2: Definitions of the output parameters for BLOOM.

Name in formulas	Name in output ¹	Definition	Units
$Calgt_i$ Cdm_i	$Phyt$ $AlgDM$	total algae biomass concentration total algae biomass conc. on a dry matter basis	$gC\ m^{-3}$ $gDM\ m^{-3}$
$Cchf_i$ Can_i	$Chlf_a$ $AlgN$	total chlorophyll-a concentration total concentration of nitrogen in algae biomass	$mgChf\ m^{-3}$ $gN\ m^{-3}$
$Caph_i$	$AlgP$	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 $Lim_G(i)$	-
–	Lim_Mor or Lim_MALG	indicator for limitation by mortality can be split into species specific $Lim_M(i)$	-
$Rnpt$ $Rrspt$ $Rfixt$	$fPPtot$ $fResptot$ $fFixNUpt$	total net primary production total maintenance respiration total uptake of nitrogen by fixation	$gC\ m^{-2}\ d^{-1}$ $gC\ m^{-2}\ d^{-1}$ $gN\ m^{-2}\ d^{-1}$
–	$RcPPAlg(i)$	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.

4.2 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, SDMixAlgj. 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 FixAlgj defines for each algae type, whether it is part of a combination of fixed and suspended types or not. If FixAlgj has the default value of 0, this type is omitted from the further analysis. If the value of FixAlgj 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:

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

And for the fixed type as:

$$dResSedj = (frFixedAlgae \times (BloomAlg_i + BloomAlg_j) - BloomAlg_j) / Delt$$

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.

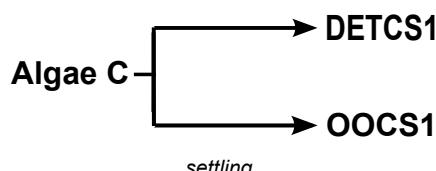
4.3 Settling of phytoplankton

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 (SEDGRID); or
- 2 DET(C,N,P,Si)S1 and OO(C,N,P,Si)S1 for the S1/2 approach (sulphur is not covered for S1/2).

When the S1/2 approach is followed phytoplankton biomass is allocated to the sediment detritus pools as follows:



Water = || = Sediment

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 stoichiometric 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 stoichiometric 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 4.3 provides the definitions of the input parameters occurring in the formulations.

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:

$$\begin{aligned} Rset_i &= ftau_i \times \frac{Fset_i}{H} \\ &\text{if } H < Hmin \quad Fset_i = 0.0 \\ &\text{else} \\ Fset_i &= \min \left(Fset'_i, \frac{Cx_i \times H}{\Delta t} \right) \\ Fset'_i &= Fset0_i + s_i \times Cx_i \\ &\text{if } \tau = -1.0 \quad ftau = 1.0 \\ &\text{else} \\ ftau_i &= \max \left(0.0, \left(1 - \frac{\tau}{\tau c_i} \right) \right) \end{aligned}$$

where:

Cx	concentration of the biomass of an algae species [gC m^{-3}]
$Fset0$	zero-order settling flux of an algae species [$\text{gC m}^{-2} \text{d}^{-1}$]
$Fset$	settling flux of an algae species [$\text{gC m}^{-2} \text{d}^{-1}$]
$ftau$	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 [$\text{gC m}^{-3} \text{d}^{-1}$]
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:

$fs_{j,i}$	stoichiometric ratio of nutrient j in algae species i [gX gC^{-1}]
$Rsn_{j,i}$	settling rate of nutrient j in algae species i [$\text{gX m}^{-3} \text{d}^{-1}$]
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 $Depth$ is smaller than minimal depth $MinDepth$ for settling, which has a default value of 0.1 m. When desired $MinDepth$ may be given a different value.

- ◊ The settling fluxes $fSedAlg$ ($\text{gDM m}^{-2} \cdot \text{d}^{-1}$) and $fSedPhyt$ ($\text{gC m}^{-2} \cdot \text{d}^{-1}$) are available as additional output parameters.

Table 4.3: Definitions of the input parameters in the above equations for SED(i), SEDPH-BLO 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	$\text{gC m}^{-2} \text{ d}^{-1}$
$fs_{j,i}$	$NCR(i)$ $PCR(i)$ $SCR(i)$ $SuCr(i)$ or $NCrat(i)$ $PCrat(i)$ $SCrat(i)$ $SuCrat(i)$	stoch. ratio N in algae species i for BLOOM stoch. ratio P in algae species i for BLOOM stoch. ratio Si in algae species i for BLOOM stoch. ratio S in algae species i for BLOOM stoch. ratio N in algae species i for DYNAMO stoch. ratio P in algae species i for DYNAMO stoch. ratio Si in algae species i for DYNAMO stoch. ratio S in algae species i for DYNAMO	gN gC^{-1} gP gC^{-1} gSi gC^{-1} gS gC^{-1} gN gC^{-1} gP gC^{-1} gSi gC^{-1} gS gC^{-1}
H $Hmin$	$Depth$ $MinDepth$	depth of the overlying water compartment minimal water depth for settling and resuspension	m m
s_i	$VSed(i)$ or $V0Sed(i)$	input or calc. settling velocity algae species i basic settling velocity of algae species i	m d^{-1} m d^{-1}
τ τc_i	Tau $TaucS(i)$	shear stress critical shear stress for settling of algae species i	Pa 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.

4.4 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 4.4 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:

<i>Calg</i>	concentration of algae biomass [gC m ⁻³]
<i>fdl</i>	daylength limitation function [-]
<i>fnut</i>	nutrient limitation function [-]
<i>frad</i>	light limitation function [-]
<i>ftp</i>	production temperature function [-]
<i>kgp</i>	gross primary production rate constant [d ⁻¹]
<i>knp</i>	net primary production rate constant [d ⁻¹]
<i>kpp</i> ²⁰	potential maximum production rate constant at 20 °C [d ⁻¹]
<i>krsp</i>	total respiration rate constant [d ⁻¹]
<i>ktp</i>	temperature constant for production [-]
<i>Rnp</i>	net primary production rate [gC m ⁻³ d ⁻¹]
<i>T</i>	water temperature [°C]
<i>i</i>	index for algae species

The limitation function for nutrients is given by:

$$fnut_i = \text{Min}(fn_i, fp_i, fsi_i)$$

$$fn_i = \frac{Cnn}{Cnn + Ksn_i}$$

$$fp_i = \frac{Cph}{Cph + Ksp_i}$$

$$fsi_i = \frac{Csi}{Csi + Kssi_i}$$

$$Cnn = Cam + \frac{Cni}{fan_i}$$

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:

$$fdl_i = \frac{\text{Min}(DL, DLo_i)}{DLo_i}$$

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]
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 4.3 \(Harris, 1986\)](#). 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:

$$\begin{aligned}
 Rnp_{max,1} &= \text{Min}\left(\frac{\text{Max}(Cni + Cam, 0.0)}{an_1 \times \Delta t}, \frac{\text{Max}(Cph, 0.0)}{ap_1 \times \Delta t}\right) \\
 Rnp_{max,2} &= \text{Min}\left(\frac{\text{Max}(Cni + Cam, 0.0)}{an_2 \times \Delta t}, \frac{\text{Max}(Cph, 0.0)}{ap_2 \times \Delta t}, \frac{\text{Max}(Csi, 0.0)}{asi_2 \times \Delta t}\right) \\
 Rnp_{max} &= \text{Max}(Rnp_{max,1}, Rnp_{max,2}) \\
 Rnp &= \text{Max}(Rnp_1, Rnp_2) \\
 \text{if } Rnp > Rnp_{max} \text{ then} \\
 Rnp_{c,2} &= \text{Min}\left(\frac{Rnp_{max}}{Rnp} \times Rnp_2, Rnp_{max,2}\right) \\
 Rnp_{c,1} &= Rnp_{max} - Rnp_{c,2} \\
 \Delta Rnp_2 &= Rnp_{c,2} - Rnp_2 \\
 \Delta Rnp_1 &= Rnp_{c,1} - Rnp_1 \\
 \text{else} \\
 Rnp_{c,1} &= Rnp_1 \text{ and } Rnp_{c,2} = Rnp_2 \\
 \Delta Rnp_{c,1} &= 0.0 \text{ and } \Delta Rnp_{c,2} = 0.0
 \end{aligned}$$

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}]
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 [$\text{gC m}^{-3} \text{ d}^{-1}$]
ΔRnp	correction of the net primary production rate [$\text{gC m}^{-3} \text{ d}^{-1}$]
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 [-]
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:

$$Rmrt_i = ftm_i \times kmrt_i^{20} \times \text{Max}((Calg_i - Calgmin_i), 0.0)$$

$$ftm_i = ktm_i^{(T-20)}$$

$$\text{if } S < Smin_i \text{ then } kmrt_i^{20} = kmrt_{min,i}^{20}$$

$$\text{if } S > Smax_i \text{ then } kmrt_i^{20} = kmrt_{max,i}^{20}$$

$$\text{else}$$

$$kmrt_i^{20} = kmrt_{min,i}^{20} + \frac{(S - Smin_i)}{(Smax_i - Smin_i)} \times (kmrt_{max,i}^{20} - kmrt_{min,i}^{20})$$

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:

$$\begin{aligned} Ruam_i &= fram \times \sum_i^{n=2} (an_i \times Rnp_{c,i}) \\ Runi_i &= (1 - fram) \times \sum_i^{n=2} (an_i \times Rnp_{c,i}) \\ Rup_i &= \sum_i^{n=2} (ap_i \times Rnp_{c,i}) \\ Rusi_i &= \sum_i^{n=2} (asi_i \times Rnp_{c,i}) \end{aligned}$$

where:

<i>an</i>	stoichiometric constant for N over C in algae biomass [gN gC ⁻¹]
<i>ap</i>	stoichiometric constant for P over C in algae biomass [gP gC ⁻¹]
<i>asi</i>	stoichiometric constant for Si over C in algae biomass [gSi gC ⁻¹]
<i>fram</i>	fraction of N consumed as ammonium [-]
<i>Ruam</i>	ammonium uptake rate [gN m ⁻³ d ⁻¹]
<i>Runi</i>	nitrate uptake rate [gN m ⁻³ d ⁻¹]
<i>Rup</i>	phosphate uptake rate [gP m ⁻³ d ⁻¹]
<i>Rusi</i>	silicate uptake rate [gSi m ⁻³ d ⁻¹]
<i>Rnp</i>	net primary production rate [gC m ⁻³ d ⁻¹]
<i>c</i>	index for corrected net primary production
<i>i</i>	index for algae species

Algae prefer ammonium over nitrate. The fraction of N consumed as ammonium follows from:

$$\begin{aligned} \text{if } Cam < Cam_c \text{ then } fram = \frac{Cam}{Cam + Cni} \\ \text{else} \\ Run = \sum_i^{n=2} (an_i \times Rnp_{c,i}) \\ \text{if } (Cam - Cam_c) \geq (Run \times \Delta t) \text{ then } fram = 1.0 \\ \text{if } (Cam - Cam_c) < (Run \times \Delta t) \text{ then} \\ fram = \frac{(Cam - Cam_c) + (Cam_c / (Cam_c + Cni)) \times (Run \times \Delta t - Cam + Cam_c)}{Run \times \Delta t} \end{aligned}$$

where:

<i>an</i>	stoichiometric constant for N over C in algae biomass [gN gC ⁻¹]
<i>Cam</i>	concentration of ammonium [gN m ⁻³]
<i>Cam_c</i>	critical concentration of ammonium [gN m ⁻³]
<i>Cni</i>	concentration of nitrate [gN m ⁻³]
<i>fram</i>	fraction of N consumed as ammonium [-]
<i>Rnp</i>	net primary production rate [gC m ⁻³ d ⁻¹]
<i>Run</i>	required nitrogen uptake in a timestep [gC m ⁻³ d ⁻¹]
<i>Δt</i>	computational timestep [d]

<i>c</i>	index for corrected net primary production
<i>i</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 nutrients are released proportional to mortality as follows:

$$\begin{aligned}
 R_{an} &= fra_i \times \sum_i^{n=2} (an_i \times Rmrt_i) \\
 R_{ap} &= fra_i \times \sum_i^{n=2} (ap_i \times Rmrt_i) \\
 R_{asi} &= fra_i \times \sum_i^{n=2} (asi_i \times Rmrt_i) \\
 R_{mc_1} &= \frac{frpoc_1}{(1 - fra_i)} \times \sum_i^{n=2} (Rmrt_i) \\
 R_{mn_1} &= frpoc_1 \times \sum_i^{n=2} (an_i \times Rmrt_i) \\
 R_{mp_1} &= frpoc_1 \times \sum_i^{n=2} (ap_i \times Rmrt_i) \\
 R_{msi_1} &= frpoc_1 \times \sum_i^{n=2} (asi_i \times Rmrt_i) \\
 R_{mc_2} &= (1 - \frac{frpoc_1}{(1 - fra_i)}) \times \sum_i^{n=2} (Rmrt_i) \\
 R_{mn_2} &= (1 - frpoc_1 - fra_i) \times \sum_i^{n=2} (an_i \times Rmrt_i) \\
 R_{mp_2} &= (1 - frpoc_1 - fra_i) \times \sum_i^{n=2} (ap_i \times Rmrt_i) \\
 R_{msi_2} &= (1 - frpoc_1 - fra_i) \times \sum_i^{n=2} (asi_i \times Rmrt_i)
 \end{aligned}$$

where:

<i>an</i>	stoichiometric constant for N over C in algae biomass [gN gC ⁻¹]
<i>ap</i>	stoichiometric constant for P over C in algae biomass [gP gC ⁻¹]
<i>asi</i>	stoichiometric constant for Si over C in algae biomass [gSi gC ⁻¹]
<i>fra</i>	fraction released by autolysis [-]
<i>frpoc₁</i>	fraction released to detritus POC/N/P1 or OPAL [-]
<i>Ran</i>	nitrogen NH4 release due to autolysis [gN m ⁻³ d ⁻¹]
<i>Rap</i>	dissolved phosphate PO4 release due to autolysis [gP m ⁻³ d ⁻¹]
<i>Rasi</i>	dissolved silicate Si release due to autolysis [gSi m ⁻³ d ⁻¹]
<i>Rmc₁</i>	detritus C release to POC1 due to mortality [gC m ⁻³ d ⁻¹]

Rmc_2	detritus C release to POC2 due to mortality [$\text{gC m}^{-3} \text{ d}^{-1}$]
Rmn_1	detritus N release to PON1 due to mortality [$\text{gN m}^{-3} \text{ d}^{-1}$]
Rmn_2	detritus N release to PON2 due to mortality [$\text{gN m}^{-3} \text{ d}^{-1}$]
Rmp_1	detritus P release to POP1 due to mortality [$\text{gP m}^{-3} \text{ d}^{-1}$]
Rmp_2	detritus P release to POP2 due to mortality [$\text{gP m}^{-3} \text{ d}^{-1}$]
$Rmsi_1$	silicate release to OPAL due to mortality [$\text{gSi m}^{-3} \text{ d}^{-1}$]
$Rmsi_2$	silicate release to OPAL due to mortality [$\text{gSi m}^{-3} \text{ d}^{-1}$]
$Rmrt$	mortality rate [$\text{gC m}^{-3} \text{ d}^{-1}$]
i	index for algae species

Directives for use

- ◊ Because the limitation function for radiation (f_{rad_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 4.2](#).
- ◊ 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 m² 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).

Table 4.4: 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
$Calg_i$ $Calgmin_i$	(i) $Min(i)$	concentration algae biomass (i) minimum conc. algae species (i)	gC m^{-3} gC m^{-3}
an_i ap_i asi_i	$NCRat(i)$ $PCRat(i)$ $SCRat(i)$	stoich. constant N over C in algae (i) stoich. constant P over C in algae (i) stoich. constant Si over C in algae (i)	gN gC^{-1} gN gC^{-1} gN gC^{-1}
Cam Cam_c Cni Cph Csi	$NH4$ $NH4Crit$ $NO3$ $PO4$ Si	concentration of ammonium critical conc. of ammonium for uptake concentration of nitrate concentration of dissolved phosphate concentration of dissolved silicate	gN m^{-3} gN m^{-3} gN m^{-3} gP m^{-3} gSi m^{-3}
DL DLo_i	$DayL$ $OptDL(i)$	daylength, fraction of a day optimal daylength for algae species (i)	- -
et	$ExtVL$	total extinction coefficient	m^{-1}
$fani$ fgr_i fra_i $frpoc_1$	$PrfNH4(i)$ $GResp(i)$ $FrAut(i)$ $FrDet(i)$	pref. ammonium over nitrate for algae (i) growth respiration factor for algae (i) fraction released by autolysis for algae (i) fraction released to detritus POC/N/P1 or OPAL for algae (i)	- - - -
H	$Depth$	water depth	m
Is Io_i^{20}	Rad $RadSat(i)$	light intensity at water surface optimal light int. at 20 °C for algae (i)	W m^{-2} W m^{-2}
kmr_i^{20} $kmrt_{min,i}^{20}$ $kmrt_{max,i}^{20}$ kpp_i^{20} $ktmi$ ktp_i	$MResp(i)$ $Mort0(i)$ $MortS(i)$ $PPMax(i)$ $TCDec(i)$ $TCGro(i)$	maint. resp. const. at 20 °C of algae (i) min. mort. constant at 20 °C of algae (i) max. mort. constant at 20 °C of algae (i) max. prod. constant at 20 °C of algae (i) temp. constant for mortality of algae (i) temp. constant for production of algae (i)	d^{-1} d^{-1} d^{-1} d^{-1} - -
Ksn_i Ksp_i $Kssi_i$	$KmDIN(i)$ $KmP(i)$ $KmSi(i)$	half satur. const. nitrogen for algae (i) half satur. const. phosphate for algae (i) half satur. const. silicate for algae (i)	gN m^{-3} gP m^{-3} gSi m^{-3}
S $Smin_i$ $Smax_i$	$Salinity$ $SalM1(i)$ $SalM2(i)$	salinity salinity limit for Mort0 of algae (i) salinity limit for MortS of algae (i)	psu psu psu
T	$Temp$	water temperature	°C
Δt	$Delt$	computational timestep	d

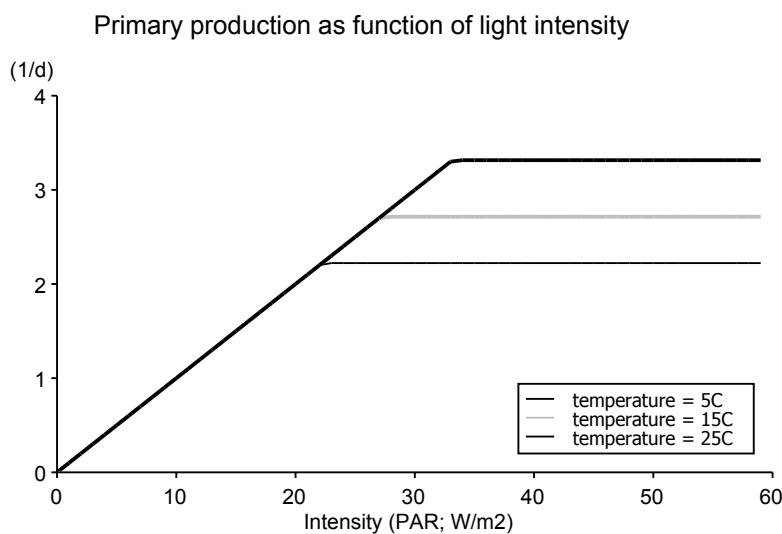


Figure 4.2: Primary production rate of algae species i as a function of temperature and radiation.

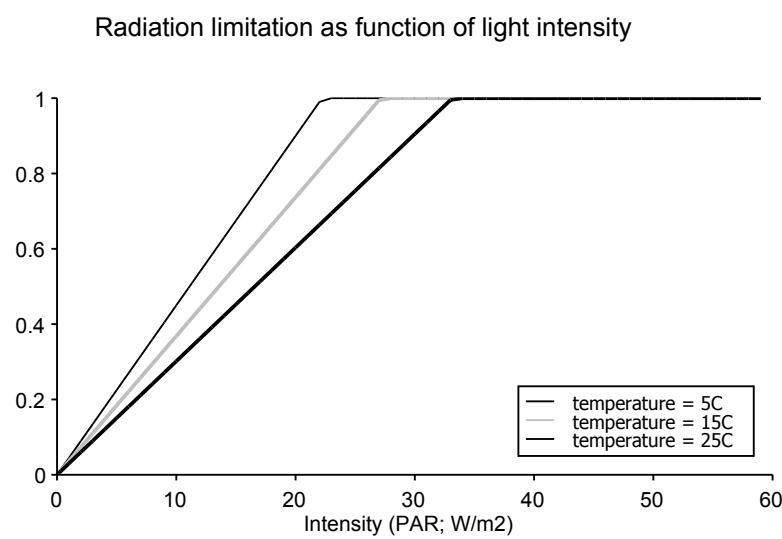


Figure 4.3: Limitation function for radiation (f_{rad_i}) for algae species i as a function of radiation (I_s, RAD) at different temperature ranging from 5 to 25 °C.

4.5 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 (ℓ) or to water (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 4.5–4.6 provide the definitions of the input and output parameters occurring in the formulations.

Formulation

The total concentrations of algae biomass components follow from:

$$\begin{aligned} Calgt_1 &= \sum_{i=1}^n Calgi \\ Calgt_2 &= \sum_{i=1}^n (fdm_i \times Calgi) \\ Calgn &= \sum_{i=1}^n (an_i \times Calgi) \\ Calgp &= \sum_{i=1}^n (ap_i \times Calgi) \\ Calgsi &= \sum_{i=1}^n (asi_i \times Calgi) \\ Cchf &= \sum_{i=1}^n (achf_i \times Calgi) \end{aligned}$$

where:

$achf$	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}]
$Calgn$	concentration of organic nitrogen in algae biomass [gC m^{-3}]
$Calgp$	concentration of organic phosphorus in algae biomass [gC m^{-3}]
$Calgsi$	concentration of silicate in algae biomass [gC m^{-3}]
$Calgt_1$	total concentration of algae biomass [gC m^{-3}]
$Calgt_2$	total concentration of algae biomass [gDM m^{-3}]
$Cchl$	concentration of chlorophyll-a [mgChf m^{-3}]
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 4.5: 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	$Ncrat(i)$	stoichiometric ratio of nitrogen in algae species (i)	gN gC^{-1}
ap_i	$PCrat(i)$	stoichiometric ratio of phosphorus in algae species (i)	gP gC^{-1}
asi_i	$SCrat(i)$	stoichiometric ratio of silicate in algae species (i)	gSi gC^{-1}
$achf_1$	$GrToChl$	stoichiometric ratio of chlorophyll-a in green algae	gChl gC^{-1}
$achf_2$	$DiToChl$	stoichiometric ratio of chlorophyll-a in diatoms	gChl gC^{-1}
$Calgi$	(i)	concentration of biomass in algae species (i)	gC m^{-3}
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	-

Table 4.6: Definitions of the output parameters in the above equations for PHY_DYN. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input ¹	Definition	Units
$Calgt_1$	$Phyt$	total algae biomass carbon concentration	$gC \text{ m}^{-3}_\ell$
$Calgt_2$	$AlgDM$	total algae biomass dry matter concentration	$gDM \text{ m}^{-3}_\ell$
$Calgn$	$AlgN$	concentration of organic nitrogen in algae biomass	$gN \text{ m}^{-3}_\ell$
$Calgp$	$AlgP$	concentration of organic phosphorus in algae biomass	$gP \text{ m}^{-3}_\ell$
$Calgsi$	$AlgSi$	concentration of silicate in algae biomass	$gSi \text{ m}^{-3}_\ell$
$Cchf$	$Chlfa$	chlorophyll-a concentration	$mgChf \text{ m}^{-3}_\ell$

4.6 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.

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 4.7 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 [$\text{gC m}^{-3} \text{ d}^{-1}$]
T	water temperature [$^{\circ}\text{C}$]

The limitation function for nutrients is given by:

$$fnut = \text{Min}(fn, fp, fsi, 1.0)$$

$$fn = \frac{(Rmn_{S1} \times (1 - frnb) + (Cnn/(Cnn + Ksn)) \times (Cnn/\Delta t)) \times A \times H}{an \times kpn \times Malg}$$

$$fp = \frac{(Rmp_{S1} + (Cph/(Cph + Ksp)) \times (Cph/\Delta t)) \times A \times H}{ap \times kpn \times Malg}$$

$$fsi = \frac{(Rmsi_{S1} + (Csi/(Csi + Kssi)) \times (Csi/\Delta t)) \times A \times H}{asi \times kpn \times Malg}$$

$$Cnn = Cam + Cni$$

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 [$\text{gN m}^{-3} \text{ d}^{-1}$]
Rmp_{S1}	mineralisation rate for DETPS1 [$\text{gP m}^{-3} \text{ d}^{-1}$]
$Rmsi_{S1}$	mineralisation rate for DETSiS1 [$\text{gSi m}^{-3} \text{ d}^{-1}$]

The limitation functions for daylength and light are given by:

$$fdl = \frac{\text{Min}(DL, DLo)}{DLo}$$

if $(Is/Io) \geq 1.0$ then
 $frad = 1.0$
 if $(Ib/Io) < 1.0$ then
 $frad = \frac{Ib}{Io}$

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 [$\text{gC m}^{-3} \text{ d}^{-1}$]
T	water temperature [°C]

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:

$$\begin{aligned}
 Ruam &= fram \times Run \\
 Runi &= (1 - fram) \times Run \\
 Run_{S1} &= \text{Min}(an \times Rnp, (1 - frnb) \times Rmn_1) \\
 Run &= \text{Max}((an \times Rnp - Run_{S1}), 0.0) \\
 Rups_{S1} &= \text{Min}(ap \times Rnp, Rmps_{S1}) \\
 Rup &= \text{Max}((ap \times Rnp - Rups_{S1}), 0.0) \\
 Rusi_{S1} &= \text{Min}(asi \times Rnp, Rmsis_{S1}) \\
 Rusi &= \text{Max}((asi \times Rnp - Rusi_{S1}), 0.0)
 \end{aligned}$$

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]
$Rups_{S1}$	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]
$Rmps_{S1}$	mineralisation rate for DETPS1 [gP m ⁻³ d ⁻¹]
$Rmsis_{S1}$	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:

$$\begin{aligned}
 &\text{if } Cam < Cam_c \text{ then } fram = \frac{Cam}{Cnn} \\
 &\text{if } (Run \times \Delta t) \leq (Cam - Cam_c) \text{ then } fram = 1.0 \\
 &\text{else} \\
 fram &= \frac{(Cam - Cam_c) + (Cam_c/(Cam_c + Cni)) \times (Run \times \Delta t - Cam + Cam_c)}{Run \times \Delta t}
 \end{aligned}$$

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]
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]

Directives for use

- ◊ The nutrient-carbon ratios for diatoms in the sediment are the same as for diatoms in the water column.

Table 4.7: 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
M_{alg}	$DiatS1$	quantity of benthic diatom biomass	gC m^{-3}
A	$Surf$	surface area	m^2
a_n a_p a_{si}	$NCRatDiat$ $PCRatDiat$ $SCRatDiat$	stoich. const. N over C in diatom biomass stoich. const. P over C in diatom biomass stoich. const. Si over C in diatom biomass	gN gC^{-1} gN gC^{-1} gN gC^{-1}
C_{am} C_{am_c} C_{ni} C_{ph} C_{si}	$NH4$ $NH4Crit$ $NO3$ $PO4$ Si	concentration of ammonium critical conc. of ammonium for uptake concentration of nitrate concentration of dissolved phosphate concentration of dissolved silicate	gN m^{-3} gN m^{-3} gN m^{-3} gP m^{-3} gSi m^{-3}
DL DLo	$DayL$ $OptDLDiaS1$	daylength, fraction of a day optimal daylength for benthic diatoms	- -
f_{gr} f_{ra} f_{rdet_1} f_{rn}	$GRespDiaS1$ $FrAutDiatS$ $FrDetDiatS$ $FrMinS1Bac$	growth respiration factor fraction released by autolysis fraction released to detritus DetC/N/P/SiS1 frac. min. N allocated to sediment bacteria	- - - -
H	$Depth$	water depth	m
I_b I_o	Rad $RadSatDiS1$	light intensity at water surface optimal light intensity for benthic diatoms	W m^{-2} W m^{-2}
k_{mr}^{20} k_{mrt}^{20} k_{pp}^{20} k_{tm} k_{tp}	$MRespDiaS1$ $MrtSedDiat$ $PPMaxDiaS1$ $TCDecDiat$ $TCDGroDiat$	maint. resp. const. at 20 °C of diatoms mortality constant at 20 °C of diatoms max. prod. constant at 20 °C of diatoms temp. constant for mortality of diatoms temp. constant for production of diatoms	d^{-1} d^{-1} d^{-1} - -
K_{sn} K_{sp} K_{ssi}	$KmDINDiaS1$ $KmPDiats1$ $KmSiDiats1$	half satur. const. nitrogen for diatoms half satur. const. phosphate for diatoms half satur. const. silicate for diatoms	gN m^{-3} gP m^{-3} gSi m^{-3}
$RmnS1$ $Rmps1$ $RmsiS1$	$dMinDetNS1$ $dMinDetPS1$ $dMinDetSiS$	mineralisation rate for DETNS1 mineralisation rate for DETPS1 mineralisation rate for DETSiS1	$\text{gN m}^{-3} \text{d}^{-1}$ $\text{gP m}^{-3} \text{d}^{-1}$ $\text{gSi m}^{-3} \text{d}^{-1}$
T	$Temp$	water temperature	°C
Δt	$Delt$	computational timestep	d

4.7 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 ran 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 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 m². 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, sulphur) in vegetation biomass are not modelled as 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 4.4](#)). 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 4.5](#)). 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 sulphur from sulphate (SO₄, preferred) and dissolved sulphide (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

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 4.8](#) provides the definitions of the input parameters occurring in the formulations, and [Table 4.9](#) 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 4.5](#)). 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:

$$M_{veg,i} = \frac{(M_{veg_{min,i}} - M_{veg_{max,i}})}{1 + \exp(sf_i \times (ag_i - ag_{hb,i})/ag_{hb,i})} + M_{veg_{max,i}}$$

where:

ag	age of vegetation [d]
ag_{hb}	age of vegetation when half of attainable biomass is reached [d]
M_{veg}	attainable biomass in all compartments [gC.m^{-2}]
$M_{veg_{max}}$	maximum biomass in all compartments [gC.m^{-2}]
$M_{veg_{min}}$	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:

$$M_{veg,i} = fa_i \times M_{veg0,i}/dmci$$

where:

$$dmci \quad \text{dry matter carbon ratio } [\text{gDM.gC}^{-1}]$$

f_a	percentage of area coverage [%]
M_{veg}	actual biomass in all compartments [gC.m^{-2}]
M_{veg_0}	initial biomass in all compartments [tDM.ha^{-1}]

If growth takes place ($SWVB(i)Gro = 1.0$), the potential (or target) growth rate of biomass per vegetation cohort results from:

$$Rgr_{p,i} = (M_{veg_{a,i}} - M_{veg_i}) / \Delta t$$

where:

Rgr_p	potential growth rate of biomass in all compartments [$\text{gC.m}^{-2}.\text{d}^{-1}$]
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:

$$Rup_{lin} = fn_{ln} \times Rgr_i \times \sum_{j=1}^5 (fb_{ij}/vn_{lij}) / H$$

$$Rup_{t,l} = \sum_{i=1}^9 \left(\sum_{n=1}^{nr} (Rup_{iln}) \right)$$

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 [$\text{gC.m}^{-2}.\text{d}^{-1}$]
Rup	uptake rate of nutrients in all compartments [$\text{gN/P/S.m}^{-3}.\text{d}^{-1}$]
$Rupt$	total uptake rate of nutrients in all compartments [$\text{gN/P/S.m}^{-3}.\text{d}^{-1}$]
vn	carbon nutrient ratio in vegetation biomass [gC.gN/P/S^{-1}]
l	index for nutrient (1=nitrogen, 2=phosphorus, 3=sulphur)
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 the nutrient concentrations (*Cam*, *Cni*, *Cph*, *Cap*, *Csu*, *Csud*) in the sediment layers within rooting depth. When not enough nutrient 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 *VBFMaxU*.

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:

if *SwEmersion* = 0.0 then *ti* = *ti* + Δt else *ti* = 0.0

if *ti* > *ti_{c,i}* then *ag_i* = 0.0 and *SwVB_iMrt* = 0.0

where:

<i>ag</i>	age of biomass [d]
<i>ti</i>	inundation period, the number of successive days of inundation [d]
<i>ti_c</i>	critical inundation period, the mortality lag time [d]
<i>SwEmersion</i>	switch for inundation (0 = yes, 1 = no)
<i>SwVB_iMrt</i>	switch for mortality (0 = yes, 1 = no)
Δt	computational time step [d]
<i>i</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 *ti₀* 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:

$$Rmrt_i = kmrt_i \times Mvegi$$

$$Rmrkd_{klij} = fh_i \times fd_{kij} \times fb_{ij} \times Rmrt_i / (vnlij \times H)$$

where:

<i>fb</i>	fraction of biomass in a compartment [-]
<i>fd</i>	fraction of biomass released into a specific detritus fraction [-]
<i>fh</i>	fraction of biomass in a layer [-]
<i>H</i>	water layer or sediment layer thickness [-]
<i>kmrt</i>	mortality rate constant [d^{-1}]
<i>Mvegi</i>	actual biomass in all compartments [$gC.m^{-2}$]
<i>Rmrkd</i>	release rate of detritus [$gC/N/P/S.m^{-3}.d^{-1}$]

$Rmrt$	mortality rate of biomass [$\text{gC.m}^{-2}.\text{d}^{-1}$]
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 = sulphur)
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:

$$Fs_i = \frac{Cveg_i(z_{max,i})}{(Mveg_{p,i}/H_{max,i})}$$

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 z_{max} , 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 F on the distribution appear from [Figure 4.6](#).

A linear distribution function is formulated using two constants, a and b . Both are fixed when F 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:

$$\begin{aligned} Cveg_i(z) &= a_i \times z + b_i \\ a_i &= \frac{Mveg_{p,i}}{H_{max,i}} \times \frac{(2 - 2 \times Fs_i)}{(H_t - z_{max,i})} \\ b_i &= \frac{Mveg_{p,i}}{H_{max,i}} \times \frac{(Fs_i \times (z_{max,i} + H_t) - 2 \times z_{max,i})}{(H_t - z_{max,i})} \end{aligned}$$

The biomass fraction fh_i in a layer n between z_n and z_{n+1} follows from:

$$\int_{z_n}^{z_{n+1}} (Cveg_i(z)/Mveg_i) dz = \frac{A}{2} (z_{n+1}^2 - z_n^2) + B (z_{n+1} - z_n)$$

$$fh_i = \begin{cases} \int_{z_n}^{z_{n+1}} (Cveg_i(z)/Mveg_i) dz & \text{if } z_n > z_{max,i} \\ \int_{z_{max,i}}^{z_{n+1}} (Cveg_i(z)/Mveg_i) dz & \text{if } z_n \leq z_{max,i} \end{cases}$$

with:

$$\int_{z_n}^{z_{n+1}} (Cveg_i(z)/Mveg_i) dz = \frac{A}{2} (z_{n+1}^2 - z_n^2) + B (z_{n+1} - z_n)$$

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:

$$fh_i = \frac{Mveg_{p,i}}{Mveg_i} \times \frac{(z_{n+1} - z_n)}{H_{max,i}} \quad \text{if } z_n > z_{max,i}$$

$$fh_i = \frac{Mveg_{p,i}}{Mveg_i} \times \frac{(z_{max,i} - z_n)}{H_{max,i}} \quad \text{if } z_n < z_{max,i} \text{ and } z_{n+1} > z_{max,i}$$

Directives for use

- 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.
- The input for initial biomasses may be generated as a GIS map representing each model grid cell, for instance based on a satellite image.
- 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 $VBFr\text{-}MaxU$ (<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.

Table 4.8: Definitions of the input parameters in the above equations for $VBMORT(i)$, $VB(i)\text{-}MRT3W$, $VB(i)\text{-}MRT3S$, $VBGROWTH(i)$, $VB(i)\text{-}UPT$, $VB(i)\text{-}UPT3D$, $VB(i)\text{-}AVAILN$ 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 sulphate	gS.m^{-3}
$Csud$	SUD	concentration of dissolved sulphide	gS.m^{-3}
dmc_i	$DMcfVB(i)$	dry matter carbon ratio	gDM.gC^{-1}
fa_i	$IniCovVB(i)$	percentage of area coverage	%
$fb_{i,j}$	$F1VB(i)$	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}	$FrootPOC1$	biomass fraction 2 (fine roots) to detr. POX1	-
fd_{2i5}	$FrootPOC2$	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}

Name in formulas ¹	Name in input ¹	Definition	Units
$M_{veg_{min,i}}$	$MinVB(i)$	minimum biomass in all five compartments	gC.m^{-2}
sf_i	$SfVB(i)$	shape factor of the growth function	-
$SWEmerison$ $SWDisVB(i)$ $SwIniVB(i)$ $IniVB(i)Dec$ $SwRegrVB(i)$	$SWEmerison$ $SWDisVB(i)$ $SwIniVB(i)$ $IniVB(i)Dec$ $SwRegrVB(i)$	switch for inundation (0 = yes, 1 = no) option vert. distr. (1=const., 2=linear, 3=exp.) option init. biomass (0=biomass,1=coverage) option mort. at start of simul. (0=no, 1=yes) option for re-growth (0=no, 1=yes)	- - - - -
$VBFrMaxU$	$VBFrMaxU$	max. fr. of nutrients taken up in a time step	-
vn_{1ij}	$CNF1VB(i)$ $CNF2VB(i)$ $CNF3VB(i)$ $CNF4VB(i)$ $CNF5VB(i)$	carbon nitrogen ratio in comp. 1 (stems) carbon nitrogen ratio in comp. 2 (foliage) carbon nitrogen ratio in comp. 3 (branches) carbon nitrogen ratio in comp. 4 (roots) carbon nitrogen ratio in comp. 5 (fine roots)	gC.gN^{-1} gC.gN^{-1} gC.gN^{-1} gC.gN^{-1} gC.gN^{-1}
vn_{2ij}	$CPF1VB(i)$ $CPF2VB(i)$ $CPF3VB(i)$ $CPF4VB(i)$ $CPF5VB(i)$	carbon phosphorus ratio in comp. 1 (stems) carbon phosphorus ratio in comp. 2 (foliage) carbon phos. ratio in comp. 3 (branches) carbon phosphorus ratio in comp. 4 (roots) carbon phos. ratio in comp. 5 (fine roots)	gC.gP^{-1} gC.gP^{-1} gC.gP^{-1} gC.gP^{-1} gC.gP^{-1}
vn_{3ij}	$CSF1VB(i)$ $CSF2VB(i)$ $CSF3VB(i)$ $CSF4VB(i)$ $CSF5VB(i)$	carbon sulphur ratio in comp. 1 (stems) carbon sulphur ratio in comp. 2 (foliage) carbon sulphur ratio in comp. 3 (branches) carbon sulphur ratio in comp. 4 (roots) carbon sulphur ratio in comp. 5 (fine roots)	gC.gS^{-1} gC.gS^{-1} gC.gS^{-1} gC.gS^{-1} gC.gS^{-1}
$t_{c,i}$ $t_{l0,i}$	$CrnsfVB(i)$ $Initnsfd$	critical inundation period, mortality lag time inundation period prior to sim. start time	d 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.

Table 4.9: 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
t_i	$AgeVB(i)$	age of vegetation biomass	d
-	$fNVB(i)UP$ $fPVB(i)UP$ $fSVB(i)UP$ $fN1VB(i)UPy$ $fN2VB(i)UPy$ $fP1VB(i)UPy$	N vegetation uptake flux P vegetation uptake flux S vegetation uptake flux ammonium N vegetation uptake flux nitrate N vegetation uptake flux dissolved phosphate P vegetation uptake flux	$\text{gN.m}^{-2}.\text{d}^{-1}$ $\text{gP.m}^{-2}.\text{d}^{-1}$ $\text{gS.m}^{-2}.\text{d}^{-1}$ $\text{gN.m}^{-2}.\text{d}^{-1}$ $\text{gN.m}^{-2}.\text{d}^{-1}$ $\text{gP.m}^{-2}.\text{d}^{-1}$

Name in formulas ¹	Name in output ¹	Definition ²	Units
	$fP2VB(i)UPy$ $fS1VB(i)UPy$ $fS2VB(i)UPy$	adsorbed phosphate P vegetation uptake flux sulphate S vegetation uptake flux dissolved sulphide S vegetation uptake flux	$\text{gP.m}^{-2}.\text{d}^{-1}$ $\text{gS.m}^{-2}.\text{d}^{-1}$ $\text{gS.m}^{-2}.\text{d}^{-1}$
-	$fC1VB(i)P5$ $fN1VB(i)P5$ $fP1VB(i)P5$ $fS1VB(i)P5$ $fC2VB(i)P1$ $fN2VB(i)P1$ $fP2VB(i)P1$ $fS2VB(i)P1$ $fC2VB(i)P2$ $fN2VB(i)P2$ $fP2VB(i)P2$ $fS2VB(i)P2$ $fC2VB(i)P3$ $fN2VB(i)P3$ $fP2VB(i)P3$ $fS2VB(i)P3$ $fC3VB(i)P5$ $fN3VB(i)P5$ $fP3VB(i)P5$ $fS3VB(i)P5$ $fC4VB(i)P5$ $fN4VB(i)P5$ $fP4VB(i)P5$ $fS4VB(i)P5$ $fC5VB(i)P1$ $fN5VB(i)P1$ $fP5VB(i)P1$ $fS5VB(i)P1$ $fC5VB(i)P2$ $fN5VB(i)P2$ $fP5VB(i)P2$ $fS5VB(i)P2$ $fC5VB(i)P3$ $fN5VB(i)P3$ $fP5VB(i)P3$ $fS5VB(i)P3$	C flux from biomass comp. 1 to detritus POC5 N flux from biomass comp. 1 to detritus POC5 P flux from biomass comp. 1 to detritus POC5 S flux from biomass comp. 1 to detritus POC5 C flux from biomass comp. 2 to detritus POC1 N flux from biomass comp. 2 to detritus POC1 P flux from biomass comp. 2 to detritus POC1 S flux from biomass comp. 2 to detritus POC1 C flux from biomass comp. 2 to detritus POC2 N flux from biomass comp. 2 to detritus POC2 P flux from biomass comp. 2 to detritus POC2 S flux from biomass comp. 2 to detritus POC2 C flux from biomass comp. 2 to detritus POC3 N flux from biomass comp. 2 to detritus POC3 P flux from biomass comp. 2 to detritus POC3 S flux from biomass comp. 2 to detritus POC3 C flux from biomass comp. 3 to detritus POC5 N flux from biomass comp. 3 to detritus POC5 P flux from biomass comp. 3 to detritus POC5 S flux from biomass comp. 3 to detritus POC5 C flux from biomass comp. 4 to detritus POC5 N flux from biomass comp. 4 to detritus POC5 P flux from biomass comp. 4 to detritus POC5 S flux from biomass comp. 4 to detritus POC5 C flux from biomass comp. 5 to detritus POC1 N flux from biomass comp. 5 to detritus POC1 P flux from biomass comp. 5 to detritus POC1 S flux from biomass comp. 5 to detritus POC1 C flux from biomass comp. 5 to detritus POC2 N flux from biomass comp. 5 to detritus POC2 P flux from biomass comp. 5 to detritus POC2 S flux from biomass comp. 5 to detritus POC2 C flux from biomass comp. 5 to detritus POC3 N flux from biomass comp. 5 to detritus POC3 P flux from biomass comp. 5 to detritus POC3 S flux from biomass comp. 5 to detritus POC3	$\text{gC.m}^{-3}.\text{d}^{-1}$ $\text{gN.m}^{-3}.\text{d}^{-1}$ $\text{gP.m}^{-3}.\text{d}^{-1}$ $\text{gS.m}^{-3}.\text{d}^{-1}$ $\text{gC.m}^{-2}.\text{d}^{-1}$ $\text{gN.m}^{-2}.\text{d}^{-1}$ $\text{gP.m}^{-2}.\text{d}^{-1}$ $\text{gS.m}^{-2}.\text{d}^{-1}$ $\text{gC.m}^{-2}.\text{d}^{-1}$ $\text{gN.m}^{-2}.\text{d}^{-1}$ $\text{gP.m}^{-2}.\text{d}^{-1}$ $\text{gS.m}^{-2}.\text{d}^{-1}$ $\text{gC.m}^{-2}.\text{d}^{-1}$ $\text{gN.m}^{-2}.\text{d}^{-1}$ $\text{gP.m}^{-2}.\text{d}^{-1}$ $\text{gS.m}^{-2}.\text{d}^{-1}$ $\text{gC.m}^{-2}.\text{d}^{-1}$ $\text{gN.m}^{-2}.\text{d}^{-1}$ $\text{gP.m}^{-2}.\text{d}^{-1}$ $\text{gS.m}^{-2}.\text{d}^{-1}$ $\text{gC.m}^{-2}.\text{d}^{-1}$ $\text{gN.m}^{-2}.\text{d}^{-1}$ $\text{gP.m}^{-2}.\text{d}^{-1}$ $\text{gS.m}^{-2}.\text{d}^{-1}$ $\text{gC.m}^{-2}.\text{d}^{-1}$ $\text{gN.m}^{-2}.\text{d}^{-1}$ $\text{gP.m}^{-2}.\text{d}^{-1}$ $\text{gS.m}^{-2}.\text{d}^{-1}$
Rgr_i	$fVB(i)$	actual vegetation biomass growth rate	$\text{gC.m}^{-2}.\text{d}^{-1}$
$NutLimVB(i)$	$NutLimVB(i)$	nutrient limitation factor for growth (≤ 1.0)	-
-	$VB(i)ha$ $VB(i)Aha$	vegetation biomass density attainable vegetation biomass density	tC.ha^{-1} tC.ha^{-1}
-	$VB(i)Navail$ $VB(i)Pavail$	available nutrient N within rooting depth available nutrient P within rooting depth	gN.m^{-2} gP.m^{-2}

Name in formulas ¹	Name in output ¹	Definition ²	Units
	$VB(i)Savail$	available nutrient S within rooting depth	gS.m^{-2}
-			-
SWVB(i)Dec	$SWVB(i)Dec$	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⁾ $(i)=01\text{--}09$ is the vegetation cohort number; $j=1\text{--}5$ is the biomass compartment number.

²⁾ Vegetation biomass compartments are 1=stems, 2=foliage, 3=branches, 4=roots and 5=fine roots.

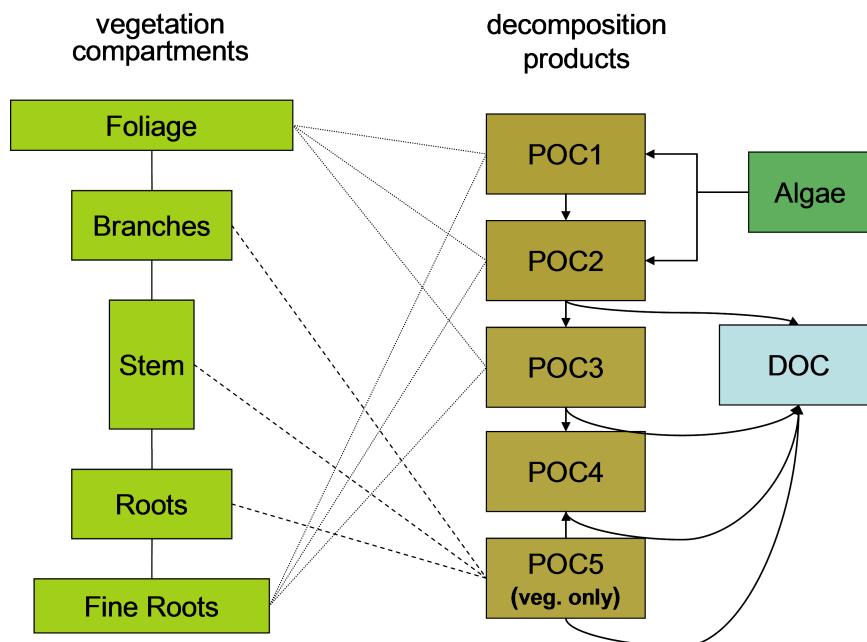


Figure 4.4: Interactions between the compartments of a vegetation cohort (left side, green) and the detritus fractions POC1–5/DOC in the model (particulate fractions brown, dissolved fraction blue). Similar schemes apply to PON1–5/DON, POP1–5/DOP and POS1–5/DOS.

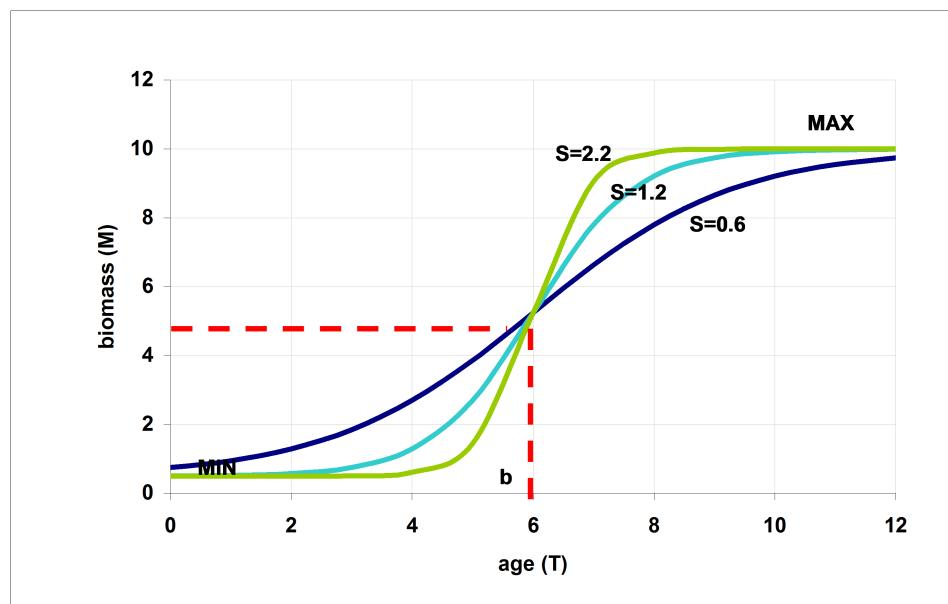


Figure 4.5: The growth curve of a vegetation cohort (y -axis) as a function of it's age is a function of 4-parameters: minimum biomass (MIN), maximum target biomass (MAX), cohort age where 50 % of maximum biomass is achieved (b) and a factor indicating how 'smooth' the growth curve is (s).

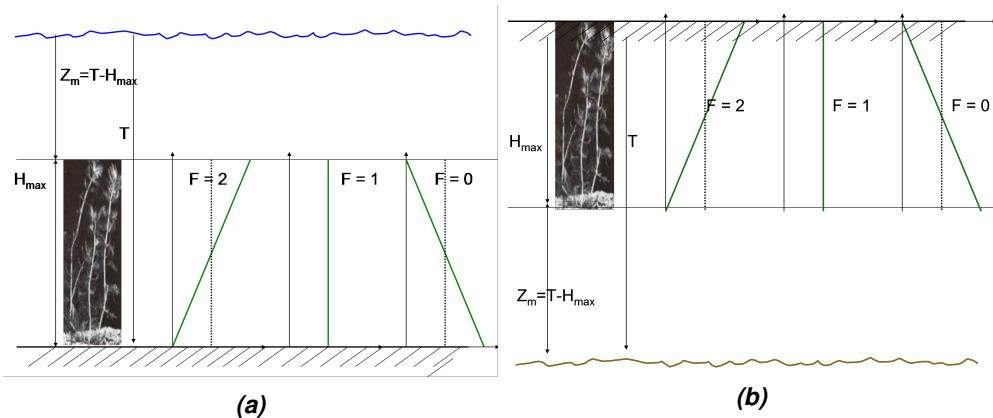


Figure 4.6: The effect of shape constant $F_s(F)$ on the distribution of vegetation biomass above the sediment (a) and vegetation biomass in the sediment (b). The symbols used are explained in the text ($T = H_t$).

5 Light regime

Contents

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5.1 Light intensity in the water column

PROCESS: CALCRAD, CALCRAADDAY, CALCRAD_UV

Due to extinction the light intensity in the water column is reduced compared to the intensity at the water surface. The light intensity is an exponential attenuation function of depth times the total extinction coefficient according to the law of Lambert-Beer. This holds for visible light as well as UV light, but with different extinction coefficients. Total visible light or photoactive radiation (PAR) is used to determine the growth rates of phytoplankton, microphytobenthos and submerged macrophytes. UV light is used to determine the mortality rate of bacterial pollutants.

The total extinction coefficient is calculated by processes Extinc_VLG and Extinc_UVG and contains contributions of algae biomass, particulate organic detritus, dissolved organic matter, suspended inorganic matter, submerged macrophytes and water itself.

Implementation

Processes CALCRAD and CALCRAADDAY deliver the intensity of total visible light (solar radiation) at the top and the bottom of the water and sediment layers in the model. Process CALCRAD_UV does the same for UV light. CALCRAD and CALCRAD_UV may deliver the daily average light intensity as well as the actual light intensity as it varies over the day. CALCRAADDAY produces the actual light intensity as it varies over the day from daily average input, and needs to be combined with additional process DAYRAD. 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.

Tables 5.1 to 5.6 provide the definitions of the parameters occurring in the user-defined input and output parameters.

Formulation

The light intensities at the top or bottom of a water layer or compartment follow from:

$$\begin{aligned} I_{top_1} &= I_s \\ I_{top_i} &= I_{bot_{i-1}} \\ I_{bot_i} &= I_{top_i} \times e^{(-et_i \times H_i)} \end{aligned}$$

with:

et	total extinction coefficient [m^{-1}]
H	thickness of the water layer [m]
I_s	light intensity at the water surface, just below the surface [$W.m^{-2}$]
I_{top}	light intensity at the top of a water layer [$W.m^{-2}$]
I_{bot}	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:

$$I_{bot_i} = a \times I_{top_i} \times e^{(-et_i \times H_i)}$$

with:

a	amplification factor due to scattering by sediment particles [-]
H	thickness of a sediment layer [m]
I_{top}	light intensity at the top of a sediment layer [$\text{W} \cdot \text{m}^{-2}$]
I_{bot}	light intensity at the bottom of a sediment layer [$\text{W} \cdot \text{m}^{-2}$]
i	index for sediment layer [-]

I_{top} at the sediment-water interface is equal to I_{bot} of the lower water layer.

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 corrected for reflection.
- ◊ Rad_UV is derived from RadSurf , when process CALCRAD_UV is active. Alternatively it can be imposed as input parameter, but this is only applicable for a model with one water layer. Process BACMORT converts Rad_UV into UV light intensity.
- ◊ Unattenuated solar radiation as visible light yields 100–500 $\text{W} \cdot \text{m}^{-2}$ at altitudes around 50 °. Always make sure that the light input (observed solar radiation) is consistent with the light related parameters of the primary producer modules used. If data are expressed in units PAR (photosynthetic active radiation), and the model is based on total visible light, the PAR data need to be converted by dividing with 0.45 (the photosynthetic fraction of the visible wave length spectrum). The radiation data should be corrected for cloudiness and sometimes also for reflection (approximately 10 %).
- ◊ Phytoplankton module BLOOM uses the daily average radiation. In its standard setting it uses total visible light and carries out corrections for both reflection and photo-synthetic fraction. DYNAMO may use the daily average radiation or the actual radiation varying over the day. The latter is delivered by process DAYRAD, which is used in addition to process CALCRADDAY. This process is used instead of or in parallel with process CALCRAD.

Additional references

[WL | Delft Hydraulics \(1991a\)](#)

Table 5.1: 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 sed. particles	-
et	$ExtVl$	total extinction coefficient of vivible light	m^{-1}
Is	$Radsurf$	light intensity at water surface	$\text{W} \cdot \text{m}^{-2}$
z_1	$Depth$	thickness of a water or sediment layer	m

Table 5.2: Definitions of the output parameters for CALCRAAD.

Name in formulas	Name in output	Definition	Units
I_{top}	Rad	light intensity at the top of a water or sediment layer	W.m^{-2}
I_{bot}	$RadBot$	light intensity at the bottom of a water or sediment layer	W.m^{-2}

Table 5.3: Definitions of the input parameters in the formulations for CALCRAADDAY.

Name in formulas	Name in output	Definition	Units
a	a_enh	amplification factor due to scattering by sed. particles	-
et	$ExtVI$	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

Table 5.4: Table IV Definitions of the output parameters for CALCRAADDAY.

Name in formulas	Name in output	Definition	Units
I_{top}	$DayRad$	light intensity at the top of a water or sediment layer	W.m^{-2}
I_{bot}	$DayRadBot$	light intensity at the bottom of a water or sediment layer	W.m^{-2}

Table 5.5: Definitions of the input parameters in the formulations for CALCRAD_UV.

Name in formulas	Name in output	Definition	Units
a	a_enh	amplification factor due to scattering by sed. particles	-
et	$ExtUv$	total extinction coefficient of UV light	m^{-1}
Is	$Radsurf$	light intensity at the water surface	W.m^{-2}
H	$Depth$	thickness of a water or sediment layer	m

Table 5.6: Definitions of the output parameters for CALCRAD_UV.

Name in formulas	Name in output	Definition	Units
I_{top}	Rad_Uv^1	light intensity at the top of a water or sediment layer	$W.m^{-2}$
I_{bot}	$RadBot_Uv^1$	light intensity at the bottom of a water or sediment layer	$W.m^{-2}$

¹Total visible light or PAR as based on UV extinction!

5.2 Extinction coefficient of the water column

PROCESS: EXTINC_VLG, EXTINABVLP (EXTINABVL), EXTPhDVL, EXTINC_UVG,
EXTINABUVP (EXTINABUV), EXTPHDUV

Primary producers like algae use a certain fraction of the visible light for assimilation. The various algae modules account for this fraction in light limitation functions and light production efficiency functions. These functions use the intensity of visible light as an input parameter.

Due to extinction the light intensity in the water column is reduced compared to the intensity at the water surface. The light intensity is an exponential attenuation function of depth times the extinction coefficient according to the law of Lambert-Beer. All light absorbing substances in particulate or dissolved form contribute to the extinction coefficient in a linear way. This includes algae biomass, suspended and dissolved organic matter (detritus), suspended inorganic matter, water itself and all remaining dissolved substances.

Most of the substances that contribute to the extinction coefficient can be modelled. The contributions of these substances are calculated on the basis of concentrations and specific extinction coefficients. Water and the remaining substances contribute in the form of a background extinction coefficient. Dissolved fulvic and humic acids may be modelled as substances *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 may be delivered by 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 matter 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 \(1991\)](#). Such a relation has been incorporated in process Extinc_VLG.

Apart of the processes for the extinction coefficient of visible light similar processes are available for the extinction coefficient of UV-light, which is relevant for the modelling of bacterial pollutants.

Processes Extinc_VLG and Extinc_UVG may apply an alternative advanced submodel of the extinction coefficient called UITZICHT. This submodel takes the optical properties of a water column into account. Given the advanced features of UITZICHT this module is not (yet) described in this manual. The user is referred to [Rijkswaterstaat/RIKZ \(1990\)](#) for background and details.

Implementation

The total extinction coefficient of visible light for the water column is delivered by three processes the names of which depend on the algae module selected. Process Extinc_VLG provides the total extinction coefficient of visible light, for which ExtinaBVLP (ExtinaBVL) or ExtPhDVL deliver the partial phytoplankton biomass extinction coefficient for BLOOM or for DYNAMO. Processes Extinc_UVG, ExtinaBUVP (ExtinaBUV), ExtPhDUV provide similar coefficients for UV light. The processes do not deliver process rates and, therefore, do not affect

mass balances.

Processes ExtinaBVLP (ExtinaBVL) and ExtinaBUVP (ExtinaBUV) have been implemented for the BLOOM algae:

- ◊ BLOOMALG01 - BLOOMALG30.

Processes ExtPhDVL and ExtPhDUV have been implemented for the DYNAMO algae:

- ◊ Diat and Green.

Processes Extinc_VLG and Extinc_UVG add the partial extinction coefficients, and have been implemented for substances:

- ◊ IM1, IM2, IM3, POC1, POC2, POC3, POC4, DOC and Salinity.

The auxiliary process UITZICHT is incorporated in this process, but it is inactivated unless specific input is provided.

All processes have been implemented in a generic way and therefore cover water as well sediment layers.

Tables 5.7 to 5.10 provide the definitions of the input parameters and the output parameters for visible light. Tables 5.11 to 5.14 provide the same for UV light.

Formulation

Two methods are available to compute the total and partial extinction coefficients.

For $SW_Uitz = 0.0$ (UITZICHT not applied) the total extinction coefficient of visible light or UV light is calculated as the sum of seven partial extinction coefficients:

$$et = eat + emt + ept + edt + est + eot + eb$$

where:

eat	partial extinction coefficient of algae biomass [m^{-1}]
eb	background extinction coefficient [m^{-1}]
edt	partial extinction coefficient of dissolved organic matter [m^{-1}]
ept	partial extinction coefficient of particulate detritus [m^{-1}]
emt	partial extinction coefficient of macrophytes [m^{-1}]
est	partial extinction coefficient of suspended inorganic matter [m^{-1}]
eot	partial extinction coefficient of other substances as a function of salinity [m^{-1}]
et	partial extinction coefficient [m^{-1}]

The background extinction coefficient and the partial extinction coefficient of macrophytes are

input parameters. The other contributions are determined according to:

$$\begin{aligned} eat &= \sum_{i=1}^n (ea_i \times Calg_i) \\ ept &= \sum_{j=1}^m (ep_j \times Cdet_j) \\ edt &= ed \times Cdoc \\ est &= \sum_{k=1}^3 (es_k \times Cim_k) \\ eot &= eo \times (1 - SAL/SALmax) \end{aligned}$$

where:

$Calg_i$	biomass concentration of algae species group i [gC.m ⁻³]
$Cdet_j$	concentration of detritus component j [gC.m ⁻³]
Cim_k	concentration of suspended inorganic matter fraction k [gC.m ⁻³]
ea	specific extinction coefficient of an algae species type [m ² .gC ⁻¹]
ed	specific extinction coefficient of dissolved organic carbon [m ² .gC ⁻¹]
eo	spec. ext. coefficient of other substances based on relative salinity [m ⁻¹]
ep	specific extinction coefficient of a particulate detritus component [m ² .gC ⁻¹]
es	spec. ext. coefficient of a suspended inorganic matter fraction [m ² .gDM ⁻¹]
SAL	actual salinity ([g.kg ⁻¹] ≈ [g.l ⁻¹])
$SALmax$	maximal salinity ([g.kg ⁻¹] ≈ [g.l ⁻¹])
i	index for algae species [-]
j	index for detritus components [-]
k	index for suspended inorganic matter fractions [-]
n	number for algae species, =30 for BLOOM, = 2 for DYNAMO [-]
m	number of detritus components, =4 for POX [-]

Besides to the total extinction coefficient the processes deliver the partial extinction coefficients of algae biomass, particulate detritus, dissolved organic matter and suspended inorganic matter.

For $SW_Uitz = 1.0$ the auxiliary process UITZICHT (Rijkswaterstaat, 1990) is applied for the calculation of the extinction coefficients based on a background extinction and the concentrations of (in)organic suspended matter, chlorophyll and dissolved organic matter (fulvic and humic acids).

Directives for use

- ◊ BLOOM corrects the visible light intensity (irradiation) for the fraction light that can be used by algae (45 %). Often available irradiation data are expressed in [J.cm⁻².week⁻¹] (PAR or TotalRAD). Notice that irradiation has to 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 .
- ◊ The user must make sure that the form of the regression equation used for eot meets the formulation in the model. An indicative equation provided by [Rijkswaterstaat/RIKZ \(1991\)](#) for the Eastern Scheldt in the Netherlands is $0.005 \times (19.4 - SAL/1.8)$ at a background extinction coefficient of 0.06 (version corrected in 2002). This function is equivalent to $0.079 \times (1.0 - SAL/SALmax)$. If salinity dependent extinction is applied, make sure there is no double counting due to simulated DOC.

- ◊ UITZICHT is applied when $SW_Uitz = 1.0$. In that case a number of additional input parameters are needed.
- ◊ For the application of the extinction processes for UV light make shure that the light intensity is calculated as UV light, and specify the specific extinction coefficients for UV light.

Table 5.7: Definitions of the input parameters in the formulations for Extinc_VLG.

Name in formulas	Name in input	Definition	Units
Cim_1	$IM1$	conc. of inorg. susp. matter fraction 1	$\text{gDM} \cdot \text{m}^{-3}$
Cim_2	$IM2$	conc. of inorg. susp. matter fraction 2	$\text{gDM} \cdot \text{m}^{-3}$
Cim_3	$IM3$	conc. of inorg. susp. matter fraction 3	$\text{gDM} \cdot \text{m}^{-3}$
$Cpoc_1$	$POC1$	concentration of fast dec. part. detritus	$\text{gC} \cdot \text{m}^{-3}$
$Cpoc_2$	$POC2$	conc. of medium dec. part. detritus	$\text{gC} \cdot \text{m}^{-3}$
$Cpoc_3$	$POC3$	concentration of slow dec. part. detritus	$\text{gC} \cdot \text{m}^{-3}$
$Cpoc_4$	$POC4$	concentration of refractory part. detritus	$\text{gC} \cdot \text{m}^{-3}$
$Cdoc$	DOC	concentration of dissolved organic carbon	$\text{gC} \cdot \text{m}^{-3}$
SAL	$Salinity$	actual salinity	$\text{psu}(\text{g} \cdot \text{kg}^{-1})$
eat	$ExtVlPhyt$	partial ext. coeff. of algae biomass	m^{-1}
eb	$ExtVlBak$	background extinction coefficient	m^{-1}
ep_1	$ExtVlPOC1$	specific ext. coefficient of detritus POC1	$\text{m}^2 \cdot \text{gC}^{-1}$
ep_2	$ExtVlPOC2$	specific ext. coefficient of detritus POC2	$\text{m}^2 \cdot \text{gC}^{-1}$
ep_3	$ExtVlPOC3$	specific ext. coefficient of detritus POC3	$\text{m}^2 \cdot \text{gC}^{-1}$
ep_4	$ExtVlPOC4$	specific ext. coefficient of detritus POC4	$\text{m}^2 \cdot \text{gC}^{-1}$
ed	$ExtVlDOC$	specific ext. coeff. of diss. detritus DOC	$\text{m}^2 \cdot \text{gC}^{-1}$
emt	$ExtVlMacro$	partial ext. coefficient of macrophytes	m^{-1}
eo	$ExtVlSal0$	spec. ext. coeff. other subst. based on rel. salinity	m^{-1}
es_1	$ExtVlIM1$	spec. ext. coefficient of inorg. matter IM1	$\text{m}^2 \cdot \text{gDM}^{-1}$
es_2	$ExtVlIM2$	spec. ext. coefficient of inorg. matter IM2	$\text{m}^2 \cdot \text{gDM}^{-1}$
es_3	$ExtVlIM3$	spec. ext. coefficient of inorg. matter IM3	$\text{m}^2 \cdot \text{gDM}^{-1}$
$SALmax$	$SalExt0$	maximal salinity	$\text{psu}(\text{g} \cdot \text{kg}^{-1})$
SW_Uitz	Sw_Uitz^1	option parameter: if 0.0 no UITZICHT (default), if 1.0 UITZICHT is applied	-
-	$UitzDEPT1^1$	diepte Z1	m
-	$UitzDEPT2^1$	diepte Z2	m
-	$UitzCorCH^1$	correctiefactor	-
-	$UitzC_Det^1$	coeff. C3 absorp. by glowing dried matter and detritus	-
-	$UitzC_GL1^1$	coeff. C1 atten. by glowing dried matter and detritus	-
-	$UitzC_GL2^1$	coeff. C2 atten. by glowing dried matter and detritus	nm^{-1}
-	$UitzHelHM^1$	constant for the spectre	-
-	$UitzTau^1$	constant for calc. of the visibility depth	-
-	$UitzAngle^1$	angle of incidence of solar radiation	degrees
-	$DMCFDetC^1$	dry matter conversion factor for detritus	$\text{gDM} \cdot \text{gC}^{-1}$

¹Only concern alternative calculation method according to UITZICHT.

Table 5.8: Definitions of the input parameters in the formulations for ExtinaBVLP (ExtinaBVL) for BLOOM algae.

Name in formulas	Name in input ¹	Definition	Units
$Calg_i$	$BLOOMALG(i)$	biomass concentration of algae species type i	gC.m^{-3}
ea_i	$ExtVlAlg(i)$	algae species type specific extinction coefficient	$\text{m}^2.\text{gC}^{-1}$
n –	$NAlgBloom^2$ $SW_fixin_y^2$	number of algae species groups = 30 indicator for algae species attached to the sediment = 1	- -
–	$Volume^3$	volume of water compartment or sediment layer	m^3
–	$FixAlg(i)^3$	identifier for pairs of algae types attaching to sediment (0 = not applying, > 0 = suspended, < 0 = attached)	-

¹(i) indicates algae species types 1–30.

²Default values are fixed and must not be changed because they refer to additional input $FixAlg(i)$.

³Parameters are added for conversion of biomass of algae attached to the sediment from $[\text{gC.m}^{-2}]$ to $[\text{gC.m}^{-3}]$.

Table 5.9: Definitions of the input parameters in the formulations for ExtPhDVL.

Name in formulas	Name in input	Definition	Units
$Calg_1$ $Calg_2$	$Diat$ $Green$	biomass concentration of diatoms biomass concentration of green algae	gC.m^{-3} gC.m^{-3}
ea_1 ea_2	$ExtVlDiat$ $ExtVlGreen$	specific ext. coefficient for diatoms specific ext. coefficient for green algae	$\text{m}^2.\text{gC}^{-1}$ $\text{m}^2.\text{gC}^{-1}$
n –	$NAlgDynamo^1$ SW_fixin_y1	number of algae species groups = 2 indicator for algae species attached to the sediment = 0	- -
–	$Volume$	volume of water compartment or sediment layer	m^3

¹The default values are fixed and must not be changed!

Table 5.10: Definitions of the output parameters for *Extinc_VLG*, *ExtinaBVLP* (*Extin-aBVL*), *ExtPhDVL*.

Name in formulas	Name in output ¹	Definition	Units
<i>eat</i>	<i>ExtVlPhyt</i>	partial ext. coefficient of algae biomass	m^{-1}
<i>edt</i>	<i>ExtVlODS</i>	partial ext. coeff. of dissolved org. matter	m^{-1}
<i>ept</i>	<i>ExtVlOSS</i>	partial ext. coefficient of part. detritus	m^{-1}
<i>est</i>	<i>ExtVlISS</i>	partial ext. coeff. of susp. inorg. matter	m^{-1}
<i>et</i>	<i>ExtVl</i>	total extinction coefficient	m^{-1}

¹Notice that the partial extinction coefficients *ExtVlBak* and *ExtVlMacro* are input parameters

Table 5.11: Definitions of the input parameters in the formulations for Extinc_UVG.

Name in formulas	Name in input	Definition	Units
Cim_1	$IM1$	conc. of inorg. susp. matter fraction 1	$\text{gDM} \cdot \text{m}^{-3}$
Cim_2	$IM2$	conc. of inorg. susp. matter fraction 2	$\text{gDM} \cdot \text{m}^{-3}$
Cim_3	$IM3$	conc. of inorg. susp. matter fraction 3	$\text{gDM} \cdot \text{m}^{-3}$
$Cpoc_1$	$POC1$	concentration of fast dec. part. detritus	$\text{gC} \cdot \text{m}^{-3}$
$Cpoc_2$	$POC2$	conc. of medium dec. part. detritus	$\text{gC} \cdot \text{m}^{-3}$
$Cpoc_3$	$POC3$	concentration of slow dec. part. detritus	$\text{gC} \cdot \text{m}^{-3}$
$Cpoc_4$	$POC4$	concentration of refractory part. detritus	$\text{gC} \cdot \text{m}^{-3}$
$Cdoc$	DOC	concentration of dissolved organic carbon	$\text{gC} \cdot \text{m}^{-3}$
SAL	$Salinity$	actual salinity	$\text{psu(g.kg}^{-1}\text{)}$
eat	$ExtUvPhyt$	partial ext. coeff. of algae biomass	m^{-1}
eb	$ExtUvBak$	background extinction coefficient	m^{-1}
ep_1	$ExtUvPOC1$	specific ext. coefficient of detritus POC1	$\text{m}^2 \cdot \text{gC}^{-1}$
ep_2	$ExtUvPOC2$	specific ext. coefficient of detritus POC2	$\text{m}^2 \cdot \text{gC}^{-1}$
ep_3	$ExtUvPOC3$	specific ext. coefficient of detritus POC3	$\text{m}^2 \cdot \text{gC}^{-1}$
ep_4	$ExtUvPOC4$	specific ext. coefficient of detritus POC4	$\text{m}^2 \cdot \text{gC}^{-1}$
ed	$ExtUvDOC$	specific ext. coeff. of diss. detritus DOC	$\text{m}^2 \cdot \text{gC}^{-1}$
emt	$ExtUvMacro$	partial ext. coefficient of macrophytes	m^{-1}
eo	$ExtUvSal0$	spec. ext. coeff. other subst. based on rel. salinity	m^{-1}
es_1	$ExtUvIM1$	spec. ext. coefficient of inorg. matter IM1	$\text{m}^2 \cdot \text{gDM}^{-1}$
es_2	$ExtUvIM2$	spec. ext. coefficient of inorg. matter IM2	$\text{m}^2 \cdot \text{gDM}^{-1}$
es_3	$ExtUvIM3$	spec. ext. coefficient of inorg. matter IM3	$\text{m}^2 \cdot \text{gDM}^{-1}$
$SALmax$	$SalExt0$	maximal salinity	$\text{psu(g.kg}^{-1}\text{)}$
SW_Uitz	Sw_Uitz^1	option parameter: if 0.0 no UITZICHT (default), if 1.0 UITZICHT is applied	-
-	$UitzDEPT1^1$	diepte Z1	m
-	$UitzDEPT2^1$	diepte Z2	m
-	$UitzCorCH^1$	correctiefactor	-
-	$UitzC_Det^1$	coeff. C3 absorp. by glowing dried matter and detritus	-
-	$UitzC_GL1^1$	coeff. C1 atten. by glowing dried matter and detritus	-
-	$UitzC_GL2^1$	coeff. C2 atten. by glowing dried matter and detritus	nm^{-1}
-	$UitzHelHM^1$	constant for the spectre	-
-	$UitzTau^1$	constant for calc. of the visibility depth	-
-	$UitzAngle^1$	angle of incidence of solar radiation	degrees
-	$DMCFDetC^1$	dry matter conversion factor for detritus	$\text{gDM} \cdot \text{gC}^{-1}$

¹Only concern alternative calculation method according to UITZICHT.

Table 5.12: Definitions of the input parameters in the formulations for ExtinaBUVP (*ExtinaBUV*) for BLOOM algae.

Name in formulas	Name in input ¹	Definition	Units
$Calg_i$	$BLOOMALG(i)$	biomass concentration of algae species type i	gC.m^{-3}
ea_i	$ExtUvAlg(i)$	algae species type specific extinction coefficient	$\text{m}^2.\text{gC}^{-1}$
n –	$NAlgBloom^2$ $SW_fixin_y^2$	number of algae species groups = 30 indicator for algae species attached to the sediment = 1	- -
–	$Volume^3$	volume of water compartment or sediment layer	m^3
–	$FixAlg(i)^3$	identifier for pairs of algae types attaching to sediment (0 = not applying, > 0 = suspended, < 0 = attached)	-

¹(i) indicates algae species types 1–30.

²Default values are fixed and must not be changed because they refer to additional input $FixAlg(i)$.

³Parameters are added for conversion of biomass of algae attached to the sediment from $[\text{gC.m}^{-2}]$ to $[\text{gC.m}^{-3}]$.

Table 5.13: Definitions of the input parameters in the formulations for ExtPhDUV.

Name in formulas	Name in input	Definition	Units
$Calg_1$ $Calg_2$	$Diat$ $Green$	biomass concentration of diatoms biomass concentration of green algae	gC.m^{-3} gC.m^{-3}
ea_1 ea_2	$ExtUvDiat$ $ExtUvGreen$	specific ext. coefficient for diatoms specific ext. coefficient for green algae	$\text{m}^2.\text{gC}^{-1}$ $\text{m}^2.\text{gC}^{-1}$
n –	$NAlgDynamo^1$ SW_fixin_y1	number of algae species groups = 2 indicator for algae species attached to the sediment = 0	- -
–	$Volume$	volume of water compartment or sediment layer	m^3

¹The default values are fixed and must not be changed!

Table 5.14: Definitions of the output parameters for *Extinc_UVG*, *ExtinaBUVP* (*ExtinaBUV*), *ExtPhDUV*.

Name in formulas	Name in output ¹	Definition	Units
<i>eat</i>	<i>ExtUvPhyt</i>	partial ext. coefficient of algae biomass	m^{-1}
<i>edt</i>	<i>ExtUvODS</i>	partial ext. coeff. of dissolved org. matter	m^{-1}
<i>ept</i>	<i>ExtUvOSS</i>	partial ext. coefficient of part. detritus	m^{-1}
<i>est</i>	<i>ExtUvISS</i>	partial ext. coeff. of susp. inorg. matter	m^{-1}
<i>et</i>	<i>ExtUv</i>	total extinction coefficient	m^{-1}

¹Notice that the partial extinction coefficients *ExtUvBak* and *ExtUvMacro* are input parameters

5.3 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.

Tables 5.15 and 5.16 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 :

$$E_t = \frac{I_0}{\pi} \frac{\bar{R}^2}{R^2} (\sin \delta \sin \phi + \cos \delta \cos \phi \cos \omega)$$

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:

$$d = \left(\frac{ITIME}{86400} - Refday \right)$$

$$h = ITIME - \text{int}(Refday) \times 86400 - \frac{Reftime}{3600}$$

$$\phi = \frac{\text{Latitude}}{360} \times 2\pi$$

where:

<i>ITIME</i>	DELWAQ time [scu]
<i>Latitude</i>	latitude of area of interest [degrees]
<i>RefDay</i>	day at start of the simulation [d]
<i>Reftime</i>	time 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 E_t 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.

References

Velds (1992)

Table 5.15: 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}
$Latitude$ $Refday$	$Latitude$ $Refday$	thickness of a water or sediment layer time at the start of the simulation	degrees -

Table 5.16: 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}

5.4 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 5.1.

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 $Tmp > 1.0$

$$DayL = 0.0 \quad (5.1)$$

If $Tmp < -1.0$

$$DayL = 1.0 \quad (5.2)$$

Else

$$DayL = 7.639437268 \times \arccos(Tmp) / 24 \quad (5.3)$$

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 at start of the simulation [d]
DayL	daylength (fraction of a day - sunrise to sunset) [-]
Tmp	temporarily variable for calculation [d]

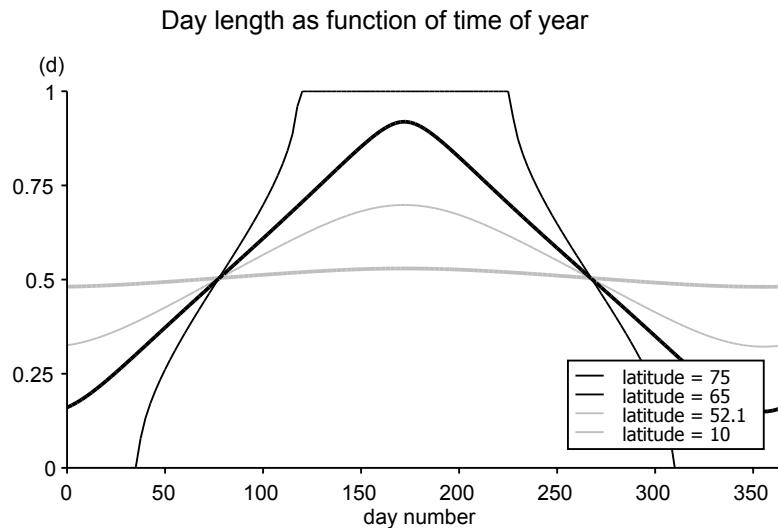


Figure 5.1: Day length calculated by the module DAYL for the latitudes 10° , 52.1° , 65° and 75° . The latitude of 52.1° refers to De Bilt, The Netherlands

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 reference day (input item RefDay) enables you to tell the day length module the actual day number at the start of a calculation. E.g. when a run starts at the first of April, the variable RefDay should be set to 91.

Additional references

[Velds \(1992\)](#)

5.5 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 optical properties of a water column into account. Given the advanced features of UITZICHT this module is not (yet) described in this manual. The user is referred to ([Rijkswaterstaat/RIKZ, 1990](#)) for background and details.

Implementation

The auxiliary process SECCHI has been implemented for the following substances:

- ◊ IM1, IM2, IM3, POC1, POC2, POC3, POC4.

Tabel 5.17 provides the definitions of the parameters occurring in the formulations.

Formulation

Two methods are available to compute the Secchi depth.

For $SW_Uitz = 0.0$ (UITZICHT not applied) the Poole-Atkins relation is applied:

$$SD = \frac{a_{pa}}{et}$$

where:

a_{pa}	Poole-Atkins constant (1.7-1.9) [-]
et	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).

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 organic matter) calculated by process $ExtincV LG$ and $Chlfa$ calculated by the active phytoplankton module.

Table 5.17: 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}	<i>PAConstant</i>	Poole-Atkins constant	-
et	<i>ExtVl</i>	total extinction coefficient	m^{-1}
SW_Uitz	<i>Sw_Uitz</i>	option parameter: if 0.0 no UITZICHT (default), if 1.0 UITZICHT is applied	-

6 Primary consumers

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6.1 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 \(1990, 1992c\); Van der 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 ($(i)FrDetBot = 1$).

CONSL 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.).

CONSL has been implemented for the following substances:

for BLOOM,

- ◊ ALGC, ALGN, ALGP, ALGSi, BLOOMALG01-BLOOMALG30, POC1, PON1, POP1, OPAL, DETCS1, DETNS1, DETPS1, DETSiS1, NH4, NO3, PO4, Si, OXY, TIC and ALKA

for DYNAMO,

- ◊ GREEN, DIAT, POC1, PON1, POP1, OPAL, DETCS1, DETNS1, DETPS1, DETSiS1, NH4, NO3, PO4, Si, OXY, TIC and ALKA

Sulphur is not considered by CONSL.

Tables 6.1 and 6.2 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 division 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 $Cgri2_i \geq Cgr1_i$,

$$Cgrc_i = Cgr1_i \times (1 + kgr_i \times \Delta t)$$

$$\begin{aligned} Cgr2_i &= Cgrc_i && \text{if } Cgri2_i > Cgrc_i \\ Cgr2_i &= Cgri2_i && \text{if } Cgri2_i \leq Cgrc_i \end{aligned}$$

$$kgr_i = kgr_i^{20} \times e^{ktgr_i \times (T-20)}$$

when $Cgri2_i < Cgr1_i$,

$$Cgrc_i = Cgr1_i \times (1 - kmrt_i \times \Delta t)$$

$$\begin{aligned} Cgr2_i &= Cgrc_i && \text{if } Cgri2_i < Cgrc_i \\ Cgr2_i &= Cgri2_i && \text{if } Cgri2_i \geq Cgrc_i \end{aligned}$$

$$kmrt_i = kmrt_i^{20} \times e^{ktgr_i \times (T-20)}$$

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 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 concentration 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:

$$Cfdc_i \quad \text{critical concentration of food for grazer group } i \text{ [gC m}^{-3}\text{]}$$

The consumption process rate is equal to either the filtration or the uptake rate according to:

$$\begin{aligned} kcns_i &= kfil_i && \text{if } Cfdi < Cfdci \\ kcns_i &= kup_i && \text{if } Cfdi \geq Cfdci \end{aligned}$$

with:

$$kcns_i \quad \text{consumption process rate of grazer group } i [\text{d}^{-1}]$$

So far, all rates are referring to organic carbon as a nutrient to grazers. Since the nutrient stoichiometry 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:

$anut_{k,j}$	stoichiometric 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, respiration 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 [-]
$fsed_i$	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 $^{-1}$]

$$Rdcns2_{k,i} \text{ net cons. rate of grazer group } i \text{ for nutrient } k \text{ in detritus [gC/N/P/Si m}^{-3} \text{ d}^{-1}]$$

$$Rsdpr1_{k,i} \text{ total nutrient } k \text{ in detr. prod. at the sediment for all grazers [gC/N/P/Si m}^{-3} \text{ d}^{-1}]$$

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 stoichiometries 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:

$bnut_{k,i}$	stoichiometric const. of nutr. k over org. carbon in grazer i [gC/N/P/Si gC $^{-1}$]
$Cgr1_i$	graizer 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 graizer i [gC/N/P/Si m $^{-3} \text{ d}^{-1}$]
$Rrsp1_{k,i}$	growth respiration rate for nutrient k and graizer i [gC/N/P/Si m $^{-3} \text{ d}^{-1}$]
$Rrsp2_{k,i}$	maintenance respiration rate for nutrient k and graizer i [gC/N/P/Si m $^{-3} \text{ d}^{-1}$]
$Ras2_{k,i}$	actual nutrient k in food ass. rate for graizer group i [gC/N/P/Si m $^{-3} \text{ d}^{-1}$],
$Ras3_{k,i}$	actual nutrient k in food ass. rate for graizer group i [gC/N/P/Si m $^{-3} \text{ d}^{-1}$], diminished with growth respiration

6. Correction of graizer biomass for the food constraint

Grazers can not assimilate more food than is available. The food that is available to a graizer group on a daily basis is equal to $Ras3_{1,i}$. Consequently, the net growth rate of a graizer group should not exceed the actual food assimilation rate. If the imposed graizer biomass at t_2 is larger than supported by food assimilation, it must be diminished in order to meet the food constraint. The corrected graizer biomass $Cgr2_{1,i}$ 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:

$$Ras_{k,i} = bnut_{k,i} \times Rgr_i$$

$$Rdcns_{k,i} = Rdcns2_{k,i} + (1 - f_{sed_i}) \times (Ras3_{k,i} - Ras_{k,i})$$

$$Rsdpr_{k,i} = Rsdpr2_{k,i} + f_{sed_i} \times (Ras3_{k,i} - Ras_{k,i})$$

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:

$$Racns_{k,j} = \sum_{i=1}^n (Racns_{k,i,j})$$

$$Rtacns_k = \sum_{j=1}^m (Racns_{k,j})$$

$$\begin{aligned}
 Rtask &= \sum_{i=1}^n (Ras_{k,i}) \\
 Rtdcns_k &= \sum_{i=1}^n (Rdcns_{k,i}) \\
 Rtsdpr_k &= \sum_{i=1}^n (Rsdpr_{k,i}) \\
 Rtrsp_k &= \sum_{i=1}^n (Rrsp_{k,i})
 \end{aligned}$$

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 $^{-1}$]
$Rtask$	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 nutrients, 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:

$$fs_i \quad \text{scaling factor for the biomass of grazer group } i \text{ [-]}$$

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 process 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.
- ◊ 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 weight 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 \(1997c\)](#), [Scholten and Van der Tol \(1994\)](#),

Table 6.1: 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	$gN\ gC^{-1}$
$anut_{2,j}$	$NCRAlg(j)$	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	$gP\ gC^{-1}$
$anut_{3,j}$	$PCRAlg(j)$	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	$gSi\ gC^{-1}$
$anut_{4,j}$	$SCRAlg(j)$	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)	$gC\ m^{-3}$

continued on next page

Table 6.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
$Calg2$	$Diat$	biomass concentration of diatoms (DY-NAMO)	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 ($1=\text{g m}^{-2}$, $0=\text{g m}^{-3}$)	-
T	$Temp$	water temperature	$^{\circ}\text{C}$
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}
$bnut_{2,i}$	(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)GRZSTS i	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 (DY-NAMO)	-
$fapr_{i,j}$	(i)ALGPR(j)	preference of grazer i for BLOOM algae group j	-
$fdpr_i$	(i)DET i	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	-
$falg_{i,j}$	(i)ALGFF(j)	egested fraction of algae j consumed by grazer i	-
$fdet_i$	(i)DETFF	egested fraction of detritus consumed by grazer i	-
$fsedi$	(i)FrDetBot	fr. of produced detr. by grazer i to sediment detr. pool	-

continued on next page

Table 6.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
f_{si}	(i)GRZML	scaling factor for the biomass of grazer i	-
$frsp1^{20}_i$	(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}
$krsp2^{20}_i$	(i)GRZSE	maintenance respiration rate for grazer i at 20 °C	d^{-1}
Ksf_{di}	(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	${}^\circ C^{-1}$
$ktgr$	(i)TMPPGM	temperature coefficient of growth for grazer i	${}^\circ C^{-1}$
$ktmrt$	(i)TMPPMM	temperature coefficient of mortality for grazer i	${}^\circ C^{-1}$
$ktrsp1$	(i)TMPRE	temperature coeff. of growth respiration for grazer i	${}^\circ C^{-1}$
$ktrsp2$	(i)TMPSE	temperature coeff. of maintenance resp. for grazer i	${}^\circ C^{-1}$
$ktup$	(i)TMPPRM	temperature coefficient of uptake for grazer i	${}^\circ C-1$

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.

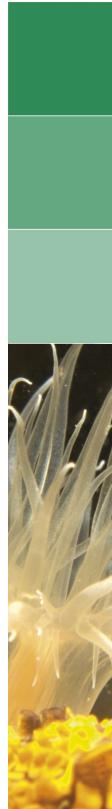
Table 6.2: Definitions of the output parameters for CONSBL.

Name in formulas	Name in output	Definition	Units
$Cgr1_1$	$CZooplank$	biomass concentration of zooplankton	$gC\ m^{-3\ or\ -2}$
$Cgr1_2$	$CMussel$	biomass concentration of mussel type zoobenthos	$gC\ m^{-3\ or\ -2}$
$Cgr1_3$	$CGrazer3$	biomass concentration of grazer type 3	$gC\ m^{-3\ or\ -2}$
$Cgr1_4$	$CGrazer4$	biomass concentration of grazer type 4	$gC\ m^{-3\ or\ -2}$
$Cgr1_5$	$CGrazer5$	biomass concentration of grazer type 5	$gC\ m^{-3\ or\ -2}$

7 Organic matter (detritus)

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7.1 Decomposition of detritus

PROCESS: DECFAST, DEC_MEDIUM, 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 sulphide 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 1) distributing the fresh detritus among the detritus fractions according to fixed ratios, and/or by 2) 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 sulphate 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 sulphur in detritus are considered as separate state variables in the model (sulphur 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 sulphur have been made a function of the nutrient stoichiometry of refractory detritus.

The rate of mineralization is also a function of the temperature. Decomposition rates tend to decrease progressively at temperatures below 4 °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 (β) or to water (ω).

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 \rightarrow detritus from vegetation only. As opposed to all other conversion processes, the decomposition of POC5 continues in grid cells when running dry.

Tables 7.1 and 7.2 provide the definitions of the input parameters occurring in the formulations.

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:

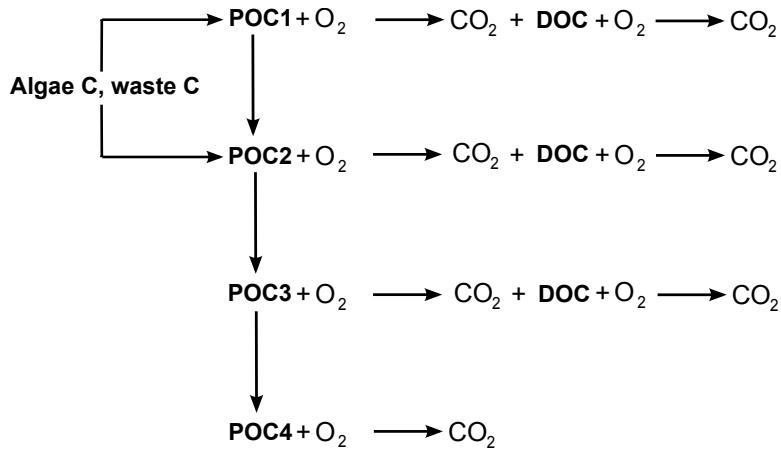


Figure 7.1: When an algae module is included.

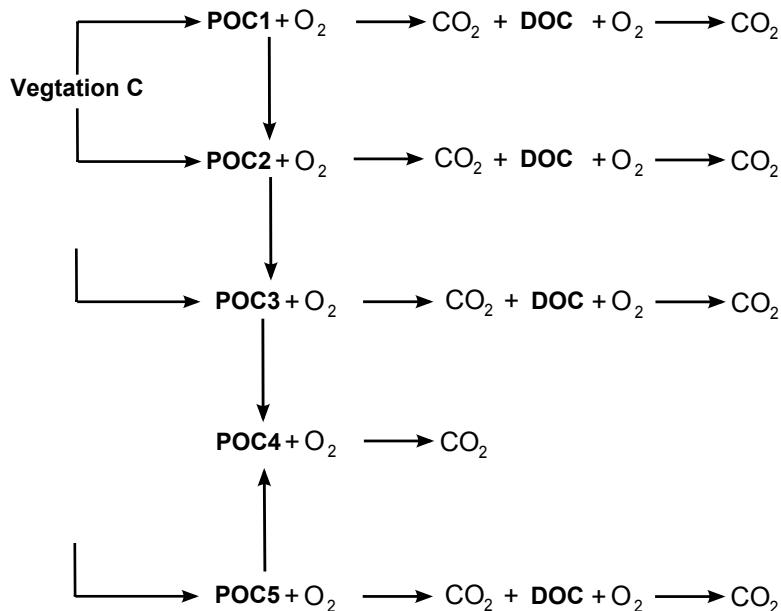


Figure 7.2: When the terrestrial vegetation module is included.

The first scheme (Figure 7.1) applies when an algae module is included in a model. The second scheme (Figure 7.2) 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

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 sulphate, 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 sulphur, for which the mineralization products are ammonium (NH₄), phosphate (PO₄) and sulphide (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 Van 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 sulphur concentration ([gC/N/P/S m ⁻³]); x is <i>oc</i> , <i>on</i> , <i>op</i> or <i>os</i>
$facc$	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 sulphur [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

$$kmin_i^{20} = kmin_{i,min}^{20} + fnut_i \times (kmin_{i,max}^{20} - kmin_{i,min}^{20})$$

$$fnut_i = \min \left\{ \frac{((Con_i/Coc_i) - an_{i,\min})}{an_{i,\max} - an_{i,\min}}, \frac{((Cop_i/Coc_i) - ap_{i,\min})}{ap_{i,\max} - ap_{i,\min}} \right\}$$

(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 sulphate 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 stoichiometric constant of refractory detritus:

$$facc_{j,i} = 1.0 + \frac{((Cx_{j,i}/Coc_i) - ar_j)}{ar_j}$$

with:

ar	stoichiometric constant of nitrogen, phosphorus or sulphur 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 sulphur 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 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 sulphur 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:

<i>b</i>	constant fraction of detritus C component <i>i</i> converted into detritus C component <i>i</i> + 1 relative to and in addition to mineralization [-]
<i>Rcon</i>	conversion rate for particulate organic carbon, nitrogen, phosphorus or sulphur to slower particulate or dissolved fractions [gC/N/P/S m ⁻³ l.d ⁻¹]

Notice that the fractions *b* are equal for organic carbon, nitrogen, phosphorus and sulphur. 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 sulphur 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, sulphate 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 POX₁₋₅ 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 stoichiometric 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 (C₁₀₆N₁₆P₁S₁) and 40% lower values may be used for the maximal and minimal values of the remaining stoichiometric 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 stoichiometric 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 Van der Molen \(1993\)](#), [Westrich and Berner \(1984\)](#), [WL | Delft Hydraulics \(1997c\)](#), [WL | Delft Hydraulics \(1980a\)](#)

Table 7.1: Definitions of the input parameters in the above equations for DECFAST, DEC_MEDIUM and DECSLOW. Volume units refer to bulk (ℓ) or to water (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

Table 7.1: Definitions of the input parameters in the above equations for DECFAST, DECMEDIUM and DECSLOW. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas ¹	Name in input	Definition	Units
"	<i>al_dNs</i>	min. st. constant N in slow dec. detritus	gN.gC^{-1}
$\text{ap}_{i,\text{max}}$	<i>au_dPf</i>	max. st. constant P in fast dec. detritus	gP.gC^{-1}
"	<i>au_dPm</i>	max. st. const. P in medium slow detr.	gP.gC^{-1}
"	<i>au_dPs</i>	max. st. constant P in slow dec. detritus	gP.gC^{-1}
$\text{ap}_{i,\text{min}}$	<i>al_dPf</i>	min. st. const. P in fast dec. detritus	gP.gC^{-1}
"	<i>al_dPm</i>	min. st. const. P in medium slow detr.	gP.gC^{-1}
"	<i>al_dPs</i>	min. st. constant P in slow dec. detritus	gP.gC^{-1}
ar_j	<i>a_dNpr</i>	stoch. constant N in refractory detritus	gN.gC^{-1}
"	<i>a_dPpr</i>	stoch. constant P in refractory detritus	gP.gC^{-1}
"	<i>a_dSpr</i>	stoch. constant S in refractory detritus	gS.gC^{-1}
b_i	<i>b_poc1poc2</i>	conv. fraction fast detr. into medium detr.	-
"	<i>b_poc2poc3</i>	conv. fraction medium detr. into slow detr.	-
"	<i>b_poc2doc</i>	conv. fr. medium detr. into diss. refr. detr.	-
"	<i>b_poc3poc4</i>	conv. fr. slow detr. into part. refr. detr.	-
"	<i>b_poc3doc</i>	conv. fr. slow detr. into diss. refr. detr.	-
b_{ni}	<i>b_ni</i>	atten. const. for nitrate as el. acceptor	-
b_{su}	<i>b_su</i>	atten. const. for sulphate as el. acceptor	-
Coc_i	<i>POC1</i>	conc. organic carbon in fast detritus	$\text{gC.m}^{-3}\ell$
"	<i>POC2</i>	conc. organic carbon in medium detritus	$\text{gC.m}^{-3}\ell$
"	<i>POC3</i>	conc. organic carbon in slow detritus	$\text{gC.m}^{-3}\ell$
Con_i	<i>PON1</i>	conc. organic nitrogen in fast detritus	$\text{gN.m}^{-3}\ell$
"	<i>PON2</i>	conc. organic nitrogen in medium detritus	$\text{gN.m}^{-3}\ell$
"	<i>PON3</i>	conc. organic nitrogen in slow detritus	$\text{gN.m}^{-3}\ell$
Cop_i	<i>POP1</i>	conc. organic phosphorus in fast detritus	$\text{gP.m}^{-3}\ell$
"	<i>POP2</i>	conc. organic phosphorus in medium detritus	$\text{gP.m}^{-3}\ell$
"	<i>POP3</i>	conc. organic phosphorus in slow detritus	$\text{gP.m}^{-3}\ell$
Cos_i	<i>POP1</i>	conc. organic sulphur in fast detritus	$\text{gS.m}^{-3}\ell$
"	<i>POP2</i>	conc. organic sulphur in medium detritus	$\text{gS.m}^{-3}\ell$
"	<i>POP3</i>	conc. organic sulphur in slow detritus	$\text{gS.m}^{-3}\ell$
Cox	<i>OXY</i>	concentration of dissolved oxygen	$\text{gO}_2 \text{ m}^{-3}\ell$
Cni	<i>NO3</i>	concentration of nitrate	$\text{gN m}^{-3}\ell$
$facc_{j,i}$	-	accel. factors nutrient strip. for six detritus components	-
fel	-	limiting factor for electron acceptors	-
$fnut_i$	-	limiting factors for nutrient availability	-
$kmin_{i,\text{max}}^{20}$	<i>ku_dFdcC20</i>	max. min. rate fast detr-C at 20 °C	d^{-1}
"	<i>ku_dMdcC20</i>	max. min. rate medium detr-C detr. at 20 °C	d^{-1}
"	<i>ku_dSdcC20</i>	max. min. rate slow detr-C at 20 °C	d^{-1}
$kmin_{i,\text{min}}^{20}$	<i>kl_dFdcC20</i>	min. min. rate fast detr-C at 20 °C	d^{-1}

Table 7.1: Definitions of the input parameters in the above equations for DECFAST, DEC_MEDIUM and DECSLOW. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas ¹	Name in input	Definition	Units
"	$kl_dMdcC20$	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}
<i>SWOMDec</i>	<i>SWOMDec</i>	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.

Table 7.2: Definitions of the input parameters in the above equations for DECREFR, DEC_DOC 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	-

Table 7.2: Definitions of the input parameters in the above equations for DECREFR, DEC-DOC and DECPOC5. Volume units refer to bulk (ℓ) or to water (ω).

Name in formulas ¹	Name in input	Definition	Units
bsu	b_{su}	attenuation constant for sulphate 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}
$kTmin$	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 .

7.2 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), sulphate 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;
- ◊ sulphate reduction; and
- ◊ methanogenesis.

In principle 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 sulphate 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 sulphate 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), sulphate 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), sulphide, methane has implications for the dissolved oxygen budget. It is possible to exclude nitrate, iron(III), sulphate or methane from simulations. The reduction of manganese is ignored, as it can be considered implicit in sulphate and iron reduction.

Denitrification, iron reduction, sulphate 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 °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, sulphate reducers and methanogens 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. 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. Sulphate 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, sulphate reduction and methanogenesis. DELWAQ converts these fluxes into the concurrent consumption fluxes for DO, nitrate, iron(III) and sulphate, 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, DEC_MEDIUM, 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 (ℓ) or to water (ω).

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 FeIIp, and added to the dissolved reducing iron FeIId.

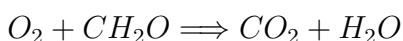
The sulphate reduced is added to dissolved sulphide SUD. [Table 7.3](#) provides the definitions of the parameters occurring in the formulations.

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 Van 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:



For simplicity it is assumed that organic matter is represented by the molecular stoichiometry 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}]
fox^{20}	unscaled relative contr. of oxygen consumption in mineralisation at 20 °C [-]
$Ksox$	half saturation constant for dissolved oxygen limitation [$\text{gO}_2 \text{ m}^{-3}$]
ϕ	porosity [-]

The relative contribution is the following function of temperature:

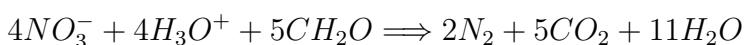
$$fox = fox^{20} \times ktoxc^{(T-20)}$$

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:



Denitrification ultimately removes nitrate from the water phase and produces elemental nitrogen that may escape into the atmosphere. The process delivers 2.86 gO₂ 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^{-3}]
fni^{20}	unscaled relative contribution of denitrification in mineralisation at 20 °C [-]
$Ksni$	half saturation constant for nitrate limitation [gN m^{-3}]
$Ksoxi$	half saturation constant for dissolved oxygen inhibition [$\text{gO}_2 \cdot \text{m}^{-3}$]

The relative contribution of denitrification needs to be adjusted for (low) temperature:

$$fni = fct \times fni^{20} \times ktden^{(T-20)}$$

$fct = 1.0$	if $T \geq T_c$
$fct = fden$	if $T < T_c$

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:

$$fni = 0.0 \quad \text{if } Cox \geq Cox_{c1} \times \phi$$

where:

$$Cox_{c1} \quad \text{critical dissolved oxygen conc. for inhibition of denitrification [g m^{-3}]}$$

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:



The resulting dissolved reducing iron may largely precipitate with sulphide. The process delivers $0.143 \text{ gO}_2 \cdot \text{gFe}^{-1}$, 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 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}]
- ffe^{20} unscaled relative contrib. of iron reduction in mineralisation at 20 °C [-]
- $Ksfe$ half saturation constant for iron limitation [gFe.m^{-3}]
- $Ksnifei$ half saturation constant for nitrate inhibition of iron reduction [gN.m^{-3}]

The relative contribution of iron reduction is adjusted for (low) temperatures in the same way as in the case of denitrification:

$$\begin{aligned} ffe &= fct \times ffe^{20} \times ktird^{(T-20)} \\ fct &= 1.0 \quad \text{if } T \geq Tc \\ fct &= fird \quad \text{if } T < Tc \end{aligned}$$

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:

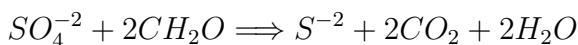
$$ffe = 0.0 \quad \text{if } Cox \geq Cox_{c2} \times \varphi$$

where:

- Cox_{c2} = critical dissolved oxygen conc. for inhibition of iron reduction ($\text{g.m}^{-3}\text{b}$)

Sulphate reduction

Sulphate 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:



Sulphate reduction removes sulphate and ultimately produces sulphide, which may largely precipitate with iron(II). The process delivers $2 \text{ gO}_2 \text{ gS}^{-1}$, instantly consumed for the oxidation of organic matter. Consequently, the process consumes 1.333 gram S per gram C. Sulphate reduction is limited by the availability of sulphate. 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 sulphate 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:

C_{su}	sulphate concentration [gS m $^{-3}$]
f_{su}^{20}	unscaled relative contrib. of sulphate reduction in mineralisation at 20 °C [-]
K_{ssu}	half saturation constant for sulphate limitation [gS m $^{-3}$]
K_{snisui}	half saturation constant for nitrate inhibition of sulphate reduction [gN m $^{-3}$]

The relative contribution of sulphate reduction is adjusted for (low) temperatures in the same way as in the case of denitrification:

$$f_{su} = f_{ct} \times f_{su}^{20} \times k_{tsrd}^{(T-20)}$$

$$\begin{aligned} f_{ct} &= 1.0 && \text{if } T \geq T_c \\ f_{ct} &= f_{srd} && \text{if } T < T_c \end{aligned}$$

where:

f_{srd}	reduction factor for sulphate reduction below critical temperature [-]
f_{su}	unscaled relative contribution of sulphate reduction in mineralisation [-]
k_{tsrd}	temperature coefficient for sulphate reduction [-]

Because sulphate reduction is not to occur when dissolved oxygen is present in significant quantity, it is necessary to exclude sulphate reduction if DO exceeds a certain critical level:

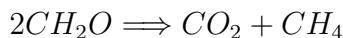
$$f_{su} = 0.0 \quad \text{if } Cox \geq Cox_{c3} \times \phi$$

where:

$$Cox_{c3} \quad \text{critical dissolved oxygen conc. for inhibition of sulphate reduction [g.m}^{-3}\text{]}$$

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 stoichiometry for organic matter the overall reaction equation is:



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 sulphate, nitrate and dissolved oxygen, but not by oxidizing iron due to the slow kinetics of iron reduction. However, it is reasonable to assume that sulphate is present in substantial quantities at the significant presence of dissolved oxygen or nitrate. Therefore, the relative contribution of sulphate in the mineralisation of organic matter is proportional to:

$$f_{ch4}^{20} = \left(1 - \frac{C_{su}}{K_{ssui} \times \phi + C_{su}} \right)$$

where:

f_{ch4}^{20}	unscaled relative contribution of methanogenesis in mineralisation at 20 °C [-]
K_{ssui}	half saturation constant for sulphate inhibition [gS m $^{-3}$]

The relative contribution of methanogenesis is adjusted for low temperatures in the same way as in the case of denitrification:

$$f_{ch4} = f_{ct} \times f_{ch4}^{20} \times k_{tmet}^{(T-20)}$$

$$\begin{aligned} f_{ct} &= 1.0 && \text{if } T \geq T_c \\ f_{ct} &= f_{met} && \text{if } T < T_c \end{aligned}$$

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:

$$fch4 = 0.0 \quad \text{if } Cox \geq Coxc_4 \times \phi \quad \text{or} \quad Cni \geq Cnic \times \phi$$

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:

$$\begin{aligned} frrox &= \frac{fox}{fox + fni + ffe + fsu + fch4} \\ frni &= \frac{fni}{fox + fni + ffe + fsu + fch4} \\ frfe &= \frac{ffe}{fox + fni + ffe + fsu + fch4} \\ frsu &= \frac{fsu}{fox + fni + ffe + fsu + fch4} \\ frch4 &= 1 - frrox - frni - ffe - frsu \end{aligned}$$

where:

- $frrox$ scaled contribution of dissolved oxygen consumption [-]
- $frni$ scaled contribution of denitrification [-]
- $frfe$ scaled contribution of iron reduction [-]
- $frsu$ scaled contribution of sulphate 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 [$\text{gC m}_w^{-3} \text{ d}^{-1}$]
- $Rmin_2$ mineralisation flux for organic carbon in the slowly decomposing detritus fraction POC2 [$\text{gC m}_w^{-3} \text{ d}^{-1}$]

$Rmin_3$	mineralisation flux for organic carbon in the very slowly decomposing detritus fraction POC3 [$\text{gC m}^{-3} \text{d}^{-1}$]
$Rmin_4$	mineralisation flux for organic carbon in the particulate refractory detritus fraction POC4 [$\text{gC m}^{-3} \text{d}^{-1}$]
$Rmin_5$	mineralisation flux for organic carbon in dead stems and roots of vegetation detritus fraction POC5 [$\text{gC m}^{-3} \text{d}^{-1}$]
$Rmin_6$	mineralisation flux for organic carbon in the dissolved refractory detritus fraction DOC [$\text{gC m}^{-3} \text{d}^{-1}$]
$Rtmin$	total mineralisation flux for organic carbon [$\text{gC m}^{-3} \text{d}^{-1}$]

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 [$\text{gC m}^{-3} \text{d}^{-1}$]
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^{-3}]
-------	--

$frni'$	corrected scaled relative contribution of denitrification [-]
$Rden$	mineralisation flux connected to denitrification [$\text{gC.m}^{-3}\text{d}^{-1}$]
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-3d]
$frfe$	corrected scaled relative contribution of iron reduction [-]
$Rird$	mineralisation flux connected to iron reduction [$\text{gC m}^{-3}\text{d}^{-1}$]

Sulphate reduction

The mineralisation flux connected to sulphate reduction needs a similar correction as made for denitrification, when the stock of sulphate is too small to satisfy the demand. The mineralisation flux and the corrected contribution are calculated as follows:

$$Rsrd = \min \left(frsu \times Rtmin, 0.9 \times \frac{Csu}{1.33 \times \Delta t} \right)$$

$$frsu' = \frac{0.9 \times Csue}{frsu \times Rtmin \times 1.33 \times \Delta t}$$

where:

Csu	sulphate concentration [gS m^{-3}]
$frsu'$	corrected scaled relative contribution of sulphate reduction [-]
$Rsrd$	mineralisation flux connected to sulphate reduction [$\text{gC m}^{-3}\text{d}^{-1}$]

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 [$\text{gC m}^{-3}\text{d}^{-1}$]

The coefficient am is in fact a stoichiometric 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 sulphate reduction have changed due to limited stocks, the contribution of the other processes need to be corrected too. This is achieved by

- ◊ 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 sulphate reduction
- ◊ if also necessary, the required decrease of the fraction of iron consumption to the fraction of sulphate reduction
- ◊ and if also necessary, the required decrease of the fraction of sulphate reduction to the fraction of methanogenesis.

The corrected contribution of methanogenesis follows from:

$$frch4' = 1 - frox' - frni' - frfe' - frsu'$$

where:

$$frch4' \quad \text{corrected scaled relative contribution of methanogenesis [-]}$$

Directives for use

- ◊ Indicative values for the limitation constants are: $KsOxCon = 1.0 \text{ gO}_2 \text{ m}^{-3} \omega$, $KsNiDen = 0.25 \text{ gN m}^{-3} \omega$, $KsFeRed = 100 000.0 \text{ gFe m}^3 \omega$, $KsSuRed = 2.0 \text{ gS m}^{-3} \omega$. Indicative values for the inhibition constants are: $KsOxDenInh = 1.0 \text{ gO}_2 \text{ m}^{-3} \omega$, $KsNiIReInh = 0.2 \text{ gN m}^{-3} \omega$, $KsNiSReInh = 0.2 \text{ gN m}^3 \omega$, $KsSuMetInh = 1.0 \text{ gS m}^{-3} \omega$.
- ◊ 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, sulphate 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, sulphate 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 $2 \text{ gO}_2 \text{ m}^{-3} \omega$, 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, sulphate 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 $2\text{--}4$ °C. In case sediment temperature is set equal to water temperature, one wants some enhancement instead of retardation because generally sediment temperature is higher than water temperature in winter time. Enhancement factors $RedFacDen$, $RedFacIRed$, $RedFacSRed$, $RedFacMet$ can be 1.25.

- ◊ The critical concentrations for inhibition of denitrification, iron reduction, sulphate 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 stoichiometric coefficients in the processes matrix of DELWAQ are:
 - The amount of oxygen consumed per amount of carbon is $2.667 \text{ gO}_2 \text{ gC}^{-1}$.
 - 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 $18.67 \text{ gFe.gC}^{-1}$.
 - The amount of sulphate 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, sulphate reduction and methanogenesis are available as the following output parameters: $FrOxCon$, $FrNitDen$, $FrFeRed$, $FrSulRed$, $FrMetGen$.
- ◊ Coefficient $FrMetGeCH_4$ 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 CH₂O. He should modify these fluxes too.

Additional references

Boudreau (1996), DiToro (2001), Luff and Moll (2004), Santschi *et al.* (1990), Smits and Van der Molen (1993), Soetaert *et al.* (1996), Vanderborght *et al.* (1977), Wang and Cappellen (1996), WL | Delft Hydraulics (2002), Wijsman *et al.* (2001)

Table 7.3: Definitions of the parameters in the above equations for CONSELAC. Volume units refer to bulk (b) or to water (w).

Name in formulas	Name in input	Definition	Units
Cox	OXY	dissolved oxygen concentration	$\text{gO}_2 \text{ m}^{-3}_b$
Cni	$NO3$	nitrate concentration	gN m^{-3}_b
$Cfea$	$FeIIIpa$	particulate amorphous oxidizing iron concentration	gFe m^{-3}_b
Csu	$SO4$	sulphate concentration	gS m^{-3}_b
$Coxc_1$	$CoxDenInh$	critical diss. oxygen conc. inhibition of denitrific.	$\text{gO}_2 \text{ m}^{-3}_w$
$Coxc_2$	$CoxIRedInh$	critical diss. oxygen conc. inhibition of iron red.	$\text{gO}_2 \text{ m}^{-3}_w$
$Coxc_3$	$CoxSRedInh$	critical diss. oxygen conc. inhibition of sulphate red.	$\text{gO}_2 \text{ m}^{-3}_w$
$Coxc_4$	$CoxMetInh$	critical diss. oxygen conc. inhib. of methanogenesis	$\text{gO}_2 \text{ m}^{-3}_w$
$Cnic$	$CniMetInb$	critical nitrate conc. inhibition of methanogenesis	gN m^{-3}_w
fox	-	unscaled rel. contr. of oxygen cons. in mineralisation	-
fni	-	unscaled rel. contr. of denitrif. in mineralisation	-

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Table 7.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
<i>ffe</i>	-	unscaled rel. contr. of iron red in mineralisation	-
<i>fsu</i>	-	unscaled rel. contr. of sulphate red. in mineralisation	-
<i>fch4</i>	-	unscaled rel. contr. of methanog. in mineralisation	-
<i>frox</i>	-	scaled rel. contr. of dissolved oxygen consumption	-
<i>frni</i>	-	scaled rel. contribution of denitrification	-
<i>frfe</i>	-	scaled rel. contribution of iron reduction	-
<i>frsu</i>	-	scaled rel. contribution of sulphate reduction	-
<i>frch4c</i>	-	scaled rel. contribution of methanogenesis	-
<i>fct</i>	-	reduction factor for temp. below critical temperature	-
<i>fden</i>	<i>RedFacDen</i>	reduction factor for denitr. below critical temperature	-
<i>fird</i>	<i>RedFacIRed</i>	reduction factor for iron red. below critical temperature	-
<i>fsrd</i>	<i>RedFacSRed</i>	reduction factor for sulphate red. below critical temperature	-
<i>fmet</i>	<i>RedFacMet</i>	reduction factor for methanog. below critical temperature	-
<i>ktoxc</i>	<i>TcOxCon</i>	temperature coefficient for oxygen consumption	-
<i>ktden</i>	<i>TcDen</i>	temperature coefficient for denitrification	-
<i>ktird</i>	<i>TcIred</i>	temperature coefficient for iron reduction	-
<i>ktsrd</i>	<i>TcSRed</i>	temperature coefficient for sulphate reduction	-
<i>ktmet</i>	<i>TcMet</i>	temperature coefficient for methanogenesis	-
<i>Ksox</i>	<i>KsOxCon</i>	half saturation constant for oxygen limitation	$\text{gO}_2 \text{ m}_w^{-3}$
<i>Ksni</i>	<i>KsNiDen</i>	half saturation constant for nitrate limitation	$\text{gN} \text{ m}_w^{-3}$
<i>Ksfe</i>	<i>KsFiRed</i>	half saturation constant for iron limitation	$\text{gFe} \text{ m}_w^{-3}$
<i>Kssu</i>	<i>KsSuRed</i>	half saturation constant for sulphate limitation	$\text{gS} \text{ m}_w^{-3}$
<i>Ksoxi</i>	<i>KsOxDenInh</i>	half sat. const. for DO inhibition of denitrification	$\text{gO}_2 \text{ m}_w^{-3}$
<i>Ksnifei</i>	<i>KsNiIRdInh</i>	half sat. const. for nitrate inhib. of iron reduction	$\text{gN} \text{ m}_w^{-3}$
<i>Ksnisui</i>	<i>KsNiSRdInh</i>	half sat. const. for nitrate inhib. of sulphate reduction	$\text{gN} \text{ m}_w^{-3}$
continued on next page			

Table 7.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
$Kssui$	$KsSuMetInh$	half sat. const. for sulphate inhib. of methanogenesis	gS m_w^{-3}
$Rcns$	-	mineralisation flux connected to oxygen consumption	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rden$	-	mineralisation flux connected to denitrification	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rird$	-	mineralisation flux connected to iron reduction	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rsrd$	-	mineralisation flux connected to sulphate reduction	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rmet$	-	mineralisation flux connected to methanogenesis	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rmin_1$	$f_MinPOC1$	mineralisation flux for organic carbon in the fast decomposing detritus fraction POC1	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rmin_2$	$f_MinPOC2$	mineralisation flux for organic carbon in the slowly decomposing detritus fraction POC2	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rmin_3$	$f_MinPOC3$	mineralisation flux for organic carbon in the very slowly decomposing detritus fraction POC3	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rmin_4$	$f_MinPOC4$	mineralisation flux for organic carbon in the particulate refractory detritus fraction POC4	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rmin_5$	$f_MinPOC5$	mineralisation flux for organic carbon in dead stems and roots, detritus fraction POC5	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
$Rmin_6$	f_MinDOC	mineralisation flux for organic carbon in the dissolved refractory detritus fraction DOC	$\text{gC m}_\ell^{-3} \text{d}^{-1}$
am	$FrMetGeCH4$	fraction of organic C converted into methane (CH_4)	-
T T_c	$Temp$ $CTBactAc$	temperature critically low temp. for specific bacterial activity	$^{\circ}\text{C}$ $^{\circ}\text{C}$
Δt	$Delt$	computational time-step	d
ϕ	$POROS$	porosity	$\text{m}_w^3 \text{m}_\ell^{-3}$

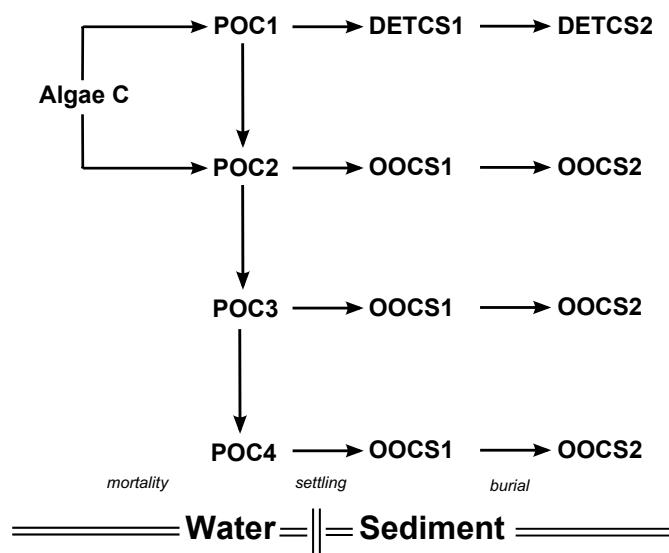
7.3 Settling of detritus

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 sulphur (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.

Processes SEDN(i) deliver the settling rates of organic nutrients (i) relative to organic carbon components (i). Process COMPOS provides the stoichiometric ratios f_s of the organic nutrients (N,P,S) for this. 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 7.4 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:

$$Rset_i = ftau_i \times \frac{Fset_i}{H}$$

$$\begin{aligned} & \text{if } H < Hmin \quad Fset_i = 0.0 \\ & \quad \text{else} \\ & \quad Fset_i = \min \left(Fset'_i, \frac{Cx_i \times H}{\Delta t} \right) \\ & \quad Fset'_i = Fset0_i + s_i \times Cx_i \end{aligned}$$

$$\begin{aligned} & \text{if } \tau = -1.0 \quad ftau = 1.0 \\ & \quad \text{else} \\ & \quad ftau_i = \max \left(0.0, \left(1 - \frac{\tau}{\tau c_i} \right) \right) \end{aligned}$$

where:

Cx	concentration of a substance [gC/P/Si m ⁻³]
$Fset0$	zero-order settling flux of a substance [gC/P/Si m ⁻² d ⁻¹]
$Fset$	settling flux of a substance [gC/P/Si m ⁻² d ⁻¹]
$ftau$	shear stress limitation function [-]
H	depth of the water column [m]
$Hmin$	minimal depth of the water column for resuspension [m]
$Rset$	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]
τc	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.

The settling of organic nutrients is coupled to the settling of organic carbon as follows:

$$Rsn_{j,i} = \frac{Rset_i}{fs_{j,i}}$$

where:

$fs_{j,i}$	stoichiometric ratios carbon over nutrient j in detritus component i [gC gX ⁻¹]
$Rsn_{j,i}$	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

- ◊ 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 $Depth$ is smaller than minimal depth $MinDepth$ 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.

Table 7.4: 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
$Fset0_i$	$ZSed(i)$	zero-order settling flux of substance (i)	gC/P/Si m ⁻² d ⁻¹
$fs_{j,i}$	$C - NPOC1^2$ $C - NPOC2$ $C - NPOC3$ $C - NPOC4$ $C - PPOC1$ $C - PPOC2$ $C - PPOC3$ $C - PPOC4$ $C - SPOC1$ $C - SPOC2$ $C - SPOC3$ $C - SPOC4$	stoch. ratio C and N in POC1 stoch. ratio C and N in POC2 stoch. ratio C and N in POC3 stoch. ratio C and N in POC4 stoch. ratio C and P in POC1 stoch. ratio C and P in POC2 stoch. ratio C and P in POC3 stoch. ratio C and P in POC4 stoch. ratio C and S in POC1 stoch. ratio C and S in POC2 stoch. ratio C and S in POC3 stoch. ratio C and S in POC4	gC gN ⁻¹ gC gN ⁻¹ gC gN ⁻¹ gC gN ⁻¹ gC gN ⁻¹ gC gP ⁻¹ gC gP ⁻¹ gC gP ⁻¹ gC gP ⁻¹ gC gS ⁻¹ gC gS ⁻¹ gC gS ⁻¹ gC gS ⁻¹
H	$Depth$	depth of the water column, thickness of water layer	m
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Table 7.4 – continued from previous page

Name in formulas	Name in input	Definition	Units
H_{min}	$MinDepth$	minimal water depth for settling and resuspension	m
s_i	$VSedPOC$ $VSedIM$ $VSedAAP$ $VSedVIVP$ $VSedAPATP$ $VSedOPAL$	settling velocity of POC settling velocity of inorg. matter settling velocity of AAP settling velocity of VIVP settling velocity of APATP settling velocity of OPAL	$m\ d^{-1}$ $m\ d^{-1}$ $m\ d^{-1}$ $m\ d^{-1}$ $m\ d^{-1}$ $m\ d^{-1}$
τ τc_i	Tau $TaucS(i)$	shear stress critical shear stress for settling of substance (I)	Pa 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 stoichiometric ratios are delivered by process COMPOS.

7.4 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 (β) or to water (ω).

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 substances:

- ◊ PO4, AAPS1 and AAPS2

[Table 7.5](#) 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:

$$Rmin_{i,k} = \begin{cases} \frac{k0min_{i,k}}{H} + \frac{kmin_{i,k} \times Mx_{i,k}}{V} & \text{if } T \geq Tc \\ \frac{k0min_{i,k}}{H} & \text{if } T < Tc \end{cases}$$

$$kmin_{i,k} = kmin_{i,k}^{20} \times ktmin_i^{(T-20)}$$

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 ⁻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 Van der Molen \(1993\)](#), [Westrich and Berner \(1984\)](#), [WL | Delft Hydraulics \(1980a\)](#)

Table 7.5: 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 (ℓ) or to water (ω).

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	$gX m^{-2}\ell$
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.

8 Inorganic substances and pH

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8.1 Air-water exchange of CO₂

PROCESS: REARCO2

Carbon dioxide (CO₂) 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 CO₂-excess or CO₂-deficit. Furthermore, the CO₂ concentration is dependent on the pH:



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 CO₂ 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 CO₂ 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. Raeaeration 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 CO₂-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 CO₂.

[Table 8.4](#) provides the definitions of the parameters occurring in the formulations.

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 CO₂ as follows:

$$R_{rear} = klrear \times [Cco2s - \max(Cco2, 0.0)] / H$$

$$klrear = klrear^{20} \times ktrear^{(T-20)}$$

$$klrear^{20} = \left(\frac{a \times v^b}{H^c} \right) + (d \times W^2)$$

$$Cco2s = f(T, Ccl \text{ or } SAL) \quad (\text{delivered by SATURCO2})$$

$$fsat = 100 \times \frac{\max(Cco2, 0.0)}{Cco2s}$$

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 [-]
R_{rear}	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, CO₂ may have negative values in the model due to the consumption of CO₂ 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.

$SWRearCO2 = 0$

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:

$$a = klrear^{20} \times H \quad b = 0.969 \quad c = 0.5 \quad d = 0.0$$

$SWRearCO2 = 1$

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

$$a = klrear^{20} \quad b = 0.969 \quad c = 0.5 \quad d = 0.0$$

SWRearCO2 = 4

The coefficients are according to ([O' Connor and Dobbins, 1956](#)) for DO, but coefficient a can be scaled for CO₂ using the transfer coefficient as input parameter. Consequently, the coefficients are:

$$a = klrear^{20} \times 3.863 \quad b = 0.5 \quad c = 0.5 \quad d = 0.0$$

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

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:

$$a = func(T) \quad b = 0.0 \quad c = 0.0 \quad d = 0.0744 \times fsc$$

$$func(T) = 2.5 \times (0.5246 + 0.016256 \times T + 0.00049946 \times T^2)$$

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

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

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

SWRearCO2 = 13

The relation according to [Guérin \(2006\); 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:

$$klrear = (a \times \exp(b_1 \times W^{b2}) + (c_1 \times P^{c2})) \times fsc \quad (8.1)$$

$$fsc = \left(\frac{Sc}{Sc^{20}} \right)^{-0.67} \quad (8.2)$$

$$Sc = d_1 - d_2 \times T + d_3 \times T^2 - d_4 \times T^3 \quad (8.3)$$

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
<i>CoefACO2</i>	<i>CoefB1CO2</i>	<i>CoefB2 CO2</i>	<i>CoefC1CO2</i>	<i>CoefC2CO2</i>
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
<i>CoefD1CO2</i>	<i>CoefD2 CO2</i>	<i>CoefD3 CO2</i>	<i>CoefD4 CO2</i>
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 8.4: Definitions of the parameters in the above equations for REARCO2.

Name in formulas ¹	Name in input	Definition	Units
$Cco2$ $Cco2s$	$DisCO2$ $SaturCO2$	concentration of carbon dioxide saturation conc. of carbon dioxide from SATURCO2	$\text{gCO}_2 \text{ m}^{-3}$ $\text{gCO}_2 \text{ m}^{-3}$
a b_1 b_2 c_1 c_2	$CoefACO2$ $CoefB1CO2$ $CoefB2CO2$ $CoefC1CO2$ $CoefC2CO2$	coefficients for option 13 only	- - - - -
d_1 d_2 d_3 d_4	$CoefD1CO2$ $CoefD2CO2$ $CoefD3CO2$ $CoefD4CO2$	coefficients for option 11 and 13	- - - -
fcs $fsat$	- -	scaling factor for the Schmidt number percentage carbon dioxide saturation	- %
H	$Depth$	depth of the top water layer	m
$klrear^{20}$ $kltemp$	$KLRearCO2$ $TCRearCO2$	water transfer coefficient for carbon dioxide ¹ temperature coefficient for reaeration	m d^{-1} -
P	$rain$	Rainfall	mm h^{-1}
$Rrear$	-	reaeration rate for carbon dioxide	$\text{gCO}_2 \text{ m}^{-3} \text{ d}^{-1}$
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	$^{\circ}\text{C}$
v W	$Velocity$ $VWind$	stream velocity windspeed at 10 m height	m s^{-1} m s^{-1}

¹ $KLRearCO2$ is a dimensionless scaling factor for option 4.

8.2 Saturation concentration of CO₂

PROCESS: SATURCO2

The reaeration of carbon dioxide proceeds proportional to the difference of the saturation CO₂ concentration and the actual dissolved CO₂ concentration. The saturation concentration of CO₂ is primarily a function of the partial atmospheric CO₂ pressure, the water temperature and the salinity. However, the partial atmospheric CO₂ 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 CO₂ saturation concentration in water required for the process REARCO2. The process has been implemented with two options for the formulations of the saturation concentration, that can be selected by means of input parameter *SWSatCO2* (= 1 – 2).

The process has been implemented in connection with substance CO₂. [Table 8.5](#) 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](#)):

$$fac = 10^{-f_{temp}}$$

$$f_{temp} = a - \frac{b}{(T + 273)} - c \times (T + 273) + fcl \times (d - m \times (T + 273))$$

$$fcl = n + o \times Ccl + p \times Ccl^2$$

For *SWSatCO2* = 2 ([Weiss, 1974](#)):

$$fac = \exp \left(a + \frac{b}{Tf} + c \times \ln(Tf) + SAL \times (m + n \times Tf + o \times Tf^2) \right)$$

$$Tf = \left(\frac{T + 273}{100} \right)$$

For both options:

$$Cco2s = Pco2 \times fac \times 44 \times 1000$$

with:

a, b, c, d coefficients with different values for the two formulations

m, n, o, p	
Ccl	chloride concentration [gCl m^{-3}]
$Cco2s$	saturation carbon dioxide concentration in water [$\text{gCO}_2 \text{ m}^{-3}$]
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 [$^{\circ}\text{C}$]
Tf	temperature function [$^{\circ}\text{C}$]
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:

$$SAL = 2 \times Cl / 1000$$

- ◊ A representative value for the atmospheric carbon dioxide pressure $PAPCO2$ is 3.162×10^{-4} atm.

Table 8.5: 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	$\text{gCO}_2 \text{ m}^{-3}$
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	$^{\circ}\text{C}$
Tf	-	temperature function	-

8.3 Calculation of the pH and the carbonate speciation

PROCESS: PH_SIMP

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; $\text{gHCO}_3 \text{ m}^{-3}$) and the total dissolved inorganic carbon concentration (TIC; gC m^{-3}). Salinity (g kg^{-1}) and temperature ($^{\circ}\text{C}$) are necessary inputs.

The dissolved $[\text{CO}_2]$ concentration is more than two orders of magnitude higher than the concentration of carbonic acid $[\text{H}_2\text{CO}_3]$. Consequently, the sum of the concentrations of these species $[\text{CO}_2^*]$ is practically identical to the concentration of $[\text{CO}_2]$, and thus TIC is defined as:

$$\text{TIC} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

The equilibrium in the carbonate system is dependent of temperature, salinity and pressure. The relative proportions of total 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 $[\text{H}^+]$ concentration is derived from the alkalinity equation and is used to calculate pH:

$$\text{ALKA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+]$$

In process pH_simp 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 pH is measured on the ‘total pH scale’ (pH_T):

$$\text{pH}_T = -10\log([\text{H}^+] + [\text{HSO}_4^-]) > -10\log([\text{H}^+]) = \text{pH}$$

Not the free $[\text{H}^+]$ is measured but $[\text{H}^+]_{\text{T}}$ ($= [\text{H}^+] + [\text{HSO}_4^-]$). In fresh water $[\text{HSO}_4^-]$ is negligible, but through the abundance of sulphate it is significant in seawater. Because in this model the pH is calculated from $[\text{H}^+]$ only, the calculated pH slightly underestimates the pH measured in seawater.

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. All processes in DELWAQ that can change pH are taken into account. [Table 8.6](#) gives a general summary of all processes that have a pH effect.

Table 8.6: Processes in D-Water Quality with effects on pH

process description	equivalent chemical reaction	stoichiometry
reaeration of CO_2	$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3^{*}_{(\text{aq})}$	TIC +0.273 ^{a)}
continued on next page		

Table 8.6 – continued from previous page

process description	equivalent chemical reaction	stoichiometry
primary production	$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$	TIC -1.000 H ₂ O -1.500 C _{org} +1.000 OXY +2.670
mineralisation of organic C	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	TIC +1.000 H ₂ O +1.500 C _{org} -1.000 OXY -2.670
denitrification	$\text{NO}_3^- + \text{H}^+ \rightarrow \frac{1}{2} \text{N}_2 + 1\frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O}$	NO3 -1.000 ^{b)} ALKA +4.357 OXY +2.857 H ₂ O +0.643
nitrification	$\text{NH}_4^+ + 2 \text{O}_2 \leftrightarrow \text{NO}_3^- + 2 \text{H}^+ + \text{H}_2\text{O}$	NH4 -1.000 OXY -4.571 NO3 +1.000 ALKA -8.714 H ₂ O +1.286
Uptake of ammonia ^{c)}	$\text{NH}_4^+ \rightarrow (\text{NH}_3)_{org} + \text{H}^+$	NH4 -1.000 N _{org} +1.000 ALKA -4.357
Uptake of phosphate ^{c)}	$\text{H}_2\text{PO}_4^- + \text{H}^+ \rightarrow (\text{H}_3\text{PO}_4)_{org}$	PO4 -1.000 P _{org} +1.000 ALK 1.968
Uptake of nitrate	$\text{NO}_3^- + \text{H}^+ + \text{H}_2\text{O} \rightarrow (\text{NH}_3)_{org} + 2 \text{O}_2$	NO3 -1.000 ALK +4.357 H ₂ O -1.286 N _{org} +1.000 OXY -4.571
Atmospheric deposition of nitrate	$\text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^-$	NO3 +1.000 H ₊ +0.071 ALK -4.357
Atmospheric deposition of ammonium	$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$	NH4 +1.000 ALK +4.357
Atmospheric deposition of sulphate	$\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$	SO4 +1.000 H ₊ +0.143 ALK -8.714
continued on next page		

Table 8.6 – continued from previous page

process description	equivalent chemical reaction	stoichiometry
---------------------	------------------------------	---------------

^aThe CO₂ flux in D-Water Quality has units gCO₂ m⁻³ d⁻¹ and is converted to gC m⁻³ d⁻¹.

^bDenitrification in the sediment is thought to be a sink for nitrate. No alkalinity, oxygen and water are added to the water column

^cMineralisation reactions are the reverse of the uptake reactions

Implementation

Process pH_simp has been implemented for the following substances:

- ◊ TIC, Alka and Salinity

Although process pH_simp has been formulated in a generic way, the calculation of the pH should be applied to water layers only. Concentrations are corrected for porosity (input parameter POROS) to allow for application to sediment layers, but buffering of the pH by minerals like calcite is not considered. Process pH_simp can be used for a model with "layered sediment" because the lapse of the pH and pH dependent processes can be avoided by constraining the pH within a user defined range. pH_simp cannot be used for pH and carbonate speciation in the sediment, when substances are modelled as 'inactive' substances according to the S1/2 approach.

Two versions for the calculation of pH are available. The original version 2 is selected with option parameter *SwpH* = 0.0 (default value), and applies to water with low salinity (< 5 psu). The other version 1 is selected with option parameter *SwpH* = 1.0, and is suitable for fresh as well as saline water. Apart from the pH both versions calculate the concentrations and the fractions of the carbonate species. Version 2 includes the calculation of *DisH2CO3* and *FrH2CO3d*, whereas this is not done by version 1 because this species is assumed included in *DisCO2*.

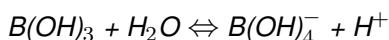
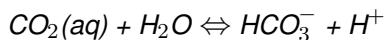
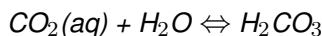
Instead of simulating the pH, it can be imposed on a model. If process *pH_simp* is activated to calculate the carbonate speciation with the formulations of version 2, this is done for option *SwpH* = -1.0. The carbonate speciation computed by pH_simp can be used by process PRIRON for the formation of iron(II) carbonate. The dissolved carbon dioxide concentration *DisCO2* computed by pH_simp can be used for process REARCO2 to calculate the CO₂ exchange flux between atmosphere and water.

[Table 8.7](#) provides the definitions of the input parameters in the formulations and [Table 8.8](#) provides the output parameters.

Formulation

Version 2 ($SwpH = 1.0$)

The hydrolysis reactions of carbonate and borate and the self-ionization of water proceed according to the following reaction equations:



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 [$\text{mol kg}^{-1} \text{ atm}^{-1}$]

K_1 first dissociation constant of carbonic acid [$\text{mol kg}^{-1} \text{ solution}$]

K_2 second dissociation constant of carbonic acid [$\text{mol kg}^{-1} \text{ solution}$]

K_B dissociation constant of boric acid [$\text{mol kg}^{-1} \text{ solution}$]

K_W dissociation constant of water [$\text{mol}^2 \text{ kg}^{-2} \text{ solution}$]

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 [$^\circ\text{C}$]

T_{abs} absolute temperature [K]

Because the model calculates bulk salinity, it is corrected for porosity as follows:

$$S = Salinity/\varphi$$

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) $< 5 \text{ g kg}^{-1}$ (psu):

$$\begin{aligned}\ln K_1 = & 290.9097 - 14554.21/T_{abs} - 45.0575 \times \ln(T_{abs}) + \\ & (-228.39774 + 9714.36839/T_{abs} + 34.485796 \times \ln(T_{abs})) \times S^{0.5} + \\ & (54.20871 - 2310.48919/T_{abs} - 8.19515 \times \ln(T_{abs})) \times S + \\ & (-3.969101 + 170.22169/T_{abs} + 0.603627 \times \ln(T_{abs})) \times S^{1.5} - \\ & 0.00258768 \times S^2 + \ln(1 - S \times 0.001005)\end{aligned}$$

$$K_1 = e^{\ln K_1}$$

$$\begin{aligned}\ln K_2 = & 207.6548 - 11843.79/T_{abs} - 33.6485 \times \ln(T_{abs}) + \\ & (-167.69908 + 6551.35253/T_{abs} + 25.928788 \times \ln(T_{abs})) \times S^{0.5} + \\ & (39.75854 - 1566.13883/T_{abs} - 6.171951 \times \ln(T_{abs})) \times S + \\ & (-2.892532 + 116.270079/T_{abs} + 0.45788501 \times \ln(T_{abs})) \times S^{1.5} - \\ & 0.00613142 \times S^2 + \ln(1 - S \times 0.001005)\end{aligned}$$

$$K_2 = e^{\ln K_2}$$

For Salinity (S) < 45 and $\geq 5 \text{ g kg}^{-1}$ (psu):

$$\begin{aligned}\ln K_1 = & 2.83655 - 2307.1266/T_{abs} - 1.5529413 \times \ln(T_{abs}) + \\ & (-0.20760841 - 4.0484/T_{abs}) \times S^{0.5} + 0.08468345 \times S \\ & - 0.00654208 \times S^{1.5} + \ln(1 - 0.001005 \times S)\end{aligned}$$

$$K_1 = e^{\ln K_1}$$

$$\begin{aligned}\ln K_2 = & -9.226508 - 3351.6106/T_{abs} - 0.2005743 \times \ln(T_{abs}) + \\ & (-0.106901773 - 23.9722/T_{abs}) \times S^{0.5} + 0.1130822 \times S \\ & - 0.00846934 \times S^{1.5} + \ln(1 - 0.001005 \times S)\end{aligned}$$

$$K_2 = e^{\ln K_2}$$

For all values of salinity:

$$\begin{aligned}\ln K_0 = & -60.2409 + 93.4517/(T_{abs}/100) - 23.3585 \times \ln(T_{abs}/100) + \\ & S \times (0.023517 - 0.023656 \times (T_{abs}/100) + 0.000447036 \times (T_{abs}/100)^2)\end{aligned}$$

$$K_0 = e^{\ln K_0}$$

$$\begin{aligned}\ln K_B = & (-8966.90 - 2890.53 \times S^{0.5} - 77.942 \times S + 1.728 \times S^{1.5} - 0.0996 \times S^2) / T_{abs} \\ & + 148.0248 + 137.1942 \times S^2 + 1.62142 \times S + \\ & (-24.4344 - 25.085 \times S^{0.5} - 0.2474 \times S) \times \ln(T_{abs}) + 0.053105 \times S^{0.5} \times T_{abs}\end{aligned}$$

$$K_B = e^{\ln K_B}$$

$$\begin{aligned}\ln K_W = & 148.96502 - 13847.26 / T_{abs} - 23.6521 \times \ln(T_{abs}) + \\ & (118.67 / T_{abs} - 5.977 + 1.0495 \times \ln(T_{abs})) \times S^{0.5} - 0.01615 \times S\end{aligned}$$

$$K_W = e^{\ln K_W}$$

$$\begin{aligned}\ln K_{Cal} = & -171.9065 - 0.077993 \times T_{abs} + 2839.319 / T_{abs} + 71.595 \times \ln(T_{abs}) + \\ & (-0.77712 + 0.0028426 \times T_{abs} + 178.34 / T_{abs}) \times S^{0.5} - \\ & 0.07711 \times S + 0.0041249 \times S^{1.5}\end{aligned}$$

$$K_{Cal} = e^{\ln K_{Cal}}$$

$$\begin{aligned}\ln K_{Arg} = & -171.9065 - 0.077993 \times T_{abs} + 2903.293 / T_{abs} + 71.595 \times \ln(T_{abs}) + \\ & (-0.068393 + 0.0017276 \times T_{abs} + 88.135 / T_{abs}) \times S^{0.5} - \\ & 0.10018 \times S + 0.0059415 \times S^{1.5}\end{aligned}$$

$$K_{Arg} = e^{\ln K_{Arg}}$$

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:

$$\begin{aligned}\rho_w &= (1000. + 0.7 \times S / (1 - S / 1000.) - 0.0061 \times (T - 4.0)^2) / 1000 \\ TICM &= mtmm \times (TIC / (MWC \times \rho_w \times m3tl \times \varphi)) \\ AlkaM &= mtmm \times (Alka / (MWHCO3 \times \rho_w \times m3tl \times \varphi)) \\ B &= mtmm \times 0.000416 \times (S / 35) \\ [Ca^{2+}] &= mtmm \times 0.01028 \times (S / 35)\end{aligned}$$

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:

$$pH = -10\log[H^+]$$

$$CO2 = mtmm \times m3tl \times MWCO2 \times \rho_w \times TICM \times \\ [H^+]^2 / ([H^+]^2 + K_1 \times [H^+] + K_1 \times K_2)$$

$$pCO2_w = FCO2 / (\exp(atpa \times (BV + 2 \times D) / (R \times T_{abs})))$$

$$FCO2 = atma \times CO2M / K_0$$

$$BV = (-1636.75 + 12.0408 \times T_{abs} - 0.0327957 \times T_{abs}^2 + 3.16528 \times 10^{-5} \times T_{abs}^3) / m3tcm3$$

$$D = (57.7 - 0.118 \times T_{abs}) / m3tcm3$$

$$HCO3 = MWC \times \rho_w \times m3tl \times \varphi \times \\ (TICM \times K_1 \times [H^+]) / ([H^+]^2 + K_1 \times [H^+] + K_1 \times K_2) \times mtmm$$

$$CO3 = MWC \times \rho_w \times m3tl \times \varphi \times$$

$$(TICM \times K_1 \times K_2) / ([H^+]^2 + K_1 \times [H^+] + K_1 \times K_2) \times mtmm$$

$$BOH4 = MWB \times \rho_w \times m3tl \times \varphi \times B / ([H^+] + K_B) \times mtmm$$

$$\Omega_{Cal} = Ca^{2+} \times CO3 / (K_{Cal} \times MWC \times \rho_w \times m3tl \times mmmtm \times \varphi)$$

$$\Omega_{Arg} = Ca^{2+} \times CO3 / (K_{Arg} \times MWC \times \rho_w \times m3tl \times mmmtm \times \varphi)$$

where:

$atma$	conversion factor for atmosphere to microatmosphere (10^6) [$\mu\text{atm atm}^{-1}$]
$atpa$	conversion factor for atmosphere to pascal (101325) [Pa atm^{-1}]
$cm3tm3$	conversion factor for cm^3 to m^3 (10^6) [$\text{cm}^3 \text{ m}^{-3}$]
BV	virial coefficient of carbon dioxide in air [$\text{m}^3 \text{ mol}^{-1}$]
D	virial coefficient of pure carbon dioxide [$\text{m}^3 \text{ mol}^{-1}$]
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 [$\text{m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$]
$CO2$	dissolved carbon dioxide concentration [$\text{gCO}_2 \text{ m}^{-3}$]
$CO2M$	molar dissolved carbon dioxide concentration [$\text{mmolCO}_2 \text{ kg}^{-1}$]
$FCO2$	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 made equal to pH_max . If the pH is smaller than pH_min , it is made equal to pH_min .

Finally, the fractions (gC gC $^{-1}$ or mol mol $^{-1}$) of the carbon dioxide and the carbonate species of total dissolved inorganic carbon (TIC) are calculated as follows:

$$\begin{aligned}fc_2 &= \frac{HCO_3}{TIC} \\fc_3 &= \frac{CO_3}{TIC} \\fc_0 &= 1 - fc_2 - fc_3\end{aligned}$$

where:

$$\begin{aligned}fc_0 &\quad \text{fraction } CO_2 \text{ of TIC } [-] \\fc_2 &\quad \text{fraction } HCO_3^- \text{ of TIC } [-] \\fc_3 &\quad \text{fraction } CO_3^{2-} \text{ of TIC } [-]\end{aligned}$$

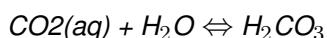
Version 1 (SwpH = 0.0)

The original version 1 uses only the formulations for K_1 and K_2 valid for salinity < 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.

Version 1 calculates the carbonate species differently. The hydrolysis reactions of carbonate proceed according to the following reaction equations:



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:

$$\begin{aligned}Kc_0 &= \frac{Ccd_0}{Ccd_1} \\Kc_1 &= \frac{Ccd_2 \times H^+}{(Ccd_0 + Ccd_1)} \\Kc_2 &= \frac{Ccd_3 \times H^+}{Ccd_2} \\Ccdt &= Ccd_0 + Ccd_1 + Ccd_2 + Ccd_3\end{aligned}$$

where:

$$\begin{aligned}Ccd_0 &\quad \text{dissolved carbon dioxide } [\text{mol.l}^{-1}] \\Ccd_1 &\quad \text{dissolved } H_2CO_3 \text{ } [\text{mol.l}^{-1}]\end{aligned}$$

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.

The concentration of the relevant carbonate species in solution can now be calculated from:

$$Ccdt = \frac{Ctic}{12\,000 \times \varphi}$$

$$Ccd_1 = \frac{Ccdt}{(1 + Kc_1/H^+ + (Kc_1 \times Kc_2)/(H^+)^2)} \times \frac{1}{(1 + Kc_0)}$$

$$Ccd_0 = Kc_0 \times Ccd_1$$

$$Ccd_2 = \frac{Kc_1 \times (Kc_0 + 1) \times Ccd_1}{H^+}$$

$$Ccd_3 = Ccdt - Ccd_0 - Ccd_1 - Ccd_2$$

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})
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 $\text{gCO}_2.\text{m}^{-3}$.

The pertinent carbonate fractions (mol mol⁻¹ or g g⁻¹) follow from:

$$\begin{aligned}fc_0 &= \frac{Ccd_0}{Ccdt} \\fc_1 &= \frac{Ccd_1}{Ccdt} \\fc_2 &= \frac{Ccd_2}{Ccdt} \\fc_3 &= 1 - fc_0 - fc_1 - fc_2\end{aligned}$$

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.

Directives for use

- ◊ Two versions for the calculation of pH are available. The original version 1 is selected with option parameter $SwpH = 0.0$ (default value). Former process SPECCARB for the calculation of the concentrations and the fractions of the carbonate species needed for processes REARCO2 and PRIRON was integrated into the pH_Simp process. Version 2 is selected with option parameter $SwpH = 1.0$, and has its own formulations for the calculation of the carbonate species.
- ◊ Version 1 is suitable for water with a salinity < 5 psu.
- ◊ 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.
- ◊ pH_Simp can be used to calculate the pH as described above, or the pH can be imposed as a function of time and space with option $SwpH = -1.0$. When the pH is imposed, pH_Simp calculates the concentrations and the fractions of the carbonate species process according to Version 1.
- ◊ Version 1 includes the calculation of $DisH2CO3$ and $FrH2CO3d$, whereas this is not done by version 2 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 8.7: Definitions of the input parameters in the above equations for *pH_simp*. Volume units refer to bulk (ℓ) or to water (ω).

Name in formulas	Name in Input	Definition	Units
<i>SwpH</i>	<i>SwpH</i>	option parameter for formulations (0.0 = old version; 1.0 = new version)	-
<i>Alka</i> <i>TIC</i>	<i>Alka</i> <i>TIC</i>	alkalinity total dissolved inorganic carbon concentration	$\text{gHCO}_3 \text{ m}^{-3} \ell$ $\text{gC.m}^{-3} \ell$
<i>pH</i> <i>pH_max</i> <i>pH_min</i>	<i>pH</i> <i>pH_max</i> <i>pH_min</i>	imposed pH, acidity maximum pH minimum pH	- - -
<i>S</i> <i>T</i>	<i>Salinity</i> <i>TEMP</i>	salinity ambient water temperature	$\text{psu } \ell$ $^{\circ}\text{C}$
φ	<i>POROS</i>	porosity	-

Table 8.8: Definitions of the output parameters of *pH_simp*. Volume units refer to bulk (ℓ) or to water (ω).

Name in formulas	Name in Input	Definition	Units
<i>pH</i>	<i>pH</i>	simulated pH, acidity	-
<i>CO2</i> or <i>Ccd₀</i>	<i>DisCO2</i>	concentration of dissolved CO_2	$\text{gCO}_2 \cdot \text{m}^{-3} \ell$
<i>HCO3</i> or <i>Ccd₁</i>	<i>DisHCO3</i>	concentration of dissolved HCO_3^-	$\text{gC.m}^{-3} \ell$
<i>CO3</i> or <i>Ccd₂</i>	<i>DisCO3</i>	concentration of dissolved CO_3^{2-}	$\text{gC.m}^{-3} \ell$
<i>H2CO3</i> or <i>Ccd₃</i>	<i>DisH2CO3</i>	concentration of dissolved H_2CO_3	$\text{gC.m}^{-3} \ell$
<i>f_{c0}</i> <i>f_{c1}</i> <i>f_{c2}</i> <i>f_{c3}</i>	<i>FrCO2dis</i> <i>FrH2CO3d</i> <i>FrHCO3dis</i> <i>FrCO3dis</i>	fraction of dissolved carbon dioxide fraction of dissolved H_2CO_3 fraction of dissolved HCO_3^- fraction of dissolved CO_3^{2-}	gC gC^{-1} gC gC^{-1} gC gC^{-1} gC gC^{-1}
<i>BOH4</i>	<i>BOH4</i>	dissolved borate B(OH)_4^- concentration	$\text{gB m}^{-3} \ell$
<i>pCO2_w</i>	<i>pCO2water</i>	partial pressure of carbon dioxide in water	μatm^{-1}
Ω_{Cal} Ω_{Arg}	<i>SatCal</i> <i>SatArg</i>	saturation state of calcite saturation state of aragonite	- -

8.4 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. Volatilisation 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 ($< 3 \text{ m s}^{-1}$). 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. Volatilisation 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 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 8.9](#) provides the definitions of the parameters occurring in the formulations.

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 CH₄ as follows:

$$Rvol = klvol \times [Cch4s - \max(Cch4, 0.0)] / H$$

$$klvol = klvol^{20} \times ktvol^{(T-20)}$$

$$klvol^{20} = \left(\frac{a \times v^b}{H^c} \right) + (d \times W^2)$$

$$Cch4s = f(T, Pch4) \quad (\text{delivered by SATURCH4})$$

$$fsat = 100 \times \frac{\max(Cch4, 0.0)}{Cch4s}$$

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. Although 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:

$$a = klvol^{20} \quad b = 0.0 \quad c = 0.0 \quad d = 0.0$$

$SWVolCH_4 = 4$

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.

 $SWVolCH_4 = 9$

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 ($W < 3 \text{ m s}^{-1}$).

 $SWVolCH_4 = 13$

The relation according to [Guérin \(2006\)](#); [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:

$$klrear = (a \times \exp(b_1 \times W^{b2}) + (c_1 \times P^{c2})) \times fsc$$

$$fsc = \left(\frac{Sc}{Sc^{20}} \right)^{-0.67}$$

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

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 [$^\circ\text{C}$]
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
<i>CoefA CH4</i>	<i>CoefB1 CH4</i>	<i>CoefB2 CH4</i>	<i>CoefC1 CH4</i>	<i>CoefC2 CH4</i>
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
<i>CoefD1 CH4</i>	<i>CoefD2 CH4</i>	<i>CoefD3 CH4</i>	<i>CoefD4 CH4</i>
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.

Table 8.9: Definitions of the parameters in the above equations for VOLATCH4.

Name in formulas ¹	Name in input	Definition	Units
$Cch4$ $Cch4s$	$CH4$ $SaturCH4$	concentration of methane saturation conc. of methane from SAT-URCH4	gC m^{-3} gC m^{-3}
a b_1 b_2 c_1 c_2	$CoefA\text{CH4}$ $CoefB1\text{CH4}$ $CoefB2\text{CH4}$ $CoefC1\text{CH4}$ $CoefC2\text{CH4}$	coefficients for option 13 only	- - - - -
d_1 d_2 d_3 d_4	$CoefD1\text{CH4}$ $CoefD2\text{CH4}$ $CoefD3\text{CH4}$ $CoefD4\text{CH4}$	coefficients for option 13 only	- - - -
fcs $fsat$	- -	scaling factor for the Schmidt number percentage methane saturation	- %
H	$Depth$	depth of the top water layer	m
$klvol^{20}$ $kvol$	$KLVol\text{CH4}$ $TCVol\text{CH4}$	water transfer coefficient for methane ¹ temperature coefficient for methane volatilisation	d^{-1} -
P	$Rain$	rainfall	mm h^{-1}
$Rvol$	-	methane volatilisation rate	$\text{gC m}^{-3} \text{ d}^{-1}$
$SWVol\text{CH4}$	$SWVol\text{CH4}$	switch for selection of options for transfer coefficient	-
T	$Temp$	temperature	$^{\circ}\text{C}$
v W	$Velocity$ $VWind$	stream velocity windspeed at 10 m height	m s^{-1} m s^{-1}

¹ See directives for use concerning the dimension of $KLVol\text{CH4}$

8.5 Saturation concentration of methane

PROCESS: SATURCH4

The volatilization of methane proceeds proportional to the difference of the saturation CH₄ concentration and the actual dissolved CH₄ concentration. The saturation concentration of CH₄ is primarily a function of water temperature, although salinity affects the saturation concentration too.

The saturation concentration at the water surface is also proportional to the partial atmospheric CH₄ 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 CH₄ 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 CH₄. [Table 8.10](#) 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 $PAPCH4$ is 0 atm.
- ◊ The name of the output parameter for the saturation concentration of methane is *SaturCH4*.

Table 8.10: The definitions 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	$^{\circ}\text{C}$

8.6 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 CH₄ 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 8.11](#) provides the definitions of the parameters occurring in the formulations.

Formulation

The methane ebullition flux follows from:

$$Rebu = f \times \left(\frac{Cch4/\phi - Cch4s}{\Delta t} \right) \quad \text{if } Cch4/\phi \geq Cch4s$$

$$Cch4s = 18.76 \times \left(1 + \frac{H}{10} \right) \times (1.024)^{(20-T)}$$

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.

Directives for use

- ◊ The scaling factor $fScEbul$ can be used to scale the ebullition flux in order to establish 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 8.11: 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	$\text{gC m}^{-3} \text{ d}^{-1}$
T	$Temp$	temperature	$^{\circ}\text{C}$
Δt	$Delt$	computational time-step	d
ϕ	$POROS$	porosity	-

8.7 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 sulphate 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. Sulphate reduction does not deliver energy at the (substantial) presence of dissolved oxygen. Therefore, the oxidation with sulphate only occurs when sulphate 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 temperatures. It may even come to a halt.

Volume units refer to bulk (ℓ) or to water (ω).

Implementation

Process METHOX has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers.

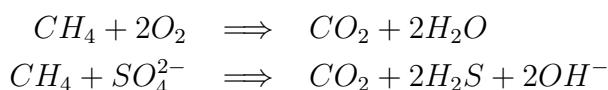
The process has been implemented for the following substances:

- ◊ CH₄, OXY and SO₄.

[Table 8.12](#) provides the definitions of the parameters occurring in the formulations.

Formulation

Methane oxidation can be described with the following overall reaction equations:



These processes require 5.33 gO₂ 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 sulphate. 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 sulphate at DO concentrations exceeding a certain critical concentration.

Methane oxidation is formulated as follows to accommodate the above features ([Smits and](#)

Van Beek (2013)):

$$Roxi_1 = k0oxi_1 + koxi_1 \times \left(\frac{Cch4}{Ksch4 \times \phi + Cch4} \right) \times \left(\frac{Cox}{Ksox \times \phi + Cox} \right)$$

$$koxi_1 = koxi_1^{20} \times ktoxi_1^{(T-20)}$$

$$koxi_1 = 0.0 \quad \text{if } T < Tc$$

$$\quad \text{or } Cox \leq 0.0$$

$$\quad \text{or } Cox \leq Coxc \times \phi$$

$$k0oxi_1 = 0.0 \quad \text{if } Cox > Coxc \times \phi$$

$$\quad \text{or } Cox \leq 0.0$$

$$Roxi_2 = k0oxi_2 + koxi_2 \times \left(\frac{Cch4}{Ksch4 \times \phi + Cch4} \right) \times \left(\frac{Csu}{Kssu \times \phi + Csue} \right)$$

$$koxi_2 = koxi_2^{20} \times ktoxi_2^{(T-20)}$$

$$koxi_2 = 0.0 \quad \text{if } T < Tc$$

$$\quad \text{or } Csue \leq 0.0$$

$$\quad \text{or } Csue \leq Csuc \times \phi$$

$$\quad \text{or } Cox > Coxc \times \phi$$

$$k0oxi_2 = 0.0 \quad \text{if } Csue > Csuc \times \phi$$

$$\quad \text{or } Csue \leq 0.0$$

$$\quad \text{or } Cox > Coxc \times \phi$$

with:

$Cch4$	dissolved methane concentration [gC m^{-3}]
Cox	dissolved oxygen concentration [$\text{gO}_2 \text{ m}^{-3}$]
$Coxc$	critical dissolved oxygen concentration for oxidation with sulphate [$\text{gO}_2 \text{ m}^{-3}$]
Csu	sulphate concentration [gS m^{-3}]
$Csuc$	critical sulphate concentration for oxidation with sulphate [gS m^{-3}]
$k0oxi_1$	zero-order methane oxidation rate for diss. oxygen consumption [$\text{gC m}^{-3} \text{ d}^{-1}$]
$k0oxi_2$	zero-order methane oxidation rate for sulphate consumption [$\text{gC m}^{-3} \text{ d}^{-1}$]
$koxi_1$	Michaelis-Menten rate for oxidation with dissolved oxygen [$\text{gC m}^{-3} \text{ d}^{-1}$]
$ktoxi_1$	temperature coefficient for oxidation with dissolved oxygen [-]
$Ksch4$	half saturation constant for methane consumption [gC m^{-3}]
$Ksox$	half saturation constant for dissolved oxygen consumption [$\text{gO}_2 \text{ m}^{-3}$]
$koxi_2$	Michaelis-Menten rate for oxidation with sulphate [$\text{gC m}^{-3} \text{ d}^{-1}$]
$ktoxi_2$	temperature coefficient for oxidation with sulphate [-]
$Kssu$	half saturation constant for sulphate consumption [gS m^{-3}]
$Roxi_1$	methane oxidation rate with DO [$\text{gC m}^{-3} \text{ d}^{-1}$]
$Roxi_2$	methane oxidation rate with sulphate [$\text{gC m}^{-3} \text{ d}^{-1}$]
T	temperature [$^{\circ}\text{C}$]
Tc	critical temperature for methane oxidation [$^{\circ}\text{C}$]
ϕ	porosity [-]

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 sulphate 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 $2 \text{ gO}_2 \text{ m}^{-3}$.
- ◊ An indicative value for the temperature coefficients $TcMetOx$ and $TcMetSu$ is 1.07.
- ◊ The oxidation with sulphate 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. \(2001\)](#)

Table 8.12: Definitions of the parameters in the above equations for OXIDCH4. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
$Cch4$	$CH4$	methane concentration	$gC \ m_\ell^{-3}$
Cox	OXY	dissolved oxygen concentration	$gO_2 \ m_\ell^{-3}$
$Coxc$	$CoxMet$	critical DO concentration for methane oxidation	$gO_2 \ m_w^{-3}$
$Csuc$	$CsuMet$	critical sulphate concentration for methane oxidation	$gS \ m_w^{-3}$
Csu	$SO4$	sulphate concentration	$gS \ m_\ell^{-3}$
$koxi_1^{20}$	$RcMetOx20$	MM-rate for methane oxidation with DO at 20 °C	$gC \ m_\ell^{-3} \ d^{-1}$
$ktoxi_1$	$TcMetOx$	temp. coefficient for methane oxidation with DO	-
$koxi_2^{20}$	$RcMetSu20$	MM-rate for methane oxid. with sulphate at 20 °C	$gC \ m_\ell^{-3} \ d^{-1}$
$ktoxi_2$	$TcMetSu$	temp. coefficient for methane oxidation with sulphate	-
$Ksch4$	$KsMet$	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 sulphate consumption	$gS \ m_w^{-3}$
$k0oxi_1$	$Rc0MetOx$	zero-order methane oxid. rate for DO consumption	$gC \ m_\ell^{-3} \ d^{-1}$
$k0oxi_2$	$Rc0MetSu$	zero-order methane oxid. rate for sulphate cons.	$gC \ m_\ell^{-3} \ d^{-1}$
$Roxi_1$	-	rate of oxidation of methane with DO	$gC \ m_\ell^{-3} \ d^{-1}$
$Roxi_2$	-	rate of oxidation of methane with sulphate	$gC \ m_\ell^{-3} \ d^{-1}$
T	$Temp$	temperature	°C
Tc	$CTMetOx$	critical temperature for methane oxidation	°C
ϕ	$POROS$	porosity	$m_w^3 \ m_\ell^{-3}$

8.8 Oxidation of sulphide

PROCESS: OXIDSUD

Sulphide 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 sulphide can be important at low dissolved oxygen concentrations. Specific autotrophic bacteria species are capable of oxidising sulphide when solar radiation is available as a source of energy. Given the specific features of sulphide 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 sulphide 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 sulphide minerals, it is assumed that only dissolved sulphide is available to quick oxidation.

Volume units refer to bulk (b) or to water (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 8.13](#) provides the definitions of the parameters occurring in the formulations.

Formulation

Sulphide oxidation can be described with following overall reaction equation:



The process requires 2.0 gO₂ gS⁻¹.

Sulphide oxidation is modelled as the sum of a zero order process and a second-order kinetic process, involving the concentrations of both total dissolved sulphide 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 sulphide oxidation when the dissolved oxygen concentration falls below a critical level. The other purpose is to have sulphide 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.

The sulphate oxidation rate is formulated as follows to accommodate the above features ([Smits and Van Beek \(2013\)](#)):

$$Roxi = k0oxi + koxi \times \left(\frac{Csud}{\phi} \right) \times \left(\frac{Cox}{\phi} \right) \times \phi$$

$$koxi = koxi^{20} \times ktoxi^{(T-20)}$$

$$koxi = 0.0 \quad \text{if } Cox \leq 0.0$$

$$k0oxi = 0.0 \quad \text{if } Cox > Coxc \times \phi$$

with:

Cox	dissolved oxygen concentration [$\text{gO}_2 \text{ m}^{-3}$]
$Coxc$	critical dissolved oxygen concentration [$\text{gO}_2 \text{ m}^{-3}$]
$Csud$	total dissolved sulphide concentration [gS m^{-3}]
$koxi$	pseudo second-order sulphide oxidation rate [$\text{gO}_2^{-1} \text{ m}^3 \text{ d}$]
$ktoxi$	temperature coefficient for sulphide oxidation [-]
$k0oxi$	zero-order sulphide oxidation rate [$\text{gS m}^{-3} \text{ d}^{-1}$]
T	temperature [$^\circ\text{C}$]
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 sulphide. Therefore, the oxidation flux is made equal to half the concentration of dissolved sulphide 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 sulphide 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 $T = 20$ $^\circ\text{C}$, and average DO concentrations. Using zero-order kinetics may cause negative sulphide 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 sulphide oxidation in a water column with negative oxygen concentrations.

Additional references

[DiToro \(2001\)](#), [Wang and Cappellen \(1996\)](#), [WL | Delft Hydraulics \(2002\)](#), [Wijisman et al. \(2001\)](#)

Table 8.13: Definitions of the parameters in the above equations for OXIDSUD. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
C_{ox}	OXY	dissolved oxygen concentration	$\text{gO}_2 \text{ m}^{-3}_\ell$
C_{oxc}	$CoxSUD$	critical dissolved oxygen concentration	$\text{gO}_2 \text{ m}^{-3}_w$
C_{sud}	SUD	total dissolved sulphide concentration	gS m^{-3}_ℓ
Δt	$Delt$	timestep	d
$koxi^{20}$	$RcSox20$	pseudo second-order sulphide oxidation rate at 20 °C	$\text{gO}_2^{-1} \text{ m}^3_w \text{ d}^{-1}$
$ktoxi$	$TcSox$	temperature coefficient for sulphide oxidation	-
$k0oxi$	$Rc0Sox$	zero-order sulphide oxidation rate	$\text{gS m}^{-3}_\ell \text{ d}^{-1}$
$Roxi$	-	sulphide oxidation rate	$\text{gS m}^{-3}_\ell \text{ d}^{-1}$
T	$Temp$	temperature	°C
ϕ	$POROS$	porosity	$\text{m}^3_w \text{ m}^{-3}_\ell$

8.9 Precipitation and dissolution of sulphide

PROCESS: PRECSUL

At reducing conditions sulphide resulting from sulphate reduction may precipitate with iron(II) as rather amorphous iron(II) sulphide. This mineral is thermodynamically unstable at oxidising conditions. At the presence of dissolved oxygen iron(II) in sulphides is oxidised into iron(III), sulphide into sulphate, resulting in the subsequent dissolution of the mineral.

Not only sulphide but also elementary sulphur is produced at sulphate reduction. Crystalline pyrite (FeS_2) is formed from iron(II) sulphide and sulphur, 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 in 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) sulphide only occurs at the absence of dissolved oxygen in a solution supersaturated with respect to free sulphide and iron(II) ions. These conditions usually occur in the reducing sediment, just below an oxidising top layer. However, sulphide 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 sulphide is subjected. The pH-dependency is taken into account via the calculation of a pH dependent free sulphide concentration with process SPECSUD.

The dissolution of iron(II) sulphide occurs when the solution is undersaturated with respect to sulphide 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 sulphide 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) sulphide. However, in reality oxidation will also take place at the mineral surface to a certain extent.

Volume units refer to bulk (b) or to water (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 sulphide 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:

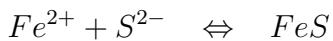
- ◊ total dissolved sulphide SUD and particulate sulphide SUP.

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 sulphide as iron sulphide in stead of process PRECSUL.

Table 8.14 provides the definitions of the parameters occurring in the formulations. The actual dissolved free sulphide concentration (C_{sd}) can be delivered by process SPECSUD or imposed to DELWAQ via the input.

Formulation

The precipitation and dissolution equilibrium of iron(II) sulphide can be described with the following simplified reaction equation:



The precipitation and dissolution rates are formulated with first-order kinetics, with the difference between the actual dissolved free sulphide concentration and the equilibrium dissolved concentration as driving force ([Smits and Van Beek \(2013\)](#)):

$$R_{prc} = 32\,000 \times k_{prc} \times (C_{sd} - C_{sde}) \times \phi \quad \text{if } C_{sd} \geq C_{dse}$$

$$R_{dis} = 32\,000 \times k_{dis} \times (C_{sde} - C_{sd}) \times \phi \quad \text{if } C_{sd} < C_{dse}$$

$$k_{prc} = k_{prc}^{20} \times k_{tprc}^{(T-20)}$$

$$k_{dis} = k_{dis}^{20} \times k_{tdis}^{(T-20)}$$

with:

C_{sd}	dissolved free sulphide concentration [mol l ⁻¹]
C_{sde}	equilibrium dissolved free sulphide concentration [mol l ⁻¹]
k_{dis}	dissolution reaction rate [d ⁻¹]
k_{prc}	precipitation rate [d ⁻¹]
k_{tdis}	temperature coefficient for dissolution [-]
k_{tprc}	temperature coefficient for precipitation [-]
R_{dis}	rate of dissolution [gS m ⁻³ d ⁻¹]
R_{prc}	rate of precipitation [gS m ⁻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 sulphide. Therefore, the dissolution flux is made equal to half the concentration of precipitated sulphide 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 sulphide and iron(II) concentrations. However, iron is currently not included in DELWAQ.

Directives for use

- ◊ The equilibrium dissolved free sulphide concentration can be calculated with process SUL-FID using an imposed total dissolved sulphide concentration. However, it is also possible to impose fixed dissolved free sulphide concentrations by assigning values to *DisSWK* as input parameter.
- ◊ The equilibrium dissolved free sulphide concentration *DisSEqFeS* is an input parameter. Its value can be deduced from the solubility product of iron(II) sulphide 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 sulphide oxidation rate *RcSox20* for process OXIDSUD.

- ◇ 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 8.14: Definitions of the parameters in the above equations for PRECSUL. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
C_{sd}	$DisSWK$	dissolved free sulphide concentration	mol l^{-l}
C_{sde}	$DisSEqFeS$	equilibrium dissolved free sulphide concentration for amorphous iron sulphide	mol l^{-1}
C_{sup}	SUP	precipitated sulphide concentration	gS m^{-3}
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	$\text{gS m}^{-3} \text{d}^{-1}$
$Rprc$	-	precipitation rate	$\text{gS m}^{-3} \text{d}^{-1}$
T	$Temp$	temperature	$^{\circ}\text{C}$
ϕ	$POROS$	porosity	$\text{m}_w^3 \text{m}_{\ell}^{-3}$

8.10 Speciation of dissolved sulphide

PROCESS: SPECSUD AND SPECSUDS1/2

Sulphide can only persist in anoxic environment, the reducing environment which usually occurs in the sediment. Being a weak acid sulphide 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 sulphide concentrations in the reducing environment. Metal sulphide complexes are formed and only the concentrations of the free metal ion and the free sulphide ion affect the precipitation and the dissolution of a solid metal sulphide.

The computed sulphide 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 sulphide.

Volume units refer to bulk (β) or to water (ω).

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 sulphide species as model input

The processes have been implemented for the following substances:

- ◊ dissolved sulphide species SUD and SUDS1/2.

Tables 8.15 and 8.16 provide the definitions of the parameters occurring in the formulations. Table 8.17 provides the output parameters.

Formulation

The hydrolysis of hydrogen sulphide proceeds according to the following reaction equations:



The chemical equilibria are described with:

$$K_{s1} = \frac{C_{sd2} \times H^+}{C_{sd1}} \quad (8.4)$$

$$K_{s2} = \frac{C_{sd3} \times H^+}{C_{sd2}} \quad (8.5)$$

$$Csdt = C_{sd1} + C_{sd2} + C_{sd3} \quad (8.6)$$

with:

C_{sd1} concentration of dissolved hydrogen sulphide [mol l⁻¹]

C_{sd_2}	concentration of hydrogen sulphide anion [mol l ⁻¹]
C_{sd_3}	concentration of free dissolved sulphide [mole l ⁻¹]
C_{sdt}	concentration of total dissolved sulphide [mol l ⁻¹]
H^+	proton concentration [mol l ⁻¹]
K_{s1}	acidity (dissociation, equilibrium) constant for H ₂ S [mol l ⁻¹]
K_{s2}	acidity (dissociation, equilibrium) constant for HS ⁻ [mol l ⁻¹]

The proton concentration H^+ and the temperature dependent equilibrium constants follow from:

$$\begin{aligned}H^+ &= 10^{-pH} \\K_{s1} &= 10^{-lK_{11}} \times kth2s^{(T-20)} \\K_{s2} &= 10^{-lK_{s2}} \times kths^{(T-20)}\end{aligned}$$

where:

$kths$	temperature coefficient for HS ⁻¹ equilibrium [-]
$kth2s$	temperature coefficient for H ₂ S equilibrium [-]
pH	acidity [-]
T	temperature [°C]

The concentration of the relevant sulphide species in solution can now be calculated from:

$$\begin{aligned}Csdt &= \frac{Csud}{32\,000 \times \phi} \\Csdt_1 &= \frac{Csdt}{(1 + K_{s1}/H^+ + (K_{s1} \times K_{s2})/(H^+)^2)} \\Csdt_2 &= \frac{K_{s1} \times Csdt_1}{H^+} \\Csdt_3 &= Csdt - Csdt_1 - Csdt_2\end{aligned}$$

if due to round off the resulting $Csdt_3 \leq 0.0$

$$Csdt_3 = \frac{K_{s2} \times Csdt_2}{H^+}$$

where:

$Csud$	concentration of total dissolved sulphide [gS m ⁻³]
ϕ	porosity [-]

The constant 32 000.0 concerns the conversion from gS m⁻³ to mol l⁻¹.

The pertinent fractions follow from:

$$\begin{aligned}fs_1 &= \frac{Csdt_1}{Csdt} \\fs_2 &= \frac{Csdt_2}{Csdt} \\fs_3 &= 1 - fs_1 - fs_2\end{aligned}$$

if due to rounding off the resulting $fs_3 = 0.0$

$$fs_3 = \frac{Csdt_3}{Csdt}$$

Directives for use

- ◊ The acidity constants for the hydrogen sulphides 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 sulphide 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 sulphide concentrations apply to the water column and the various sediment layers.

Additional references

[Stumm and Morgan \(1996\)](#)

Table 8.15: Definitions of the input parameters in the above equations for SPECSUD.

Name in formulas	Name in input	Definition	Units
Csd _t	-	concentration of total dissolved sulphide	mol l $^{-1}$
Csud	SUD	concentration of total dissolved sulphide	gS.m $^{-3}$
IKs ₁	lKstH2S	log acidity constant for H ₂ S (mol l $^{-1}$)	log(-)
IKs ₂	lKstHS	log acidity constant for HS $^{-}$ (mol l $^{-1}$)	log(-)
kth _{2s}	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 3 w.m $^{-3}$

Table 8.16: Definitions of the input parameters in the above equations for SPECSUDS1/2.

Name in formulas	Name in input	Definition	Units
Csdt Csud	— SUDS1/2	concentration of total dissolved sulphide concentration of total dissolved sulphide	mol l^{-1} $\text{g S.m}^{-3}\ell$
IKhs IKh ₂ s kth ₂ s kths	IKstHS IKstH2S TcKstH2S TcKstHS	log acidity constant for HS^- (mol l^{-1}) log acidity constant for H_2S (mol l^{-1}) temperature coefficient for KstH2S temperature coefficient for KstHS	log(-) log(-) - -
H ⁺ pH	— pH	proton concentration acidity	mol l^{-1} -
T	TEMP	ambient temperature (currently not used)	°C
φ	PORS1/2	porosity	$\text{m}^3\text{w.m}^{-3}\ell$

Table 8.17: Definitions of the output parameters of SPECSUD and SPECSUDS1/2.

Name in formulas	Name in input	Definition	Units
Csd ₁ Csd ₂ Csd ₃	DisH2SWK DisHSWK DisSWK	of dissolved hydrogen sulphide concentration of hydrogen sulphide anion concentration of free dissolved sulphide	mol l^{-1} mol l^{-1} mol l^{-1}
fs ₁ fs ₂ fs ₃	FrH2Sdis FrHSdis FrS2dis	fraction of dissolved hydrogen sulphide fraction of hydrogen sulphide anion fraction of free dissolved sulphide	- - -
Csd ₁ Csd ₂ Csd ₃	DisH2SWKS1 DisHSWKS1 DisSWKS1	concentration of dissolved hydrogen sulphide in S1 concentration of hydrogen sulphide anion in S1 concentration of free dissolved sulphide in S1	mol l^{-1} mol l^{-1} mol l^{-1}
Csd ₁ Csd ₂ Csd ₃	DisH2SWKS2 DisHSWKS2 DisSWKS2	concentration of dissolved hydrogen sulphide in S2 concentration of hydrogen sulphide anion in S2 concentration of free dissolved sulphide in S2	mol l^{-1} mol l^{-1} mol l^{-1}

8.11 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 $\text{Fe}(\text{OH})_3$ 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) sulphide 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) sulphide 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) sulphide. Precipitation of Fe^{2+} adds to the FeS whereas FeS_2 is formed from FeS and S . Elementary sulphur is produced at sulphate 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) sulphide and pyrite are thermodynamically unstable at oxidizing conditions. At the presence of dissolved oxygen the sulphide is oxidized into sulphate 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) sulphide 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) sulphide 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 sulphide 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 FeIIpc FeIId FeS FeS2 FeCO3 Felld and SUD.

Tables 8.18 and 8.19 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 SPEC-IRON or imposed on the model as an input parameter. The fraction dissolved free sulphide 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 SPEC-CARB 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 SWT/CCO₂ 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:



The precipitation and dissolution rates are formulated with approximate kinetics with the difference of the ion activity and solubility products as driving force:

$$Rpfe3 = kpfe3 \times \left(\frac{IAP_1}{Ksp_1} - 1 \right) \times \varphi \quad \text{if } IAP_1 \geq Ksp_1$$

$$Rdfe3 = kdfe3 \times Cfea \times \left(1 - \frac{IAP_1}{Ksp_1} \right) \quad \text{if } IAP_1 < Ksp_1$$

$$IAP_1 = Cfe3d \times (\text{OH}^-)^3$$

$$Cfe3d = ffe3_1 \times Cfe3dt \times \frac{1}{56\,000 \times \varphi}$$

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

$$Ksp_1 = 10^{lKsp_1}$$

$$Kfe_1 = 10^{lKfe_1}$$

$$kpfe3 = kpfe3^{20} \times ktpfe3^{(T-20)}$$

$$kdfe3 = kdfe3^{20} \times ktdfe3^{(T-20)}$$

where:

Cfea particulate amorphous oxidizing iron concentration [gFe.m⁻³]
Cfe3dt dissolved oxidizing iron concentration [gFe.m⁻³]
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 ⁻¹⁴]
Ksp_1	solubility product for Fe(OH)_3 [mol.l ⁻¹⁴]
$kdf3e$	specific iron(III) dissolution rate [d ⁻¹]
$kpf3e$	specific iron(III) precipitation rate [gFe.m ⁻³ .d ⁻¹]
$ktdfe3$	temperature coefficient for iron(III) dissolution [-]
$ktpfe3$	temperature coefficient for iron(III) precipitation [-]
OH^-	hydroxyl concentration [mol.l ⁻¹]
pH	acidity [-]
$Rdf3e$	rate of amorphous iron(III) dissolution [gFe.m ⁻³ .d ⁻¹]
$Rpfe3$	rate of amorphous iron(III) precipitation [gFe.m ⁻³ .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 $Cfea/\Delta t$.

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:



The rate of aging is equal to:

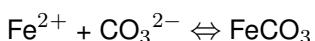
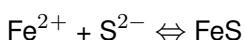
$$\begin{aligned} Rafe3 &= kafe3 \times Cfea \\ kafe3 &= kafe3^{20} \times ktafe3^{(T-20)} \end{aligned}$$

where:

$Cfea$	particulate amorphous oxidizing iron concentration [gFe.m ⁻³]
$kafe3$	specific iron(III) aging rate [d ⁻¹]
$ktafe3$	temperature coefficient for iron(III) aging [-]
$Rafe3$	rate of amorphous iron(III) aging [gFe.m ⁻³ .d ⁻¹]
T	temperature [°C]

Precipitation and dissolution of iron(II)

The precipitation of iron(II) minerals in the model includes iron(II) sulphide (FeS) and siderite (FeCO_3). The precipitation and dissolution equilibria can be described with the following simplified reaction equations:



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

sulphide formation are:

$$\begin{aligned}
 Rpfes &= kpifes \times \left(\frac{IAP_2}{Ksp_2} - 1 \right) \times \phi && \text{if } IAP_2 \geq Ksp_2 \\
 Rdfes &= kdfes \times Cfes \times \left(1 - \frac{IAP_2}{Ksp_2} \right) && \text{if } IAP_2 < Ksp_2 \\
 IAP_2 &= Cfe2d \times Csd_3 \\
 Cfe2d &= ffe2_1 \times Cfe2dt \times \frac{1}{56\,000 \times \varphi} \\
 Csd_3 &= fs_3 \times Csdt \times \frac{1}{32\,000 \times \varphi} \\
 Ksp_2 &= 10^{lKsp_2} \\
 kpifes &= kpifes^{20} \times ktpfes^{(T-20)} \\
 kdfes &= kdfes^{20} \times ktdfes^{(T-20)}
 \end{aligned}$$

where:

$Cfes$	iron(II) sulphide concentration [gFe.m $^{-3}$]
$Cfe2dt$	dissolved reducing iron concentration [gFe.m $^{-3}$]
$Cfe2d$	equilibrium dissolved free iron(II) concentration [mol.l $^{-1}$]
$Csdt$	total dissolved sulphide concentration [gS.m $^{-3}$]
Csd_3	dissolved free sulphide concentration [mol.l $^{-1}$]
fs_3	fraction dissolved free sulphide [-]
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 $^{-1}$]
$kpifes$	specific FeS precipitation rate [gFe.m $^{-3}.d^{-1}$]
$ktdfes$	temperature coefficient for FeS dissolution [-]
$ktpfes$	temperature coefficient for FeS precipitation [-]
$Rdfes$	rate of FeS dissolution [gFe.m $^{-3}.d^{-1}$]
$Rpfes$	rate of FeS precipitation [gFe.m $^{-3}.d^{-1}$]
T	temperature [°C]
φ	porosity [-]

The constant of 56 000 concerns the conversion of gFe.m $^{-3}$ to mol.l $^{-1}$.

The formulations for iron carbonate formation are:

$$\begin{aligned}
 R_{pfeco3} &= kp_{feco3} \times \left(\frac{IAP_3}{Ksp_3} - 1 \right) \times \phi && \text{if } IAP_3 \geq Ksp_3 \\
 R_{dfeco3} &= kdfeco3 \times C_{feco3} \times \left(1 - \frac{IAP_3}{Ksp_3} \right) && \text{if } IAP_3 < Ksp_3 \\
 IAP_3 &= C_{fe2d} \times C_{co3d} \\
 C_{fe2d} &= ffe2_1 \times C_{fe2td} \times \frac{1}{56\,000 \times \varphi} \\
 C_{co3d} &= fc_3 \times Ctic \times \frac{1}{12\,000 \times \varphi} \\
 Ksp_3 &= 10^{lKsp_3} \\
 kp_{feco3} &= kp_{feco3}^{20} \times ktp_{feco3}^{(T-20)} \\
 kdfeco3 &= kdfeco3^{20} \times ktdfeco3^{(T-20)}
 \end{aligned}$$

where:

C_{feco3}	iron(II) carbonate concentration [gFe.m^{-3}]
C_{fe2td}	dissolved reducing iron concentration [gFe.m^{-3}]
C_{fe2d}	equilibrium dissolved free iron(II) concentration [mol.l^{-1}]
$Ctic$	total dissolved inorganic carbon concentration [gC.m^{-3}]
C_{co3d}	total dissolved free carbonate concentration [mol.l^{-1}]
fc_3	fraction dissolved free carbonate [-]
IAP_3	ion activity product for FeCO_3 [mol.l^{-12}]
Ksp_3	solubility product for FeCO_3 ($[\text{mol.l}^{-12}]$)
$kdfeco3$	specific FeCO_3 dissolution rate [d^{-1}]
kp_{feco3}	specific FeCO_3 precipitation rate [$\text{gFe.m}^{-3}.\text{d}^{-1}$]
$ktdfeco3$	temperature coefficient for FeCO_3 dissolution [-]
ktp_{feco3}	temperature coefficient for FeCO_3 precipitation [-]
R_{dfeco3}	rate of FeCO_3 dissolution [$\text{gFe.m}^{-3}.\text{d}^{-1}$]
R_{pfeco3}	rate of FeCO_3 precipitation [$\text{gFe.m}^{-3}.\text{d}^{-1}$]
T	temperature [$^{\circ}\text{C}$]
φ	porosity [-]

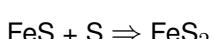
The constant of 12 000 concerns the conversion of gC.m^{-3} to mol.l^{-1} .

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 C_{fes} or C_{feco3} divided with timestep Δt when the flux as calculated with the above formulation is larger than $C_{fes}/\Delta t$ or $C_{feco3}/\Delta t$.

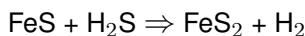
The total inorganic carbonate concentration is derived from TIC when $SWTICCO2 = 0.0$ (default) or from $\text{CO}_2 * 12/44$ when $SWTICCO2 = 1.0$.

Formation of pyrite

The formation of pyrite (FeS_2) can be described with the following simplified reaction equations:



or



Nor elemental sulphide nor elemental hydrogen is included in the model consequently the electrons transferred cannot be accounted for. Pragmatically the formation rate is formulated as follows:

$$R_{\text{pyr}} = k_{\text{pyr}} \times C_{fes} \times f_{s1} \times C_{sdt} / \varphi$$

$$k_{\text{pyr}} = k_{\text{pyr}}^{20} \times k_{\text{tpyr}}^{(T-20)}$$

where:

C_{fes}	iron(II) sulphide concentration [gFe.m^{-3}]
C_{sdt}	total dissolved sulphide concentration [gS.m^{-3}]
f_{s1}	fraction dissolved hydrogen sulphide [-]
k_{pyr}	specific pyrite formation rate ($\text{gS}^{-1} \cdot \text{m}^3 \cdot \text{d}^{-1}$)
k_{tpyr}	temperature coefficient for iron(III) aging [-]
R_{pyr}	rate of pyrite formation [$\text{gFe.m}^{-3} \cdot \text{d}^{-1}$]
T	temperature [$^{\circ}\text{C}$]
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 sulphide $FrS2dis$ can be calculated with process SPECSUD using an imposed or simulated total dissolved sulphide concentration.
- ◊ The fraction dissolved free carbonate $FrCO3dis$ can be calculated with process SPEC-CARB 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:
 $IKspFeOH3 = -38.7$ $IKspFeS = -18.1$ and $IKspFeCO3 = -10.7$.
- ◊ 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)

Table 8.18: Definitions of the parameters in the above equations for PRIRON concerning oxidizing iron. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in Input	Definition	Units
Cfea	Felli _{pa}	particulate amorphous oxidizing iron concentration	gFe.m^{-3}_ℓ
Cfe3dt	Felli _d	dissolved oxidizing iron concentration	gFe.m^{-3}_ℓ
Cfe3d	—	equilibrium dissolved free iron(III) concentration	mol.l^{-l}
ffe3 ₁	FrFe3dis	fraction dissolved free iron(III)	
IAP ₁	—	ion activity product for Fe(OH)_3	mol.l^{-14}
IKsp ₁	IKspFeOH3	log solubility product for Fe(OH)_3 [mol.l^{-14}]	log(-)
kafe3 ²⁰	RcAgFe320	specific iron(III) aging rate at 20 °C	d^{-1}
kdf _{e3} ²⁰	RcDisFe320	specific iron(III) dissolution rate at 20 °C	d^{-1}
kpfe3 ²⁰	RcPrcFe320	specific iron(III) precipitation rate at 20 °C	$\text{gFe.m}^{-3}_\ell \cdot \text{d}^{-1}$
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	$\text{gFe.m}^{-3}_\ell \cdot \text{d}^{-1}$
Rdfe3	—	rate of amorphous iron(III) dissolution	$\text{gFe.m}^{-3}_\ell \cdot \text{d}^{-1}$
Rpfe3	—	rate of amorphous iron(III) precipitation	$\text{gFe.m}^{-3}_\ell \cdot \text{d}^{-1}$
T	Temp	temperature	°C
Δt	Delt	timestep	d
φ	POROS	porosity	$\text{m}^3_w \cdot \text{m}^{-3}_\ell$

Table 8.19: 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
Cfes	FeS	iron(II) sulphide concentration	gFe.m^{-3}_ℓ
Cfe2dt	Felli _d	total dissolved reducing iron concentration	gFe.m^{-3}_ℓ
Cfe2d	—	equilibrium dissolved free iron(II) concentration	mol.l^{-l}
ffe2 ₁	FrFe2dis	fraction dissolved free iron(II)	-

Table 8.19: Definitions of the parameters in the above equations for PRIRON concerning reducing iron. Volume units refer to bulk (ℓ) or to water (ω).

Name in formulas	Name in Input	Definition	Units
Csd _t	SUD	total dissolved sulphide concentration	gS.m^{-3}
Csd ₃	-	dissolved free sulphide concentration	mol.l^{-1}
fs ₁	FrH2Sdis	fraction dissolved hydrogen sulphide	-
fs ₃	FrS2dis	fraction dissolved free sulphide	-
Cfeco3	FeCO ₃	iron(II) carbonate concentration	gFe.m^{-3}
Ctic	TIC or CO ₂	total dissolved inorganic carbon concentration	gC.m^{-3}
Cco3d	-	total dissolved sulphide concentration	$\text{gCO}_2\text{.m}^{-3}$
fc ₃	FrCO3dis	fraction dissolved free carbonate	mol.l^{-1}
IAP ₂	-	ion activity product for FeS	[mol.l^{-12}]
IKsp ₂	IKspFeS	log solubility product for FeS [mol.l^{-12}]	log(-)
IAP ₃	-	ion activity product for FeCO ₃	[mol.l^{-12}]
Ksp ₃	IKspFeCO ₃	log solubility product for FeCO ₃ [mol.l^{-12}]	log(-)
kpyr ²⁰	RcPyrite20	specific pyrite formation rate at 20 °C	$\text{gS}^{-1}\text{.m}^3\text{.d}^{-1}$
kdfes ²⁰	RcDisFeS20	specific iron(II) sulphide dissolution rate at 20 °C	d^{-1}
kpfes ²⁰	RcPrcFeS20	specific iron(II) sulphide precipitation rate at 20 °C	$\text{gFe.m}^{-3}\text{.d}^{-1}$
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	$\text{gFe.m}^{-3}\text{.d}^{-1}$
ktpyr	TcPyrite	temperature coefficient for pyrite formation	-
ktdfes	TcDisFeS	temperature coefficient for iron(II) sulphide diss.	-
ktpfes	TcPrcFeS	temperature coefficient for iron(II) sulphide prec.	-
ktdfeco3	TcDisFeCO ₃	temperature coefficient for iron(II) carbonate diss.	-
ktpfeco3	TcPrcFeCO ₃	temperature coefficient for iron(II) carbonate prec.	-
Rpyr	-	rate of pyrite formation	$\text{gFe.m}^{-3}\text{.d}^{-1}$
Rdfes	-	rate of iron(II) sulphide dissolution	$\text{gFe.m}^{-3}\text{.d}^{-1}$
Rpfes	-	rate of iron(II) sulphide precipitation	$\text{gFe.m}^{-3}\text{.d}^{-1}$
Rdfeco3	-	rate of iron(II) carbonate dissolution	$\text{gFe.m}^{-3}\text{.d}^{-1}$
Rpfeco3	-	rate of iron(II) carbonate precipitation	$\text{gFe.m}^{-3}\text{.d}^{-1}$
SWTICCO2	SWTICCO2	option parameter (0.0 = use TIC; 1.0 = use CO ₂)	-
T	Temp	temperature	°C

Table 8.19: 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
Δt	Delt	timestep	d
φ	POROS	porosity	$m_w^3 \cdot m_\ell^{-3}$

8.12 Reduction of iron by sulphides

PROCESS: IRONRED

Particulate oxidizing iron in the model consists of iron(III) oxyhydroxide, chemically indicated with $\text{Fe}(\text{OH})_3$ or FeOOH . Particulate oxidizing iron can be reduced abiotically by dissolved sulphides and particulate iron sulphides ([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 sulphate. 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 Fellpa. The less reactive crystalline fraction is indicated as substance Fellpc. The latter fraction reacts much more slowly due to the additional activation energy needed to detach ions from its crystal lattice.

Implementation

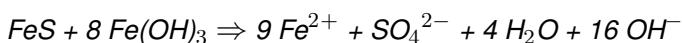
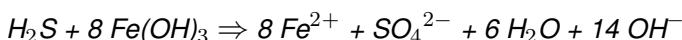
Process IRONRED has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. It covers all simulated abiotic particulate oxidizing iron reduction processes and has been implemented for the following substances:

- ◊ Fellpa, Fellpc, FeS, Felld, SUD and SO4

The reducing iron produced is added to Felld, the sulphate 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:



The reduction of iron oxyhydroxide requires $0.0714 \text{ gS.gFe}^{-1}$ in the cases of H_2S and FeS , and $0.125 \text{ gFe.gFe}^{-1}$ in the case of FeS .

The reduction reactions are formulated according to double first-order kinetics:

$$Rire_1 = kire_1 \times Cfea \times \left(\frac{fs_1 \times Csdt}{\varphi} \right) \times \varphi$$

$$Rire_2 = kire_2 \times Cfec \times \left(\frac{fs_1 \times Csdt}{\varphi} \right) \times \varphi$$

$$Rire_3 = kire_3 \times Cfes \times Cfea$$

$$Rire_4 = kire_4 \times Cfes \times Cfec$$

where:

$Cfes$ particulate iron sulphide concentration [gFe.m^{-3}]

$Cfea$ particulate amorphous oxidizing iron concentration [gFe.m^{-3}]

C_{fec}	particulate crystalline oxidizing iron concentration [gFe.m $^{-3}$]
C_{sdt}	total dissolved sulphide [gS.m $^{-3}$]
f_{s1}	fraction hydrogen sulphide [-]
$kire_1$	specific rate of amorphous iron reduction with H ₂ S [1/(gS.m $^{-3}$.d)]
$kire_2$	specific rate of crystalline iron reduction with H ₂ S [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 ₂ S [gFe.m $^{-3}$.d $^{-1}$]
$Rire_2$	rate of crystalline iron reduction with H ₂ S [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 sulphide or particulate iron sulphide. Therefore, each of the reduction fluxes is made equal to half the concentration of amorphous oxidizing iron or crystalline oxidizing iron or hydrogen sulphide or iron sulphide 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 H₂S 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)

Table 8.20: Definitions of the parameters in the above equations for IRONRED. Volume units refer to bulk (ℓ) or to water (ω).

Name in formulas	Name in Input	Definition	Units
Cfes	FeS	particulate iron sulphide concentration	gFe.m $^{-3}$

Table 8.20: Definitions of the parameters in the above equations for IRONRED. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in Input	Definition	Units
Cfea	Felliipa	particulate amorphous oxidizing iron concentration	gFe.m^{-3}_ℓ
Cfec	Felliipc	particulate crystalline oxidizing iron concentration	gFe.m^{-3}_ℓ
Csdt	SUD	total dissolved sulphide concentration	gS.m^{-3}_ℓ
fs ₁	FrH2Sdis	fraction dissolved hydrogen sulphide (H_2S)	-
kire ₁ ²⁰	RcFeaH2S20	spec. rate of amorphous iron red. with H_2S at 20 °C	$\text{gS}^{-1}.\text{m}^3_w.\text{d}^{-1}$
kire ₂ ²⁰	RcFecH2S20	spec. rate of crystalline iron red. with H_2S at 20 °C	$\text{gS}^{-1}.\text{m}^3_w.\text{d}^{-1}$
kire ₃ ²⁰	RcFeaFeS20	spec. rate of amorphous iron red. with FeS at 20 °C	$\text{gFe}^{-1}.\text{m}^3_w.\text{d}^{-1}$
kire ₄ ²⁰	RcFecFeS20	spec. rate of crystalline iron red. with FeS at 20 °C	$\text{gFe}^{-1}.\text{m}^3_w.\text{d}^{-1}$
ktire	TcFeRed	temperature coeff. for abiotic iron reduction at 20 °C	-
Rire ₁	-	rate of amorphous iron reduction with H_2S	$\text{gFe.m}^{-3}_\ell.\text{d}^{-1}$
Rire ₂	-	rate of crystalline iron reduction with H_2S	$\text{gFe.m}^{-3}_\ell.\text{d}^{-1}$
Rire ₃	-	rate of amorphous iron reduction with FeS	$\text{gFe.m}^{-3}_\ell.\text{d}^{-1}$
Rire ₄	-	rate of crystalline iron reduction with FeS	$\text{gFe.m}^{-3}_\ell.\text{d}^{-1}$
T	Temp	temperature	°C
Δt	Delt	timestep	d
φ	POROS	porosity	$\text{m}^3_w.\text{m}^{-3}_\ell$

8.13 Oxidation of iron sulphides

PROCESS: SULPHOX

Particulate components FeS and FeS₂ 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 sulphides proceeds in two steps. First the sulphide part is oxidized into sulphate. Secondly, the iron released as Fe²⁺ is oxidized. The latter process is taken care of in process IRONOX.

The particulate component FeCO₃ is assumed not to be oxidized directly. The iron in this component is oxidized after dissolution.

The oxidation of dissolved sulphide is taken care of in process OXIDSUD.

Implementation

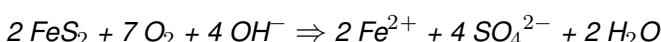
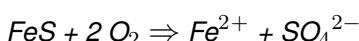
Process SULPHOX has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. It covers all simulated iron sulphide oxidation processes and has been implemented for the following substances:

- ◊ place FeS, FeS₂, Felld, OXY and SO₄

The iron from FeS and FeS₂ is added to the dissolved reducing iron Felld. The oxygen consumed is removed from the model as water, which is not simulated. The sulphide oxidized is added to sulphate. Table I provides the definitions of the parameters occurring in the formulations.

Formulation

The following oxidation reactions are included in the model:



The oxidation of iron sulphide requires 1.143 gO₂.gFe⁻¹ or 2.0 gO₂.gS⁻¹. The oxidation of pyrite requires 2.0 gO₂.gFe⁻¹ or 1.75 gO₂.gS⁻¹.

The oxidation reactions are formulated according to double first-order kinetics:

$$R_{sox1} = k_{sox1} \times C_{fes} \times \left(\frac{C_{ox}}{\varphi} \right) \times \varphi$$

$$R_{sox2} = k_{sox2} \times C_{fes2} \times \left(\frac{C_{ox}}{\varphi} \right) \times \varphi$$

where:

C_{fes} iron sulphide concentration [gFe.m⁻³]

C_{fes2} pyrite concentration [gFe.m⁻³]

C_{ox} dissolved oxygen concentration [gO₂.m⁻³]

k_{sox1} specific rate of iron sulphide oxidation [1/(gO₂.m⁻³.d)]

k_{sox_1}	specific rate of pyrite oxidation [$1/(gO_2 \cdot m^{-3} \cdot d)$]
R_{sox_2}	rate of iron sulphide oxidation [$gFe \cdot m^{-3} \cdot d^{-1}$]
R_{sox_2}	rate of pyrite oxidation [$gFe \cdot m^{-3} \cdot d^{-1}$]
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:

$$k_{sox_i} = k_{sox_i}^{20} \times k_{tsox}^{(T-20)}$$

$$k_{sox_i} = 0.0 \quad \text{if } Cox \leq 0.0$$

where:

$k_{sox_i}^{20}$	specific rate of iron sulphide or pyrite oxidation at 20 °C [$1/(gO_2 \cdot m^{-3} \cdot d)$]
k_{tsox}	temperature coefficient for iron sulphide oxidation [-]
T	temperature [°C]

The oxidation process must stop at the depletion of iron sulphide. Therefore, each of the oxidation fluxes is made equal to half the concentration of the iron sulphide concerned divided with timestep Δt , when this flux as calculated with the above formulations is larger than $C_{FeS}/\Delta t$ or $C_{FeS2}/\Delta t$.

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 sulphide.

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 8.21: Definitions of the parameters in the above equations for SULPHOX. Volume units refer to bulk (b) or to water (w)

Name in formulas	Name in Input	Definition	Units
C_{FeS}	FeS	particulate iron sulfide concentration	$gFe \cdot m_b^{-3}$
C_{FeS2}	FeS2	pyrite concentration	$gFe \cdot m_b^{-3}$
C_{OXY}	OXY	dissolved oxygen concentration	$gO_2 \cdot m_b^{-3}$
$k_{sox_1}^{20}$	RcFeSox20	specific rate of iron sulphide oxidation at 20 °C	$gO_2^{-1} \cdot m_w^3 \cdot d^{-1}$
$k_{sox_2}^{20}$	RcFeS2ox20	specific rate of pyrite oxidation at 20 °C	$gO_2^{-1} \cdot m_w^3 \cdot d^{-1}$

Table 8.21: Definitions of the parameters in the above equations for SULPHOX. Volume units refer to bulk (ℓ) or to water (w)

Name in formulas	Name in Input	Definition	Units
ktsox	TcFeSox	temperature coefficient for iron sulphide oxidation	-
Rioo ₁	-	rate of iron sulphide oxidation	$\text{gFe.m}^{-3}\cdot\text{d}^{-1}$
Rioo ₂	-	rate of pyrite oxidation	$\text{gFe.m}^{-3}\cdot\text{d}^{-1}$
T	Temp	temperature	°C
Δt	Delt	timestep	d
φ	POROS	porosity	$\text{m}_w^3 \cdot \text{m}_\ell^{-3}$

8.14 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 sulphides proceeds in two steps. First the sulphide part is oxidized into sulphate, 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

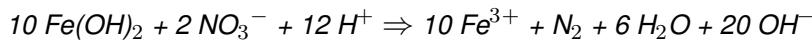
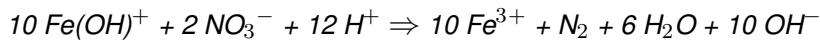
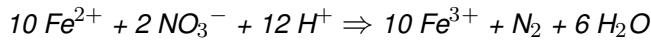
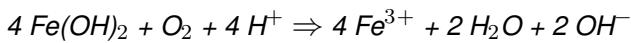
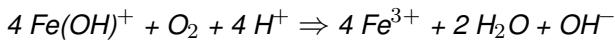
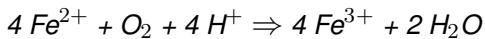
Process IRONOX has been implemented in a generic way, meaning that it can be applied both to water layers and sediment layers. It covers all simulated iron oxidation processes and has been implemented for the following substances:

- ◊ FeIId , FeIIId , OXY and NO_3^-

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:



The processes require $0.143 \text{ gO}_2 \cdot \text{gFe}^{-1}$ or $0.05 \text{ gN} \cdot \text{gFe}^{-1}$.

The oxidation reactions are formulated according to double first-order kinetics:

$$R_{ioo} = (k_{ioo1} \times ffe_1 + k_{ioo2} \times ffe_2 + k_{ioo3} \times ffe_3) \times \left(\frac{C_{feIId}}{\varphi} \right) \times \left(\frac{C_{ox}}{\varphi} \right) \times \varphi$$

$$R_{ion} = (k_{ion1} \times ffe_1 + k_{ion2} \times ffe_2 + k_{ion3} \times ffe_3) \times \left(\frac{C_{feIId}}{\varphi} \right) \times \left(\frac{C_{ni}}{\varphi} \right) \times \varphi$$

where:

C_{feIId}	total dissolved reducing iron concentration [gFe.m $^{-3}$]
C_{ox}	dissolved oxygen concentration [gO $_2$.m $^{-3}$]
C_{ni}	nitrate concentration [gN.m $^{-3}$]
ffe_i	fraction Fe $^{2+}$ (i=1), Fe(OH) $^+$ (i=2) or Fe(OH) $_2$ (i=3) in FeIId [-]
k_{ioo_i}	specific rate of iron i oxidation with dissolved oxygen [1/(gO $_2$.m $^{-3}$.d)]
k_{ion_i}	specific rate of iron i oxidation with nitrate [1/(gN.m $^{-3}$.d)]
R_{ioo}	total rate of iron oxidation with oxygen [gFe.m $^{-3}$.d $^{-1}$]
R_{ion}	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:

$$k_{ioo_i} = k_{ioo_i}^{20} \times ktiox^{(T-20)}$$

$$k_{ioo_i} = 0.0 \quad \text{if } Cox \leq 0.0$$

$$k_{ion_i} = k_{ion_i}^{20} \times ktiox^{(T-20)}$$

$$k_{ion_i} = 0.0 \quad \text{if } Cox \leq 0.0$$

where:

$k_{ioo_i}^{20}$	specific rate of iron i oxidation with oxygen at 20 °C [1/(gO $_2$.m $^{-3}$.d)]
$k_{ion_i}^{20}$	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 ($R_{ioo}+R_{ion}$) 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 $FeIId/\Delta t$.

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),
 Soetaert *et al.* (1996),

Wang and Cappellen (1996),
 WL | Delft Hydraulics (2002),
 Wijsman *et al.* (2001)

Table 8.22: Definitions of the parameters in the above equations for IRONOX. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in Input	Definition	Units
Cfeld	Felld	dissolved reducing iron concentration	gFe.m^{-3}_ℓ
Cox	OXY	dissolved oxygen concentration	$\text{gO}_2.\text{m}^{-3}_\ell$
Cni	NO3	nitrate concentration	gN.m^{-3}_ℓ
ffe ₁	FrFe2dis	fraction of Fe^{2+} in Felld	-
ffe ₂	FrFe2OHd	fraction of FeOH^+ in Felld	-
ffe ₃	FrFe2OH2d	fraction of Fe(OH)_2 in Felld	-
kioo ₁ ²⁰	Rcl1oxox20	specific rate of Fe^{2+} oxidation with oxygen at 20 °C	$\text{gO}_2^{-1}.\text{m}^3_w.\text{d}^{-1}$
kioo ₂ ²⁰	Rcl2oxox20	specific rate of FeOH^+ oxid. with oxygen at 20 °C	$\text{gO}_2^{-1}.\text{m}^3_w.\text{d}^{-1}$
kioo ₃ ²⁰	Rcl3oxox20	specific rate of Fe(OH)_2 oxid. with oxygen at 20 °C	$\text{gO}_2^{-1}.\text{m}^3_w.\text{d}^{-1}$
kion ₁ ²⁰	Rcl1oxni20	specific rate of Fe^{2+} oxidation with nitrate at 20 °C	$\text{gN}^{-1}.\text{m}^3_w.\text{d}^{-1}$
kion ₂ ²⁰	Rcl2oxni20	specific rate of FeOH^+ oxidation with nitrate at 20 °C	$\text{gN}^{-1}.\text{m}^3_w.\text{d}^{-1}$
kion ₃ ²⁰	Rcl3oxni20	specific rate of Fe(OH)_2 oxid. with nitrate at 20 °C	$\text{gN}^{-1}.\text{m}^3_w.\text{d}^{-1}$
ktiox	Tclox	temperature coefficient for iron oxidation	
Rioo	-	rate of iron oxidation with dissolved oxygen	$\text{gFe.m}^{-3}_\ell.\text{d}^{-1}$
Rion	-	rate of iron oxidation with nitrate	$\text{gFe.m}^{-3}_\ell.\text{d}^{-1}$
T	Temp	temperature	°C
Δt	Delt	timestep	d
φ	POROS	porosity	$\text{m}^3_w.\text{m}^{-3}_\ell$

8.15 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 sulphide 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:

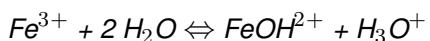
- ◊ FeIId and Felld.

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:



The chemical equilibria are described with:

$$K_{fe3_1} = \frac{C_{fe3d_2} \times H^+}{C_{fe3d_1}}$$

$$K_{fe3_2} = \frac{C_{fe3d_3} \times (H^+)^2}{C_{fe3d_1}}$$

$$C_{fe3dt} = (C_{fe3d_1} + C_{fe3d_2} + C_{fe3d_3}) \times 56\,000 \times \varphi$$

where

C_{fe3d_1} concentration of free dissolved Fe^{3+} [mol.l⁻¹]

C_{fe3d_2} concentration of dissolved FeOH^{2+} [mol.l⁻¹]

C_{fe3d_3} concentration of dissolved Fe(OH)_2^+ [mol.l⁻¹]

C_{fe3dt} concentration of total dissolved oxidizing iron [gFe.m⁻³]

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:

$$\begin{aligned} H^+ &= 10^{-pH} \\ Kfe3_1 &= 10^{lKfe3_1} \times ktfe3_1^{(T-20)} \\ Kfe3_2 &= 10^{lKfe3_2} \times ktfe3_2^{(T-20)} \end{aligned}$$

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:

$$\begin{aligned} Cfe3d_1 &= \frac{Cfe3dt}{(1 + Kfe3_1/H^+ + Kfe3_2/(H^+)^2)} \times \frac{1}{56\,000 \times \varphi} \\ Cfe3d_2 &= \frac{Kfe3_1 \times Cfe3d_1}{H^+} \\ Cfe3d_3 &= \frac{Cfe3dt}{56\,000 \times \varphi} - Cfe3d_1 - Cfe3d_2 \end{aligned}$$

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:

$$\begin{aligned} ffe3_1 &= \frac{Cfe3d_1}{Cfe3dt} \times 56\,000 \times \varphi \\ ffe3_2 &= \frac{Cfe3d_2}{Cfe3dt} \times 56\,000 \times \varphi \\ ffe3_3 &= 1 - ffe3_1 - ffe3_2 \end{aligned}$$

if due to rounding off the resulting $ffe_3 < 0.0$

$$ffe3_3 = \frac{Cfe3d_3}{Cfe3dt} \times 56\,000 \times \varphi$$

Iron(II)

The hydrolysis of dissolved reducing iron proceeds according to the following reaction equations:



The chemical equilibria are described with:

$$K_{fe2_1} = \frac{C_{fe2d_2} \times H^+}{C_{fe2d_1}}$$

$$K_{fe2_2} = \frac{C_{fe2d_3} \times (H^+)^2}{C_{fe2d_1}}$$

$$C_{fe2dt} = (C_{fe2d_1} + C_{fe2d_2} + C_{fe2d_3}) \times 56\,000 \times \varphi$$

where

C_{fe2d_1} concentration of free dissolved Fe^{2+} [mol.l⁻¹]

C_{fe2d_2} concentration of dissolved FeOH^+ [mol.l⁻¹]

C_{fe2d_3} concentration of dissolved Fe(OH)_2 [mol.l⁻¹]

C_{fe2dt} concentration of total dissolved reducing iron [gFe.m⁻³]

H^+ proton concentration [mol.l⁻¹]

K_{fe2_1} stability (equilibrium, hydrolysis) constant for FeOH^+ [mol.l⁻¹]

K_{fe2_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:

$$H^+ = 10^{-pH}$$

$$K_{fe2_1} = 10^{lK_{fe2_1}} \times ktfe2_1^{(T-20)}$$

$$K_{fe2_2} = 10^{lK_{fe2_2}} \times ktfe2_2^{(T-20)}$$

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:

$$C_{fe2d_1} = \frac{C_{fe2dt}}{(1 + K_{fe2_1}/H^+ + K_{fe2_2}/(H^+)^2)} \times \frac{1}{56\,000 \times \varphi}$$

$$C_{fe2d_2} = \frac{K_{fe2_1} \times C_{fe2d_1}}{H^+}$$

$$C_{fe3d_2} = \frac{C_{fe2dt}}{56\,000 \times \varphi} - C_{fe2d_1} - C_{fe2d_2}$$

if due to rounding off the resulting $C_{fe2d_3} = 0.0$

$$C_{fe2d_3} = \frac{K_{fe2_2} \times C_{fe2d_1}}{(H^+)^2}$$

The pertinent fractions follow from:

$$ffe2_1 = \frac{C_{fe2d_1}}{C_{fe2dt}} \times 56\,000 \times \varphi$$

$$ffe2_2 = \frac{C_{fe2d_2}}{C_{fe2dt}} \times 56\,000 \times \varphi$$

$$ffe2_3 = 1 - ffe2_1 - ffe2_2$$

if due to rounding off the resulting $ffe_2 = 0.0$

$$ffe2_3 = \frac{C_{fe2d_3}}{C_{fe2dt}} \times 56\,000 \times \varphi$$

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:
 $\text{IKstFe3OH} = -3.05$ and $\text{IKstFe3OH}_2 = -6.31$.
 $\text{IKstFe2OH} = -9.50$ and $\text{IKstFe2OH}_2 = -17.0$ (?)
- ◊ 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 $TcKFe2OH_2$.
- ◊ 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 $5.6 \cdot 10^{-4}$ 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 8.23: Definitions of the input parameters in the above equations for SPECIRON.

Name in formulas	Name in Input	Definition	Units
Cfe3dt	Felld	concentration of total dissolved oxidizing iron(III)	gFe.m ⁻³
Cfe2dt	Felld	concentration of total dissolved reducing iron(II)	gFe.m ⁻³
IKfe3 ₁	IKstFe3OH	log stability constant for Fe3OH^{2+} (l.mol ⁻¹)	log(-)
IKfe3 ₂	IKstFe3OH ₂	log stability constant for Fe3OH_2^+ (l.mol ⁻¹)	log(-)
ktfe3 ₁	TcKFe3OH	temperature coefficient for KstFe3OH	-
ktfe3 ₂	TcKFe3OH ₂	temperature coefficient for KstFe3OH ₂	-
IKfe2 ₁	IKstFe2OH	log stability constant for Fe2OH^+ (l.mol ⁻¹)	log(-)
IKfe2 ₂	IKstFe2OH ₂	log stability constant for Fe2OH_2 (l.mol ⁻¹)	log(-)

Table 8.23: Definitions of the input parameters in the above equations for SPECIRON.

Name in formulas	Name in Input	Definition	Units
ktfe2 ₁	TcKFe2OH	temperature coefficient for KstFe2OH	-
ktfe2 ₂	TcKFe2OH2	temperature coefficient for KstFe2OH2	-
H ⁺ pH	— pH	proton concentration acidity	mol.l ⁻¹ -
T	Temp	temperature	°C
φ	POROS	porosity	m _w ³ .m _f ⁻³

Table 8.24: 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	-

8.16 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 ($gCl \cdot L^{-1}$). 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 $gCl \cdot m^{-3}$ when density is expressed as $kg \cdot m^{-3}$.

Volume units refer to bulk (ℓ) or to water (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 8.25](#) provides the definitions of the parameters occurring in the formulations.

Formulation

The conversion of chloride into salinity follows from ($SWSa/Cl = 0.0$):

$$\begin{aligned} \rho_w &= 1000 + \frac{0.7 \times Cl}{1000} \times r_{scl} - 0.0061 \times (T - 4.0)^2 \\ S &= S_0 + \frac{r_{scl} \times Cl}{\rho_w} \end{aligned}$$

The conversion of salinity into chloride follows from ($SWSa/Cl = 1.0$):

$$\begin{aligned} \rho_w &= 1000 + \frac{700 \times S}{(1000 - S)} \times r_{scl} - 0.0061 \times (T - 4.0)^2 \\ Cl &= \frac{(S - S_0) \times \rho_w}{r_{scl}} \end{aligned}$$

where:

Cl	chloride concentration ($g.m^{-3} \ell$)
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 ($^{\circ}C$)
ρ_w	density of water with dissolved salts ($kg.m^{-3} \ell$)

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 8.25: Definitions of the parameters in the above equations for SALINCHLOR. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
Cl	Cl	chloride concentration	$g.m^{-3} \ell$
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	$^{\circ}C$
ρ_w	–	density of water with dissolved salt	$kg.m^{-3} \ell$

9 Organic micropollutants

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9.1 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 $\text{g m}^{-3}w$). 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 (hexachlorohexane),
- ◊ HCB (hexachlorobenzene),
- ◊ 153 (PCB 153);
- ◊ BaP (Benzo[a]pyrene),
- ◊ Flu (fluoranthene),
- ◊ Diu (diuron),
- ◊ Atr (atrazine), and
- ◊ Mef (mevinphos).

OMP can be any micro-pollutant. The default values of the input parameters for OMP are meaningless. For instance, PCB52 can be simulated as OMP (but also as PCB153) by replacing the values of the input parameters by those for PCB52.

The above substance names concern the situation, where equilibrium partitioning is simu-

lated. 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 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 9.1 and 9.2 provide the definitions of the input parameters occurring in the formulations. Tables 9.3 and 9.4 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:

$$\begin{aligned} fdf &= \frac{\phi}{\phi + Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg} \\ fdoc &= (1 - fdf) \times \frac{Kppoc' \times Xdoc \times Cdoc}{Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg} \\ fpoc &= (1 - fdf) \times \frac{Kppoc' \times Cpoc}{Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg} \\ falg &= (1 - fdf - fdoc - fpoc) \end{aligned}$$

where:

<i>Calg/poc/doc</i>	concentration of algae biomass, dead particulate organic matter matter, and dissolved organic matter [gC m^{-3}]
<i>falg/poc/doc</i>	fraction of a micropollutant adsorbed to algae, dissolved organic matter, dead particulate organic matter [-]
<i>fdf</i>	freely dissolved fraction of a micropollutant [-]
<i>Kpalg/poc'</i>	partition coefficient for algae and dead particulate organic matter [$\text{m}^3 \text{w gC}^{-1}$]
<i>Xdoc</i>	adsorption efficiency of DOC relative to POC [-]
ϕ	porosity ($[\text{m}^3 \text{w m}^{-3}]$; 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 [$\text{m}^3 \text{w.gC}^{-1}$] are derived from the input parameters expressed in [${}^{10}\log(\text{l.kgC}^{-1})$], corrected for temperature:

$$\log K_{ppoc} = \log K_{ppoc}^{20} + a \times \left(\frac{1}{(T + 273.15)} - \frac{1}{293.15} \right)$$

$$\log K_{palg} = \log K_{palg}^{20} + a \times \left(\frac{1}{(T + 273.15)} - \frac{1}{293.15} \right)$$

$$K_{ppoc}' = 10^{\log K_{ppoc}} \cdot 10^{-6}$$

$$K_{palg}' = 10^{\log K_{palg}} \cdot 10^{-6}$$

where:

a	temperature coefficient [°K]
K_{palg}/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:

$$fp' = fpoc' + falg' = \frac{C_{mpp'}}{C_{mpf'}}$$

$$fpe = fpoc + falg$$

if $fp < fpe$ then

$$ksorp = \frac{\ln(2)}{tads}$$

else

$$ksorp = \frac{\ln(2)}{tdes}$$

and

$$\begin{aligned} fp &= fpe - (fpe - fp') \times \exp(-ksorp \times \Delta t) \\ fd\bar{f} &= fdfe \times \frac{(1 - fp)}{(1 - fpe)} \\ fdoc &= fdoce \times \frac{(1 - fp)}{(1 - fpe)} \\ fpoc &= fpoce \times \frac{fp}{fpe} \\ falg &= falg \times \frac{fp}{fpe} \end{aligned}$$

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:

$$\frac{Rsorp}{\Delta t} \quad \begin{array}{l} \text{sorption rate [g m}^{-3}\text{/d}^{-1}] \\ \text{timestep of DELWAQ [d}^{-1}\text{]} \end{array}$$

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:

$$\begin{aligned} Cmpdf &= \frac{fd\bar{f} \times Cmpt'}{\phi} \\ Cmpdoc &= \frac{fdoc \times Cmpt'}{\phi} \\ Cmpd &= Cmpdf + Cmpdoc \\ Cmpp &= (fpoc + falg) \times Cmpt' \\ Cmppoc &= \frac{fpoc \times Cmpt'}{Cpoc} \\ Cmpalg &= \frac{falg \times Cmpt'}{Calg} \end{aligned}$$

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:

$$C_{mppt} = \frac{C_{mpp} \times 10^6}{C_{ss}}$$

$$K_{pt} = \frac{C_{mppt} \times 10^{-3}}{C_{mpd} + C_{mpdoc}}$$

where:

- | | |
|-----------|---|
| C_{ss} | the total suspended solids concentration [g m^{-3}]. |
| C_{mpp} | the micropollutant content of total suspended solids [mg kg^{-1}]. |
| K_{pt} | the apparent overall partition coefficient [$\text{m}^3 \text{kg}^{-1}$]. |

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 $\log(K_{ppoc}) = a \log(K_{ow}) + b$ ($a = 0.8 - 1.0$ and $b = 0.0 - 0.3$; these coefficients are different for the various types of micropollutants).
- ◊ The input parameters *SW Sed Yes/No* and *OMP Group* 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.

Additional references

WL | Delft Hydraulics (1992b), DiToro and Horzempa (1982), Karickhoff *et al.* (1979), O' Connor and Connolly (1980), Connolly *et al.* (2000)

Table 9.1: Definitions of the input parameters in the above equations for PARTWK_(i). (i) is a substance name. Volume units refer to bulk (ℓ) 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	$gC\ m^{-3}\ell$
$Cdoc$	DOC	dissolved organic matter concentration	$gC\ m^{-3}\ell$
Cim_i	IMi	conc. inorg. particulate fractions i=1,2,3	$gDW\ m^{-3}\ell$
$Cpoc$	$POCnoa^2$	particulate organic matter concentration without algae	$gC\ m^{-3}\ell$
$Cmpt$	(i)	total micropollutant concentration	$g\ m^{-3}\ell$
$Cmpd$	(i) - dis	total dissolved micropollutant conc.	$g\ m^{-3}w$
$Cmpp$	(i) - par	totsl particulate micropollutant conc.	$g\ m^{-3}\ell$
Css	SS	total suspended matter concentration	$gDW\ m^{-3}\ell$
$logKpalg$	$lKphy(i)$	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	$^{\circ}K$
-	$WSedNo^3$	option for process in water column (default = 0.0)	-
$tads$	$HLTAds(i)$	half-life-time adsorption process	d
$tdes$	$HTLDes(i)$	half-life-time desorption process	d
T	$Temp$	temperature	$^{\circ}K$
V	$Volume$	volume	$^{\circ}K$
$Xdoc$	$XDOC(i)$	adsorption efficiency of DOC relative to POC	-
ϕ	$POROS$	porosity	$m^3w\ m^{-3}\ell$
Δt	$Delt$	timestep	d^{-1}

¹⁾ Delivered by processes PHY_BLO (BLOOM) or PHY_DYN (DYNAMO).

²⁾ Delivered by process COMPOS.

³⁾ Default value must not be changed.

Table 9.2: 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 (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
A	$Surf$	surface area	m^2
$Calg$ $Cdoc$ Cim_i	$PHYTS(k)^1$ $DOCS(k)$ $IMiS(k)$	phytoplankton quantity dissolved organic matter concentration quantity inorg. particulate fractions $i=1,2,3$	gC $gC m^{-3}w$ gDW
$Cpoc$ $Cmpt$ $Cmpd$ $Cmpp$ Css	$POCS(k)^1$ $(i)S(k)$ $(i)S(k) - dis$ $(i)S(k) - par$ $DMS(k)^1$	part. organic matter without algae quantity of total micropollutant quantity of total diss. org. micro-poll. quantity of total part. org. micro-poll. total quantity of total sediment	gC g g g gDW
$logKp_{alg}$ $logKp_{poc}$ a	$lKphy(i)S(k)$ $lKpoc(i)S(k)$ $TcKp(i)S(k)$	10 logarithm of part. coeff. for phyt. 10 logarithm of part. coeff. for POC temperature coefficient of partition coefficient	$\log(L kgC^{-1})$ $\log(L kgC^{-1})$ $^\circ K$
-	SW_{SedYes}^2	identifier for processes PARTS1/2	-
$tads$ $tdes$	$HLTAds(i)S(k)$ $HTLDes(i)S(k)$	half-life-time adsorption process half-life-time desorption process	d d
$Xdoc$	$XDOC(i)$	adsorption efficiency of DOC relative to POC	-
T	$Temp$	temperature	$^\circ K$
V Z ϕ Δt	$Volume$ $ActThS(k)$ $PORS(k)$ $Delt$	volume thickness of sediment layer porosity timestep	$m^{-3}\ell$ m $m^3w m^{-3}\ell$ d^{-1}

¹⁾ Delivered by processes S1_COMP and S1_COMP.

²⁾ Default value must not be changed.

Table 9.3: Definitions of the output parameters for PARTWK_(i). (i) is a substance name. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
$Cmpt$ $Cmpd$ $Cmpdoc$	$(i)tot$ $Dis(i)$ $Doc(i)$	total micropollutant concentration freely dissolved micropollutant conc. DOC adsorbed micropollutant conc.	$g m^{-3}\ell$ $g m^{-3}w$ $g m^{-3}w$
fdf	$Fr(i)Dis$	freely diss. micropoll. fraction (not bound to DOC!)	-

Table 9.3: Definitions of the output parameters for PARTWK_(i). (i) is a substance name.
Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
f_{doc}	$Fr(i)DOC$	fraction micropollutant adsorbed to DOC	-
f_{poc}	$Fr(i)POC$	fraction micropollutant adsorbed to POC	-
f_{alg}	$Fr(i)PHYT$	fraction micropollutant adsorbed to phytoplankton	-
Kpt	$Kd(i)SS$	apparent overall partition coefficient for susp. solids	$m^3 \text{ kgDW}^{-1}$
-	$Q(i)POC$	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 9.4: 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 (ℓ) or to water (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.	$\text{g m}^{-3}w$
$Cmpdoc$	$Doc(i)S(k)$	DOC adsorbed micropollutant conc.	$\text{g m}^{-3}w$
fdf	$Fr(i)DisS(k)$	freely diss. micropoll. fraction (not bound to DOC!)	-
f_{doc}	$Fr(i)DOCS(k)$	fraction micropollutant adsorbed to DOC	-
f_{poc}	$Fr(i)POCS(k)$	fraction micropollutant adsorbed to POC	-
f_{alg}	$Fr(i)PHYTS(k)$	fraction micropollutant adsorbed to phytoplankton	-
Kpt	$Kd(i)DMS(k)$	apparent overall partition coefficient for susp. solids	$m^3 \text{ kgDW}^{-1}$
-	$Q(i)POCS(k)$	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}

9.2 Calculation of organic matter

PROCESS: MAKOOC AND MAKOOC51/2

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, MAKOOC51 and MAKOOC52 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, MAKOOC51 and MAKOOC52. 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 MAKOOC51 and MAKOOC52 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, MAKOOC51 and MAKOOC52 require total quantities per sediment layer as input. The formulations for the processes are identical.

Tables 9.5 and 9.6 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:

$$C_{poc} = \sum_{i=1}^3 (f_{ocsed_i} \times \frac{C_{im_i}}{1 - f_{ocsed_i} \times f_{ctr}})$$

where:

C_{im}	the concentration or quantity of inorganic matter [gDM m^{-3} or gDM]
C_{poc}	the concentration or quantity of particulate organic carbon [gC m^{-3} or gOC]
f_{ctr}	weight conversion factor [gDM gOC^{-1}]
f_{ocsed}	content organic carbon in total of sediment fraction [gOC gDM^{-1}]
i	index for sediment component

The conversion factor f_{ctr} enters the equation because the content of organic matter f_{ocsed} 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 f_{ocsed} again, the C_{poc} is calculated from the total sediment dry weight for each fraction, and summed.

Table 9.5: Definitions of the input parameters in the above equations for MAKOOC, MAKOOC51 and MAKOOC52.

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 9.6: 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!)	$gC m^{-3} \ell$
$Cpoc$	$POCS(k)$	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.

9.3 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 (b) or to water (w).

Implementation

Process DISOMP_(i) has been implemented for the following substances:

- ◊ OMP-ios, OMP, OMP-dis (any micropollutant); and
- ◊ 153-ios, 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 9.7](#) provides the definitions of the input parameters occurring in the formulations.

Formulation

Assuming the eventual dissolution of all micropollutant in a solvent the dissolution is formulated as a first order kinetic process:

$$R_{dis} = -k_{dis} \times C_{ios}$$

$$k_{dis} = k_{dis}^{20} \times k_{tdis}^{(T-20)}$$

where:

C_{ios}	concentration of micropollutant in organic solvent in water [$g.m^{-3}\ell$]
k_{dis}^{20}	dissolution rate constant at 20 °C [d^{-1}]
k_{tdis}	temperature constant for dissolution [-]
R_{dis}	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 9.7: 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 (ω).

Name in formulas	Name in input	Definition	Units
C_{ios}	(i)-ios	micropollutant in organic solvent concentration	$g.m^{-3}\ell$
k_{dis}^{20} k_{tdis}	$RcDis(i)$ $TcDis(i)$	dissolution rate constant at 20 °C temperature constant of dissolution	d^{-1} —
R_{dis}	—	dissolution rate	$g.m^{-3}\ell.d^{-1}$

9.4 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 instead.

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 instead 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 [9.8](#) and [9.9](#) 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.

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 oxidizing or reducing conditions can be delivered by auxiliary process SWOXY-PAR 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:

$$Rdeg = k0deg \quad \text{if } T < T_c$$

and else equal to:

$$Rdeg = k0deg + (k1deg^{20} \times ktdeg^{(T-20)} \times frdeg \times Cmpt)$$

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 $k1deg1^{20}$ [d⁻¹] depends on the redox conditions according to:

$$k1deg^{20} = \begin{cases} kdego^{20} & \text{if } SWOXY = 1 \\ kdogr^{20} & \text{if } SWOXY = 0 \end{cases}$$

where:

$kdego$	first order degradation rate at oxidising conditions [d ⁻¹]
$kdogr$	first order degradation rate at reducing conditions [d ⁻¹]

The switch is determined as function of the dissolved oxygen concentration in process SWOXY-PAR.

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]!)

Factor *frdeg* is different for various options imposed with *SWDeg* with respect to the concentration fraction that is subjected to degradation.

Option 0

$$frdeg = 1.0 \quad (\text{default})$$

Option 1

$$frdeg = fdf$$

Option 2

$$frdeg = fdf + fdoc$$

where:

<i>fdf</i>	freely dissolved fraction of the micropollutant [-]
<i>fdoc</i>	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:

$$Rdeg = k0deg \quad \text{if} \quad T < T_c$$

and else equal to:

$$Rdeg = k0deg + (k1deg^{20} \times ktdeg^{(T-20)} \times fdf \times Cmpt)$$

where:

<i>Cmpt</i>	total micropollutant concentration [g.m ⁻³]
<i>fdf</i>	freely dissolved fraction of the micropollutant [-]
<i>k0deg</i>	zeroth order degradation rate [g.m ⁻³ .d ⁻¹]
<i>k1deg</i>	first order degradation rate [d ⁻¹]
<i>ktdeg</i>	temperature coefficient of degradation [-]
<i>Rdeg</i>	degradation rate [g.m ⁻³ .d ⁻¹]
<i>T</i>	temperature [°C]
<i>T_c</i>	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* · *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]!)

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 \(1982\)](#)

Table 9.8: 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
$Cmpt$ $frdeg$ fdf $fdoc$	(i) - $Fr(i)Dis$ $Fr(i)Doc$	total micropollutant concentration fraction subjected to degradation freely dissolved micropollutant fraction DOC-bound dissolved micropollutant fraction	g m^{-3} - - -
$SWDeg$ $SWOXY$ -	$SWDeg(i)$ $SWWaterCh$ $SWVnDegMP$	switch for selection of one of the options switch for oxidising and reducing conditions, computed with SWOXPAR switch for selection of formulations (no redox dependency = 0.0, with redox dependency = 1.0)	- - -
$k0deg$ $kdego^{20}$ $kdegr^{20}$ $k1deg^{20}$ $ktdeg$	$ZLoss(i)$ $RcDegO(i)$ $RcDegR(i)$ $Rc(i)$ $Tc(i)$	zeroth-order degradation rate first-order degr. rate at oxid. cond. and at 20 °C first-order degr. rate at red. cond. and at 20 °C first-order degradation rate at 20 °C temperature constant of degradation	$\text{g m}^{-3} \text{ d}^{-1}$ d^{-1} d^{-1} d^{-1} -
$Rdeg$	-	overall degradation rate	$\text{g m}^{-3} \text{ d}^{-1}$
T T_c	$Temp$ $CTLoss$	ambient temperature critical temperature for degradation	°C °C

Table 9.9: 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
$Cmtt$ $frdeg$	$(i)S1/2$ -	total micropollutant concentration factor for conc. fraction subjected to degradation	g -
fdf $fdoc$	$Fr(i)DisS1/2$ $Fr(i)DocS1/2$	freely dissolved micropollutant fraction 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 SWOXPAR	-
-	$SWVnDegMP$	switch for selection of formulations (no redox dependency = 0.0, with redox dependency = 1.0)	-
$k0deg$ $kdego^{20}$	$ZLoss(i)S1/2$ $RcDgO(I)S1/2$	zeroth-order degradation rate first-order degr. rate at oxid. cond. and at 20 °C	$g\ m^{-2}\ d^{-1}$ d^{-1}
$kdegr^{20}$	$RcDgR(i)S1/2$	first-order degr. rate at red. cond. and at 20 °C	d^{-1}
$k1deg^{20}$ $ktdeg$	$Rc(i)S1/2$ $Tc(i)Sed$	first-order degradation rate at 20 °C temperature constant of degradation	d^{-1} -
$Rdeg$	-	overall degradation rate	$g\cdot d^{-1}$
T T_c	$Temp$ $CTLoss$	ambient temperature critical temperature for degradation	°C °C
V	$Volume$	volume	m^3

9.5 Redox status

PROCESS: SWOXYPAR

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).

Volume units refer to bulk (ℓ) or to water (w).

Implementation

Process SWOXYPAR is generic and can be used for water and sediment compartments. When substances in the sediment are modeled as 'inactive' substances, SWOXYPAR affects both the water compartments and the S1/2 partitioning processes. See [Table 9.10](#) below for definition of the parameters.

Volume units refer to bulk (ℓ) or to water (w).

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:

$$\begin{aligned} SWOXY &= 1 && \text{if } Cox/\phi > Cox_c \\ SWOXY &= 0 && \text{if } Cox/\phi \leq Cox_c \end{aligned}$$

with:

$$\begin{aligned} Cox &\quad \text{actual dissolved oxygen concentration [g m}^{-3}\ell\text{]} \\ Cox_c &\quad \text{critical dissolved oxygen concentration [g m}^{-3}w\text{]} \\ \phi &\quad \text{porosity [-]} \end{aligned}$$

The critical concentration Cox_c 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.

Directives for use

- ◊ The critical dissolved oxygen concentration Cox_{Part} is generally below 2 ppm, 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 ppm seems appropriate considering that such an average concentration may imply the presence of rather large anaerobic water masses within a compartment.

Table 9.10: Definitions of the parameters in the above equations for SWOXYPAR. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input/output	Definition	Units
Cox	OXY	dissolved oxygen concentration	$g m_\ell^{-3}$
$Coxc$	$CoxPart$	critical dissolved oxygen concentration	$g m_w^{-3}$
ϕ	$POROS$	porosity	-
$SWOXY$	$SWWaterKch$	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 S1	-

9.6 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 9.11](#) 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 f_{df} concentration is also input to VOLAT_(*i*) . This parameter is calculated with partitioning process PARTWK_(*i*)

Formulation

The volatilization rate for a specific water segment is equal to:

$$R_{vol} = \frac{k_{vol} \times (Cd - Cde)}{H}$$

with:

Cd	freely dissolved micropollutant concentration [g m^{-3}]
Cde	freely dissolved micropollutant concentration in equilibrium [g m^{-3}]
H	water depth [m]
k_{vol}	overall transfer coefficient for volatilization [m d^{-1}]
R_{vol}	volatilization rate [$\text{g m}^{-3} \text{ d}^{-1}$]

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 $\text{Pa.m}^3.\text{mol}^{-1}$) 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:

$$He = \frac{Ng}{Nl} \times e^{(a_1 + a_2 / (T + 273.15))}$$

$$Ng = \frac{P}{Rg \times (T_{ref} + 273.15)}$$

$$a_2 = (T_{ref} + 273.15) \times (\ln(He_{mr}) - a_1)$$

$$He_{mr} = He_{pr} \times \frac{Nl}{P}$$

with:

a_1	temperature coefficient for volatilization entropy [-]
a_2	temperature coefficient for volatilization enthalpy [K^{-1}]

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:

$$He_p = \frac{Pm}{Cd} = He \times R \times (T_{ref} + 273.15)$$

$$He_p = He_m \times R \times (T_{ref} + 273.15) \times \frac{Ng}{Nl} = He_m \times \frac{P}{Nl}$$

$$He_m = e^{\frac{-\Delta H^\circ}{Rg \times (T+273.15)} + \frac{\Delta S^\circ}{Rg}}$$

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 ($= THe$) 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 10^2 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.

- ◇ 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.* \(1992\)](#)

Table 9.11: 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 volatilization 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>i</i>)	total micropollutant concentration in the water	$g.m^{-3}$
fdf	-	freely dissolved micropollutant fraction	-
H	<i>Depth</i>	depth of the upper water segment	m
He	-	dimensionless Henry's constant of micropollutant (<i>i</i>) at ambient temperature $[(mol.m^{-3}).(mol.m^{-3})^{-1}]$	-
He_{mr}	-	Henry's constant of micropoll. (<i>i</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>i</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	$^{\circ}C$
T_{ref}	$Tref(i)$	reference temperature	$^{\circ}C$

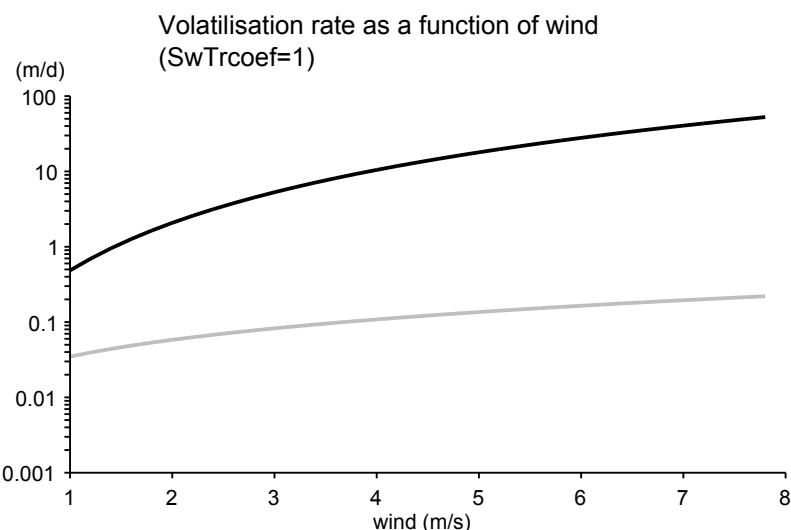
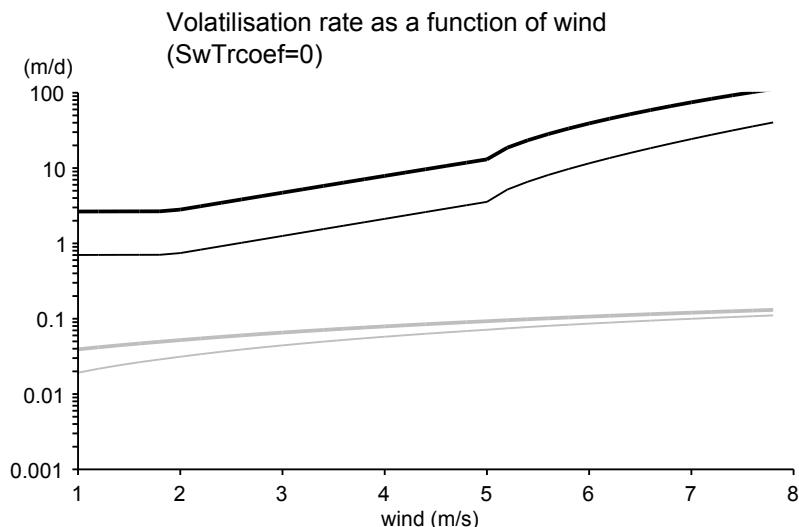


Figure 9.1: Liquid-air exchange rate (k_{vol}) for a very volatile pollutant: toluene (dashed lines: $H_{epr} = 660$) and a non-volatile pollutant lindane (solid lines: $H_{epr} = 0.48 \text{ Pa.m}^3.\text{mole}^{-1}$). Values of k_l and k_g for k_{vol} were calculated using the two options implemented in process TRCOEF (n : Water flow velocity = 0.5 m.s^{-1} , f : Water flow velocity = 2.0 m.s^{-1}).

9.7 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 m³ 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 IMPAQ; [IMPAQT \(1996\)](#)), 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 9.11](#) 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 $W < 1.9 \text{ m s}^{-1}$:

$$k_l = 5.64 \times \left(\frac{v^{0.969}}{H^{0.673}} \right) \times \sqrt{\frac{32}{Mw}}$$

for $1.9 \text{ m s}^{-1} \leq W < 5 \text{ m s}^{-1}$:

$$k_l = 5.64 \times \left(\frac{v^{0.969}}{H^{0.673}} \right) \times \sqrt{\frac{32}{Mw}} \times e^{(0.526 \times (W - 1.9))}$$

for $W \geq 5 \text{ m s}^{-1}$:

$$k_l = 5.64 \times \left(\frac{v^{0.969}}{H^{0.673}} \right) \times \sqrt{\frac{32}{Mw}} \times e^{(0.526 \times (5.0 - 1.9))} \times (1 + (W - 5.0)^{0.7})$$

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 $u < 0.3 \text{ m s}^{-1}$:

$$k_l = 86\,400 \times \left(10^{-6} + 0.0144 \times \frac{u^{2.2}}{\sqrt{Sc_l}} \right)$$

for $u \geq 0.3 \text{ m s}^{-1}$:

$$k_l = 86\,400 \times \left(10^{-6} + 0.00341 \times \frac{u}{\sqrt{Sc_l}} \right)$$

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.

$$u = 0.01 \times W \times \sqrt{(6.1 + 0.63 \times W)}$$

$$Sc_g = 86\,400 \times \frac{\eta_g}{\rho_g \times D_g}$$

$$Sc_l = 86\,400 \times \frac{\eta_l}{\rho_l \times D_l}$$

$$\rho_g = \frac{1.293}{1 + 0.00367 \times T}$$

$$\rho_l = 1000 - 0.088 \times T$$

$$\eta_g = 10^{-5} \times (1.32 + 0.009 \times T)$$

$$\eta_l = 0.001$$

with:

D_g	molecular diffusion coeff. of micropollutant in air [$\text{m}^2 \text{ d}^{-1}$]
D_l	molecular diffusion coeff. of micropollutant in water [$\text{m}^2 \text{ d}^{-1}$]
T	ambient temperature [$^\circ\text{C}$]
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 9.1](#) 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 \(1982\)](#)

Table 9.12: 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	$\text{m}^2 \text{ d}^{-1}$
D_l	$LDif(i)$	molecular diffusion coeff. of micropol. (i) in water	$\text{m}^2 \text{ d}^{-1}$
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}
<i>option</i>	$SWTrCoe f$	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 v W	$Velocity$ $VWind$	friction velocity at the water surface water flow velocity wind speed at 10 meter above water level	m s^{-1} m s^{-1} m s^{-1}
T	$Temp$	ambient water temperature	$^{\circ}\text{C}$
η_g η_l ρ_g ρ_l	-	dynamic viscosity of air [Pa s^{-1}] dynamic viscosity of water [Pa s^{-1}] density of air density of water	$\text{kg m}^{-1}\text{s}^{-1}$ $\text{kg m}^{-1}\text{s}^{-1}$ kg m^{-3} kg m^{-3}

9.8 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:

$$\begin{array}{c} \text{MP} \implies \text{MPS1} \implies \text{MPS2} \\ \text{settling} \quad \text{burial} \\ \hline \hline \text{Water} = || = \text{Sediment} \end{array}$$

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; sulphide forming heavy metals)
- Cr (group 2; hydroxide forming metal)
- As and Va (group 3; anion forming “metals”)

organic micropollutants,

- OMP (unspecified organic micropollutant)
- HCH (hexachloroheptane), 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.

Table [Table 9.13](#) 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:

$$Rset_j = ftau_j \times \frac{Fset_j}{H}$$

$$\begin{aligned} \text{if } H < Hmin \quad Fset_j = 0.0 \\ \text{else} \\ Fset_j = \min \left(Fset'_j, \frac{Cx_j \times H}{\Delta t} \right) \\ Fset'_j = Fset0_j + s_j \times Cx_j \end{aligned}$$

$$\begin{aligned} \text{if } \tau = -1.0 \quad ftau = 1.0 \\ \text{else} \\ ftau_j = \max \left(0.0, \left(1 - \frac{\tau}{\tau c_j} \right) \right) \end{aligned}$$

where:

<i>Cx</i>	concentration of a carrier substance ([gDM m ⁻³] or [gC m ⁻³])
<i>Fset0</i>	zero-order settling flux of a carrier substance ([gDM m ⁻² d ⁻¹] or [gC m ⁻² d ⁻¹])
<i>Fset</i>	settling flux of a carrier substance ([gDMm ⁻² d ⁻¹] or [gC m ⁻² d ⁻¹])
<i>ftau</i>	shear stress limitation function [-]
<i>H</i>	depth of the water column [m]
<i>Hmin</i>	minimum depth of the water column for settling and resuspension [m]
<i>Rset</i>	settling rate of a carrier substance ([gDM m ⁻³ d ⁻¹] or [gC m ⁻³ d ⁻¹])
<i>s</i>	settling velocity of a carrier substance [m d ⁻¹]
<i>τ</i>	shear stress [Pa]
<i>τc</i>	critical shear stress for the settling of a carrier substance [Pa]
<i>Δt</i>	timestep in DELWAQ (d)
<i>j</i>	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:

$$fs_{i,j} \quad \text{conc. of micro-pollutant i in carrier substance j ([gX gDM⁻¹] or [gX gC⁻¹])}$$

$Rset_j$	settling rate carrier substance j ([gDW m ⁻³ d ⁻¹] or [C m ⁻³ d ⁻¹])
$Rsm_{i,j}$	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 $Depth$ is smaller than minimal depth $MinDepth$ 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 9.13: 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
$Fset0_j$ $Fset_j$	$ZSed(j)$ $fSedIM1^2$ $fSedIM2^2$ $fSedIM3^2$ $fSedPHYT^2$ $fSedPOCnoa^2$	zero-order sett. flux of carrier subst. (j) settling flux of carrier substance IM1 settling flux of carrier substance IM2 settling flux of carrier substance IM3 settling flux of carrier substance PHYT settling flux of carrier substance POC without algae biomass	gC/DM.m ⁻² d ⁻¹ gDM m ⁻² d ⁻¹ gDM m ⁻² d ⁻¹ gDM m ⁻² d ⁻¹ gC m ⁻² d ⁻¹ gC m ⁻² d ⁻¹
$f_{s,i,j}$	$Q(i)IM1^3$ $Q(i)IM2$ $Q(i)IM3$ $Q(i)PHYT$ $Q(i)POC$	metal conc. in inorg. part. fraction IM1 metal conc. in inorg. part. fraction IM2 metal conc. in inorg. part. fraction IM3 micro-pollutant conc. in algae PHYT micro-pollutant conc. in POC	g gDW ⁻¹ g gDW ⁻¹ g gDW ⁻¹ g gC ⁻¹ g gC ⁻¹
- - - - -	$Fr(i)IM1^3$ $Fr(i)IM2$ $Fr(i)IM3$ $Fr(i)PHYT$ $Fr(i)POC$	fraction metal ads. to inorg. IM1 fraction metal ads. to inorg. IM2 fraction metal ads. to inorg. IM3 fraction micro-pollutant ads. to phytoplankton fraction micro-pollutant ads. to POC	- - - - -
H $Hmin$	$Depth$ $MinDepth$	depth of the overlying water compartment minimum water depth for settling and resuspension	m m
s_j	$VSed(j)$	settling velocity of carrier substance (j)	m d ⁻¹
τ τc_j	Tau $TaucS(j)$	shear stress crit. shear stress for settling of carrier substance (j)	Pa Pa
Δt	$Delt$	timestep in DELWAQ	d

Table 9.13: Definitions of the input parameters in the above equations for SED_(i).

Name in formulas	Name in input	Definition	Units
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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.

9.9 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 calculated 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 (β) or to water (ω).

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 9.14 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)

Formulation

The advective transport flux at the sediment-water interface due to seepage is formulated as follows:

$$R_{seep} = v_{seep} \times C_{mpd}$$

$$C_{mpd} = \begin{cases} C_{mpd_{s1}} = C_{mpdf_{s1}} + C_{mpdoc_{s1}} & \text{if } v_{seep} \geq 0.0 \\ C_{mpd_w} = C_{mpdf_w} + C_{mpdoc_w} & \text{if } v_{seep} < 0.0 \end{cases}$$

where:

C_{mpd} total dissolved micropollutant concentration [g.m^{-3}]

C_{mpdoc} DOC-bound dissolved micropollutant concentration [g.m^{-3}]

C_{mpdf} freely dissolved micropollutant concentration [g.m^{-3}]

R_{seep} seepage transport flux [$\text{g.m}^{-2}.d^{-1}$]

v_{seep} 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:

$$C_{mpd} = \begin{cases} C_{mpd_{s2}} = C_{mpdf_{s2}} + C_{mpdoc_{s2}} & \text{if } v_{seep} \geq 0.0 \\ C_{mpd_{s1}} = C_{mpdf_{s1}} + C_{mpdoc_{s1}} & \text{if } v_{seep} < 0.0 \end{cases}$$

where:

$s1$ index for the top sediment S1

$s2$ index for the deep sediment S2

V_{seep} 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:

$$R_{disp} = \phi_{s1} \times D_{sw} \times \frac{(C_{mpd_{s1}} - C_{mpd_w})}{L_{sw}}$$

where:

D dispersion coefficient ($\text{m}^2.\text{d}^{-1}$)

L mixing length (m)

R_{disp} dispersive transport flux ($\text{g.m}^{-2}.d^{-1}$)

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.

The dispersive transport flux between the top and deep sediment S1 and S2 is formulated as follows:

$$R_{disp} = \phi_{s2} \times D_{ss} \times \frac{(Cmpd_{s2} - Cmpd_{s1})}{L_{ss}}$$

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:

$$R_{seep} = 0.0, \text{ if } |v_{seep}| < \varphi \cdot s1 \cdot D_{sw} / L_{sw}$$

$$R_{disp} = 0.0, \text{ if } |v_{seep}| \geq \varphi \cdot s1 \cdot D_{sw} / L_{sw}$$

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 V_{Seep} 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 φ^2 (φ = porosity).
- 3 An indicative value for $MixLsw$ and $MixLss$ is 0.02 m.

References

None.

Table 9.14: 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	$g.m^{-3}w$
$Cmpdf_{s1}$	$Dis(i)S1$	freely dissolved micropollutant conc. in sediment S1	$g.m^{-3}w$

Table 9.14: Definitions of the parameters in the above equations for SWEOMP_(i). (i) is a substance name. Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
$Cmpdf_{s2}$	$Dis(i)S2$	freely dissolved micropollutant conc. in sediment S2	$g.m^{-3}w$
$Cmpdoc_w$	$Doc(i)$	DOC-bound micropollutant concentration in water	$g.m^{-3}w$
$Cmpdoc_{s1}$	$Doc(i)S1$	DOC-bound micropollutant conc. in sediment S1	$g.m^{-3}w$
$Cmpdoc_{s2}$	$Doc(i)S2$	DOC-bound micropollutant conc. in sediment S2	$g.m^{-3}w$
$Cmpd$	(i)-dis	total dissolved micropollutant concentration in water	$g.m^{-3}w$
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	-
φ_{s2}	$PORS2$	porosity of the deep sediment S2	-

10 Heavy metals

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10.1 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, sulphide and sulphate. 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 sulphide forming heavy metals like zinc and copper, since they are present in anionic forms instead 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 sulphide forming heavy metals may precipitate as sulphides at reducing conditions, especially in sediments. The co-precipitation with iron(II) sulphides 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 (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 $\text{g m}^{-3}\omega$). 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, sulphide 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 input parameters *HMGGroup1/2/3* 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 COM-POS, 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 sulphide concentrations can be generated by processes SPECSUD, SPESUDS1 and SPECSUDS2. Process SWOXYPARWK generates the input parameter *SWWaterKCh*, that indicates the oxidising (oxic) or reducing (anoxic) conditions.

Tables 10.1, 10.2 and 10.3 provide the definitions of the input parameters occurring in the formulations. Tables 10.4 and 10.5 contain the definitions of the output parameters.

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 *SWOXYPAR* 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:

$$fim_i = (1 - fdf) \times \frac{Kpim'_i \times Cim_i}{\sum_{i=1}^3 (Kpim'_i \times Cim_i) + Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

$$fdoc = (1 - fdf) \times \frac{Kppoc' \times Xdoc \times Cdoc}{\sum_{i=1}^3 (Kpim'_i \times Cim_i) + Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

$$fpoc = (1 - fdf) \times \frac{Kppoc' \times Cpoc}{\sum_{i=1}^3 (Kpim'_i \times Cim_i) + Kppoc' \times (Cpoc + Xdoc \times Cdoc) + Kpalg' \times Calg}$$

$$falg = (1 - fdf - fim_1 - fim_2 - fim_3 - fdoc - fpoc)$$

where:

<i>Calg/poc/doc</i>	concentration of algae biomass, dead particulate organic matter matter, and dissolved organic matter [gC m ⁻³]
<i>Cim_i</i>	concentration of inorganic matter fractions i = 1, 2 and 3 [gDW m ⁻³]
<i>falg/poc/doc</i>	fraction of micropollutant adsorbed to algae, dead particulate organic matter dissolved organic matter, [-]
<i>fim_i</i>	fraction of micropollutant adsorbed to inorganic matter fractions i = 1, 2 and 3 [-]
<i>fdf</i>	freely dissolved fraction of a micropollutant [-]
<i>Kpalg/poc'</i>	partition coefficient for algae and dead particulate organic matter [m ³ w gC ⁻¹]
<i>Kpim'_i</i>	partition coefficient for inorganic matter fractions i = 1, 2 and 3 [m ³ w gDW ⁻¹]
<i>Xdoc</i>	adsorption efficiency of DOC relative to POC [-]
<i>ϕ</i>	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* · *A*).

The partition coefficients in the above equations expressed in $[m_w^3 \text{ gC}^{-1}]$ or in $[m_w^3 \text{ gDW}^{-1}]$ are derived from the input parameters expressed in $[m_w^3 \text{ kgC}^{-1}]$ or $[m_w^3 \text{ kgDW}^{-1}]$:

$$Kpim'_i = \frac{Kpim_i}{1000} \quad \text{for } i = 1, 2 \text{ and } 3$$

$$Kppoc' = \frac{Kppoc}{1000}$$

$$Kppoc' = \frac{Kppoc}{1000}$$

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

$$fp = fpe - (fpe - fp') \times \exp(-ksorp \times \Delta t)$$

$$fdf = fdfe \times \frac{(1 - fp)}{(1 - fpe)}$$

$$fdoc = fdoce \times \frac{(1 - fp)}{(1 - fpe)}$$

$$fim_i = fime_i \times \frac{fp}{fpe} \quad \text{for } i = 1, 2 \text{ and } 3$$

$$fpoc = fpoce \times \frac{fp}{fpe}$$

$$falg = falge \times \frac{fp}{fpe}$$

where:

$Chmt/hmp'$	total and particulate conc. of metal after the previous time-step [g m ⁻³]
$fimi'$	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:

$$\begin{array}{ll} Rsorp & \text{sorption rate [g m}^{-3} \text{ d}^{-1}\text{]} \\ \Delta t & \text{timestep of DELWAQ [d}^{-1}\text{]} \end{array}$$

The calculation of the rate also requires division with the volume of the volume of the sediment layer ($V = Z \cdot A$) in case of PARTS1_(i) and PARTS2_(i).

The dissolved and particulate metal concentrations and the quality of the particulate organic fractions follow from:

$$Chmdf = \frac{fdf \times Chmt'}{\phi}$$

$$Chmoc = \frac{fdoc \times Chmt'}{\phi}$$

$$Chmd = Chmdf + Chmoc$$

$$Chmp = (fim_1 + fim_2 + fim_3 + fpoc + falg) \times Chmt'$$

$$Chmim_i = \frac{fim_i \times Chmt'}{Cpoc} \quad \text{for } i = 1, 2 \text{ or } 3$$

$$Chmpoc = \frac{fpoc \times Chmt'}{Cpoc}$$

$$Chmalg = \frac{falg \times Chmt'}{Calg}$$

For PARTS1_(i) and PARTS2_(i) the calculation of the dissolved concentrations also requires division with the volume of the layer ($V = Z \cdot A$).

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 from 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:

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

$$Crfr'_m = \frac{Crdf'_m}{1 + 10^{\log KCr_1} \times OH + 10^{\log KCr_2} \times OH^2 + 10^{\log KCr_3} \times OH^3}$$

where:

$Crfr'_m$	molar free chromium ion concentration [mol l ⁻¹]
$\log KCr_1/2/3$	the three equilibrium constants for hydroxyl complexation of chromium [$10^{\log((l\text{ mol}^{-1})^{1,2\text{ or }3})}$]
OH	the hydroxyl concentration [mol l ⁻¹]
pH	acidity [-]

The ion activity product based on this concentration and the solubility product are:

$$IAP = Crfr'_m \times OH^3$$

$$SOL = 10^{\log KCrS}$$

where:

$$\log KCrS \text{ solubility equilibrium constant for chromium hydroxide } [10^{\log(\text{mol l}^{-1})^4}]$$

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:

$$Crfr_m = \frac{10^{\log KCrS}}{OH^3}$$

$$Crdf_m = Crfr_m \times (1 + 10^{\log KCr_1} \times OH + 10^{\log KCr_2} \times OH^2 + 10^{\log KCr_3} \times OH^3)$$

$$Crdf = Crdf_m \times Mw \times 10^{+3}$$

$$f_{cor} = \frac{Crdf}{Crdf'}$$

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 precipitated fraction f_{pr} must be equal to:

$$f_{pr} = 1 - f_{cor}$$

The corrected sorbed fractions and concentrations for chromium are:

$$fdf = fdf' \times (1 - f_{pr})$$

$$fdoc = fdoc' \times (1 - f_{pr})$$

$$fim_i = fim'_i \times (1 - f_{pr}) \quad \text{for } i = 1, 2 \text{ or } 3$$

$$fpoc = fpoc' \times (1 - f_{pr})$$

$$falg = falg' \times (1 - f_{pr})$$

$$Chmdf = Crdf \times (1 - f_{pr})$$

$$Chmoc = Chmoc' \times (1 - f_{pr})$$

$$Chmd = Chmd' \times (1 - f_{pr})$$

$$Chmp = (fim_1 + fim_2 + fim_3 + fpoc + falg + fpr) \times Chmt'$$

$$Chmim_i = Chmim'_i \times (1 - f_{pr}) \quad \text{for } i = 1, 2 \text{ or } 3$$

$$Chmpoc = Chmpoc' \times (1 - f_{pr})$$

$$Chmalg = Chmalg' \times (1 - f_{pr})$$

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 sulphide forming metals, precipitate as sulphides at reducing conditions and form two sulphide complexes at the same time (MeS^0 and MeHS^+). The solubility of the metal sulphides 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:

$$Chmdf_m = \frac{1 + 10^{\log K_{hm1}} \times Csd + 10^{\log K_{hm2}} \times Chsd}{10^{\log K_{hmS}} \times Csd}$$

$$Chmdf = Chmdf_m \times Mw \times 10^{+3}$$

where:

$Chmdf_m$ molar total dissolved metal concentration [mol l^{-1}]

Csd molar dissolved sulphide S^{2-} concentration [mol l^{-1}]

$Chsd$ molar dissolved hydrogen sulphide HS^- concentration [mol l^{-1}]

$\log K_{hm1/2}$	the two equilibrium constants for sulphide complexation of a metal [$^{10}\log(I \text{ mol}^{-1})$]
$\log K_{hmS}$	solubility equilibrium constant for metal sulphide [$^{10}\log((I \text{ mol}^{-1})^2)$]
M_w	molecular weight of the metal [g mol^{-1}]

The molar dissolved sulphide and hydrogen sulphide concentrations are computed in processes SPECSUD(S1/2), using the pH, the total dissolved sulphide 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 suspended solids, particulate inorganic matter fractions, detritus and phytoplankton.

The metal content of total suspended solids and the apparent partition coefficient follow from:

$$Chmpt = \frac{Chmp \times 10^{+6}}{C_{ss}}$$

$$Kpt = \frac{Chmpt \times 10^{-3}}{Chmd + Chmdoc}$$

where:

C_{ss} 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 [$\text{m}^3 \text{ kg}^{-1}$].

The contents of the individual particulate fractions are calculated in a similar way.

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 [$\text{m}^{-3} \text{ kg C}^{-1}$] or [$\text{m}^{-3} \text{ kg DW}^{-1}$].
- ◊ 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 input parameters *SW SedYes/No* and *HMGroupl/2/3* always have the same default value, respectively 1.0/0.0 and 1.0/2.0/3.0, 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.

Additional references

[WL | Delft Hydraulics \(1992b\)](#), [DiToro and Horzempa \(1982\)](#), [O' Connor and Connolly \(1980\)](#), [Rai et al. \(1989\)](#), [Schnoor et al. \(1987\)](#)

Table 10.1: 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 (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
-	<i>HMGroupl</i>	identifier of metal group 1	-
-	<i>HMGroup2</i>	identifier of metal group 2	-
-	<i>HMGroup3</i>	identifier of metal group 3	-
<i>Calg</i>	<i>PHYT</i> ¹	phytoplankton concentration	$\text{gC m}^{-3} \ell$
<i>Cdoc</i>	<i>DOC</i>	dissolved organic matter conc.	$\text{gC m}^{-3} \ell$
<i>Cim_i</i>	<i>IMi</i>	conc. inorg. part. fractions i = 1,2,3	$\text{gDW m}^{-3} \ell$
<i>Cpoc</i>	<i>POCnoa</i> ²	particulate organic matter concentration without algae	$\text{gC m}^{-3} \ell$
<i>Chmt</i>	(i)	total metal concentration	$\text{g m}^{-3} \ell$
<i>Chmd</i>	(i) – dis	total dissolved metal concentration	$\text{g m}^{-3} \ell$
<i>Chmp</i>	(i) – par	total particulate metal concentration	$\text{g m}^{-3} \ell$
<i>Css</i>	<i>SS</i> ²	total suspended matter concentration	$\text{gDW m}^{-3} \ell$
<i>Kpalg</i>	<i>Kd(i)PHYT</i>	partition coefficient for phytoplankton (see directives!)	$\text{m}^{-3} \text{kgC}^{-1}$
<i>Kpim_i</i>	<i>Kd(i)IMi</i>	part. coeff. for inorg. fractions i = 1,2,3	$\text{m}^{-3} \text{kgDW}^{-1}$
<i>Kppoc</i>	<i>Kd(i)POC</i>	partition coefficient for POC	$\text{m}^{-3} \text{kgC}^{-1}$
continued on next page			

Table 10.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
<i>SWOXY</i>	<i>SWWaterKCh</i> ³	switch for oxidising or reducing conditions	-
—	<i>SWSedNo</i> ⁴	option for process in water column (default = 0.0)	-
<i>tads</i>	<i>HLTAds(i)</i>	half-life-time adsorption process	d
<i>tdes</i>	<i>HLTDes(i)</i>	half-life-time desorption process	d
<i>Xdoc</i>	<i>XDOC(i)</i>	ads. efficiency of DOC relative to POC	-
<i>V</i>	<i>Volume</i>	volume	$\text{m}^{-3} \ell$
φ	<i>POROS</i>	porosity	$\text{m}^3 w \text{ m}^{-3} \ell$
Δt	<i>Delt</i>	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 10.2: 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 (ℓ) or to water (w).

Name in formulas	Name in input	Definition	Units
<i>A</i>	<i>Surf</i>	surface area	m^2
<i>Calg</i>	<i>PHYTS(k)</i> ¹	phytoplankton quantity	gC
<i>Cdoc</i>	<i>DOCS(k)</i>	dissolved organic matter concentration	$\text{gC m}^{-3} w$
<i>Cim_i</i>	<i>IMiS(k)</i>	quantity of inorganic particulate fractions i = 1,2,3	gDW
<i>Cpoc</i>	<i>POCS(k)</i> ¹	particulate organic matter quantity	gC
<i>Chmt</i>	<i>(i)S(k)</i>	quantity total heavy metal	g
<i>Chmd</i>	<i>(i)S(k) - dis</i>	quantity total dissolved heavy metal	g
<i>Chmp</i>	<i>(i)S(k) - par</i>	quantity total particulate heavy metal	g
<i>Css</i>	<i>DMS(k)</i> ¹	quantity of total sediment	gDW
<i>Kpalg</i>	<i>Kd(i)PHYTS(k)</i>	partition coeff. for phytoplankton (see directives!)	$\text{m}^{-3} \text{ kgC}^{-1}$
<i>Kpimi</i>	<i>Kd(i)IMiS(k)</i>	part. coeff. for inorg. fractions i = 1,2,3	$\text{m}^{-3} \text{ kgDW}^{-1}$
<i>Kppoc</i>	<i>Kd(i)POCS(k)</i>	part. coeff. for POC (see directives!)	$\text{m}^{-3} \text{ kgC}^{-1}$
<i>SWOXY</i>	<i>SWPoreChS(k)</i> ²	switch for oxidising or reducing conditions	-

continued on next page

Table 10.2 – continued from previous page

Name in formulas	Name in input	Definition	Units
-	$SW\text{Sed}Yes^3$	option for process in sediment (default = 1.0)	-
$tads$ $tdes$	$HLTAds(i)S(k)$ $HLTDes(i)S(k)$	half-life-time adsorption process half-life-time desorption process	d d
$Xdoc$	$XDOC(i)$	ads. efficiency of DOC relative to POC	-
V Z φ	- $ActThS(k)$ $PORS(k)$	volume thickness of sediment layer porosity	$m^{-3}\ell$ m $m^3 w m^{-3}\ell$
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 10.3: 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 sulphide HS^- concentration	$mol l^{-1}$
Csd	$DisSWK$ or $DisSS(k)$	molar dissolved sulphide 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 sulphide S^{2-} complexation constant (group 1)	$^{10}\log(l mol^{-1})$
$logKhm2$	$logK(i)HSaq$	metal hydr. sulphide HS^- compl. constant (group 1)	$^{10}\log(l mol^{-1})$
$logKhmS$	$logK(i)Ss$	metal sulphide solubility const. (group 1)	$^{10}\log((l mol^{-1})^2)$
Mw_i	$MolWt(i)$	molecular weight of a metal	$g mol^{-1}$

continued on next page

Table 10.3 – continued from previous page

Name in formulas	Name in input	Definition	Units
pH	pH or $pHS(k)$	acidity	-

¹⁾ The sulphide concentrations can be generated by processes SPECSUD, SPESUDS1 and SPECSUDS2.

Table 10.4: Definitions of the output parameters for $PARTWK_{(i)}$. (i) is a substance name.
Volume units refer to bulk (ℓ) or to water (w).

Name in formulas	Name in output	Definition	Units
$Chmt$	$(i)tot$	total metal concentration	$g m^{-3} \ell$
$Chmd$	$Dis(i)$	freely dissolved metal concentration	$g m^{-3} w$
$Chmoc$	$Doc(i)$	DOC adsorbed metal concentration	$g m^{-3} w$
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	$mg kgDW^{-1}$

Table 10.5: 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 (ℓ) or to water (w).

Name in formulas	Name in output	Definition	Units
$Chmt$	$(i)S(k)tot$	total metal concentration	$g m^{-3} \ell$
$Chmd$	$Dis(i)S(k)$	freely dissolved metal concentration	$g m^{-3} w$
$Chmdoc$	$Doc(i)S(k)$	DOC adsorbed metal concentration	$g m^{-3} w$
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	$mg kgDW^{-1}$

10.2 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 sulphide 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:

- the sulphide forming metals Cd, Cu, Zn, Ni, Hg, Pb;
- the hydroxide forming metal Cr; and
- the anion forming “metal” As.

See [Table 10.6](#) for the definition of input and output parameters.

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:

$$Kp_0 = 10^a \times 10^{(b \times pH)} \times 10^{c \times pH^2} \times ALK^d \times Ccl^g \times DOC^l \times ALK^{m \times pH} \times ALK^{n \times pH \times \log(ALK)} \times ALK^{o \times pH^2}$$

$$Kpim_i = Kp_0 \times \frac{(10^3 \times CEC_i)}{0.2} \quad \text{for } i = 1, 2 \text{ and } 3$$

with:

Kp_0	reference partition coefficient [$m^3 \text{ kgDW}^{-1}$]
$Kpim_i$	partition coefficient with respect to sediment fraction i [$m^3 \text{ kgDW}^{-1}$]
ALK	alkalinity [mole $\text{HCO}_3^- \text{ m}^{-3}$]
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	I	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).

SWRepro = 2

The North Sea repro-function is applied. This function reads:

$$Kp_0 = 10^a \times 10^{b \times pH} \times (1.8 \times 10^{+3} \times Ccl + c)^d$$

$$Kpim_i = Kp_0 \times 10^3 \times CEC_i \quad \text{for } i = 1, 2 \text{ and } 3$$

with:

Kp_0	reference partition coefficient per unit CEC [$\text{m}^3 \text{ eq}^{-1}$]
$Kpim_i$	partition coefficient with respect to sediment fraction i [$\text{m}^3 \text{ kgDW}^{-1}$]
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 $2.0-3.0 \text{ eq kg}^{-1}$. The CEC of suspended sediment can be estimated with:

$$CEC = CEC_{poc} \times foc + CEC_{silt} \times fsilt$$

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 adsorption 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 \(1991\)](#)

Table 10.6: 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 $i = 1, 2, 3$	$\text{m}^3 \text{kgDW}^{-1}$
a	$CaRFKp(i)$	metal specific coefficients in the repro-functions	various
b	$CbRFKp(i)$		(formula defined)
c	$CcRFKp(i)$		
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)	-

* $\text{mol m}^{-3} = \text{meq L}^{-1}$

11 Bacterial pollutants

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11.1 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. The lethal effect of light is associated with short wavelengths, ultraviolet radiation in particular. Approximately half of the lethal effect is due to light with wavelength below 370 nm. Wavelengths over 500 nm are ineffective.

However, little or no mortality may occur at low temperatures. Distinction is made between *Escherigia 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. The formulations are equal for each coliform species, the coefficients can be specified by the user.

Implementation

Process (I)MORT has been implemented for four “substances” (i), namely:

- ◊ ECOLI, FCOLI, TCOLI and ENCOC.

Processes CALCRAV_UV and CALCRAADDAY can be used to deliver the intensity of UV light at the top and the bottom of the water layers in the model as derived from visible light (solar radiation). Process DAYLENGTH can be used to calculate daylength. Process Extinc_UVG can be used to provide the total extinction coefficient of UV light.

[Table 11.2](#) 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 $T > Tc_i$:

$$Rmrt_i = kmrt_i \times Cx_i \quad (11.1)$$

$$kmrt_i = (kmb_i + kmcl_i) \times ktmrt_i^{(T-20)} + kmrd \quad (11.2)$$

$$kmcl_i = kcl_i \times Ccl \quad (11.3)$$

$$kmrd = krd \times DL \times fuv \times I0 \times \frac{(1 - e^{-\varepsilon \times H})}{\varepsilon \times H} \quad (11.4)$$

For $T \leq Tc_i$:

$$Rmrt_i = 0.0 \quad (11.5)$$

where:

Cx	concentration of coliform bacteria species i [MPN.m $^{-3}$]
DL	daylength, fraction of a day [-]
ε	extinction of UV-radiation [m $^{-1}$]
fuv	fraction of UV-radiation as derived from visible light [-]

H	water depth [m]
I_0	daily solar radiation as visible light at the water surface [$\text{W} \cdot \text{m}^{-2}$]
kcl	chloride related mortality constant [$\text{m}^3 \cdot \text{g}^{-1} \cdot \text{d}^{-1}$]
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 [$\text{m}^2 \cdot \text{W}^{-1} \cdot \text{d}^{-1}$]
$ktmrt$	temperature coefficient of the mortality rate [-]
$Rmrt$	mortality rate of coliform bacteria [$\text{MPN} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$]
T	temperature [$^\circ\text{C}$]
T_c	critical temperature for mortality [$^\circ\text{C}$]
Ccl	chloride concentration [$\text{g} \cdot \text{m}^{-3}$]
i	index for coliform species, ECOLI, FCOLI, TCOLI and ENCOC

The daily average solar radiation is calculated by multiplying the total daily radiation with the day length (hours of daylight per 24 hours). 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 RAD_{uv} as input parameter, but this is derived from RadSurf when process CalcRad_UV is active. This process must be active for models with more than one water layer. If $RadSurf$ is solar radiation (measured as visible light), RAD_{uv} is also solar radiation (measured as visible light), but calculated with the extinction coefficient of UV light. The mortality process converts visible light into UV light using $FrUVVL$.
- ◊ 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 fraction of UV-radiation of total light at the surface of the earth is 6 percent, that is approximately 12 percent of solar radiation measured as visible light, because visible light is approximately 50 percent of total light. The default value of $FrUVVL$ is therefore 0.12. ($FrUVVL$ should be equal to 1.0 if Rad_{UV} is imposed as UV light).
- ◊ The value of the radiation dependent mortality constant krd depends on the units in which Rad_{uv} ($RadSurf$) is specified. A value of $1.0 \text{ h langley}^{-1} \text{ d}^{-1}$ 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 $0.0862 (\text{m}^2 \text{ W}^{-1} \text{ d}^{-1})$.
- ◊ For other units of Rad_{uv} ($RadSurf$) the conversion constants listed in [Table 11.1](#) can be helpful.

Table 11.1: Conversion constants

1 langley	1 cal cm^{-2}	4.18 J cm^{-2}
$1 \text{ einstein m}^{-2} \text{ s}^{-1}$	12.1 W m^{-2}	$370 < l < 540 \text{ nm}$
1 kLux	3.75 W m^{-2}	
$1 \text{ ergs m}^{-2} \text{ s}^{-1}$	10^{-7} W m^{-2}	
1 lumen	0.005 W	White light

- ◊ The UV-extinction coefficient $ExtUV$ is high compared to the extinction coefficient of visible light. A value of 3 m^{-1} is indicative.

Table 11.2: 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_{fuv}	$ExtUV$ $FrUVVL$	extinction of UV-radiation fraction of UV-radiation as derived from visible light	m^{-1} -
H	$Depth$	water depth (layer thickness)	m
$I0$	RAD_{-uv}	daily solar radiation as visible light at water surface	W.m ⁻²
kcl_i kmb_i $kmcl_i$ $kmrd_i$ $kmrt_i$ krd $ktmrt$	$SpMrt(i)$ $RcMrt(i)$ - - - $CFRAD$ $TcMrt(i)$	chloride dependent mortality constant basic mortality rate chloride dependent mortality rate radiation dependent mortality rate first order mortality rate radiation dependent mortality constant temperature coefficient of the mortality rate	$m^3.g^{-1}.d^{-1}$ d^{-1} d^{-1} d^{-1} d^{-1} $m^2.W^{-1}.d^{-1}$ -
$Rmrt_i$	-	mortality rate of coliform bacteria	MPN.m ⁻³ .d ⁻¹
T Tc_i	$Temp$ $CTMrt(i)$	temperature critical temperature for mortality	°C °C

¹substances (i) are ECOLI, FCOLI, TCOLI and ENCOC

12 Sediment and mass transport

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12.1 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 "inactive" 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 12.1](#) 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:

$$Rset_i = ftau_i \times \frac{Fset_i}{H}$$

$$\text{if } H < Hmin \text{ } Fset_i = 0.0$$

else

$$Fset_i = \min \left(Fset'_i, \frac{Cx_i \times H}{\Delta t} \right)$$

$$Fset'_i = Fset0_i + s_i \times Cx_i$$

$$\begin{aligned}
 & \text{if } \tau = -1.0 \quad ftau = 1.0 \\
 & \text{else} \\
 & \quad ftau_i = \max \left(0.0, \left(1 - \frac{\tau}{\tau_{ci}} \right) \right)
 \end{aligned}$$

where:

Cx	concentration of a substance [gDM/O ₂ m ⁻³]
$Fset0$	zero-order settling flux of a substance [gDM/O ₂ m ⁻² d ⁻¹]
$Fset$	settling flux of a substance [gDM/O ₂ m ⁻² d ⁻¹]
$ftau$	shear stress limitation function [-]
H	depth of the water column [m]
$Hmin$	minimal depth of the water column for resuspension [m]
$Rset$	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)

The settling velocity as dependent on flocculation is formulated as follows:

$$\begin{aligned}
 s_i &= ftemp \times fsal \times fcon \times s0_i \\
 ftemp &= kt^{(T-20)} \\
 fsal &= \left(\frac{a_i + 1}{2} \right) - \left(\frac{a_i - 1}{2} \right) \times \cos\left(\frac{\pi \times S}{S_{max}}\right) \\
 fcon &= \left(\frac{Cs}{Csc} \right)^{n_i}
 \end{aligned}$$

where:

a	coefficient for the enhancement of flocculation [-]
Cs	concentration of total suspended solids [gDM m ⁻³]
Csc	critical concentration of total susp. solids above which flocc. occurs [gDM m ⁻³]
$fcon$	function for the concentration dependency of flocculation, see Figure 12.1A [-]
$fsal$	function for the salinity function dependency of flocculation, range [0,EnhSedi], see Figure 12.1B [-]
$ftemp$	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 $Hmin$ 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 $Fset$ (output 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 Csc ($CrSS$) and the coefficient $n(i)$ determine the increase of the settling velocity at concentrations above the critical concentrations, see [Figure 12.1, 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 12.2](#).

Table 12.1: 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	$EnhSed(i)$	coefficient for the enhancement of flocculation of substance (i)	-
$Fset0_i$	$ZSed(i)$	zero-order settling flux of substance (i)	$\text{gDM m}^{-2} \text{ d}^{-1}$
H	$Depth$	depth of the water column, thickness of water layer	m
$Hmin$	$MinDepth$	minimal water depth for settling and re-suspension	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 $Salmax$	$Salinity$ $SMax$	salinity salinity at which the salinity function is at its maximum	psu psu
Cs	SS	concentration of total suspended solids	gDM m^{-3}
continued on next page			

Table 12.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
Csc	$CrSS$	critical concentration of total suspended solids for flocculation	gDM m^{-3}
n_i	$N(i)$	constant for concentration effect on flocculation	-
T	$Temp$	temperature	$^{\circ}\text{C}$
kt	$TcSed$	temperature coefficient for settling	-
τ	Tau	shear stress	Pa
τc_i	$TaucS(i)$	critical shear stress for settling of substance (I)	Pa
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.

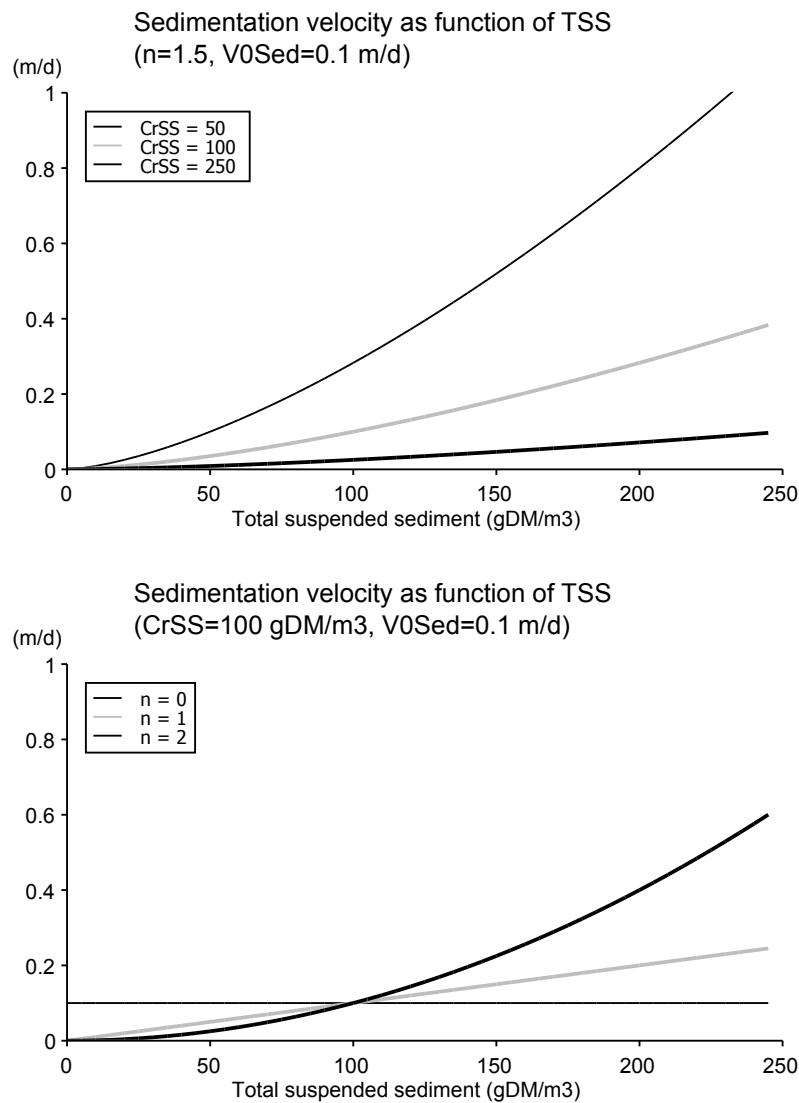


Figure 12.1: Sedimentation velocity (V_{sed}) as a function of total suspended solid concentration (SS) solely (no effect of salinity and density included) at A): a critical suspended solid concentration and B) at one value of n (constant in the sedimentation formulation)

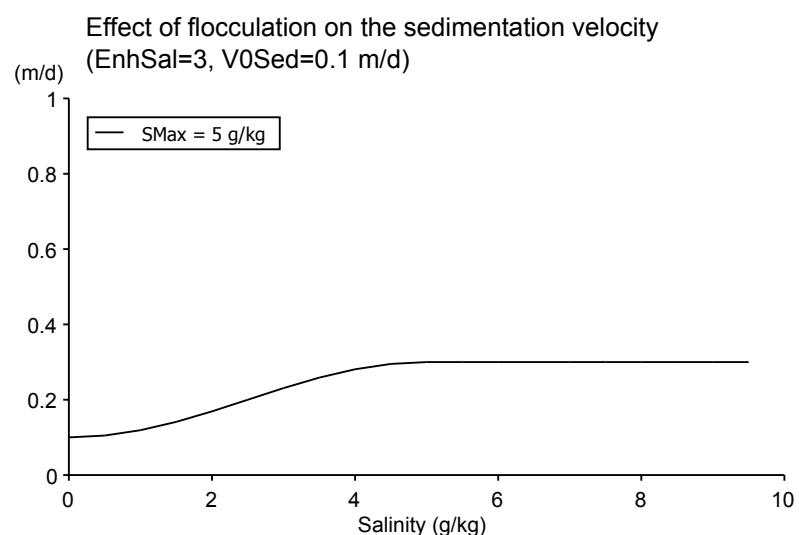


Figure 12.2: Sedimentation velocity (V_{Sed}) as a function of salinity solely (effect of flocculation and density not included).

12.2 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 $f_{SedAlgDM}$ for BLOOM. Process SEDPHDYN delivers the algae biomass settling flux $f_{SedAlgDM}$ for DYNAMO.

The output parameters f_{SedTIM} and $f_{SedPOCnoa}$ are used to calculate the settling fluxes of organic micro-pollutants and heavy metals. Tabel 12.2 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 f_{SedSOD} , the settling flux of total BOD and or COD. Tabel 12.3 provides the definitions of the input parameters.

Formulation

The formulations for *Sum_Sedim* are:

$$\begin{aligned}
 f_{SedTIM} &= \sum_{i=1}^3 f_{SedIM_i} \\
 f_{SedPOMnoa} &= \sum_{j=1}^4 f_{SedPOC_j} \times DMCFPOC_j \\
 f_{SedDM} &= \sum_{i=1}^3 f_{SedIM_i} \times DMCFIM_i + f_{SedPOMnoa} + f_{SedAlgDM} \\
 f_{SedPOCnoa} &= \sum_{j=1}^4 f_{SedPOC_j} \\
 f_{SedPOC} &= f_{SedPOCnoa} + f_{SedPhyt}
 \end{aligned}$$

where:

fSedPHYT	settling flux of total phytoplankton [gC m ⁻² d ⁻¹]
fSedAlgDM	settling flux of total phytoplankton [gDM m ⁻² d ⁻¹]
fSedPOC	settling flux of total particulate organic carbon [gC m ⁻² d ⁻¹]
fSedPOC_j	settling flux of detritus fraction j [gC m ⁻² d ⁻¹]
fSedPOCnoa	settling flux of POC excluding algae [gC m ⁻² d ⁻¹]
fSedPOMnoa	settling flux of POC excluding algae [gDM m ⁻² d ⁻¹]
fSedTIM	settling flux of total inorganic matter [gDM m ⁻² d ⁻¹]
fSedIM_i	settling flux of inorganic matter fraction i [gDM m ⁻² d ⁻¹]
fSedDM	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;

$$fSedSOD = fSedBOD5 + fSedBOD5_2 + fSedBOD5_3 + fSedBODu + \\ + fSedBODu_2 + fSedNBOD5 + fSedNBODu$$

if *SWOxyDem* = 1;

$$fSedSOD = fSedCODCr + fSedCODMn$$

if *SWOxyDem* = 2;

$$fSedSOD = fSedCODCr + fSedCODMn + fSedBOD5 + fSedBOD5_2 + fSedBOD5_3 + \\ + fSedBODu + fSedBODu_2 + fSedNBOD5 + fSedNBODu$$

where:

fSedSOD	settling flux of sediment oxygen demand [gO m ⁻² d ⁻¹]
fSed(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.

Table 12.2: 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
$fSedIM_i$	$fSed(i)$	settling flux of inorganic matter fraction (i)	$\text{gDM m}^{-2}\text{d}^{-1}$
$fSedPOC_j$	$fSed(j)$	settling flux of detritus fraction (j)	$\text{gC m}^{-2}\text{d}^{-1}$
$fSedAlgDM$ $fSedPHYT$	$fSedAlgDM$ $fSedPHYT$	settling flux of total phytoplankton settling flux of total phytoplankton	$\text{gDM m}^{-2}\text{d}^{-1}$ $\text{gC m}^{-2}\text{d}^{-1}$

Table 12.3: 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)	-
$fSedBOD5$ $fSedBOD5_2$ $fSedBOD5_3$ $fSedBODu$ $fSedBODu_2$	$fSedBOD5$ $fSedBOD5_2$ $fSedBOD5_3$ $fSedBODu$ $fSedBODu_2$	settling flux of CBOD5 settling flux of CBOD5_2 settling flux of CBOD5_3 settling flux of CBODu settling flux of CBODu_2	$\text{gO}_2 \text{ m}^{-2}\text{d}^{-1}$ $\text{gO}_2 \text{ m}^{-2}\text{d}^{-1}$ $\text{gO}_2 \text{ m}^{-2}\text{d}^{-1}$ $\text{gO}_2 \text{ m}^{-2}\text{d}^{-1}$ $\text{gO}_2 \text{ m}^{-2}\text{d}^{-1}$
$fSedNBOD5$ $fSedNBODu$	$fSedNBOD5$ $fSedNBODu$	settling flux of NBOD5 settling flux of NBODu_2	$\text{gO}_2 \text{ m}^{-2}\text{d}^{-1}$ $\text{gO}_2 \text{ m}^{-2}\text{d}^{-1}$
$fSedCODCr$ $fSedCODMn$	$fSedCODCr$ $fSedCODMn$	settling flux of COD_Cr settling flux of COD_Mn	$\text{gO}_2 \text{ m}^{-2}\text{d}^{-1}$ $\text{gO}_2 \text{ m}^{-2}\text{d}^{-1}$

12.3 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 (β), water (ω) or solids (δ).

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
- ◊ Fellipa, Fellipc, Fellid, FeS, FeS2, FeCO3, Felld
- ◊ OMP, 153, Atr, BaP, Diu, Flu, HCB, HCH, Mef
- ◊ As, Cd, Cr, Hg, Ni, Pb, Va, Zn
- ◊ Cl, Salinity

◇ 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 12.4](#) 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):

$$\begin{aligned} Fres' &= ftau \times Fres0 \\ \text{if } H < Hmin \quad Fres' &= 0.0 \quad \text{else} \\ Fres &= \min \left(Fres', \frac{Cdm}{A \times \Delta t} \right) \\ \text{if } \tau = -1.0 \quad ftau &= 1.0 \quad \text{else} \\ ftau &= \max \left(0.0, \left(\frac{\tau}{\tau_c} - 1.0 \right) \right) \end{aligned}$$

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]
τ_c	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 [$g.m^{-2}.d^{-1}$]
f_p	particulate fraction of a substance [—]
vp	volumetric burial or digging velocity [$m.d^{-1}$]
j	porosity [—]

Fraction f_p is equal to 1.0 for all particulate substances, except for organic micro-pollutants and heavy metals. The model calculates f_p 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:

$$\varphi = 1 - \sum_{i=1}^{i=n} \left(\frac{f_{p_i} \times Cx_i}{\rho_i} \right)$$

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 $fd = 1 - f_p$ is equal to 1.0 for all dissolved substances, except for organic micro-pollutants and heavy metals.

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.

- 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 $5.0 \cdot 10^{-4} \text{ m}^2/\text{d}$. 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 $0.25 \cdot 10^{-4} \text{ m}^2/\text{d}$.
- 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 $2.0 \cdot 10^{-6} \text{ m}^2/\text{d}$. 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 Van Beek \(2013\)](#)

Table 12.4: Definitions of the input parameters in the above equations for ADVTRA, DSP-TRA and TRASE2_(i) (or TRSE2_(i) or TRSE2(i)). Volume units refer to bulk (β), water (ω) or solids (δ).

Name in formulas	Name in input	Definition	Units
A	$Surf$	surface area of overlying water compartment	m^2
Dd Dp	$DifCoef^1)$ $TurCoef^1)$	dispersion coefficient for solutes dispersion coefficient for particulates	$\text{m}^2 \cdot \text{d}^{-1}$ $\text{m}^2 \cdot \text{d}^{-1}$
$Fres0$	$ZResDM$	zero order resuspension flux	$\text{gDM} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$

$Hmin$	$MinDepth$	minimal water depth 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	$g.m^{-3}\delta$
	$RhoOM$	density of organic matter	$g.m^{-3}\delta$
j	$Porinp^2$	input porosity	—
τ	Tau	shear stress	Pa
τ_c	$TauCrDM$	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.

12.4 Transport in sediment and resuspension (S1/2)

PROCESSES: S12TRA(i), RES_DM, BUR_DM, DIG_DM, S1_COMP, S2_COMP, PARTS1_(i), PARTS2_(i)

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 phosphorus, organic micropollutants and heavy metals are allocated 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 (β), water (ω) or solids (δ).

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:

- ◊ POC2, OOCS1, OOCS2, PON2, OONS1, OONS2, POP2, OOPS1, OOPS2, Opal, OOSiS1 and OOSiS2.

Process S12TRAAP 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 stoichiometric 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 12.5](#) to [12.8](#) provide the definitions of the input parameters occurring in the formulations.

Formulation

Resuspension

The resuspension flux of sediment dry matter is described as the sum of zero-order and first-order kinetics according to:

$$\begin{aligned}
 Fres'_j &= ftau_j \times (Fres0 + r \times Cdm_j / A) \\
 \text{if } H < Hmin \quad Fres'_j &= 1.0 \quad \text{else} \\
 Fres_j &= \min \left(Fres'_j, \frac{Cdm}{A \times \Delta t} \right) \\
 \text{if } DMS1 > 0.0 \quad FresS2 &= 0.0 \\
 \text{if } \tau = -1.0 \quad f_\tau &= 1.0 \quad \text{else} \\
 ftau_j &= \max(0.0, (\frac{\tau}{\tau_{Cj}} - 1.0))
 \end{aligned}$$

where:

A	surface area of overlying water compartment [m^2]
Cdm	amount of sediment dry matter [gDM]
$Fres_0$	zero-order resuspension flux of sediment [$gDM.m^{-2}.d^{-1}$]
$Fres$	resuspension flux of sediment [$gDM.m^{-2}.d^{-1}$]
$f\tau_a$	shear stress limitation function [—]
H	depth of the water column, thickness overlying water layer [m]
H_{min}	minimal depth of the water column for resuspension [m]
r	first-order resuspension rate [d^{-1}]
τ	shear stress [Pa]
τ_c	critical shear stress for resuspension [Pa]
Δt	timestep in DELWAQ [d]
j	index for sediment layer S1 or S2.

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:

$$Rres_{i,j} = f_{s,i,j} \times fr_{i,j} \times Fres_j / H$$

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 [$gX.m^{-3}\mathcal{L}.d^{-1}$]
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 stoichiometric 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 *SW*Sediment=0.0 layer thicknesses are kept constant. The burial fluxes of sediment dry matter follows from:

$$Fbur_j = \begin{cases} Fin_j + \frac{(Z_j - Zfix_j) \times \rho_j \times (1 - \phi_j)}{\Delta t} & \text{if } Z_j \geq Zfix_j \\ 0.0 & \text{otherwise} \end{cases}$$

$$Fin_1 = Fset$$

$$Fin_2 = Fbur_1$$

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 ($g.m^{-3}$)
Δt	timestep in DELWAQ [d]
j	index for sediment layer S1 or S2.

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:

$$\begin{aligned} F_{bur_j} &= \min ((F_{bin_j} + F_{bad_j}), F_{bmax_j}) \\ F_{bin_j} &= F_{bur0_j} + rb_j \times Cdm_j / A \\ F_{bad_j} &= \max \left(0, \frac{(Z_j - Z_{max_j}) \times \rho_j \times (1 - \phi_j)}{\Delta t} \right) \\ F_{bmax_j} &= Fin_j - Fout_j + \frac{Cdm_j}{A \times \Delta t} \\ Cdm_j &= A \times Z_j \times \rho_j \times (1 - \phi_j) \end{aligned}$$

$$\begin{aligned} Fin_1 &= Fset \\ Fin_2 &= F_{bur_1} \end{aligned}$$

$$\begin{aligned} Fout_1 &= Fres_1 \\ Fout_2 &= Fdig_1 \end{aligned}$$

where:

A	surface area of overlying water compartment [m^2]
Cdm	amount of sediment dry matter [gDM]
F_{bad}	additional burial flux to obey maximal layer thickness [$gDM.m^{-2}.d^{-1}$]
F_{bin}	burial flux of sediment based on input parameters [$gDM.m^{-2}.d^{-1}$]
F_{bmax}	maximal possible burial based on available sediment [$gDM.m^{-2}.d^{-1}$]
F_{bur0}	zero-order burial flux of sediment [$gDM.m^{-2}.d^{-1}$]
F_{bur}	burial flux of sediment [$gDM.m^{-2}.d^{-1}$]
F_{dig}	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]
Z_{fix}	fixed thickness of sediment layer [m]
Z_{max}	maximal 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 burial of inorganic sediment components, organic carbon, nitrogen, phosphorus and silicate components, adsorbed phosphate, micro-pollutants and heavy metals in the sediment follows from:

$$\begin{aligned} F_{bur_{i,j}} &= fs_{i,j} \times fr_{i,j} \times F_{bur_j} \\ R_{bur_{i,j}} &= F_{bur_{i,j}} / H \end{aligned}$$

where:

f_r	fraction of a component in sediment dry matter [$gX.gDM^{-1}$]
f_s	scaling factor [–] or [$gX.gY^{-1}$]
H	depth of the water column, thickness overlying water layer [m]
F_{bur}	burial flux of a component [$gX.m^{-2}.d^{-1}$]
R_{bur}	burial rate of a component [$gX.m^{-3}.l.d^{-1}$]
i	index for component i
j	index for sediment layer S1 or S2.

The ratio f_s is a scaling factor that is equal to 1.0 for most substances. It is component specific for the organic nutrients, in fact the stoichiometric 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 *SW*Sediment=0.0 layer thicknesses are kept constant. The burial fluxes of sediment dry matter follows from:

if $Z_j < Z_{fix_j}$ then

$$F_{dig_j} = F_{out_j} + \frac{(Z_{fix_j} - Z_j) \times \rho_j \times (1 - \phi_j)}{\Delta t}$$

if $Z_j = Z_{fix_j}$ then

$$F_{dig_j} = F_{out_j}$$

and

$$F_{out_1} = F_{res_1}$$

$$F_{out_2} = F_{dig_1}$$

where:

F_{dig}	digging flux of sediment [$gDM.m^{-2}.d^{-1}$]
F_{out}	outflux of sediment [$gDM.m^{-2}.d^{-1}$]
F_{res}	resuspension flux of sediment [$gDM.m^{-2}.d^{-1}$]
Z	actual thickness of sediment layer [m]
Z_{fix}	fixed 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.

For option *SW*Sediment=1.0 layer the digging fluxes of sediment dry matter are described with zero-order kinetics according to:

$$F_{dig_j} = \min(F_{dig0_j}, F_{dm2})$$

$$F_{dm2} = \frac{C_{dm2}}{A \times \Delta t}$$

$$F_{dm2} = \infty$$

$$C_{dm2} = A \times Z_2 \times \rho_2 \times (1 - \phi_2)$$

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 [$gX.m^{-3}\ell.d^{-1}$]
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 stoichiometric 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.

- 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 $Depth$ is smaller than minimal depth $MinDepth$ for settling, which has a default value of 0.1 m. When desired $MinDepth$ may be given a different value.
- 4 The 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 Usually only the zeroth-order part of the resuspension formulation is used.
- 7 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.
- 8 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.
- 9 The option parameter $SWDigS1 = 0.0$ (default) leads to the allocation of the quality of layer S1 ($f_{r,i,1}$, $f_{s,i,1}$) 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 ($f_{r,i,2}$, $f_{s,i,2}$) to the digging flux for layer S2.
- 10 The option parameter $SWDigS1 = 1.0$ leads to the allocation of the quality of underlying boundary layer S2 ($f_{r,i,2}$, $f_{s,i,2}$) 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 ($f_{r,i,3}$, $f_{s,i,3}$) to the digging flux for layer S2. Boundary S3 is not simulated but imposed.
- 11 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)

Table 12.5: Definitions of the input parameters in the above equations for S12TRA(i).

Name in formulas	Name in input	Definition	Units
$F_{bur,j}$ $F_{dig,j}$ $F_{res,j}$	$fBur(i)DM3$ $fDig(i)DM3$ $fRes(i)DM3$	burial flux of sediment from layer j digging flux of sediment to layer j resuspension flux of sediment from layer j	$gDM.m^{-2}.d^{-1}$ $gDM.m^{-2}.d^{-1}$ $gDM.m^{-2}.d^{-1}$
$f_{r,i,j}$	$Fr(i)(j)$	fraction of a component in sediment layer j for inorganic sediment components, micro-phytobenthos, detritus components, and AAP	$gX.gDM^{-1}$
$f_{r,i,j}$	$Q(i)DM(j)$	content in sediment layer j for organic micro-pollutants and heavy metals	$mgX.kgDM^{-1}$
$f_{s,i,j}$	N-CDetC(j) P-CDetC(j)	ratio of DetN and DetC in sediment layer j ratio of DetP and DetC in sediment layer j	$gN.gC^{-1}$ $gP.gC^{-1}$

	S-CDetC(j) or N-COOC(j) P-COOC(j) S-COOC(j)	ratio of DetSi and DetC in sediment layer j ratio of OON and OOC in sediment layer j ratio of OOP and OOC in sediment layer j ratio of OOSi and OOC in sediment layer j	$gSi.gC^{-1}$ $gN.gC^{-1}$ $gP.gC^{-1}$ $gSi.gC^{-1}$
$f_{s_{i,j}}$	<i>ScalCar</i>	scaling factor for all other components	-
H	<i>Depth</i>	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) (j) 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 $f_{s_{i,j}}$ (j) also concerns underlying boundary layer S3.
- 3) These fluxes are calculated by processes SUM_SEDIM, RES_DM, BUR_DM and DIG_DM.

Table 12.6: 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	$gDM.m^{-2}.d^{-1}$
A H $Hmin$	Surf Depth MinDepth	surface area of overlying water comp. depth of the overlying water compartment minimal water depth for resusp. and settling	m^2 m m
r	$VResDM$	first-order resuspension rate of sediment	d^{-1}
τ	Tau	shear stress	Pa
τ_{c_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 12.7: Definitions of the input parameters in the above equations for BUR_DM.

Name in formulas	Name in input ¹⁾	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	<i>Surf</i>	surface area of overlying water compartment	m^2
Z_j	<i>ActTh(j)</i>	actual thickness of sediment layer j	m
$Zfix_j$	<i>FixTh(j)</i>	fixed thickness of sediment layer j	m
$Zmax_j$	<i>MaxTh(j)</i>	maximal thickness of sediment layer j	m
rb_j	<i>VBurDM(j)</i>	first-order burial rate of sediment in layer j	d^{-1}
<i>SW Sediment</i>	<i>SW Sediment</i>	option parameter, =0.0 apply fixed layer thickness, =1.0 apply burial kinetics	-
φ_j ρ_j	<i>Por(j)</i> <i>Rho(j)</i>	shear stress critical shear stress for resusp. from sediment layer j	Pa Pa
Δt	<i>Delt</i>	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 12.8: Definitions of the input parameters in the above equations for DIG_DM.

Name in formulas	Name in input ¹⁾	Definition	Units
$Fdig0_j$	<i>ZDigDM(j)</i>	zero-order digging flux of sediment in layer j	$gDM.m^{-2}.d^{-1}$
$Fres_1$	<i>fResS1DM2</i>	resuspension flux of sediment in layer 1	$gDM.m^{-2}.d^{-1}$
A Z_j $Zfix_j$	<i>Surf</i> <i>ActTh(j)</i> <i>FixTh(j)</i>	surface area of overlying water comp. actual thickness of sediment layer j fixed thickness of sediment layer j	m^2 m m
<i>SW Sediment</i>	<i>SW Sediment</i>	option parameter, =0.0 apply fixed layer thickness, =1.0 apply burial kinetics	-
φ_j ρ_j	<i>Por(j)</i> <i>Rho(j)</i>	shear stress critical shear stress for resusp. from sediment layer j	Pa Pa
Δt	<i>Delt</i>	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.

12.5 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 by using Pythagoras.

Formulation

$$\begin{aligned} VelocAvg_1 &= \frac{\frac{Flow_{1,1}}{Area_{1,1}} + \frac{Flow_{1,2}}{Area_{1,2}}}{2} \\ VelocAvg_2 &= \frac{\frac{Flow_{2,1}}{Area_{2,1}} + \frac{Flow_{2,2}}{Area_{2,2}}}{2} \\ Veloc &= \sqrt{VelocAvg_1^2 + VelocAvg_2^2} \end{aligned}$$

where

- $Flow_{1,1}$ horizontal "from"-flow direction 1 [$\text{m}^3 \text{s}^{-1}$]
- $Flow_{1,2}$ horizontal "to"-flow direction 1 [$\text{m}^3 \text{s}^{-1}$]
- $Flow_{2,1}$ horizontal "from"-flow direction 2 [$\text{m}^3 \text{s}^{-1}$]
- $Flow_{2,2}$ horizontal "to"-flow direction 2 [$\text{m}^3 \text{s}^{-1}$]
- $Area_{1,1}$ 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}]

Directives for use

The process VELOC uses flows in the horizontal direction and therefore is only applicable if one or 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.

12.6 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

$$C_{2D} = 18^{10} \log \left(12 \frac{H}{k_s} \right)$$

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 be derived as follows:

Roughness height z_0 of the bed:

$$z_0 = H \cdot e^{-\left(1 + \frac{\kappa \cdot C_{2D}}{\sqrt{g}}\right)} \quad (12.1)$$

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 [$m^{1/2} s^{-1}$]

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 [$\text{m}^{1/2} \text{ s}^{-1}$]
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 [Delft3D-FLOW \(2013\)](#)).

Additional references

[Delft3D-FLOW \(2013\)](#)

12.7 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 $\text{IniDepth} \leq 0$: $\text{IniDepth} = \text{TotalDepth}$

$$F_S = \frac{g \times \text{Fetch}}{v \text{Wind}^2}$$

$$d_S = \frac{g \times \text{IniDepth}}{v \text{Wind}^2}$$

$$H_S = 0.24 \times \tanh(0.71 \times d_S^{0.763}) \times \tanh\left(\frac{0.015 \times F_S^{0.45}}{\tanh(0.71 \times d_S^{0.763})}\right)$$

$$H = \frac{H_S \times \text{Wind}^2}{g}$$

$$T_S = 2\pi \times \tanh(0.855 \times d_S^{0.365}) \tanh\left(\frac{0.0345 \times F_S^{0.37}}{\tanh(0.855 \times d_S^{0.365})}\right)$$

$$T = \frac{T_S \times \text{Wind}}{g}$$

$$L = \frac{g \times T^2}{2 \times \pi} \tanh\left(\frac{2 \times \pi \times \text{IniDepth}}{L_0}\right)$$

F_S standardized fetch [-]

TotalDepth total water depth [m]

IniDepth 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 can be calculated by a one-step iteration:

$$L_0 = \frac{g \times T^2}{2\pi}$$

The wave length L , wave period T and water depth h satisfy the dispersion relation:

$$\omega = \frac{2 \times \pi}{T}$$

$$k = \frac{2 \times \pi}{L}$$

$$\omega^2 = g \times k \times \tanh(k \times \text{TotalDepth})$$

ω	radial frequency (1/s)
k	wave number (1/m)

Directives for use

- ◊ By default the depth at the origin of the wave (IniDepth) equals the actual depth (TotalDepth), because the default value for IniDepth is -1 . IniDepth 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.

12.8 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

For $WinDir_{i-1} < WindDir \leq WinDir_i$

$$\begin{aligned} Fetch &= WFetch_i \\ InitDepth &= WDepth_i \end{aligned}$$

with: $WinDir_0 = 0^\circ$

$WindDir$ 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 eighth 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*.

12.9 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:

$$\tau_{wind} = \frac{1}{4} \times \rho_l \times Fw \times U_{bg,max}^2$$

$$U_{bg,max} = \frac{\pi \times H}{T \times \sinh\left(\frac{2 \times \pi \times TotalDepth}{L}\right)}$$

$$\omega = \frac{2 \times \pi}{T}$$

$$A_g = \frac{U_{bg,max}}{\omega}$$

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 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](#)):

$$H = \min(0.55 \times TotalDepth, H)$$

The wave friction factor f_w can be calculated according to [Tamminga \(1987\)](#); [Swart \(1974\)](#) or [Soulsby \(1997\)](#).

SWTau = 1 (Tammainga, 1987):

$$f_w = 0.16 \sqrt{\frac{Rough}{U_{bg} \times T/2\pi}}$$

SWTau = 2 (Swart, 1974):

$$r = \frac{H}{2 \times Rough \times \sinh(\frac{2\pi \times TotalDepth}{L})}$$

if $r > \pi/2$ then

$$f_w = 0.00251 \exp(5.213r^{-0.19})$$

else

$$f_w = 0.32$$

SWTau = 3 (Soulsby, 1997):

$$r = \frac{H}{2 \times Rough \times \sinh(\frac{2\pi \times TotalDepth}{L})}$$

$$f_w = 0.237r^{-0.52}$$

<i>SWTau</i>	switch to calculate the wave fraction factor [-]
<i>SWTauVeloc</i>	switch to calculate the bottom shear stress due to flow from the flow velocity or rely on <i>TauFlow</i> instead [-]
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]
τ_{ship}	part of bottom shear stress defined by you, e.g. to describe the effect of ships [Pa]
<i>Veloc</i>	flow velocity [$m s^{-1}$]
$U_{bg,max}$	amplitude of the wave orbital velocity [$m s^{-1}$]
<i>Rough</i>	Nikuradse bottom roughness length scale [m]
<i>g</i>	acceleration of gravity [$m s^{-2}$]
ρ_l	density of water [$kg m^{-3}$]
<i>H</i>	wave height [m]
<i>T</i>	wave period [s]
<i>L</i>	wave length [m]
<i>Fw</i>	wave (friction) factor [-]
<i>TauFlow</i>	bottom shear stress due to flow (used only if <i>SWTauVeloc</i> 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.)

12.10 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:

$$D_H = a \times V^b \times H^c + D_{H,background}$$

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:

$$\text{velocity} = \begin{cases} \text{abs}(flow/area), & \text{if } area > 10^{-10} \\ 0 & \text{otherwise} \end{cases}$$

$$\text{horzdisp} = \begin{cases} Dfact_a \times \text{velocity}^{Dfact_b} \times \text{TotalDepth}^{Dfact_c} + D_{back} \\ \max(\min(\text{horzdisp}, D_{max}), D_{min}) \end{cases}$$

<i>flow</i>	Flow rate at exchange (automatically available) [m^3/s]
<i>area</i>	Area at exchange (automatically available) [m^2]
<i>velocity</i>	Computed flow velocity at exchange [m/s]
<i>horzdisp</i>	Computed horizontal dispersion coefficient at exchange [m^2/s]
<i>Dfact_a</i>	Factor a in dispersion calculation [-]
<i>Dfact_b</i>	Factor b in dispersion calculation [-]
<i>Dfact_c</i>	Factor c in dispersion calculation [-]
<i>D_{back}</i>	Background dispersion coefficient [m^2/s]
<i>D_{min}</i>	Minimum dispersion coefficient to be used [m^2/s]
<i>D_{max}</i>	Maximum dispersion coefficient to be used [m^2/s]
<i>TotalDepth</i>	Mean total depth at the segments on either side of the exchange [m]

12.11 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:

$$D_H = DispConst \times \frac{Velocity \times Width^2 \times Chezy}{TotalDepth \times \sqrt{g}}$$

<i>Velocity</i>	mean of the specified flow velocity at the <i>segments</i> on both sides of the exchange [m/s]
<i>Width</i>	mean of the specified width at the <i>segments</i> on both sides of the exchange [m]
<i>TotalDepth</i>	mean of the total depth at the <i>segments</i> on both sides of the exchange [m]
<i>Chezy</i>	mean of the Chézy coefficients <i>segments</i> on both sides of the exchange [$m^{1/2}/s$]
<i>DispConst</i>	horizontal dispersion coefficient (again specified at the segments and averaged) [-]
<i>g</i>	gravitational acceleration (fixed at 9.81) [m/s ²]

12.12 Computation of vertical dispersion

PROCESS: VERTDISP

The vertical dispersion coefficient in a well-mixed water body may be approximated by [Fisher et al. \(1979\)](#):

$$D_0 = \frac{\kappa u_* H}{6} \quad (12.2)$$

D_0 dispersion coefficient in a well-mixed water body [$\text{m}^2 \text{ s}^{-1}$]

κ constant of Von Kármán, 0.4 [-]

u_* shear stress velocity [m s^{-1}]

H thickness of the water layer [m]

For the wind induced mixing phenomenon this formula holds only if the boundary layer is fully developed over the thickness of the water layer H . Based on data from [Wu \(1982\)](#), the following relation between the shear stress velocity and the wind velocity can be derived.

$$u_* = 7 \times 10^{-4} W_{10}^{1.25} \quad (12.3)$$

W_{10} wind velocity at 10 meters above the water surface [m s^{-1}]

The effect of vertical density gradients on the dispersive transport is commonly expressed by a relation of the Munck-Andersen type

$$D = \frac{c D_0}{(1 + a Ri)^b} \quad (12.4)$$

a model constant [-]

b model constant [-]

c linear model constant [-]

D vertical dispersion coefficient in a stratified water body [$\text{m}^2 \text{ s}^{-1}$]

Ri local Richardson number [-]

The local Richardson number is defined as:

$$Ri = \frac{-g \frac{\partial \rho}{\partial z}}{\rho \left(\frac{\partial u}{\partial z} \right)^2} \quad (12.5)$$

g acceleration due to gravity [m s^{-2}]

ρ density [kg m^{-3}]

z vertical co-ordinate [m]

u velocity [m s^{-1}]

Implementation

This process is implemented for all active substances. Inactive substances are part of the sediment and obviously are not subject to vertical dispersion in the water column.

Formulation

$$VertDisp0 = \frac{0.4 (7 \times 10^{-4} V_{wind})^{1.25} TotalDepth}{6} \quad (12.6)$$

$VertDisp0$ dispersion coefficient in a well-mixed water body [$\text{m}^2 \text{ s}^{-1}$]

$TotalDepth$ thickness of the water layer [m]

V_{wind} wind velocity at 10 meter above the water surface [m s^{-1}]

$$localRi = \frac{-9.81 \times RhoGrad}{RhoExc \times VelocGrad^2} \quad (12.7)$$

$RhoExc$ density at an exchange area [kg m^{-3}]

$VelocGrad$ gradient in flow velocity at an exchange area [m s^{-2}]

$RhoGrad$ gradient in density at an exchange area [kg m^{-4}]

$$VertDisp = \frac{c VertDisp0}{(1 + a LocalRi)^b} \quad (12.8)$$

$VertDisp$ vertical dispersion coefficient in a stratified water body [$\text{m}^2 \text{ s}^{-1}$]

$VertDisp0$ vertical dispersion coefficient in a non stratified water body [$\text{m}^2 \text{ s}^{-1}$]

$LocalRi$ local Richardson number [-]

a model constant [-]

b model constant [-]

c linear model constant [-]

Directives for use

This process can only be active if the third direction is defined: only if layers in the vertical are used (1DV, 2DV or 3D schematisations).

12.13 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.

12.14 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.

12.15 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.

13 Temperature

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13.1 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 \(1976\)](#)

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 [$^{\circ}\text{C}$]
$SwitchTemp$	switch modelled temperature is absolute (0) or surplus (1) [-]
$SurTemp$	surplus temperature [$^{\circ}\text{C}$]
T	ambient water temperature [$^{\circ}\text{C}$]
$NatTemp$	ambient natural background water temperature [$^{\circ}\text{C}$]
$Depth$	depth of a DELWAQ segment [m]
V_{wind}	wind velocity [m s^{-1}]
C_p	specific heat of water [$\text{J kg}^{-1} ^{\circ}\text{C}^{-1}$]
$RcHeat$	rate constant for surplus temperature exchange [d^{-1}]
$FactRcHeat$	factor on rate constant for surplus temperature exchange [-]
ρ_w	density of water at ambient water temperature [kg m^{-3}]
$ZHeatExch$	zeroth order temperature exchange flux [$^{\circ}\text{C d}^{-1}$]
$dModTemp$	temperature exchange flux [$^{\circ}\text{C d}^{-1}$]

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.

13.2 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 simplifications 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 13.1](#) 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 *SWelevation* 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:

$$\begin{aligned} Tts &= Ta + \DeltaTrad - \DeltaTev & (13.1) \\ \DeltaTrad &= \Delta t \times RTrad + \DeltaTrad_0 \quad \text{and} \quad \DeltaTrad = \DeltaTreq \\ RTrad &= RTrmax \times \frac{I}{Imax} \\ \DeltaTreq &= \DeltaTrmax \times \frac{I}{Imax} \\ T &= Tts \end{aligned}$$

with:

I	solar radiation intensity [W m^{-2}]
$Imax$	maximal solar radiation intensity [W m^{-2}]
T	temperature [$^{\circ}\text{C}$]
Ta	air temperature [$^{\circ}\text{C}$]
Tts	top sediment temperature in run-dry segments [$^{\circ}\text{C}$]
$RTrad$	rate of temperature increase due to solar radiation [$^{\circ}\text{C d}^{-1}$]
$RTrmax$	maximal rate of temperature increase due to solar radiation [$^{\circ}\text{C d}^{-1}$]
Δt	timestep [d]
ΔTev	temperature decrease due to evaporation [$^{\circ}\text{C}$]
\DeltaTrad	temperature increase due to solar radiation [$^{\circ}\text{C}$]
\DeltaTrad_0	temperature increase due to solar radiation in the previous timestep [$^{\circ}\text{C}$]
\DeltaTreq	equilibrium temperature increase due to solar radiation [$^{\circ}\text{C}$]
\DeltaTrmax	maximal temperature increase due to solar radiation [$^{\circ}\text{C}$]

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. \(2000\)](#)

Table 13.1: Definitions of the parameters in the above equations for TEMPERATUR.

Name in formulas	Name in input/output	Definition	Units
Hst	$ThSedDT$	thickness top sed. layer subjected to temp. change	m
I I_{max}	$DayRadSurf$ $RadMax$	solar radiation intensity maximal solar radiation intensity	W m^{-2} W m^{-2}
$RTrmax$	$RTradMax$	maximal rate of temp. increase due to solar rad.	$^{\circ}\text{C d}^{-1}$
$SWemersion$	$SWemersion$	switch that determines emersion or submersion	-
$SWTempDF$	$SWTempDF$	switch that (de)activates modification of temperature (default 0 = inactive; 1 = active)	-
T Ta Tst	$Temp$ $NatTemp$ $ModTemp$	actual temperature air temperature top sediment temperature	$^{\circ}\text{C}$ $^{\circ}\text{C}$ $^{\circ}\text{C}$
Δt ΔTev	$Delt$ $DelTev$	timestep temperature decrease due to evaporation	d $^{\circ}\text{C}$
$\Delta Trmax$	$DelRadMax$	maximal temperature increase due to solar radiation	$^{\circ}\text{C}$

14 Various auxiliary processes

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14.1 Computation of aggregate substances

PROCESS: COMPOS

The simulated substances for detrital organic matter and algae biomass do not provide all essential information to interpret 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 stoichiometric ratios of nitrogen, phosphorus, sulphur and silicon in the individual detritus fractions for this purpose.

Process COMPOS also delivers the total particulate matter, carbon, nitrogen, phosphorus, silicon and sulphur 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 (b) or to water (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 14.1 provides the definitions of the output parameters as related to the formulations.

Formulation

The individual stoichiometric nutrient ratios follow from:

$$\begin{aligned} an_i &= \frac{Coc_i}{Con_i} \\ ap_i &= \frac{Coc_i}{Cop_i} \\ as_i &= \frac{Coc_i}{Cos_i} \end{aligned}$$

where:

an	stoichiometric ratio of carbon and nitrogen in organic matter [gC gN ⁻¹]
ap	stoichiometric ratio of carbon and phosphorus in organic matter [gC gP ⁻¹]
as	stoichiometric ratio of carbon and sulphur in organic matter [gC gS ⁻¹]
Coc	concentration of detritus carbon [gC m ⁻³] b

<i>Con</i>	concentration of detritus nitrogen [gN m^{-3}]
<i>Cop</i>	concentration of detritus phosphorus [gP m^{-3}]
<i>Cos</i>	concentration of detritus sulphur [gS m^{-3}]
<i>i</i>	index for the particulate detritus fraction [-]

The total particulate detritus pools follow from:

$$\begin{aligned} C_{poc} &= \sum_{i=1}^4 C_{oc_i} \\ C_{pon} &= \sum_{i=1}^4 C_{on_i} \\ C_{pop} &= \sum_{i=1}^4 C_{op_i} \\ C_{pos} &= \sum_{i=1}^4 C_{os_i} \\ C_{pom} &= \sum_{i=1}^4 (fdm_i \times C_{oc_i}) \end{aligned}$$

where:

<i>Cpoc</i>	concentration of total particulate detritus carbon [gC m^{-3}]
<i>Cpon</i>	concentration of total particulate detritus nitrogen [gN m^{-3}]
<i>Cpop</i>	concentration of total particulate detritus phosphorus [gP m^{-3}]
<i>Cpos</i>	concentration of total particulate detritus sulphur [gS m^{-3}]
<i>Cpom</i>	concentration of total particulate detritus dry matter [gC m^{-3}]
<i>fdm</i>	dry matter conversion factor [gDM gC^{-1}]
<i>i</i>	index for the particulate detritus fraction [-]

The concentration of total inorganic sediment follows from:

$$C_{tim} = \sum_{j=1}^3 (fidm_j \times C_{im_j})$$

where:

<i>Cim</i>	concentration of inorganic sediment fraction [gDM m^{-3}]
<i>Ctim</i>	concentration of total inorganic dry matter [gDM m^{-3}]
<i>fidm</i>	dry matter ratio of inorganic sediment fraction [gDM gDM^{-1}]
<i>j</i>	index for the inorganic sediment fraction [-]

The other "total" concentrations arise from summing the various simulated substances as follows:

$$\begin{aligned} POC &= C_{poc} + Phyt \\ TOC &= POC + DOC \end{aligned}$$

$$PON = Cpon + AlgN$$

$$TON = PON + DON$$

$$KjelN = TON + NH4$$

$$DIN = NH4 + NO3$$

$$TOTN = TON + DIN$$

$$POP = Cpop + AlgP$$

$$TOP = POP + DOP$$

$$PIP = AAP + VIVP + APATP$$

$$TOTP = TOP + PO4 + PIP$$

$$POS = Cpos + AlgS$$

$$TOS = POS + DOS$$

$$TOTS = TOS + SO4 + SUD + SUP$$

$$TOTSi = AlgSi + Opal + Si$$

$$TPMnoa = Ctim + Cpom$$

$$TPM = SS = TPMnoa + AlgDM$$

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).
- ◊ Sulphur 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.

Table 14.1: 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}
asi	$C - S(i)$	stoch. ratio of carbon and sulphur in detritus fraction i	gC gS^{-1}
TOC	TOC	concentration total organic carbon	$\text{gC m}^{-3}\ell$
POC	POC	conc. total part. organic carbon	$\text{gC m}^{-3}\ell$
POM	POM	conc. total part. dry matter	$\text{gDM m}^{-3}\ell$
$Cpoc$	$POCnoa$	conc. total total part. org. carbon without algae	$\text{gC m}^{-3}\ell$
$Cpom$	$POMnoa$	conc. total part. dry matter without algae	$\text{gDM m}^{-3}\ell$
$TOTN$	$TOTN$	concentration total nitrogen	$\text{gN m}^{-3}\ell$
TON	TON	conc. total organic nitrogen	$\text{gN m}^{-3}\ell$
PON	PON	conc. total part. organic nitrogen	$\text{gN m}^{-3}\ell$
$Cpon$	$PONnoa$	conc. total part. org. nitrogen without algae	$\text{gN m}^{-3}\ell$
DIN	DIN	conc. total diss. inorganic nitrogen	$\text{gN m}^{-3}\ell$
$KjelN$	$KjelN$	conc. total Kjeldahl nitrogen	$\text{gN m}^{-3}\ell$
$TOTP$	$TOTP$	concentration total phosphorus	$\text{gP m}^{-3}\ell$
TOP	TOP	conc. total organic phosphorus	$\text{gP m}^{-3}\ell$
POP	POP	conc. total part. org. phosphorus	$\text{gP m}^{-3}\ell$
$Cpop$	$POPnoa$	conc. total part. org. phosphorus without algae	$\text{gP m}^{-3}\ell$
PIP	PIP	conc. total part. inorg. phosphorus	$\text{gP m}^{-3}\ell$
$TOTS$	$TOTS$	conc. total sulphur	$\text{gS m}^{-3}\ell$
TOS	TOS	conc. total organic sulphur	$\text{gS m}^{-3}\ell$
POS	POS	conc. total part. organic sulphur	$\text{gS m}^{-3}\ell$
$Cpos$	$POSnoa$	conc. total part. org. sulphur without algae	$\text{gS m}^{-3}\ell$
$TOTSi$	$TOTSi$	concentration total silicon	$\text{gSi m}^{-3}\ell$
TMP	SS	conc. total (susp.) sediment (solids)	$\text{gDM m}^{-3}\ell$
$Ctim$	TIM	conc. total inorganic sediment	$\text{gDM m}^{-3}\ell$
TMP	TMP	conc. total part. matter with algae	$\text{gDM m}^{-3}\ell$
$TM\!Pnoa$	$TM\!Pnoa$	conc. total part. matter without algae	$\text{gDM m}^{-3}\ell$

14.2 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 components 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 phytoplankton 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 14.2 and 14.3 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:

$$Mdm_k = \sum_{l=1}^n (fdm_{i,k} \times Mx_{i,k})$$

$$frx_{i,k} = \frac{Mx_{i,k}}{Mdm_k}$$

$$frpha_k = \frac{Mphak}{Mdm_k}$$

where:

Mdm	total amount of dry matter in a layer [gDM]
$Mphak$	amount of adsorbed phosphate 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]

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 stoichiometric 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	stoichiometric ratio of carbon over nitrogen in detritus fraction k [gC gN ⁻¹]
ap	stoichiometric ratio of carbon over phosphorus in detritus fraction k [gC gP ⁻¹]
asi	stoichiometric 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:

$$Mimt_k = \sum_{j=1}^3 (Mim_{j,k})$$

$$Moct_k = \sum_{i=1}^2 (Moc_{i,k})$$

$$Malgt_k = \sum_{l=1}^n (Malgt_{l,k})$$

$$Mpom_k = \sum_{l=1}^n (fdm_l \times Malgt_l) + \sum_{i=1}^2 (fdm_i \times Moc_{i,k})$$

where:

fdm	dry matter conversion factor [gDM gC ⁻¹]
$Malgt$	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 [-]

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 [$\text{gDM m}^{-3}\text{DM}$]
ρdm	density of sediment dry matter [$\text{gDM m}^{-3}\text{DM}$]
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.

Table 14.2: 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
$fdm_{j,k}$ or $fdm_{i,k}$ $fdm_{l,k}$	$DMCFIM1$ $DMCFIM2$ $DMCFIM3$ $DMCFDetCS$ $DMCFOOCS$ $DMCFDiatS$	dry matter conv. factor sed. inorg. matter fraction 1 dry matter conv. factor sed. inorg. matter fraction 2 dry matter conv. factor sed. inorg. matter fraction 3 dry matter conv. factor detr. fraction 1 dry matter conv. factor detr. fraction 2 dry matter conv. factor algae species 1	gDM gDM^{-1} gDM gDM^{-1} gDM gDM^{-1} gDM gC^{-1} gDM gC^{-1} gDM gC^{-1}
$Malg_{l,k}$	$DiatS(k)$	amount of biomass of algae species 1	gC
$Mim_{j,k}$	$IM1S(k)$ $IM2S(k)$ $IM3S(k)$	amount of sed. inorg. matter fraction 1 amount of sed. inorg. matter fraction 2 amount of sed. inorg. matter fraction 3	gDW gDW gDW
$Moc_{i,k}$ $Mon_{i,k}$ $Mop_{i,k}$ $Mosi_{i,k}$	$DetCS(k)$ $OOCs(k)$ $DetNS(k)$ $OONS(k)$ $DetPS(k)$ $OOPS(k)$ $DetSiS1(k)$ $OOSiS1(k)$	amount of detr. C in part. fraction 1 amount of detr. C in part. fraction 2 amount of detr. N in part. fraction 1 amount of detr. N in part. fraction 2 amount of detr. P in part. fraction 1 amount of detr. P in part. fraction 2 amount of detr. Si in part. fraction 1 amount of detr. Si in part. fraction 2	gC gC gN gN gP gP gSi gSi
$Mpha$	$AAPS(k)$	amount of adsorbed phosphate	gP
ϕ	$PORS(k)$	sediment porosity	-
ρ_i	$RHOIM1$ $RHOIM2$ $RHOIM3$ $RHODetC$ $RHOOC$ $RHODiat$	density of sed. inorg. matter fr. 1 density of sed. inorg. matter fr. 2 density of sed. inorg. matter fr. 3 density of detritus fraction 1 density of detritus fraction 2 density of biomass of algae species 1	gDM m^{-3} gDM m^{-3} gDM m^{-3} gDM m^{-3} gDM m^{-3} gDM m^{-3}

¹(k) is sediment layer 1 or 2.

Table 14.3: Definitions of the output parameters in the above equations for S1_COMP and S2_COMP .

Name in formulas	Name in output	Definition	Units
$an_{i,k}^1$ or $ap_{i,k}$	C $-NDetCS(k)$ $C - NOOC(k)$ C $-PDetCS(k)$ $C - POOCS(k)$ $C - SDetCS(k)$ $C - SOOCS(k)$	stoch. ratio C over N in detr. fraction 1 stoch. ratio C over N in detr. fraction 2 stoch. ratio C over P in detr. fraction 1 stoch. ratio C over P in detr. fraction 2 stoch. ratio C over Si in detr. fraction 1 stoch. ratio C over Si in detr. fraction 2	$gC\ gN^{-1}$ $gC\ gN^{-1}$ $gC\ gP^{-1}$ $gC\ gP^{-1}$ $gC\ gSi^{-1}$ $gC\ gSi^{-1}$
$Calgl_k$	$DiatS(k)M2$	surface conc. of algae species 1	$gC\ m^{-2}$
$Cim_{j,k}$	$IM1S(k)M2$ $IM2S(k)M2$ $IM3S(k)M2$	surf. conc. of sed. inorg. matter fr. 1 surf. conc. of sed. inorg. matter fr. 2 surf. conc. of sed. inorg. matter fr. 3	$gDW\ m^{-2}$ $gDW\ m^{-2}$ $gDW\ m^{-2}$
$Coc_{i,k}$ or $Con_{i,k}$ or $Cop_{i,k}$ or $Cosi_{i,k}$	$DetCS(k)M2$ $OOCS(k)M2$ $DetNS(k)M2$ $OONS(k)M2$ $DetPS(k)M2$ $OOPS(k)M2$ $DetSiS1(k)M2$ $OOSiS1(k)M2$	surf. conc. of detr. C in part. fr. 1 surf. conc. of detr. C in part. fr. 2 surf. conc. of detr. N in part. fr. 1 surf. conc. of detr. N in part. fr. 1 surf. conc. of detr. P in part. fr. 1 surf. conc. of detr. P in part. fr. 1 surf. conc. of detr. Si in part. fr. 1 surf. conc. of detr. Si in part. fr. 1	$gC\ m^{-2}$ $gC\ m^{-2}$ $gN\ m^{-2}$ $gN\ m^{-2}$ $gP\ m^{-2}$ $gP\ m^{-2}$ $gSi\ m^{-2}$ $gSi\ m^{-2}$
Cxi_k	$AAPS(k)M2$	surface conc. of adsorbed phosphate	$gP\ m^{-2}$
Zk	$ActThS(k)$	thikness of sediment layer	m
$frx_{i,k}$	$FrIM1S(k)$ $FrIM2S(k)$ $FrIM3S(k)$ $FrDetCS(k)$ $FrOOCS(k)$ $FrCFDiatS(k)$	fraction inorg. matter 1 in sediment fraction inorg. matter 2 in sediment fraction inorg. matter 3 in sediment fraction detritus 1 in sediment fraction detritus 2 in sediment fraction algae species 1 in sediment	$gDM\ gDM^{-1}$ $gDM\ gDM^{-1}$ $gDM\ gDM^{-1}$ $gC\ gDM^{-1}$ $gC\ gDM^{-1}$ $gC\ gDM^{-1}$
Mdm_k $Mimt_k$ $Moct_k$ $Malgt_k$ $Mpom_k$	$DMS(k)$ $TIMS(k)$ $POCS(k)$ $PHYTS(k)$ $POMS(k)$	total amount of dry matter total amount of sed. inorganic matter total amount of part. organic carbon total amount of algae biomass total amount of organic matter	gDM gDM gC gC gDM
pdm_k	$RHOS(k)$	density of sediment dry matter	$gDM\ m^{-3}$

¹(k) is sediment layer 1 or 2.

14.3 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:

$$dDfWast_i = \frac{fDfWast_i}{depth} \quad (14.1)$$

Atmospheric deposition:

$$dAtmDep_i = \frac{fAtmDep_i}{depth} \quad (14.2)$$

$dDfWast_i$ 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.

14.4 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

$$\begin{aligned} Depth &= \frac{Volume}{Surf} \\ TotalDepth &= \sum_{i=1}^n Depth_i \\ LocalDepth_m &= \sum_{j=1}^m Depth_j \end{aligned}$$

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]

Directives for use

- ◊ Either $Depth$ or $Surf$ must be supplied by you (or a water quantity model)!

14.5 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

<i>Depth</i>	depth of a DELWAQ segment [m]
<i>Volume</i>	volume of a DELWAQ segment [m^3]
<i>Surf</i>	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)!

14.6 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 [$\text{m s}^{-1} \text{ m}^{-1}$]
	(b) RhoGrd gradient in density of water [$\text{kg m}^{-3} \text{ m}^{-1}$]
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.

14.7 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 [$\text{m}^3 \text{ s}^{-1}$] — as derived from SOBEK, Delft3D or another hydrodynamic model. *Dispersion* is not taken into account.

Formulation

$$\text{ResTim} = \frac{\text{Volume}}{\sum_{\text{exchanges}} |\text{Flow}| / 2} \quad (14.3)$$

where

<i>ResTim</i>	residence time [s]
<i>Volume</i>	DELWAQ water volume of a segment [m^3]
<i>Flow</i>	DELWAQ water flow over an exchange [$\text{m}^3 \text{ s}^{-1}$]

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’.

14.8 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

$$\begin{aligned} ageTr_i &= \frac{\ln\left(\frac{dTr_i}{cTr_i}\right)}{RcDecTr_i} \\ dDecTr_i &= RcDecTr_i \times dTr_i \end{aligned}$$

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 [$\text{g m}^{-3} \text{ d}^{-1}$]

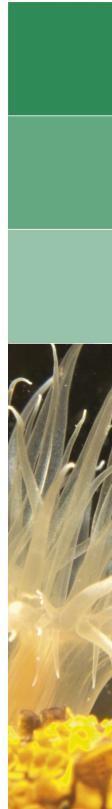
Directives for use

- ◊ 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.

15 Deprecated processes descriptions

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15.1 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, re-suspension 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 Van der 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 [$\text{gO}_2 \text{ m}^{-3}$]. 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 stoichiometric 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.

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 15.1](#) 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}]
kpg^{10}	potential gross primary production rate at 10 °C [d^{-1}]

k_{tp}	temperature coefficient for primary production [-]
R_{gp}	gross primary production rate [$\text{gC m}^{-3} \text{ d}^{-1}$]
T	water temperature [$^{\circ}\text{C}$]
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:

$$f_{nut_i} = f_{am_i} + (1 - f_{am_i}) \times f_{ni_i}$$

$$f_{am_i} = \frac{Cam \times Cph \times Csi}{(Ks_{am_i} \times Cph \times Csi + Cam \times Ks_{ph_i} \times Csi + Cam \times Cph \times Ks_{si_i} + Cam \times Cph \times Csi)}$$

$$f_{ni_i} = \frac{Cni \times Cph \times Csi}{(Ks_{ni_i} \times Cph \times Csi + Cni \times Ks_{ph_i} \times Csi + Cni \times Cph \times Ks_{si_i} + Cni \times Cph \times Csi)}$$

with:

f_{am}	ammonium specific nutrient limitation factor [-]
f_{ni}	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}]
Ks_{am}	half saturation constant for ammonium [gN m^{-3}]
Ks_{ni}	half saturation constant for nitrate [gN m^{-3}]
Ks_{ph}	half saturation constant for phosphate [gP m^{-3}]
Ks_{si}	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 \(1988\)](#):

$$f_{lt_i} = \frac{\left(\sum_{k=1}^n \sum_{j=1}^m (R_{rgp_{i,j,k}} \times \Delta z \times \Delta t) \right)}{(86400 \times H)}$$

$$R_{rgp_{i,j,k}} = \frac{Ir_{i,j,k} \times (c_i + 2)}{(Ir_{i,j,k}^2 + c_i \times Ir_{i,j,k} + 1)}$$

$$Ir_{i,j,k} = \frac{I_{j,k}}{Io_i}$$

$$c_i = \frac{Io_i}{(kgp_i/d_i)} - 2$$

$$Io_i = Io_i^{10} \times ktpg_i^{(T-10)}$$

$$I_{j,k} = Itop_k \times e^{(-et \times z_j)}$$

with:

c	shape coefficient of the production factor [-]
d	initial slope of the light-production curve [$\text{gC d}^{-1} \cdot \text{W m}^{-2}$] $^{-1}$]
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}]
$ktpg$	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:

$$Rrsp_i = krsp_i \times Calgi + frsp_i \times Rgp_i$$

$$krsp_i = krsp_i^{10} \times ktrsp_i^{(T-10)}$$

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 [$\text{gC m}^{-3} \text{ d}^{-1}$]

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:

f_{exc}	fraction of gross production excreted at the absence of nutrient limitation [-]
R_{exc}	excretion rate [$\text{gC m}^{-3} \text{d}^{-1}$]

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:

$$Rmrt_i = kmrt_i \times Calg_i$$

$$kmrt_i = kmrt_i^{10} \times ktmrt_i^{(T-10)}$$

$$kmrt_i^{10} = \frac{m1_i - m2_i}{1 + e^{(b1_i \times (Ccl - b2_i))}} + m2_i \quad \text{for fresh water algae, } MND(i)Type = 2.0$$

$$kmrt_i^{10} = \frac{m2_i - m1_i}{1 + e^{(b1_i \times (Ccl - b2_i))}} + m1_i \quad \text{for marine algae, } MND(i)Type = 1.0$$

with:

$b1$	coefficient 1 of salinity stress function [$\text{g}^{-1} \text{m}^3$]
$b2$	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 [$\text{gC m}^{-3} \text{d}^{-1}$]

$m1$ 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 15.1. 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:

$$Rprd_{ox,i} = (Rgp_i - Rrsp_i) \times aox_i$$

$$Rcns_{am,i} = (Rgp_i - Rrsp_i) \times an_i \times fam_i / fnut_i$$

$$Rcns_{ni,i} = (Rgp_i - Rrsp_i) \times an_i \times (1 - fam_i / fnut_i)$$

$$Rcns_{ph,i} = (Rgp_i - Rrsp_i) \times aph_i$$

$$Rcns_{si,i} = (Rgp_i - Rrsp_i) \times asi_i$$

$$Rprd_{oc,i} = (Rmrt_i + Rexc_i)$$

$$Rprd_{on,i} = (Rmrt_i + Rexc_i) \times an_i$$

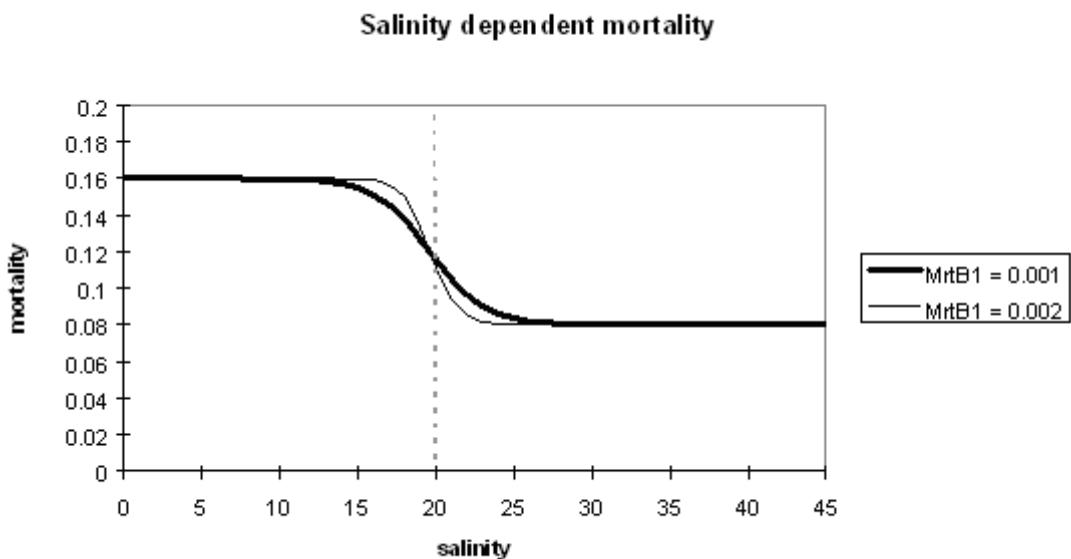


Figure 15.1: Example of the salinity dependent mortality function. $m1 = 0.08 \text{ d}^{-1}$; $m2 = 0.16 \text{ d}^{-1}$; $b2 = 11000$ (equivalent with 20 ppt salinity) [gCl m^{-3}]; $b1 = 0.001$ and $0.002 \text{ m}^3 \cdot \text{gCl}^{-1}$.

$$Rprd_{op,i} = (Rmrt_i + Rexci) \times aph_i$$

$$Rprd_{osi,i} = (Rmrt_i + Rexci) \times asi_i$$

with:

an	stoichiometric constant for nitrogen over carbon in algae biomass [gN.gC^{-1}]
aph	stoichiometric constant for phosphorus over carbon in algae biomass [gP.gC^{-1}]
aox	stoichiometric constant for oxygen over carbon in algae biomass [$\text{gO}_2\text{.gC}^{-1}$]
asi	stoichiometric constant for silicon over carbon in algae biomass [gSi.gC^{-1}]
$Rcns_{am}$	net consumption rate for ammonium [$\text{gN m}^{-3} \text{ d}^{-1}$]
$Rcns_{ni}$	net consumption rate for nitrate [$\text{gN m}^{-3} \text{ d}^{-1}$]
$Rcns_{ph}$	net consumption rate for phosphate [$\text{gP m}^{-3} \text{ d}^{-1}$]
$Rcns_{si}$	net consumption rate for silicate [$\text{gSi m}^{-3} \text{ d}^{-1}$]
$Rprd_{ox}$	net production rate for dissolved oxygen [$\text{gO}_2 \text{ m}^{-3} \text{ d}^{-1}$]
$Rprd_{oc}$	net production rate for detritus organic carbon [$\text{gC m}^{-3} \text{ d}^{-1}$]
$Rprd_{on}$	net production rate for detritus organic nitrogen [$\text{gN m}^{-3} \text{ d}^{-1}$]
$Rprd_{op}$	net production rate for detritus organic phosphorus [$\text{gP m}^{-3} \text{ d}^{-1}$]
$Rprd_{osi}$	net production rate for opal silicate [$\text{gSi m}^{-3} \text{ d}^{-1}$]

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]
$achf_{min}$	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 (1997c)

Table 15.1: 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	$gP\ m^{-3}$
Csi	Si	dissolved inorganic silicate concentration	$gSi\ m^{-3}$
$Calg1$	$MND1Diat-m$	biomass concentration of marine diatoms	$gC\ m^{-3}$

continued on next page

¹(i) indicates species groups 1-4.

²This parameter is only used for initialisation during the first timestep.

³This parameter is calculated by processes ExtPhGVL and Extinc_VL.

⁴This parameter is not part of the input.

Table 15.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
$Calg_2$	$MND2Flag-m$	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)	-
$achf_i$	$MND(i)AChl^2$	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	$\text{gO}_2.\text{gC}^{-1}$
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	$\text{g}^{-1} \text{m}^3$
$b2_i$	$MND(i)b2$	group specific coefficient 2 of salinity stress function	g m^{-3}
d_i	$MND(i)schl$	group spec initial slope of the light-production curve	$\text{gC m}^{-2})^{-1} \cdot (\text{W m}^{-1})$
et	$ExtVL^3$	total extinction coefficient of visible light	
gi	$MND(i)b$	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}

continued on next page

¹(i) indicates species groups 1-4.²This parameter is only used for initialisation during the first timestep.³This parameter is calculated by processes ExtPhGVL and Extinc_VL.⁴This parameter is not part of the input.

Table 15.1 – continued from previous page

Name in formulas	Name in input	Definition	Units
f_{exc_i}	$MND(i)b_{ex}$	group spec. frac. gross prod. excrat abs. of nutr. lim.	-
$frsp_i$	$MND(i)r_p r$	group specific fraction of gross production respired	-
H	$Depth$	depth of a water compartment or water layer	m
Io_i I_{top}	$MND(i)I_{opt}$ Rad	group specific optimal light intensity light intensity at top of layer or compartment	W m^{-2} 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.	-
$kmrt_{s,i}$	$MND(i)MorS_{\text{ed}}$	group spec. mortality process rate in sediment	d^{-1}
T	$Temp$	water temperature	°C
- Δt	$ITIME$ IDT	time time interval, that is the DELWAQ timestep	s s
m	Nr_dz	number of depth intervals in a water comp. or layer	-

¹(i) indicates species groups 1-4.²This parameter is only used for initialisation during the first timestep.³This parameter is calculated by processes ExtPhGVL and Extinc_VL.⁴This parameter is not part of the input.

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