The Coupled Cycles of Carbon, Oxygen, Nitrogen and Sulfur in Marine Sediments

Exercises Accompanying the Course Reaction Transport Modelling in the Hydrosphere

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Introduction

After mineral and organic matter particles are deposited from the water column onto the sediment surface, they undergo a series of physical and chemical transformations resulting from the water-mineral interactions, microbial activity and compaction. The process that encompasses these transformations is called *diagenesis*.

In this exercise, you will implement a model of early diagenesis in marine sediments. The model will be simplified in the sense that it will only consider a *subset* of possible diagenetic transformations including aerobic mineralisation, nitrification, denitrification, sulphate reduction, sulphide oxidation, and methanogenesis. The model will also include the effects of transport (deposition, molecular diffusion, and bioturbation) and sediment compaction (decrease in porosity with sediment depth). However, for the sake of simplicity, the model will ignore many important processes, such as dissolution and precipitation of minerals, the cycling of manganese, iron, or phosphorus, etc.

The overall objective of this exercise is to demonstrate how to *approach* modelling of coupled biogeochemical cycles of C, O, N, and S in marine sediments, and to illustrate the so-called *biogeochemical cascade*, a concept where the organic matter mineralisation pathway switches on or off depending on the availability of substances such as O_2, NO_3^-, SO_4^{2-}, or CO_2 and the free energy they yield when used as oxidants of organic matter.

Key state variable and assumptions

The key state variable considered in this exercise is organic matter, denoted as $Corg$. Although organic matter is a highly complex and diverse ensemble of molecules, we will represent it in this exercise by a chemical formula $(CH_2O)_1(NH_3)_{NC}(H_3PO_4)_{PC}$, where $NC = 16/106$ and $PC = 1/106$.[1] This simplification reflects the aim of the model, which is to describe the effects of the processes mentioned above on the *mass balance* and dynamics of C, O, N, and S.

Although all processes considered in this exercise are mediated by organisms (e.g., bacteria, archaea, but also more complex organisms), these organisms will *not* be explicitly included in the model. Instead, we will only model the result of their activity, assuming that the organisms are present and actively performing a specific process as long as the required chemical conditions are present. In other words, we will assume that the processes are limited by substrates but *not* by the organisms that mediate them (i.e., the "workers").

[1] This corresponds to the so-called Redfield organic matter, where the (molar!) $C : N : P$ ratio is equal to $106 : 16 : 1$.

On the other hand, we do consider important principles that govern the growth and fitness of organisms involved in the modelled processes. Specifically, we assume that if the amount of free energy gained from a process ‘A’ is greater than that from a process ‘B’, the organisms performing the process ‘A’ will outcompete those performing the process ‘B’. Thus, in effect, we will consider that the process ‘B’ can only become quantitatively important if the conditions become unfavourable for the process ‘A’. We will model this by assuming specific limitation and inhibition terms in the expressions for the process rates (as explained in class).

Processes and their reaction stoichiometry

To model mass balances of C, O, N and S in the system, we need to specify how these elements are coupled by the different processes involved. We do this by specifying the stoichiometry and rates of the net reactions that transform the elements from one form to another.

Organic matter mineralisation

Microbial mineralisation of organic matter[2] can proceed via different pathways depending on the availability of oxidants (i.e., terminal electron acceptors), as described in the following.

In *aerobic mineralisation*, molecular oxygen (O_2) is the oxidant and the corresponding reaction stoichiometry is

$$AeroMin: \qquad (CH_2O)_1(NH_3)_{NC}(H_3PO_4)_{PC} + O_2 \rightarrow CO_2 + NC \cdot NH_3 + PC \cdot H_3PO_4 + H_2O.$$

This reaction yields the greatest amount of free (Gibbs) energy and thus is the dominant process of organic matter mineralisation if O_2 is available. If O_2 becomes depleted, suboxic or anaerobic mineralisation processes can take over.

The most favoured suboxic process is *denitrification*, where nitrate (NO_3^-) is used as the oxidant. The corresponding reaction stoichiometry is

$$Denitri: \qquad (CH_2O)_1(NH_3)_{NC}(H_3PO_4)_{PC} + \frac{4}{5} \cdot HNO_3 \rightarrow CO_2 + \frac{2}{5} \cdot N_2 + NC \cdot NH_3 + PC \cdot H_3PO_4 + \frac{7}{5} \cdot H_2O$$

Denitrification is an important biogeochemical process as it produces N_2 gas and thus leads to a loss of reactive N species (NO_3^-) from the system.

Excluding manganese and iron reduction, the next favoured anaerobic process is *sulphate reduction*, where sulphate (SO_4^{2-}) is used as the oxidant. The corresponding reaction stoichiometry is

$$Sred: \qquad (CH_2O)_1(NH_3)_{NC}(H_3PO_4)_{PC} + \frac{1}{2} \cdot SO_4^{2-} + H^+ \rightarrow CO_2 + \frac{1}{2} \cdot H_2S + NC \cdot NH_3 + PC \cdot H_3PO_4 + H_2O$$

Sulphate reduction is important because a large fraction of organic matter is mineralised via this pathway, which is due to the relatively high seawater concentration of sulphate compared to O_2 or NO_3^-. Additionally, it is environmentally relevant because it produces free sulphide (H_2S), which is a toxic gas soluble in water.

When O_2, NO_3^- and SO_4^{2-} are not available, organic matter is mineralised by a process called *methanogenesis*, where CO_2 is used as the terminal electron acceptor and methane is produced. Although this process involves

[2] Depending on the perspective, there are several terms used when referring to the process of organic matter mineralisation, including organic matter decay, respiration, or oxidation.

several steps, we write its stoichiometry in the following simplified form:

$$CH4gen: \qquad (CH_2O)_1(NH_3)_{NC}(H_3PO_4)_{PC} \rightarrow \frac{1}{2}\cdot CO_2 + \frac{1}{2}\cdot CH_4 + NC\cdot NH_3 + PC\cdot H_3PO_4$$

This process is environmentally relevant because the produced methane is a very potent greenhouse gas.

Secondary reactions

As shown by the above reactions, organic matter mineralisation leads to the production of compounds that are relevant in the context of early diagenesis. Of interest in this exercise are ammonia (NH_3) and free sulphide (H_2S), because they can be used as energy sources for chemosynthetic organisms when reacting with molecular oxygen. Specifically, ammonia can be utilized by a process called nitrification according to the stoichiometry

$$Nitri: \qquad NH_3 + 2\cdot O_2 \rightarrow HNO_3 + H_2O$$

leading to the production of nitrate. Similarly, free sulphide can be utilized by a process called sulphide oxidation according to the stoichiometry

$$Sox: \qquad H_2S + 2\cdot O_2 \rightarrow SO_4^{2-} + 2\cdot H^+$$

Process rates

Assuming that aerobic mineralisation is limited by O_2 (Michaelis-Menten kinetics, half-saturation parameter $k_{O_2} = 0.001\ mol\ m^{-3}$) and is first-order with respect to organic carbon (rate constant $rMin = 0.01\ d^{-1}$), its rate can be mathematically formulated as[3]

$$AeroMin = rMin \cdot \frac{O_2}{O_2 + k_{O_2}} \cdot Corg$$

Because $Corg$ is a solid substance (units of $mol\ C\ m_S^{-3}$), the rate is expressed in units of $mol\ C\ m_S^{-3}\ d^{-1}$.

Task 1

Formulate rate expressions for the remaining processes, assuming that

- Nitrification is
  - limited by oxygen (Michaelis-Menten kinetics, the same half-saturation parameter $k_{O_2} = 0.001\ mol\ m^{-3}$),
  - first-order with respect to ammonia (rate constant $rNit = 10\ d^{-1}$).
- Denitrification is
  - limited by nitrate (Michaelis-Menten kinetics, half-saturation *limitation* parameter $k_{NO3} = 0.0001\ mol\ N\ m^{-3}$),
  - first-order with respect to organic carbon (rate constant $rMin = 0.01\ d^{-1}$),

[3] Note that, for simplicity, we omit the brackets when denoting the concentration of a specific component. Thus, for instance, $Corg$ concentration is denoted as $Corg$ (instead of $[Corg]$), O_2 concentration is denoted as O_2 (instead of $[O_2]$), etc.

  - inhibited by O_2 (use the previously defined parameter k_{O_2} as the corresponding half-saturation *inhibition* constant).

- Sulphate reduction is
  - limited by sulphate (Michaelis-Menten kinetics, $k_{SO4} = 0.1\ mol\ S\ m^{-3}$),
  - first-order with respect to organic carbon (rate constant $rMin = 0.01\ d^{-1}$),
  - inhibited by both oxygen (k_{O_2}) and nitrate (k_{NO3}).
- Sulphide oxidation is
  - limited by oxygen (Michaelis-Menten kinetics, k_{O_2}),
  - first-order with respect to sulphide (rate constant $rSox = 10\ d^{-1}$).
- Methanogenesis is
  - first-order with respect to organic carbon (rate constant $rMin = 0.01\ d^{-1}$),
  - inhibited by both oxygen (k_{O_2}), nitrate (k_{NO3}) and sulphate (k_{SO4}).

What are the units of the rates?

Mass balance equations

Assuming the following transport and reaction processes in the system

- transport: molecular diffusion, sediment accretion and mixing by bioturbation,
- reactions: aerobic mineralisation and nitrification,

we can write the following mass balance equations for the solid substance $Corg$ (units of $mol\ C\ m_S^{-3}$) and the dissolved substances O_2, NO_3^-, NH_3 and CO_2 (in units of $mol\ m_L^{-3}$):

$$\frac{\partial Corg}{\partial t} = \frac{1}{1-\phi} \cdot \frac{\partial}{\partial x}\left[(1-\phi)\cdot D_b \cdot \frac{\partial Corg}{\partial x}\right] - \frac{1}{1-\phi} \cdot \frac{\partial}{\partial x}\left[(1-\phi)\cdot v \cdot Corg\right] - AeroMin$$

$$\frac{\partial O_2}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{O2} \cdot \frac{\partial O_2}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot O_2\right] - AeroMin \cdot f_{2L} - 2 \cdot Nitri$$

$$\frac{\partial NH_3}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{NH_3} \cdot \frac{\partial NH_3}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot NH_3\right] + \frac{16}{106} \cdot AeroMin \cdot f_{2L} - Nitri$$

$$\frac{\partial NO_3^-}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{NO_3^-} \cdot \frac{\partial NO_3^-}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot NO_3^-\right] + Nitri$$

$$\frac{\partial CO_2}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{CO_2} \cdot \frac{\partial CO_2}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot CO_2\right] + AeroMin \cdot f_{2L}$$

where f_{2L} is a factor that converts from $mol\ m_S^{-3}$ (solid) to $mol\ m_L^{-3}$ (liquid), i.e., $f_{2L} = \frac{1-\phi}{\phi}$.

Task 2

Assuming that transport processes are the same for all dissolved substances, update the mass balance equations above to include the processes of denitrification, sulphate reduction, sulphide oxidation, and methanogenesis.

Model domain and boundary conditions

To find a unique solution to differential equations, we need to specify the model domain and boundary conditions. In this exercise, the model domain is a sediment column with a depth of 0.1 m. The porosity, ϕ, exponentially decreases with depth according to

$$\phi(x) = 0.7 + 0.2 \cdot e^{-porcoef \cdot x}$$

where $porcoef = 100\ m^{-1}$.

With respect to the boundary conditions, we impose

- the flux of $Corg$ at the sediment-water interface ($depoPOC$, see below)
- concentrations for the dissolved species at the sediment-water interface, equal to the bottom-water concentrations:
  - $O_{2,bw} = 0.3\ mol\ O_2\ m^{-3}$
  - $NO^-_{3,bw} = 0.01\ mol\ N\ m^{-3}$
  - $NH_{3,bw} = 0.001\ mol\ N\ m^{-3}$
  - $CO_{2,bw} = 2\ mol\ C\ m^{-3}$
  - $SO^{2-}_{4,bw} = 28\ mol\ S\ m^{-3}$
  - $H_2S_{bw} = 0\ mol\ S\ m^{-3}$
  - $CH_{4,bw} = 0\ mol\ C\ m^{-3}$
- zero concentration gradient at the lower boundary of the sediment column.

Model implementation in R

Task 3: Add aerobic mineralisation and nitrification

Open the template file that describes the dynamics of particulate organic carbon and DIC.[4] Change this model so that it describes the effects of aerobic mineralisation and nitrification on $Corg$, O_2, NO_3^-, NH_3, and CO_2 according to the reactions above.

- Add oxygen, ammonia, and nitrate as new state variables. To implement the transport and reaction terms for these new state variables, you can use the R-code lines for DIC as a "template", as this is also a dissolved substance.[5]
  - Add the new parameters to the parameter vector: rNit = 10 d^{-1}, kO2 = 0.001 $mol\ m^{-3}$, bwO2 = 0.3 $mol\ m^{-3}$, bwNO3 = 0.01 $mol\ m^{-3}$, bwNH3 = 0.001 $mol\ m^{-3}$.
  - You need to change the *names* of the state variables (5 species), and unpack the new state variables at the beginning of the model function in the *correct order*.
  - You also need to estimate the sediment diffusion coefficients for the new dissolved substances. To do that, use the package *marelac* and the lecture notes to account for tortuosity.
  - Implement transport of O_2, NH_3, NO_3^-, using these diffusion coefficients (beware that they are dissolved substances).
  - Implement rate expressions for aerobic mineralisation and nitrification, and use them to estimate the mass balances for all state variables in the model.
  - Implement depth-integration of the rates of aerobic mineralisation and nitrification.

[4] In Rstudio: File → new file → R markdown → from template → RTM_porous1D.

[5] Be careful when copying and pasting code chunks!

  - In addition to time derivatives, include depth-integrated process rates (expressed in $mol\ m^{-2}\ d^{-1}$) as well as fluxes at the top and bottom of the model domain as output variables from the model function. These will be useful to construct budgets.

- Run the model in steady state for three values of the $Corg$ deposition flux:
  - $depoPOC = 1 \times 10^{-3}\ mol\ m^{-2}\ d^{-1}$ (default)
  - $depoPOC = 20 \times 10^{-3}\ mol\ m^{-2}\ d^{-1}$
  - $depoPOC = 200 \times 10^{-3}\ mol\ m^{-2}\ d^{-1}$
- Plot depth profiles of state variables ($Corg$, CO_2, O_2, NH_3, etc.) for these three runs.
- Plot depth profiles of the process rates as well. Why are the processes stratified?

Task 4: Add denitrification

Expand the model from Task 3 to include denitrification.

- Although it is not essential, you can add N_2 as a new state variable to your model, if you want. It is a useful quantity to track N in the system. If you do so, you can assume the bottom-water concentration of $N_{2,bw} = 0$.
- Implement depth-integration of the denitrification rate.

Task 5: Add sulphate reduction and sulphide oxidation

Expand the model from Task 4 to include sulphate reduction and sulphide oxidation. This expansion adds basic S cycling to your model.

- Add two new state variables: SO_4^{2-} and H_2S.
- Implement depth-integration of the rates of sulphate reduction and sulphide oxidation.

Task 6: Add methanogenesis

Expand the model from Task 5 to include methanogenesis.

- Add CH_4 as a new state variable.
- Implement depth-integration of the methanogenesis rate.

Model application

Task 7: Quantify the contributions of mineralisation pathways

For each of the three runs, calculate the relative contribution of the aerobic mineralisation, denitrification, sulphate reduction, and methanogenesis to the total mineralisation of organic matter.

- When is organic matter mineralisation mostly aerobic?
- Why is the contribution of denitrification so low?
- When, and why, is the contribution of sulphate reduction high?
- When is the contribution of methanogenesis significant?

Task 8: Oxygen budget

Create an oxygen budget for the three runs.

- Which process consumes most of the oxygen diffusing into the sediment from the overlying water column?
- How does this depend on the POC deposition flux?

Task 9: Sulphur budget

If you have time, it is also interesting to create a sulphur budget. Here you can, for instance, look at the flux of sulphate that is recycled within the sediment and compare it with the flux of sulphate that enters the sediment from the overlying water.

Answers

Rate expressions

$$AeroMin = rMin \cdot \frac{O_2}{O_2+k_{O_2}} \cdot Corg$$

$$Nitri = rNit \cdot \frac{O_2}{O_2+k_{O_2}} \cdot NH_3$$

$$Denitri = rMin \cdot \frac{k_{O_2}}{O_2+k_{O_2}} \cdot \frac{NO_3^-}{NO_3^-+k_{NO_3}} \cdot Corg$$

$$Sred = rMin \cdot \frac{k_{O_2}}{O_2+k_{O_2}} \cdot \frac{k_{NO_3}}{NO_3^-+k_{NO_3}} \cdot \frac{SO_4^{2-}}{SO_4^{2-}+k_{SO_4}} \cdot Corg$$

$$Sox = rSox \cdot \frac{O_2}{O_2+k_{O_2}} \cdot H_2S$$

$$CH4gen = rMin \cdot \frac{k_{O_2}}{O_2+k_{O_2}} \cdot \frac{k_{NO_3}}{NO_3^-+k_{NO_3}} \cdot \frac{k_{SO_4}}{SO_4^{2-}+k_{SO_4}} \cdot Corg$$

Units of the rates:

- $AeroMin$, $Denitri$, $Sred$ and $CH4gen$ are in $mol\ C\ m_S^{-3}\ d^{-1}$.
- $Nitri$ is in $mol\ N\ m_L^{-3}\ d^{-1}$.
- Sox is in $mol\ S\ m_L^{-3}\ d^{-1}$.

Note that $AeroMin + Denitri + Sred + CH4gen$ is equal to $rMIN \cdot Corg$, as follows directly from the fact that the sum of the limitation and inhibition terms for a specific substrate is 1. Thus, the *total* mineralisation rate is first-order with respect to $Corg$ and independent of the terminal electron acceptor. The limitation and inhibition terms only dictate the *contributions* of the different oxidants to the overall mineralisation process.

Mass balance equations

The updated mass balance equations that include all processes mentioned are:[6]

$$\frac{\partial Corg}{\partial t} = \frac{1}{1-\phi} \cdot \frac{\partial}{\partial x}\left[(1-\phi) \cdot D_b \cdot \frac{\partial Corg}{\partial x}\right] - \frac{1}{1-\phi} \cdot \frac{\partial}{\partial x}\left[(1-\phi) \cdot v \cdot Corg\right] - AeroMin - Denitri - Sred - CH4gen$$

$$\frac{\partial O_2}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{O2} \cdot \frac{\partial O_2}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot O_2\right] - AeroMin \cdot f_{2L} - 2 \cdot Nitri - 2 \cdot Sox$$

$$\frac{\partial NH_3}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{NH_3} \cdot \frac{\partial NH_3}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot NH_3\right] + \frac{16}{106} \cdot (AeroMin + Denitri + Sred + CH4gen) \cdot f_{2L} - Nitri$$

$$\frac{\partial NO_3^-}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{NO_3^-} \cdot \frac{\partial NO_3^-}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot NO_3^-\right] - 0.8 \cdot Denitri + Nitri$$

$$\frac{\partial SO_4^{2-}}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{SO_4^{2-}} \cdot \frac{\partial SO_4^{2-}}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot SO_4^{2-}\right] - 0.5 \cdot Sred \cdot f_{2L} + Sox$$

$$\frac{\partial H_2S}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{H_2S} \cdot \frac{\partial H_2S}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot H_2S\right] + 0.5 \cdot Sred \cdot f_{2L} - Sox$$

$$\frac{\partial CO_2}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{CO_2} \cdot \frac{\partial CO_2}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot CO_2\right] + (OxicMin + Denitri + Sred + 0.5 \cdot CH4gen) \cdot f_{2L}$$

$$\frac{\partial CH_4}{\partial t} = \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot D_{CH_4} \cdot \frac{\partial CH_4}{\partial x}\right] - \frac{1}{\phi} \cdot \frac{\partial}{\partial x}\left[\phi \cdot v \cdot CH_4\right] + 0.5 \cdot CH4gen \cdot f_{2L}$$

where $f_{2L} = (1-\phi)/\phi$.

[6] Note the factors ϕ or $1-\phi$, which cannot be canceled out from the spatial derivative because the porosity varies with depth.

R implementation

```
require(marelac)
require(ReacTran)
```

The model grid and associated properties

```
# spatial domain: total length of 0.10 m, 500 boxes
Length    <- 0.1   # [m]
N         <- 500

# grid with an exponentially increasing grid size, first cell 0.05 cm (5e-4m)
Grid      <- setup.grid.1D(L = Length, N = N, dx.1 = 0.05/100)

# function describing the variation of porosity (volume fraction of LIQUID) with depth
porFun.L  <- function(x, por.SWI, por.deep, porcoef)
  return( por.deep + (por.SWI-por.deep)*exp(-x*porcoef) )

# function describing the SOLID volume fraction (svf = 1-porosity)
porFun.S  <- function(x, por.SWI, por.deep, porcoef)
  return( 1-porFun.L(x, por.SWI, por.deep, porcoef) )

# calculate porosity and svf on the grid (mid-points and box interfaces, etc.)
porLiquid <- setup.prop.1D(func=porFun.L, grid=Grid, por.SWI=0.9, por.deep=0.7, porcoef=100)
porSolid  <- setup.prop.1D(func=porFun.S, grid=Grid, por.SWI=0.9, por.deep=0.7, porcoef=100)

# molecular diffusion coefficients (m2/d) from the marelac package
diff.O2   <- diffcoeff(S=35, t=20)$O2  * 3600*24
diff.CO2  <- diffcoeff(S=35, t=20)$CO2 * 3600*24
diff.CH4  <- diffcoeff(S=35, t=20)$CH4 * 3600*24
diff.NH3  <- diffcoeff(S=35, t=20)$NH3 * 3600*24
diff.NO3  <- diffcoeff(S=35, t=20)$NO3 * 3600*24
diff.SO4  <- diffcoeff(S=35, t=20)$SO4 * 3600*24
diff.H2S  <- diffcoeff(S=35, t=20)$H2S * 3600*24

# effective diffusion coefficients in the sediment (corrected for tortuosity)
porInt    <- porLiquid$int                # porosity at the box interfaces
diffO2    <- diff.O2 /(1-log(porInt^2))
diffCO2   <- diff.CO2/(1-log(porInt^2))
diffCH4   <- diff.CH4/(1-log(porInt^2))
diffNO3   <- diff.NO3/(1-log(porInt^2))
diffNH3   <- diff.NH3/(1-log(porInt^2))
diffSO4   <- diff.SO4/(1-log(porInt^2))
diffH2S   <- diff.H2S/(1-log(porInt^2))
```

Other model parameters

```
parms <- c(
 Dbio     = 5e-4/365,   # [m2/d]      bioturbation mixing coefficient
 v_adv    = 5e-6,       # [m/d]       advection velocity = sediment accretion rate
 rMin     = 0.005,      # [/d]        POC mineralisation rate constant
 depoPOC  = 1e-3,       # [mol/m2/d]  POC deposition rate at SWI (sediment-water interface)
 rNit     = 10,         # [/d]        Nitrification rate constant
 rSox     = 10,         # [/d]        H2S reoxidation rate constant
 kO2      = 0.001,      # [mol/m3]    half-saturation O2 concentration
 kNO3     = 0.0001,     # [mol/m3]    half-saturation NO3 concentration
 kSO4     = 0.1,        # [mol/m3]    half-saturation SO4 concentration
 bwO2     = 0.300,      # [mol/m3]    O2 concentration at SWI
 bwCO2    = 2,          # [mol/m3]    CO2 concentration at SWI
 bwNO3    = 0.010,      # [mol/m3]    NO3 concentration at SWI
 bwNH3    = 0.001,      # [mol/m3]    NH3 concentration at SWI
 bwSO4    = 28,         # [mol/m3]    SO4 concentration at SWI
 bwH2S    = 0,          # [mol/m3]    H2S concentration at SWI
 bwCH4    = 0           # [mol/m3]    CH4 concentration at SWI
)
```

Definition and initialisation of state variables

```
names    <- c("POC", "CO2", "O2", "NH3", "NO3", "SO4", "H2S", "CH4")
nspec    <- length(names)
POC.ini  <- rep(0, length = N)      # initial conditions
CO2.ini  <- rep(0, length = N)
O2.ini   <- rep(0, length = N)
NH3.ini  <- rep(0, length = N)
NO3.ini  <- rep(0, length = N)
SO4.ini  <- rep(0, length = N)
H2S.ini  <- rep(0, length = N)
CH4.ini  <- rep(0, length = N)
state    <- c(POC.ini, CO2.ini, O2.ini, NH3.ini, NO3.ini, SO4.ini, H2S.ini, CH4.ini)
```

Definition of the model function

```
Diamodel <- function (t, state, pars)   # state is a LONG vector
{
  with (as.list(pars),{

    # unpack state variables
    POC <- state[     1 :   N ]     # first N elements: POC
    CO2 <- state[  (N+1):(2*N)]     # next N elements:  CO2
    O2  <- state[(2*N+1):(3*N)]     # next N elements:  O2
    NH3 <- state[(3*N+1):(4*N)]     # next N elements:  NH3
```

```
NO3 <- state[(4*N+1):(5*N)]    # next N elements:  NO3
SO4 <- state[(5*N+1):(6*N)]    # next N elements:  SO4
H2S <- state[(6*N+1):(7*N)]    # next N elements:  H2S
CH4 <- state[(7*N+1):(8*N)]    # next N elements:  CH4

# === transport rates ===
# note: zero gradient by default at lower boundaries

# solid substances, VF = solid volume fraction = 1-porosity!
tran.POC <- tran.1D(C = POC, flux.up = depoPOC,  # upper boundary: flux
                    dx = Grid, VF = porSolid,    # grid and volume fraction (1-por)
                    D = Dbio, v = v_adv)         # mixing (bioturbation) and advection

# dissolved substances, VF = liquid volume fraction = porosity!
tran.CO2 <- tran.1D(C = CO2, C.up = bwCO2,       # upper boundary: concentration
                    dx = Grid, VF = porLiquid,   # grid and volume fraction (por)
                    D = diffCO2, v = v_adv)      # diffusive mixing and advection

tran.O2 <- tran.1D(C = O2, C.up = bwO2,
                    dx = Grid, VF = porLiquid,
                    D = diffO2, v = v_adv)

tran.NH3 <- tran.1D(C = NH3, C.up = bwNH3,
                    dx = Grid, VF = porLiquid,
                    D = diffNH3, v = v_adv)

tran.NO3 <- tran.1D(C = NO3, C.up = bwNO3,
                    dx = Grid, VF = porLiquid,
                    D = diffNO3, v = v_adv)

tran.SO4 <- tran.1D(C = SO4, C.up = bwSO4,
                    dx = Grid, VF = porLiquid,
                    D = diffSO4, v = v_adv)

tran.H2S <- tran.1D(C = H2S, C.up = bwH2S,
                    dx = Grid, VF = porLiquid,
                    D = diffH2S, v = v_adv)

tran.CH4 <- tran.1D(C = CH4, C.up = bwCH4,
                    dx = Grid, VF = porLiquid,
                    D = diffCH4, v = v_adv)

# === reaction rates ===

# [mol/m3 SOLID/d] (per volume of solid)
AeroMin      <- rMin *  O2/(O2+kO2)                                    * POC
Denitri      <- rMin * kO2/(O2+kO2) *  NO3/(NO3+kNO3)                  * POC
SO4reduction <- rMin * kO2/(O2+kO2) * kNO3/(NO3+kNO3) *  SO4/(SO4+kSO4) * POC
```

```
CH4genesis   <- rMin * kO2/(O2+kO2) * kNO3/(NO3+kNO3) * kSO4/(SO4+kSO4) * POC

Mineralisation  <- AeroMin  + Denitri + SO4reduction + CH4genesis

# [mol/m3 LIQUID/d] (per volume of liquid)
Nitri   <- rNit * O2/(O2+kO2) *NH3
Sox     <- rSox * O2/(O2+kO2) *H2S

# === mass balances : dC/dt = transport + reactions ===

# solid substances [mol/m3 SOLID/d]
dPOC.dt   <- ( tran.POC$dC                                    # transport
             - AeroMin - Denitri - SO4reduction - CH4genesis) # reactions,

# dissolved substances  [mol/m3 LIQUID/d]
poro      <- porLiquid$mid
f2Liquid  <- (1-poro)/poro  # to convert from /solid to /liquid

dCO2.dt   <- ( tran.CO2$dC
               + (AeroMin + Denitri + SO4reduction + 0.5*CH4genesis)*f2Liquid )
dO2.dt    <- ( tran.O2$dC - 2*Nitri - 2*Sox - AeroMin*f2Liquid )
dNH3.dt   <- ( tran.NH3$dC - Nitri
               + 16/106*(AeroMin + Denitri + SO4reduction + CH4genesis)*f2Liquid )
dNO3.dt   <- ( tran.NO3$dC + Nitri - 4/5*Denitri*f2Liquid )
dSO4.dt   <- ( tran.SO4$dC - 0.5*SO4reduction*f2Liquid + Sox)
dH2S.dt   <- ( tran.H2S$dC + 0.5*SO4reduction*f2Liquid - Sox)
dCH4.dt   <- ( tran.CH4$dC + 0.5*CH4genesis*f2Liquid)

# === depth-integrated rates: [mol/m2 BULK/d]
TotalAero   <- sum(AeroMin       *Grid$dx*porSolid$mid)
TotalDenit  <- sum(Denitri       *Grid$dx*porSolid$mid)
TotalSO4red <- sum(SO4reduction  *Grid$dx*porSolid$mid)
TotalCH4gen <- sum(CH4genesis    *Grid$dx*porSolid$mid)
TotalMin    <- sum(Mineralisation*Grid$dx*porSolid$mid)

TotalNit    <- sum(Nitri         *Grid$dx*porLiquid$mid)
TotalSox    <- sum(Sox           *Grid$dx*porLiquid$mid)

return(list(c(dPOC.dt, dCO2.dt, dO2.dt, dNH3.dt, dNO3.dt,
              dSO4.dt, dH2S.dt, dCH4.dt),  # time-derivatives
      AeroMin        = AeroMin,            # rate profiles
      Denitri        = Denitri,
      SO4reduction   = SO4reduction,
      CH4genesis     = CH4genesis,
      Mineralisation = Mineralisation,
      Nitri          = Nitri,
      Sox            = Sox,
        # part of mineralisation due to aero, denit, SO4red, CH4genesis
          pAero          = TotalAero/TotalMin,
          pDenit         = TotalDenit/TotalMin,
          pSO4red        = TotalSO4red/TotalMin,
          pCH4gen        = TotalCH4gen/TotalMin,

        # for creating budgets - all in [mol/m2 BULK/d]
          TotalAero      = TotalAero,
          TotalDenit     = TotalDenit,
          TotalSO4red    = TotalSO4red,
          TotalCH4gen    = TotalCH4gen,
          TotalMin       = TotalMin,
          TotalNit       = TotalNit,
          TotalSox       = TotalSox,
          CO2.SWI.Flux   = tran.CO2$flux.up,
          CO2.Deep.Flux  = tran.CO2$flux.down,
          O2.SWI.Flux    = tran.O2$flux.up,
          O2.Deep.Flux   = tran.O2$flux.down,
          NH3.SWI.Flux   = tran.NH3$flux.up,
          NH3.Deep.Flux  = tran.NH3$flux.down,
          NO3.SWI.Flux   = tran.NO3$flux.up,
          NO3.Deep.Flux  = tran.NO3$flux.down,
          SO4.SWI.Flux   = tran.SO4$flux.up,
          SO4.Deep.Flux  = tran.SO4$flux.down,
          H2S.SWI.Flux   = tran.H2S$flux.up,
          H2S.Deep.Flux  = tran.H2S$flux.down,
          CH4.SWI.Flux   = tran.CH4$flux.up,
          CH4.Deep.Flux  = tran.CH4$flux.down,
          POC.SWI.Flux   = tran.POC$flux.up,
          POC.Deep.Flux  = tran.POC$flux.down))
 })
}
```

Model application

Steady-state solution

Here, we find steady state solutions of the model for the three POC fluxes.

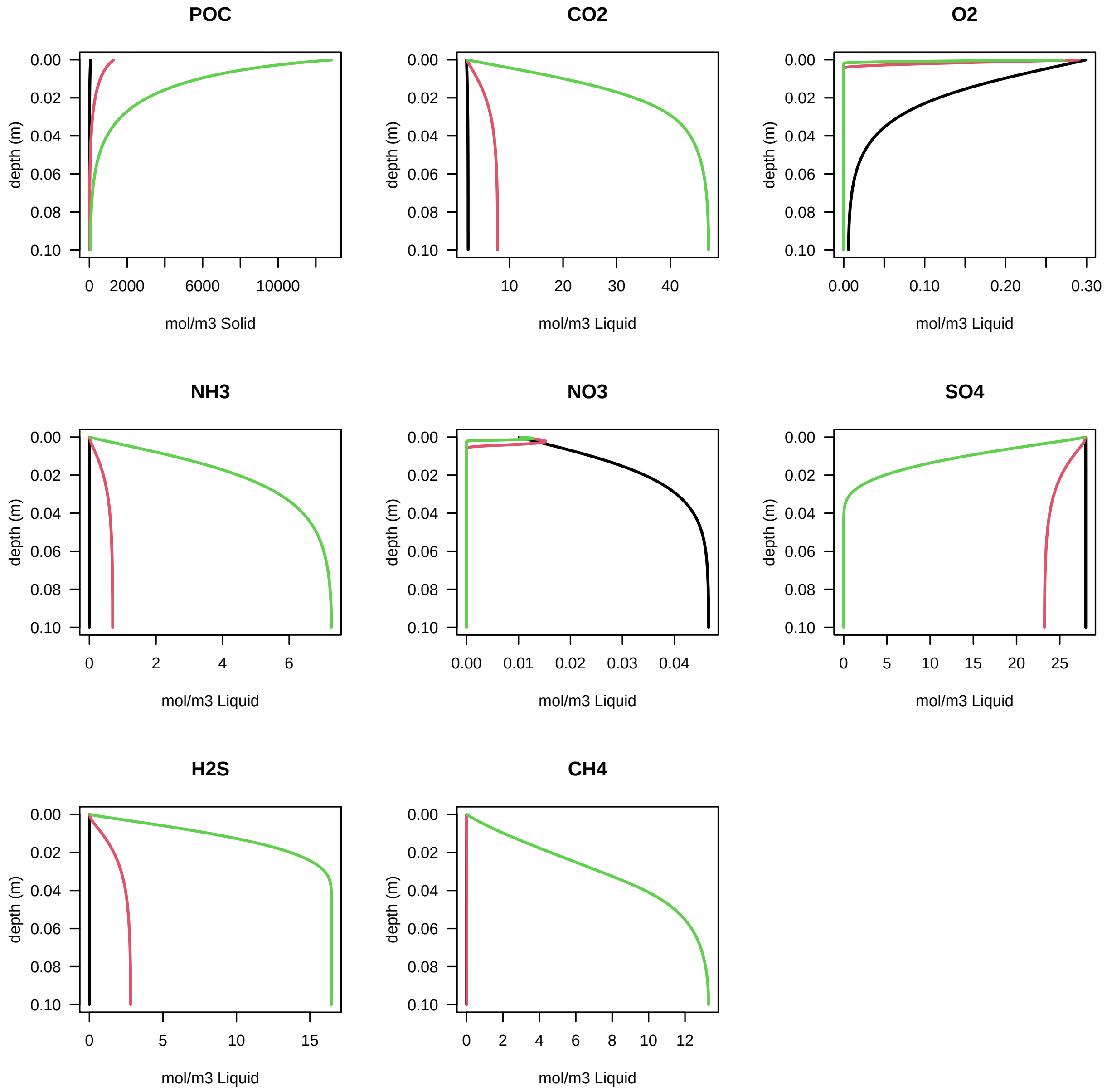
```
std <- steady.1D (y=state, func=Diamodel, parms=parms,
                  nspec=nspec, dimens=N, names=names,
                  positive = TRUE)     # to have only positive values!

p1 <- parms
p1["depoPOC"]  <- 20e-3 # [mol/m2/d]  POC deposition rate (flux at SWI)
std1 <- steady.1D (y=state, func=Diamodel, parms=p1,
                  nspec=nspec, dimens=N, names=names, positive = TRUE)
```

```
p2 <- parms
p2["depoPOC"]  <- 200e-3 # [mol/m2/d]  POC deposition rate (flux at SWI)
std2 <- steady.1D (y=state, func=Diamodel, parms=p2,
                   nspec=nspec, dimens=N, names=names, positive = TRUE)
```

Plotting

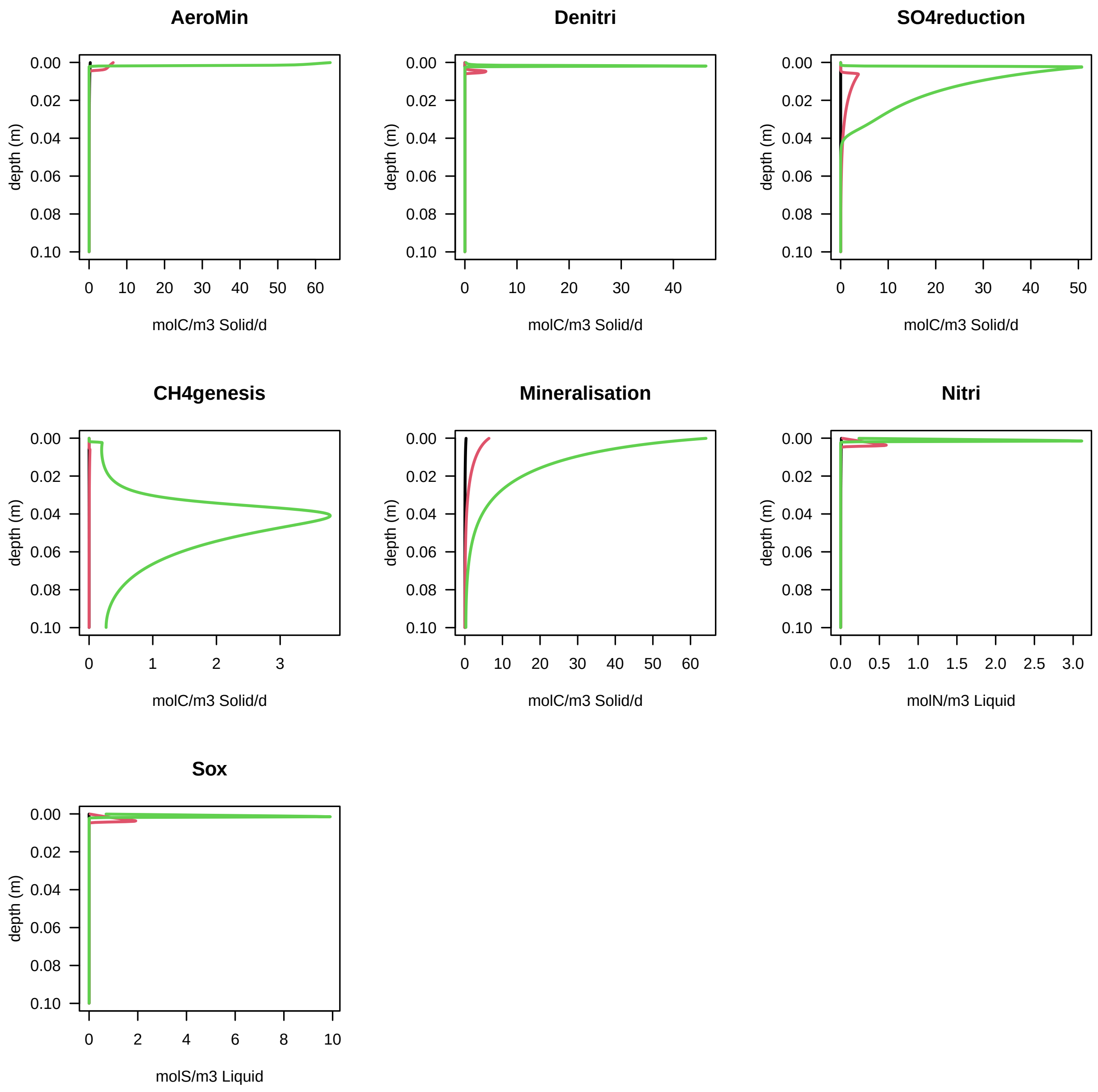
First, we plot depth profiles of the concentrations of state variables, all runs in one graph.

```
plot(std, std1, std2,
     grid=Grid$x.mid, xyswap=TRUE, ylim=c(Length,0), lty=1, lwd=2, las=1,
     ylab="depth (m)", xlab=c("mol/m3 Solid", rep("mol/m3 Liquid",nspec-1)))
```



Next, we plot depth profiles of the process rates, all runs in one graph.

```
plot(std, std1, std2,
 which = c("AeroMin","Denitri","SO4reduction","CH4genesis","Mineralisation","Nitri","Sox"),
 grid=Grid$x.mid, xyswap=TRUE, ylab="depth (m)", ylim=c(Length,0), lty=1, lwd=2, las=1,
 xlab=c(rep("molC/m3 Solid/d",5), "molN/m3 Liquid", "molS/m3 Liquid"))
```

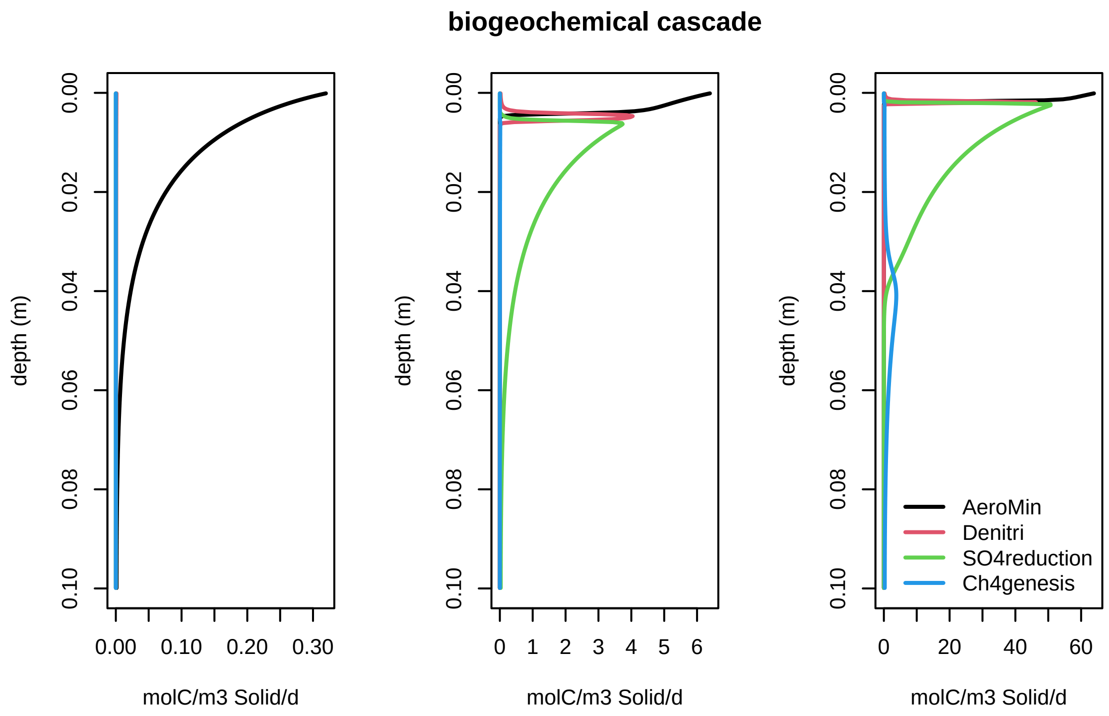


Finally, we plot depth profiles of all mineralisation rates in one graph, separately for each model run. The graphs show that the organic matter is mineralised by aerobic mineralisation at the very top of the sediment (where O_2 is available), then by denitrification in a narrow band (where NO_3^- is available but O_2 is depleted), then by sulphate reduction in the deeper sediment (where SO_4^{2-} is available but O_2 and NO_3^- are depleted).[7] Finally, methanogenesis occurs at depths where O_2, NO_3^- and SO_4^{2-} have been depleted and organic matter is still available (only visible in the run with the largest POC deposition flux). The plots thus illustrate the

[7] Note that the latter two processes do not occur in the run with the lowest POC deposition flux.

so-called biogeochemical cascade.

```
# all process rates in one graph
par(mfrow=c(1,3))
s <- std
matplot(y=Grid$x.mid, x=cbind(s$AeroMin, s$Denitri, s$SO4reduction, s$CH4genesis),
        type="l", ylim=c(Length,0), col=1:4, lwd=2, lty=1,
        xlab="molC/m3 Solid/d", ylab="depth (m)")
s <- std1
matplot(y=Grid$x.mid, x=cbind(s$AeroMin, s$Denitri, s$SO4reduction, s$CH4genesis),
        type="l", ylim=c(Length,0), col=1:4, lwd=2, lty=1,
        xlab="molC/m3 Solid/d", ylab="depth (m)", main="biogeochemical cascade")
s <- std2
matplot(y=Grid$x.mid, x=cbind(s$AeroMin, s$Denitri, s$SO4reduction, s$CH4genesis),
        type="l", ylim=c(Length,0), col=1:4, lwd=2, lty=1,
        xlab="molC/m3 Solid/d", ylab="depth (m)")
legend("bottomright",legend=c("AeroMin", "Denitri", "SO4reduction", "Ch4genesis"),
       lwd=2, col=1:4, lty=1, bty="n")
```



Contributions of mineralisation pathways

The following table shows that for the lowest POC deposition flux (`std`), organic matter mineralisation is primarily aerobic (almost 99% of total mineralisation). For the second largest POC deposition flux (`std1`), about 80% of organic matter is mineralised via sulphate reduction, while aerobic mineralisation and denitrification contribute by about 15% and 6%, respectively. Methanogenesis is significant (about 16%) only for the largest POC deposition flux (`std2`). Note that the depth-integrated total mineralisation (last line, values in $mol\ C\ m^{-2}\ d^{-1}$) is equal to the POC deposition flux, showing that at the bottom of the modelled sediment column, all deposited POC was mineralised and converted to either CO_2 or CH_4.

```
toselect <- c("pAero", "pDenit", "pSO4red", "pCH4gen", "TotalMin")
PATH     <- std[toselect]
PATH1    <- std1[toselect]
PATH2    <- std2[toselect]
CONTRIB  <- data.frame(std=unlist(PATH), std1=unlist(PATH1), std2=unlist(PATH2))
knitr::kable(CONTRIB, digits = 4)
```

	std	std1	std2
pAero	0.9866	0.1464	0.0568
pDenit	0.0134	0.0551	0.0143
pSO4red	0.0000	0.7954	0.7677
pCH4gen	0.0000	0.0032	0.1611
TotalMin	0.0010	0.0200	0.1999

Oxygen budget

The following table (O_2 fluxes in $mol\ O_2\ m^{-2}\ yr^{-1}$) shows that for the lowest POC deposition flux (`std`), about 2/3 of the sedimentary O_2 consumption occurs due to the aerobic mineralisation of the organic matter, while the remaining 1/3 is due to nitrification. In contrast, for the larger POC deposition fluxes, sedimentary O_2 consumption occurs primarily (50% or more) due to oxidation of the free sulphide produced by sulphate reduction, while the contributions of aerobic mineralisation and nitrification are lower.

```
toselect <- c("TotalAero", "TotalNit", "TotalSox", "O2.SWI.Flux", "O2.Deep.Flux")
fac      <- 365  # to molO2/m2/yr
BUDGET   <- std[toselect]
BUDGET1  <- std1[toselect]
BUDGET2  <- std2[toselect]
O2budget <- rbind(std=unlist(BUDGET), std1=unlist(BUDGET1), std2=unlist(BUDGET2))*fac

O2BUDG   <-
  data.frame(O2FluxIn       =  O2budget[,"O2.SWI.Flux"],
             O2FluxOut      = -O2budget[,"O2.Deep.Flux"],
             O2consByAeroMin = -O2budget[,"TotalAero"],
             O2consByNitri   = -O2budget[,"TotalNit"]*2, # 2 moles per mole of NH3 nitrified
             O2consBySox     = -O2budget[,"TotalSox"]*2) # 2 moles per mole of H2S oxidised

knitr::kable(O2BUDG, digits = 2)
```

	O2FluxIn	O2FluxOut	O2consByAeroMin	O2consByNitri	O2consBySox
std	0.48	0	-0.36	-0.12	0.00
std1	4.74	0	-1.07	-0.90	-2.78
std2	12.81	0	-4.15	-2.09	-6.57

The output below demonstrates that the difference between the O_2 fluxes at the domain boundaries and the sum of all depth-integrated rates of O_2 consumption is equal to (nearly) zero, consistent with the mass conservation law.

```
rowSums(O2BUDG)
```

```
##          std         std1         std2 
## 3.167488e-09 4.596323e-14 1.465494e-14
```

Sulphur budget

The following table (S fluxes in $mol\ S\ m^{-2}\ yr^{-1}$) shows that if sulphate reduction is significant, the *total* amount of SO_4^{2-} consumed in the sediment by sulphate reduction is always greater than the amount of SO_4^{2-} that enters the sediment from the overlying water. This is only possible if SO_4^{2-} is additionally produced within the sediment, i.e., if the free sulphide produced by sulphate reduction is *recycled* back to sulphate. The process responsible for this recycling is the aerobic oxidation of sulphide, which, as noted in the previous section, is a major contributor to the sedimentary oxygen consumption.

```
toselect <- c("TotalSO4red", "TotalSox", "SO4.SWI.Flux", "SO4.Deep.Flux",
              "H2S.SWI.Flux", "H2S.Deep.Flux")
fac <- 365  # to molS/m2/yr
BUDGET   <- std[toselect]
BUDGET1  <- std1[toselect]
BUDGET2  <- std2[toselect]
SBUDG <- rbind(std=unlist(BUDGET), std1=unlist(BUDGET1), std2=unlist(BUDGET2))*fac
SBUDG[,"TotalSO4red"] <- SBUDG[,"TotalSO4red"]*0.5  # 0.5 moles of SO4 per mole of C
knitr::kable(SBUDG, digits = 4)
```

	TotalSO4red	TotalSox	SO4.SWI.Flux	SO4.Deep.Flux	H2S.SWI.Flux	H2S.Deep.Flux
std	0.0000	0.0000	0.0358	0.0358	0.0000	0.0000
std1	2.9019	1.3893	1.5424	0.0297	-1.5091	0.0036
std2	28.0106	3.2867	24.7239	0.0000	-24.7029	0.0210

This conclusion is confirmed by the following output, which shows that the net flux of sulphate consumed in the sediment (which is equal to `SO4.SWI.Flux - SO4.Deep.Flux`) together with the gross flux of sulphide production (`TotalSox`) is equal to the gross (total) rate of sulphate reduction in the sediment (`TotalSO4red`).

```
Scheck <- cbind(SBUDG[,"SO4.SWI.Flux"]-SBUDG[,"SO4.Deep.Flux"] # net SO4 consumed
                + SBUDG[,"TotalSox"],                          # + H2S recycled
                SBUDG[,"TotalSO4red"])                         # gross SO4 consumed
Scheck
```

```
##              [,1]         [,2]
## std  6.929439e-06 6.929442e-06
## std1 2.901937e+00 2.901937e+00
## std2 2.801062e+01 2.801062e+01
```

References

R Core Team (2020). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.

Soetaert Karline (2009). rootSolve: Nonlinear root finding, equilibrium and steady-state analysis of ordinary differential equations. R-package version 1.6

Soetaert Karline, Thomas Petzoldt, R. Woodrow Setzer (2010). Solving Differential Equations in R: Package deSolve. Journal of Statistical Software, 33(9), 1–25. URL http://www.jstatsoft.org/v33/i09/ DOI 10.18637/jss.v033.i09

Soetaert, Karline and Meysman, Filip (2012). Reactive transport in aquatic ecosystems: Rapid model prototyping in the open source software R Environmental Modelling & Software, 32, 49-60.

Soetaert Karline and Thomas Petzoldt (2020). marelac: Tools for Aquatic Sciences. R package version 2.1.10. https://CRAN.R-project.org/package=marelac