

Supplementary material to

Model of Early Diagenesis in the Upper Sediment
with Adaptable complexity – MEDUSA (v. 2):
a time-dependent biogeochemical sediment module for
Earth System Models, process analysis and teaching

Setting up a simplified version of the early diagenesis model of Jourabchi et al. (2008) with MEDUSA

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1 Model equations

Jourabchi et al. (2008) use the steady-state version of the general early diagenesis equation, which they write as (see Electronic Annex to the paper)

$$\frac{\partial(\zeta_k C_k)}{\partial t} = 0 = -\frac{\partial(\zeta_k \omega_k C_k)}{\partial x} + \frac{\partial}{\partial x} \left((D_b + D_k) \zeta_k \frac{\partial C_k}{\partial x} \right) + \sum_i s_k^i R_i \quad (1)$$

where

- t is time ([yr])
- x is depth below the sediment water interface ([cm])
- C_k is the concentration of species k , expressed in mol/L_{pw} for solutes (i.e., moles per litre of porewater) and in mol/g_{ss} for solids (i.e., moles per gram of solid sediment);
- ω_k is the advection rate of k ([cm/yr])
- D_b is the bioturbation (biodiffusion) coefficient ([cm²/yr]), constant for all species;
- D_k is the molecular diffusion coefficient ([cm²/yr]), set to zero for solids;

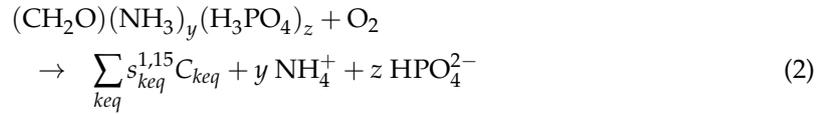
- $\bar{\zeta}_k$ is the volume fraction of the phase that species k belongs to ($\bar{\zeta}_k = \varphi$ for solutes and $\bar{\zeta}_k = (1 - \varphi)$ for solids);
- R_i is the rate at which reaction i proceeds (apparently expressed in moles per cubic centimeter of total sediment per year [$\text{mol}/\text{cm}_{\text{ts}}^3/\text{yr}$]);[†]
- s_k^i is the stoichiometric coefficient for the species k in the reaction i .

2 Original formulation

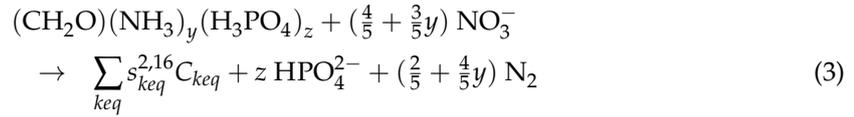
2.1 Model reactions

The equations used by Jourabchi et al. (2008) are written here for the special Redfield composition $(\text{CH}_2\text{O})(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z$ (i.e., with x set to 1) and using the main reagents.

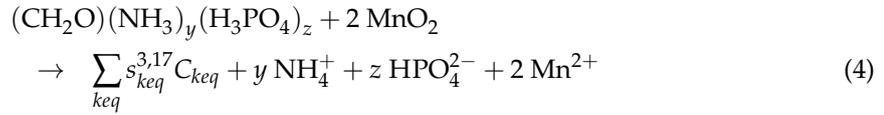
R^1 & R^{15} (oxic respiration):



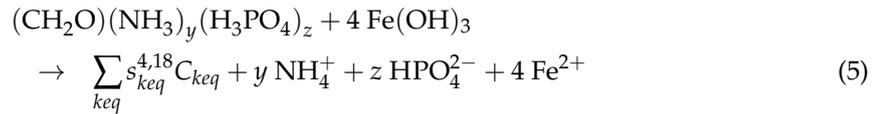
R^2 & R^{16} (denitrification):



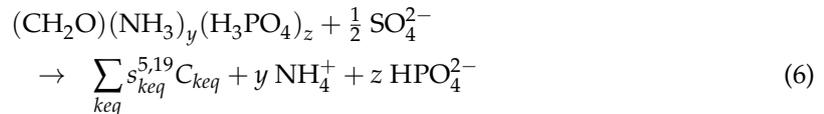
R^3 & R^{17} (Mn(IV) reduction):



R^4 & R^{18} (Fe(III) reduction):



R^5 & R^{19} (sulfate reduction):



[†]Units for the different R^i are not clearly stated in Jourabchi et al. (2008). They nevertheless provide the following expression for the oxic degradation rates of fast and slowly degradable organic matter:

$$R^{1,15} = f_{\text{O}_2} k [\text{CH}_2\text{O}] (1 - \varphi) \rho_s.$$

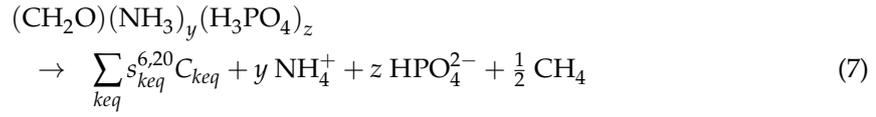
Here f_{O_2} is dimensionless (the ramp function detailed in a later section in this memo), k is the rate constant in [yr^{-1}], $[\text{CH}_2\text{O}]$ is the organic matter concentration in [$\text{mol C}/\text{g}_{\text{ss}}$], $(1 - \varphi)$ is the volume fraction of solids in the total sediment (in [$\text{L}_{\text{ss}}/\text{L}_{\text{ts}}$] or equivalently [$\text{cm}_{\text{ss}}^3/\text{cm}_{\text{ts}}^3$]) and ρ_s is the solids' bulk density, whose units are not specified. They are most probably [$\text{g}_{\text{ss}}/\text{cm}_{\text{ss}}^3$] — the units used by Jourabchi et al. (2005) and also by Aguilera et al. (2005) who use a variant of the same model. In this case, units for $R^{1,15}$ would be [$\text{mol C}/\text{cm}_{\text{ts}}^3/\text{yr}$].

The re-oxidation rate of Fe^{2+} by O_2 (in the porewater phase) is written as

$$R^9 = k_9 [\text{Fe}^{2+}] [\text{O}_2] \varphi \left(\frac{1 \text{L}}{10^3 \text{cm}^3} \right)$$

where k_9 is expressed in [$(\text{mol}/\text{L}_{\text{pw}})^{-1} \text{yr}^{-1}$], the two species concentrations in [$\text{mol}/\text{L}_{\text{pw}}$] and the porosity φ in [$\text{L}_{\text{pw}}/\text{L}_{\text{ts}}$]. Accordingly, units for R^9 would be [$\text{mol}/\text{cm}_{\text{ts}}^3/\text{yr}$].

R^6 & R^{20} (methanogenesis):



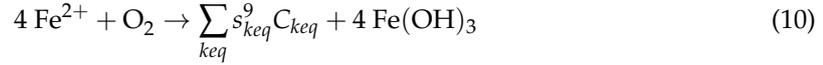
R^7 (nitrification):



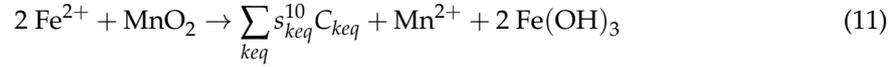
R^8 (Mn^{2+} re-oxidation by O_2):



R^9 (Fe^{2+} re-oxidation by O_2):



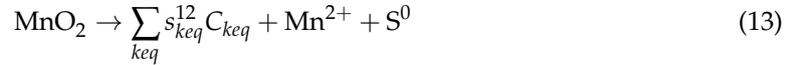
R^{10} (Fe^{2+} re-oxidation by MnO_2):



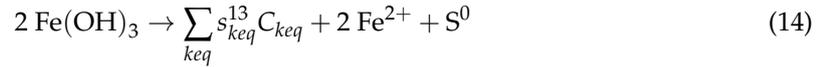
R^{11} (sulfide re-oxidation by O_2):



R^{12} (sulfide re-oxidation by MnO_2):



R^{13} (sulfide re-oxidation by $\text{Fe}(\text{OH})_3$):



R^{14} (CaCO_3 dissolution):



2.2 Equilibria

E^1 (first dissociation of carbonic acid):



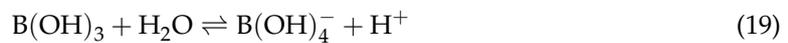
E^2 (second dissociation of carbonic acid):



E^3 (sulfide dissociation):



E^4 (boric acid dissociation):

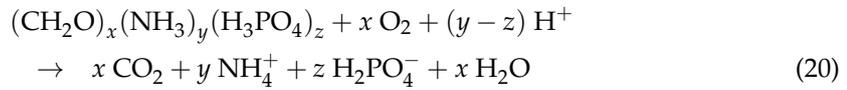


3 Reformulation and simplification

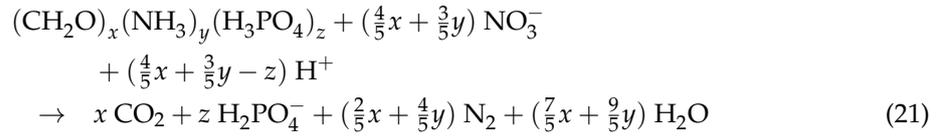
We reformulate the problem for a complete organic composition and without the stoichiometric sums for the species involved in equilibria. We

- introduce the general Redfield composition $(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z$;
- simplify the reaction network by neglecting organic matter oxidation by sulfate reduction (reactions R^6 and R^{19}), by methanogenesis (reactions R^7 and R^{20}), sulfide re-oxidation (reactions R^{11} , R^{12} and R^{13});
- explicitly introduce back H_2O , H^+ , and individual reagents from the equilibria;
- add a x stoichiometric coefficient for the carbon bearing organic compound;
- switch to H_2PO_4^- as the representative phosphate system solute: H_2PO_4^- is the zero-level component for the alkalinity system, and so the alkalinity balance becomes more coherent.

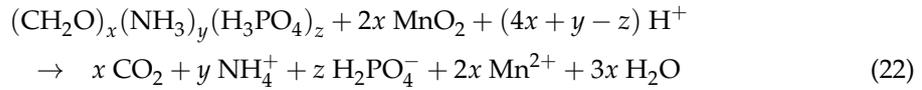
R^1 & R^{15} (oxic respiration):



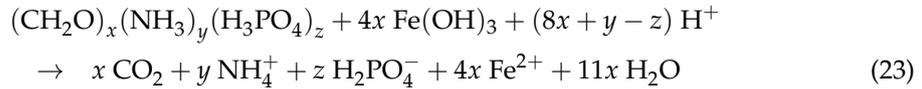
R^2 & R^{16} (denitrification):



R^3 & R^{17} (Mn(IV) reduction):



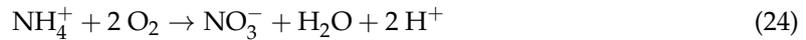
R^4 & R^{18} (Fe(III) reduction):



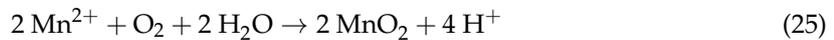
[R^5 & R^{19} (sulfate reduction) – neglected here]

[R^6 & R^{20} (methanogenesis) – neglected here]

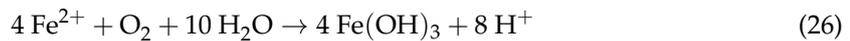
R^7 (nitrification):



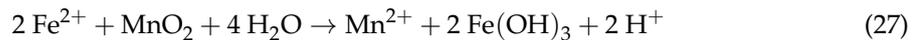
R^8 (Mn^{2+} re-oxidation by O_2):



R^9 (Fe^{2+} re-oxidation by O_2):



R^{10} (Fe^{2+} re-oxidation by MnO_2):



[R^{11} (sulfide re-oxidation by O_2) – neglected here]

[R^{12} (sulfide re-oxidation by MnO_2) – neglected here]

[R^{13} (sulfide re-oxidation by $\text{Fe}(\text{OH})_3$) – neglected here]

R^{14} : CaCO_3 dissolution



3.1 Equilibria

E^1 (first dissociation of carbonic acid):

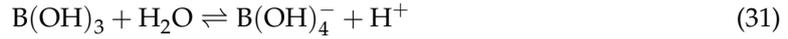


E^2 (second dissociation of carbonic acid):



[E^3 (sulfide dissociation) – neglected here]

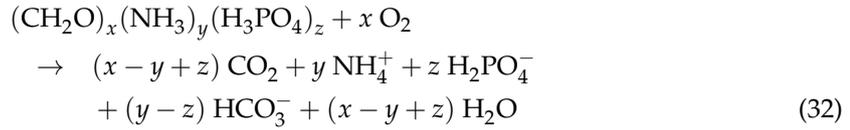
E^4 (boric acid dissociation):



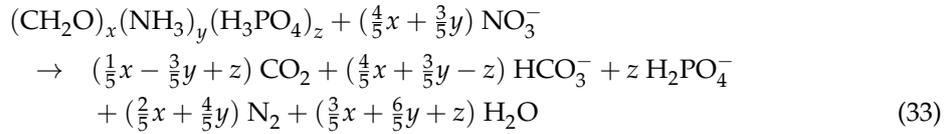
4 Unified formulation

The equations from the previous section are modified in order to discard the H^+ ion, by introduction of the $\text{CO}_2\text{-HCO}_3^-$ equilibrium $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$.

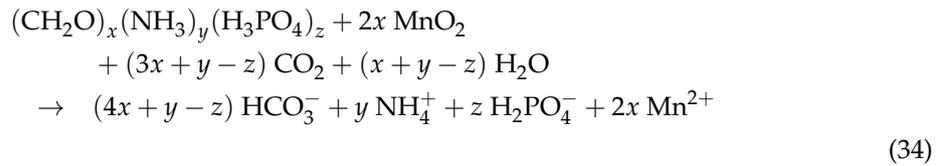
R^1 & R^{15} (oxic respiration):



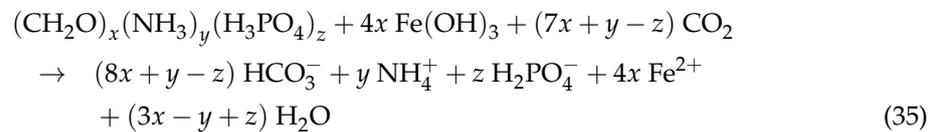
R^2 & R^{16} (denitrification):



R^3 & R^{17} (Mn(IV) reduction):



R^4 & R^{18} (Fe(III) reduction):



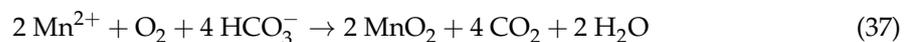
[R^5 & R^{19} (sulfate reduction) – neglected here]

[R^6 & R^{20} (methanogenesis) – neglected here]

R^7 (nitrification):



R^8 (Mn^{2+} re-oxidation by O_2):



R^9 (Fe^{2+} re-oxidation by O_2):



R^{10} (Fe^{2+} re-oxidation by MnO_2):



[R^{11} (sulfide re-oxidation by O_2) – neglected here]

[R^{12} (sulfide re-oxidation by MnO_2) – neglected here]

[R^{13} (sulfide re-oxidation by $\text{Fe}(\text{OH})_3$) – neglected here]

R^{14} : CaCO_3 dissolution



4.1 Equilibria

E^1 (first dissociation of carbonic acid):

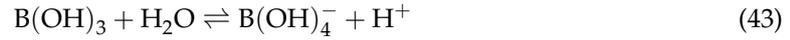


E^2 (second dissociation of carbonic acid):



[E^3 (sulfide dissociation) – neglected here]

E^4 (boric acid dissociation):



5 Rate laws and equilibria

5.1 General

Two classes of organic matter are considered: a slowly and a fast metabolizable fraction.

The degradation rate of the slowly metabolizable fraction, k_s , is derived from a constitutive relationship (Boudreau, 1997):

$$k_s / [\text{yr}^{-1}] = 2.2 \times 10^{-5} (F_{\text{orgC}} / [\mu\text{molC cm}^{-2} \text{yr}^{-1}])^{2.1} \quad (44)$$

For a given F_{orgC} , k_s is calculated, and the fraction f of fast degradable organic carbon and the corresponding rate constant k_f are adjusted.

Initially $f = 0.9$, $k_s = 0.001 \text{ yr}^{-1}$ and $k_f = 0.1 \text{ yr}^{-1}$

In the course of the adjustment, the following constraints are used: $f \leq 1$ and $k_f \leq 10 \text{ yr}^{-1}$

Here, sulfate reduction is neglected. It was included in the model configuration adopted by Jourabchi et al. (2008), where it did, however, only play a role at three of the thirteen sites (disregarding one site, where it contributed for only 0.1% of the remineralization of the slowly degradable organic matter fraction, which accounted for 18% of the total organic matter rain).

5.1.1 OM degradation by oxidic respiration

Oxidic respiration (eqs. 2, 20, 32): Ramp function of $[\text{O}_2]$ multiplied by $[\text{OM}]$, with a saturation concentration K_{O_2} of $8 \times 10^{-6} \text{ mol/L} = 8 \times 10^{-3} \text{ mol/m}^3$:

$$\hat{R}_1 = k_f(1 - \varphi) \cdot [\text{OM}_f] \cdot \text{ramp}([\text{O}_2]; K_{\text{O}_2})$$

and similarly for $[\text{OM}_s]$ (rate \hat{R}_{15}), with a rate constant k_s .

5.1.2 OM degradation by nitrate reduction and denitrification

Denitrification (eq. 21): Ramp function of $[\text{NO}_3^-]$ multiplied by $[\text{OM}]$ and by a complementary ramp function in $[\text{O}_2]$

$$\hat{R}_2 = k_f(1 - \varphi) \cdot [\text{OM}_f] \cdot \text{ramp}([\text{NO}_3^-]; K_{\text{NO}_3}) \cdot \text{rampc}([\text{O}_2]; K_{\text{O}_2})$$

with $K_{\text{NO}_3} = 10^{-5} \text{ mol/L} = 10^{-2} \text{ mol/m}^3$, and similarly for $[\text{OM}_s]$ (rate \hat{R}_{16}).

5.1.3 OM degradation by Mn(IV) reduction

Mn(IV) reduction (eqs. 4, 22, 34): proportional to concentration of organic carbon and solid-phase MnO_2

$$\hat{R}_3 = k_f(1 - \varphi) \cdot [\text{OM}_f] \cdot \text{ramp}([\text{MnO}_2]; K_{\text{MnO}_2}) \cdot \text{rampc}([\text{NO}_3^-]; K_{\text{NO}_3}) \cdot \text{rampc}([\text{O}_2]; K_{\text{O}_2})$$

with $K_{\text{MnO}_2} = 2 \times 10^{-6} \text{ mol/g}_{\text{ss}}$. This value can be converted to MEDUSA units, by noting that $K_{\text{MnO}_2} / [\text{kg/m}_{\text{ss}}^3] = K_{\text{MnO}_2} / [\text{mol/g}_{\text{ss}}] \times M_{\text{MnO}_2} / [\text{kg/mol}] \times \rho_s / [\text{g}_{\text{ss}}/\text{cm}_{\text{ss}}^3] \times 10^6$, where the factor 10^6 is $1 \text{ g}_{\text{ss}}/\text{cm}_{\text{ss}}^3 / [\text{g}_{\text{ss}}/\text{m}_{\text{ss}}^3]$. Hence $K_{\text{MnO}_2} / [\text{kg/m}_{\text{ss}}^3] = 2 \times 10^{-6} \times 0.08694 \times 2.5 \times 10^6 = 0.4347$.

5.1.4 OM degradation by Fe(III) reduction

Fe(III) reduction (eqs. 5, 23, 35): proportional to concentration of organic carbon and solid-phase $\text{Fe}(\text{OH})_3$, resp.

$$\hat{R}_4 = k_f(1 - \varphi) \cdot [\text{OM}_f] \cdot \text{ramp}([\text{Fe}(\text{OH})_3]; K_{\text{Fe}(\text{OH})_3}) \cdot \text{rampc}([\text{MnO}_2]; K_{\text{MnO}_2}) \cdot \text{rampc}([\text{NO}_3^-]; K_{\text{NO}_3}) \cdot \text{rampc}([\text{O}_2]; K_{\text{O}_2})$$

with $K_{\text{Fe}(\text{OH})_3} = 5 \times 10^{-6} \text{ mol/g}_{\text{ss}}$. In MEDUSA units, $K_{\text{Fe}(\text{OH})_3} / [\text{kg/m}_{\text{ss}}^3] = K_{\text{Fe}(\text{OH})_3} / [\text{mol/g}_{\text{ss}}] \times M_{\text{Fe}(\text{OH})_3} / [\text{kg/mol}] \times \rho_s / [\text{g}_{\text{ss}}/\text{cm}_{\text{ss}}^3] \times 10^6$. Therefore, $K_{\text{Fe}(\text{OH})_3} / [\text{kg/m}_{\text{ss}}^3] = 5 \times 10^{-6} \times 0.08986 \times 2.5 \times 10^6 = 1.123$.

5.1.5 Ammonium oxidation by O_2

Oxidation of NH_4^+ by O_2 (eq. 24): first order in both $[\text{NH}_4^+]$ and $[\text{O}_2]$.

$$\hat{R}_7 = k_7 \varphi \cdot [\text{NH}_4^+] \cdot [\text{O}_2]$$

The rate constant k_7 is set to $10^7 (\text{mol/L})^{-1} \text{yr}^{-1} = 10^4 (\text{mol/m}^3)^{-1} \text{yr}^{-1}$.

5.1.6 Mn oxidation by O_2

For Mn oxidation by O_2 (eqs. 9, 25, 37), proportional in $[\text{Mn}^{2+}]$ and $[\text{O}_2]$:

$$\hat{R}_8 = k_{\text{mox}} \varphi \cdot [\text{Mn}^{2+}] \cdot [\text{O}_2]$$

The rate constant k_8 is set to $10^9 (\text{mol/L})^{-1} \text{yr}^{-1} = 10^6 (\text{mol/m}^3)^{-1} \text{yr}^{-1}$.

5.1.7 Fe oxidation by O_2

Oxidation of Fe^{2+} by O_2 (eqs. 10, 26, 38): first order in both $[\text{Fe}^{2+}]$ and $[\text{O}_2]$

$$\hat{R}_9 = k_9 \varphi \cdot [\text{Fe}^{2+}] \cdot [\text{O}_2]$$

The rate constant k_9 is set to $10^9 (\text{mol/L})^{-1} \text{yr}^{-1} = 10^6 (\text{mol/m}^3)^{-1} \text{yr}^{-1}$.

5.1.8 Fe oxidation by solid MnO₂

Oxidation of Fe²⁺ by solid MnO₂ (eq. 27): first order in both [Fe²⁺] and [MnO₂]

$$\hat{R}_{10} = k_{10}(1 - \varphi) \cdot [\text{Fe}^{2+}] \cdot [\text{MnO}_2]$$

The rate constant k_{10} is set to $10^4 \text{ (mol/L)}^{-1}\text{yr}^{-1} = 10 \text{ (mol/m}^3\text{)}^{-1}\text{yr}^{-1}$.

6 Material and milieu characteristics

Exponentially decreasing porosity profiles is used. The control parameter values (porosity at the sediment-water interface, asymptotic porosity and scale of decrease) depend on each site and are taken from Table 2 in Jourabchi et al. (2008).

7 Grid

From the information provided in (Jourabchi et al., 2008), the model sediment extends to a depth of 82 cm. No information is given on the number of grid elements. It is only specified that the grid has a variable resolution, ranging from 0.01 cm near the sediment-water interface to 2 cm at the bottom of the modelled domain. Here, we use a grid with 321 nodes, distributed quadratically near the surface and shifting to a linear distribution towards the bottom.

8 Transport parameters

In the absence of independent estimates for the transport parameters (biodiffusion coefficient, advection rate), Jourabchi et al. (2008) call upon empirical relationships between these parameters and water depth established by Middelburg et al. (1997) to derive the required information for the different sites.

8.1 Advection

The *sedimentation rate* parameter, denoted by ω in Jourabchi et al. (2008), derives from the relationship (Middelburg et al., 1997)

$$\omega / [\text{cm/yr}] = 10^{(-0.87478367 - 0.00043512 \times Z / [\text{m}])} \times 3.3 \quad (45)$$

The notation and the terminology used by Jourabchi et al. (2008) is unfortunately somewhat ambiguous, as the mass balance equations solved by BRNS-GLOBAL include an ω that is depth-dependent (see the electronic annex to the paper). According to Middelburg et al. (1997), the above relationship is for the sediment accumulation rate. For the sake of clarity, we therefore denote the rate derived from eq. (45) by ω_{acc} hereafter. In BRNS, reaction processes do not have any impact on the transport parameters (Aguilera et al., 2005).^{*} We therefore adopt the following relationship to calculate the advection rate profile $\omega(z)$:

$$\omega(z)(1 - \varphi(z)) = \omega_{\text{acc}}(1 - \varphi_{\infty}) \quad (46)$$

where φ_{∞} is the asymptotic porosity at great depth. In MEDUSA the advection rate profile is normally also influenced by the volume loss due to reactions. This dependency can nevertheless be ignored by using the the `-DSOLIDS.VOLUMELESS` option at compile time. This sets the partial specific volumes (ϑ) of all solids except for the main inert solid (dubbed clay here) to zero and

^{*}The effect of chemical reactions on the compaction in deep-sea sediments was analysed in a subsequent study by Jourabchi et al. (2010).

thus cancels the influence of chemical reactions, as they do not lead to volume changes any more. The clay deposition rate at the sediment-water interface is then chosen so that $\omega_{\text{acc}}(1 - \varphi_{\infty}) = F_{\text{clay}}\theta_{\text{clay}}$. The advection rate profile then exactly follows the profile defined by eq. (46).

8.2 Bioturbation

Bioturbation is represented as a diffusive process (biodiffusion). Jourabchi et al. (2008) assume that the bioturbation coefficient that controls this process decreases with depth below the sediment-water interface, “following a complementary error function whose value falls to 50% at a depth of 20 cm.” Unfortunately, the scale of the decrease is not reported. Jourabchi et al. (2005) nevertheless specify that they use

$$D_b(x) = \frac{D_{b0}}{2} \operatorname{erfc}\left(\frac{x - 20}{4}\right) \quad (47)$$

where erfc is the complementary error function, D_{b0} the value that D_b takes near the sediment-water interface and x denotes depth below the sediment-water interface in centimetres. As this expression is consistent with the description in Jourabchi et al. (2008), we use it to set the depth-dependent biodiffusion coefficient. The bioturbation coefficient D_{b0} near the surface of the sediment is calculated from the empirical relationship between D_b values based up ^{210}Pb and water depth from Middelburg et al. (1997):

$$D_{b0}/[\text{cm}^2/\text{yr}] = 10^{(0.76241122 - 0.00039724 \times Z/[\text{m}])} \times 5.2 \quad (48)$$

A Organic Matter Degradation: Sequence of Oxidants and Inhibitors

Here we show how the rate law expressions used by Jourabchi et al. (2008) for the sequence of organic matter degradation by different oxidants in a simpler and more compact way allowing easier differentiation.

The model uses ramp functions and complementary ramp functions to parametrize dependencies of rate laws and of inhibition effects:

$$\text{ramp}(c; K) = \begin{cases} 0 & \text{for } c \leq 0 \\ c/K & \text{for } 0 \leq c \leq K \\ 1 & \text{for } K \leq c \end{cases}$$

and

$$\text{rampc}(c; K) = 1 - \text{ramp}(c; K)$$

where $K > 0$ is a constant critical concentration.

A.1 First oxidant

The oxidation rate of component ‘O’ (concentration O) by the first oxidant (typically O_2) of concentration C_1 is:

$$R_1 = f_1 k O$$

where

$$f_1 = \begin{cases} 1 & \text{for } C_1 > K_1 \\ C_1/K_1 & \text{for } C_1 \leq K_1 \end{cases}$$

or, equivalently, by definition

$$f_1 = \text{ramp}(C_1; K_1).$$

A.2 Second oxidant

The oxidation rate of component 'O' (concentration O) by the second oxidant (typically NO_3^-) is:

$$R_2 = f_2 k O$$

where

$$f_2 = \begin{cases} 0 & \text{for } f_1 = 1 \\ (1 - f_1) & \text{for } f_1 < 1 \text{ and } C_2 > K_2 \\ (1 - f_1)C_2/K_2 & \text{for } f_1 < 1 \text{ and } C_2 \leq K_2 \end{cases}$$

This can obviously be reformulated in an equivalent way as

$$f_2 = \begin{cases} (1 - f_1) & \text{for } f_1 \leq 1 \text{ and } C_2 > K_2 \\ (1 - f_1)C_2/K_2 & \text{for } f_1 \leq 1 \text{ and } C_2 \leq K_2 \end{cases}$$

Since $f_1 \leq 1$ anyway, the condition on f_1 is redundant

$$f_2 = \begin{cases} (1 - f_1) & \text{for } C_2 > K_2 \\ (1 - f_1)C_2/K_2 & \text{for } C_2 \leq K_2 \end{cases}$$

Hence

$$f_2 = (1 - f_1) \cdot \text{ramp}(C_2; K_2) = \text{ramp}(C_1; K_1) \cdot \text{ramp}(C_2; K_2)$$

A.3 Third oxidant

The oxidation rate of component 'O' (concentration O) by the third oxidant (typically Mn(IV)) is:

$$R_3 = f_3 k O$$

where

$$f_3 = \begin{cases} 0 & \text{for } f_1 + f_2 = 1 \\ (1 - f_1 - f_2) & \text{for } f_1 + f_2 < 1 \text{ and } C_3 > K_3 \\ (1 - f_1 - f_2)C_3/K_3 & \text{for } f_1 + f_2 < 1 \text{ and } C_3 \leq K_3 \end{cases}$$

This can obviously again be reformulated in an equivalent way as

$$f_3 = \begin{cases} (1 - f_1 - f_2) & \text{for } f_1 + f_2 \leq 1 \text{ and } C_3 > K_3 \\ (1 - f_1 - f_2)C_3/K_3 & \text{for } f_1 + f_2 \leq 1 \text{ and } C_3 \leq K_3 \end{cases}$$

$$\begin{aligned} 1 - f_1 - f_2 &= 1 - f_1 - (1 - f_1) \cdot \text{ramp}(C_2; K_2) \\ &= (1 - f_1) \cdot (1 - \text{ramp}(C_2; K_2)) \\ &= \text{ramp}(C_1; K_1) \cdot \text{ramp}(C_2; K_2) \\ &= \prod_{i=1}^2 \text{ramp}(C_i; K_i) \end{aligned}$$

Hence,

$$0 \leq 1 - f_1 - f_2 \leq 1$$

and thus

$$-1 \leq f_1 + f_2 - 1 \leq 0$$

and finally

$$0 \leq f_1 + f_2 \leq 1$$

Therefore, the condition on $f_1 + f_2$ is redundant and we may rewrite f_3 as

$$\begin{aligned} f_3 &= (1 - f_1 - f_2) \cdot \text{ramp}(C_3; K_3) \\ &= \text{ramp}(C_1; K_1) \cdot \text{ramp}(C_2; K_2) \cdot \text{ramp}(C_3; K_3) \end{aligned}$$

A.4 Fourth oxidant

The oxidation rate of component 'O' (concentration O) by the fourth oxidant (typically Fe(III)) is:

$$R_4 = f_4 k O$$

where

$$f_4 = \begin{cases} 0 & \text{for } f_1 + f_2 + f_3 = 1 \\ (1 - f_1 - f_2 - f_3) & \text{for } f_1 + f_2 + f_3 < 1 \text{ and } C_4 > K_4 \\ (1 - f_1 - f_2 - f_3)C_4/K_4 & \text{for } f_1 + f_2 + f_3 < 1 \text{ and } C_4 \leq K_4 \end{cases}$$

This can obviously again be reformulated in an equivalent way as

$$f_4 = \begin{cases} (1 - f_1 - f_2 - f_3) & \text{for } f_1 + f_2 + f_3 \leq 1 \text{ and } C_4 > K_4 \\ (1 - f_1 - f_2 - f_3)C_4/K_4 & \text{for } f_1 + f_2 + f_3 \leq 1 \text{ and } C_4 \leq K_4 \end{cases}$$

$$\begin{aligned} 1 - f_1 - f_2 - f_3 &= 1 - f_1 - f_2 - (1 - f_1 - f_2) \cdot \text{ramp}(C_3; K_3) \\ &= (1 - f_1 - f_2) \cdot (1 - \text{ramp}(C_3; K_3)) \\ &= \text{rampc}(C_1; K_1) \cdot \text{rampc}(C_2; K_2) \cdot \text{rampc}(C_3; K_3) \\ &= \prod_{i=1}^3 \text{rampc}(C_i; K_i) \end{aligned}$$

Hence,

$$0 \leq 1 - f_1 - f_2 - f_3 \leq 1$$

and again

$$0 \leq f_1 + f_2 + f_3 \leq 1.$$

Therefore, the condition on $f_1 + f_2 + f_3$ is, once again, redundant, and we may rewrite f_4 as

$$\begin{aligned} f_4 &= (1 - f_1 - f_2 - f_3) \cdot \text{ramp}(C_4; K_4) \\ &= \text{rampc}(C_1; K_1) \cdot \text{rampc}(C_2; K_2) \cdot \text{rampc}(C_3; K_3) \cdot \text{ramp}(C_4; K_4) \end{aligned}$$

A.5 Oxidant $N - 1$

From the preceding, it can be demonstrated that we have, for I oxidants whose oxidation rates follow the scheme outlined before,

$$1 - \sum_{i=1}^I f_i = \prod_1^I \text{rampc}(C_i; K_i).$$

The oxidation rate of component 'O' (concentration O) by oxidant $N - 1$ (typically CO_4^{2-}) is:

$$R_{N-1} = f_{N-1} k O$$

where

$$\begin{aligned} f_{N-1} &= \left(1 - \sum_1^{N-2} f_i\right) \cdot \text{ramp}(C_{N-1}; K_{N-1}) \\ &= \left(\prod_1^{N-2} \text{rampc}(C_i; K_i)\right) \cdot \text{ramp}(C_{N-1}; K_{N-1}) \end{aligned}$$

A.6 Oxidant N

The oxidation rate of component 'O' (concentration O) by the last oxidant N (typically 'O' itself – by fermentation) is

$$R_N = f_N k O$$

where, in deviation to the previous,

$$f_N = 1 - \sum_1^{N-1} f_i.$$

Accordingly,

$$\begin{aligned} f_N &= 1 - \sum_1^{N-2} f_i - f_{N-1} \\ &= 1 - \sum_1^{N-2} f_i - (1 - \sum_1^{N-2} f_i) \cdot \text{ramp}(C_{N-1}; K_{N-1}) \\ &= (1 - \sum_1^{N-2} f_i) \cdot \text{ramp}(C_{N-1}; K_{N-1}) \\ &= \left(\prod_1^{N-2} \text{ramp}(C_i; K_i) \right) \cdot \text{ramp}(C_{N-1}; K_{N-1}) \\ &= \prod_1^{N-1} \text{ramp}(C_i; K_i). \end{aligned}$$

Obviously, by construction,

$$\sum_1^N f_i = 1$$

and thus

$$\sum_{i=1}^N R_N = \sum_1^N f_i k O = k O \sum_1^N f_i = k O.$$

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