

Radi.jl

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Abstract

Radi.jl is the one-dimensional reactive-advective-diffusive-irrigative diagenetic sediment module implemented in Julia. Here, we define the variables and the equations used in this implementation. This document focuses on the mathematics of the model and this specific implementation. It is not intended to explain the underlying science.

1 Model grid

1.1 Time

Time units are always in years.

- T (`stoptime` in a) is the total time that the model runs for.
- dt (`interval` in a) is the time resolution (i.e. the interval between each timestep).
- t (`timesteps` in a) refers to the array of modelled timepoints.

The model therefore runs from time 0 to T in intervals of dt .

1.2 Depth within the sediment

Depth units are always in metres.

- Z (`z_max` in m) is the total height of the sediment column being modelled.
- dz (`z_res` in m) is the depth resolution (i.e. the height of each model layer).
- z (`depths` in m) refers to the array of modelled depths within the sediment.

The model layers are therefore at depths within the sediment from 0 to Z in increments of dz , where 0 represents the interface between the surface sediment and overlying seawater.

2 Parameters

Model parameters are the external drivers of the simulation. They can either be constant or vary through time, but either way they cannot be affected by the processes operating in the sediment.

2.1 Overlying water

Properties of the water immediately above the sediment surface:

- T_w (T in $^{\circ}\text{C}$) is the conservative temperature.
- S_w (S in $\text{g}\cdot\text{kg}^{-1}$) is the absolute salinity.
- $\rho(w)$ is the seawater density (rho_sw in $\text{kg}\cdot\text{m}^{-3}$), calculated from salinity, temperature and pressure using the function `gsw_rho` of McDougall and Barker [2011]. **Currently just using pressure = 1.**
- $[\text{O}_2]_w$ (`oxy_w` in $\text{mol}\cdot\text{m}^{-3}$) is the seawater dissolved oxygen concentration.
- $[\text{PO}_4]_w$ (`po4_w` in $\text{mol}\cdot\text{m}^{-3}$) is the seawater total dissolved phosphate concentration.
- δ (`dbl` in m) is the diffusive boundary layer thickness.

Note that T is also used for the total model runtime...

2.2 Organic matter

2.2.1 Stoichiometry

Particulate organic matter (POM) is assumed to consist of:

$$(\text{CH}_2\text{O})_c(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p \quad (1)$$

which requires c moles of dissolved oxygen (O_2) to completely degrade into CO_2 , NH_3 , H_3PO_4 and H_2O . **In the future it should be possible to use a different C:O₂ ratio here.**

The “Redfield” ratios for the stoichiometry of POM are calculated as follows. For carbon (c) and phosphorus (p), following Galbraith and Martiny [2015]:

$$\text{RC} = c/p = \left(\frac{6.9 \cdot [\text{PO}_4]_w}{\rho(w) \cdot 10^{-3}} + 6 \cdot 10^{-3} \right)^{-1} \quad (2)$$

For nitrogen (n) and p , following Martiny et al. [2013] at 60 $^{\circ}\text{S}$:

$$\text{RN} = n/p = 11 \quad (3)$$

By convention:

$$\text{RP} = p = 1 \quad (4)$$

2.2.2 Flux of POM to the seafloor

The total mass flux of POM arriving at the seafloor is G_T (`Ftot` in $\text{g}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$).

Given the following relative molecular masses:

- $M_{\text{CH}_2\text{O}} = M(\text{CH}_2\text{O}) = 30.031 \text{ g}\cdot\text{mol}^{-1}$;
- $M_{\text{NH}_3} = M(\text{NH}_3) = 17.031 \text{ g}\cdot\text{mol}^{-1}$; and
- $M_{\text{H}_3\text{PO}_4} = M(\text{H}_3\text{PO}_4) = 97.994 \text{ g}\cdot\text{mol}^{-1}$;

the molar mass of POM ($M(\text{POM})$, `M_POM` in $\text{g}\cdot\text{mol}^{-1}$) is therefore:

$$\text{M_POM} = M(\text{POM}) = cM(\text{CH}_2\text{O}) + nM(\text{NH}_3) + pM(\text{H}_3\text{PO}_4) \quad (5)$$

The molar flux of POM to the seafloor (F_T , `Ftot_mol` in $\text{mol}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$) is:

$$\text{Ftot_mol} = F_T = \frac{G_T}{M(\text{POM})} \quad (6)$$

and the molar particulate organic carbon (POC) flux (F_c , `Foc` in $\text{mol}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$):

$$\text{Foc} = F_c = cF_T \quad (7)$$

2.3 Porosity and tortuosity

In the current set-up of `RADI.jl`, the porosity parameters ϕ_∞ and ϕ_0 are set to 0.74 and 0.85 respectively (`phiInf` and `phi0`, both dimensionless), and $\beta = 33 \text{ m}^{-1}$ (`beta`). These values were obtained by fitting real data from station 7, mooring 3 of cruise NBP98-2 [Sayles et al., 2001].

The porosity (ϕ_z , `phi`, dimensionless) is parameterised following Boudreau [1996b]:

$$\text{phi} = \phi_z = \phi_\infty + (\phi_0 - \phi_\infty) \exp(-\beta z) \quad (8)$$

The corresponding “solid porosity” ($\phi_{s,z}$, `phiS`, dimensionless) is:

$$\text{phiS} = \phi_{s,z} = 1 - \phi_z \quad (9)$$

`RADI.jl` also uses the related convenience variable `phiS_phi` = $\phi_{s,z}/\phi_z$.

The derivatives of the porosities with respect to z are:

$$\text{delta_phi} = \frac{d\phi_z}{dz} = -\beta(\phi_0 - \phi_\infty) \exp(-\beta z) \quad (10)$$

$$\text{delta_phiS} = \frac{d\phi_{s,z}}{dz} = -\frac{d\phi_z}{dz} \quad (11)$$

Following Boudreau [1996a], the sediment tortuosity ($\theta_z^2 = \text{tort2}$, $\theta_z = \text{tort}$, dimensionless) is:

$$\text{tort2} = \theta_z^2 = 1 - 2 \log \phi_z \quad (12)$$

Its derivative with respect to z is:

$$\text{delta_tort2i} = \frac{d(1/\theta_z^2)}{dz} = \frac{2d\phi_z/dz}{\phi_z \theta_z^4} \quad (13)$$

2.4 Bioturbation

Following Archer et al. [2002], the surface sediment bioturbation coefficient b_0 (`D_bio_0` in $\text{m}^2\cdot\text{a}^{-1}$) is:

$$\text{D_bio_0} = b_0 = (0.0232 \cdot 10^{-4})(F_c \cdot 10^2)^{0.85} \quad (14)$$

The bioturbation coefficient propagates down through the sediment as b_z (D_{bio} in $\text{m}^2 \cdot \text{a}^{-1}$):

$$D_{\text{bio}} = b_z = b_0 \exp(-[z/\lambda_b]^2) \cdot \frac{[\text{O}_2]_w}{[\text{O}_2]_w + 0.02 \cdot \text{mol} \cdot \text{m}^{-3}} \quad (15)$$

where λ_b (lambda_b in m) is the characteristic depth of 0.08 m, following Sayles et al. [2001]. **The magic 0.02 number comes from Archer et al. [2002], it is the "half-saturation constant" for oxygen (i.e. the concentration needed for bioturbators to act at half their maximum speed).**

Its derivative with respect to z is:

$$\text{delta_D_bio} = \frac{db_z}{dz} = -\frac{2zb_z}{\lambda_b^2} \quad (16)$$

2.4.1 Organic matter degradation

The rate constant k_z for organic matter degradation ($k_{\text{refractory}}$ in a^{-1}) is [Archer et al., 2002]:

$$k_{\text{refractory}} = k_z = 80.25 b_0 \exp(-z) \quad (17)$$

2.5 Advection through burial

The bulk burial velocity at the sediment-water interface (x_0 , x0 in $\text{m} \cdot \text{a}^{-1}$) is:

$$\text{x0} = x_0 = \frac{G_T}{\rho(\text{POM}) \cdot \phi_{s,0}} \quad (18)$$

where $\rho(\text{POM}) = 2.65 \cdot 10^6 \cdot \text{g} \cdot \text{m}^{-3}$ (rho_pom) is the density of particulate organic matter (POM). The bulk burial velocity at "infinite" depth in the sediment (x_∞ , xinf in $\text{m} \cdot \text{a}^{-1}$) is:

$$\text{xinf} = x_\infty = x_0 \phi_{s,0} / \phi_{s,z} \quad (19)$$

The porewater burial velocity (u_z , u in $\text{m} \cdot \text{a}^{-1}$) is therefore:

$$\text{u} = u_z = x_\infty \phi_z / \phi_z \quad (20)$$

and the solid burial velocity (w_z , w in $\text{m} \cdot \text{a}^{-1}$) is:

$$\text{w} = w_z = x_\infty \phi_{s,z} / \phi_{s,z} \quad (21)$$

$P_{e_h,z}$ (Peh) is one-half of the cell Peclet number, following Boudreau [1996b]:

$$\text{Peh} = P_{e_h,z} = w_z dz / (2b_z) \quad (22)$$

where σ_z (sigma) is:

$$\text{sigma} = \sigma_z = 1 / \tanh(P_{e_h,z}) - 1 / P_{e_h,z} \quad (23)$$

3 Variables

Model variables are the results of the simulation. Their values cannot be directly controlled, but rather emerge from the modelled parameters and processes.

There are two arrays for each variable in `RADI.jl`. In general, the values of the variable at the current timestep are `var`, while the values from the previous timestep are stored as `var0`.

3.1 Porewater solutes

Within the sediment porewaters:

- $[O_2]$ (oxy, oxy0 in $\text{mol} \cdot \text{m}^{-3}$) is the dissolved oxygen concentration.

3.2 Solids

Within the sediment itself:

- $[POC]$ (poc, poc0 in $\text{mol} \cdot \text{m}^{-3}$) is the particulate organic carbon concentration.

4 Master equation

For each modelled variable v at time t and depth z :

$$v_{(t+dt),z} = v_{t,z} + [R_{t,z}(v) + A_{t,z}(v) + D_{t,z}(v) + I_{t,z}(v)] \cdot dt \quad (24)$$

where:

- $R_{t,z}(v)$ quantifies the rate of change of $v_{t,z}$ due to **reactions** (section 5).
- $A_{t,z}(v)$ quantifies the rate of change of $v_{t,z}$ due to **advection** (section 6).
- $D_{t,z}(v)$ quantifies the rate of change of $v_{t,z}$ due to **diffusion** (section 7).
- $I_{t,z}(v)$ quantifies the rate of change of $v_{t,z}$ due to **irrigation** (section 8).

In general, only the subscript zs are explicitly written out in this document. The ts are implicit but excluded for clarity.

4.1 Above and below the modelled sediment

Advection and diffusion processes require values for each model variable not only at the depth being modelled (z) but also in the layers above and below ($z - dz$ and $z + dz$). These values exist within the sediment (i.e. $0 < z < Z$) but not at its extremes. At the sediment-water interface ($z = 0$) we require a value for the variable at $z = -dz$, effectively within the overlying water. At the very bottom of the modelled sediment ($z = Z$) we require a value for the next layer down, at $z = Z + dz$.

Effective values of each variable in these “next layers” just beyond the modelled domain are calculated following Boudreau [1996b]. These effective values can then be used to calculate the effects of advection and diffusion in the top and bottom layers using exactly the same equations as within the sediment itself.

4.1.1 Above the sediment-water interface

Following Boudreau [1996b], we calculate advection and diffusion at $z = 0$ using following substitutions for solutes:

$$v_{(-dz)} = v_{dz} + \frac{2\theta^2 dz}{\delta} (v_w - v_0) \quad (25)$$

and for solids:

$$v_{(-dz)} = v_{dz} + \frac{2dz}{b_0} \left(\frac{F_v}{\phi_{s,0}} - w_0 v_0 \right) \quad (26)$$

4.1.2 Below the bottom of the modelled sediment

At sediment depth $z = Z$ only, $v_{(Z+dz)}$ falls outside the depth range of the model. However, the model has a boundary condition demanding that the slope of each variable with respect to z is zero at the bottom of the modelled domain. This dictates that:

$$v_{(Z+dz)} = v_{(Z-dz)} \quad (27)$$

Therefore (27) is used to calculate advection and diffusion at $z = Z$ for both solutes and solids.

5 Reaction

Biogeochemical reactions operate on solutes and solids throughout the entire sediment column, including the very top and bottom layers. $R_z(v)$ is the net rate at which v is being consumed (negative R_z) or created (positive R_z) by these reactions.

5.1 Organic matter degradation

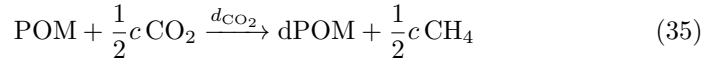
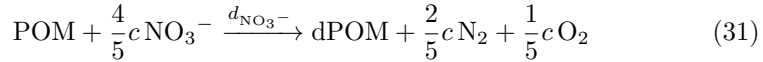
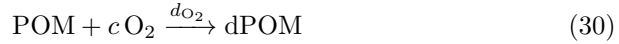
5.1.1 Pathways

For convenience:

$$\text{POM} = (\text{CH}_2\text{O})_c(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p(\text{s}) \quad (28)$$

$$\text{dPOM} = c \text{CO}_2(\text{aq}) + n \text{NH}_3(\text{aq}) + p \text{H}_3\text{PO}_4(\text{aq}) \quad (29)$$

The pathways, simplified to include only the species tracked by the model:



Each of the reactions above can be balanced by adding to the products the appropriate amounts of OH^- to balance the charges and then H_2O to balance the residual H and O budgets.

These degradation reactions are all first-order with respect to all reactants. The rate constants (d) follow a Monod scheme, as follows. Each reactant v has an *inhibition factor*, denoted f' :

$$f'(v) = \frac{k'(v)}{k'(v) + [v]} \quad (36)$$

where the k' are inhibition constants following Soetaert et al. [1996] and van Cappellen and Wang [1996]. There are a corresponding set of k reaction constants.

The respiration pathway rate constants (d) for the reactions above are composed from the reaction constants and inhibition factors:

$$d_{\text{O}_2} = \frac{[\text{O}_2]}{k(\text{O}_2) + [\text{O}_2]} \quad (37)$$

$$d_{\text{NO}_3^-} = \frac{[\text{NO}_3^-]}{k(\text{NO}_3^-) + [\text{NO}_3^-]} \cdot f'_{\text{O}_2} \quad (38)$$

$$d_{\text{MnO}_2} = \frac{[\text{MnO}_2]}{k(\text{MnO}_2) + [\text{MnO}_2]} \cdot f'_{\text{O}_2} f'_{\text{NO}_3} \quad (39)$$

$$d_{\text{Fe}(\text{OH})_3} = \frac{[\text{Fe}(\text{OH})_3]}{k(\text{Fe}(\text{OH})_3) + [\text{Fe}(\text{OH})_3]} \cdot f'_{\text{O}_2} f'_{\text{NO}_3} f'_{\text{MnO}_2} \quad (40)$$

$$d_{\text{SO}_4^{2-}} = \frac{[\text{SO}_4^{2-}]}{k(\text{SO}_4^{2-}) + [\text{SO}_4^{2-}]} \cdot f'_{\text{O}_2} f'_{\text{NO}_3} f'_{\text{MnO}_2} f'_{\text{Fe}(\text{OH})_3} \quad (41)$$

$$d_{\text{CH}_4} = f'_{\text{O}_2} f'_{\text{NO}_3} f'_{\text{MnO}_2} f'_{\text{Fe}(\text{OH})_3} f'_{\text{SO}_4} \quad (42)$$

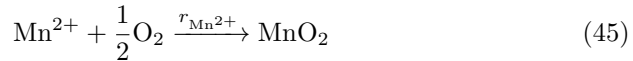
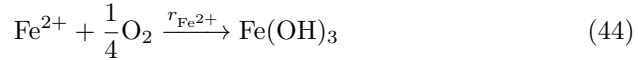
The overall reaction rate of each reaction is then given by:

$$R = kd \cdot [\text{POC}] \quad (43)$$

with separate k and $[\text{POC}]$ for the slow- and fast-reacting fractions.

5.1.2 Redox reactions

These reactions have been simplified to include only the species tracked by the model. They can be balanced by adding the appropriate quantities of H_2O , OH^- and/or H^+ .



These redox reactions are all first-order with respect to all reactants. The rate constants have constant values following Boudreau [1996b].

5.1.3 Previous version

Organic matter degradation affects dissolved oxygen and particulate organic carbon:

$$\text{R}_{\text{poc}} = R_z(\text{POC}) = -k_z[\text{POC}]_z \quad (48)$$

$$\text{R}_{\text{oxy}} = R_z(\text{O}_2) = R_z(\text{POC}) \cdot \phi_{s,z}/\phi_z \quad (49)$$

5.1.4 Validity check

The losses of O_2 and POC through organic matter degradation are coupled, so if one of these variables is exhausted then the other can no longer be used up. The initial calculations of the R_z values therefore represent the maximum possible changes. At each timestep, we test whether these are possible in the following sequence:

$$[O_2]_{(t+dt,z)} + R_{t,z}(O_2) \cdot dt < 0 \quad (50)$$

Note that the O_2 concentration tested is from the current (new) timepoint, after adding the effects of advection, diffusion, and irrigation, but before adding the reaction.

If equality (50) is true, then the values of $R_{t,z}(O_2)$ and $R_{t,z}(POC)$ are sequentially updated as follows:

$$R_{t,z}(O_2) = -[O_2]_{(t+dt,z)}/dt \quad (51)$$

$$R_{t,z}(POC) = R_{t,z}(O_2) \cdot \phi_{t,z}/\phi_{s,t,z} \quad (52)$$

Next, the validity of the current value of $R_{t,z}(POC)$ is tested:

$$[POC]_{(t+dt,z)} + R_{t,z}(POC) \cdot dt < 0 \quad (53)$$

If equality (53) is true, then the values of $R_{t,z}(POC)$ is updated as follows:

$$R_{t,z}(POC) = -[POC]_{(t+dt,z)}/dt \quad (54)$$

and finally $R_{t,z}(O_2)$ is updated with (49).

6 Advection

Advection is modelled differently for solutes and solids.

6.1 Advection of solutes

At sediment depth z , for solutes (e.g. O_2):

$$A_z(v) = - \left(u_z - \frac{d_z(v)}{\phi_z} \cdot \frac{d\phi_z}{dz} - d^\circ(v) \cdot \frac{d(1/\theta_z^2)}{dz} \right) \cdot \frac{v_{(z+dz)} - v_{(z-dz)}}{2dz} \quad (55)$$

6.2 Advection of solids

For solids (e.g. POC):

$$A_z(v) = - \left(w_z - \frac{db_z}{dz} - \frac{b_z}{\phi_{s,z}} \cdot \frac{d\phi_{s,z}}{dz} \right) \cdot \frac{(1 - \sigma_z)v_{(z+dz)} + 2\sigma_z v_z - (1 + \sigma_z)v_{(z-dz)}}{2dz} \quad (56)$$

7 Diffusion

7.1 Effective diffusion coefficients

Diffusion is controlled by each variable's effective diffusion coefficient, which varies with depth in the sediment (generically denoted $d_z(v)$ for variable v , `D_var`, always in $m^2 \cdot a^{-1}$).

7.1.1 Effective diffusion coefficients for solutes

Each solute has a “free-solution” molecular/ionic diffusion coefficient $d^\circ(v)$, which can be estimated from temperature, salinity and pressure. For dissolved oxygen, following Li and Gregory [1974]:

$$d^\circ(\text{O}_2) = 0.034862 + 0.001409T_w \quad (57)$$

The $d^\circ(v)$ can be converted into the $d_z(v)$ required by RADI following Boudreau [1996b]:

$$d_z(v) = \frac{d^\circ(v)}{(\theta_z)^2} \quad (58)$$

7.1.2 Effective diffusion coefficients for solids

For particulate organic carbon:

$$d_z(\text{POC}) = b_z \quad (59)$$

7.2 Diffusion within the sediment

At sediment depth z , where $0 < z < Z$, for both solutes and solids:

$$D(v_z) = d_z(v) \cdot (v_{(z-dz)} - 2v_z + v_{(z+dz)})/(dz)^2 \quad (60)$$

where $d_z(v)$ is the relevant diffusion coefficient.

8 Irrigation

Irrigation only affects the solutes, not the solids. Its effect varies with depth throughout the sediment:

$$I(v_z) = \alpha_z (v_w - v_z) \quad (61)$$

where α_z (**alpha** in a^{-1}) at the sediment-water interface (i.e. where $z = 0$, denoted α_0 , **alpha_0**) is, following **where does this equation actually come from?**:

$$\alpha_0 = 11 \left[\text{atan} \left(\frac{5F_c \cdot 10^2 - 400}{400\pi} \right) + 0.5 \right] - 0.9 + \frac{20[\text{O}_2]_w}{[\text{O}_2]_w + 0.01} \cdot \frac{F_c \cdot 10^2}{F_c \cdot 10^2 + 30} \cdot \exp \left(\frac{-[\text{O}_2]_w}{0.01} \right) \quad (62)$$

Within the sediment itself:

$$\alpha_z = \alpha_0 \exp[-(z/\lambda_i)^2] \quad (63)$$

where $\lambda_i = 0.05 \text{ m}$ (**lambda_i**) is the characteristic depth of Archer et al. [2002]. **The value of λ_i should be easily adjustable by the user.**

References

- D. E. Archer, J. L. Morford, and S. R. Emerson. A model of suboxic sedimentary diagenesis suitable for automatic tuning and gridded global domains. *Global Biogeochem. Cy.*, 16(1):17–17–21, 2002. doi: 10.1029/2000GB001288.
- B. P. Boudreau. The diffusive tortuosity of fine-grained unlithified sediments. *Geochim. Cosmochim. Acta*, 60(16):3139–3142, 1996a. doi: 10.1016/0016-7037(96)00158-5.
- B. P. Boudreau. A method-of-lines code for carbon and nutrient diagenesis in aquatic sediments. *Comput. Geosci.*, 22(5):479–496, 1996b. doi: 10.1016/0098-3004(95)00115-8.
- E. D. Galbraith and A. C. Martiny. A simple nutrient-dependence mechanism for predicting the stoichiometry of marine ecosystems. *Proc. Natl. Acad. Sci. U.S.A.*, 112(27):8199–8204, 2015. doi: 10.1073/pnas.1423917112.
- Y.-H. Li and S. Gregory. Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta*, 38(5):703–714, 1974. doi: 10.1016/0016-7037(74)90145-8.
- A. C. Martiny, C. T. A. Pham, F. W. Primeau, J. A. Vrugt, J. K. Moore, S. A. Levin, and M. W. Lomas. Strong latitudinal patterns in the elemental ratios of marine plankton and organic matter. *Nature Geosci.*, 6(4):279–283, 2013. doi: 10.1038/ngeo1757.
- T. J. McDougall and P. M. Barker. *Getting started with TEOS-10 and the Gibbs SeaWater (GSW) Oceanographic Toolbox*. SCOR/IAPSO WG127, 2011. ISBN 978-0-646-55621-5.
- F. L. Sayles, W. R. Martin, Z. Chase, and R. F. Anderson. Benthic remineralization and burial of biogenic SiO_2 , CaCO_3 , organic carbon, and detrital material in the Southern Ocean along a transect at 170° West. *Deep-Sea Res. Pt II*, 48(19):4323–4383, 2001. doi: 10.1016/S0967-0645(01)00091-1.
- K. Soetaert, P. M. J. Herman, and J. J. Middelburg. A model of early diagenetic processes from the shelf to abyssal depths. *Geochim. Cosmochim. Acta*, 60(6):1019–1040, 1996. doi: 10.1016/0016-7037(96)00013-0.
- P. van Cappellen and Y. Wang. Cycling of iron and manganese in surface sediments; a general theory for the coupled transport and reaction of carbon, oxygen, nitrogen, sulfur, iron, and manganese. *Am. J. Sci.*, 296(3):197–243, 1996. doi: 10.2475/ajs.296.3.197.