Accessory publication

A three-dimensional reactive transport model for sediments, incorporating microniches

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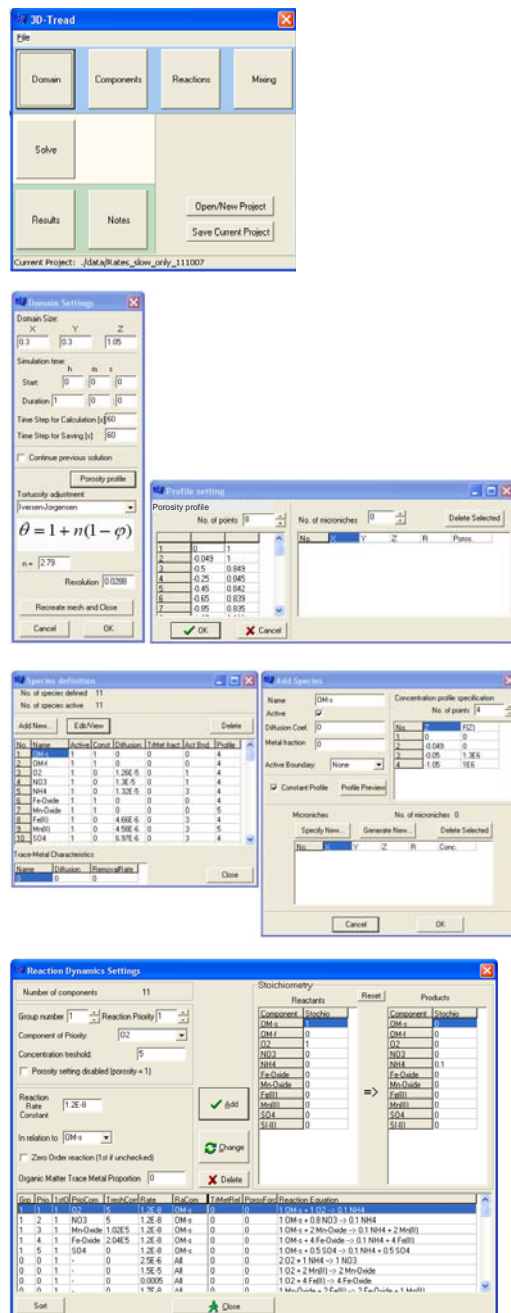[B]Corresponding author. Email: w.davison@lancaster.ac.uk

Fig. A1. User interface for 3-D TREAD. From top to bottom, left to right; menu screen that links to data input modules, domain settings input and porosity input, species list and species definition box, reaction setting box.

Model output

Simulation results are generated by the main calculations module in the form of text files that contain concentration values of every component saved for every specified time step at every node of the mesh. They are usually very large (up to hundreds of megabytes depending on simulation parameters and mesh complexity). Because it is impossible to interpret the 3-D results directly in such a format, a Results module is provided to present them in a graphical form. Users can specify any *x-y* or *y-x* cross-section of the domain to be plotted as a set of charts of concentration profiles (at that selected cross-section).

Resolution explained

As an approximation, the 'resolution' value can be assumed to be the minimum linear resolution resolved by the mesh. This is the case for the 3-D TREAD model as it uses maximum element size (maximum distance between nodes in element – MEL) as a mesh parameter in the GUI. If cubic elements were used, then the linear resolution would be equal to the maximum distance (elements arranged as bricks). As the mesh in our model uses tetrahedrons, then on the boundary, resolution is approximately MEL, while inside the domain it could be as high as ~MEL/1.7.

Further details on mesh implementation

The mesh, built of tetrahedral elements (each having four nodes), is interactively created to fit the desired shape of sediment column by specifying the overall distribution of the *x*, *y* and *z* coordinates. The nodes contain information about the porosity, φ, in the domain (and hence tortuosity by calculation) and the distribution of chemical components of defined concentrations (represented in the form of a vector for each species). Reactions and transport occur within all parts of the mesh. The model state updates are calculated at each timestep, which is specified by the user. Porosity can be specified for the entire domain as a function of depth and separately for each microniche.

A microniche in the model is defined as a location of a spherical shape within the domain, specified by the four values *x*, *y*, *z*, and *R*, where *x*, *y* and *z* are spatial coordinates and *R* is the radius. This specification of any microniches is transferred to the FEM mesh used for domain representation. Although commonly considered for organic matter (OM), microniches can be defined for any chemical component of the system. The user can specify microniches one by one using a dialogue window that sets their positions, size (radius) and component concentration.

Model implementation

The model was implemented in an Object Orientated fashion. Analysis of functionality was conducted to identify information carriers (such as species or reactions). Then all processes and routines were associated with appropriate data carriers based on their function. These information clusters – objects – were later used to define the calculation path for each simulation. New reactions can be added to the application without interfering with any other object (such as species or domain), allowing short

implementation times and limited errors, while sustaining system stability. It allows easy and efficient modifications and optimisations of the built-in functionality, providing a framework for future extensions.

The solving process takes advantage of the small timesteps and the small size of the mesh elements. It exploits the superposition principle, so that at each timestep we isolate the reaction equations from the transport equations and solve them in an interleaved manner. In other words, at each timestep the reaction and the transport equations are solved sequentially. This separation allows substantial flexibility in the reaction model. With this assumption, any reaction becomes an algebraic operation on a set of vectors of data. This approach allows introduction of a large number of reaction types without the constraints of the transport calculation engine interface.

We have used a uniform mesh for the model domain, where edges of the niche are not implemented as discrete boundaries. An alternative approach is to introduce spherical subdomains into the mesh, potentially allowing the specification of boundary conditions for the microniche–sediment interface. Although providing much better precision to the model, it is very difficult to implement in such a dynamic environment, where microniches (subdomains) may change in size (get smaller in time) and may be relocated at any time (simulation of particle relocation). Every such modification to the domain would require recreating the mesh and initiating the solver – according to our tests, this can take as long as 12% of the entire simulation time (when doing this once) depending on the number of timesteps in a simulation. After careful consideration, the uniform mesh approach was taken to allow easy definition and introduction of particle relocation mechanisms. Satisfactory results can be obtained by decreasing the mesh size (finer resolution), which does not introduce much longer simulation times even with many components in the system. Moreover, this approach makes the simulation time independent of the number of microniches, providing an excellent opportunity to build and solve very complex heterogeneous systems (consisting of multiple microniches) in hours.

Solutes are specified as porewater concentrations (per unit volume of solution) and the solid phases are specified as solid phase concentrations (per unit volume of dry sediment). As the model does not account for density of the solid phase, input concentrations relevant to solid phases need to be specified in volume units (of dry sediment) by prior correction using density (Eqn A1).

$$\text{mmol g}^{-1} \times \text{dry weight density (g cm}^{-3}） = \text{mmol cm}^{-3} = M \text{ (mol L}^{-1}) \tag{A1}$$

Additional options for microniche specification

A more advanced stochastic method has also been implemented, where a specified number of microniches are generated with predefined probability distributions (univariate, as a function of depth) for size, position and species concentrations of the simulated microniches.

In another development, a Monte Carlo technique can be optionally used to simulate the effects of mixing. This technique allows an exchange of two randomly chosen parts of the sediment matrix (the volume transferred is also randomly generated). Such processes mimic the microniche creation when the locations chosen for exchange have different biogeochemical characteristics.

Example equation for validation procedure

$$-d\,[\text{OM}] = k_{\text{OM}} \times \psi \times \left(\underbrace{\frac{[O_2]}{[O_2]_{\text{lim}}}}_{f_1} + \underbrace{\frac{[MnO_2]}{[MnO_2]_{\text{lim}}} \times \left[1 - \frac{[O_2]}{[O_2]_{\text{lim}}} \right]}_{f_2} + \underbrace{\frac{[FeOOH]}{[FeOOH]_{\text{lim}}} \times \left[1 - \frac{[O_2]}{[O_2]_{\text{lim}}} - \frac{[MnO_2]}{[MnO_2]_{\text{lim}}} \times \left[1 - \frac{[O_2]}{[O_2]_{\text{lim}}} \right] \right]}_{f_3} \right) [\text{OM}] \times t_s$$

Fig. A2. Change in organic matter (OM) concentration where three oxidants are available, all below their limiting concentrations. The fractional contribution of each primary reaction, f_j, is shown (see Eqn 3). To calculate production or loss of the reactant or product of an individual reaction with a single oxidant (e.g. Fe^{II} in the case of FeOOH), the value of f for that fraction only can be used. The product evolved from that reaction over a set timescale can then be calculated. The stoichiometry of the reaction equation also needs to be considered.

Tortuosity

Tortuosity (θ) is used to represent non-linear diffusion induced by physical constraints caused by particles in sediment. Boudreau[5] plotted several empirical porosity–tortuosity relationships together with observed values to determine those equations that gave the best fit. The three best-fitting relationships are available in the model, together with a relationship recently presented by Boudreau and Meysman.[44] An option is also available for tortuosity to be ignored. This may be useful if porosity is constant in a modelled domain and manual calculation of tortuosity is required (to test other relationships, for example). The equations and published best fit values are provided in Table A1. Best fit values are numbers for the equation variables (n, b, d, h, m) that give the closest relationship to the experimental data (see Boudreau[5]).

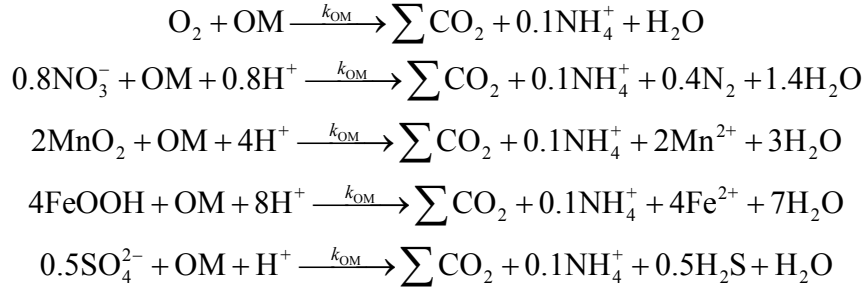**Table A1. Tortuosity options available in the 3-D TREAD model**

Label	Equation	Best fit values for equation variables	Reference
Iversen–Jørgensen[A]	$\theta^2 = 1 + n(1 - \varphi)$	$n = 2.79$[B]	Iversen and Jørgensen[44]
Modified Weissberg	$\theta^2 = 1 - b \times \ln(\varphi)$	$b = 2.02$[B]	Boudreau[5]
Modified Archie's Law	$\theta^2 = d \times \varphi^{(1-m)}$	$d = 1$[B] $m = 2.14$[B]	Boudreau[5]
Boudreau–Meysman	$\theta^2 = \left[1 + \frac{32h}{9\pi}(1 - \varphi) \right]^2$	$h = 1$[C]	Boudreau and Meysman[45]
No adjustment	$\theta^2 = 1$		

[A]A similar relationship was previously independently presented as the Burger–Frieke relationship (see Boudreau[5]). [B]Best fit values from Boudreau.[5] [C]Best fit value from Boudreau and Meysman.[45]

Data used as model input parameters

Table A2.   Primary and secondary reactions used to model microniche processes using the 3-D TREAD model (after Fossing et al.[41])

H_2O, H^+, N_2, $\sum CO_2$ and S^0 are included in the reaction stoichiometry for balancing, but are not modelled as reactants for these model simulations. Ammonium production in primary reactions is based on an organic matter (OM) $C:N$ ratio of 10

Primary reactions

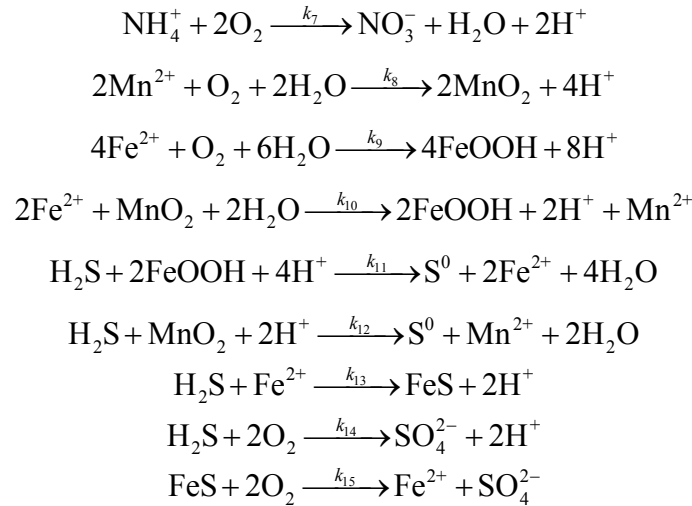$$O_2 + OM \xrightarrow{\ k_{OM}\ } \sum CO_2 + 0.1NH_4^+ + H_2O$$

$$0.8NO_3^- + OM + 0.8H^+ \xrightarrow{\ k_{OM}\ } \sum CO_2 + 0.1NH_4^+ + 0.4N_2 + 1.4H_2O$$

$$2MnO_2 + OM + 4H^+ \xrightarrow{\ k_{OM}\ } \sum CO_2 + 0.1NH_4^+ + 2Mn^{2+} + 3H_2O$$

$$4FeOOH + OM + 8H^+ \xrightarrow{\ k_{OM}\ } \sum CO_2 + 0.1NH_4^+ + 4Fe^{2+} + 7H_2O$$

$$0.5SO_4^{2-} + OM + H^+ \xrightarrow{\ k_{OM}\ } \sum CO_2 + 0.1NH_4^+ + 0.5H_2S + H_2O$$

Secondary reactions

$$NH_4^+ + 2O_2 \xrightarrow{\ k_7\ } NO_3^- + H_2O + 2H^+$$

$$2Mn^{2+} + O_2 + 2H_2O \xrightarrow{\ k_8\ } 2MnO_2 + 4H^+$$

$$4Fe^{2+} + O_2 + 6H_2O \xrightarrow{\ k_9\ } 4FeOOH + 8H^+$$

$$2Fe^{2+} + MnO_2 + 2H_2O \xrightarrow{\ k_{10}\ } 2FeOOH + 2H^+ + Mn^{2+}$$

$$H_2S + 2FeOOH + 4H^+ \xrightarrow{\ k_{11}\ } S^0 + 2Fe^{2+} + 4H_2O$$

$$H_2S + MnO_2 + 2H^+ \xrightarrow{\ k_{12}\ } S^0 + Mn^{2+} + 2H_2O$$

$$H_2S + Fe^{2+} \xrightarrow{\ k_{13}\ } FeS + 2H^+$$

$$H_2S + 2O_2 \xrightarrow{\ k_{14}\ } SO_4^{2-} + 2H^+$$

$$FeS + 2O_2 \xrightarrow{\ k_{15}\ } Fe^{2+} + SO_4^{2-}$$

Table A3. Model input parameters (from Fossing et al.[41] unless otherwise stated)

Parameter	Value
Domain (user defined)	x,y,z: 0.6, 0.6, 1.05 cm
	5- and 3.75-mm niches
	x,y,z: 0.3, 0.3, 1.05 cm
	2.5- and 1-mm niches
Resolution (user-defined)	0.0290 (smallest domain)
See text for explanation	0.0472 (largest domain)
Porosity	$\varphi = 0.763 + 0.086e^{-0.216x}$
(entered as finite values in the 3-D model)	microniche porosity = 0.8
Tortuosity option	Iversen–Jørgensen, n = 2.79
Diffusion coefficients (9°C)[A]	
O_2	12.6×10^{-6} cm^2 s^{-1}
NO_3^-	13.0×10^{-6} cm^2 s^{-1}
NH_4^-	13.2×10^{-6} cm^2 s^{-1}
SO_4^{2-}	6.97×10^{-6} cm^2 s^{-1}
$\sum H_2S$	12.9×10^{-6} cm^2 s^{-1}
Boundary conditions[B] U = Upper, L = lower	
[O_2]	U 200 μM
[NO_3^-]	U 5 μM; L 0 μM
[NH_4^-]	U 0.6 μM; L 50 μM
[SO_4^{2-}]	U and L 2000 μM
[ΣH_2S]	U 0 μM
Limiting concentrations	
[O_2]	Bulk 5 μM[C]
	Niche 0.4 μM
[NO_3^-]	Bulk 5 μM
	Niche 0.1 μM
[MnO_2]	Bulk 1.02×10^5 μM
[FeOOH]	Bulk 2.04×10^5 μM
Rate constants	
k_{OM-s}	1.2×10^{-8} s^{-1}
k_{OM-f}	9.6×10^{-6} s^{-1}
k_7	2.5×10^{-6} μM^{-1} s^{-1}
k_8	1.5×10^{-5} μM^{-1} s^{-1}
k_9	5.0×10^{-4} μM^{-1} s^{-1}
k_{10}	$1.7. \times 10^{-8}$ μM^{-1} s^{-1}
k_{11}	2.0×10^{-8} μM^{-1} s^{-1}
k_{12}	3.0×10^{-9} μM^{-1} s^{-1}
k_{13}	7.5×10^{-7} μM^{-1} s^{-1}
k_{14}	6.0×10^{-7} μM^{-1} s^{-1}
k_{15}	5.0×10^{-5} μM^{-1} s^{-1}

[A]Diffusion coefficients are calculated from equations presented in Boudreau[5]. [B]Fe and Mn are excluded as these concentrations are fixed in the modelled scenarios. Upper boundaries are obtained from the cited reference, lower conditions are user-defined (based on the 1-D profiles from the cited reference). [C]User-defined, other limiting concentration values for the microniche modelling taken from Fossing et al.[41] and niche values set at 2% of the values of Fossing et al.[41]
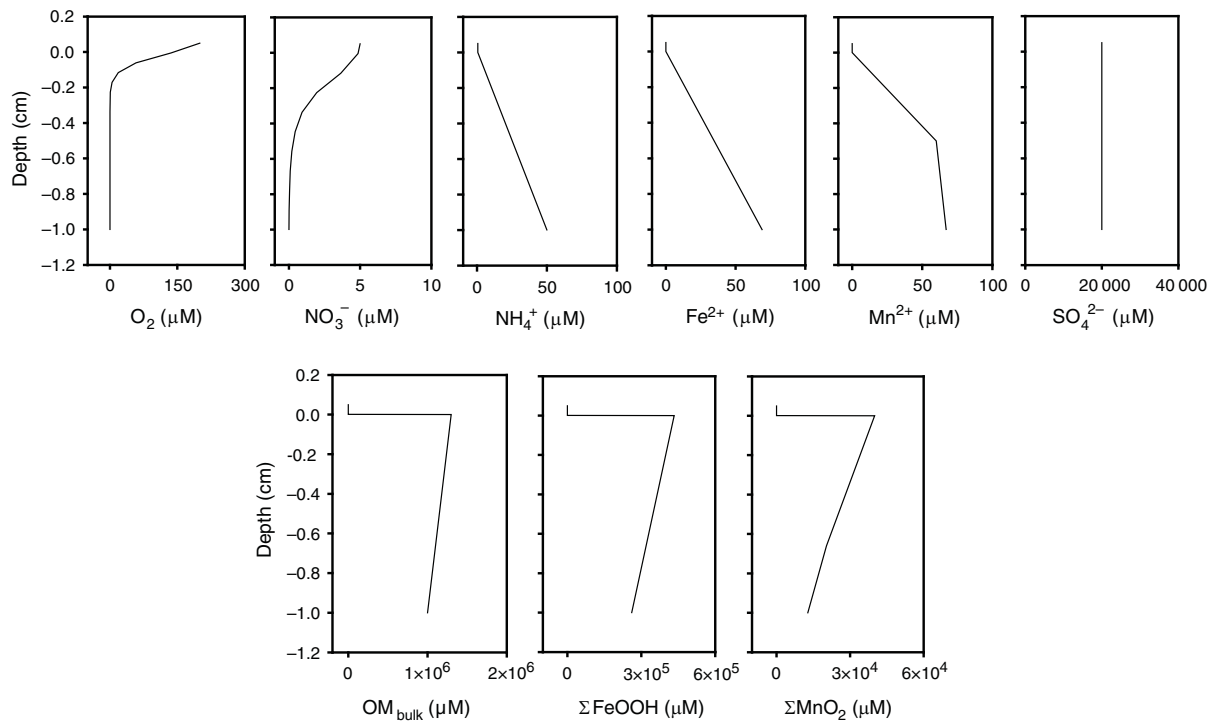
Initial Profiles

Fig. A3. Initial profile inputs. Oxygen and nitrate are based on steady-state profiles where no niches are present (i.e. bulk organic matter (OM) only). Other components are based on the data of Fossing et al.[41] Solid phases (bottom row) have been adjusted for density to give unified units.

Additional references

[44]   B. P. Boudreau, F. J. R. Meysman, Predicted tortuosity of muds. *Geology* **2006**, *34*, 693. doi:10.1130/G22771.1

[45]   N. Iversen, B. B. Jørgensen, Diffusion coefficients of sulfate and methane in marine sediments: influence of porosity. *Geochim. Cosmochim. Acta* **1993**, *57*, 571. doi:10.1016/0016-7037(93)90368-7