

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

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Environmental context

Modelling of discrete sites of diagenesis in sediments (microniches) has typically been performed in 1-D and has involved a limited set of components. Here we present a new 3-D model for microniches within a traditional vertical sequence of redox reactions, and show example modelled niches with a range of sizes, close to the sediment-water interface. Microniche processes may have implications for understanding trace metal diagenesis, via formation of sulphides. The model provides a quantitative framework for examining microniche data and concepts.

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Abstract

Most reactive transport models have represented sediments as one-dimensional (1-D) systems and have solely considered the development of vertical concentration gradients. However, application of recently developed micro-scale and 2-D measurement techniques have demonstrated more complicated solute structures in some sediments, including discrete localized sites of depleted oxygen, and elevated trace metals and sulphide, referred to as microniches. A model of transport and reaction in sediments, that can simulate the dynamic development of concentration gradients occurring in 3-D, was developed. Its graphical user interface (GUI) allows easy input of user-specified reactions and provides flexible schemes that prioritise their execution. The 3-D capability was demonstrated by quantitative modelling of hypothetical solute behaviour at organic matter microniches covering a range of sizes. Significant effects of microniches on the profiles of oxygen and nitrate are demonstrated. Sulphide is shown to be readily generated in microniches within one centimetre of the sediment surface, provided the diameter of the reactive organic material is greater than one millimetre. These modelling results illustrate the geochemical complexities that arise when processes occur in 3-D and demonstrate the need for such a model. Future use of high-resolution measurement techniques should include the collection of data for relevant major components, such as reactive iron and manganese oxides, to allow full, multi-component modelling of microniche processes.

Keywords: early diagenesis, diffusion, high resolution, organic matter, redox reactions, sulfide, trace metals

Introduction

Understanding of the cycling of carbon, nitrogen, manganese, iron and sulphur in sediments is largely based on measurement of solution and solid phase components in vertically arranged slices of cores. The dynamic interactions of the various components have been successfully modelled by coupling the reactions to one-dimensional (1-D) diffusion, with the implicit assumption of horizontal uniformity.^[1-3] Although transport and reaction in relation to idealized burrows and mounds has been treated quantitatively (Aller^[4] and references therein), processes of bioturbation and bio-irrigation are commonly modelled by considering their average effects on transport.^[5]

The true heterogeneous nature of the solid phase of sediments, especially at the sub-mm scale, is well recognized, but these variations are implicitly assumed to be averaged within the typical volume (20-100 ml) of a sediment slice.^[6] Various techniques have emerged that can measure concentrations of solutes directly, on a small scale, without the volumetric averaging inherent in core slices. They are showing that solute concentrations may vary markedly on a small (sub-mm) scale. Data from planar optodes has demonstrated the temporary development of small spheres (1-2 mm diameter) of anoxia within sediment^[7] and at the sediment surface,^[8] as particles of highly reactive organic matter consume all available oxygen. Sharp dips in oxygen concentration in otherwise smooth vertical profiles obtained using micro-electrodes, may be similarly explained.^[6]

Two-dimensional maps of concentrations of metals and sulphide, obtained using DGT (diffusive gradients in thin-films),^[9-13] have demonstrated that the maxima and minima can occur at discrete sites. These observations are consistent with the idea of microniches, where

discrete patches of reactive material bring about pronounced local changes in sediment chemistry.

We define the term *microniche* as a small-scale location within the 3-D sediment matrix where the geochemical behaviour differs significantly from the average for that depth. An example might be a particle of organic matter or other component (e.g. iron oxide) that has biogeochemical reaction rates which are higher (or lower) than the surrounding environment.^[6]

Modelling of microniches

Jørgensen^[14] modelled the depletion of oxygen within such niches and concluded that sulphate reduction may occur within pellets as small as 100 μm in diameter. Brandes and Devol^[15] modelled numerically the 2-D distribution of oxygen and nitrate by considering their reactions at points of reactive organic material distributed stochastically in a planar grid of 100 μm resolution. The averaged vertical profiles were able to explain the similar penetration of O_2 and NO_3^- observed in pore waters obtained by whole core squeezing at 1mm resolution. This stochastic approach was extended to 3-D by Harper et al.^[16] They showed that the production of dissolved metal ions within local sources (>100 μm diameter) set in sediment acting as a uniform sink for metals, resulted in much more sharply defined solute maxima (typically 0.5 mm wide) than would be possible with diffusion restricted to 1-D. Reactive transport models for sediments, which include advective contaminant exchange, have been developed.^[17-20] Such models have included 3-D simulations of the effects of various sediment-water interface geometries,^[21, 22] and these models have been further developed to include the effects of bioirrigation.^[23] A 3-D model by Meile et al.^[24] was devised to include organic matter diagenesis reactions and was applied to assessing the effect of burrow

irrigation on solute distributions. Using this model the significance of burrowing organisms in locally enhancing penetration of both oxygen and nitrate was demonstrated.

Microniche sources and life-span

As the term microniche can apply to any discrete site of reactive organic matter (OM), it can encompass material from a range of different sources. Microniches can be attributed to decaying organisms (observed using a pH optode^[25]), algal aggregates (added to sediment to study sulphidic microniches^[12]) and faecal pellets (photographed after resin embedding and thin sectioning of an intact core^[26]). Root systems can also generate microniches.^[27] Such niches will have a range of different properties. For example: algal aggregates will tend to have a high porosity and a low concentration of authigenic oxides; faecal pellets may possess a peritrophic membrane, be more compact than the ambient sediment (lower porosity) and in some cases have been shown to contain a greater proportion of fine mineral grains than the ambient sediment,^[26] potentially affecting tortuosity.

The life-span of niches will depend upon organic matter degradation reaction rates and the supply of oxidants, with niche size affecting oxidant supply to the centre of the niche. The duration of anoxia within a microniche occupying the oxic zone may be unlikely to exceed 2.5 days, as Alldredge and Cohen^[28] found little or no O₂ depletion in faecal pellets of this age or older. Zhu et al^[25] measured pH at a decaying organism and observed that the generation of protons from the niche was not measurable after approximately 80 hours. These studies indicate that microniches tend to have life-spans of days rather than weeks or months.

Aims and approach

Here we present a dynamic diagenetic model set within a 3-D framework, for the investigation of geochemical processes at microniches. The model's novelty lies in considering in three dimensions both diffusion and organic matter diagenesis (and associated secondary reactions) in small-scale volumes of sediment. It provides for the generation of vertical concentration gradients according to recent 1-D models, while allowing the definition of localized spherical zones of various diameters that may differ in the concentrations, transport or reactivity of components (microniches).

Engineering software packages such as COMSOL are now being used to model diagenetic processes (e.g. Cardenas and Wilson^[21]). While we could have alternatively built and presented specific model simulations using such a package, we chose to develop a self contained, flexible model, capable of representing a wide range of microniche environments, that will be made freely available. It incorporates a graphical user interface (figure included as Accessory Materials), which allows geochemists with no prior modelling expertise to set up and run quite complex problems within a few hours. It can be used to model observed field data or to test hypotheses. In contrast to traditional 1-D models, e.g. Berg et al^[3], the model is not intended to be used to investigate sediment at the 'bulk' scale, where transport by biota needs to be considered. Therefore, features such as tubes, and the transport processes associated with them (e.g. irrigation or advection) are not incorporated. In practise, the small, mm-scale, features being modelled may occur between burrows. Consequently, on the timescales of a few days that characterize the lifetime of microniches, they and the burrows can be regarded as separate entities. Consistent with this view, bioturbation may be responsible for relocating a microniche, while not affecting the physical properties of its localized domain. As sedimentation will not be significant over the time-scales of days, it is not considered. Validation was achieved by comparison of model outputs with known

analytical solutions. Examples of distributions of solutes in the vicinity of microniches of a range of sizes (one to five mm) are shown. We show the effect of microniches on solute concentrations within and around niches that are positioned close to sediment water interface within ambient oxic and suboxic sediment.

Model Formulation

Modelling in 3-D presents conceptual and computational challenges. The models must be geochemically sound with respect to transport and reactions, while allowing specific examples of heterogeneity (microniches). The model we have developed uses existing understanding of reaction and transport gained from measurements and modelling in 1-D. A similar system that allows input and simulation of vertical profiles of components is constructed within a 3-D framework. Spherical zones that represent microniches, may be created at any location within the 3-D grid (based on the principle that microniches in nature are likely to be introduced at various depths by the actions of biota). As the lifetime of microniches is generally relatively short (days) we have focused on short spatial scales (sub-mm to cm) and times, and have disregarded longer-term processes such as sediment recruitment and accumulation. The ultimate aim was to model the heterogeneous distribution of a range of components in sediments in response to the existence of microniches. To achieve this goal it was necessary to consider the oxidation of organic matter (OM) and all associated redox processes normally considered in diagenetic models. To allow ease of use, an executable form of the model has been developed with a graphical user interface (GUI). Flexibility was preserved by allowing the user to define all reactions and the initial spatial set up. The result is a versatile model for considering solute transport and reaction dynamics in sediments (known as 3D-TREAD), which can be used for a wide range of applications.

The model was divided into three modules: a GUI to allow user-friendly control of the simulation setup, a Calculation Unit where all simulations are solved, and a Reporting and Graphics module that was implemented in Matlab. It provides plots and output text files of concentration profiles of species for specified coordinates (details of model output and data extraction are provided in the Accessory Materials). Module one (GUI) allows the user to control the entire simulation process from designing the problem to solving and viewing the results.

The calculations unit contains all the solving routines, its input being the setup files prepared by the GUI unit. The transport and reaction formulation is implemented using the long-established Finite Element Method (FEM).^[29] For this it uses OFELI (Object Finite Element Library)^[30] to create the FEM mesh, interpret the user requirements and solve the model equations. The model space is subdivided into a large number of small parts to discretise the continuous volume. Each of these parts is considered to be homogeneous. These parts are called elements and together they form a mesh. Every element is identified by its nodes – points in space stored in the form of a vector (or array) of numbers. For microniches, elements are identified as being inside or outside the niche. Figure 1 illustrates the equivalent 2-D situation. In 3-D, the circle becomes a sphere and the triangles become tetrahedrons. By increasing the mesh size, elements become smaller, leading to better spherical definition. Spatial resolution is set by a value that controls the number of nodes per volume unit: the calculation precision increases as this value decreases. As an approximation this value can be assumed to be the minimum linear resolution resolved by the mesh. For example if the resolution is set at 0.05 (and the domain dimensions are in cm), the linear resolution will be at least as good as 500 μm (explained more fully in the Accessory Materials). Further

descriptions of mesh, model implementation and of more advanced features for the specification of microniches are provided as Accessory Materials.

Model inputs and calculations

The simulated system can be defined using the GUI, which allows the following input of data.

(a) Initial vertical concentration profiles and concentrations within microniches for all chemical components. (b) Diffusion coefficients in water for each component separately. (c) Porosity – allows calculation of effective diffusion coefficients at each depth and for each microniche. (d) Selection of tortuosity equation – selects equation and variable values to be applied to the diffusion coefficient calculation. (e) Nature of the boundary for solute components – boundaries can be specified at the top and/or bottom of the domain. (f) Domain – input of domain dimensions, mesh resolution, model simulation run-time and calculation time-step. (g) Reaction stoichiometry, rates, and priorities.

With these data all the possible components that are in the simulated system are specified. Each individual pool of OM is considered as a separate component, which effectively provides a very flexible multi-G model.^[31-33] The multi-G approach is particularly suitable for this model, which considers sufficiently short periods of diagenesis that accumulation and burial processes can be disregarded. For other models where longer-term processes are considered, the power model ('continuous-G') of Middelburg^[34] may be equally valid. Ultimately, knowledge of the behaviour and distributions of microbial communities and the degradation of known organic molecules and functional groups may lead to a more advanced understanding of OM degradation. However, given the current status of our understanding the more holistic approach of multi-G is the best available option.

All the reactive species participate in reactions that each have a set of user-specified values.

(a) Priority group and order within this group (i.e. for organic matter pools and the order of oxidant utilisation) (b) Reference component and concentration threshold (for specification of oxidants in OM reactions). (c) Reaction rate constant (with specification to which reactant it is related – i.e. OM in case of OM decomposition reactions, or all components for secondary reactions). (d) Type of reaction kinetics (zero or first order). (e) Chemical equation of the reaction (stoichiometric values).

To calculate the effective reaction rate for a first order reaction we use the following formulae (Eq. 1):

$$R_e = [C_{spec}] R_c \Psi \quad (1)$$

where R_e is the effective reaction rate, $[C_{spec}]$ is the concentration of the appropriate component, R_c is the reaction rate constant and Ψ accounts for the effect of porosity, ϕ , on the rate, by adjusting to concentration in unit volume of sediment. These porosity adjustments are specified according to Berg et al.^[3]

$$\Psi = \begin{cases} 1-\phi & (\text{reaction involving OM}) \\ \phi & (\text{Solute - Solute reaction}) \\ 1-\phi & (\text{Solute - Solid reaction}) \\ (1-\phi)^2 & (\text{Solid - Solid reaction}) \\ 1-\phi & (\text{Solid transformations}) \\ \phi & (\text{Solute transformations}) \end{cases} \quad (2)$$

As porosity can be specified as both a vertical profile and separately for microniches, Ψ introduces variations in the reaction rates with depth and within microniches (Eq. 2). Transformation reactions are included in the model for processes involving single species; for example reactive iron oxides converting into a form not reactive to OM^[3] or the adsorption of a solute onto a solid phase.

There are two main types of reactions: primary and secondary. The difference between them lies in regulation of their execution, which follow the principles used by Hunter et al^[35] and Berg et al.^[3]

Organic matter (involved only in primary reactions) can be defined as a series of separate components, each with their individual concentration profiles and distributions of microniches. A set of electron acceptors (EA; solutes or solids) facilitates the decomposition of each component of OM through a set of j primary reactions. Each reaction is assigned a priority index. When the concentration of the highest priority EA is above a prescribed threshold concentration $[EA]_{lim}$, it is the only EA that reacts. The EA with the next highest priority can only be used when the concentration falls below $[EA]_{lim}$. Each fraction of OM is consumed at a single prescribed rate that is first order with respect to OM, irrespective of the participating EAs. When $[EA] < [EA]_{lim}$ the reaction still proceeds provided $[EA] > 0$, but its rate then becomes proportional to $[EA]$, so that the primary redox reaction of OM degradation no longer follows a first order process. This complex system of priorities and rates was implemented in the model by calculating the fraction, f_i , of electrons consumed by the j^{th} primary reaction using the elegant formula of Hunter et al^[35] (Eq. 3).

for $j=1, 2, \dots, P-1$

if $[EA_j] > [EA_j]_{lim}$ then $f_j = 1 - \sum_{n=0}^{j-1} f_n$

else $f_j = \left(1 - \sum_{n=0}^{j-1} f_n\right) \frac{[EA_j]}{[EA_j]_{lim}}$

for $j=P$ $f_j = 1 - \sum_{n=0}^{P-1} f_n$ (3)

P is the number of primary reactions in a group. $[EA_j]$ is the concentration and $[EA_j]_{lim}$ is the limiting (threshold) concentration of the reference component. If overlap of OM

decomposition by two or more EA's is undesirable, the electron acceptor limiting concentrations can be set to a very low number (this avoids dividing by zero). Other reactions, that do not involve OM, are considered secondary and are allowed to proceed simultaneously at each time step of the calculation according to their specified rate. Secondary reactions are considered to proceed with first order kinetics with respect to each component. However, the model retains the flexibility to specify overall first order (for a chosen component) or zero order, if required.

The reactive transport equation for the i^{th} (mobile) aqueous component is shown in Eq. 4.

$$\frac{\partial C_i}{\partial t} = \nabla(D_i \nabla C_i) + v_i \nabla C_i + R_{\text{reac},i} \quad (4)$$

where C_i is the total aqueous concentration, $R_{\text{reac},i}$ is a source or sink rate due to chemical reaction, D_i is the diffusivity coefficient (matrix) and v_i is the pore-water velocity vector of the i^{th} component. Given the model does not consider advection ($v_i = 0$), transport of the i^{th} component is driven by reaction and diffusion processes only (Eq. 5)^[36, 37]

$$\frac{\partial C_i}{\partial t} = \nabla(D_i \nabla C_i) + R_{\text{reac},i} \quad (5)$$

The diffusion coefficient (D_i) at a particular point is calculated from Eq. 6.

$$D_i = \frac{D_o \varphi}{\theta^2} \quad (6)$$

Where D_o is the diffusion coefficient in water, θ is the tortuosity and φ is the porosity. A description of tortuosity and the various relationships built into the model are provided as Accessory Materials.

There are six boundaries in the modelled domain and, with the focus on small scale features, the simulated volume will not necessarily encompass all diagenetic regimes. Boundary

conditions can only be specified for solute species. Where upper or lower boundary concentrations are specified they are considered to be Dirichlet boundaries (i.e. fixed concentrations) by the transport process solver. There are four options for specifying solute boundaries; only upper or lower boundary specified, both boundaries specified or no boundaries specified (this option assumes zero flux at the boundary so that the gradients of concentration are equal to zero). Specified boundaries are defined by fixed concentrations entered by the user. Boundary conditions can not be individually specified for the four sides of the domain (zero flux applies).

The top interface is commonly the surface of the diffusive boundary layer, where fixed concentrations that are representative of values in the overlying water are appropriate. The bottom interface does not have such a simple conceptual analogue. It is necessary because all solutes may not be generated by the model if a small vertical zone is being simulated to accommodate limited computing power. For example, if maxima in dissolved iron or manganese concentrations were expected to occur in the sediment considered, but below the depth included in the simulation, there would be an upward flux of solute iron and manganese, which would be oxidized within the modelled zone. In this case, a lower boundary condition with fixed concentrations of Fe and Mn can be specified, allowing inclusion of the solute flux due to processes outside the modelled domain.

The functionality of the OFELI software (diffusion process), has been verified independently by a large user base. Validation of all the reaction mechanisms was achieved by comparing outputs to known solutions. For example to test both the organic matter oxidation reaction (which include variables for porosity, time-step and [OM]) and the proper functioning of the limiting concentrations, requires initial profiles for two or more oxidants, with the highest

order oxidant being allowed to drop below the limiting concentration. Consider a case where: (a) oxygen is present at the interface, but is quickly depleted, (b) manganese oxides are present equally throughout the domain, but below the limiting concentration, and (c) iron oxides are present equally throughout the domain and are above the limiting concentration. If OM is present at equal concentrations throughout the domain and the degradation rate is equal for all three oxidants, then the reduction in concentration of OM should be equal and predictable for all areas of the domain. By specifying a solid phase (immobile) product for each reactant, the consumption of reactants and generation of products can be calculated manually for each reaction using equations 1 to 3 and the reaction stoichiometry. Agreement of these calculations with modelled values provided verification of the framework for the primary metabolic pathways (see Accessory Materials for a more explicit example).

Modelling solute dynamics at microniches of varying size

To demonstrate the capabilities of the model and to provide some insight into why microniche processes may be important, this section quantitatively investigates the effect of microniche size on solute distributions and the nature of the sulphide release from these hypothetical microniches. Previous modelling of microniches, as detailed in the introduction, has tended to investigate a limited number of components (O_2 , NO_3^- , N_2) in one or two dimensions.^[14,15,38] Investigations into the behaviour of marine snow microniches have been similarly limited,^[28,39] although, sulphide production in these environments has been measured.^[40]

Here we sought to extend the pioneering work of Jørgensen^[14] to model, in 3-D, multiple components at a microniche within an appropriate diagenetic framework. The modelling structure is largely based on a comprehensive data set for a Danish marine sediment compiled by Fossing et al.^[41] As data for microniches is limited, selecting input data for the model is

not trivial. Assumptions about the ambient conditions and reaction priorities are required. Here we set reaction rates, starting concentrations and boundary concentrations to those modelled in 1-D by Fossing et al.^[41] Within a simple 1-D description based on horizontally averaged sediment, overlap in redox zones is likely to be due to the heterogeneity of the sediment rather than specific biogeochemical controls occurring at given limiting concentrations. However, within a microniche, it may be more reasonable to assume that there will tend to be a dominant process at all times. This situation was recognised by setting limiting concentrations for oxidants of the bulk OM outside the microniche to those values used by Fossing et al.^[41]. The limiting concentrations for the oxidants of the OM within the microniche were set much lower (2% of the Fossing et al.^[41] values). Use of lower thresholds recognises that a single oxidant is likely to be largely responsible for OM degradation at discrete sites, while also accounting for both the likelihood that oxidant concentrations will become limiting before reaching zero and observations that microbial OM reducers utilising different electron acceptors can co-exist in the same locality (e.g. sulphate reduction and methanogenesis).^[42] We have also assumed that resupply or removal of porewater Fe(II) and Mn(II) from or to the solid phase is sufficient to buffer porewater concentrations for the 24 hrs modelled (these porewater concentrations were fixed for this modelling). OM microniches were assumed to contain negligible concentrations of metal oxides. Therefore, the only OM-oxidising components within the microniches are in solution, and oxidation will follow the progression of O₂, NO₃⁻, SO₄²⁻. Microniche OM concentration was set at ~4-5 times the ambient OM concentration, consistent with observations by Kristensen and Pilgaard.^[43] Rates for OM degradation were based on the multi-G based Fossing et al.^[41] data, with the bulk OM degradation rates based on the slow reacting phase (with rate k_{OM-s}) and the microniche rates based on the fast reacting OM pool (with rate k_{OM-f}). The ratio of the rates ($k_{om-f} : k_{om-s}$) was 800. This rate results in the microniche OM concentration being depleted by ~12% of the

initial value over the period modelled; one third of the initial value will be reached after approximately 200 hrs. Initial profiles and tables of input parameters and reactions are provided as Accessory Materials.

With the input parameters described above and a domain of maximum x, y, z, dimensions of $0.6 \times 0.6 \times 1.05$ cm, microniches of varying diameters were introduced at a depth of 0.25 cm below the sediment-water interface at the x, y coordinates of the centre of the domain. Given that the oxygen and nitrate penetration depths (defined here as the depth where the microniche limiting concentration is reached) in the absence of microniches are 0.26 mm and 0.67 mm respectively, the microniches have the potential to affect the profiles of multiple solutes. The largest niche has an upper edge at the sediment-water interface.

The 3-D distribution of solutes at four spherical microniches, of diameters 5, 3.75, 2.5 and 1 mm, was modelled. Figure 2 shows the porewater profiles for O_2 , NO_3^- , and total sulphide (sum of S^{-2} , HS^- and H_2S , referred to from this point as $\Sigma S(-II)$) through the centre of the microniches. The smaller niches (≤ 2.5 mm) have NO_3^- minima (barely discernible in the Figure) centred within the niche. The slightly higher values below the niche centre are due to lateral diffusion, which would not be observed using a 1-D model. A NO_3^- maximum is created at the sediment surface by the intermediate sized niche (2.5 mm). High sulphide concentrations are observed at the largest niches, with only limited sulphate reduction in the 2.5 mm niche and no sulphate reduction in the one millimetre niche where nitrate is not completely exhausted. Clearly the local geochemistry is very dependent on the size of any aggregate of OM. It will also be dependent on location. At greater depths where nitrate is absent, sulphide would be expected to be produced in small microniches, as observed by Widerlund and Davison.^[12]

The significant localized changes in solute profiles that can be induced by the presence of microniches is further illustrated by Figure 3, which shows the profiles for all 3 solutes arising from a 3.75 mm diameter niche. The existence of sulphidic microniches in otherwise non-sulphidic zones of the sediment may have implications for the formation of metal sulphides. Trace metal sulphides are used as paleoredox proxies. Removal of metals from solution in sediments, where no removal is expected according to bulk data, may complicate interpretation of such paleo-data.^[13] Measurements of metals in porewaters at sulphidic microniches, using DGT, have shown that there may be localized supersaturation with respect to metal sulphides.^[11]

Time series data can be obtained from 3-D TREAD, as shown in Figure 4, for NO_3^- and $\Sigma\text{S}(-\text{II})$ profiles at the 2.5 mm microniche over the first 24 hrs of the model run. Sulphide rapidly increases as the initial NO_3^- concentration within the niche is limited. As more NO_3^- is produced within the oxic sediment layer (due to oxidation of ammonia released from the niche as OM is oxidized) less of the OM in the niche is oxidized by sulphate and the peak reduces to a plateau where a balance is achieved between NO_3^- production and loss. We recognise that this ammonia release may to some extent be retarded via uptake by OM-oxidising bacteria, as depletions in porewater nutrients (phosphate) at microniches has been observed.^[13] Figure 5 represents graphically a plane of the 3-D data that can be produced from the model output. It shows how the magnitude of the concentration in a 2-D image is very dependent on how close the plane is to the centre of the microniche. Data from this study corroborate the hypothesis of Brandes and Devol,^[15] that microniches may influence the general porewater chemistry of sediments via diffusion extending away from the discrete sites.

Conclusions

We have developed a model that considers reactions and transport occurring in 3-D within a sediment. Its graphical user interface allows it to be used by geochemists without expert modelling skills. Flexibility in the specification of reactions and the priority with which they occur facilitates detailed diagenetic modelling using a wide range of solutes and solid phases. Spherical microniches, where different rates and/or concentrations produce a localized chemistry, may be specified. The model has been tested by separately verifying individual reaction types. Modelling of the hypothetical cases of microniches in the near surface sediment showed that, for the conditions selected, sulphide was readily generated, provided the microniche diameter was greater than 1 mm.

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Accessory Materials

Further details of model implementation and additional Tables and Figures. This material is available on the journal website.

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Figure Captions

Figure 1. Illustration in 2-D of the approximation involved in representing a circular microniche (circle) by a Finite Element Method (FEM) mesh of triangles. The darkest grey indicates elements that lay completely within the microniche and the white those completely outside. The lightest grey elements have a significant proportion of their area (>34%) outside the microniche, while intermediate grey shows elements with most of their area (>66%, <100%) inside the microniche, as used by the model.

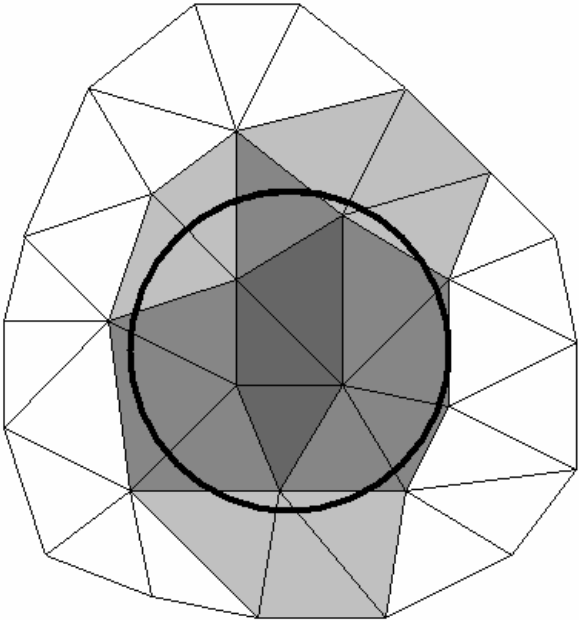
Figure 2. Vertical porewater profiles at the x, y co-ordinates of the microniche centres, through the modelled domain (z), 24 hours after the introduction of the microniches of diameters from one to five millimetres. The horizontal line at zero depth represents the sediment-water interface and at -0.25 cm it represents the centre of the microniches.

Figure 3. Comparisons of vertical O_2 , NO_3^- , and total sulphide, $\Sigma S(-II)$, profiles at the 3.75 mm microniche (24 h) and profiles when no microniches are present (x, y values were set at the centre of the niche). The horizontal line at -0.25 cm represents the centre of the microniche; the grey shading represents the niche area.

Figure 4. Time series of solute profiles at the x, y co-ordinates of the centre of the 2.5 mm microniche. z co-ordinates are at the peak concentration for each solute.

Figure 5. Contour plots of sulphide concentrations across the domain in the presence of a 3.75 mm diameter niche. x co-ordinates are (a) 0.05 cm – outside the niche, (b) 0.13 cm – just within the niche, (c) 0.22 cm and (d) 0.30 cm – the centre of the niche.

Figure 1



Pre-Print Version

Figure 2.

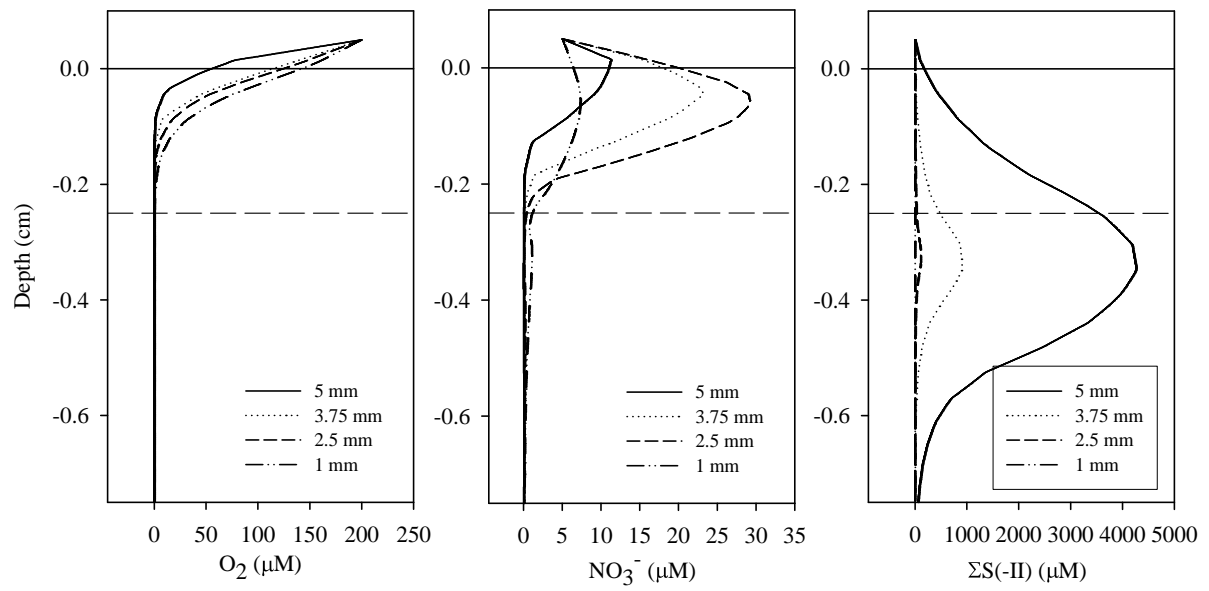


Figure 3.

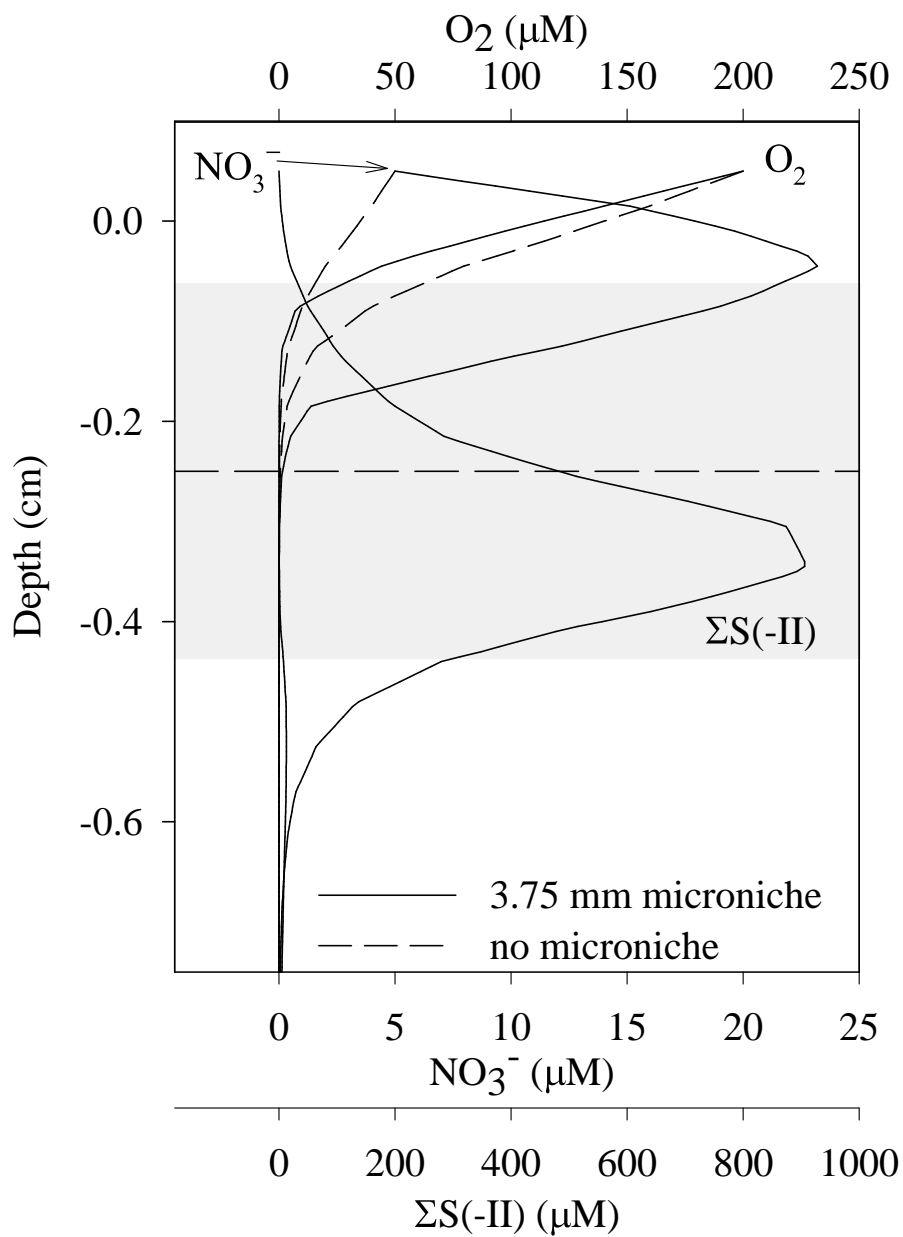
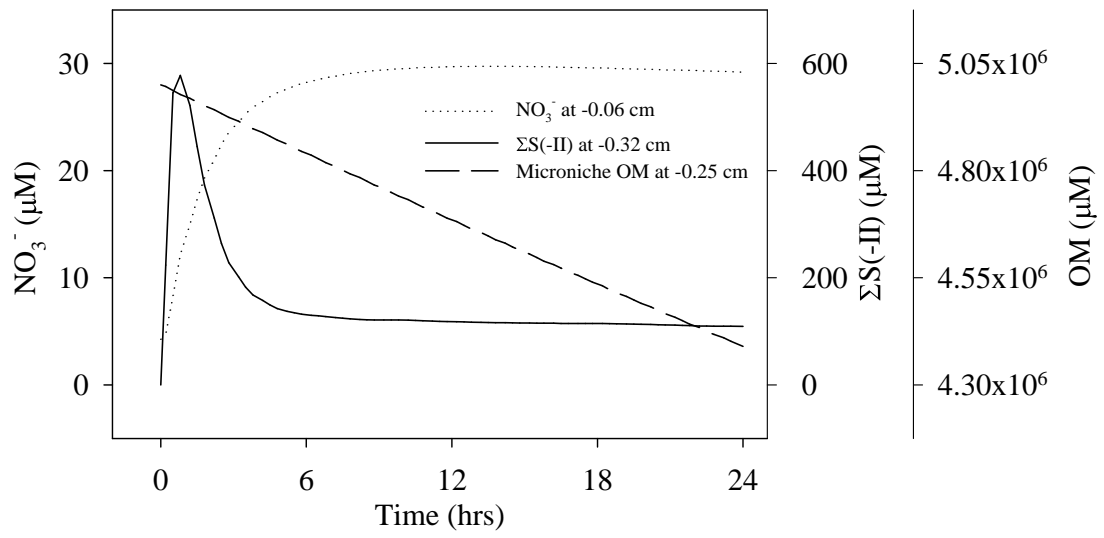
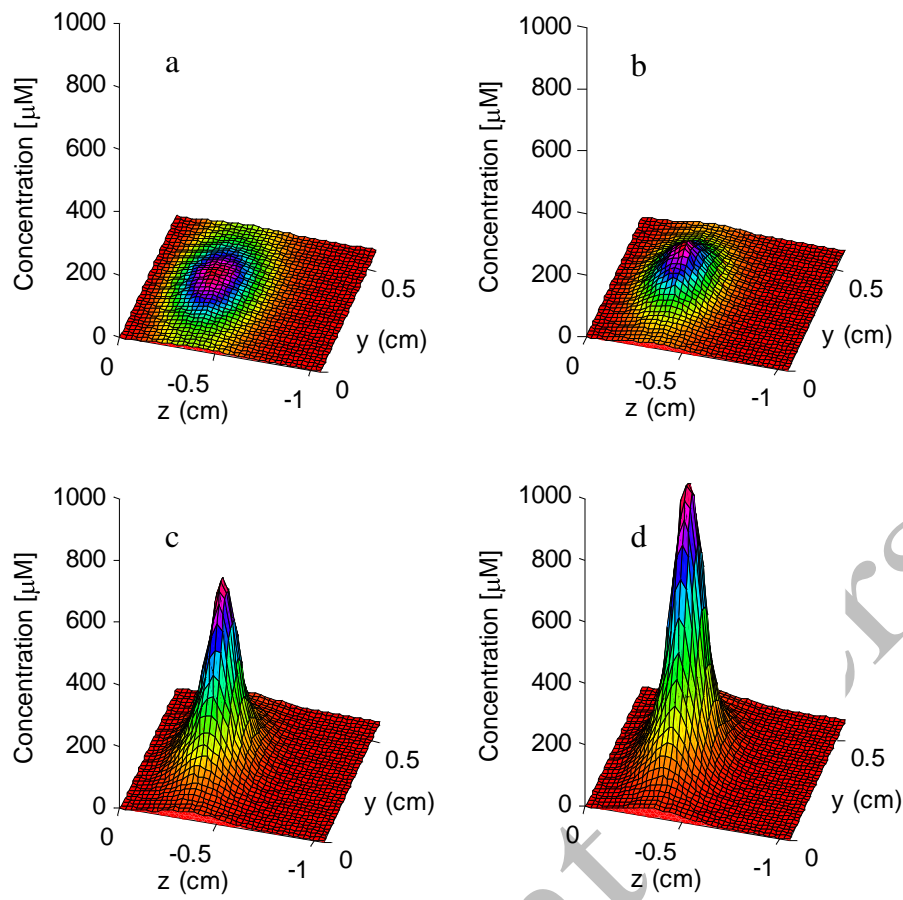


Figure 4.



Pre-Print Ver

Figure 5.



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

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Accessory Materials

In the order they are referred to in the main manuscript.

Pre-Print Version

The GUI

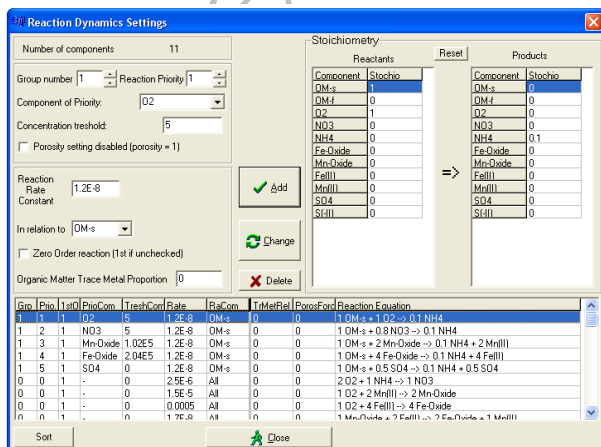
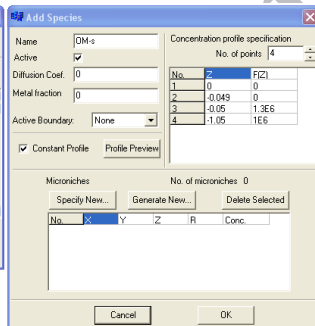
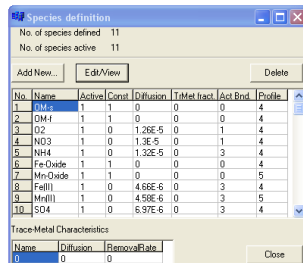
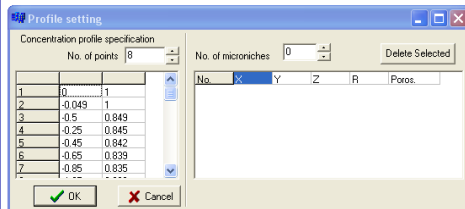
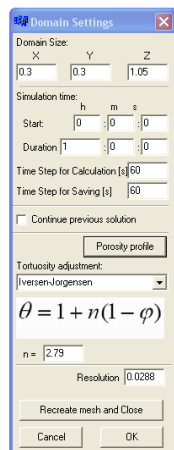
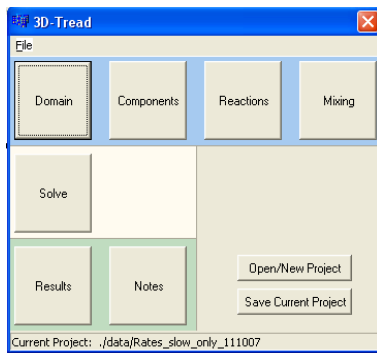


Figure S1. User interface for 3D-TREAD. From top to bottom, left to right; menu screen that links to data input modules, domain settings input and porosity input, species list and species definition box, reaction setting box.

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 3D-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 $\sim \text{MEL} / 1.7$.

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 time step,

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 OM, microniches can be defined for any chemical component of the system. The user can specify microniches one-by-one using a dialog 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 – are 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 time steps and the small size of the mesh elements. It exploits the superposition principle, so that at each time step we isolate the reaction equations from the transport equations and solve them in an interleaved manner. In other words, at each time step 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 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 sub-domains 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 (sub-domains) 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 time-steps in 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 (Eq. S1).

$$\text{mmol g}^{-1} \times \text{dry weight density (g cm}^{-3}\text{)} = \text{mmol cm}^{-3} = M \text{ (mol L}^{-1}\text{)} \quad (\text{S1})$$

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

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

Figure S2. 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 equation 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 time-scale 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 which gave the best fit. The three best fitting relationships are available in the model, together with a relationship recently presented by Boudreau and Meysman (2006). 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 S1. 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 S1. Tortuosity options available in the 3D-Tread model.

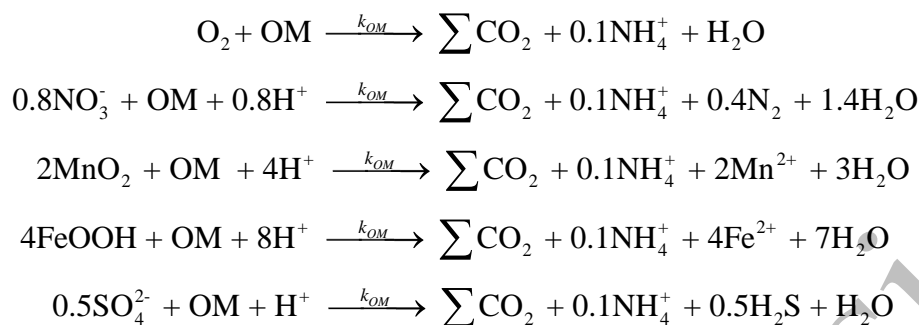
Label	Equation	Best fit values for equation variables	Reference
Iversen- Jørgensen ^a	$\theta^2 = 1 + n(1 - \varphi)$	$n = 2.79^b$	Iversen and Jørgensen, 1993
Modified Weissberg	$\theta^2 = 1 - b \cdot \ln(\varphi)$	$b = 2.02^b$	[5]
Modified Archie's Law	$\theta^2 = d \cdot \varphi^{(1-m)}$	$d = 1^b$ $m = 2.14^b$	[5]
Boudreau-Meysman	$\theta^2 = \left[1 + \frac{32h}{9\pi}(1 - \varphi) \right]^2$	$h = 1^c$	Boudreau and Meysman, 2006
No Adjustment	$\theta^2 = 1$		

^aA similar relationship was previously independently presented as the Burger-Frieke relationship (see Boudreau,^[5] 1997). ^bBest fit values from Boudreau (1997).^[5] ^cBest fit value from Boudreau and Meysman (2006).

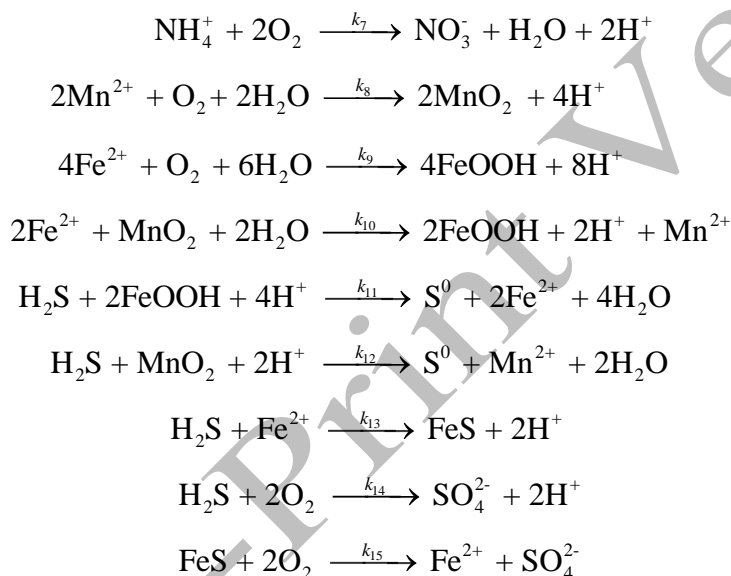
Data used as model input parameters

Table S2. Primary and secondary reactions used to model microniche processes using the 3D-TREAD model (after Fossing et al^[41]).^a

Primary reactions



Secondary reactions



^aH₂O, H⁺, N₂, \sum CO₂ and S⁰ 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 a OM C:N ratio of 10.

Table S3. 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 mm and 3.75 mm niches x,y,z: 0.3, 0.3, 1.05 cm – 2.5 mm and 1 mm niches
Resolution (user defined)	0.0290 (smallest domain)
See text for explanation	0.0472 (largest domain)
Porosity	$\phi = 0.763 + 0.086e^{-0.216x}$
(entered as finite values in the 3d 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
	ΣH ₂ S 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 & L 2000 μM
	[ΣH ₂ S] 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. × 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

^aDiffusion coefficients are calculated from equations presented in [5]. ^bFe 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). ^cUser defined, other limiting concentration values for the microniche modelling taken from [41] and niche values set at 2% of the [41] values.

Initial Profiles

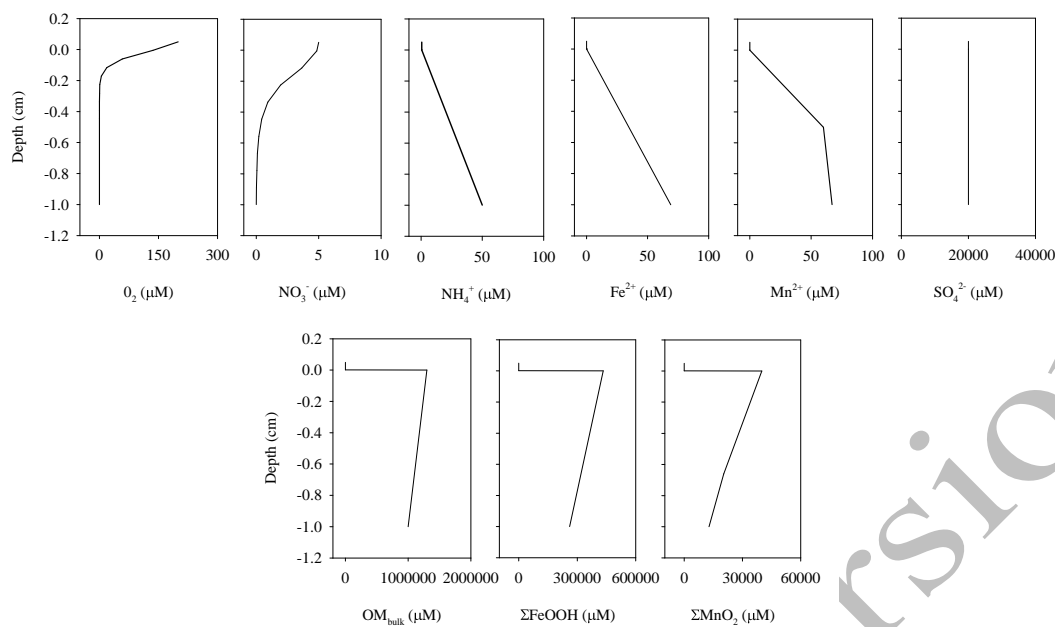


Figure S3. Initial profile inputs. Oxygen and nitrate are based on steady state profiles where no niches are present (i.e. bulk OM only). Other components are based on the Fossing et al data.^[41] Solid phases (bottom row) have been adjusted for density to give unified units.

Additional references not cited in main manuscript

Boudreau, B.P.; Meysman, F.J.R. Predicted tortuosity of muds. *Geology* 2006, 34, 693-696.

Iversen, N., Jørgensen, B.B., 1993. Diffusion coefficients of sulfate and methane in marine sediments: Influence of porosity. *Geochimica et Cosmochimica Acta*, 57, 571-578.