

OMEN-SED 1.0: A new, numerically efficient sediment module for the coupling to Earth System Models

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Abstract. Here we describe the first version of the Organic Matter ENabled SEDiment model (OMEN-SED 1.0).

1 Introduction

DH: How to include comments.

- Marine surface sediments are key components in the Earth system. They host the largest carbon reservoir within the surficial Earth system, provide the only long term sink for atmospheric CO₂, recycle nutrients and represent the most important geochemical archive used for deciphering past changes in biogeochemical cycles and climate. Physical and chemical processes in sediments (diagenesis) depend on the water column and vice versa: Diagenesis is mainly donor controlled, as it is fuelled by the external supply of solid material (e.g. organic matter, calcium carbonate, opal) from the water column and is affected by overlying bottom water concentrations of solutes. At the same time, diagenesis in the sediments transforms the deposited material and returns the resulting products (e.g. nutrients, DIC) to the water column. This so-called benthic-pelagic coupling is essential for understanding global biogeochemical cycles and climate (e.g. Archer and Maier-Reimer, 1994; Archer et al., 2000; Mackenzie, 2005; Ridgwell and Zeebe, 2005).
- In the marine sediments, most biogeochemical reactions can be related either directly or indirectly to the degradation of organic matter (OM) (e.g. Boudreau and Ruddick, 1991; Arndt et al., 2013). Organic matter degradation, for instance, releases metabolic CO₂ to the pore water, causing it to have a lower pH and provoking the dissolution of CaCO₃ (Emerson and Bender, 1981). **TODO: which cycles are affected!?**

TODO: next paragr. think about better logical structure!

On the other hand, over long timescales production of OM is generally greater than degradation which results in some organic matter being buried in marine sediments and oxygen accumulating in the atmosphere. Thus burial of OM leads to net oxygen input to, and CO₂ removal from, the atmosphere (Berner, 2004). Furthermore, the sediments form an important sink for organic phosphorus and nitrogen. Therefore, changes in the burial rate of OM can profoundly affect the oxygen and nutrient inventory of the ocean and thus marine biogeochemical cycling and primary productivity (e.g. Lenton and Watson, 2000; ?). Furthermore, burial of OM represents an important connection between carbon stored in more climate-relevant reservoirs like oceans, atmosphere, and surficial sediments and carbon that is sequestered for much longer, geological timescales in sedimentary rock or coal (Mackenzie, 2005; Burdige, 2007).

Furthermore, nutrient recycling from the sediments has been used by modelling and data studies to explain the occurrence of extreme events in Earth history, for instance Oceanic Anoxic Events (OAEs) (Bjerrum et al., 2006; Mort et al., 2007; Tsandev and Slomp, 2009). OAEs represent severe disturbances of the global carbon, oxygen and nutrient cycles of the ocean and are usually characterized by widespread bottom water anoxia and photic zone euxinia (occurrence of free hydrogen sulfide) (?). One possible mechanism to explain the genesis and persistence of OAEs is increased oxygen demand due to enhanced primary productivity (PP). Increased nutrient inputs to fuel PP may have come from marine sediments as the burial efficiency of phosphorus declines when bottom waters become anoxic (e.g. Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1994).

Difference for oxic vs. anoxic sediments and impacts on atmospheric CO₂.

TODO: Give examples when and why important (also in Paleo-context).

- general dynamics: first e.g. CaCO₃ then nutrients and the OM!
- 45 - then more focus on paleo!
 - glacial/interglacial atmospheric pCO₂ cycles
 - maybe important for OMZ (see Kriest + Oschlies 2013)
 -
 - Carbon burial events
- 50 Degradation of organic matter (OM) in marine sediments fuels benthic biogeochemical processes and the resulting fluxes across the sediment-water interface are of considerable importance for many global biogeochemical cycles (Arndt et al., 2013). Burial of OM represents an important connection between carbon stored in more climate-relevant reservoirs like the oceans, atmosphere, and the marine sediments and carbon that is sequestered for much longer, geological timescales in sedimentary rock or coal (Mackenzie, 2005; Burdige, 2007). Biological primary production of organic matter (CH₂O in equation R1) and the reverse process of degradation can be written in a greatly simplified

reaction as:



On long timescales production of OM is generally greater than degradation which results in some organic matter being buried in marine sediments and oxygen accumulating in the atmosphere. Thus burial of OM leads to net oxygen input to, and CO₂ removal from, the atmosphere (Berner, 2004). Therefore, globally quantifying the degradation of organic matter in marine sediments and related biogeochemical dynamics is important for understanding climate and the cycling of many chemical elements on various timescales. Such studies and quantifications are possible through the application of idealised mathematical representations of diagenesis, or so-called diagenetic models (e.g. Berner, 1980; Boudreau, 1997). The number of research questions that can be addressed with diagenetic models is infinite and a plethora of different approaches have been developed, mainly following two distinct directions (Arndt et al., 2013). First, state-of-the art diagenetic models simulating all of the essential coupled redox and equilibrium reactions within marine sediments that control carbon burial and benthic recycling fluxes (e.g. BRNS, Aguilera et al., 2005; MEDIA, Meysman et al., 2003; OMEXDIA, Soetaert et al., 1996b). These “complete” models generally use a so-called multi-G approach, thus dividing the bulk organic carbon pool into a number of compound classes that are characterised by different degradabilities k_i . However, their global applicability is limited by the high computation cost of simulating all biogeochemical reactions. The second group of models is less sophisticated and comprehensive than the “complete” diagenetic models and is used for the coupling to global Earth System Models (e.g. DCESS, Shaffer et al., 2008; HAMOCC, Heinze et al., 1999; MEDUSA, Munhoven, 2007). In particular, these models consider fewer biogeochemical reactions and apply the so-called 1G approach, thus just representing a single organic matter pool which is degraded at a constant rate. Obviously, such a simplification can neither account for the observed vast structural complexity in natural organic matter and its resulting different degradation rates nor for the decrease in OM degradability during diagenesis (Arndt et al., 2013). A further problem of both approaches (and models in general) are model parameters which implicitly account for processes not explicitly described. These parameters are either derived through profile fitting for a specific site or follow different global relationships with a related, readily available sediment characteristic, such as water depth (Middelburg et al., 1997) or sedimentation rate (Tromp et al., 1995). However, also these relationships are mostly based on simple fitting exercises to limited data sets and cannot replace a mechanistic representation of the underlying processes, especially when applying the model for different geological timescales.

Even though there is potential to use more appropriate global sediment representations, in most current Earth System models sediment-water exchange of OM and chemical elements is generally treated in a very simplistic way (Soetaert et al., 2000; Hülse et al., 2016). Most Earth system Models of Intermediate Complexity (EMICs) for instance represent the sediment-water interface either as a reflective or a conservative/semi-reflective boundary (Hülse et al., 2016). Thus, all particulate ma-

terial deposited on the seafloor is either instantaneously consumed (reflective boundary), or a fixed
95 fraction is buried in the sediments (conservative/semi-reflective boundary). Both highly simplified approaches furthermore completely neglect the exchange of solute species through the sediment-water interface and, therefore, cannot resolve the complex benthic-pelagic coupling. However, due to their computational efficiency, both representations are often used in global biogeochemical models (e.g. Najjar et al., 2007; Ridgwell et al., 2007; Goosse et al., 2010)

100 **TODO:** Sandra review: large scale of published model parameters illustrates the complex nature of organic matter dynamics! Very difficult to find global relationships to relate model parameters to available environmental characteristics, such as water depth, deposition rate. Sentence about: even though there is some potential most ESM use the following:

See e.g. (Soetaert et al., 2000; Mackenzie et al., 2004).

105

How are sediment resolved in Earth System models

See e.g. (Soetaert et al., 2000)

Problem with that:

110 The spatial variability in e.g. benthic particulate organic carbon (POC) mineralization kinetics throughout the ocean is currently unknown. This creates considerable uncertainties when diagenetic models are used to couple benthic and pelagic biogeochemical cycles in global models. (Kriest and Oschlies, 2011)

Alternative Model approaches, e.g. from coastal research

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Here, we present the OrganicMatter ENabled SEDiment model (OMEN-SED 1.0), a new, one-dimensional, numerically efficient reactive transport model (RTM) that describes OM cycling as well as the associated dynamics of the most important terminal electron acceptors (O_2 , NO_3^- , SO_4^{2-} , CH_4), related reduced substances (NH_4^+ , H_2S) and macronutrients (PO_4^{3-}). OMEN-SEDS computational efficiency allows its coupling to Earth System Models and therefore the investigation of coupled global biogeochemical dynamics over geological timescales. Also mention here presented as a 2G-Model, however OMEN-SED can easily be extended to a Multi-G approach.

125 See Van Cappellen and Wang (1996): “Metal cycling in surface sediments: Modeling the interplay or transport and reaction” for some good basic info!

2 Model Description

The following section provides a detailed description of the new model. Table 1 summarizes the biogeochemical reaction network and a glossary of parameters along with their respective units is provided in Tables 7 and 8.

130 2.1 General Model Approach

The calculation of benthic return/uptake and burial fluxes is based on the vertically resolved conservation equation for solid and dissolved species in porous media is given by (e.g. Berner, 1980; Boudreau, 1997):

$$135 \quad \frac{\partial \xi C_i}{\partial t} = -\frac{\partial F}{\partial z} + \xi \sum_j R_i^j \quad (1)$$

where C_i is the concentration of the biogeochemical species i , ξ equals the porosity ϕ for solute species and $(1 - \phi)$ for solid species, hence represents the partitioning of species i into the solute and dissolved phase. The term z is the sediment depth, t denotes the time, F summarises the transport fluxes and $\sum_j R_i^j$ represents the sum of production/consumption rates j that affect species i .

140 The reaction network has to account for the most important primary and secondary redox reactions, equilibrium reactions, mineral dissolution and precipitation, as well as adsorption and desorption processes that affect the explicitly resolved chemical species.

State-of-the-art reaction-transport models generally solve the ordinary differential equation (ODE) (eq. 1) numerically and thus allow to account for transient dynamics, depth-varying parameters or 145 a high degree of coupling between different chemical species. Yet, numerical models are computational expensive, thus rendering their application in an Earth System Model framework prohibitive. An analytical solution of equation (1) provides an alternative and computational more efficient approach. Analytical models enjoyed great popularity in the early days of diagenetic modelling and computer technology due to their low computational demands. However, early analytical models 150 were often very problem-specific and only considered one or two coupled species ([e.g. Lehrman, Berner](#)) ?? which pubs?. Over the next decades, a number of more complex analytical models describing the coupled dynamics of ...were developed (e.g. Billen, 1982; Goloway and Bender, 1982; Jahnke et al., 1982), before the boost in computing power enabled the development of fully-coupled, multi-species, numerical models (e.g. Van Cappellen and Wang, 1995; Soetaert et al., 1996b).

155 Finding an analytical solution to Eq. (1), especially when complex reaction networks are to be considered, is not straightforward and generally requires the assumption of steady state. In addition, the complexity of the reaction network can be reduced by dividing the sediment into distinct zones and accounting for the most pertinent biogeochemical processes within each zone, thus increasing the likelihood of finding an analytical solution to Eq. (1).



Figure 1. Schematic of the different modelled species and layers in our sediment model. Here showing the case $z_{\text{ox}} < z_{\text{bio}} < z_{\text{NO}_3} < z_{\text{SO}_4}$.

160 Therefore, OMEN-SED assumes that benthic dynamics can be represented by a series of steady-states. Because the Earth system model relevant variability in boundary conditions and fluxes is generally longer than the characteristic timescales of the reaction-transport processes, the sediment can be described by a series of pseudo steady-states. In addition, it divides the sediment into a bioturbated and a non-bioturbated zone defined by the constant bioturbation depth z_{bio} (see Fig. 1).
 165 Furthermore, it accounts for the dynamic redox zonation of marine sediments by dividing the sediment into: 2) an oxic zone delineated by the oxygen penetration depth z_{ox} , 3) a denitrification zone situated between z_{ox} and the nitrate penetration depth z_{NO_3} , 4) a sulfate reduction zone situated between z_{NO_3} and the sulfate penetration depth z_{SO_4} and 5) a methanogenic zone situated below z_{SO_4} (Fig. 1). All penetration depths are dynamically calculated by the model. Each zone is characterised
 170 by a set of diagenetic equations that encapsulate the most pertinent reaction and transport processes in this zone (see section 2.2 and 2.3 for more details).

OMEN calculates and feeds back to the Earth System model the fraction of POC preserved in the sediments and the sediment-water interface fluxes of the dissolved species C_i :

$$\text{Flux_SWI}(C_i) = \phi \cdot \left(D_i \frac{\partial C_i}{\partial z} + w C_i(0) \right) \quad (2)$$

175 where w is the deposition rate, D_i is the diffusion coefficient and $C_i(0)$ the sediment-water concentration of species i .

2.2 Transport

The model accounts for both the advective, as well as the diffusive transport of dissolved and solid species, assuming that sediment compaction is negligible (i.e. $\frac{\partial \phi}{\partial z} = 0$). The molecular diffusion of dissolved species is described via a species-specific apparent diffusion coefficient, $D_{\text{mol},i}$. In addition, the activity of infaunal organisms in the bioturbated zone of the sediment ($z < z_{\text{bio}}$) that causes random displacements of sediments and porewaters is simulated using a diffusive term (e.g. Boudreau, 1986), with a constant bioturbation coefficient D_{bio} in the bioturbated zone. The pumping activity by burrow-dwelling animals and the resulting ventilation of tubes, the so-called bioirrigation, is encapsulated in a factor, f_{ir} that enhances the molecular diffusion coefficient (hence, $D_{i,0} = D_{\text{mol},i} \cdot f_{\text{ir}}$, Soetaert et al., 1996a). The flux divergence can thus be formulated as:

$$\frac{\partial F}{\partial z} = -\frac{\partial}{\partial z} \left(-\xi D_i \frac{\partial C_i}{\partial z} + \xi w C_i \right) \quad (3)$$

where D_i is the diffusion coefficient of species i ($D_i = D_{i,0} + D_{\text{bio}} = D_{\text{mol},i} \cdot f_{\text{ir}} + D_{\text{bio}}$ for dissolved species and $D_i = D_{\text{bio}}$ for solid species) and w is the deposition rate. The bioturbation coefficient D_{bio} is set to zero below z_{bio} . In addition, infaunal activity ceases ($D_{\text{bio}} = 0$) once bottom waters become anoxic ($O_2 < ??? \text{ mol cm}^{-3}$). check for good value + add if-query in code!!

2.3 Reaction Network

Earth System models generally track the biogeochemical dynamics of organic and inorganic carbon, essential nutrients (nitrogen, phosphorus) and oxygen with the aim of investigating the evolution of the ocean's redox structure and carbonate system and its feedbacks on global climate. This general aim thus defines a minimum set of state variables and reaction processes that need to be resolved for an efficient representation of the benthic-pelagic coupling in Earth system models. A suitable sediment model must provide a robust quantification of organic (and inorganic) carbon burial fluxes, as well as the benthic return fluxes of growth-limiting nutrients, equilibrium invariant and reduced species, and oxygen uptake fluxes. As a consequence, the reaction network must account for the most important primary and secondary redox reactions, equilibrium reactions, mineral precipitation/dissolution and adsorption/desorption, resulting in a complex set of coupled reaction-transport equations. The following subsections provide a short discussion of the reaction processes included in the model and give an overview of the vertically resolved conservation equations and boundary conditions for solid and dissolved species in each layer. Table 1 provides a summary of the reactions and variables considered in the reaction network. Table 10 summarises their reaction stoichiometry and Table ?? provides an overview of their description in the model.

2.3.1 Organic matter

In marine sediments, organic matter (OM) is degraded by heterotrophic activity coupled to the sequential utilisation of terminal electron acceptors (TEAs), typically in the order of O_2 , NO_3^- ,

Table 1. Reactions and variables implemented in the Reaction Network of OMEN-SED (1.0). The primary and secondary redox reactions are listed in the sequence they occur with increasing sediment depth.

Description	
Primary redox reactions	Degradation of organic matter via aerobic respiration, denitrification, sulfate reduction, methanogenesis (implicit)
Secondary redox reactions	Oxidation of ammonium and sulfide by oxygen, anaerobic oxidation of methane by sulfate
Adsorption/Desorption	Ad-/Desorption of P on/from Fe(OH) ₃ , NH ₄ adsorption, PO ₄ adsorption
Mineral precipitation	Formation of authigenic P
Variables	Organic matter, oxygen, nitrate, ammonium, sulfate, sulfide (hydrogen sulfide), phosphate, Fe-bound P, DIC, ALK

Mn(VI), Fe(III) and SO₄²⁻ followed by methanogenesis and/or fermentation. Here, organic matter degradation is described via a multi-G model approach (Arndt et al., 2013, and references therein), assuming that the bulk OM consists of a number of discrete compound classes C_i characterised by specific degradation rate constants k_i . Such a multi-G approach allows for selective preservation of compound classes according to their reactivity, k_i and, thus, accounts for the change in organic matter reactivity during burial. Each compound class is degraded according to first-order kinetics. The conservation equation for organic matter dynamics is thus given by:

$$\frac{\partial C_i}{\partial t} = 0 = D_{C_i} \frac{\partial^2 C_i}{\partial z^2} - w \frac{\partial C_i}{\partial z} - k_i \cdot C_i \quad (4)$$

The analytical solution of Eq. (4) (see section ?? for details) requires the definition of a set of boundary conditions (Table 2). The model assumes a known concentration/flux at the sediment-water interface and continuity across the bottom of the bioturbated zone, z_{bio} .

2.3.2 Oxygen

In marine sediments, oxygen is consumed through the aerobic degradation of organic matter and a number of secondary redox reactions. In the oxic layer ($z < z_{\text{ox}}$), the model explicitly accounts for the aerobic degradation of OM, which consumes oxygen with a fixed O:C ratio (OC, Tab. 8) and produces ammonium, which is partially nitrified to nitrate (γ_{NH_4}). In addition, the oxygen consumption through the oxidation of reduced species (Fe²⁺, Mn²⁺, NH₄, H₂S) produced in the suboxic and anoxic layers of the sediment is implicitly taken into account through the flux boundary condition at the dynamic oxygen penetration depth z_{ox} . This simplification can be justified as it has been shown that these secondary redox reactions mainly occur at the oxic/suboxic interface (Soetaert et al., 1996b). The factor $\frac{1-\phi}{\phi}$ accounts for the volume conversion from the solid to the dissolved

Table 2. Boundary conditions for organic matter and oxygen. For the boundaries we define: $z_-^- := \lim_{h \rightarrow 0} (z_- - h)$ and $z_+^+ := \lim_{h \rightarrow 0} (z_- + h)$.

Boundary	Condition	
$z = 0$ $z = z_{\text{bio}}$	known concentration continuity	1) $C_i(0) = C_{i0}$ 2) $C_i(z_{\text{bio}}^-) = C_i(z_{\text{bio}}^+)$ 3) $-D_{\text{bio}} \cdot \frac{\partial C_i}{\partial z} _{z_{\text{bio}}^-} = 0$
$z = 0$ $z = z_{\text{bio}}$ $z = z_{\text{ox}}$	known concentration continuity O ₂ consumption ($z_{\text{ox}} = z_\infty$)	1) $O_2(0) = O_{20}$ 2) $O_2(z_{\text{bio}}^-) = O_2(z_{\text{bio}}^+)$ 3) $-(D_{O_2,0} + D_{\text{bio}}) \cdot \frac{\partial O_2}{\partial z} _{z_{\text{bio}}^-} = -D_{O_2,0} \cdot \frac{\partial O_2}{\partial z} _{z_{\text{bio}}^+}$ 4) IF ($O_2(z_\infty) > 0$) $\frac{\partial O_2}{\partial z} _{z_{\text{ox}}} = 0$ ELSE $O_2(z_{\text{ox}}) = 0$ and $-D_{O_2} \cdot \frac{\partial O_2}{\partial z} _{z_{\text{ox}}} = F_{\text{red}}(z_{\text{ox}})$
	($z_{\text{ox}} < z_\infty$) with flux from below	$F_{\text{red}}(z_{\text{ox}}) = \frac{1-\phi}{\phi} \cdot \int_{z_{\text{ox}}}^\infty \sum_i (2\gamma_{\text{NH}_4} \text{NC}_i + \gamma_{\text{H}_2\text{S}} \text{SO}_4 \text{C}) k_i C_i dz$

phase. Oxygen dynamics are thus described by:

$$235 \quad \frac{\partial O_2}{\partial t} = 0 = D_{O_2} \frac{\partial^2 O_2}{\partial z^2} - w \frac{\partial O_2}{\partial z} - \frac{1-\phi}{\phi} \sum_i k_i \cdot [OC + 2\gamma_{\text{NH}_4} \text{NC}_i] \cdot C_i(z) \quad (5)$$

The analytical solution of Eq. (5) (see section ??) requires the definition of boundary conditions (Table 2). The model assumes a known bottom water concentration and the complete consumption of oxygen at the oxygen penetration depth (or zero flux if $z_{\text{ox}} = z_\infty$). It considers equal oxygen concentration and diffusive flux above (z_{bio}^-) and below (z_{bio}^+) the bioturbation boundary. In addition,

240 the model imposes a flux of reduced species through the bottom of the oxic zone that is calculated as the reduced substances produced through anoxic mineralization of organic matter below z_{ox} . Thus, assuming that fractions (γ_{NH_4} and δ) of these reduced species are oxidised at the oxic/suboxic interface.

2.3.3 Nitrate and Ammonium

245 To model nitrate and ammonium dynamics the sediment is partitioned into two geochemical layers (oxic and suboxic), where different equations describe the biogeochemical processes. Above the oxygen penetration depth organic matter mineralization produces ammonium, which is partly nitrified to nitrate (the fraction γ_{NH_4}). In the suboxic zone ($z > z_{\text{ox}}$), oxygen concentration is zero and nitrate serves as the electron acceptor to respire organic matter, thus nitrate is consumed by denitrification and ammonium is produced. Below the nitrate penetration depth z_{NO_3} , ammonium is still produced through OM mineralization. Therefore the diagenetic equations for nitrate and ammonium are given by:

1. Layer ($z \leq z_{\text{ox}}$)

$$255 \quad \frac{\partial NO_3^I}{\partial t} = 0 = D_{NO_3} \frac{\partial^2 NO_3^I}{\partial z^2} - w \frac{\partial NO_3^I}{\partial z} + \gamma_{\text{NH}_4} \frac{1-\phi}{\phi} \cdot \sum_i \text{NC}_i \cdot k_i \cdot C_i(z) \quad (6)$$

$$\frac{\partial \text{NH}_4^I}{\partial t} = 0 = \frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \frac{\partial^2 \text{NH}_4^I}{\partial z^2} - w \frac{\partial \text{NH}_4^I}{\partial z} + \frac{1-\gamma_{\text{NH}_4}}{1+K_{\text{NH}_4}} \cdot \frac{1-\phi}{\phi} \cdot \sum_i \text{NC}_i \cdot k_i \cdot C_i(z) \quad (7)$$

2. Layer ($z_{\text{ox}} < z \leq z_{\text{NO}_3}$)

$$\frac{\partial NO_3^{II}}{\partial t} = 0 = D_{NO_3} \frac{\partial^2 NO_3^{II}}{\partial z^2} - w \frac{\partial NO_3^{II}}{\partial z} - \frac{1-\phi}{\phi} NO_3 C \cdot \sum_i k_i \cdot C_i(z) \quad (8)$$

$$260 \quad \frac{\partial \text{NH}_4^{II}}{\partial t} = 0 = \frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \frac{\partial^2 \text{NH}_4^{II}}{\partial z^2} - w \frac{\partial \text{NH}_4^{II}}{\partial z} \quad (9)$$

3. Layer ($z_{\text{NO}_3} < z \leq z_\infty$)

$$\frac{\partial \text{NH}_4^{III}}{\partial t} = 0 = \frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \frac{\partial^2 \text{NH}_4^{III}}{\partial z^2} - w \frac{\partial \text{NH}_4^{III}}{\partial z} + \frac{1}{1+K_{\text{NH}_4}} \cdot \frac{1-\phi}{\phi} \cdot \sum_i \text{NC}_i \cdot k_i \cdot C_i(z) \quad (10)$$

265 The boundary conditions to solve Equations 6 - 10 are summarized in Table 3. The model assumes known bottom water concentrations for both species, the complete consumption of nitrate at the nitrate penetration depth (or zero flux if $z_{\text{NO}_3} = z_\infty$) and no change in ammonium flux at z_∞ . It considers equal concentrations and diffusive fluxes at z_{bio} and z_{ox} . In addition, the re-oxidation of upward-diffusing reduced ammonium is considered in the oxic-suboxic boundary condition for
270 nitrate and ammonium.

2.3.4 Sulfate and Sulfide

When nitrate is depleted, sulfate reduction is the pathway to mineralize organic matter, thus consuming sulfate (SO_4) and producing hydrogen sulfide (H_2S) until the sulfate penetration depth (z_{SO_4}).
275 Sulfate and sulfide dynamics are thus described by:

1. Layer ($z \leq z_{\text{NO}_3}$)

$$\frac{\partial \text{SO}_4^I}{\partial t} = 0 = D_{\text{SO}_4} \frac{\partial^2 \text{SO}_4^I}{\partial z^2} - w \frac{\partial \text{SO}_4^I}{\partial z} \quad (11)$$

$$\frac{\partial \text{H}_2\text{S}^I}{\partial t} = 0 = D_{\text{H}_2\text{S}} \frac{\partial^2 \text{H}_2\text{S}^I}{\partial z^2} - w \frac{\partial \text{H}_2\text{S}^I}{\partial z} \quad (12)$$

280 2. Layer ($z_{\text{NO}_3} < z \leq z_{\text{SO}_4}$)

$$\frac{\partial \text{SO}_4^{II}}{\partial t} = 0 = D_{\text{SO}_4} \frac{\partial^2 \text{SO}_4^{II}}{\partial z^2} - w \frac{\partial \text{SO}_4^{II}}{\partial z} - \frac{1-\phi}{\phi} \cdot \sum_i \text{SO}_4 C \cdot k_i \cdot C_i(z) \quad (13)$$

$$\frac{\partial \text{H}_2\text{S}^{II}}{\partial t} = 0 = D_{\text{H}_2\text{S}} \frac{\partial^2 \text{H}_2\text{S}^{II}}{\partial z^2} - w \frac{\partial \text{H}_2\text{S}^{II}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{SO}_4 C \cdot k_i \cdot C_i(z) \quad (14)$$

Table 3. Boundary conditions for nitrate and ammonium.

Boundary	Condition	
$z = 0$	known concentration	1) $NO_3(0) = NO_{30}$
$z = z_{\text{bio}}$	continuity	2) $NO_3(z_{\text{bio}}^-) = NO_3(z_{\text{bio}}^+)$ 3) $-(D_{NO_3,0} + D_{\text{bio}}) \cdot \frac{\partial NO_3}{\partial z} _{z_{\text{bio}}^-} = -D_{NO_3,0} \cdot \frac{\partial NO_3}{\partial z} _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $NO_3(z_{\text{ox}}^-) = NO_3(z_{\text{ox}}^+)$ 5) $-D_{NO_3} \cdot \frac{\partial NO_3}{\partial z} _{z_{\text{ox}}^-} + \gamma_{NH_4} \cdot F_{NH_4}(z_{\text{ox}}) = -D_{NO_3} \cdot \frac{\partial NO_3}{\partial z} _{z_{\text{ox}}^+}$ $F_{NH_4}(z_{\text{ox}}) = \frac{1}{1+K_{NH_4}} \cdot \frac{1-\phi}{\phi} \cdot \int_{z_{NO_3}}^{\infty} \sum_i k_i \cdot NC_i \cdot C_i dz$
$z = z_{NO_3}$	NO ₃ consumption ($z_{NO_3} = z_\infty$)	6) IF ($NO_3(z_\infty) > 0$) $\frac{\partial NO_3}{\partial z} _{z_{NO_3}} = 0$ ELSE $NO_3(z_{NO_3}) = 0$
$z = 0$	known concentration	1) $NH_4(0) = NH_{40}$
$z = z_{\text{bio}}$	continuity	2) $NH_4(z_{\text{bio}}^-) = NH_4(z_{\text{bio}}^+)$ 3) $-\frac{D_{NH_4,0} + D_{\text{bio}}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} _{z_{\text{bio}}^-} = -\frac{D_{NH_4,0}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $NH_4(z_{\text{ox}}^-) = NH_4(z_{\text{ox}}^+)$ 5) $-\frac{D_{NH_4}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} _{z_{\text{ox}}^-} - \gamma_{NH_4} \cdot F_{NH_4}(z_{\text{ox}}) = -\frac{D_{NH_4}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} _{z_{\text{ox}}^+}$ $F_{NH_4}(z_{\text{ox}}) = \frac{1}{1+K_{NH_4}} \cdot \frac{1-\phi}{\phi} \cdot \int_{z_{NO_3}}^{\infty} \sum_i k_i \cdot NC_i \cdot C_i dz$
$z = z_{NO_3}$	continuity flux	6) $NH_4(z_{NO_3}^-) = NH_4(z_{NO_3}^+)$ 7) $-\frac{D_{NH_4}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} _{z_{NO_3}^-} = -\frac{D_{NH_4}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} _{z_{NO_3}^+}$
$z = z_\infty$	zero NH ₄ flux	8) $\frac{\partial NH_4}{\partial z} _{z_\infty} = 0$

3. Layer ($z_{SO_4} < z \leq z_\infty$)

$$285 \quad \frac{\partial H_2S^{III}}{\partial t} = 0 = D_{H_2S} \frac{\partial^2 H_2S^{III}}{\partial z^2} - w \frac{\partial H_2S^{III}}{\partial z} \quad (15)$$

To solve equations 11 - 15 the model assumes known concentrations at the sediment-water interface and continuity across the bioturbation depth and the nitrate penetration depth (see Table 4).

The re-oxidation of reduced H₂S to SO₄ is considered in the oxic-suboxic boundary condition for both species, here including the methanic zone, as H₂S is also produced during anaerobic oxidation of methane (AOM). Furthermore, sulfate is used at z_{SO_4} to oxidize methane from below and thus producing H₂S. In case $z_{SO_4} < z_\infty$, sulfate concentration is zero at z_{SO_4} and its diffusive flux must equal the amount of methane produced below; or, in case $z_{SO_4} = z_\infty$, a zero flux condition for sulfate is considered. At lower boundary (z_∞) zero flux of H₂S is considered. **correct??**

295

2.3.5 Phosphate

To model phosphorus (P) in the sediments the model takes into account the change with depth of phosphate (PO₄) and iron-bound P, thereby mainly following the description of Slomp et al. (1996)

Table 4. Boundary conditions for sulfate and sulfide.

Boundary	Condition	
$z = 0$	known concentration	1) $\text{SO}_4(0) = \text{SO}_{40}$
$z = z_{\text{bio}}$	continuity	2) $\text{SO}_4(z_{\text{bio}}^-) = \text{SO}_4(z_{\text{bio}}^+)$
	flux	3) $-(D_{\text{SO}_4,0} + D_{\text{bio}}) \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{bio}}^-} = -D_{\text{SO}_4,0} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $\text{SO}_4(z_{\text{ox}}^-) = \text{SO}_4(z_{\text{ox}}^+)$
	flux	5) $-D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{ox}}^-} + \gamma_{\text{H}_2\text{S}} \cdot F_{\text{H}_2\text{S}}(z_{\text{ox}}) = -D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{ox}}^+}$
	where:	$F_{\text{H}_2\text{S}}(z_{\text{ox}}) = \frac{1-\phi}{\phi} \cdot \left(\int_{z_{\text{NO}_3}}^{\text{SO}_4} \sum_i \text{SO}_4 \text{C} \cdot k_i \cdot C_i dz + \gamma_{\text{CH}_4} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot C_i dz \right)$
$z = z_{\text{NO}_3}$	continuity	6) $\text{SO}_4(z_{\text{NO}_3}^-) = \text{SO}_4(z_{\text{NO}_3}^+)$
	flux	7) $-D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{NO}_3}^-} = -D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{NO}_3}^+}$
$z = z_{\text{SO}_4}$	SO_4 consumption ($z_{\text{SO}_4} = z_\infty$)	8) IF ($\text{SO}_4(z_\infty) > 0$) $\frac{\partial \text{SO}_4}{\partial z} _{z_{\text{SO}_4}} = 0$ ELSE $\text{SO}_4(z_{\text{SO}_4}) = 0$ and $-D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{SO}_4}} = \gamma_{\text{CH}_4} \cdot F_{\text{CH}_4}(z_{\text{SO}_4})$ $F_{\text{CH}_4}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot C_i dz$
	$(z_{\text{SO}_4} < z_\infty)$ with flux from below:	
$z = 0$	known concentration	1) $\text{H}_2\text{S}(0) = \text{H}_2\text{S}_0$
$z = z_{\text{bio}}$	continuity	2) $\text{H}_2\text{S}(z_{\text{bio}}^-) = \text{H}_2\text{S}(z_{\text{bio}}^+)$
	flux	3) $-(D_{\text{H}_2\text{S},0} + D_{\text{bio}}) \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{bio}}^-} = -D_{\text{H}_2\text{S},0} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $\text{H}_2\text{S}(z_{\text{ox}}^-) = \text{H}_2\text{S}(z_{\text{ox}}^+)$
	flux	5) $-D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{ox}}^-} - \gamma_{\text{H}_2\text{S}} F_{\text{H}_2\text{S}}(z_{\text{ox}}) = -D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{ox}}^+}$
	where:	$F_{\text{H}_2\text{S}}(z_{\text{ox}}) = \frac{1-\phi}{\phi} \cdot \left(\int_{z_{\text{NO}_3}}^{\text{SO}_4} \sum_i \text{SO}_4 \text{C} \cdot k_i \cdot C_i dz + \gamma_{\text{CH}_4} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot C_i dz \right)$
$z = z_{\text{NO}_3}$	continuity	6) $\text{H}_2\text{S}(z_{\text{NO}_3}^-) = \text{H}_2\text{S}(z_{\text{NO}_3}^+)$
	flux	7) $-D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{NO}_3}^-} = -D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{NO}_3}^+}$
$z = z_{\text{SO}_4}$	continuity flux (with AOM)	8) $\text{H}_2\text{S}(z_{\text{SO}_4}^-) = \text{H}_2\text{S}(z_{\text{SO}_4}^+)$ 9) $-D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{SO}_4}^-} + \gamma_{\text{CH}_4} \cdot F_{\text{CH}_4}(z_{\text{SO}_4}) = -D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{SO}_4}^+}$ $F_{\text{CH}_4}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot C_i dz$
$z = z_\infty$	zero H_2S flux	10) $\frac{\partial \text{H}_2\text{S}}{\partial z} _{z_\infty} = 0$

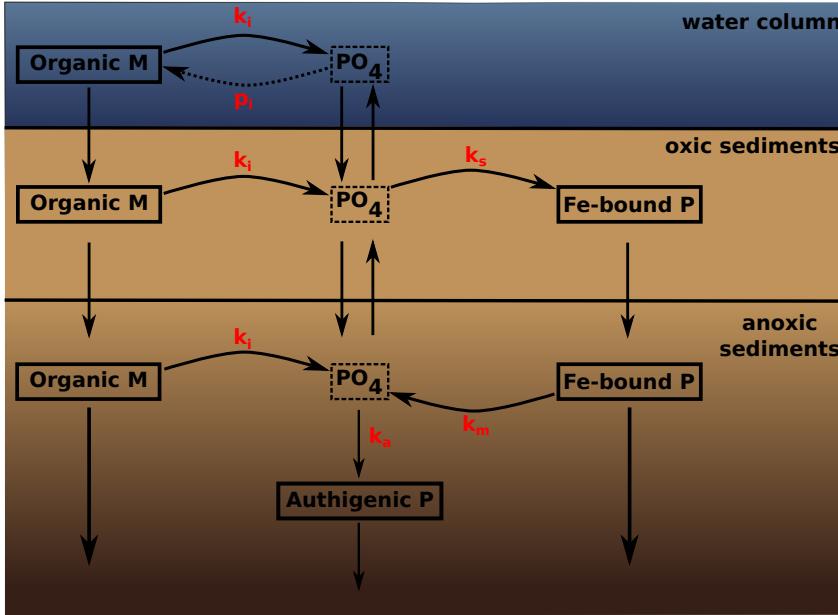


Figure 2. A schematic of the sedimentary P cycle in OMEN-SED (1.0). Red numbers represent kinetic rate constants for phosphorus dynamics (compare Table 8; p_i represents uptake rate of PO_4 via primary production in shallow environments). Adapted from Slomp et al. (1996).

and Gypens et al. (2008). Throughout the sediment column organic matter is mineralized resulting
 300 in a release of phosphate to the pore water. In the oxic part of the sediment, this PO_4 either diffuses upward to the water column or is adsorbed to Fe oxides forming Fe-bound P (or M)(Slomp et al., 1998). In the suboxic/anoxic zone, PO_4 is not only produced through organic matter degradation but is also released from the Fe-bound P pool due to the reduction of Fe oxides. Furthermore, phosphate concentrations can become high enough in this layer for authigenic mineral formation to occur
 305 (Cappellen and Berner, 1988). This phosphorus bound in authigenic minerals represents a permanent sink for reactive phosphorus (Slomp et al., 1996). See Figure 2 for a schematic overview of the sedimentary P cycle. Therefore the diagenetic equations for phosphorus are written:

1. Layer ($z \leq z_{\text{ox}}$)

$$\frac{\partial \text{PO}_4^I}{\partial t} = \frac{D_{\text{PO}_4}}{1 + K_{\text{PO}_4}^I} \frac{\partial^2 \text{PO}_4^I}{\partial z^2} - w \frac{\partial \text{PO}_4^I}{\partial z} + \frac{1 - \phi}{\phi} \frac{1}{1 + K_{\text{PO}_4}^I} \sum_i (\text{PC}_i \cdot k_i \cdot C_i(z)) - \frac{k_s}{1 + K_{\text{PO}_4}^I} (\text{PO}_4^I - \text{PO}_4^s) \quad (16)$$

$$\frac{\partial M^I}{\partial t} = D_M \frac{\partial^2 M^I}{\partial z^2} - w \frac{\partial M^I}{\partial z} + \frac{\phi}{1 - \phi} k_s (\text{PO}_4^I - \text{PO}_4^s) \quad (17)$$

Table 5. Boundary conditions for phosphate and Fe-bound P (M).

Boundary	Condition	
$z = 0$	known concentration	1) $\text{PO}_4(0) = \text{PO}_{40}$
$z = z_{\text{bio}}$	continuity	2) $\text{PO}_4(z_{\text{bio}}^-) = \text{PO}_4(z_{\text{bio}}^+)$
	flux	3) $(D_{\text{PO}_4,0} + D_{\text{bio}}) \cdot \frac{\partial \text{PO}_4}{\partial z} \Big _{z_{\text{bio}}^-} = D_{\text{PO}_4,0} \cdot \frac{\partial \text{PO}_4}{\partial z} \Big _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $\text{PO}_4(z_{\text{ox}}^-) = \text{PO}_4(z_{\text{ox}}^+)$
	flux	5) $-\frac{D_{\text{PO}_4}}{1+K_{\text{PO}_4}^{II}} \cdot \frac{\partial \text{PO}_4}{\partial z} \Big _{z_{\text{ox}}^-} = -\frac{D_{\text{PO}_4}}{1+K_{\text{PO}_4}^{II}} \cdot \frac{\partial \text{PO}_4}{\partial z} \Big _{z_{\text{ox}}^+}$
$z = z_{\infty}$	flux	10) $\frac{\partial \text{PO}_4}{\partial z} \Big _{z_{\infty}} = 0$
$z = 0$	known concentration	1) $M(0) = M_0$
$z = z_{\text{bio}}$	continuity	2) $M(z_{\text{bio}}^-) = M(z_{\text{bio}}^+)$
	flux	3) $\frac{\partial M}{\partial z} \Big _{z_{\text{bio}}^-} = \frac{\partial M}{\partial z} \Big _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $M(z_{\text{ox}}^-) = M(z_{\text{ox}}^+)$
	flux	5) $\frac{\partial M}{\partial z} \Big _{z_{\text{ox}}^-} = \frac{\partial M}{\partial z} \Big _{z_{\text{ox}}^+}$
$z = z_{\infty}$	assymptotic concentration	10) $M(z_{\infty}) = M_{\infty}$

2. Layer ($z_{\text{ox}} < z$)

$$315 \quad \frac{\partial M^{II}}{\partial t} = D_M \frac{\partial^2 M^{II}}{\partial z^2} - w \frac{\partial M^{II}}{\partial z} - k_m (M^{II} - M^{\infty}) \quad (18)$$

$$\frac{\partial \text{PO}_4^{II}}{\partial t} = \frac{D_{\text{PO}_4}}{1+K_{\text{PO}_4}^{II}} \frac{\partial^2 \text{PO}_4^{II}}{\partial z^2} - w \frac{\partial \text{PO}_4^{II}}{\partial z} + \frac{1-\phi}{\phi} \frac{1}{1+K_{\text{PO}_4}^{II}} \sum_i (\text{PC}_i \cdot k_i \cdot C_i(z)) \\ - \frac{k_a}{1+K_{\text{PO}_4}^{II}} (\text{PO}_4^{II} - \text{PO}_4^a) + \frac{(1-\phi)}{\phi} \frac{k_m}{1+K_{\text{PO}_4}^{II}} (M^{II} - M^{\infty}) \quad (19)$$

(20)

- 320 The boundary conditions to solve Equations 16 - 19 are summarized in Table 5. The model assumes known bottom water concentrations and equal concentrations and diffusive fluxes at z_{bio} and z_{ox} for both species. Additionally it considers no change in phosphate flux and an assymptotic Fe-bound P concentration at z_{∞} .

325 @ Sandra: SWI Flux for M does not exist, right???

2.3.6 Dissolved Inorganic Carbon (DIC)

Dissolved inorganic carbon (DIC) is produced by when organic matter is degraded. Explain different ratios for the two layers.

330 1. Layer ($z \leq z_{\text{SO}_4}$)

$$\frac{\partial \text{DIC}^I}{\partial t} = 0 = D_{\text{DIC}} \frac{\partial^2 \text{DIC}^I}{\partial z^2} - w \frac{\partial \text{DIC}^I}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{DICC}^I \cdot k_i \cdot C_i(z) \quad (21)$$

Table 6. Boundary conditions for DIC and alkalinity.

Boundary	Condition	
$z = 0$	known concentration	1) $\text{DIC}(0) = \text{DIC}_0$
$z = z_{\text{bio}}$	continuity	2) $\text{DIC}(z_{\text{bio}}^-) = \text{DIC}(z_{\text{bio}}^+)$
	flux	3) $-(D_{\text{DIC},0} + D_{\text{bio}}) \cdot \frac{\partial \text{DIC}}{\partial z} \Big _{z_{\text{bio}}^-} = -D_{\text{DIC},0} \cdot \frac{\partial \text{DIC}}{\partial z} \Big _{z_{\text{bio}}^+}$
$z = z_{\text{SO}_4}$	continuity	8) $\text{DIC}(z_{\text{SO}_4}^-) = \text{DIC}(z_{\text{SO}_4}^+)$
	flux (with AOM)	9) $-D_{\text{DIC}} \cdot \frac{\partial \text{DIC}}{\partial z} \Big _{z_{\text{SO}_4}^-} + \gamma_{\text{CH}_4} \cdot F_{\text{CH}_4}(z_{\text{SO}_4}) = -D_{\text{DIC}} \cdot \frac{\partial \text{DIC}}{\partial z} \Big _{z_{\text{SO}_4}^+}$
	where:	$F_{\text{CH}_4}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot C_i dz$
$z = z_{\infty}$	zero DIC flux	10) $\frac{\partial \text{DIC}}{\partial z} \Big _{z_{\infty}} = 0$
$z = 0$	known concentration	1) $\text{ALK}(0) = \text{ALK}_0$
$z = z_{\text{bio}}$	continuity	2) $\text{ALK}(z_{\text{bio}}^-) = \text{ALK}(z_{\text{bio}}^+)$
	flux	3) $-(D_{\text{ALK},0} + D_{\text{bio}}) \cdot \frac{\partial \text{ALK}}{\partial z} \Big _{z_{\text{bio}}^-} = -D_{\text{ALK},0} \cdot \frac{\partial \text{ALK}}{\partial z} \Big _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $\text{ALK}(z_{\text{ox}}^-) = \text{ALK}(z_{\text{ox}}^+)$
	flux	5) $-D_{\text{ALK}} \cdot \frac{\partial \text{ALK}}{\partial z} \Big _{z_{\text{ox}}^-} + F_{\text{ALK}}(z_{\text{ox}}) = -D_{\text{ALK}} \cdot \frac{\partial \text{ALK}}{\partial z} \Big _{z_{\text{ox}}^+}$
	where:	$F_{\text{ALK}}(z_{\text{ox}}) = \frac{1-\phi}{\phi} \cdot \left(\text{ALK}^{\text{H}_2\text{S}} \gamma_{\text{H}_2\text{S}} \int_{z_{\text{NO}_3}}^{z_{\text{SO}_4}} \sum_i \text{SO}_4 \text{C} \cdot k_i \cdot C_i dz \right) + \frac{1-\phi}{\phi} \cdot \left(\text{ALK}^{\text{NIT}} \frac{\gamma_{\text{NH}_4}}{1+k_{\text{NH}_4}} \int_{z_{\text{NO}_3}}^{\infty} \sum_i \text{NC}_i \cdot k_i \cdot C_i dz \right)$
$z = z_{\text{NO}_3}$	continuity	6) $\text{ALK}(z_{\text{NO}_3}^-) = \text{ALK}(z_{\text{NO}_3}^+)$
	flux	7) $-D_{\text{ALK}} \cdot \frac{\partial \text{ALK}}{\partial z} \Big _{z_{\text{NO}_3}^-} = -D_{\text{ALK}} \cdot \frac{\partial \text{ALK}}{\partial z} \Big _{z_{\text{NO}_3}^+}$
$z = z_{\text{SO}_4}$	continuity	8) $\text{ALK}(z_{\text{SO}_4}^-) = \text{ALK}(z_{\text{SO}_4}^+)$
	flux (with AOM)	9) $-D_{\text{ALK}} \cdot \frac{\partial \text{ALK}}{\partial z} \Big _{z_{\text{SO}_4}^-} + F_{\text{ALK}}(z_{\text{SO}_4}) = -D_{\text{ALK}} \cdot \frac{\partial \text{ALK}}{\partial z} \Big _{z_{\text{SO}_4}^+}$
	where:	$F_{\text{ALK}}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \left(\text{ALK}^{\text{AOM}} \gamma_{\text{CH}_4} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot C_i dz \right)$
$z = z_{\infty}$	zero ALK flux	10) $\frac{\partial \text{ALK}}{\partial z} \Big _{z_{\infty}} = 0$

2. Layer ($z_{\text{SO}_4} < z \leq z_{\infty}$)

$$\frac{\partial \text{DIC}^{II}}{\partial t} = 0 = D_{\text{DIC}} \frac{\partial^2 \text{DIC}^{II}}{\partial z^2} - w \frac{\partial \text{DIC}^{II}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{DIC}^{II} \cdot k_i \cdot C_i(z) \quad (22)$$

335

To solve equations 21 and 22 the model assumes the boundary conditions summarised in Table 6.

2.3.7 Alkalinity

Alkalinity is produced and consumed by when organic matter is degraded. Explain why it is produced/consumed, where and how in the different layers $j \in \{I, II, III, IV\}$ and talk earlier on in

340 the model description why it matters.

1. Layer ($z \leq z_{\text{ox}}$)

$$\frac{\partial \text{ALK}^I}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^I}{\partial z^2} - w \frac{\partial \text{ALK}^I}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i (\gamma_{\text{NH}_4} \text{NC}_i \text{ALK}^{\text{NIT}} + \text{ALK}^{\text{OX}}) \cdot k_i \cdot C_i(z) \quad (23)$$

345 2. Layer ($z_{\text{ox}} < z \leq z_{\text{NO}_3}$)

$$\frac{\partial \text{ALK}^{II}}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^{II}}{\partial z^2} - w \frac{\partial \text{ALK}^{II}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{ALK}^{\text{DEN}} \cdot k_i \cdot C_i(z) \quad (24)$$

3. Layer ($z_{\text{NO}_3} < z \leq z_{\text{SO}_4}$)

$$350 \quad \frac{\partial \text{ALK}^{III}}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^{III}}{\partial z^2} - w \frac{\partial \text{ALK}^{III}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{ALK}^{\text{SUL}} \cdot k_i \cdot C_i(z) \quad (25)$$

4. Layer ($z_{\text{SO}_4} < z \leq z_{\infty}$)

$$\frac{\partial \text{ALK}^{IV}}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^{IV}}{\partial z^2} - w \frac{\partial \text{ALK}^{IV}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{ALK}^{\text{MET}} \cdot k_i \cdot C_i(z) \quad (26)$$

To solve equations 23 and 26 the model assumes the boundary conditions summarised in Table 6.

355 **2.4 Model Parameters**

This section describes the parameters used in OMEN-SED (1.0) to describe sediment transport and biogeochemical reactions related to the burial and mineralization of organic matter under a wide range of environmental conditions. Table 7 states the parameters for sediment characteristics and Table 8 summarizes the stoichiometric factors and secondary reaction parameters used in the model.

360 **2.4.1 Transport Parameters**

Advection is the bulk flow of sediments and can be directly related to the accumulation of new material on the seafloor (i.e. sedimentation, Burdige, 2006). This results in a downward flux of older sediment material and porewater in relation to the sediment-water interface. OMEN-SED (1.0) uses the empirical global relationship between sediment accumulation rate (cm yr^{-1}) and seafloor depth

365 (m) of Middelburg et al. (1997):

$$w = 3.3 \cdot 10^{-0.87478367 - 0.00043512 \cdot \text{depth}} \quad (27)$$

As discussed before (Sec. 2.2), the diffusion coefficient of species i is calculated as $D_i = D_{i,0} + D_{\text{bio}} = D_{\text{mol},i} \cdot f_{ir} + D_{\text{bio}}$ for dissolved species and $D_i = D_{\text{bio}}$ for solid species. The bioturbation coefficient D_{bio} ($\text{cm}^2 \text{yr}^{-1}$) is constant in the bioturbated zone and also follows the empirical relationship by Middelburg et al. (1997):

$$D_{\text{bio}} = 5.2 \cdot 10^{0.76241122 - 0.00039724 \cdot \text{depth}} \quad (28)$$

Studies showed that bioturbational effects on a global scale are largely restricted to the upper 10 cm of the sediments and are only marginally related to seafloor depth (e.g. Boudreau, 1998; Teal et al., 2010). Therefore, OMEN-SED (1.0) imposes a globally invariant bioturbation depth of 10 cm. Bioirrigation can enhance the molecular diffusion coefficient $D_{i,0} = D_{\text{mol},i} \cdot f_{ir}$ (Soetaert et al.,

1996a). However, here we do not consider this effect and set f_{ir} to a constant value of 1. The specific molecular diffusion coefficients $D_{\text{mol},i}$ are corrected for sediment porosity ϕ , tortuosity F and are linearly interpolated for an ambient temperature T using zero-degree coefficients D_i^0 and temperature dependent diffusion coefficients D_i^T (compare Gypens et al., 2008):

$$380 \quad D_{\text{mol},i} = (D_i^0 + D_i^T \cdot T) \cdot \frac{1}{\phi \cdot F}$$

Tortuosity can be expressed in terms of porosity as $F = \frac{1}{\phi^m}$ (Ullman and Aller, 1982) with the exponent m varying according to the type of sediment (here we use $m=3$). Values for D_i^T and D_i^0 are summarized in Table 7 and are adapted from Li and Gregory (1974) and Gypens et al. (2008).

2.4.2 Reaction Parameters

- 385 The applied multi-G approach for organic matter degradation considers specific degradation rate constants k_i (yr^{-1}) for each compound class. The degradation constants are generally taken from the coupled Earth System model and are assumed invariant along the sediment column, therefore independent of the nature of the terminal electron acceptor. The stoichiometry of organic matter is represented by the factors NC_i and PC_i denoting the molecular nitrogen to carbon and phosphorus
 390 to carbon ratio. In the sulfidic and methanic zone the reduction of 1 mol organic matter additionally produces 0.5 mol of hydrogen sulfide (SO_4C) and 0.5 mol of methane (MC). In the total sediment column organic matter mineralization consumes the specific terminal electron acceptor with a fixed ratio (OC , NO_3C and SO_4C respectively). See Table 8 for a complete summary of the parameters and their values.

395 **2.5 Module Structure**

- TODO:** An analytical steady-state solution is found for the reaction-transport equation of each chemical species in each layer. At each boundary (i.e. z_{ox} , z_{bio} , z_{NO_3} and z_{SO_4}) the model has to match continuity and flux for different ODE solutions of the layer above and below the specific boundary. In particular the bioturbation boundary is problematic as it can theoretically occur in any
 400 geochemical layer. In order to simplify this recurring boundary matching problem it is implemented in an independent algorithm which is described in Section 2.5.1. Instructions and requirements for coupling OMEN-SED (1.0) to a global Earth Sytem Model are given in Section 2.5.2.

2.5.1 Generic boundary condition matching (GBCM)

A general steady-state advection-diffusion-reaction (ADR) diagenetic equation looks like:

$$405 \quad \frac{\partial C}{\partial t} = 0 = D \frac{\partial^2 C}{\partial z^2} - w \frac{\partial C}{\partial z} - \sum_i \alpha_i \exp(-\beta_i z) - k \cdot C + Q. \quad (29)$$

Table 7. Fixed sediment characteristics and transport parameters. **TODO:** Update table!

Parameter	Unit	Value	Description/Source
ρ_{sed}	g cm^{-3}	2.5	Sediment density
w	cm yr^{-1}	Fct. of seafloor depth	Advection/Sediment accumulation rate Middelburg et al. (1997)
z_{bio}	cm	10	Bioturbation depth Boudreau (1998); Teal et al. (2010)
D_{bio}	$\text{cm}^2 \text{yr}^{-1}$	Fct. of seafloor depth	Bioturbation coefficient Middelburg et al. (1997)
ϕ	-	0.8	Porosity
F	-	$\frac{1}{\phi^m}$	Tortuosity, here $m=3$
$f_i r$	-	1	Irrigation factor
PO_4^s	mol cm^{-3}	$1 \cdot 10^{-9}$	equilibrium conc. for P sorption Slomp et al. (1996)
PO_4^a	mol cm^{-3}	$3.7 \cdot 10^{-9}$	equilibrium conc. for authigenic P precipitation Slomp et al. (1996)
M^∞	mol cm^{-3}	$1.99 \cdot 10^{-9}$	asymptotic concentration for Fe-bound P Slomp et al. (1996)
Diffusion coefficients (Li and Gregory, 1974; Gypens et al., 2008)			
$D_{\text{O}_2}^0$	$\text{cm}^2 \text{yr}^{-1}$	348.62172	Molecular diffusion coefficient of oxygen at 0°C
$D_{\text{O}_2}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ }^\circ\text{C}^{-1}$	14.08608	Diffusion coefficient for linear temp. dependence of oxygen
$D_{\text{NO}_3}^0$	$\text{cm}^2 \text{yr}^{-1}$	308.42208	Molecular diffusion coefficient of nitrate at 0°C
$D_{\text{NO}_3}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ }^\circ\text{C}^{-1}$	12.2640	Diffusion coefficient for linear temp. dependence of nitrate
$D_{\text{NH}_4}^0$	$\text{cm}^2 \text{yr}^{-1}$	308.42208	Molecular diffusion coefficient of ammonium at 0°C
$D_{\text{NH}_4}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ }^\circ\text{C}^{-1}$	12.2640	Diffusion coefficient for linear temp. dependence of ammonium
$D_{\text{SO}_4}^0$	$\text{cm}^2 \text{yr}^{-1}$	157.68	Molecular diffusion coefficient of sulfate at 0°C
$D_{\text{SO}_4}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ }^\circ\text{C}^{-1}$	7.884	Diffusion coefficient for linear temp. dependence of sulfate
$D_{\text{H}_2\text{S}}^0$	$\text{cm}^2 \text{yr}^{-1}$	307.476	Molecular diffusion coefficient of sulfide at 0°C
$D_{\text{H}_2\text{S}}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ }^\circ\text{C}^{-1}$	9.636	Diffusion coefficient for linear temp. dependence of sulfide
$D_{\text{PO}_4}^0$	$\text{cm}^2 \text{yr}^{-1}$	112.90764	Molecular diffusion coefficient of phosphate at 0°C
$D_{\text{PO}_4}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ }^\circ\text{C}^{-1}$	5.586252	Diffusion coefficient for linear temp. dependence of phosphate

Table 8. Values for biogeochemical parameters used in OMEN-SED (1.0).

Parameter/Variable	Unit	Value	Description
Stoichiometric factors and molecular ratios			
NC ₁	mol/mol	0.1509	nitrogen to carbon ratio refractory fraction, two different ones? why these values?
NC ₂	mol/mol	0.13333	nitrogen to carbon ratio labile fraction
PC _i	mol/mol	0.0094	phosphorus to carbon ratio
MC	mol/mol	0.5	methane to carbon ratio produced during methanogenesis
OC	mol/mol	1.0	oxygen to carbon ratio
NO ₃ C	mol/mol	94.4/106	nitrate to carbon ratio
SO ₄ C	mol/mol	0.5	sulfate to carbon ratio
ALK ^{OX}	mol/mol	15/106	ALK from aerobic degradation
ALK ^{NIT}	mol/mol	-2	ALK from nitrification
ALK ^{DEN}	mol/mol	93.4/106	ALK from denitrification
ALK ^{SUL}	mol/mol	15/106	ALK from sulfate reduction
ALK ^{MET}	mol/mol	14/106	ALK from methanogenesis
ALK ^{H2S}	mol/mol	-1	ALK from H ₂ S oxidation CORRECT???
ALK ^{AOM}	mol/mol	2	ALK from methanogenesis
Secondary reaction parameters			
γ _{NH₄}	-	0.8	fraction of NH ₄ that is oxidised in oxic layer
γ _{H₂S}	-	0.95	fraction of H ₂ S that is oxidised in oxic layer
γ _{CH₄}	-	1.0	fraction of CH ₄ that is oxidised at z _{SO₄}
Rate constants			
k _i	yr ⁻¹	from Earth System Model	OM degradation rate constants
k _s	yr ⁻¹	???	rate constant for P sorption
k _m	yr ⁻¹	???	rate constant for Fe-bound P release
k _a	yr ⁻¹	???	rate constant for authigenic P formation

where z is the sediment depth, t the time, D is the diffusion coefficient and w is the advection rate.

The ODE solution is of the general form:

$$C(z) = A \exp(az) + B \exp(bz) + \sum_i \frac{\alpha_i}{D\beta_i^2 - w\beta_i - k} \cdot \exp(-\beta_i z) + \frac{Q}{k} \quad (30)$$

and can therefore be expressed as:

$$C(z) = A \cdot E(z) + B \cdot F(z) + G(z) \quad (31)$$

where $E(z)$, $F(z)$ are the homogeneous solutions of the ODE, $G(z)$ the particular integral, and A , B are the integration constants.

415

Each boundary matching problem involves matching continuity and flux for the two solutions $C_U(z)$ ($=$ 'upper') and $C_L(z)$ ($=$ 'lower') across a boundary at $z = z_b$. Therefore, we get two ODE solutions of the genral form:

$$C_U(z) = A_U \cdot E_U(z) + B_U \cdot F_U(z) + G_U(z) \quad (32)$$

$$420 \quad C_L(z) = A_L \cdot E_L(z) + B_L \cdot F_L(z) + G_L(z). \quad (33)$$

The two boundary conditions are: for continuity (where for generality we allow a discontinuity V_b)

$$C_U(z_b) = C_L(z_b) + V_b \quad (34)$$

425 and for flux

$$D_U C'_U(z_b) + w C_U(z_b) = D_L C'_L(z_b) + w C_L(z_b) + F_b \quad (35)$$

where w is advection, D are the diffusion coefficients and F_b is any flux discontinuity.

In terms of the ODE solutions (32), (33), the boundary conditions represent two equations connecting

430 the four integration constants:

$$\begin{pmatrix} E_U & F_U \\ D_U E'_U & D_U F'_U \end{pmatrix} \begin{pmatrix} A_U \\ B_U \end{pmatrix} = \begin{pmatrix} E_L & F_L \\ D_L E'_L & D_L F'_L \end{pmatrix} \begin{pmatrix} A_L \\ B_L \end{pmatrix} + \begin{pmatrix} G_L - G_U + V_b \\ D_L G'_L - D_U G'_U + F_b - wV_b \end{pmatrix} \quad (36)$$

where the ODE solutions E , F , G are all evaluated at z_b .

Equation (36) can be solved to give A_U and B_U as a function of the integration constants from the

435 layer below (A_L and B_L), thereby constructing a piecewise solution for the whole region, with now just two integration constants A_L and B_L .

In the code the function **benthic_utils.matchsoln** provides this solution in the form:

$$\begin{pmatrix} A_U \\ B_U \end{pmatrix} = \begin{pmatrix} c_1 & c_2 \\ c_3 & c_4 \end{pmatrix} \begin{pmatrix} A_L \\ B_L \end{pmatrix} + \begin{pmatrix} d_1 \\ d_2 \end{pmatrix}. \quad (37)$$

Using (37) we can now rewrite $C_U(z)$ in (32) as a function of A_L and B_L :

440 $C_U(z) = (c_1 A_L + c_2 B_L + d_1) \cdot E_U(z) + (c_3 A_L + c_4 B_L + d_2) \cdot F_U(z) + G_U(z)$

and hence define the “transformed” basis functions $E_U^*(z)$, $F_U^*(z)$, $G_U^*(z)$ such that:

$$C_U(z) = A_L \cdot E_U^*(z) + B_L \cdot F_U^*(z) + G_U^*(z) \quad (38)$$

where

$$E_U^*(z) = c_1 E_U(z) + c_3 F_U(z)$$

445 $F_U^*(z) = c_2 E_U(z) + c_4 F_U(z) \quad (39)$

$$G_U^*(z) = G_U(z) + d_1 E_U(z) + d_2 F_U(z)$$

(in the code this is done by **benthic_utils.xformsoln**).

Solving the sediment layer stack

450 Equations (37), (38) and (39) can now be applied for each layer boundary, working up from the bottom of the sediments. The net result is to construct a piecewise solution with just two integration constants (coming from the lowest layer), which can then be solved for by applying one boundary condition for the sediment-water interface and one for the bottom of the sediments (e.g. a concentration condition at the bottom of the sediments, and a flux condition at the SWI).

455 **TODO: Add figure, illustrating this e.g. for nitrate...**

Abstracting out the bioturbation boundary

The bioturbation boundary affects the diffusion coefficient of the modelled solutes and the conservation equation of organic matter which is available for mineralization. The boundary is particularly inconvenient as it can in principle occur in the middle of any “geochemical” layer and therefore generates multiple cases. To simplify this for solutes, the “piecewise solution construction” above is used to abstract out the bioturbation boundary. An initial test for each layer is made to identify its “bioturbation-status” (fully bioturbated, fully non-bioturbated or crossing the bioturbation boundary) and (if needed) a piecewise solution is constructed by matching boundary conditions across the bioturbation boundary. The “outside” code therefore never needs to know whether it is dealing with a piecewise solution (i.e. matched across a bioturbation boundary) or a “simple” solution (i.e. the layer is fully bioturbated or fully non-bioturbated).

In the code, this is performed by **zTOC.prepfg_l12** which hands back a structure `ls` containing the “bioturbation-status” for each layer and (if needed) the description of the piecewise solution (coefficients $c_1, c_2, c_3, c_4, d_1, d_2$ as above). So e.g. for sulfate, **zTOC.prepfg_l12** is called three times at 470 the beginning of **zSO4.calcbc** (one for each “geochemical” layer: oxic, suboxic, sulfidic) handing back three structures `ls` describing the layer’s “bioturbation-status”, abstracting away the bioturbation boundary and all associated conditional logic. When calculating the solutions for the different layers, the pre-calculated structure `ls` is passed to the function **zTOC.calcfg_l12** which sorts out the correct solution type to use.

475 2.5.2 Coupling to an Earth System Model

3 Test Cases

3.1 Sediment profiles

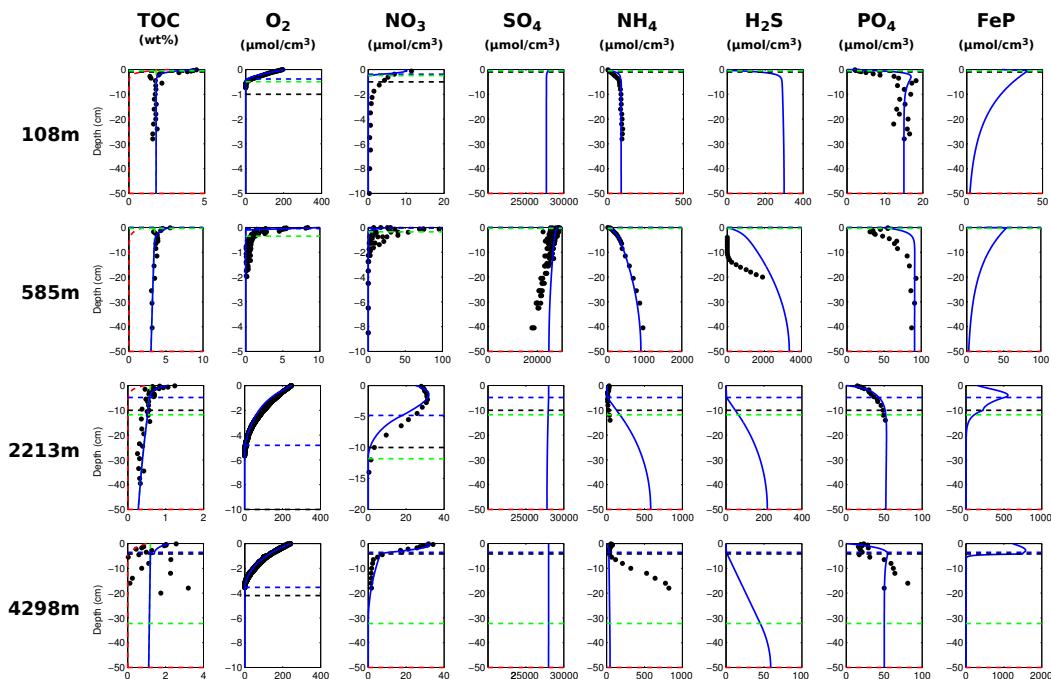


Figure 3. Modelled (curves) and measured (filled dots) dissolved and solid phase pore water profiles for four different sediment cores. Note that different scales are used for different stations. The blue TOC curve represents the sum of the refractory (green) and labile (red) TOC fraction.

Table 9. Model boundary conditions for the sampling stations in Figure 3.

Sediment characteristics:							
Depth (m)	Temp. (°C)	z_{bio} (cm)	D_{bio} ($\text{cm}^2 \text{yr}^{-1}$)	TOC_1 (wt%)	TOC_2 (wt%)	k_1 (yr^{-1})	k_2 (yr^{-1})
108	12.5	1.0	0.02	2.66	1.8	0.5	$1.0e^{-5}$
585	5.85	0.01	0.02	2.0	3.5	0.035	$5.0e^{-5}$
2213	3.2	10.0	0.17	0.45	0.6	0.15	$9.0e^4$
4298	2.5	4.2	0.18	1.0	1.2	0.055	$1e^{-5}$

Bottom water concentrations of solutes (all in $\mu\text{mol cm}^{-3}$):							
Depth	O_2	NO_3	SO_4	NH_4	H_2O	PO_4	PO_4^{a}
108	210.0	9.6	28,000	0.4	0.0	0.0	15.0
585	10.0	25.0	28,000	0.0	0.0	50.0	90.0
2213	250	25	28,000	0.6	0.0	0.0	5.0
4298	243	30.1	28,000	0.22	0.0	0.0	5.0

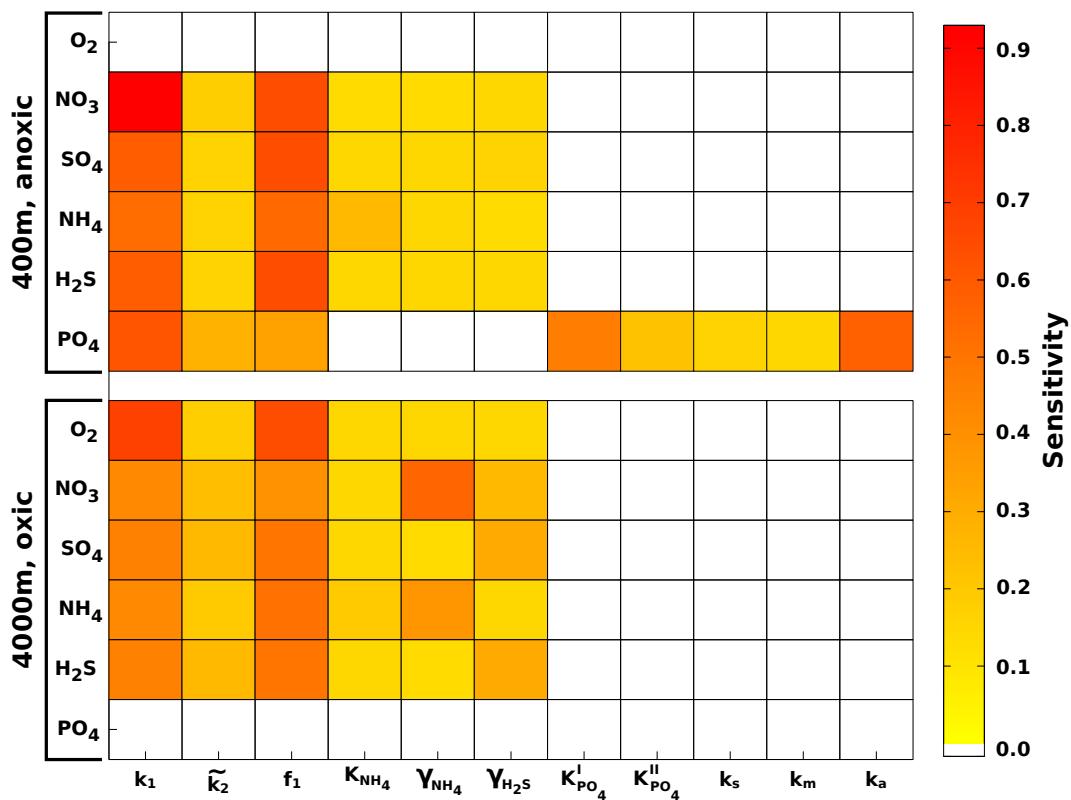


Figure 4. Pattern plot, showing the output sensitivity for each SWI flux (i.e. the chemical compounds on the horizontal axis) and each input factor (i.e. the model parameters on the vertical axis) for two hypothetical sediment cores.

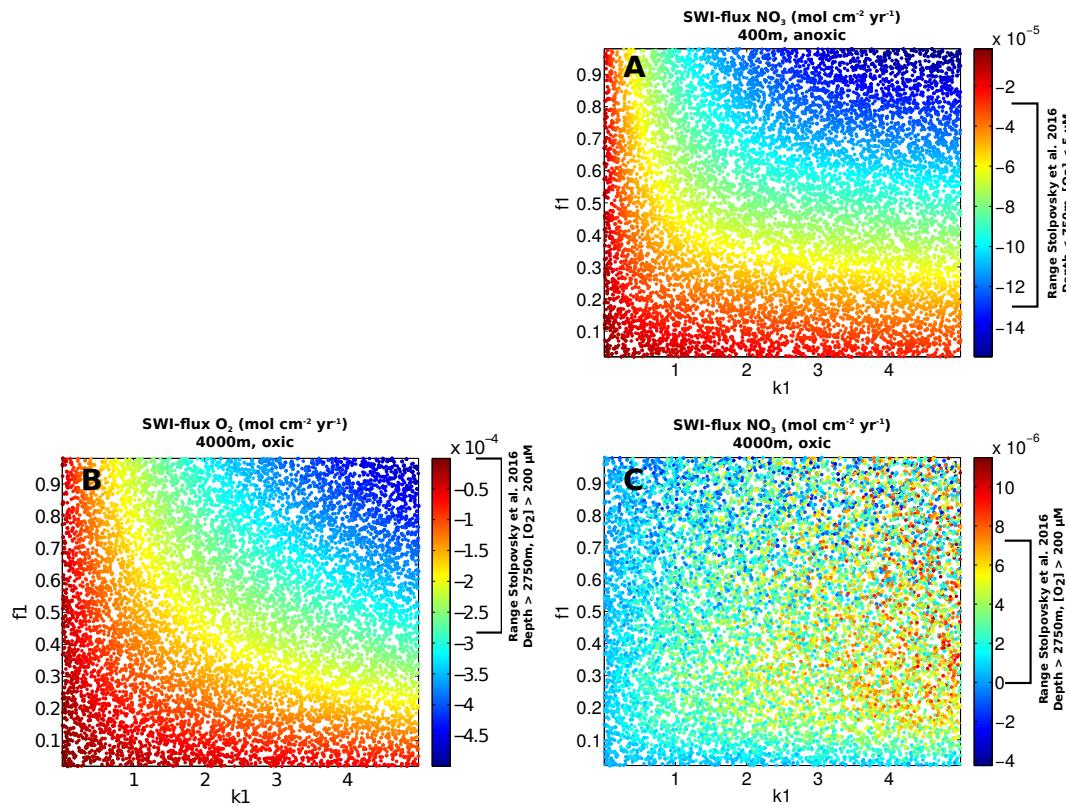


Figure 5.

3.2 Sensitivity Analysis

3.3 Benthic fluxes on a global scale

480 Application to Seitert, 2004 OM, burwiczk see rate data and evaluation based on global data (Archer)

3.4 GENIE-Cretaceous test?

4 Scope of applicability and model limitations

5 Conclusions

TEXT

Table 10. Primary pathways of organic matter degradation, secondary redox reactions and stoichiometries implemented in the reaction network.

Pathway	Stoichiometry
Primary Redox Reactions	
Aerobic degradation	$(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + (\text{x} + 2\text{y})\text{O}_2 + (\text{y} + 2\text{z})\text{HCO}_3^- \rightarrow (\text{x} + \text{y} + 2\text{z})\text{CO}_2 + \text{yNO}_3^- + \text{zHPO}_4^{2-} + (\text{x} + 2\text{y} + 2\text{z})\text{H}_2\text{O}$
Denitrification	$5(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + (\text{4x} + 3\text{y})\text{NO}_3^- \rightarrow (\text{2x} + 4\text{y})\text{N}_2 + (\text{x} - 3\text{y} + 10\text{z})\text{CO}_2 + (\text{4x} + 3\text{y} - 10\text{z})\text{HCO}_3^- + 5\text{zHPO}_4^{2-} + (\text{3x} + 6\text{y} + 10\text{z})\text{H}_2\text{O}$
Sulfate reduction	$2(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + \text{xSO}_4^{2-} + 2(\text{y} - 2\text{z})\text{CO}_2 + 2(\text{y} - 2\text{z})\text{H}_2\text{S} \rightarrow \text{xH}_2\text{O} + 2(\text{x} + \text{y} - 2\text{z})\text{HCO}_3^- + 2\text{yNH}_4^+ + 2\text{zHPO}_4^{2-}$
Methanogenesis	—
Secondary Redox Reactions	
Nitrification	$\text{NH}_4^+ + 2\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{NO}_3^- + 2\text{CO}_2 + 3\text{H}_2\text{O}$
Sulfide oxidation	$\text{H}_2\text{S} + 2\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{SO}_4^{2-} + 2\text{CO}_2 + 2\text{H}_2\text{O}$
AOM	$\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$ how get H_2S? $\rightarrow \text{CO}_3^{2-} + \text{H}_2\text{S} + \text{H}_2\text{O}$

Appendix A: Reaction Network

A1

Acknowledgements. TEXT

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