

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 a new, analytical early diagenetic model resolving organic matter cycling and associated biogeochemical dynamics in marine sediments called OMEN-SED (Organic Matter ENabled SEDiment model). Most biogeochemical cycles and reactions in the surface sediments can be related either directly or indirectly to the degradation of organic matter.

5 Despite its fundamental importance, an appropriate Earth System model of the coupled atmosphere-ocean-sediment system which is able to model all relevant processes and feedbacks over geological time-scales currently does not exist. The major problem is the high computational cost of simulating the essential redox reactions in marine sediments which are important to calculate burial of organic matter and benthic recycling fluxes of chemical compounds. In most Earth System models sediment-
10 water dynamics are either neglected or treated in a very simplistic way. To provide a more realistic description of organic matter degradation and nutrient cycles in marine sediments we have developed OMEN-SED, a new, one-dimensional, numerically efficient reactive transport model. OMEN-SED is the first analytical model to explicitly describe organic matter cycling as well as associated dynamics of the most important terminal electron acceptors (i.e. O₂, NO₃, SO₄), related reduced substances
15 (NH₄, H₂S), the full suite of secondary-redox reactions, macronutrients (PO₄) and associated pore water quantities (ALK, DIC). To represent a redox-dependent sedimentary P cycle we consider the formation and burial of Fe-bound P and authigenic Ca-P minerals. Thus, OMEN-SED captures most of the features of a complex, numerical diagenetic model, however, its computational efficiency allows the coupling to global Earth System models and therefore the investigation of coupled global
20 biogeochemical dynamics over different timescales. This paper provides a detailed description of

the new sediment model, **tested with observations, SA and global observations** and describes it's coupling to the Earth System model cGENIE.

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1 Introduction

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Role of marine sediments for climate and global biogeochemical cycles:

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 (e.g. Berner, 1991; Archer and Maier-Reimer, 1994; Ridgwell and Zeebe, 2005; Arndt et al., 2013). Physical and chemical processes in sediments (i.e. diagenetic processes) 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, sediments impact the water column directly either by short- and long-term storage of deposited material or diagenesis transforms deposited material and returns some of the resulting products (e.g. nutrients, DIC) to the bottom waters. 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; Soetaert et al., 2000; Mackenzie, 2005).

Biological primary production of organic matter (OM, CH₂O in equation R1) and the reverse process of degradation can be written in a greatly simplified reaction as:



On geological 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). On shorter timescales, the upper few meters of the sediments (i.e. early diagenesis) are specifically important as it is decided here if a substance is recycled to the water column or buried for a longer period of time in the deeper sediments (Hensen et al., 2006). Most biogeochemical cycles and reactions in this part of marine sediments can be related either directly or indirectly to the degradation of organic matter (e.g. Boudreau and Ruddick, 1991; Arndt et al., 2013). Organic matter degradation releases metabolic CO₂ to the pore water, causing it to have a lower pH and provoking the dissolution of CaCO₃ (Emerson and Bender, 1981). Oxygen and nitrate for instance, the most powerful electron acceptors, are consumed in the course of the degradation of organic matter, resulting in the release of ammonium and phosphorous to the pore water. As such, degradation of OM in the sediments can profoundly affect the oxygen and nutrient inventory of the ocean and thus primary productivity (Van Cappellen and Ingall, 1994; Lenton and Watson, 2000).

Nutrient recycling from marine sediments has been suggested to play a key role for climate and ocean biogeochemistry for different events during Earth history. For example, feedbacks between phosphorous storage and erosion from shelf sediments and marine productivity have been hypothesised to play an important role for glacial/interglacial atmospheric CO₂ changes (Broecker, 1982;

Ruttenberg, 1993). Furthermore, nutrient recycling from anoxic sediments has been invoked to explain the occurrence of more extreme events in Earth history, for instance Oceanic Anoxic Events (OAEs, e.g. 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 (Jenkyns, 2010). One way to explain the genesis and persistence of OAEs is increased oxygen demand due to enhanced primary productivity. Increased nutrient inputs to fuel primary productivity may have come from marine sediments as the burial efficiency of phosphorus declines when bottom waters become anoxic (Ingall and Jahnke, 1994; Van Cappellen and Ingall, 1994). The recovery from OAE like conditions is thought to involve the permanent removal of excess CO_2 from the atmosphere and ocean by burying carbon in the form of organic matter in marine sediments (e.g. Arthur et al., 1988; Jarvis et al., 2011), which is consistent with the geological record of widespread black shale formation (Stein et al., 1986). However, the overall amount, exact timing and the rate of organic matter burial remain a topic of an ongoing debate.

Diagenetic Models:

Therefore, globally quantifying the burial and 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 (see 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 vertically resolved numerical models simulating the entire suite of essential coupled redox and equilibrium reactions within marine sediments (e.g. BRNS, Aguilera et al., 2005; CANDI, Boudreau, 1996; MEDIA, Meysman et al., 2003; STEADYSED, Van Cappellen and Wang, 1996). These “complete”, non-steady-state models, thus resolve the resulting characteristic redox-zonation of marine sediments through explicitly including oxic OM degradation, denitrification, oxidation by manganese and iron (hydr)oxides, sulphate reduction and methanogenesis as well as the reoxidation of reduced byproducts (i.e. NH_4 , Mn^{2+} , Fe^{2+} , H_2S , CH_4). Furthermore, they incorporate various mineral dissolution and precipitation reactions, as well as fast equilibrium sorption processes for example of NH_4 , PO_4 and metal ions (i.e. Mn^{2+} , Fe^{2+} and Mg^{2+} , compare Van Cappellen and Wang, 1996; Meysman et al., 2003). Modelled, depth-dependent, transport processes usually comprise advection, diffusion, bioturbation and bio-irrigation. This group of diagenetic models generally uses a so-called multi-G approach (Jørgensen, 1978; Berner, 1980), thus dividing the bulk organic matter pool into a number of compound classes that are characterised by different degradabilities k_i , which are generally dependent on the type and concentration of the specific terminal electron acceptor (TEA). These complex models have a great potential for quantifying

OM degradation dynamics for sites where enough observations are available to constrain its model parameters (see e.g. Boudreau et al., 1998; Wang and Van Cappellen, 1996; Thullner et al., 2009, for applications). However, due to the high degree of coupled processes and depth-varying parameters the diagenetic equation needs to be solved numerically, thus resulting in a very high computational demand and consequently rendering their application in an Earth system model framework prohibitive. Additionally, their global applicability is limited by the restricted transferability of model parameters from one site to the global scale (Arndt et al., 2013).

The second group of models solves the diagenetic equation analytically or semi-analytically, thus providing an alternative and computationally more efficient approach. However, finding an analytical solution, especially when complex reaction networks are to be considered, is not straightforward and generally requires the assumption of steady state. The complexity of the reaction network can be reduced by dividing the sediment column into distinct zones and accounting for the most pertinent biogeochemical processes within each zone, thus increasing the likelihood of finding an analytical solution. In general, analytical diagenetic models are less sophisticated and comprehensive than numerical models and are used for the coupling to global ESMs (e.g. HAMOCC and NorESM use the model of Heinze et al. (1999)) or box models (e.g. DCESS, Shaffer et al., 2008 or MBM using MEDUSA, Munhoven, 2007). These analytic or semi-analytical models account for the most important transport processes (i.e. advection, bioturbation and molecular diffusion) through basic parametrizations and include fewer biogeochemical reactions which are generally restricted to the upper, bioturbated 10 cm of the sediments. They assume that the sedimentary organic matter pool is composed of just a single compound class which is either degraded with a globally invariant degradation rate constant (Munhoven, 2007) or a fixed rate constant depending on local oxygen concentrations (Shaffer et al., 2008; Palastanga et al., 2011). Pore water tracers explicitly represented in DCESS (Shaffer et al., 2008) and the HAMOCC model of Heinze et al. (1999) and Palastanga et al. (2011) are restricted to DIC, TA, PO_4 and O_2 . The MEDUSA model (Munhoven, 2007) considers CO_2 , HCO_3^- , CO_3^{2-} and O_2 . Other species produced or consumed during OM degradation are neglected. Thus, with oxygen being the only TEA explicitly modelled the influence of reduced species is only implicitly included in the boundary conditions for O_2 . A newer versions of the HAMOCC model, being a notable exception, as Ilyina et al. (2013) include NO_3 and denitrification explicitly. Furthermore, the version of Palastanga et al. (2011) represents an redox-dependent explicit sedimentary phosphorus cycle. Yet, secondary redox reactions involving reduced substances or sorption processes are not included in any of the discussed models.

How are sediments resolved in Earth system models:

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 has to provide a robust quantification of organic (and inorganic) carbon burial fluxes, as well as benthic uptake/return fluxes of oxygen, growth-limiting nutrients and reduced species. 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.

Even though there are more appropriate sediment representations, in most current ESMs sediment-water dynamics are either neglected or treated in a very simplistic way (Soetaert et al., 2000; Hülse et al., 2017). Most Earth system Models of Intermediate Complexity (EMICs) and also some of the higher resolution global carbon cycle models represent the sediment-water interface either as a reflective or a conservative/semi-reflective boundary (Hülse et al., 2017). Thus, all particulate material deposited on the seafloor is either instantaneously consumed (reflective boundary), or a fixed 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). A superior approach is the vertically integrated dynamic model, which represents the whole sediment column as a single box (Hülse et al., 2017). Here, OM deposited on the seafloor is added to the sediment box where it gets degraded and dissolved species diffuse through the sediment-water interface in accordance with these transformations. This approach thus ignores the vertical extent of the sediments and the temporary storage of dissolved species (Soetaert et al., 2000). Yet, it is computationally efficient and allows differentiating between various fractions of organic matter. Most EMICs incorporate a vertically integrated dynamic model for particulate inorganic carbon only (i.e. mainly CaCO_3) and just a few consider oxic-only sediment degradation of organic matter (Hülse et al., 2017).

The most complex description of diagenetic organic matter degradation in Earth system models is the second group of vertically resolved diagenetic models as discussed above (e.g. Heinze et al., 1999; Munhoven, 2007; Shaffer et al., 2008). These models solve the one-dimensional reaction-transport equation for a number of solid and dissolved species for the upper, bioturbated 10 cm of the sediments. Examples of global ESMs employing a vertically resolved diagenetic model are NorESM (Tjiputra et al., 2013) and HAMOCC (Palastanga et al., 2011; Ilyina et al., 2013), both using a version of Heinze et al. (1999). None of the EMICs reviewed by Hülse et al. (2017) use such a sediment representation. DCESS (Shaffer et al., 2008) and MBM (Munhoven, 2007) are box models employing a vertically resolved diagenetic model. However, in general oxygen is the only TEA explicitly modelled and secondary redox reactions and reduced species are completely neglected in these approaches. Furthermore, all models represent the bulk OM pool as a single fraction with a fixed degradation rate constant.

Problem with that:

Obviously, such a simplification of the OM pool can neither account for the observed vast structural complexity in natural organic matter and its resulting different degradation rates nor for the rapid decrease in OM degradability in the uppermost centimetres of the sediments (Arndt et al., 2013). It has been suggested that at least a 3G approach is necessary to accurately represent organic matter dynamics in this part of the sediments where most OM is degraded (e.g. Soetaert et al., 1996b). Even more restrictive is the use of O_2 as the only TEA and the complete absence of reduced substances and related secondary redox reactions. Even though for the majority of the modern sediments (i.e. in the deep-ocean) O_2 is the primary electron acceptor and Archer et al. (2002) suggested that aerobic degradation accounts for 66% of total organic matter respiration more recent model and data studies have reported that sulfate reduction is the dominant degradation pathway on a global average (with contributions of 55-76% Canfield et al., 2005; Jørgensen and Kasten, 2006; Thullner et al., 2009). O_2 becomes progressively less important as TEA with decreasing seafloor depth and in shallow waters most of it is used to reoxidise reduced substances produced during anaerobic degradation (Canfield et al., 2005; Thullner et al., 2009). Thus, the in situ production of e.g. NO_3 and SO_4 through oxidation of NH_4 and H_2S forms an important sink for O_2 which is entirely neglected in current sediment representations in global models. In addition, due to the lack of an appropriate sedimentary P cycle (with the exception of the HAMOCC version of Palastanga et al. (2011)), no current global ESM is able to model the redox dependent P release from marine sediments and its implications for primary productivity, global biogeochemical cycles and climate.

Solution presented here:

In order to provide a more realistic description of organic matter degradation and nutrient cycles in marine sediments we have developed the OrganicMatter ENabled SEDiment model (OMEN-SED), a new, one-dimensional, numerically efficient reactive transport model. OMEN-SED is the first analytical model to explicitly describe OM cycling as well as associated dynamics of the most important TEAs (i.e. O_2 , NO_3 , SO_4), related reduced substances (NH_4 , H_2S), the full suite of secondary-redox reactions, macronutrients (PO_4) and associated pore water quantities (ALK, DIC). To represent a redox-dependent sedimentary P cycle we consider the formation and burial of Fe-bound P and authigenic Ca-P minerals. Thus, OMEN-SED captures most of the features of a complex, numerical diagenetic model, however, its computational efficiency allows the coupling to global Earth system models and therefore the investigation of coupled global biogeochemical dynamics over different timescales. Here, the model is presented as a 2G-approach, however, a third, non-degradable OM fraction can easily be added and OMEN-SED can be further extended to a Multi-G approach.

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 9 and 10.

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 (e.g. Berner, 1980; Boudreau, 1997):

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

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 . The reaction network accounts 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.

In order to find an analytical solution to Eq. (1), OMEN-SED assumes that benthic dynamics can be represented by a series of 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). Furthermore, it accounts for the dynamic redox zonation of marine sediments by dividing the sediment into an oxic zone delineated by the oxygen penetration depth z_{ox} , a denitrification zone situated between z_{ox} and the nitrate penetration depth z_{NO_3} , a sulfate reduction zone situated between z_{NO_3} and the sulfate penetration depth z_{SO_4} , and a methanogenic zone situated below z_{SO_4} (Fig. 1). All penetration depths are dynamically calculated by the model. Each zone is characterised 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 (in $\text{mol cm}^{-2} \text{ year}^{-1}$):

$$\text{Flux_SWI}(C_i) = \phi \left(D_i \frac{\partial C_i(z)}{\partial z} \Big|_0 - w [C_i(0) - C_i(z_\infty)] \right) \quad (2)$$

where w is the deposition rate, D_i is the diffusion coefficient and $C_i(0)$, $C_i(z_\infty)$ the concentration of species i at the SWI and at the lower sediment boundary.

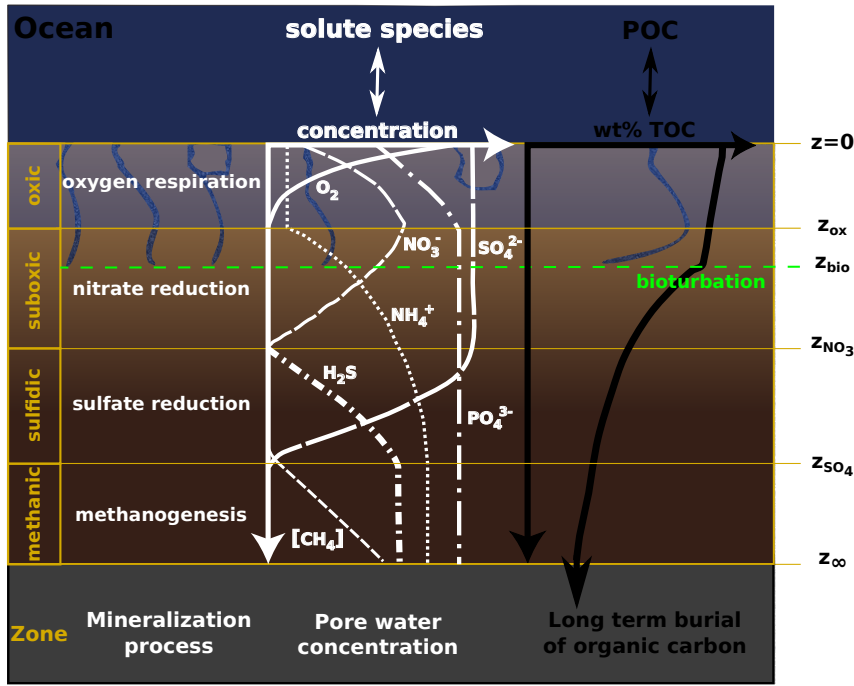


Figure 1. Schematic of the different modelled species and layers in OMEN-SED. Here showing the case $z_{\text{ox}} < z_{\text{bio}} < z_{\text{NO}_3} < z_{\text{SO}_4}$.

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, $D_{i,0} = D_{\text{mol},i} \cdot f_{ir}$, 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 ($D_i = D_{i,0} + D_{\text{bio}} = D_{\text{mol},i} \cdot f_{ir} + D_{\text{bio}}$ 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} .

Table 1. Reactions and biogeochemical tracers implemented in the Reaction Network of OMEN-SED. 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 degradation, 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 $\text{Fe}(\text{OH})_3$, NH_4 adsorption, PO_4 adsorption
Mineral precipitation	Formation of authigenic P
Biogeochemical tracers	Organic matter (2-G), oxygen, nitrate, ammonium, sulfate, sulfide (hydrogen sulfide), phosphate, Fe-bound P, DIC, ALK

2.3 Reaction Network

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 biogeochemical tracers considered in the reaction network. Table 15 summarises their reaction stoichiometry and Table ?? provides an overview of their description in the model.

2.3.1 Organic matter or Particulate Organic Carbon (POC)

In marine sediments, organic matter (OM) is degraded by heterotrophic activity coupled to the sequential utilisation of terminal electron acceptors. Here, organic matter degradation is described via a 2G-model approach (Arndt et al., 2013, and references therein), assuming that the bulk OM consists of two discrete compound classes C_i characterised by specific first-order degradation rate constants k_i . The degradation constants are assumed independent of the nature of the TEA, thus invariant along the sediment column. Nevertheless, the 2G-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. The conservation equation for organic matter dynamics is thus given by:

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

with $D_{C_i} = D_{\text{bio}}$ for $z \leq z_{\text{bio}}$ and $D_{C_i} = 0$ for $z > z_{\text{bio}}$.

Equation (4) has the following general solutions depending on the bioturbation depth:

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

Boundary	Condition	
$z = 0$	known concentration	1) $C_i(0) = C_{0i}$
$z = z_{\text{bio}}$	continuity	2) $C_i(z_{\text{bio}}^-) = C_i(z_{\text{bio}}^+)$
		3) $-D_{\text{bio}} \cdot \frac{\partial C_i}{\partial z} \Big _{z_{\text{bio}}^-} = 0$

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

$$C_{1i}(z) = A_{1i} \cdot \exp(a_{1i}z) + B_{1i} \cdot \exp(b_{1i}z) \\ \stackrel{\text{BC1)}}{=} A_{1i} \cdot [\exp(a_{1i}z) - \exp(b_{1i}z)] + C_{0i} \cdot \exp(b_{1i}z) \quad (5)$$

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

305 $C_{2i}(z) = A_{2i} \cdot \exp(a_{2i}z)$

where

$$a_{1i} = \frac{w - \sqrt{w^2 + 4D_{C_i} \cdot k_i}}{2D_{C_i}}, \quad b_{1i} = \frac{w + \sqrt{w^2 + 4D_{C_i} \cdot k_i}}{2D_{C_i}}, \quad a_{2i} = -\frac{k_i}{w} \quad (6)$$

The integration constants ($A_{1,i}$, $B_{1,i}$, $A_{2,i}$) are derived by assuming a set of boundary conditions (Table 2). The model assumes a known concentration/flux at the sediment-water interface and continuity across the bioturbation boundary as transport is solely advective below z_{bio} . The steady-state solutions follow a simple exponential decay (see Eq. 5 and ??) and drives the oxygen and nutrient dynamics. See Section 2.5.1 for further details on how to find the analytical solution.

2.3.2 Oxygen

315 In marine sediments, oxygen is consumed via 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 $\text{O}_2 : \text{C}$ ratio (O_2C , Tab. 10) and produces ammonium, which is partially nitrified to nitrate (γ_{NH_4}). In addition, the oxygen consumption due to oxidation of reduced species (NH_4 , H_2S) 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 phase. Oxygen concentration is driven by the organic matter dynamics and can thus generally be described by:

325 $\frac{\partial \text{O}_2}{\partial t} = 0 = D_{\text{O}_2} \frac{\partial^2 \text{O}_2}{\partial z^2} - w \frac{\partial \text{O}_2}{\partial z} - \frac{1-\phi}{\phi} \sum_i k_i \cdot [\text{O}_2\text{C} + 2\gamma_{\text{NH}_4}\text{NC}_i] \cdot C_i(z) \quad (7)$

and therefore results in two representations depending on the bioturbation depth:

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

$$330 \quad \frac{\partial O_2}{\partial t} \stackrel{5}{=} D_{O_2}^1 \frac{\partial^2 O_2}{\partial z^2} - w \frac{\partial O_2}{\partial z} - \frac{1-\phi}{\phi} \sum_i k_i \cdot [O_2C + 2\gamma_{NH_4}NC_i] \cdot \left(A_{1i} \cdot [\exp(a_{1i}z) - \exp(b_{1i}z)] + C_{0i} \cdot \exp(b_{1i}z) \right)$$

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

$$\frac{\partial O_2^{II}}{\partial t} \stackrel{??}{=} D_{O_2}^2 \frac{\partial^2 O_2}{\partial z^2} - w \frac{\partial O_2}{\partial z} - \frac{1-\phi}{\phi} \sum_i k_i \cdot [O_2C + 2\gamma_{NH_4}NC_i] \cdot \left(A_{2i} \cdot \exp(a_{2i}z) \right)$$

335 with $D_{O_2}^1$ and $D_{O_2}^2$ being the O_2 diffusion coefficient for the bioturbated and non-bioturbated layer, respectively. The analytical solutions depending on bioturbation depth are given by:

1. Layer ($z \leq z_{bio}$):

$$O_2^I(z) = A_{O_2}^1 + B_{O_2}^1 \cdot \exp(b_{O_2}^1 z) + \sum_i \Phi_{1,i}^I \cdot \exp(a_{1i}z) + \sum_i \Phi_{1,i}^{II} \cdot \exp(b_{1i}z) + \sum_i \Phi_{1,i}^{III} \cdot \exp(b_{1i}z)$$

340 (8)

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

$$O_2^{II}(z) = A_{O_2}^2 + B_{O_2}^2 \cdot \exp(b_{O_2}^2 z) + \sum_i \Phi_{i,2}^I \cdot \exp(a_{2i}z)$$

(9)

with

$$345 \quad b_{O_2}^1 = \frac{w}{D_{O_2}^1}, \quad b_{O_2}^2 = \frac{w}{D_{O_2}^2}$$

$$\Phi_{1,i}^I = \frac{1-\phi}{\phi} \cdot \frac{k_i \cdot (O_2C + 2\gamma_{NH_4}NC_i) \cdot A_{1i}}{D_{O_2}^1(-a_{1i})^2 - w \cdot (-a_{1i})}, \quad \Phi_{1,i}^{II} = -\frac{1-\phi}{\phi} \cdot \frac{k_i \cdot (O_2C + 2\gamma_{NH_4}NC_i) \cdot A_{1i}}{D_{O_2}^1(-b_{1i})^2 - w \cdot (-b_{1i})}$$

$$\Phi_{1,i}^{III} = \frac{1-\phi}{\phi} \cdot \frac{k_i \cdot (O_2C + 2\gamma_{NH_4}NC_i) \cdot C_{0i}}{D_{O_2}^1(-b_{1i})^2 - w \cdot (-b_{1i})}$$

$$\Phi_{i,2}^I := \frac{1-\phi}{\phi} \cdot \frac{k_i \cdot (O_2C + 2\gamma_{NH_4}NC_i) \cdot A_{2i}}{D_{O_2}^2(-a_{2i})^2 - w \cdot (-a_{2i})}$$

350 To determine the four integration constants ($A_{O_2}^1, B_{O_2}^1, A_{O_2}^2, B_{O_2}^2$) and to solve the diagenetic equations a set of boundary conditions needs to be defined (see Table 3). OMEN-SED assumes a known bottom water concentration and the complete consumption of oxygen at the oxygen penetration depth (or zero flux if $z_{ox} = z_{\infty}$). Equal oxygen concentration and diffusive flux above (z_{bio}^-) and below (z_{bio}^+) the bioturbation boundary is considered. In addition, the model accounts for reduced species produced by anaerobic mineralization diffusing into the oxic layer from below, assuming

355 that respective fractions (γ_{NH_4} and γ_{H_2S}) are re-oxidised at the oxic/suboxic interface.

Table 3. Boundary conditions for oxygen. For the boundaries we define: $z_{\text{bio}}^- := \lim_{h \rightarrow 0} (z_{\text{bio}} - h)$ and $z_{\text{bio}}^+ := \lim_{h \rightarrow 0} (z_{\text{bio}} + h)$.

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

2.3.3 Nitrate and Ammonium

To model nitrate and ammonium dynamics the sediment column 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 via OM mineralization. The model assumes that adsorption of ammonium to sediment particles is fast compared with the characteristic transport time scales. Thus, a constant equilibrium adsorption coefficient K_{NH_4} is used to parameterize the loss of dissolved NH_4 to adsorbed NH_4 (Wang and Van Cappellen, 1996). Therefore the diagenetic equations for nitrate and ammonium are given by:

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

$$\frac{\partial \text{NO}_3^I}{\partial t} = 0 = D_{\text{NO}_3} \frac{\partial^2 \text{NO}_3^I}{\partial z^2} - w \frac{\partial \text{NO}_3^I}{\partial z} + \gamma_{\text{NH}_4} \frac{1-\phi}{\phi} \cdot \sum_i \text{NC}_i \cdot k_i \cdot C_i(z) \quad (10)$$

$$\frac{\partial \text{NH}_4^I}{\partial t} = 0 = \frac{D_{\text{NH}_4}}{1 + K_{\text{NH}_4}} \frac{\partial^2 \text{NH}_4^I}{\partial z^2} - w \frac{\partial \text{NH}_4^I}{\partial z} + \frac{1 - \gamma_{\text{NH}_4}}{1 + K_{\text{NH}_4}} \cdot \frac{1-\phi}{\phi} \cdot \sum_i \text{NC}_i \cdot k_i \cdot C_i(z) \quad (11)$$

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

$$\frac{\partial \text{NO}_3^{II}}{\partial t} = 0 = D_{\text{NO}_3} \frac{\partial^2 \text{NO}_3^{II}}{\partial z^2} - w \frac{\partial \text{NO}_3^{II}}{\partial z} - \frac{1-\phi}{\phi} \text{NO}_3\text{C} \cdot \sum_i k_i \cdot C_i(z) \quad (12)$$

$$\frac{\partial \text{NH}_4^{II}}{\partial t} = 0 = \frac{D_{\text{NH}_4}}{1 + K_{\text{NH}_4}} \frac{\partial^2 \text{NH}_4^{II}}{\partial z^2} - w \frac{\partial \text{NH}_4^{II}}{\partial z} \quad (13)$$

Table 4. Boundary conditions for nitrate and ammonium. For the boundaries we define: $z_-^- := \lim_{h \rightarrow 0} (z_- - h)$ and $z_-^+ := \lim_{h \rightarrow 0} (z_- + h)$.

Boundary	Condition	
$z = 0$	known concentration	1) $NO_3(0) = NO_{30}$
$z = z_{\text{bio}}$	continuity	2) $NO_3(z_{\text{bio}}^-) = NO_3(z_{\text{bio}}^+)$
$z = z_{\text{ox}}$	continuity	3) $-(D_{NO_3,0} + D_{\text{bio}}) \cdot \frac{\partial NO_3}{\partial z} \Big _{z_{\text{bio}}^-} = -D_{NO_3,0} \cdot \frac{\partial NO_3}{\partial z} \Big _{z_{\text{bio}}^+}$
		4) $NO_3(z_{\text{ox}}^-) = NO_3(z_{\text{ox}}^+)$
	where:	5) $-D_{NO_3} \cdot \frac{\partial NO_3}{\partial z} \Big _{z_{\text{ox}}^-} + \gamma_{NH_4} \cdot F_{NH_4}(z_{\text{ox}}) = -D_{NO_3} \cdot \frac{\partial NO_3}{\partial z} \Big _{z_{\text{ox}}^+}$
$z = z_{NO_3}$	NO_3 consumption ($z_{NO_3} = z_{\infty}$)	$F_{NH_4}(z_{\text{ox}}) = \frac{1}{1+K_{NH_4}} \cdot \frac{1-\phi}{\phi} \cdot \int_{z_{NO_3}}^{\infty} \sum_i k_i \cdot NC_i \cdot C_i dz$
	($z_{NO_3} < z_{\infty}$)	6) IF ($NO_3(z_{\infty}) > 0$) $\frac{\partial NO_3}{\partial z} \Big _{z_{NO_3}} = 0$ ELSE $NO_3(z_{NO_3}) = 0$
$z = 0$	known concentration	1) $NH_4(0) = NH_{40}$
$z = z_{\text{bio}}$	continuity	2) $NH_4(z_{\text{bio}}^-) = NH_4(z_{\text{bio}}^+)$
$z = z_{\text{ox}}$	continuity	3) $-\frac{D_{NH_4,0} + D_{\text{bio}}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} \Big _{z_{\text{bio}}^-} = -\frac{D_{NH_4,0}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} \Big _{z_{\text{bio}}^+}$
		4) $NH_4(z_{\text{ox}}^-) = NH_4(z_{\text{ox}}^+)$
	where:	5) $-\frac{D_{NH_4}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} \Big _{z_{\text{ox}}^-} - \gamma_{NH_4} \cdot F_{NH_4}(z_{\text{ox}}) = -\frac{D_{NH_4}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} \Big _{z_{\text{ox}}^+}$
$z = z_{NO_3}$	continuity	$F_{NH_4}(z_{\text{ox}}) = \frac{1}{1+K_{NH_4}} \cdot \frac{1-\phi}{\phi} \cdot \int_{z_{NO_3}}^{\infty} \sum_i k_i \cdot NC_i \cdot C_i dz$
	flux	6) $NH_4(z_{NO_3}^-) = NH_4(z_{NO_3}^+)$
$z = z_{\infty}$	zero NH_4 flux	7) $-\frac{D_{NH_4}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} \Big _{z_{NO_3}^-} = -\frac{D_{NH_4}}{1+K_{NH_4}} \cdot \frac{\partial NH_4}{\partial z} \Big _{z_{NO_3}^+}$ 8) $\frac{\partial NH_4}{\partial z} \Big _{z_{\infty}} = 0$

3. Layer ($z_{NO_3} < z \leq z_{\infty}$)

$$\frac{\partial NH_4^{III}}{\partial t} = 0 = \frac{D_{NH_4}}{1+K_{NH_4}} \frac{\partial^2 NH_4^{III}}{\partial z^2} - w \frac{\partial NH_4^{III}}{\partial z} + \frac{1}{1+K_{NH_4}} \cdot \frac{1-\phi}{\phi} \cdot \sum_i NC_i \cdot k_i \cdot C_i(z) \quad (14)$$

The boundary conditions to solve Equations 10 - 14 are summarized in Table 4. The analytical solutions are not further stated here but follow the same logic as for oxygen (for more details on how to find the analytical solution see Section 2.5.1). The model assumes known bottom water concentrations for both species, the complete consumption of nitrate at the nitrate penetration depth (or zero flux if $z_{NO_3} = z_{\infty}$) 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 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}). Sulfate and sulfide dynamics are thus described by:

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

$$\frac{\partial \text{SO}_4^I}{\partial t} = 0 = D_{\text{SO}_4} \frac{\partial^2 \text{SO}_4^I}{\partial z^2} - w \frac{\partial \text{SO}_4^I}{\partial z} \quad (15)$$

$$\frac{\partial \text{H}_2\text{S}^I}{\partial t} = 0 = D_{\text{H}_2\text{S}} \frac{\partial^2 \text{H}_2\text{S}^I}{\partial z^2} - w \frac{\partial \text{H}_2\text{S}^I}{\partial z} \quad (16)$$

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

$$\frac{\partial \text{SO}_4^{II}}{\partial t} = 0 = D_{\text{SO}_4} \frac{\partial^2 \text{SO}_4^{II}}{\partial z^2} - w \frac{\partial \text{SO}_4^{II}}{\partial z} - \frac{1-\phi}{\phi} \cdot \sum_i \text{SO}_4\text{C} \cdot k_i \cdot C_i(z) \quad (17)$$

$$\frac{\partial \text{H}_2\text{S}^{II}}{\partial t} = 0 = D_{\text{H}_2\text{S}} \frac{\partial^2 \text{H}_2\text{S}^{II}}{\partial z^2} - w \frac{\partial \text{H}_2\text{S}^{II}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{SO}_4\text{C} \cdot k_i \cdot C_i(z) \quad (18)$$

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

$$\frac{\partial \text{H}_2\text{S}^{III}}{\partial t} = 0 = D_{\text{H}_2\text{S}} \frac{\partial^2 \text{H}_2\text{S}^{III}}{\partial z^2} - w \frac{\partial \text{H}_2\text{S}^{III}}{\partial z} \quad (19)$$

To solve equations 15 - 19 the model assumes known concentrations at the sediment-water interface and continuity across the bioturbation depth and the nitrate penetration depth (see Table 5). The re-oxidation of reduced H_2S to SO_4 is considered in the oxic-suboxic boundary condition for both species, here including the methanic zone, as H_2S 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 H_2S . In case $z_{\text{SO}_4} < z_\infty$, sulfate concentration is zero at z_{SO_4} and its diffusive flux must equal the amount of methane produced below; or, in case $z_{\text{SO}_4} = z_\infty$, a zero flux condition for sulfate is considered. At the lower boundary z_∞ zero flux of H_2S is considered. **correct??**

2.3.5 Phosphate

To model phosphorus (P) dynamics in the sediments OMEN-SED takes into account the change with depth of phosphate (PO_4) and iron-bound P, thereby mainly following the description of Slomp et al. (1996) and Gypens et al. (2008). Throughout the sediment column organic matter is mineralized resulting 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 via organic matter degradation

Table 5. Boundary conditions for sulfate and sulfide. For the boundaries we define: $z_-^- := \lim_{h \rightarrow 0} (z_- - h)$ and $z_-^+ := \lim_{h \rightarrow 0} (z_- + h)$.

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) $-(D_{\text{SO}_4,0} + D_{\text{bio}}) \cdot \frac{\partial \text{SO}_4}{\partial z} \Big _{z_{\text{bio}}^-} = -D_{\text{SO}_4,0} \cdot \frac{\partial \text{SO}_4}{\partial z} \Big _{z_{\text{bio}}^+}$ DH: @Sandra: BC 5)
$z = z_{\text{ox}}$	continuity	4) $\text{SO}_4(z_{\text{ox}}^-) = \text{SO}_4(z_{\text{ox}}^+)$ Include $\int_{z_{\text{SO}_4}}^\infty$ here?
	flux	5) $-D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} \Big _{z_{\text{ox}}^-} + \gamma_{\text{H}_2\text{S}} \cdot F_{\text{H}_2\text{S}}(z_{\text{ox}}) = -D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} \Big _{z_{\text{ox}}^+}$
	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) $-D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} \Big _{z_{\text{NO}_3}^-} = -D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} \Big _{z_{\text{NO}_3}^+}$ DH: @Sandra: think yes,
$z = z_{\text{SO}_4}$	SO_4 consumption	8) IF $(\text{SO}_4(z_\infty) > 0)$ because at 8) CH_4 from
	$(z_{\text{SO}_4} = z_\infty)$	$\frac{\partial \text{SO}_4}{\partial z} \Big _{z_{\text{SO}_4}} = 0$ $\int_{z_{\text{SO}_4}}^\infty$ is oxidised to H_2S,
	$(z_{\text{SO}_4} < z_\infty)$	ELSE $\text{SO}_4(z_{\text{SO}_4}) = 0$ and $-D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} \Big _{z_{\text{SO}_4}} = \gamma_{\text{CH}_4} \cdot F_{\text{CH}_4}(z_{\text{SO}_4})$ at 5) this H_2S to SO_4
	with flux from below:	$F_{\text{CH}_4}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \int_{z_{\text{SO}_4}}^\infty \sum_i \text{MC} \cdot k_i \cdot C_i \, dz$
$z = 0$	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) $-(D_{\text{H}_2\text{S},0} + D_{\text{bio}}) \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} \Big _{z_{\text{bio}}^-} = -D_{\text{H}_2\text{S},0} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} \Big _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $\text{H}_2\text{S}(z_{\text{ox}}^-) = \text{H}_2\text{S}(z_{\text{ox}}^+)$
	flux	5) $-D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} \Big _{z_{\text{ox}}^-} - \gamma_{\text{H}_2\text{S}} F_{\text{H}_2\text{S}}(z_{\text{ox}}) = -D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} \Big _{z_{\text{ox}}^+}$
	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) $-D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} \Big _{z_{\text{NO}_3}^-} = -D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} \Big _{z_{\text{NO}_3}^+}$
$z = z_{\text{SO}_4}$	continuity	8) $\text{H}_2\text{S}(z_{\text{SO}_4}^-) = \text{H}_2\text{S}(z_{\text{SO}_4}^+)$
	flux (with AOM)	9) $-D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} \Big _{z_{\text{SO}_4}^-} + \gamma_{\text{CH}_4} \cdot F_{\text{CH}_4}(z_{\text{SO}_4}) = -D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} \Big _{z_{\text{SO}_4}^+}$
	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 H_2S flux	10) $\frac{\partial \text{H}_2\text{S}}{\partial z} \Big _{z_\infty} = 0$

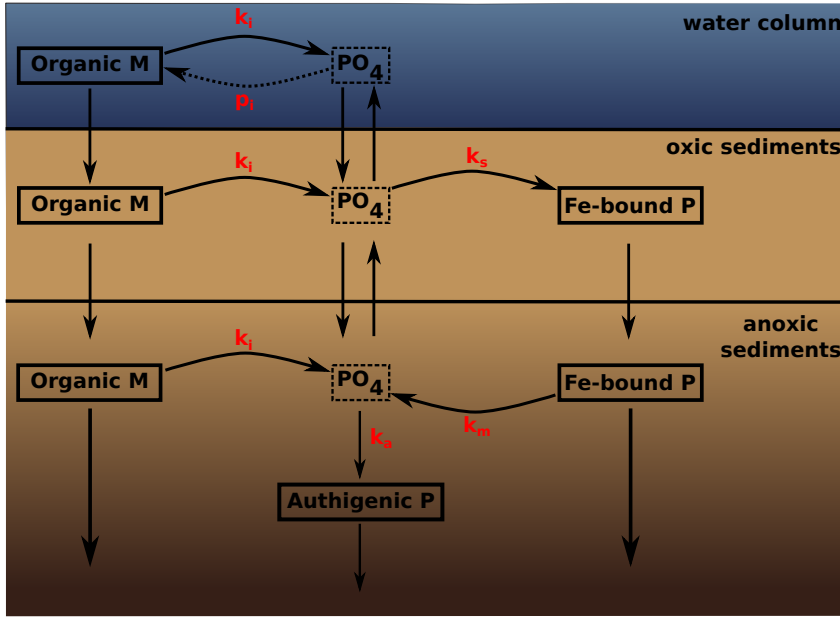


Figure 2. A schematic of the sedimentary P cycle in OMEN-SED. Red numbers represent kinetic rate constants for phosphorus dynamics (compare Table 10; p_i represents uptake rate of PO_4 via primary production in shallow environments). Adapted from Slomp et al. (1996).

420 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 (Van 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. As for ammonium, the adsorption of P to the sediment matrix is treated as
 425 an equilibrium processes, parameterized with dimensionless adsorption coefficients for the oxic and anoxic zone ($K_{\text{PO}_4}^{\text{ox}}$, $K_{\text{PO}_4}^{\text{anox}}$ Slomp et al., 1998). Therefore the diagenetic equations for phosphate are written as:

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

$$\begin{aligned}
 \frac{\partial \text{PO}_4^I}{\partial t} = & \frac{D_{\text{PO}_4}}{1 + K_{\text{PO}_4}^{\text{ox}}} \frac{\partial^2 \text{PO}_4^I}{\partial z^2} - w \frac{\partial \text{PO}_4^I}{\partial z} + \frac{1 - \phi}{\phi} \frac{1}{1 + K_{\text{PO}_4}^{\text{ox}}} \sum_i (\text{PC}_i \cdot k_i \cdot C_i(z)) \\
 & - \frac{k_s}{1 + K_{\text{PO}_4}^{\text{ox}}} (\text{PO}_4^I - \text{PO}_4^s)
 \end{aligned} \tag{20}$$

$$\frac{\partial M^I}{\partial t} = D_M \frac{\partial^2 M^I}{\partial z^2} - w \frac{\partial M^I}{\partial z} + \frac{\phi}{1 - \phi} k_s (\text{PO}_4^I - \text{PO}_4^s) \tag{21}$$

Table 6. Boundary conditions for phosphate and Fe-bound P (M). For the boundaries we define: $z_-^- := \lim_{h \rightarrow 0} (z_- - h)$ and $z_-^+ := \lim_{h \rightarrow 0} (z_- + h)$.

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) $-\frac{D_{\text{PO}_4}}{1+K_{\text{PO}_4}^{\text{ox}}} \cdot \frac{\partial \text{PO}_4}{\partial z} \Big _{z_{\text{ox}}^-} = -\frac{D_{\text{PO}_4}}{1+K_{\text{PO}_4}^{\text{anox}}} \cdot \frac{\partial \text{PO}_4}{\partial z} \Big _{z_{\text{ox}}^+}$
$z = z_{\infty}$	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) $\frac{\partial M}{\partial z} \Big _{z_{\text{ox}}^-} = \frac{\partial M}{\partial z} \Big _{z_{\text{ox}}^+}$
$z = z_{\infty}$	asymptotic concentration	10) $M(z_{\infty}) = M_{\infty}$

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

$$\frac{\partial M^{II}}{\partial t} = D_M \frac{\partial^2 M^{II}}{\partial z^2} - w \frac{\partial M^{II}}{\partial z} - k_m (M^{II} - M^{\infty}) \quad (22)$$

$$\begin{aligned} \frac{\partial \text{PO}_4^{II}}{\partial t} = & \frac{D_{\text{PO}_4}}{1 + K_{\text{PO}_4}^{\text{anox}}} \frac{\partial^2 \text{PO}_4^{II}}{\partial z^2} - w \frac{\partial \text{PO}_4^{II}}{\partial z} + \frac{1 - \phi}{\phi} \frac{1}{1 + K_{\text{PO}_4}^{\text{anox}}} \sum_i (\text{PC}_i \cdot k_i \cdot C_i(z)) \\ & - \frac{k_a}{1 + K_{\text{PO}_4}^{\text{anox}}} (\text{PO}_4^{II} - \text{PO}_4^a) + \frac{(1 - \phi)}{\phi} \frac{k_m}{1 + K_{\text{PO}_4}^{\text{anox}}} (M^{II} - M^{\infty}) \end{aligned} \quad (23)$$

$$(24)$$

with $D_M = D_{\text{bio}}$ for $z \leq z_{\text{bio}}$ and $D_M = 0$ for $z > z_{\text{bio}}$. The boundary conditions to solve Equations 20 - 23 are summarized in Table 6. 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 asymptotic Fe-bound P concentration at z_{∞} .

2.3.6 Dissolved Inorganic Carbon (DIC)

Organic matter degradation produces dissolved inorganic carbon (DIC) with a stoichiometric DIC:C ratio of 1:2 in the methanic zone and 1:1 in the rest of the sediment column. DIC dynamics in OMEN-SED are thus described by equations 25 and 25 and boundary conditions as summarized in Table 7. The model assumes a known DIC concentration at the sediment-water interface, a zero flux condition at the lower boundary z_{∞} and continuity across the bioturbation and sulfate penetration depth. In

Table 7. Boundary conditions for DIC. For the boundaries we define: $z_-^- := \lim_{h \rightarrow 0} (z_- - h)$ and $z_-^+ := \lim_{h \rightarrow 0} (z_- + h)$.

Boundary	Condition	
$z = 0$	known concentration	1) $DIC(0) = DIC_0$
$z = z_{\text{bio}}$	continuity	2) $DIC(z_{\text{bio}}^-) = DIC(z_{\text{bio}}^+)$
	flux	3) $-(D_{\text{DIC},0} + D_{\text{bio}}) \cdot \frac{\partial DIC}{\partial z} \Big _{z_{\text{bio}}^-} = -D_{\text{DIC},0} \cdot \frac{\partial DIC}{\partial z} \Big _{z_{\text{bio}}^+}$
$z = z_{\text{SO}_4}$	continuity	4) $DIC(z_{\text{SO}_4}^-) = DIC(z_{\text{SO}_4}^+)$
	flux (with AOM)	5) $-D_{\text{DIC}} \cdot \frac{\partial DIC}{\partial z} \Big _{z_{\text{SO}_4}^-} + \gamma_{\text{CH}_4} \cdot F_{\text{CH}_4}(z_{\text{SO}_4}) = -D_{\text{DIC}} \cdot \frac{\partial DIC}{\partial z} \Big _{z_{\text{SO}_4}^+}$
	where:	$F_{\text{CH}_4}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i MC \cdot k_i \cdot C_i dz$
$z = z_{\infty}$	zero DIC flux	6) $\frac{\partial DIC}{\partial z} \Big _{z_{\infty}} = 0$

addition, the anaerobic oxidation of methane at z_{SO_4} produces DIC (with 1:1 stoichiometry) which is accounted for through the flux boundary condition at z_{SO_4} (Table 7 eq. 5)

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

$$\frac{\partial DIC^I}{\partial t} = 0 = D_{\text{DIC}} \frac{\partial^2 DIC^I}{\partial z^2} - w \frac{\partial DIC^I}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{DICC}^I \cdot k_i \cdot C_i(z) \quad (25)$$

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

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

2.3.7 Alkalinity

Organic matter degradation and secondary redox reactions exert a complex influence on alkalinity with opposite effects depending on the TEA involved (Wolf-Gladrow et al., 2007). To model alkalinity in OMEN-SED the sediment column is partitioned into four geochemical layers, where different equations describe the biogeochemical processes using variable stoichiometric coefficients (compare Tables 10 and 15). Above z_{ox} , the combined effects of NH_4 and P release due to aerobic OM mineralization increases alkalinity according to ALK^{OX} whereas nitrification decreases alkalinity with stoichiometry ALK^{NIT} . In the remaining three zones anaerobic OM mineralization increases alkalinity with variable stoichiometric coefficients (i.e. ALK^{DEN} , ALK^{SUL} , ALK^{MET}). Thus, the diagenetic equations for alkalinity are written as:

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

$$\begin{aligned} \frac{\partial \text{ALK}^I}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^I}{\partial z^2} - w \frac{\partial \text{ALK}^I}{\partial z} \\ + \frac{1-\phi}{\phi} \cdot \sum_i \left(\text{ALK}^{\text{NIT}} \cdot \frac{\gamma_{\text{NH}_4}}{1+K_{\text{NH}_4}} \text{NC}_i + \text{ALK}^{\text{OX}} \right) \cdot k_i \cdot C_i(z) \end{aligned} \quad (27)$$

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

$$\frac{\partial \text{ALK}^{II}}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^{II}}{\partial z^2} - w \frac{\partial \text{ALK}^{II}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{ALK}^{\text{DEN}} \cdot k_i \cdot C_i(z) \quad (28)$$

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

$$\frac{\partial \text{ALK}^{III}}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^{III}}{\partial z^2} - w \frac{\partial \text{ALK}^{III}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{ALK}^{\text{SUL}} \cdot k_i \cdot C_i(z) \quad (29)$$

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

$$\frac{\partial \text{ALK}^{IV}}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^{IV}}{\partial z^2} - w \frac{\partial \text{ALK}^{IV}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{ALK}^{\text{MET}} \cdot k_i \cdot C_i(z) \quad (30)$$

To solve equations 27 - 30 the model assumes a known concentration at the sediment-water interface and continuity across the bioturbation depth and the penetration depths of O_2 , NO_3 and SO_4 (see Table 8). The decrease of alkalinity due to oxidation of reduced species produced in the suboxic and anoxic layers (with stoichiometry ALK^{NIT} and $\text{ALK}^{\text{H}_2\text{S}}$) is implicitly taken into account through the flux boundary condition at z_{ox} (Table 8 Eq. 5). Furthermore, the oxidation of methane by sulphate reduction increases alkalinity with stoichiometry ALK^{AOM} which is accounted for through the flux boundary condition at z_{SO_4} (Table 8 eq. 9). At the lower boundary z_{∞} a zero flux condition is applied.

2.4 Model Parameters

This section describes the parameters used in OMEN-SED to describe sediment transport and biogeochemical reactions related to the burial and mineralization of organic matter under a wide range of environmental conditions. Table 9 states the parameters for sediment characteristics and table 10 summarizes the stoichiometric factors and secondary reaction parameters used in the model.

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. When coupled to an ocean model, its sedimentation flux can be readily used in OMEN-SED. The stand-alone version of

Table 8. Boundary conditions for alkalinity. For the boundaries we define: $z_-^- := \lim_{h \rightarrow 0} (z_- - h)$ and $z_-^+ := \lim_{h \rightarrow 0} (z_- + h)$.

Boundary	Condition	
$z = 0$	known concentration	1) $ALK(0) = ALK_0$
$z = z_{\text{bio}}$	continuity	2) $ALK(z_{\text{bio}}^-) = ALK(z_{\text{bio}}^+)$
	flux	3) $-(D_{\text{ALK},0} + D_{\text{bio}}) \cdot \frac{\partial ALK}{\partial z} \Big _{z_{\text{bio}}^-} = -D_{\text{ALK},0} \cdot \frac{\partial ALK}{\partial z} \Big _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $ALK(z_{\text{ox}}^-) = ALK(z_{\text{ox}}^+)$
	flux	5) $-D_{\text{ALK}} \cdot \frac{\partial ALK}{\partial z} \Big _{z_{\text{ox}}^-} + F_{\text{ALK}}(z_{\text{ox}}) = -D_{\text{ALK}} \cdot \frac{\partial ALK}{\partial z} \Big _{z_{\text{ox}}^+}$
	where:	$F_{\text{ALK}}(z_{\text{ox}}) = \frac{1-\phi}{\phi} \cdot \left(ALK^{\text{H}_2\text{S}} \cdot \gamma_{\text{H}_2\text{S}} \int_{z_{\text{NO}_3}}^{z_{\text{SO}_4}} \sum_i \text{SO}_4\text{C} \cdot k_i \cdot C_i dz \right) + \frac{1-\phi}{\phi} \cdot \left(ALK^{\text{NIT}} \frac{\gamma_{\text{NH}_4}}{1+k_{\text{NH}_4}} \int_{z_{\text{NO}_3}}^{\infty} \sum_i \text{NC}_i \cdot k_i \cdot C_i dz \right)$
$z = z_{\text{NO}_3}$	continuity	6) $ALK(z_{\text{NO}_3}^-) = ALK(z_{\text{NO}_3}^+)$
	flux	7) $-D_{\text{ALK}} \cdot \frac{\partial ALK}{\partial z} \Big _{z_{\text{NO}_3}^-} = -D_{\text{ALK}} \cdot \frac{\partial ALK}{\partial z} \Big _{z_{\text{NO}_3}^+}$
$z = z_{\text{SO}_4}$	continuity	8) $ALK(z_{\text{SO}_4}^-) = ALK(z_{\text{SO}_4}^+)$
	flux (with AOM)	9) $-D_{\text{ALK}} \cdot \frac{\partial ALK}{\partial z} \Big _{z_{\text{SO}_4}^-} + F_{\text{ALK}}(z_{\text{SO}_4}) = -D_{\text{ALK}} \cdot \frac{\partial ALK}{\partial z} \Big _{z_{\text{SO}_4}^+}$
	where:	$F_{\text{ALK}}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \left(ALK^{\text{AOM}} \gamma_{\text{CH}_4} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i k_i \cdot C_i dz \right)$
$z = z_{\infty}$	zero ALK flux	10) $\frac{\partial ALK}{\partial z} \Big _{z_{\infty}} = 0$

OMEN-SED uses the empirical global relationship between sediment accumulation rate (cm yr^{-1}) and seafloor depth (m) of Middelburg et al. (1997):

$$w = 3.3 \cdot 10^{-0.87478367 - 0.00043512 \cdot \text{depth}}, \quad (31)$$

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):

$$D_{\text{bio}} = 5.2 \cdot 10^{0.76241122 - 0.00039724 \cdot \text{depth}} \quad (32)$$

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 imposes a globally invariant bioturbation depth z_{bio} of 10 cm. In case the bottom water oxygen concentration is below 5 nanomole cm^{-3} infaunal activity is assumed to cease and $z_{\text{bio}} = 0.01 \text{ cm}$.

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

520 temperature-dependent diffusion coefficients D_i^T (compare Gypens et al., 2008):

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

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 9 and are adapted from Li and Gregory (1974) and Gypens et al. (2008).

525 2.4.2 Reaction Parameters and Stoichiometries

The applied 2G-approach for organic matter degradation considers specific degradation rate constants k_i (yr^{-1}) for each compound class which are assumed invariant along the sediment column and therefore independent of the nature of the terminal electron acceptor. The rate constants can be altered manually to fit observed sediment profiles (compare Section 3.1) or related to a master
530 variable (e.g. sedimentation rate or POC-flux) provided by a coupled Earth system model (compare Section 2.5.2 and 3.4). The rate constants for P related processes (i.e. sorption of PO_4 to Fe oxides, release of PO_4 from Fe-bound P due to Fe-oxide reduction and authigenic CFA precipitation) are k_s , k_m , k_a respectively. The pore water equilibrium concentrations for P sorption and CFA precipitation (PO_4^s , PO_4^a) and the asymptotic concentration for Fe-bound P (M^∞) are taken from
535 Slomp et al. (1996) **maybe change to Palastanga et al. (2011) as these are values used in a global model...** The stoichiometry of organic matter is represented by the factors NC_i and PC_i denoting the molecular nitrogen to carbon and phosphorus to carbon ratio. In the sulfidic and methanic zone the reduction of 1 mol organic matter additionally produces $\text{SO}_4\text{C} = \frac{138}{212}$ mol of hydrogen sulfide and $\text{MC} = 0.5$ mol of methane. In the total sediment column organic matter mineralization consumes the
540 specific TEA with a fixed ratio (O_2C , NO_3C and SO_4C respectively). See Table 10 for a complete summary of the parameters and their values.

2.5 Module Structure

An analytical steady-state solution is found for the reaction-transport equation of each chemical species for every layer. At each boundary (i.e. z_{ox} , z_{bio} , z_{NO_3} and z_{SO_4}) the model has to match
545 continuity and flux for the 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 geochemical layer (compare Fig. 3). 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 to a global Earth Sytem Model are given in Section 2.5.2.

Table 9. Sediment characteristics and transport parameters. **TODO: PO4 adsorption coefficients okay?**

Parameter	Unit	Value	Description/Source
ρ_{sed}	g cm^{-3}	2.6	Sediment density
w	cm yr^{-1}	Fct. of seafloor depth or from ESM	Advection/Sediment accumulation rate (Middelburg et al., 1997)
z_{bio}	cm	10 or 0.01	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	-	0.85	Porosity
F	-	$\frac{1}{\phi^m}$	Tortuosity, here $m=3$
f_{ir}	-	1	Irrigation factor
Adsorption coefficients			
K_{NH_4}	-	1.3	NH_4 adsorption coefficient, (see Wang and Van Cappellen, 1996)
$K_{\text{PO}_4}^{\text{ox}}$	-	200.0	PO_4 adsorption coefficient (oxic), (see Slomp et al., 1998)
$K_{\text{PO}_4}^{\text{anox}}$	-	1.3	PO_4 adsorption coefficient (anoxic), (see Slomp et al., 1998)
Diffusion coefficients (Li and Gregory, 1974; Schulz, 2006; Gypens et al., 2008)			
$D_{\text{O}_2}^0$	$\text{cm}^2 \text{yr}^{-1}$	348.62	Molecular diffusion coefficient of oxygen at 0°C
$D_{\text{O}_2}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ } ^\circ\text{C}^{-1}$	14.09	Diffusion coefficient for linear temp. dependence of oxygen
$D_{\text{NO}_3}^0$	$\text{cm}^2 \text{yr}^{-1}$	308.42	Molecular diffusion coefficient of nitrate at 0°C
$D_{\text{NO}_3}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ } ^\circ\text{C}^{-1}$	12.26	Diffusion coefficient for linear temp. dependence of nitrate
$D_{\text{NH}_4}^0$	$\text{cm}^2 \text{yr}^{-1}$	309.05	Molecular diffusion coefficient of ammonium at 0°C
$D_{\text{NH}_4}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ } ^\circ\text{C}^{-1}$	12.26	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
$D_{\text{SO}_4}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ } ^\circ\text{C}^{-1}$	7.88	Diffusion coefficient for linear temp. dependence of sulfate
$D_{\text{H}_2\text{S}}^0$	$\text{cm}^2 \text{yr}^{-1}$	307.48	Molecular diffusion coefficient of sulfide at 0°C
$D_{\text{H}_2\text{S}}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ } ^\circ\text{C}^{-1}$	9.64	Diffusion coefficient for linear temp. dependence of sulfide
$D_{\text{PO}_4}^0$	$\text{cm}^2 \text{yr}^{-1}$	112.91	Molecular diffusion coefficient of phosphate at 0°C
$D_{\text{PO}_4}^T$	$\text{cm}^2 \text{yr}^{-1} \text{ } ^\circ\text{C}^{-1}$	5.59	Diffusion coefficient for linear temp. dependence of phosphate
D_{DIC}^0	$\text{cm}^2 \text{yr}^{-1}$	151.69	Molecular diffusion coefficient of DIC at 0°C
D_{DIC}^T	$\text{cm}^2 \text{yr}^{-1} \text{ } ^\circ\text{C}^{-1}$	7.93	Diffusion coefficient for linear temp. dependence of DIC
D_{ALK}^0	$\text{cm}^2 \text{yr}^{-1}$	151.69	Molecular diffusion coefficient of ALK at 0°C
D_{ALK}^T	$\text{cm}^2 \text{yr}^{-1} \text{ } ^\circ\text{C}^{-1}$	7.93	Diffusion coefficient for linear temp. dependence of ALK
Note: DIC and ALK coefficients are the values of HCO_3^- from Schulz (2006).			

Table 10. Values for biogeochemical parameters used in OMEN-SED. The variables x , y and z denote the atomic ratio of carbon, nitrogen and phosphorous of the degrading organic matter (here set to $C : N : P = 106 : 16 : 1$). **P related coefficients okay?**

Parameter/Variable	Unit	Value	Description
Stoichiometric factors and molecular ratios			
NC_i	mol/mol	$\frac{y}{x} = \frac{16}{106}$	nitrogen to carbon ratio
PC_i	mol/mol	$\frac{z}{x} = \frac{1}{106}$	phosphorus to carbon ratio
MC	mol/mol	0.5	methane to carbon ratio
			produced during methanogenesis
$DICC^I$	mol/mol	1.0	DIC to carbon ratio until z_{SO_4}
$DICC^{II}$	mol/mol	0.5	DIC to carbon ratio below z_{SO_4}
O_2C	mol/mol	$\frac{x+2y}{x} = \frac{138}{106}$	oxygen to carbon ratio
NO_3C	mol/mol	$\frac{4x+3y}{5x} = \frac{94.4}{106}$	nitrate to carbon ratio
SO_4C	mol/mol	$\frac{1}{2} O_2C = \frac{138}{212}$	sulfate to carbon ratio
ALK^{OX}	mol/mol	$\frac{y-2z}{x} = \frac{14}{106}$	ALK from aerobic degradation
ALK^{NIT}	mol/mol	-2	ALK from nitrification
ALK^{DEN}	mol/mol	$\frac{4x+3y-10z}{5x} = \frac{92.4}{106}$	ALK from denitrification
ALK^{SUL}	mol/mol	$\frac{x+y-2z}{x} = \frac{120}{106}$	ALK from sulfate reduction
ALK^{MET}	mol/mol	$\frac{y-2z}{x} = \frac{14}{106}$	ALK from methanogenesis
ALK^{H_2S}	mol/mol	-2	ALK from H_2S oxidation
ALK^{AOM}	mol/mol	2	ALK from AOM
Secondary reaction parameters			
γ_{NH_4}	-	0.9	fraction of NH_4 that is oxidised in oxic layer
γ_{H_2S}	-	0.95	fraction of H_2S that is oxidised in oxic layer
γ_{CH_4}	-	0.99	fraction of CH_4 that is oxidised at z_{SO_4}
P related parameters			
k_s	yr^{-1}	1.0	Rate constant for PO_4 sorption
k_m	yr^{-1}	0.02	Rate constant for Fe-bound P release
k_a	yr^{-1}	10.0	Rate constant for authigenic CFA precipitation
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^∞	$mol\ cm^{-3}$	$1.99 \cdot 10^{-10}$	asymptotic concentration for Fe-bound P (Slomp et al., 1996)

DH: ALK^{OX} correct?:
 $y = NH_4$ prod.; $-2z = P$
release

550 2.5.1 Generic Boundary Condition Matching (GBCM)

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

$$\frac{\partial C}{\partial t} = 0 = D \frac{\partial^2 C}{\partial z^2} - w \frac{\partial C}{\partial z} - \sum_i \alpha_i \exp(-\beta_i z) - k \cdot C + Q. \quad (33)$$

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

555 The ODE solution is of the general form:

$$C(z) = A \exp(az) + B \exp(bz) + \sum_i \frac{\alpha_i}{D\beta_i^2 - w\beta_i - k} \cdot \exp(-\beta_i z) + \frac{Q}{k} \quad (34)$$

and can therefore be expressed as:

$$560 \quad C(z) = A \cdot E(z) + B \cdot F(z) + G(z) \quad (35)$$

where $E(z)$, $F(z)$ are the homogeneous solutions of the ODE, $G(z)$ the particular integral, and A , B are the integration constants (compare Fig. 3 for the whole sediment column).

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

565 of the genral form:

$$C_U(z) = A_U \cdot E_U(z) + B_U \cdot F_U(z) + G_U(z) \quad (36)$$

$$C_L(z) = A_L \cdot E_L(z) + B_L \cdot F_L(z) + G_L(z). \quad (37)$$

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

$$570 \quad C_U(z_b) = C_L(z_b) + V_b \quad (38)$$

and for flux

$$D_U C'_U(z_b) + w C_U(z_b) = D_L C'_L(z_b) + w C_L(z_b) + F_b \quad (39)$$

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

575

In terms of the ODE solutions (36), (37), the boundary conditions represent two equations connecting the four integration constants:

$$\begin{pmatrix} E_U & F_U \\ D_U E'_U & D_U F'_U \end{pmatrix} \begin{pmatrix} A_U \\ B_U \end{pmatrix} = \begin{pmatrix} E_L & F_L \\ D_L E'_L & D_L F'_L \end{pmatrix} \begin{pmatrix} A_L \\ B_L \end{pmatrix} + \begin{pmatrix} G_L - G_U + V_b \\ D_L G'_L - D_U G'_U + F_b - w V_b \end{pmatrix} \quad (40)$$

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

580

Equation (40) can be solved to give A_U and B_U as a function of the integration constants from the layer below (A_L and B_L), thereby constructing a piecewise solution for both layers, with just two integration constants.

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

$$585 \quad \begin{pmatrix} A_U \\ B_U \end{pmatrix} = \begin{pmatrix} c_1 & c_2 \\ c_3 & c_4 \end{pmatrix} \begin{pmatrix} A_L \\ B_L \end{pmatrix} + \begin{pmatrix} d_1 \\ d_2 \end{pmatrix}. \quad (41)$$

Using (41) we can now rewrite $C_U(z)$ in (36) as a function of A_L and B_L :

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

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

$$C_U(z) = A_L \cdot E_U^*(z) + B_L \cdot F_U^*(z) + G_U^*(z) \quad (42)$$

590 where

$$\begin{aligned} E_U^*(z) &= c_1 E_U(z) + c_3 F_U(z) \\ F_U^*(z) &= c_2 E_U(z) + c_4 F_U(z) \\ G_U^*(z) &= G_U(z) + d_1 E_U(z) + d_2 F_U(z) \end{aligned} \quad (43)$$

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

Solving the sediment layer stack

Equations (41), (42) and (43) can now be applied for each layer boundary, working up from the bottom of the sediments. The net result is a piecewise solution of the whole sediment column 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 SWI and a zero flux condition at z_∞).

600

Abstracting out the bioturbation boundary

The bioturbation boundary affects the diffusion coefficient of the modelled solutes and the conservation equation of organic matter. The boundary is particularly inconvenient as it can, in principle, occur in the middle of any “geochemical” layer and therefore generates multiple cases (compare Fig. 3). To simplify this for solutes, the GBCM algorithm above is used to construct a piecewise solution and to abstract out the bioturbation boundary. An initial test for each “geochemical” 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

605

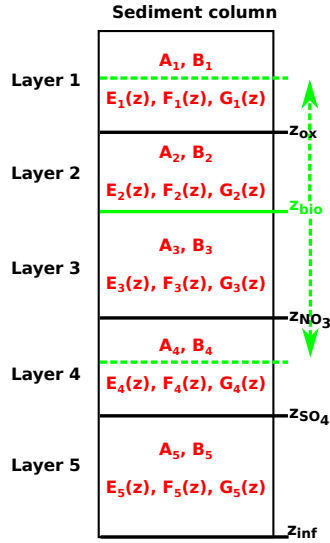


Figure 3. Schematic of the generic boundary condition matching (GBCM) problem. Showing the resulting integration constants (A_i , B_i) and ODE solutions (E_i , F_i , G_i) for the different sediment layers and the variable bioturbation boundary.

610 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_I12** 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). For example in the case of sulfate, **zTOC.prepfg_I12** is called
615 three times before the actual profile is calculated (once per layer: oxic, suboxic, sulfidic) and hands back three structures **ls** with information about the layer’s “bioturbation-status” 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_I12** which sorts out the correct solution type to use.

620 2.5.2 Coupling to an Earth System Model

The coupling of OMEN-SED to the carbon-centric version of the “GENIE” Earth system model (cGENIE Ridgwell et al., 2007) is described (Fig. 4). Results from pre-industrial experiments are presented in Section 3.4. cGENIE is a model of Intermediate Complexity based on the efficient climate model “C-GOLDSTEIN” of Edwards and Marsh (2005), featuring a frictional-geostrophic 3D-
625 ocean circulation model coupled to a fast Energy-Moisture Balance 2D-atmosphere together with a dynamic-thermodynamic sea-ice component. The version of cGENIE used here includes the marine geochemical cycling of carbon, oxygen, phosphorus and sulfur (Ridgwell et al., 2007), preservation of carbonates in deep-sea sediments (Ridgwell and Hargreaves, 2007) and terrestrial weathering

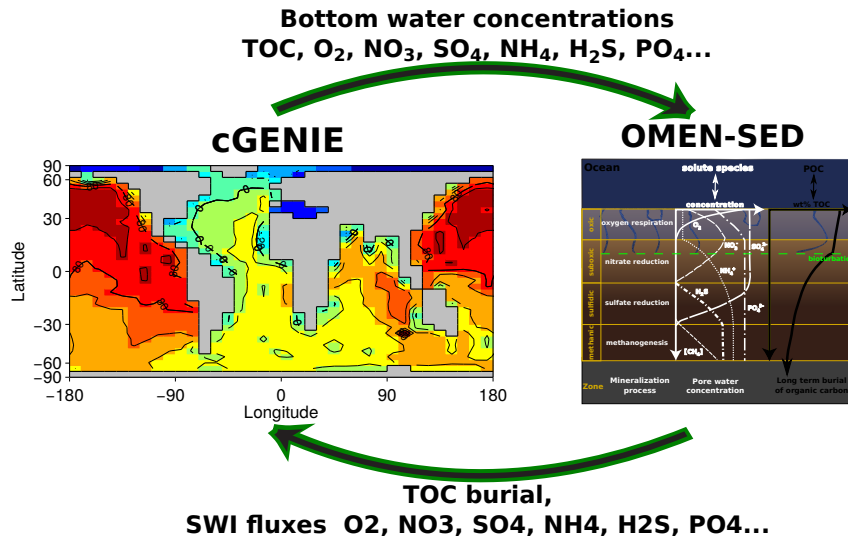


Figure 4. Schematic of the relationship between OMEN-SED and cGENIE. Arrows and accompanied text represent the information transferred between models.

(Colbourn et al., 2013). The ocean model is implemented on a 36×36 equal-area horizontal grid with 16 vertical levels using the pre-industrial continental configuration and bathymetry as in Archer et al. (2009). In contrast to Archer et al. (2009) the same grid resolution (36×36) is used for the sediment geochemistry model SEDGEM. Instead of completely degrading POC at the seafloor, OMEN-SED is called by SEDGEM for each wet ocean grid point. Depending on the overlying biogeochemical ocean model, processes can be included or excluded in OMEN-SED and stoichiometric factors need to be adjusted to ensure preservation of mass. As nitrogen is not modelled explicitly in the employed cGENIE configuration the related stoichiometries in OMEN-SED are set to zero (i.e. NC_i , ALK^{NIT} and ALK^{DEN}). cGENIE, however, implicitly includes the effects of NH_4 release and its nitrification on Alkalinity and neglects the impact of P release; therefore, related stoichiometries are changed to $ALK^{OX} = -16/106$ and $ALK^{SUL} = 122/106$.

Several biogeochemical tracers and parameters are transferred from SEDGEM to OMEN-SED and have to be converted into the required units. Bottom water concentrations of solutes are converted from mol kg^{-1} to mol cm^{-3} and the depositional flux of POC (POC_{flux}) is converted from $\text{cm}^3 \text{cm}^{-2} \text{yr}^{-1}$ to $\text{mol cm}^{-2} \text{yr}^{-1}$ assuming an average density of POC of $1.0 \text{ cm}^3 \text{g}^{-1}$. Other parameters used from cGENIE are seafloor depth, local temperature and the partitioning of bulk POC into the slower and faster degrading pool (as cGENIE represents a labile and a refractory POC fraction, see Ridgwell et al. (2007)). The advection/sediment accumulation rate is generally taken from cGENIE, however, a minimum value of $w = 0.5 \text{ cm kyrs}^{-1}$ is imposed as OMEN-SED tends to be unstable for lower values. The bulk POC_{flux} is separated into the labile and refractory component and the routine to calculate the sedimentary POC profiles is called. Here, the two POC deposi-

650 tional fluxes are first converted into SWI concentrations (in mol cm^{-3}) by solving Eq. (3) for $z=0$. OMEN-SED computes the resulting SWI-fluxes of solutes (in $\text{mol cm}^{-2} \text{yr}^{-1}$) and the fraction of POC preserved in the sediment at a depth of 100 cm (POC_{pres}) and returns the results to cGENIE. In case no POC is deposited on the seafloor (i.e. $\text{POC}_{\text{flux}} = 0$), OMEN-SED is not called and the SWI-fluxes of solutes and POC_{pres} are set to zero. In order to reduce memory requirements the sediment profiles (e.g. as shown in Fig. 5) are not calculated in the FORTRAN version of OMEN-SED, 655 however, the boundary conditions are saved at the end of the experiment and sediment profiles for specific grid-cells, ocean basins and/or ocean transects can be plotted using the stand-alone matlab version of OMEN-SED.

3 Model Applications

660 To validate our approach, model results were compared with observed pore water profiles (Section 3.1), an extensive sensitivity analysis for the most important model parameters was performed and resulting sediment-water interface fluxes were compared with a global database (Section 3.2). Furthermore, OMEN-SED was coupled to the cGENIE Earth system model and different published parameterisations for the OM degradation rate constants are tested on a global scale (Section 3.4).

665 3.1 Sediment profiles

Modelled profiles were compared with measured pore water data from different ocean depths (Figure 5) including the continental shelf (108 m), upper slope (585 m), lower slope (2213 m) and the deep sea (4298 m). The site at 585 m depth located in the Santa Barbara Basin is characterised by anoxic bottom waters and high POC concentrations ($\text{POC} \sim 5.5 \text{ wt\%}$, Reimers et al., 1996), whereas the 670 other sites at the Iberian margin (108 and 2213 m) and the Nazaré Canyon (4298 m, Epping et al., 2002) are oxic. Sediment-water interface characteristics and concentrations of POC and dissolved species in OMEN-SED were set to the observed values where available (Table 11). The POC and pore water profiles were fitted by optimizing the POC partitioning into the fast and slow degrading pool and their respective first order degradation rate constants (priority given to reproduce the POC 675 and O_2 profiles). For phosphorus the equilibrium concentration for authigenic P formation (PO_4^3) was adjusted to fit the PO_4 concentration at z_∞ . For the two open Iberian margin stations (108 and 2213 m) OMEN-SED fits all observations well. OMEN-SED does especially well at depth 2213m by reproducing the deep O_2 penetration and the subsurface maximum in NO_3 concentration due to the nitrification of NH_4 . For the Santa Barbara basin (585 m) a misfit is observed for H_2S and PO_4 in the 680 upper 20 cm of the sediment. This can be explained by the presence of Mn^{2+} , Fe^{2+} and dissolved Fe at this site which are either reduced to degrade POC and/or react with H_2S to form iron sulfides, therefore inhibiting the rise in concentration of H_2S (Reimers et al., 1996). Phosphorus is adsorbed to Fe oxides and incorporated into carbonate fluorapatite (CFA) which is highly parameterised in

Table 11. Model boundary conditions for the sampling stations in Figure 5. (For all sites DIC bottom water concentration of 2,400 nanomole cm^{-3} is assumed.)

Sediment characteristics:							
Depth	Temp.	z_{bio}	D_{bio}	POC ₁	POC ₂	k ₁	k ₂
(m)	($^{\circ}\text{C}$)	(cm)	($\text{cm}^2\text{yr}^{-1}$)	(wt%)	(wt%)	(yr^{-1})	(yr^{-1})
108	12.5	1.0	0.02	2.64	1.8	0.65	$1.0e^{-5}$
585	5.85	0.01	0.02	2.0	3.5	0.2	$8.0e^{-4}$
2213	3.2	10.0	0.17	0.45	0.5	0.1	$4.0e^{-4}$
4298	2.5	4.2	0.18	0.83	1.2	0.052	$1e^{-5}$

Bottom water concentrations of solutes (all in nanomole cm^{-3}):								
Depth	O ₂	NO ₃	SO ₄	NH ₄	H ₂ S	PO ₄	PO ₄ ^a	Alkalinity
108	210	9.6	28,000	0.4	0.0	0.0	15.0	2,400
585	10	25.0	28,000	0.0	0.0	50.0	90.0	2,480
2213	250	25.0	28,000	0.6	0.0	0.0	5.0	2,400
4298	243	30.1	28,000	0.22	0.0	0.0	5.0	2,400

OMEN-SED and not modelled explicitly. For the Nazaé Canyon station (4298 m) satisfactory fits could be realised apart from NH₄. However, also the original study (Epping et al., 2002) had the same problem using a more complex diagenetic model and suggested non-local solute exchange being responsible for the higher NH₄ concentrations at this site.

DH: P explanation correct/okay?
Also, say something about [ALK] at 585m?

3.2 Sensitivity Analysis

Model parameters implicitly account for processes not explicitly described, they are notoriously difficult to constrain and a source of uncertainty for numerical and analytical models. One strategy to explore and quantify this model uncertainty that can always be applied is sensitivity analysis (SA). SA is a term used for mathematical techniques to investigate how the variations in the outputs (y_1, \dots, y_N) of a model can be attributed to variations in the different input parameters (x_1, \dots, x_M) (Pianosi et al., 2016). Different types of sensitivity indices, which quantify this relative influence with a scalar S_i , can be calculated, ranging from simple one-at-a-time methods to statistical evaluations of the output distribution (e.g. variance-based or density-based approaches Pianosi et al., 2016). Especially the latter indices are easy to interpret and can be compared across different parameters and/or different model outputs as they generally take values between zero and one ($S_i \in [0, 1]$). An index of zero indicates a non-influential parameter and a higher value a more influential parameter. Here, we use SA mainly to identify which parameters have the largest impact on the different model outputs and therefore require careful calibration. As the probability density functions of our model outputs (i.e. the resulting SWI-fluxes) are generally highly-skewed towards extreme organic matter degradation rates (not shown) variance-based sensitivity indices are not very reliable uncer-

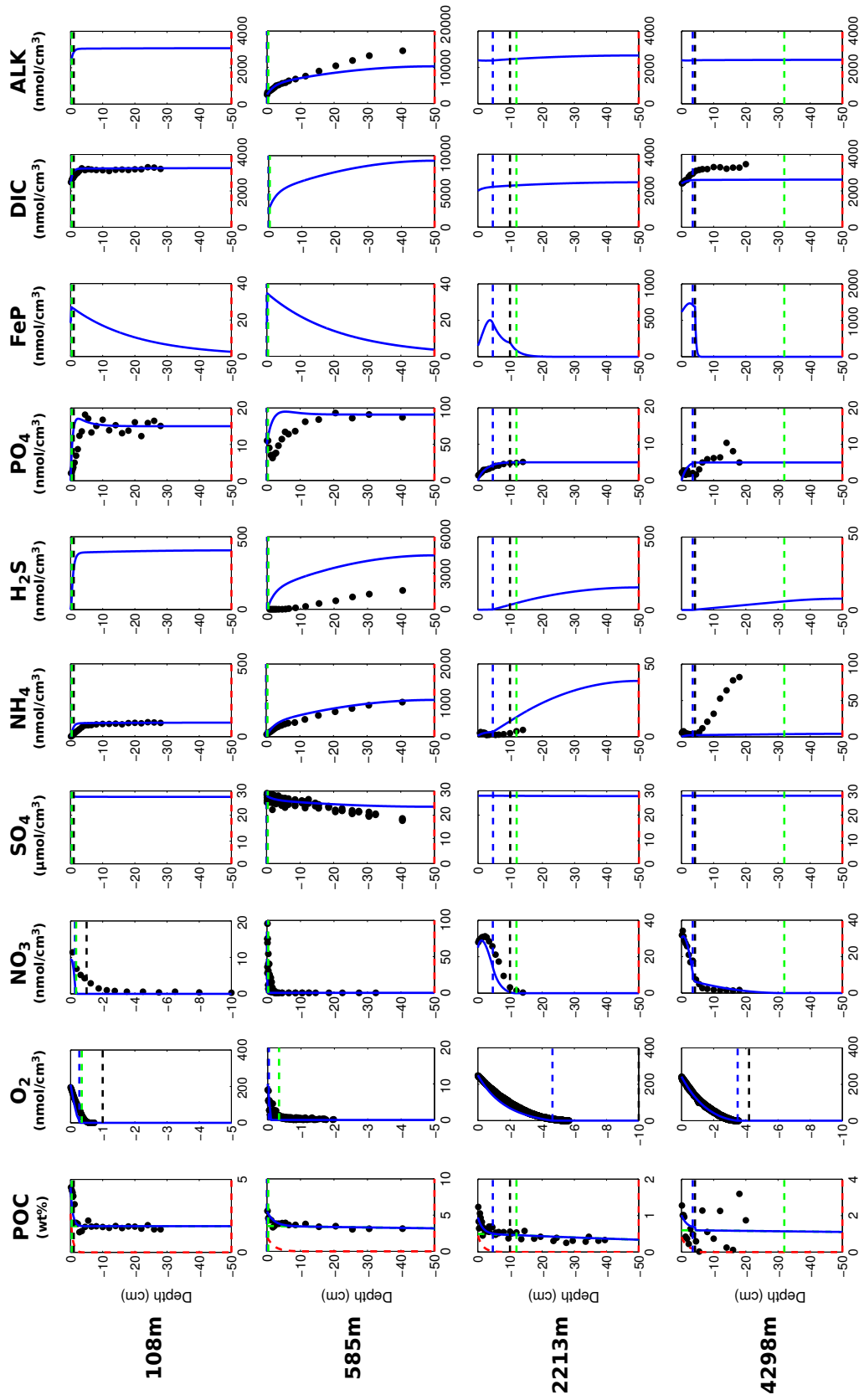


Figure 5. Modelled (curves) and measured (filled dots) dissolved and solid phase pore water profiles for four different sediment cores. Note that different scales are used for different stations. The blue POC curve represents the sum of the refractory (green) and labile (red) POC fraction.

tainty indicators (Pianosi et al., 2016). Rather than just considering the variance we employ the novel
 705 density-based PAWN method by Pianosi and Wagener (2015) which considers the entire conditional
 and unconditional Cumulative Distribution Function (CDF) of the model output. The sensitivity
 index of parameter i is calculated as the difference between the two CDFs, i.e.

$$S_i = \max_{x_i} \max_y |F_y(y) - F_{y|x_i}(y)| \quad (44)$$

where $F_y(y)$ is the unconditional CDF of the output y and $F_{y|x_i}(y)$ represents the conditional CDF
 710 when the i -th parameter is fixed to x_i . For a more detailed description of the method we refer the
 interested reader to Pianosi and Wagener (2015).

Due to the model complexity it is impossible to compute the sensitivity indices analytically there-
 fore they are approximated from a Latin-Hypercube sampling of parameter inputs and calculated
 outputs. The PAWN method, as implemented within the Sensitivity Analysis for Everyone (SAFE)
 715 matlab toolbox (Pianosi et al., 2015), is used to investigate 11 model parameters for ranges as speci-
 fied in Table 12. Sensitivity indices for all resulting SWI-fluxes for two idealised sediment conditions
 (i.e. anoxic at 400 m and oxic at 4000 m, see Table 13) are calculated. We use 200 samples to es-
 timate the unconditional CDF, 100 samples to estimate the conditional CDFs and 10 conditioning
 points, thus 11,200 evaluations are performed for each sediment condition. The resulting indices
 720 (compare Fig. 10 in the Appendix) are then translated into a color code and summarised in a pattern
 plot to simplify comparison (Fig. 6). The most significant parameters for all model outputs are the
 degradation rate for the labile OM part (k_1) and its share in the total OM pool (f_1). For the anoxic
 setup, where no oxidation occurs, the secondary redox parameters (i.e. γ_{NH_4} , $\gamma_{\text{H}_2\text{S}}$) are essentially
 non-influential. Whereas in the oxic scenario, SWI-fluxes of NH_4 , SO_4 and H_2S are very sensitive
 725 to changes in the secondary redox parameters. The PO_4 SWI-flux appears to be insensitive espe-
 cially under for the oxic condition as the majority is absorbed to Fe-oxides. The sensitivities change
 if other PO_4 related equilibrium concentrations PO_4^s , PO_4^a and M^∞ are used (not shown).

To test if OMEN-SED is able to reproduce the magnitude of observed SWI-fluxes, another set
 of Latin-Hypercube samplings is produced for the two idealised sediment conditions (sample sizes
 730 $N = 3500$). Here just the two most sensitive parameters k_1 and f_1 and also \tilde{k}_2 are varied, the other
 parameters are set to their default values (Tables 9 and 10). For the deep sea condition we account for
 the presence of more refractory OM by sampling $f_1 \in [0.02, 0.3]$. Minimum and maximum values
 for k_1 , \tilde{k}_2 and f_1 in the shallow ocean are as in Table 12. The results are compared with a global
 database of benthic fluxes of O_2 and NO_3 (Bohlen et al., 2012). The coloured scatter plots in Figure
 735 7 show that the observed fluxes fall well in the range of SWI-fluxes calculated with OMEN-SED.
 Also highlighted by the emergence of colour patterns in Figure 7 A+B are the strong interactions
 between the amount of labile OM f_1 and its degradation rate k_1 for the resulting SWI-fluxes of the
 most powerful TEA available. In general, a higher degradation rate in combination with more labile
 OM available leads to a higher SWI-flux.

DH: explanation for
 small P sensitivity
 correct?

Table 12. Range of model parameters used for sensitivity analysis of model predicted output.

Parameter	Description	Units	Minimum	Maximum	Source
k_1	labile OM degradation constant	yr^{-1}	$1e^{-4}$	5.0	(1)
\tilde{k}_2	order of refractory OM degradation constant ($k_2 = \tilde{k}_2 \cdot k_1$)	-	$1e^{-4}$	$1e^{-1}$	(1)
f_1	fraction of labile OM	-	0.02	0.98	-
K_{NH_4}	Adsorption coefficient	-	0.8	1.7	(2)
γ_{NH_4}	NH_4 fraction oxidised		0.5	1.0	-
$\gamma_{\text{H}_2\text{S}}$	H_2S fraction oxidised		0.5	1.0	-
$K_{\text{PO}_4}^{\text{ox}}$	Adsorption coeff. oxic	-	100.0	400.0	(3)
$K_{\text{PO}_4}^{\text{anox}}$	Adsorption coeff. anoxic	-	1.3	2.0	(3)
k_s	kinetic P sorption	yr^{-1}	0.1	100.0	(4, 5)
k_m	Fe-bound P release	yr^{-1}	0.015	0.02	(4, 5)
k_a	authigenic P formation	yr^{-1}	0.001	10.0	(4, 6)

Sources: (1) Arndt et al. (2013); (2): Van Cappellen and Wang (1996); (3): Krom and Berner (1980)
(4): Gypens et al. (2008); (5): Slomp et al. (1996); (6): Van Cappellen and Berner (1988)

Table 13. Model boundary conditions for the two idealised sediment conditions used for the sensitivity analysis (Fig. 6 and 7). All solute concentrations are in nanomole cm^{-3} .

Depth (m)	Temp. ($^{\circ}\text{C}$)	OC (wt%)	O_2	NO_3	SO_4	PO_4	z_{bio} (cm)
400	8.0	2.0	0.0	40.0	28,000	40.0	0.001
4000	1.5	1.0	300.0	20.0	28,000	40.0	10.0

740 3.3 Global Hypsometric Analysis of TEA Fluxes

In this section we test to which degree OMEN-SED is capable of capturing the dynamics of organic matter degradation pathways and related TEA-fluxes as simulated with a complete, numerical diagenetic model. Therefore, we reproduce the simulations of typical conditions along a global ocean hypsometry of Thullner et al. (2009). To explore the global remineralisation of OM in the seafloor

745 Thullner et al. (2009) quantified various diagenetic processes using the Biogeochemical Reaction Network Simulator (BRNS, Aguilera et al., 2005). In their study many model parameters (e.g. w , D_{bio} or ϕ) are related to the master variable seafloor depth (SFD) using existing empirical relationships. Organic matter degradation is described with a 1-G approach and the first order rate constant follows the empirical relationship of Boudreau (1997): $k = 0.38 \cdot w^{0.59}$. BRNS simulations were

750 performed using boundary conditions and parameters for representative SFD of 100m, 200m, 500m, 1000m, 2000m, 3500m and 5000m. In order to reproduce these results, OMEN-SED is configured as a 1-G model and boundary conditions and model parameters are defined as given in Table 3 of (Thullner et al., 2009). As OMEN-SED assumes a fixed fraction of reduced substances to be re-

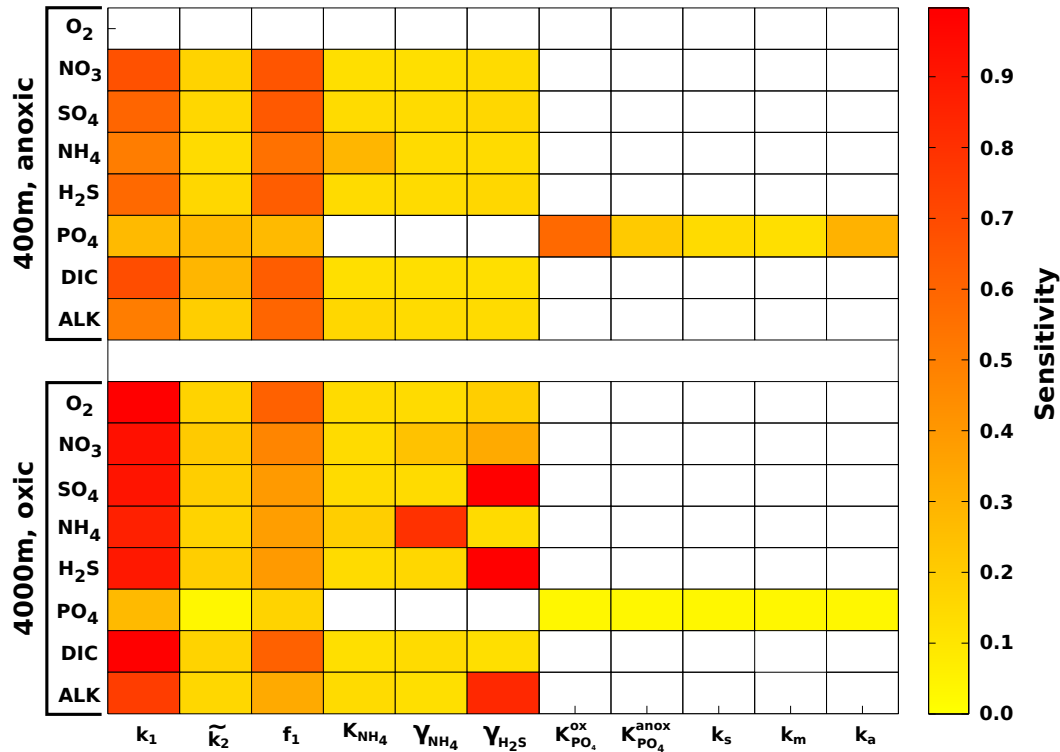
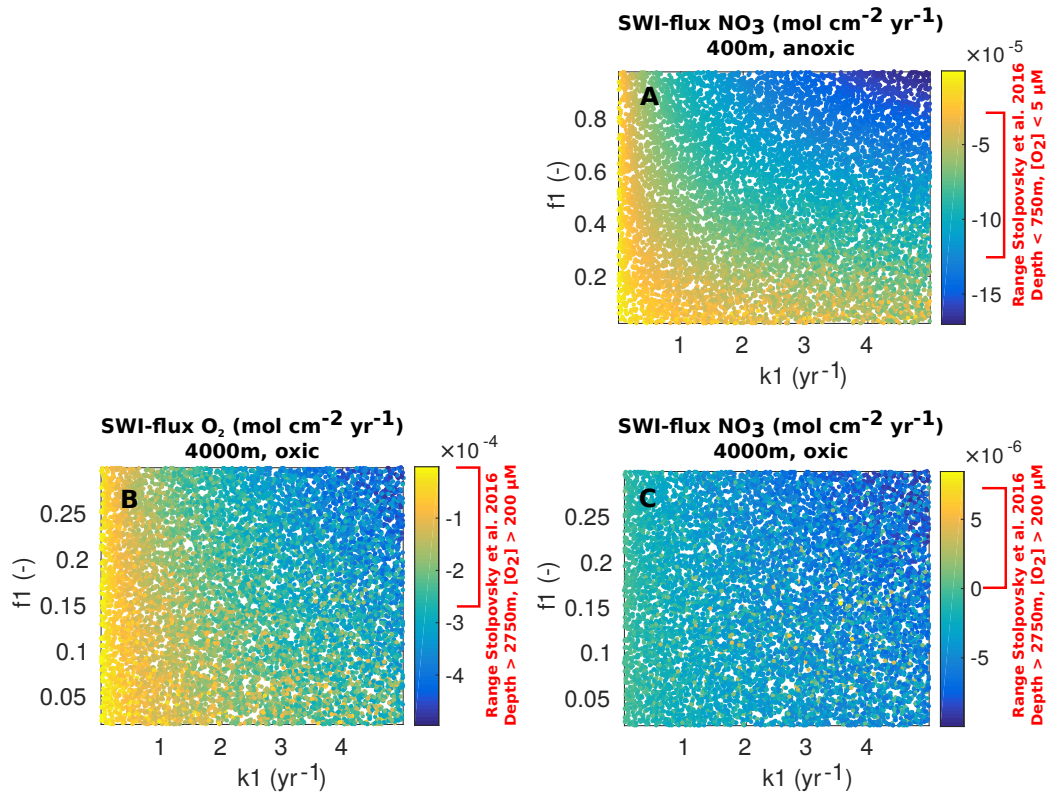


Figure 6. Pattern plot, showing the output sensitivity for each SWI flux (i.e. the chemical compounds on the vertical axis) and each input factor (i.e. the model parameters on the horizontal axis) for two idealised sediment cores. White patterns are assigned where the SWI flux is independent of the specific parameter.

DH: Rather low PO_4 sensitivity - bc of Equil. concentr.?

oxidised which exerts a large impact on the resulting SWI-fluxes (compare Section 3.2) we perform two sets of simulations in order to show the range of possible model outputs. In the first setup 95% of the reduced substances are re-oxidised (i.e. $\gamma_{NH_4} = \gamma_{H_2S} = 0.95$) and in the second only 5% are re-oxidised (all other model parameters and boundary conditions are equal).

Figure 8 compares simulated SWI-fluxes of TEAs (i.e. O_2 , NO_3 and SO_4) along the global hypsometry using OMEN-SED (black lines) with the results of Thullner et al. (2009) (red lines). Observations for O_2 and NO_3 fluxes are taken from Middelburg et al. (1996). Also plotted in Fig. 8A are the total oxygen uptake (TOU) estimates of Thullner et al. (2009) (filled red symbols), who assumed the organic matter flux to be equivalent to TOU. Considering the spatial variability in available data, Figure 8 shows that OMEN-SED is capable of reproducing the major observed trends in depth distributions of TEA fluxes. In general, fluxes calculated with BRNS fall within the range of possible OMEN-SED results (with the exception of NO_3 in the shallow ocean). In particular, the observed O_2 fluxes in the upper 2000m are well predicted by the two OMEN-SED simulations (Fig. 8A). Oxygen fluxes for the deep-sea sediments, however, are slightly underestimated. These deviations



DH: Why mainly negative NO₃-flux 4000m in contrast to database!?... might change when using diff. gamma

Figure 7. Coloured scatter plots (k_1 vs f_1) of resulting OMEN-SED SWI-fluxes for the 400m anoxic (A: NO₃) and 4000m oxic (B: O₂, C: NO₃) scenario. Negative values representing a flux from the water column into the sediments. Indicated area in red at the respective colour scale represents the range of benthic fluxes in the global database of Bohlen et al. (2012).

can presumably be related to the assumed 1-G description of organic matter degradation, which neglects the more labile OM pool. This highly reactive pool is degraded close to the sediment surface, thus promoting higher aerobic degradation rates and higher O₂ fluxes. Nitrate fluxes in the upper 500m of the Atlantic Ocean are well predicted. However, as in Middelburg et al. (1996) the direction of calculated nitrate fluxes in the upper 1000m of the Pacific Ocean differ from the observations. Middelburg et al. (1996) related these discrepancies to the globally averaged model parameters and the applied boundary conditions. They could reduce the disagreements significantly by using more representative bottom water concentrations for the eastern Pacific and a higher flux of labile organic matter for their 2-G model. By changing the boundary conditions and the NC-atomic ratio of organic matter for the whole hypsometry, it is possible to obtain a better model-data fit with OMEN-SED for the shallow Pacific Ocean (green line in Fig. 8B). Following Bohlen et al. (2012), who could show that the atomic NC-ratio strongly deviates from Redfield stoichiometry (0.151) with specifi-

780 cally lower values for the East Pacific Ocean, we adopt their globally averaged value of 0.067. In addition, bottom water conditions are changed to low oxygen/high nitrate levels more likely to be found in the shallow Pacific Ocean ($O_2 = 10$ nanomole cm^{-3} and $NO_3 = 80$ nanomole cm^{-3}).

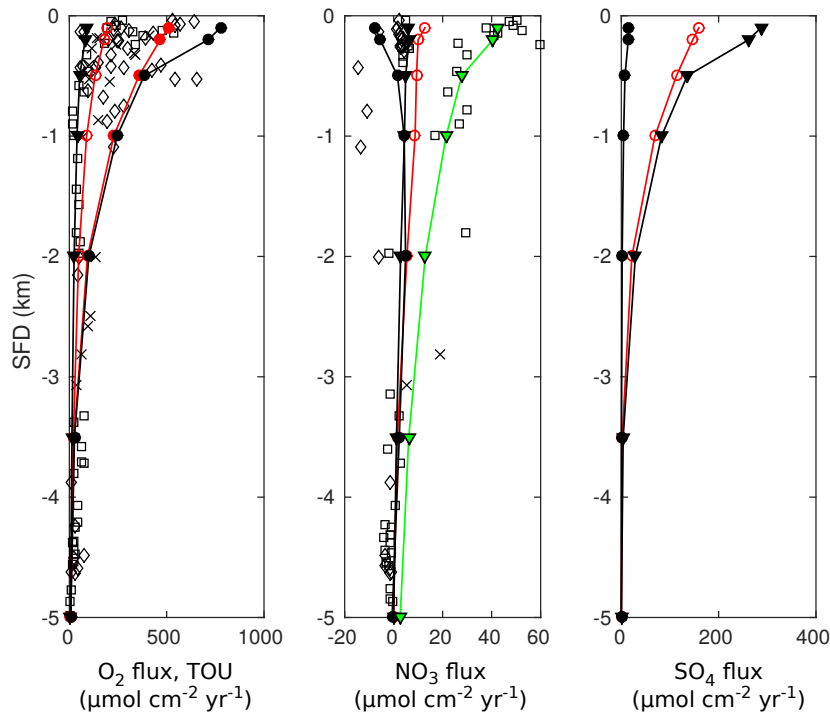


Figure 8. Fluxes of O_2 , NO_3 and SO_4 to the sediment along the global hypsometry. Red lines (with open symbols) are modelled fluxes from Thullner et al. (2009) using BRNS; black lines are results from OMEN-SED (● : $\gamma_{NH_4} = \gamma_{H_2S} = 0.95$; ▼ : $\gamma_{NH_4} = \gamma_{H_2S} = 0.05$). Observations of TEA fluxes are taken from Middelburg et al. (1996) (◇: Atlantic, □: Pacific, ×: Arctic/Indian Ocean). Also plotted in Figure (A) are the total oxygen uptake (TOU) estimates of Thullner et al. (2009) (filled red symbols). The green line indicates OMEN-SED results for low oxygen/high nitrate levels and the lower NC-ratio. Negative values are directed out of the sediments.

3.4 Pre-industrial cGENIE coupling and the OM degradation rate

OMEN-SED has been coupled to the global Earth system model cGENIE as described in Section 2.5.2. Our objective is not to perform and discuss a detailed calibration of the two models, as this is beyond the scope of this model development paper. We rather want to showcase, that a coupling is possible and the results show main sediment features one would expect to see on a global scale. All simulations are run for 20,000 years to steady-state. OMEN-SED is called for each grid-cell in every time step, feeding back the resulting SWI-fluxes and the fraction of POC preserved in the sediments to cGENIE.

Table 14. List of coupled OMEN-cGENIE experiments with oxic and anoxic rate constants (k_1 , yr^{-1}). The rate constant k_2 for the more refractory component is calculated as $k_2 = k_1/100$, apart from the Control experiment where $k_2 = 1.0$. D : seafloor depth.

Experiment	oxic rate constant	anoxic rate constant	Reference/Description
Control	1.0	1.0	All OM is degraded
Tromp	$2.97 \cdot w^{0.62}$	$0.057 \cdot w^{1.94}$	Tromp et al. (1995)
Boudreau_Toht	$0.38 \cdot w^{0.59}$	$0.04 \cdot w^2$	Boudreau (1997) oxic Toht and Lerman (1977) anoxic
Stolpovsky_Toht	$1.02 \cdot w^{0.5}$	$0.04 \cdot w^2$	Stolpovsky et al. (2015) oxic Toht and Lerman (1977) anoxic
Palastanga	0.01	0.008	$D \leq 2000$ Palastanga et al. (2011)
	0.005	0.002	$D > 2000$ Palastanga et al. (2011)

As shown in our sensitivity analysis (Figure 6) and discussed by Arndt et al. (2013) the degradation rate constants for OM (k_i) are the most influential parameters and strongly determine the SWI-flux of redox-sensitive elements as well as the burial rate of OM. Yet, their spatial variability is unknown at the global scale and reported rate constants can vary by almost 10 orders of magnitude (Arndt et al., 2013), thus defining appropriate OM degradation rate constants is a major challenge and source of uncertainty for diagenetic models. The rate constants in models are either determined through profile fitting for a specific site or, for global applications, they are related to a single, readily available characteristic (or master variable) of the local environmental conditions. For instance, considerable effort has been expended to relate the apparent rate constant for oxic and anoxic OM degradation to sedimentation rate (w) and various empirical relations have been proposed (Toht and Lerman, 1977; Tromp et al., 1995; Boudreau, 1997; Stolpovsky et al., 2015). Nevertheless, these relationships are generally based on limited data sets and their global applicability is questionable (Arndt et al., 2013).

Here, we test globally invariant values for the OM degradation rate constants as well as the empirical relation of Boudreau (1997). Modelled mean POC content in the upper 5cm of the sediments are compared to the global POC observations in surface sediments ($< 5\text{cm}$ sediment depth) of Seiter et al. (2004). The original data field is interpolated on a $1^\circ \times 1^\circ$ grid and has been transformed onto the 72×72 SEDGEM grid (Figure ??).

Describe Figure 9 and compare with what we know. E.g. Thullner et al. 2009!

Schulz and Zabel: The basic mechanism inducing microbial activity is the supply of organic matter to the seafloor and this is generally coupled to surface water productivity. Most of the highly productive areas in the global ocean are adjacent to the continents, so that we can expect a decrease of degradation intensity from the coastal marine environments over the continental shelves and slopes into the deep-sea. This becomes evident when we look at the data compiled by Middelburg

815 et al. (1993) which indicate that 83% mineralization and 87% burial in marine sediments occurs in the coastal zone occupying only 9% of the total ocean area. This means that the sediments with the highest respi- ration rates also have the highest burial efficiency in marine environments. Fluxes of oxygen and nitrate, therefore, vary over several orders of magnitude between oligo- trophic open ocean areas and continental shelf and slope areas. This is about 50 to 6,000 mmol m⁻² yr⁻¹ for
820 oxygen and -600 to 380 mmol m⁻² yr⁻¹ for nitrate ...

(SHOW O₂, NO₃ AND E.G. PO₄ SWI-fluxes).

Could also plot Figure 4 from Palastanga et al. (2011) with POC wt% for different sites in the ocean! **UNITS of Fe-P! This is a solid! Therefore not nmol/cm³ rather mol/g as in Palastanga...**

825 Also check what water column features to show and maybe sediment P or Fe-P concentrations (see PALASTANGA et al. 2011, 2013).

Stolpovsky: bioturbated sediments deposited at continental margins quickly become anoxic within a few millimeters [Wenzhöfer and Glud, 2002].

4 Scope of applicability and model limitations

830 State-of-the art numerical models representing the full complexity of the diagenetic processes typically perform adequately at reproducing site-specific biogeochemical dynamics, however, tuning model parameters is laborious, the computational demand is high and, thus, their transferability to the global scale is limited. On the other hand, analytical models are very efficient, but existing approaches coupled to global models generally use highly simplified reaction networks, often restricted
835 to oxic degradation with a limited number of explicit pore water tracers. However, our ability to assess the role of organic matter dynamics for global biogeochemical cycles and climate requires tools that resolve the most important biogeochemical processes and tracers explicitly, while at the same time are computationally efficient and have a degree of predictive capability to extrapolate knowledge to data poor areas. The new model OMEN-SED presented here is a legitimate compro-
840 mise between complexity of biogeochemical processes and computational efficiency. Its scope of applicability covers the entire range from regional to global scales. OMEN-SED's computational efficiency facilitates its use in two very different ways. Firstly, it can be coupled to global Earth system models and therefore allows the investigation of coupled global biogeochemical dynamics over different timescales. Secondly, it can be used to calculate quantitative sensitivity indices requiring
845 large sample sizes such as variance- or density-based approaches. Therefore, OMEN-SED can help to quantitatively investigate how systematic variations in model parameters impact the model output, for instance when the model has been tuned to a site-specific problem. Due to the represented anaerobic processes and secondary-redox reactions, OMEN-SED is also useful to investigate the role of benthic-pelagic coupling on the development of ocean anoxia and euxinia for instance during

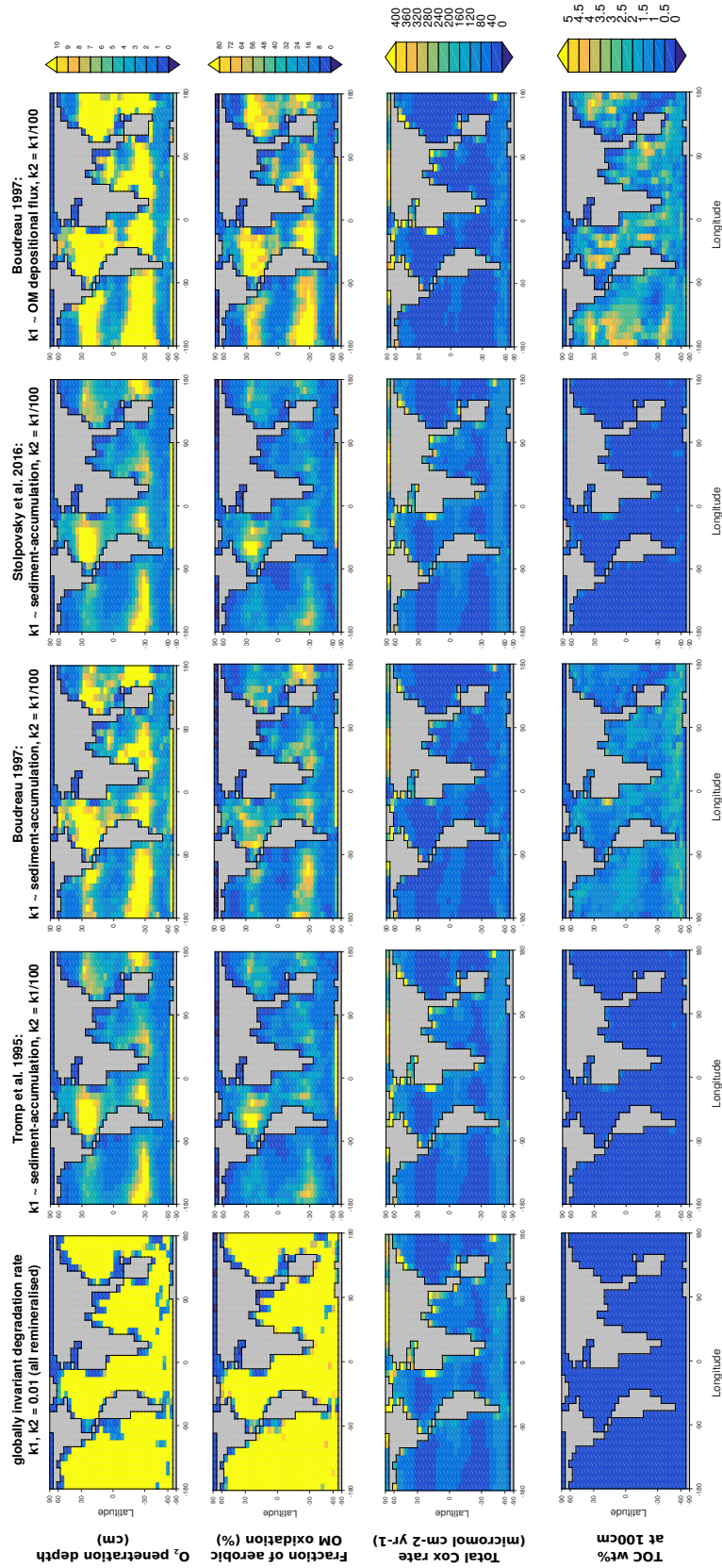


Figure 9. Results of OMEN-cGENIE coupling using different, published parameterisations for the OM degradation rates (k_1 , k_2 , compare Table ??) coupled to the same cGENIE ocean setup. All results shown are sediment characteristics calculated by OMEN-SED. **NOTE: Preliminary results (here frac2 still constant!) TODO: plot wt% just until 3%.**

extreme climate events such as OAEs. On more regional scales it can be applied to systems like continental margins or estuaries which are characterised by complex interactions between different pathways of organic matter degradation and redox reactions. Here, the model can help to disentangle the complex process interplay that drives the biogeochemical dynamics and give quantifications for upper and lower constraints of carbon and nutrient budgets for these dynamic systems. In addition, OMEN-SED can be used to model eutrophication processes in shallow coastal waters as sediment-water oxygen and nutrient exchange fluxes are explicitly modelled and depend on re-oxidation of reduced substances which causes a substantial part of oxygen consumption in these environments.

However, the model presented here, even more complete than previous analytical models, is still associated with a certain degree of simplifications. In order to solve the diagenetic equation analytically important assumptions have been made, which limit the general applicability of the model. One of the most important simplifications is assuming steady-state. When coupled to an Earth system model this assumption is only valid if the relevant variability in boundary conditions and fluxes is generally longer than the characteristic timescales of the reaction-transport processes. In that case the sediment column can be described by a series of pseudo steady-states as it is done in OMEN-SED. Consequently, the model can be used for investigating the long term effects of changes in boundary conditions such as the the input of OM or bottom water oxidation state on degradation and burial dynamics, as for instance during OAEs. Yet, it is not able to predict the system response to short-term or seasonal variations of boundary conditions. The separation of the sediment column into distinct biogeochemical zones and the resulting lack of overlap in degradation pathways may cause distorted organic matter degradation rates for the different TEAs. For instance, in OMEN-SED denitrification does not occur in the oxic layer, while in reality, although inhibited by the presence of oxygen, denitrification can still occur in the oxic zone, even at shallow sediments depths with high OM contents. Manganese and iron are not represented and as such OMEN-SED is not able to model all processes important in coastal marine environments and highly accumulating upwelling regions. This can cause problems when modelling H_2S and PO_4 profiles in anoxic environments as their concentrations are affected by these metal ions (compare Section 3.1). In addition the depth invariant porosity limits the correct calculation of the sediment-water interface flux of dissolved species as in reality porosity decreases with sediment depth.

5 Conclusions

In this paper we have described and tested a new, analytical early diagenetic model resolving organic matter cycling and associated biogeochemical dynamics called OMEN-SED. Our new model is the first of this class of analytical approaches to explicitly represent oxic degradation, denitrification, sulfate reduction and implicitly methanogenesis, as well as the re-oxidation of reduced substances produced during organic matter degradation. Pore water tracers include O_2 , NO_3 , NH_4 , SO_4 , H_2S ,

885 DIC and ALK and the solid phase includes two fractions of organic matter, Fe-bound P and authi-
genic Ca-P minerals. We have shown that the new analytical model is able to reproduce observed
pore water profiles from different ocean depths when organic matter partitioning and degradation
rate constants are tuned to site specific conditions. An extensive sensitive analysis, based on the
novel density-based PAWN method (Pianosi and Wagener, 2015), has been performed to asses the
890 importance of 11 internal model parameters for all resulting SWI-fluxes. The results reveal that the
degradation rate constant for labile organic matter is the most influential parameter for all model
outputs. Under anoxic conditions secondary redox parameters exert an important control on related
SWI-fluxes of SO_4 , H_2S , NH_4 and alkalinity. In addition, the sensitivity analysis showed that glob-
ally observed benthic O_2 and NO_3 fluxes fall well into the range of produced model results.
895 Furthermore, the coupling of OMEN-SED to the Earth system model cGENIE is described and
various published parameterisations for the apparent first order degradation rate constant are tested
to fit the model to observed global organic matter concentrations. **TODO: write about results.** ...in
order to investigate the role of sediments for global biogeochemical cycles and cimate.

6 Code Availability

900 The OMEN-SED source code (Fortran and Matlab) related to this article is provided as a supple-
mentary package together with a ReadMe file, where hardware and software requirements, source
code files and model output file management are fully described.

Appendix A: Reaction Network

Appendix B: Sensitivity Analysis

905 **B1**

Acknowledgements. Thank you...

Table 15. 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	$(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + \frac{(4\text{x}+3\text{y})}{5}\text{NO}_3^- \rightarrow \frac{(2\text{x}+4\text{y})}{5}\text{N}_2 + \frac{(\text{x}-3\text{y}+10\text{z})}{5}\text{CO}_2 + \frac{(4\text{x}+3\text{y}-10\text{z})}{5}\text{HCO}_3^- + \text{zHPO}_4^{2-} + \frac{(3\text{x}+6\text{y}+10\text{z})}{5}\text{H}_2\text{O}$
Sulfate reduction	$(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + \frac{\text{x}}{2}\text{SO}_4^{2-} + (\text{y} - 2\text{z})\text{CO}_2 + (\text{y} - 2\text{z})\text{H}_2\text{O} \rightarrow \frac{\text{x}}{2}\text{H}_2\text{S} + (\text{x} + \text{y} - 2\text{z})\text{HCO}_3^- + \text{yNH}_4^+ + \text{zHPO}_4^{2-}$
Methanogenesis	$(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + (\text{y} - 2\text{z})\text{H}_2\text{O} \rightarrow \frac{\text{x}}{2}\text{CH}_4 + \frac{\text{x}-2\text{y}+4\text{z}}{2}\text{CO}_2 + (\text{x} - 2\text{z})\text{HCO}_3^- + \text{yNH}_4^+ + \text{zHPO}_4^{2-}$
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	$\text{CH}_4 + \text{CO}_2 + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}$
Adsorption reactions and mineral precipitation	
NH ₄ adsorption	$\text{NH}_4^+ \xrightarrow{K_{\text{NH}_4}} \text{NH}_4^+(\text{ads})$
P ad-/desorption ???	$\text{PO}_4^{2-} \xrightarrow{K_{\text{PO}_4}^{\text{L,II}}} \text{PO}_4^{2-}(\text{ads}); \quad \text{HPO}_4^{2-} \xrightarrow{k_s} \text{Fe-bound P} \xrightarrow{k_m} \text{HPO}_4^{2-}$
CFA precipitation	$\text{PO}_4^{2-} \xrightarrow{k_a} \text{CFA}$

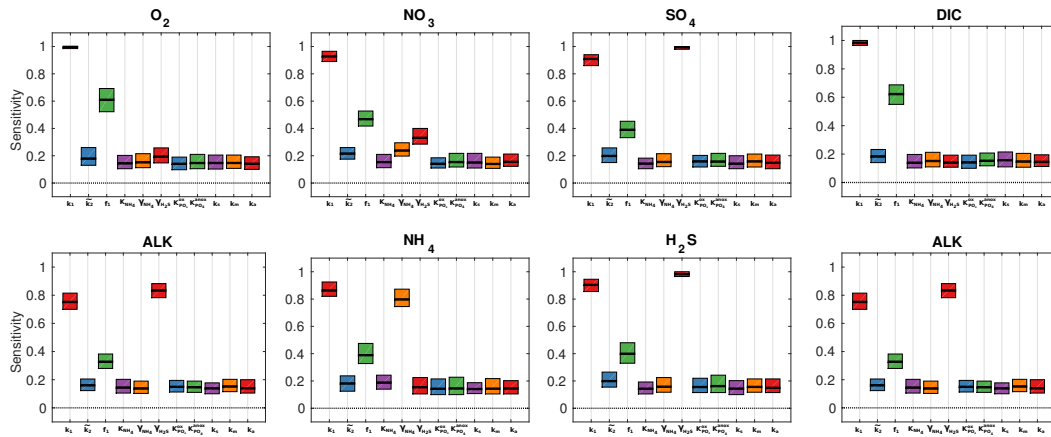


Figure 10. Move to Appendix Box plot of parameter sensitivities for the calculated SWI-fluxes for the 4000m oxic condition. Average sensitivities (black lines) and 90% confidence intervals using $N = 11200$ model evaluations and $Nboot = 100$ bootstrap resamples.

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