

OMEN-SED 0.9: A novel, numerically efficient organic matter sediment diagenesis module for coupling to Earth System Models

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Abstract. We present the first version of OMEN-SED (Organic Matter ENabled SEDiment model), a new, one-dimensional analytical early diagenetic model resolving organic matter cycling and associated biogeochemical dynamics in marine sediments designed to be coupled to Earth system models. OMEN-SED explicitly describes organic matter (OM) cycling as well as associated dynamics of the
5 most important terminal electron acceptors (i.e. O₂, NO₃, SO₄) and methane (CH₄), related reduced substances (NH₄, H₂S), macronutrients (PO₄) and associated pore water quantities (ALK, DIC). Its 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 associated with OM dynamics that affect the dissolved and solid species explicitly resolved in the
10 model. To represent a redox-dependent sedimentary P cycle we also include a representation of the formation and burial of Fe-bound P and authigenic Ca-P minerals. Thus, OMEN-SED is able to capture the main features of diagenetic dynamics in marine sediments and, therefore, offers similar predictive abilities than a complex, numerical diagenetic model. Yet, its computational efficiency allows its coupling to global Earth system models and therefore the investigation of coupled global
15 biogeochemical dynamics over a wide range of climate relevant timescales. This paper provides a detailed description of the new sediment model, as well as an extensive sensitivity analysis using a novel method which considers the entire cumulative distribution functions of the model outputs. In addition, OMEN-SED's performance is evaluated through comprehensive comparisons with observations and results from a more complex numerical model. We find solid phase and dissolved
20 porewater profiles for different ocean depths are reproduced with good accuracy and simulated terminal electron acceptor fluxes fall well within the range of globally observed fluxes. Finally, we

illustrate its application in an Earth system model framework by coupling OMEN-SED to the Earth system model cGENIE and tune the organic matter degradation rate constants to optimise the fit of simulated benthic OM contents to global observations. We find simulated sediment characteristics of the coupled model framework, such as OM degradation rates, oxygen penetration depths and sediment-water interface fluxes are generally in good agreement with observations and in line with what one would expect on a global scale. Coupled to an Earth system model, OMEN-SED is thus a powerful tool that will not only help elucidate the role of benthic-pelagic exchange processes in the evolution and, in particular, the termination of a wide range of climate events, but will also allows a direct comparison of model output with the sedimentary record - the most important climate archive on Earth.

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1 Introduction

I have slightly moved things around. There was some redundancy in the text regarding the paragraph concerning analytical diagenetic models and analytical models in ESM, as well as a part of the solution paragraph. It should flow nicely now, but go through the text and see if it

75 is well integrated.

Role of marine sediments for climate and global biogeochemical cycles:

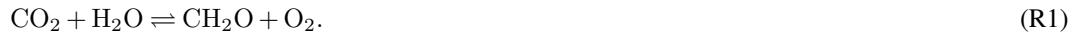
Marine surface sediments are key components in the Earth system. They host the largest carbon reservoir within the surficial Earth system, provide the primary long term sink for atmospheric CO₂, recycle nutrients, and represent the most important geochemical archive used for deciphering past

80 changes of 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 controlled 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

85 impact the water column directly either by short- and long-term storage of deposited material or diagenetic processing of deposited material and transport of terminal electron acceptors (e.g. O₂, SO₄) into, as well as metabolic products (e.g. nutrients, DIC) to the overlying 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,

90 2005).

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



95 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 deep into the sediment leads to net oxygen input to, and CO₂ removal from the atmosphere (Berner, 2004). On shorter timescales, the upper few meters of the sediments, where early diagenesis occurs are specifically important, as this zone controls whether a substance is re-

100 cycled 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 (Middelburg et al., 1993; Arndt et al., 2013). Oxygen and nitrate for instance, the highest energy yielding electron acceptors, are preferentially consumed in the course of the degradation of organic matter, resulting in the release of ammonium and phosphorus 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). Furthermore, organic matter degradation releases metabolic CO₂ to the pore water, causing it to have a lower pH and carbonate ion concentration, thus provoking the dissolution of calcium carbonate CaCO₃ (Emerson and Bender, 110 1981).

Benthic nutrient recycling from marine sediments has been suggested to play a key role for climate and ocean biogeochemistry throughout Earth history. For example, feedbacks between phosphorus 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, 115 1993). Furthermore, benthic 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. Van Cappellen and Ingall, 1994; 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 120 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 in turn 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 CO₂ from the atmosphere and ocean by burying 125 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). Models capable of simulating not only the expansion and intensification of oxygen minimum zones, but also of predicting how the underlying sediments interact are hence needed.

Diagenetic Models in general:

130 Quantifications of diagenetic processes in the sediments are possible through the application of idealised mathematical representations, or so-called diagenetic models (see e.g. Berner, 1980; Boudreau, 1997). A plethora of different approaches have been developed, mainly following two distinct directions (see Arndt et al., 2013, for an overview). First, state-of-the art vertically resolved numerical 135 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; MUDS, Archer et al., 2002; **OMEXDIA Soetaert 1995**; STEADYSED, Van Cappellen and Wang, 1996). These “complete”, multi-component steady-state or non-steady-state models, thus resolve the resulting characteristic redox-zonation of marine sediments through explicitly accounting for oxic OM degradation, denitrification, oxidation by manganese and iron (hydr)oxides, sulfate 140 reduction and methanogenesis as well as the reoxidation of reduced byproducts (i.e. NH₄, Mn²⁺, Fe²⁺, H₂S, CH₄, see e.g. Regnier et al., 2011). Furthermore, they incorporate various mineral dissolution and precipitation reactions, as well as fast equilibrium sorption processes for example of NH₄, PO₄ and metal ions (i.e. Mn²⁺, Fe²⁺ and Mg²⁺, 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 describes OM degradation via 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 . Alternative approaches, so-called continuum models (Middelburg, 1989; Boudreau and Ruddick, 1991), assume a continuous distribution of reactive types but, although conceptually superior, are much less popular (Arndt et al., 2013). These complex, multi-component models have a great potential for quantifying diagenetic dynamics at sites where comprehensive observational data sets 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 (ESM) framework with a large number of grid points prohibitive. Additionally, their global applicability is seriously compromised by the restricted transferability of model parameters from one site to the global scale (Arndt et al., 2013).

The second group of diagenetic models emerged during the early days of diagenetic modelling when computing power was severely restricted (e.g. Berner, 1964). These models solve the diagenetic equation analytically, thus providing an alternative and computationally more efficient approach. Finding an analytical solution, especially when complex reaction networks are to be considered, is not straightforward and analytical models are thus usually less sophisticated and comprehensive than numerical models and generally require the assumption of steady state conditions. It has been shown that 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 without oversimplifying the problem. Analytical approaches with distinct biogeochemical zones were implemented and used in the seventies and eighties to describe observed pore water profiles (e.g. Vanderborgh and Billen, 1975; Vanderborgh et al., 1977; Billen, 1982; Goloway and Bender, 1982; Boudreau and Westrich, 1984) and later for inclusion into multi-box ecosystem models (e.g. Ruardij and Van Raaphorst, 1995; Gypens et al., 2008) and global Earth system models (Tromp et al., 1995). However, in addition to the oxic zone these models generally only describe one anoxic zone explicitly, either a denitrification (Vanderborgh and Billen, 1975; Billen, 1982; Goloway and Bender, 1982; Ruardij and Van Raaphorst, 1995; Gypens et al., 2008) or a sulfate reduction zone (Boudreau and Westrich, 1984; Tromp et al., 1995). Furthermore, the approaches of Vanderborgh and Billen (1975), Goloway and Bender (1982) and Tromp et al. (1995) do not explicitly account for reduced species (i.e. NH_4^+ and H_2S , respectively).

How are sediments resolved in Earth system models:

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 Earth system/climate 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). Analytical diagenetic model represent the most complex description of diagenetic dynamics in Earth system models. 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. These analytic 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. Pore water species 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, PO₄ and O₂. The MEDUSA model (Munhoven, 2007) considers CO₂, HCO₃⁻, CO₃²⁻ and O₂. 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 O₂. A newer versions of the HAMOCC model is a notable exception, as Ilyina et al. (2013) include NO₃ and denitrification explicitly. Furthermore, the version of Palastanga et al. (2011) represents an redox-dependent explicit sedimentary phosphorus cycle. Yet, reoxidation of reduced byproducts, so-called secondary redox reactions (e.g. oxidation of NH₄, H₂S or CH₄), or sorption processes are not included in any of the discussed models. Furthermore, these global models 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).

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., 1996). Even

more restrictive is the use of O₂ as the only TEA and the complete absence of reduced substances and related secondary redox reactions. For the majority of the modern sediments (i.e. in the deep-ocean) O₂ is the primary electron acceptor, however, 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). Oxygen becomes progressively less important as TEA with decreasing seafloor depth and sulfate reduction has been shown to account for 83% of OM degradation in coastal sediments (Krumins et al., 2013). In these environments most O₂ 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. NO₃ and SO₄ through oxidation of NH₄ and H₂S forms an important sink for O₂ which is entirely neglected in current sediment representations in global models. In addition, the lack of anoxic degradation pathways in these models limits their application to oxic oceans. Currently no analytical sediment model exists that can be used under anoxic conditions. 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. A sediment model suitable for the coupling to an ESM and enabling a wide range of paleo questions to be addressed has to provide a robust quantification of organic (and inorganic) carbon burial fluxes, benthic uptake/return fluxes of oxygen, growth-limiting nutrients and reduced species, as well as anoxic degradation pathways. 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.

240 Solution presented here:

Therefore, we developed the OrganicMatter ENabled SEDiment model (OMEN-SED), a new, one-dimensional, numerically efficient diagenetic model. OMEN-SED builds upon and stands in the tradition of earlier stand-alone, analytical diagenetic models (Vanderborght et al., 1977; Billen, 1982; Goloway and Bender, 1982; Boudreau, 1991), as well as of analytical diagenetic models developed for the coupling to regional scale ecosystem or global Earth system models (Ruardij and Van Raaphorst, 1995; Tromp et al., 1995; Heinze et al., 1999; Gypens et al., 2008).

OMEN-SED is the first analytical model to explicitly describe OM cycling as well as associated dynamics of the most important TEAs (i.e. O₂, NO₃, SO₄), related reduced substances (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, while OMEN-SED captures most of the features of a complex, numerical diagenetic model, 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,

255 OMEN-SED can be easily extended to a Multi-G approach. The first part of the paper provides a detailed description of OMEN-SED (Section 2). This includes descriptions of the general model approach (Section 2.1), of the conservation equations for all explicitly represented biogeochemical tracers (Section 2.2), as well as a summary of global relationships used to constrain reaction and transport parameters in OMEN-SED (Section 2.4). In addition, a generic algorithm is described
 260 which is used to match internal boundary conditions and to determine the integration constants for the analytical solutions (Section 2.3). In order to validate the stand-alone version of OMEN-SED, the second part of the paper performs an extensive sensitivity analysis for the most important model parameters and resulting sediment-water interface fluxes are compared with a global database (Section 3.1). In addition, results of the stand-alone model are compared with observed pore water pro-
 265 files from different ocean depths (Section 3.2) and OMEN-SED simulations of TEA-fluxes along a typical ocean transect are compared with observations and results from a complete, numerical diagenetic model (Section 3.3). Thereafter, OMEN-SED is coupled to the carbon-centric version of the “GENIE” Earth system model (cGENIE, Ridgwell et al., 2007, Section 4.1). Sensitivity studies are carried out using this coupled model and modelled organic matter concentrations in the surface
 270 sediments are compared to a global database (Seiter et al., 2004, Section 4.2). We finally discuss potential applicabilities of OMEN-SED and critically analyse model limitations (Section 5).

2 Model Description

OMEN-SED is implemented as a FORTRAN version that can be easily coupled to any pelagic, biogeochemical model via the coupling routine **OMEN_SED_main**. In addition, OMEN-SED exists as
 275 a stand-alone version implemented in MATLAB and the entire model can be executed on a standard personal computer in less than 0.1 seconds. The source code of both, the Fortran and the MATLAB stand-alone version, as well as instructions for executing OMEN-SED and for plotting model results are available as a supplement to this paper.

The following section provides a detailed description of OMEN-SED and the fundamental equations underlying the model are highlighted. Tables 1 and 15 summarise the biogeochemical reaction network and Tables 9 and 10 provide a glossary of model parameters along with their respective units.
 280

2.1 General Model Approach

In OMEN-SED, the calculation of benthic uptake, recycling 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):

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

where C_i is the concentration of biogeochemical species i , ξ equals the porosity ϕ for solute species and $(1 - \phi)$ for solid species. The term z is the sediment depth, t denotes the time, D_i is the apparent diffusion coefficient of species i , w is the burial rate and $\sum_j R_i^j$ represents the sum of all biogeochemical rates j affecting species i .

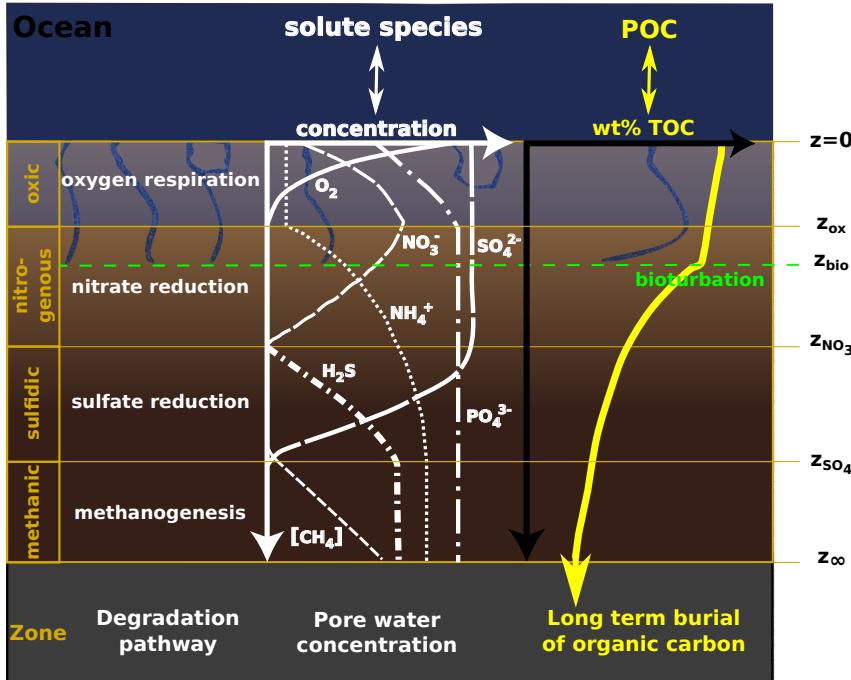


Figure 1. Schematic of the different modelled species and zones in OMEN-SED. Here showing the case $z_{ox} < z_{bio} < z_{NO_3^-} < z_{SO_4^{2-}}$.

OMEN-SED accounts for both the advective, as well as the diffusive transport of solid and dissolved species. They are buried in the sediment according to a constant burial rate w , thus neglecting the effect of sediment compaction (i.e. $\frac{\partial \phi}{\partial z} = 0$) due to mathematical constraints. The molecular diffusion of dissolved species is described by Fick's law applying a species-specific apparent diffusion coefficient, $D_{mol,i}$. In addition, the activity of infaunal organisms in the bioturbated zone is simulated using a diffusive term (e.g. Boudreau, 1986), with a constant bioturbation coefficient D_{bio} in the bioturbated zone, while D_{bio} is set to zero below the maximum bioturbation depth, z_{bio} . 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, $D_{i,0} = D_{mol,i} \cdot f_{ir}$, Soetaert et al., 1996). The reaction network of OMEN-SED accounts for the most important primary and secondary redox reactions, equilibrium reactions, mineral dissolution and precipitation, as well as adsorption and desorption processes associated with OM dynamics that affect the dissolved and solid species explicitly resolved in the model. Tables 1 and 15 provide a

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 Fe(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

305 summary of the reactions and biogeochemical tracers considered in OMEN-SED together with their respective reaction stoichiometries.

All parameters in Eq. (1) may vary with depth and many reaction rate expressions depend on the concentration of other species. Expressing Eq. (1) for a set of chemical species thus results in a non-linear, coupled set of equations that can only be solved numerically. However, OMEN-SED is 310 designed for the coupling to Earth system models and, therefore, cannot afford a computationally expensive numerical solution. Instead, similar to early, analytical diagenetic models, a computationally efficient analytical solution of Eq. (1) can be derived by 1) assuming steady state conditions (i.e. $\frac{\partial C_i}{\partial t} = 0$) and 2) reducing the vertical variability in parameters and reaction rate expressions by dividing the sediment column into a number of functional biogeochemical zones (Fig. 1, compare 315 e.g. Billen, 1982; Goloway and Bender, 1982; Ruardij and Van Raaphorst, 1995; Tromp et al., 1995; Gypens et al., 2008, for similar solutions). More specifically, OMEN-SED divides the sediment column into: I) a bioturbated and II) a non-bioturbated zone defined by an imposed, constant 320 bioturbation depth z_{bio} (Fig. 1). Furthermore, it resolves the dynamic redox stratification of marine sediments by dividing the sediment into 1) an oxic zone delineated by the oxygen penetration depth z_{ox} ; 2) a denitrification (or nitrogenous) zone situated between z_{ox} and the nitrate penetration depth z_{NO_3} ; 3) a sulfate reduction zone situated between z_{NO_3} and the sulfate penetration depth z_{SO_4} ; and 4) a methanogenic zone situated below z_{SO_4} (Fig. 1). Although in each of these zones Eq. (1) is applied with depth invariant parameters, parameter values may differ across zones. The biogeochemical zones are linked by stating continuity in both concentrations and fluxes at the dynamic, internal 325 boundaries ($z_b \in \{z_{\text{bio}}, z_{\text{ox}}, z_{\text{NO}_3}, z_{\text{SO}_4}\}$, compare e.g. Billen, 1982; Ruardij and Van Raaphorst, 1995). Note that these boundaries are dynamic because their depth varies in response to changing ocean boundary conditions and forcings (see Section 2.3.1 for details). Furthermore, the maximum bioturbation depth is not restricted to a specific biogeochemical zone, hence OMEN-SED allows bioturbation to occur in the anoxic zones of the sediment (here all zones $z > z_{\text{ox}}$ combined).

330 The formulation of the reaction term in Eq. (1) varies between zones and encapsulates the most
pertinent reaction processes within the respective zone (see Section 2.2), thus simplifying the mathematical
description of the reaction network while retaining most of its biogeochemical complexity.
All consumption or production processes of dissolved species related to the degradation of organic
matter are a function of the organic matter concentration. Because organic matter degradation is de-
335 scribed as a first-order degradation, these processes can be expressed as a series of exponential terms
($\sum_j \alpha_j \exp(-\beta_j z)$, see Eq. (2)). In addition, slow adsorption/desorption and mineral precipitation
processes can be expressed as zero or first order (reversible) reaction (Q or $k \cdot (C_i - \tilde{C})$, in Eq. (2)).
Fast adsorption is described as an instantaneous equilibrium reaction using a constant adsorption
coefficient K_i . The reoxidation of reduced substances is accounted for implicitly by adding a (con-
340 sumption/production) flux to the internal boundary conditions (see Sections 2.2.2, 2.2.3 and 2.2.4).
This simplification has been used previously by Gypens et al. (2008) for nitrate and ammonium
and can be justified as it has been shown that the reoxidation mainly occurs within a thin layer at
the oxic/anoxic interface (Soetaert et al., 1996). The general reaction-transport equation underlying
OMEN-SED is thus given by:

$$\frac{\partial C_i}{\partial t} = 0 = \frac{D_i}{1+K_i} \frac{\partial^2 C_i}{\partial z^2} - w \frac{\partial C_i}{\partial z} - \frac{1}{1+K_i} \left(\sum_j \alpha_j \exp(-\beta_j z) + \sum_l k_l \cdot C_i - \sum_m Q_m \right)$$

(2)

345

where $1/\beta_j$ can be interpreted as the length scale and α_j as the relative importance (or the magnitude
at $z = 0$) of reaction j (Boudreau, 1997), k_l are generic first order reaction rate constants and Q_m
are zero-order (or constant) reaction rates.

350 The analytical solution of Eq. (2) is of the general form:

$$C_i(z) = A \cdot \exp(az) + B \cdot \exp(bz) + \sum_j \frac{\alpha_j}{D\beta_j^2 - w\beta_j - \sum_l k_l} \cdot \exp(-\beta_j z) + \frac{\sum_m Q_m}{\sum_l k_l} \quad (3)$$

with

$$a = \frac{w - \sqrt{w^2 + 4 \cdot D \cdot \sum_l k_l}}{2 \cdot D}, \quad b = \frac{w + \sqrt{w^2 + 4 \cdot D \cdot \sum_l k_l}}{2 \cdot D} \quad (4)$$

355 where A and B are integration constants that can be determined by applying a set of internal bound-
ary conditions (see Section 2.3).

Based on Eq. (2) and its analytical solution Eq. (3), OMEN-SED returns the fraction of particulate
organic carbon (POC) buried in the sediment, f_{POC} , as well as the benthic uptake/return fluxes F_{C_i}
of dissolved species C_i (in $\text{mol cm}^{-2} \text{ year}^{-1}$) in response to the dynamic interplay of transport and

360 reaction processes under changing boundary conditions and forcings:

$$f_{\text{POC}} = \frac{\text{POC}(z_\infty)}{\text{POC}(0)} \quad (5)$$

$$F_{C_i} = \phi(0) \left(D_i \frac{\partial C_i(z)}{\partial z} \Big|_{z=0} - w \cdot C_i(0) \right) \quad (6)$$

where w is the deposition rate, D_i is the diffusion coefficient and $\text{POC}(0)$, $\text{POC}(z_\infty)$, $C_i(0)$ denote
365 the concentration of POC and dissolved species i at the SWI and at the lower sediment boundary,
respectively.

2.2 Conservation Equations and Analytical Solution

The following sections provide a detailed description of the conservation equations and analytical
solutions for each chemical species that is resolved in this version of OMEN-SED.

370 **2.2.1 Organic Matter or Particulate Organic Carbon (POC)**

In marine sediments, organic matter (or in the following called particulate organic carbon, POC) is
degraded by heterotrophic activity coupled to the sequential utilisation of terminal electron acceptors
(TEAs) according to the free energy gain of the half-reaction ($\text{O}_2 > \text{NO}_3^- > \text{MnO}_2 > \text{Fe(OH)}_3 >$
 SO_4^{2-} , e.g. Stumm and Morgan, 2012). Once all TEAs are depleted, organic matter is degraded
375 via methanogenesis. Here, organic matter degradation is described via a multi G-model approach
(Jørgensen, 1978), dividing the bulk OM into a number i of discrete compound classes POC_i char-
acterised by class-specific first-order degradation rate constants k_i . The conservation equation for
organic matter dynamics is thus given by:

$$\frac{\partial \text{POC}_i}{\partial t} = 0 = D_{\text{POC}_i} \frac{\partial^2 \text{POC}_i}{\partial z^2} - w \frac{\partial \text{POC}_i}{\partial z} - k_i \cdot \text{POC}_i \quad (7)$$

380 with $D_{\text{POC}_i} = D_{\text{bio}}$ for $z \leq z_{\text{bio}}$ and $D_{\text{POC}_i} = 0$ for $z > z_{\text{bio}}$. Integration of equations (7) yields the
following general solutions for the bioturbated and non-bioturbated layers:

I. Bioturbated zone ($z \leq z_{\text{bio}}$)

$$385 \text{POC}_i^I(z) = A_{1i} \cdot \exp(a_{1i}z) + B_{1i} \cdot \exp(b_{1i}z) \quad (8)$$

II. Non-bioturbated zone ($z_{\text{bio}} < z$)

$$\text{POC}_i^{II}(z) = A_{2i} \cdot \exp(a_{2i}z) \quad (9)$$

where

$$390 a_{1i} = \frac{w - \sqrt{w^2 + 4 \cdot D_{\text{POC}_i} \cdot k_i}}{2 \cdot D_{\text{POC}_i}}, \quad b_{1i} = \frac{w + \sqrt{w^2 + 4 \cdot D_{\text{POC}_i} \cdot k_i}}{2 \cdot D_{\text{POC}_i}}, \quad a_{2i} = -\frac{k_i}{w} \quad (10)$$

Determining the integration constants ($A_{1,i}$, $B_{1,i}$, $A_{2,i}$) requires the definition of a set of boundary
conditions (Table 2). For organic matter, OMEN-SED applies a known concentration/flux at the

Table 2. OM Boundary conditions applied in OMEN-SED. 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) $\text{POC}_i(0) = \text{POC}_{0i}$
$z = z_{\text{bio}}$	continuity	2) $\text{POC}_i(z_{\text{bio}}^-) = \text{POC}_i(z_{\text{bio}}^+)$ 3) $-D_{\text{bio}} \cdot \frac{\partial \text{POC}_i}{\partial z} \Big _{z_{\text{bio}}^-} = 0$

sediment-water interface and assumes continuity across the bottom of the bioturbated zone, z_{bio} . The integration constants ($A_{1,i}$, $B_{1,i}$, $A_{2,i}$) are thus given by:

$$395 \quad \begin{aligned} B_{1i} &\stackrel{\text{BC1)}}{=} \text{POC}_{0i} - A_{1i} \\ A_{2i} &\stackrel{\text{BC2)}}{=} \frac{A_{1i} \cdot \exp(a_{1i} z_{\text{bio}}^-) + B_{1i} \cdot \exp(b_{1i} z_{\text{bio}}^-)}{\exp(a_{2i} z_{\text{bio}}^+)} \\ A_{1i} &\stackrel{\text{BC3)}}{=} -\frac{B_{1i} b_{1i} \cdot \exp(b_{1i} z_{\text{bio}}^-)}{a_{1i} \cdot \exp(a_{1i} z_{\text{bio}}^-)} \end{aligned} \quad (11)$$

See Section 2.3.1 for further details on how to find the analytical solution.

400 2.2.2 Oxygen

OMEN-SED explicitly accounts for oxygen consumption by the aerobic degradation of organic matter within the oxic zone, as well as the oxidation of reduced species (i.e. NH_4 , H_2S) produced in the anoxic zones of the sediment. In the oxic zone ($z < z_{\text{ox}}$), the aerobic degradation consumes oxygen with a fixed $\text{O}_2 : \text{C}$ ratio (O_2C , Tab. 10). A predefined fraction, γ_{NH_4} , of the ammonium produced 405 during the aerobic degradation of OM is nitrified to nitrate, consuming two moles of oxygen per mole of ammonium produced. In addition, OMEN-SED implicitly accounts for the oxygen consumption due to oxidation of reduced species (NH_4 , H_2S) produced below the oxic zone through the flux boundary condition at the dynamically calculated (see section 2.4.2 for details) oxygen penetration depth z_{ox} . All oxygen consumption processes can thus be formulated as a function of organic matter 410 degradation. The conservation equation for oxygen is given by:

$$\frac{\partial \text{O}_2}{\partial t} = 0 = D_{\text{O}_2} \frac{\partial^2 \text{O}_2}{\partial z^2} - w \frac{\partial \text{O}_2}{\partial z} - \frac{1-\phi}{\phi} \sum_i k_i \cdot [\text{O}_2\text{C} + 2\gamma_{\text{NH}_4} \text{NC}_i] \cdot \text{POC}_i(z) \quad (12)$$

For illustrative purposes, we here substitute the analytical solution for the POC depth profile and provide the analytical solution. The remaining paragraphs only outline the general equation, whose analytical solution can be derived in an identical manner. Substituting Eq. (8) and (9) for $\text{POC}_i(z)$ and Eq. (11) for B_{1i} gives:

415 I Bioturbated zone ($z \leq z_{\text{bio}}$)

$$\frac{\partial O_2^I}{\partial t} = 0 \stackrel{8\&11}{=} D_{O_2}^I \frac{\partial^2 O_2}{\partial z^2} - w \frac{\partial O_2}{\partial z} - \frac{1-\phi}{\phi} \sum_i k_i \cdot [O_2 C + 2\gamma_{NH_4} NC_i] \cdot \left(A_{1i} \cdot [exp(a_{1i}z) - exp(b_{1i}z)] + POC_{0i} \cdot exp(b_{1i}z) \right)$$

II Non-bioturbated zone ($z_{\text{bio}} < z < z_{\text{ox}}$)

$$420 \quad \frac{\partial O_2^{II}}{\partial t} = 0 \stackrel{9}{=} D_{O_2}^{II} \frac{\partial^2 O_2}{\partial z^2} - w \frac{\partial O_2}{\partial z} - \frac{1-\phi}{\phi} \sum_i k_i \cdot [O_2 C + 2\gamma_{NH_4} NC_i] \cdot \left(A_{2i} \cdot exp(a_{2i}z) \right)$$

where $D_{O_2}^I$ and $D_{O_2}^{II}$ denote the O_2 diffusion coefficient for the bioturbated and non-bioturbated zone, respectively. The term $\frac{1-\phi}{\phi}$ accounts for the volume conversion from solid to dissolved phase and NC_i is the nitrogen to carbon ratio in POC. Integration yields the following analytical solution

425 for each zone:

I Bioturbated zone ($z \leq z_{\text{bio}}$):

$$O_2^I(z) = A_{O_2}^1 + B_{O_2}^1 \cdot exp(b_{O_2}^1 z) + \sum_i \Phi_{1,i}^I \cdot exp(a_{1i}z) + \sum_i \Phi_{1,i}^{II} \cdot exp(b_{1i}z) + \sum_i \Phi_{1,i}^{III} \cdot exp(b_{1i}z) \quad (13)$$

430 II Non-bioturbated zone ($z_{\text{bio}} < z < z_{\text{ox}}$)

$$O_2^{II}(z) = A_{O_2}^2 + B_{O_2}^2 \cdot exp(b_{O_2}^2 z) + \sum_i \Phi_{i,2}^I \cdot exp(a_{2i}z) \quad (14)$$

with

$$435 \quad \begin{aligned} b_{O_2}^1 &= \frac{w}{D_{O_2}^I}, \quad b_{O_2}^2 = \frac{w}{D_{O_2}^{II}} \\ \Phi_{1,i}^I &= \frac{1-\phi}{\phi} \cdot \frac{k_i \cdot (O_2 C + 2\gamma_{NH_4} NC_i) \cdot A_{1i}}{D_{O_2}^I (-a_{1i})^2 - w \cdot (-a_{1i})}, \quad \Phi_{1,i}^{II} = -\frac{1-\phi}{\phi} \cdot \frac{k_i \cdot (O_2 C + 2\gamma_{NH_4} NC_i) \cdot A_{1i}}{D_{O_2}^I (-b_{1i})^2 - w \cdot (-b_{1i})} \\ \Phi_{1,i}^{III} &= \frac{1-\phi}{\phi} \cdot \frac{k_i \cdot (O_2 C + 2\gamma_{NH_4} NC_i) \cdot POC_{0i}}{D_{O_2}^I (-b_{1i})^2 - w \cdot (-b_{1i})} \\ \Phi_{i,2}^I &:= \frac{1-\phi}{\phi} \cdot \frac{k_i \cdot (O_2 C + 2\gamma_{NH_4} NC_i) \cdot A_{2i}}{D_{O_2}^{II} (-a_{2i})^2 - w \cdot (-a_{2i})} \end{aligned}$$

Determining the four integration constants ($A_{O_2}^1, B_{O_2}^1, A_{O_2}^2, B_{O_2}^2$, see Section 2.3 for details), as well as the *a priori* unknown oxygen penetration depth requires the definition of five boundary conditions (see Table 3). At the sediment-water interface, OMEN-SED applies a Dirichlet condition (i.e. known concentration) and assumes concentration and flux continuity across the bottom of the bioturbated zone, z_{bio} . The oxygen penetration depth z_{ox} marks the lower boundary and is dynamically calculated as the depth at which $O_2(z) = 0$. Therefore, OMEN-SED applies a Dirichlet boundary condition $O_2(z_{\text{ox}}) = 0$. In addition, a flux boundary is applied that implicitly accounts for the oxygen consumption by the partial oxidation of NH_4 and H_2S diffusing into the oxic zone from below

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) $O_2(z_{\text{bio}}^-) = O_2(z_{\text{bio}}^+)$
$z = z_{\text{ox}}$	O_2 consumption ($z_{\text{ox}} = z_\infty$)	3) $-(D_{O_2,0} + D_{\text{bio}}) \cdot \frac{\partial O_2}{\partial z} \Big _{z_{\text{bio}}^-} = -D_{O_2,0} \cdot \frac{\partial O_2}{\partial z} \Big _{z_{\text{bio}}^+}$ 4) IF ($O_2(z_\infty) > 0$) 4.1) $\frac{\partial O_2}{\partial z} \Big _{z_{\text{ox}}} = 0$ ELSE 4.2) $O_2(z_{\text{ox}}) = 0$ and $-D_{O_2} \cdot \frac{\partial O_2}{\partial z} \Big _{z_{\text{ox}}} = F_{\text{red}}(z_{\text{ox}})$ $F_{\text{red}}(z_{\text{ox}}) = \frac{1-\phi}{\phi} \cdot \int_{\tilde{z}_{\text{NO}_3}}^{\infty} \sum_i (2\gamma_{\text{NH}_4} \text{NC}_i + 2\gamma_{\text{H}_2\text{S}} \text{SO}_4 \text{C}) k_i \text{POC}_i dz$
	($z_{\text{ox}} < z_\infty$) with	

Note: $\tilde{z}_{\text{NO}_3} = z_{\text{ox}}$ as upper boundary here, as z_{NO_3} is not known at this point.

(BC 4.2, Table 3). It is assumed that respective fractions (γ_{NH_4} and $\gamma_{\text{H}_2\text{S}}$) are directly reoxidised at the oxic/anoxic interface and the remaining fraction escapes reoxidation. OMEN-SED iteratively solves for z_{ox} by first testing if there is oxygen left at z_∞ (i.e. $O_2(z_\infty) > 0$). If that is not the case, it 450 determines the root for the flux boundary condition 4.2 (Table 3). If $z_{\text{ox}} = z_\infty$, a zero diffusive flux boundary condition is applied as lower boundary condition.

2.2.3 Nitrate and Ammonium

Nitrogen dynamics in OMEN-SED are controlled by the metabolic production of ammonium, nitrification, denitrification as well as ammonium adsorption. Ammonium is produced by organic matter 455 degradation in both the oxic and anoxic zones, while denitrification consumes nitrate in the denitrification zone with a fixed $\text{NO}_3^- : \text{C}$ ratio ($\text{NO}_3^- \text{C}$, Tab. 10).

The adsorption of ammonium to sediment particles is formulated as an equilibrium process with constant equilibrium adsorption coefficient K_{NH_4} , thus assuming that the adsorption is fast compared to the characteristic time scales of transport processes (Wang and Van Cappellen, 1996). In 460 addition, a defined fraction, γ_{NH_4} , of metabolically produced ammonium is directly nitrified to nitrate in the oxic zone, while the nitrification of upward diffusing ammonium produced in the sulfidic and methanic zones is implicitly accounted for in the boundary conditions. The conservation equations for ammonium and nitrate are thus given by:

465

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

$$\frac{\partial \text{NO}_3^I}{\partial t} = 0 = D_{\text{NO}_3} \frac{\partial^2 \text{NO}_3^I}{\partial z^2} - w \frac{\partial \text{NO}_3^I}{\partial z} + \gamma_{\text{NH}_4} \frac{1-\phi}{\phi} \cdot \sum_i \text{NC}_i \cdot k_i \cdot \text{POC}_i(z) \quad (15)$$

$$\frac{\partial \text{NH}_4^I}{\partial t} = 0 = \frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \frac{\partial^2 \text{NH}_4^I}{\partial z^2} - w \frac{\partial \text{NH}_4^I}{\partial z} + \frac{1-\gamma_{\text{NH}_4}}{1+K_{\text{NH}_4}} \cdot \frac{1-\phi}{\phi} \cdot \sum_i \text{NC}_i \cdot k_i \cdot \text{POC}_i(z) \quad (16)$$

470 2. Denitrification (or nitrogenous) zone ($z_{\text{ox}} < z \leq z_{\text{NO}_3}$)

$$\frac{\partial \text{NO}_3^{II}}{\partial t} = 0 = D_{\text{NO}_3} \frac{\partial^2 \text{NO}_3^{II}}{\partial z^2} - w \frac{\partial \text{NO}_3^{II}}{\partial z} - \frac{1-\phi}{\phi} \text{NO}_3 \text{C} \cdot \sum_i k_i \cdot \text{POC}_i(z) \quad (17)$$

$$\frac{\partial \text{NH}_4^{II}}{\partial t} = 0 = \frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \frac{\partial^2 \text{NH}_4^{II}}{\partial z^2} - w \frac{\partial \text{NH}_4^{II}}{\partial z} \quad (18)$$

3. Sulfidic and methanic zone ($z_{\text{NO}_3} < z \leq z_{\infty}$)

$$\frac{\partial \text{NH}_4^{III}}{\partial t} = 0 = \frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \frac{\partial^2 \text{NH}_4^{III}}{\partial z^2} - w \frac{\partial \text{NH}_4^{III}}{\partial z} + \frac{1}{1+K_{\text{NH}_4}} \cdot \frac{1-\phi}{\phi} \cdot \sum_i \text{NC}_i \cdot k_i \cdot \text{POC}_i(z) \quad (19)$$

475

where D_{NO_3} and D_{NH_4} denote the diffusion coefficients for NO_3 and NH_4 which depend on the bioturbation status of the respective geochemical zone (compare Section 2.3.1). Integration of Eq. (15) - (19) yields the analytical solutions, which are not further developed here but follow the procedure outlined in Section 2.2.2 for oxygen (also see Section 2.3.1 for more details on how to find the analytical solution). Table 4 summarises the boundary conditions applied in OMEN-SED to solve Eq. (15) - (19) and to find the *a priori* unknown nitrate penetration depth, z_{NO_3} . The model assumes known bottom water concentrations for both NO_3 and NH_4 , the complete consumption of nitrate at the nitrate penetration depth (in case $z_{\text{NO}_3} < z_{\infty}$) and no change in ammonium flux at z_{∞} .

480 In addition, concentration and diffusive flux continuity across z_{bio} and z_{ox} is considered for NO_3 and NH_4 . Furthermore, the reoxidation of upward-diffusing reduced ammonium is accounted for in the oxic-anoxic boundary condition for nitrate and ammonium. OMEN-SED iteratively solves for z_{NO_3} by first testing if there is nitrate left at z_{∞} (i.e. $\text{NO}_3(z_{\infty}) > 0$) and, otherwise, by finding the root for the flux boundary condition 6.2 (Table 4).

490 **2.2.4 Sulfate and Sulfide**

Below the denitrification zone ($z > z_{\text{NO}_3}$), organic matter degradation is coupled to sulfate reduction, consuming sulfate and producing hydrogen sulfide with a fixed $\text{SO}_4 : \text{C}$ ratio ($\text{SO}_4 \text{C}$, Tab. 10). In addition, the anaerobic oxidation of upward diffusing methane (AOM) produced below the sulfate penetration and the associated consumption of sulfate and production of sulfide; as well as the 495 production of sulfate and consumption of sulfide through sulfide oxidation are implicitly accounted for through the boundary conditions (Table 5). The conservation equations for sulfate and sulfide are thus given by:

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) $\text{NO}_3(0) = \text{NO}_{30}$
$z = z_{\text{bio}}$	continuity	2) $\text{NO}_3(z_{\text{bio}}^-) = \text{NO}_3(z_{\text{bio}}^+)$
$z = z_{\text{ox}}$	continuity	3) $-(D_{\text{NO}_3,0} + D_{\text{bio}}) \cdot \frac{\partial \text{NO}_3}{\partial z} _{z_{\text{bio}}^-} = -D_{\text{NO}_3,0} \cdot \frac{\partial \text{NO}_3}{\partial z} _{z_{\text{bio}}^+}$
	where:	4) $\text{NO}_3(z_{\text{ox}}^-) = \text{NO}_3(z_{\text{ox}}^+)$
$z = z_{\text{NO}_3}$	NO_3 consumption ($z_{\text{NO}_3} = z_\infty$)	5) $-D_{\text{NO}_3} \cdot \frac{\partial \text{NO}_3}{\partial z} _{z_{\text{ox}}^-} + \gamma_{\text{NH}_4} \cdot F_{\text{NH}_4}(z_{\text{ox}}) = -D_{\text{NO}_3} \cdot \frac{\partial \text{NO}_3}{\partial z} _{z_{\text{ox}}^+}$ $F_{\text{NH}_4}(z_{\text{ox}}) = \frac{1}{1+K_{\text{NH}_4}} \cdot \frac{1-\phi}{\phi} \cdot \int_{z_{\text{NO}_3}}^\infty \sum_i \text{NC}_i \cdot k_i \cdot \text{POC}_i dz$
		6) IF ($\text{NO}_3(z_\infty) > 0$)
		6.1) $\frac{\partial \text{NO}_3}{\partial z} _{z_{\text{NO}_3}} = 0$
		ELSE
		6.2) $\text{NO}_3(z_{\text{NO}_3}) = 0 \quad \text{and} \quad \frac{\partial \text{NO}_3}{\partial z} _{z_{\text{NO}_3}} = 0$
$z = 0$	known concentration	1) $\text{NH}_4(0) = \text{NH}_{40}$
$z = z_{\text{bio}}$	continuity	2) $\text{NH}_4(z_{\text{bio}}^-) = \text{NH}_4(z_{\text{bio}}^+)$
$z = z_{\text{ox}}$	continuity	3) $-\frac{D_{\text{NH}_4,0} + D_{\text{bio}}}{1+K_{\text{NH}_4}} \cdot \frac{\partial \text{NH}_4}{\partial z} _{z_{\text{bio}}^-} = -\frac{D_{\text{NH}_4,0}}{1+K_{\text{NH}_4}} \cdot \frac{\partial \text{NH}_4}{\partial z} _{z_{\text{bio}}^+}$
	where:	4) $\text{NH}_4(z_{\text{ox}}^-) = \text{NH}_4(z_{\text{ox}}^+)$
$z = z_{\text{NO}_3}$	continuity flux	5) $-\frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \cdot \frac{\partial \text{NH}_4}{\partial z} _{z_{\text{ox}}^-} - \gamma_{\text{NH}_4} \cdot F_{\text{NH}_4}(z_{\text{ox}}) = -\frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \cdot \frac{\partial \text{NH}_4}{\partial z} _{z_{\text{ox}}^+}$ $F_{\text{NH}_4}(z_{\text{ox}}) = \frac{1}{1+K_{\text{NH}_4}} \cdot \frac{1-\phi}{\phi} \cdot \int_{z_{\text{NO}_3}}^\infty \sum_i \text{NC}_i \cdot k_i \cdot \text{POC}_i dz$
$z = z_\infty$	zero NH_4 flux	6) $\text{NH}_4(z_{\text{NO}_3}^-) = \text{NH}_4(z_{\text{NO}_3}^+)$
		7) $-\frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \cdot \frac{\partial \text{NH}_4}{\partial z} _{z_{\text{NO}_3}^-} = -\frac{D_{\text{NH}_4}}{1+K_{\text{NH}_4}} \cdot \frac{\partial \text{NH}_4}{\partial z} _{z_{\text{NO}_3}^+}$
		8) $\frac{\partial \text{NH}_4}{\partial z} _{z_\infty} = 0$

500 1. Oxic and nitrogenous zone ($z \leq z_{\text{NO}_3}$)

$$\frac{\partial \text{SO}_4^{II}}{\partial t} = 0 = D_{\text{SO}_4} \frac{\partial^2 \text{SO}_4^{II}}{\partial z^2} - w \frac{\partial \text{SO}_4^{II}}{\partial z} \quad (20)$$

$$\frac{\partial \text{H}_2\text{S}^{II}}{\partial t} = 0 = D_{\text{H}_2\text{S}} \frac{\partial^2 \text{H}_2\text{S}^{II}}{\partial z^2} - w \frac{\partial \text{H}_2\text{S}^{II}}{\partial z} \quad (21)$$

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

$$\frac{\partial \text{SO}_4^{III}}{\partial t} = 0 = D_{\text{SO}_4} \frac{\partial^2 \text{SO}_4^{III}}{\partial z^2} - w \frac{\partial \text{SO}_4^{III}}{\partial z} - \frac{1-\phi}{\phi} \cdot \sum_i \text{SO}_4 \text{C} \cdot k_i \cdot \text{POC}_i(z) \quad (22)$$

$$\frac{\partial \text{H}_2\text{S}^{III}}{\partial t} = 0 = D_{\text{H}_2\text{S}} \frac{\partial^2 \text{H}_2\text{S}^{III}}{\partial z^2} - w \frac{\partial \text{H}_2\text{S}^{III}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{SO}_4 \text{C} \cdot k_i \cdot \text{POC}_i(z) \quad (23)$$

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

$$\frac{\partial \text{H}_2\text{S}^{IV}}{\partial t} = 0 = D_{\text{H}_2\text{S}} \frac{\partial^2 \text{H}_2\text{S}^{IV}}{\partial z^2} - w \frac{\partial \text{H}_2\text{S}^{IV}}{\partial z} \quad (24)$$

where D_{SO_4} and D_{H_2S} denote the diffusion coefficients for SO_4 and H_2S which depend on the bioturbation status of the respective geochemical zone (compare Section 2.3.1). Integration of Eq. (20) - (24) yields the analytical solution and Table 5 summarises the boundary conditions applied. OMEN-SED assumes known concentrations at the sediment-water interface and continuity across the bioturbation depth and the nitrate penetration depth. The reoxidation of reduced H_2S to SO_4 is accounted for implicitly via the oxic-anoxic boundary condition for both species, while reduction of SO_4 and the associated production of H_2S via AOM is accounted for through the respective boundary conditions at z_{SO_4} . In case $z_{SO_4} < z_\infty$, OMEN-SED assumes zero sulfate concentration at z_{SO_4} and its diffusive flux must equal the amount of methane produced below (with a methane to carbon ratio of MC); or, in case $z_{SO_4} = z_\infty$, a zero diffusive flux condition for sulfate is considered. OMEN-SED iteratively solves for z_{SO_4} by first testing if there is sulfate left at z_∞ (i.e. $SO_4(z_\infty) > 0$) and, otherwise, by finding the root for the flux boundary condition 8.2 (Table 5). At the lower boundary z_∞ zero diffusive flux of H_2S is considered.

2.2.5 Phosphate

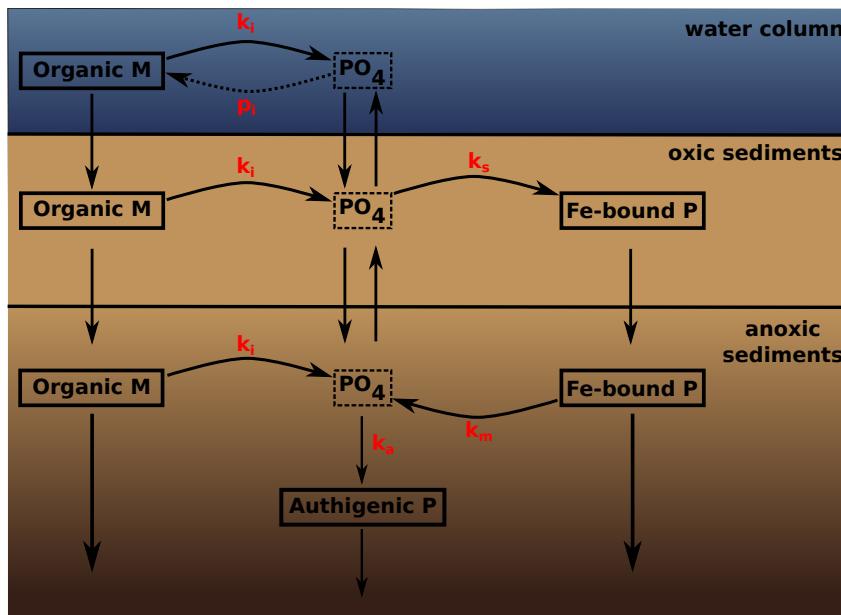


Figure 2. A schematic of the sedimentary P cycle in OMEN-SED. Red numbers represent kinetic rate constants for phosphorus dynamics (compare Table 10; p_i represents uptake rate of PO_4 via primary production in shallow environments). Adapted from Slomp et al. (1996).

The biogeochemical description of phosphorus (P) dynamics builds on earlier models developed by Slomp et al. (1996) and accounts for phosphorus recycling through organic matter degradation, adsorption onto sediments and iron(III) hydroxides (Fe-bound P), as well as carbonate fluorapatite

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) $-(D_{\text{SO}_4,0} + D_{\text{bio}}) \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{bio}}^-} = -D_{\text{SO}_4,0} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $\text{SO}_4(z_{\text{ox}}^-) = \text{SO}_4(z_{\text{ox}}^+)$
	flux	5) $-D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{ox}}^-} + \gamma_{\text{H}_2\text{S}} \cdot F_{\text{H}_2\text{S}}(z_{\text{ox}}) = -D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{ox}}^+}$
	where:	$F_{\text{H}_2\text{S}}(z_{\text{ox}}) = \frac{1-\phi}{\phi} \cdot \left(\int_{z_{\text{NO}_3}}^{\text{SO}_4} \sum_i \text{SO}_4 \cdot k_i \cdot \text{POC}_i dz + \gamma_{\text{CH}_4} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot \text{POC}_i dz \right)$
$z = z_{\text{NO}_3}$	continuity	6) $\text{SO}_4(z_{\text{NO}_3}^-) = \text{SO}_4(z_{\text{NO}_3}^+)$
	flux	7) $-D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{NO}_3}^-} = -D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{NO}_3}^+}$
$z = z_{\text{SO}_4}$	SO ₄ consumption ($z_{\text{SO}_4} = z_\infty$)	8) IF ($\text{SO}_4(z_\infty) > 0$) 8.1) $\frac{\partial \text{SO}_4}{\partial z} _{z_{\text{SO}_4}} = 0$ ELSE
	($z_{\text{SO}_4} < z_\infty$) with	8.2) $\text{SO}_4(z_{\text{SO}_4}) = 0 \quad \text{and} \quad -D_{\text{SO}_4} \cdot \frac{\partial \text{SO}_4}{\partial z} _{z_{\text{SO}_4}} = \gamma_{\text{CH}_4} \cdot F_{\text{CH}_4}(z_{\text{SO}_4})$ $F_{\text{CH}_4}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot \text{POC}_i dz$
$z = 0$	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) $-(D_{\text{H}_2\text{S},0} + D_{\text{bio}}) \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{bio}}^-} = -D_{\text{H}_2\text{S},0} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $\text{H}_2\text{S}(z_{\text{ox}}^-) = \text{H}_2\text{S}(z_{\text{ox}}^+)$
	flux	5) $-D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{ox}}^-} - \gamma_{\text{H}_2\text{S}} F_{\text{H}_2\text{S}}(z_{\text{ox}}) = -D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{ox}}^+}$
	where:	$F_{\text{H}_2\text{S}}(z_{\text{ox}}) = \frac{1-\phi}{\phi} \cdot \left(\int_{z_{\text{NO}_3}}^{\text{SO}_4} \sum_i \text{SO}_4 \cdot k_i \cdot \text{POC}_i dz + \gamma_{\text{CH}_4} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot \text{POC}_i dz \right)$
$z = z_{\text{NO}_3}$	continuity	6) $\text{H}_2\text{S}(z_{\text{NO}_3}^-) = \text{H}_2\text{S}(z_{\text{NO}_3}^+)$
	flux	7) $-D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{NO}_3}^-} = -D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{NO}_3}^+}$
$z = z_{\text{SO}_4}$	continuity flux (with AOM) where:	8) $\text{H}_2\text{S}(z_{\text{SO}_4}^-) = \text{H}_2\text{S}(z_{\text{SO}_4}^+)$ 9) $-D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{SO}_4}^-} + \gamma_{\text{CH}_4} \cdot F_{\text{CH}_4}(z_{\text{SO}_4}) = -D_{\text{H}_2\text{S}} \cdot \frac{\partial \text{H}_2\text{S}}{\partial z} _{z_{\text{SO}_4}^+}$ $F_{\text{CH}_4}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot \text{POC}_i dz$
$z = z_\infty$	zero H ₂ S flux	10) $\frac{\partial \text{H}_2\text{S}}{\partial z} _{z_\infty} = 0$

(CFA or authigenic P) formation (see Figure 2 for a schematic overview of the sedimentary P cycle). In the oxic zone of the sediment, PO_4 liberated through organic matter degradation can adsorb to iron(III) hydroxides forming Fe-bound P (or FeP, Slomp et al., 1998). Below the oxic zone, PO_4 is not only produced via organic matter degradation but can also be released from the Fe-bound P pool due to the reduction of iron(III) hydroxides under anoxic conditions. Furthermore, in these zones phosphate concentrations build up and pore waters can thus become supersaturated with respect to carbonate fluorapatite, thus triggering the authigenic formation of CFA (Van Cappellen and Berner, 1988). Phosphorus bound in these authigenic minerals represents a permanent sink for reactive phosphorus (Slomp et al., 1996). As for ammonium, the adsorption of P to the sediment matrix is treated as an equilibrium processes, parameterised with dimensionless adsorption coefficients for the oxic and anoxic zone, respectively ($K_{\text{PO}_4}^{\text{ox}}$, $K_{\text{PO}_4}^{\text{anox}}$ Slomp et al., 1998). The sorption and desorption of P to iron(III) hydroxides as well as the authigenic fluorapatite formation are described as first-order reactions with rate constants k_s , k_m and k_a , respectively (Table 10). The rate of the respective process is calculated as the product of the rate constant and the difference between the current concentration (of PO_4 and FeP) and an equilibrium or asymptotic concentration Slomp et al. (1996). The asymptotic Fe-bound P concentration is FeP^∞ and the equilibrium concentration for P sorption and authigenic fluorapatite formation are PO_4^s and PO_4^a , respectively (Table 10). The last term in Eq. (25) and (26) represents sorption of PO_4 to FeP in the oxic zone, the last term in Eq. (27) and (28) is the release of PO_4 from the FeP pool and the 4th term in Eq. (28) represents the permanent loss of PO_4 to authigenic fluorapatite formation. The conservation equations for phosphate and Fe-bound P are thus given by:

550 1. Oxic zone ($z \leq z_{\text{ox}}$)

$$\frac{\partial \text{PO}_4^I}{\partial t} = \frac{D_{\text{PO}_4}}{1 + K_{\text{PO}_4}^{\text{ox}}} \frac{\partial^2 \text{PO}_4^I}{\partial z^2} - w \frac{\partial \text{PO}_4^I}{\partial z} + \frac{1-\phi}{\phi} \frac{1}{1 + K_{\text{PO}_4}^{\text{ox}}} \sum_i (\text{PC}_i \cdot k_i \cdot \text{POC}_i(z)) - \frac{k_s}{1 + K_{\text{PO}_4}^{\text{ox}}} (\text{PO}_4^I - \text{PO}_4^s) \quad (25)$$

$$\frac{\partial \text{FeP}^I}{\partial t} = D_{\text{FeP}} \frac{\partial^2 \text{FeP}^I}{\partial z^2} - w \frac{\partial \text{FeP}^I}{\partial z} + \frac{\phi}{1-\phi} k_s (\text{PO}_4^I - \text{PO}_4^s) \quad (26)$$

555 2. Anoxic zones ($z_{\text{ox}} < z \leq z_\infty$)

$$\frac{\partial \text{FeP}^{II}}{\partial t} = D_{\text{FeP}} \frac{\partial^2 \text{FeP}^{II}}{\partial z^2} - w \frac{\partial \text{FeP}^{II}}{\partial z} - k_m (\text{FeP}^{II} - \text{FeP}^\infty) \quad (27)$$

$$\frac{\partial \text{PO}_4^{II}}{\partial t} = \frac{D_{\text{PO}_4}}{1 + K_{\text{PO}_4}^{\text{anox}}} \frac{\partial^2 \text{PO}_4^{II}}{\partial z^2} - w \frac{\partial \text{PO}_4^{II}}{\partial z} + \frac{1-\phi}{\phi} \frac{1}{1 + K_{\text{PO}_4}^{\text{anox}}} \sum_i (\text{PC}_i \cdot k_i \cdot \text{POC}_i(z)) - \frac{k_a}{1 + K_{\text{PO}_4}^{\text{anox}}} (\text{PO}_4^{II} - \text{PO}_4^a) + \frac{(1-\phi)}{\phi} \frac{k_m}{1 + K_{\text{PO}_4}^{\text{anox}}} (\text{FeP}^{II} - \text{FeP}^\infty) \quad (28)$$

560 where D_{PO_4} denotes the diffusion coefficient for PO_4 which depends on the bioturbation status of the respective geochemical zone and $D_{\text{FeP}} = D_{\text{bio}}$ for $z \leq z_{\text{bio}}$ and $D_{\text{FeP}} = 0$ for $z > z_{\text{bio}}$ (compare

Table 6. Boundary conditions for phosphate and Fe-bound P (FeP). 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) $(D_{\text{PO}_4,0} + D_{\text{bio}}) \cdot \frac{\partial \text{PO}_4}{\partial z} _{z_{\text{bio}}^-} = D_{\text{PO}_4,0} \cdot \frac{\partial \text{PO}_4}{\partial z} _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $\text{PO}_4(z_{\text{ox}}^-) = \text{PO}_4(z_{\text{ox}}^+)$
	flux	5) $-\frac{D_{\text{PO}_4}}{1 + K_{\text{PO}_4}^{2z}} \cdot \frac{\partial \text{PO}_4}{\partial z} _{z_{\text{ox}}^-} = -\frac{D_{\text{PO}_4}}{1 + K_{\text{PO}_4}^{\text{anox}}} \cdot \frac{\partial \text{PO}_4}{\partial z} _{z_{\text{ox}}^+}$
$z = z_\infty$	flux	10) $\frac{\partial \text{PO}_4}{\partial z} _{z_\infty} = 0$
$z = 0$	known concentration	1) $\text{FeP}(0) = \text{FeP}_0$
$z = z_{\text{bio}}$	continuity	2) $\text{FeP}(z_{\text{bio}}^-) = \text{FeP}(z_{\text{bio}}^+)$
	flux	3) $\frac{\partial \text{FeP}}{\partial z} _{z_{\text{bio}}^-} = \frac{\partial \text{FeP}}{\partial z} _{z_{\text{bio}}^+}$
$z = z_{\text{ox}}$	continuity	4) $\text{FeP}(z_{\text{ox}}^-) = \text{FeP}(z_{\text{ox}}^+)$
	flux	5) $\frac{\partial \text{FeP}}{\partial z} _{z_{\text{ox}}^-} = \frac{\partial \text{FeP}}{\partial z} _{z_{\text{ox}}^+}$
$z = z_\infty$	asymptotic concentration	10) $\text{FeP}(z_\infty) = \text{FeP}_\infty$

Section 2.3.1). Integration of Eq. (25) - (28) yields the analytical solution and Table 6 summarises the boundary conditions applied in OMEN-SED. The model assumes known bottom water concentrations and equal concentrations and diffusive fluxes at z_{bio} and z_{ox} for both species. Additionally

565 OMEN-SED considers no change in phosphate flux and an asymptotic Fe-bound P concentration at z_∞ .

2.2.6 Dissolved Inorganic Carbon (DIC)

OMEN-SED accounts for the production of dissolved inorganic carbon (DIC) through organic matter degradation, as well as methane oxidation. Organic matter degradation produces dissolved inor-

570 ganic carbon with a stoichiometric DIC : C ratio of 1:2 in the methanic zone and 1:1 in the rest of the sediment column (DICC^{II} and DICC^{I} respectively). DIC production through methane oxidation is implicitly taken into account through the boundary condition at z_{SO_4} . A mechanistic description of DIC production from CaCO_3 dissolution would lead to significant mathematical problems and is therefore not included in the current version of OMEN-SED. The conservation equations for DIC

575 are thus given by:

1. Oxic, nitrogenous and sulfidic zone ($z \leq z_{\text{SO}_4}$)

$$\frac{\partial \text{DIC}^{\text{I}}}{\partial t} = 0 = D_{\text{DIC}} \frac{\partial^2 \text{DIC}^{\text{I}}}{\partial z^2} - w \frac{\partial \text{DIC}^{\text{I}}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{DICC}^{\text{I}} \cdot k_i \cdot \text{POC}_i(z) \quad (29)$$

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

$$\frac{\partial \text{DIC}^{\text{II}}}{\partial t} = 0 = D_{\text{DIC}} \frac{\partial^2 \text{DIC}^{\text{II}}}{\partial z^2} - w \frac{\partial \text{DIC}^{\text{II}}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{DICC}^{\text{II}} \cdot k_i \cdot \text{POC}_i(z) \quad (30)$$

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) $\text{DIC}(0) = \text{DIC}_0$
$z = z_{\text{bio}}$	continuity	2) $\text{DIC}(z_{\text{bio}}^-) = \text{DIC}(z_{\text{bio}}^+)$
	flux	3) $-(D_{\text{DIC},0} + D_{\text{bio}}) \cdot \frac{\partial \text{DIC}}{\partial z} _{z_{\text{bio}}^-} = -D_{\text{DIC},0} \cdot \frac{\partial \text{DIC}}{\partial z} _{z_{\text{bio}}^+}$
$z = z_{\text{SO}_4}$	continuity	4) $\text{DIC}(z_{\text{SO}_4}^-) = \text{DIC}(z_{\text{SO}_4}^+)$
	flux (with AOM)	5) $-D_{\text{DIC}} \cdot \frac{\partial \text{DIC}}{\partial z} _{z_{\text{SO}_4}^-} + \gamma_{\text{CH}_4} \cdot F_{\text{CH}_4}(z_{\text{SO}_4}) = -D_{\text{DIC}} \cdot \frac{\partial \text{DIC}}{\partial z} _{z_{\text{SO}_4}^+}$
	where:	$F_{\text{CH}_4}(z_{\text{SO}_4}) = \frac{1-\phi}{\phi} \cdot \int_{z_{\text{SO}_4}}^{\infty} \sum_i \text{MC} \cdot k_i \cdot \text{POC}_i dz$
$z = z_\infty$	zero DIC flux	6) $\frac{\partial \text{DIC}}{\partial z} _{z_\infty} = 0$

where D_{DIC} denotes the diffusion coefficient for DIC which depends on the bioturbation status of the respective geochemical zone. Integration of Eq. (29) and (30) yields the analytical solution
 585 and Table 7 summarises the boundary conditions applied in OMEN-SED. A Dirichlet condition is applied at the sediment-water interface. In addition, the model assumes a zero diffusive flux through the lower boundary z_∞ and continuity across the bottom of the bioturbated zone, as well as the sulfate penetration depth. An additional flux boundary condition at z_{SO_4} , implicitly accounts for DIC production through anaerobic oxidation of methane (Table 7 Eq. 5).

590 2.2.7 Alkalinity

Organic matter degradation and secondary redox reactions exert a complex influence on alkalinity (e.g. Jourabchi et al., 2005; Wolf-Gladrow et al., 2007; Krumins et al., 2013). To model alkalinity, OMEN-SED divides the sediment column into four geochemical zones, where different equations describe the biogeochemical processes using variable stoichiometric coefficients (compare values in
 595 Table 10). Above z_{ox} , the combined effects of NH_4 and P release due to aerobic OM degradation increases alkalinity according to ALK^{OX} whereas nitrification decreases alkalinity with stoichiometry ALK^{NIT} . In the remaining three zones anaerobic OM degradation generally results in an increase in alkalinity, with the exact magnitude depending on the nature of the terminal electron acceptor used (i.e. ALK^{DEN} , ALK^{SUL} , ALK^{MET}). In addition, the effect of secondary redox reactions, such
 600 as nitrification, sulfide and methane oxidation are implicitly accounted for in the boundary conditions. Note that the alkalinity description in the current version of OMEN-SED does not account for CaCO_3 dissolution/precipitation due to the mathematical complexity of the problem. In OMEN-SED, the conservation equations for alkalinity are thus given by:

605 1. Oxic zone ($z \leq z_{\text{ox}}$)

$$\frac{\partial \text{ALK}^I}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^I}{\partial z^2} - w \frac{\partial \text{ALK}^I}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \left(\text{ALK}^{\text{NIT}} \cdot \frac{\gamma_{\text{NH}_4}}{1+K_{\text{NH}_4}} \text{NC}_i + \text{ALK}^{\text{OX}} \right) \cdot k_i \cdot \text{POC}_i(z) \quad (31)$$

2. Denitrification or nitrogenous zone ($z_{\text{ox}} < z \leq z_{\text{NO}_3}$)

$$610 \frac{\partial \text{ALK}^{II}}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^{II}}{\partial z^2} - w \frac{\partial \text{ALK}^{II}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{ALK}^{\text{DEN}} \cdot k_i \cdot \text{POC}_i(z) \quad (32)$$

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

$$\frac{\partial \text{ALK}^{III}}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^{III}}{\partial z^2} - w \frac{\partial \text{ALK}^{III}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{ALK}^{\text{SUL}} \cdot k_i \cdot \text{POC}_i(z) \quad (33)$$

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

$$\frac{\partial \text{ALK}^{IV}}{\partial t} = 0 = D_{\text{ALK}} \frac{\partial^2 \text{ALK}^{IV}}{\partial z^2} - w \frac{\partial \text{ALK}^{IV}}{\partial z} + \frac{1-\phi}{\phi} \cdot \sum_i \text{ALK}^{\text{MET}} \cdot k_i \cdot \text{POC}_i(z) \quad (34)$$

where D_{ALK} denotes the diffusion coefficient for alkalinity which depends on the bioturbation status of the respective geochemical zone. Integration of Eq. (31) - (34) yields the analytical solution
620 and Table 8 summarises the boundary conditions applied in OMEN-SED. A Dirichlet boundary condition is applied at the sediment-water interface. The decrease of alkalinity due to oxidation of reduced species produced in the anoxic zones (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 sulfate reduction increases alkalinity with stoichiometry ALK^{AOM} which
625 is accounted for through the flux boundary condition at z_{SO_4} (Table 8 Eq. 9). At the lower boundary z_{∞} a zero diffusive flux condition is applied.

2.3 Determination of Integration Constants

The integration constants of all general analytical solutions derived above change in response to changing boundary conditions. Thus, OMEN-SED has to re-determine integration constants for each
630 dynamic zone (i.e. $z_{\text{ox}}, z_{\text{bio}}, z_{\text{NO}_3}$ and z_{SO_4}) at every time step for all biogeochemical species. The bioturbation boundary poses a particular challenge as it can theoretically occur in any of the dynamic geochemical zones (Fig. 3). Therefore, in order to generalise and simplify this recurring boundary matching problem, an independent, generic algorithm (Generic Boundary Condition Matching) is implemented (rather than using multiple fully-worked-out algebraic solutions for each possible
635 case and every biogeochemical species). As a consequence, the algorithm only has to solve a two-simultaneous-equation problem.

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

2.3.1 Generic Boundary Condition Matching (GBCM)

As discussed in Section 2.1, the solution of the general steady-state transport-reaction equation (Eq. (2)) for a generic species C is of the general form:

$$640 \quad C(z) = A \exp(az) + B \exp(bz) + \sum_j \frac{\alpha_j}{D\beta_j^2 - w\beta_j - k} \cdot \exp(-\beta_j z) + \frac{Q}{k} \quad (35)$$

and can therefore be expressed as:

$$645 \quad C(z) = A \cdot E(z) + B \cdot F(z) + G(z) \quad (36)$$

where $E(z)$, $F(z)$ are the homogeneous solutions of the ODE, $G(z)$ the particular integral (collectively called the basis functions), and A , B are the integration constants that must be determined using the boundary conditions (shown in Fig. 3 for the whole sediment column).

Each internal boundary matching problem (i.e. excluding $z = 0$ and $z = z_\infty$) involves matching continuity and flux for the two solutions of the respective reaction-transport equation above, $C_U(z)$ (= 'upper'), and below, $C_L(z)$ (= 'lower'), the dynamic boundary at $z = z_b$:

$$650 \quad C_U(z) = A_U \cdot E_U(z) + B_U \cdot F_U(z) + G_U(z) \quad (37)$$

$$C_L(z) = A_L \cdot E_L(z) + B_L \cdot F_L(z) + G_L(z). \quad (38)$$

OMEN-SED generally applies concentration continuity and flux boundary conditions at its internal, dynamic boundaries:

Continuity (where for generality we allow a discontinuity V_b)

$$C_U(z_b) = C_L(z_b) + V_b \quad (39)$$

Flux

$$660 \quad D_U C'_U(z_b) + w C_U(z_b) = D_L C'_L(z_b) + w C_L(z_b) + F_b \quad (40)$$

where w is advection, D are the diffusion coefficients and F_b is any flux discontinuity (e.g. resulting from secondary redox reactions).

Considering that the advective flux above and below the boundary is equal (i.e. $w C_U(z_b) = w C_L(z_b)$)
665 and substituting the general ODE solutions (37), (38), the boundary conditions can be represented as two equations connecting the four integration constants:

$$\begin{pmatrix} E_U & F_U \\ D_U E'_U & D_U F'_U \end{pmatrix} \begin{pmatrix} A_U \\ B_U \end{pmatrix} = \begin{pmatrix} E_L & F_L \\ D_L E'_L & D_L F'_L \end{pmatrix} \begin{pmatrix} A_L \\ B_L \end{pmatrix} + \begin{pmatrix} G_L - G_U + V_b \\ D_L G'_L - D_U G'_U + F_b - w V_b \end{pmatrix} \quad (41)$$

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

Equation (41) can now be solved to give A_U and B_U as a function of the integration constants from
670 the layer below (A_L and B_L), thereby constructing a piecewise solution for both layers, with just two integration constants (this is implemented in the function **benthic_utils.matchsoln** of OMEN-SED):

$$\begin{pmatrix} A_U \\ B_U \end{pmatrix} = \begin{pmatrix} c_1 & c_2 \\ c_3 & c_4 \end{pmatrix} \begin{pmatrix} A_L \\ B_L \end{pmatrix} + \begin{pmatrix} d_1 \\ d_2 \end{pmatrix}. \quad (42)$$

Using Eq. (42), $C_U(z)$ in (37) can now be rewritten as a function of A_L and B_L (implemented in
675 **benthic_utils.xformsoln**):

$$C_U(z) = (c_1 A_L + c_2 B_L + d_1) \cdot E_U(z) + (c_3 A_L + c_4 B_L + d_2) \cdot F_U(z) + G_U(z) \quad (43)$$

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

$$C_U(z) = A_L \cdot E_U^*(z) + B_L \cdot F_U^*(z) + G_U^*(z) \quad (44)$$

where

$$\begin{aligned} 680 \quad E_U^*(z) &= c_1 E_U(z) + c_3 F_U(z) \\ F_U^*(z) &= c_2 E_U(z) + c_4 F_U(z) \\ G_U^*(z) &= G_U(z) + d_1 E_U(z) + d_2 F_U(z) \end{aligned} \quad (45)$$

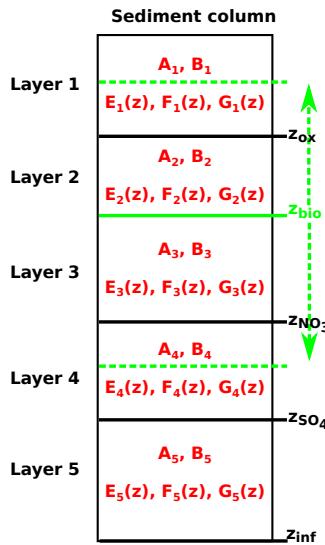


Figure 3. Schematic of the generic boundary condition matching (GBCM) problem. Showing the resulting integration constants (A_i, B_i) and ODE solutions (E_i, F_i, G_i) for the different sediment layers and the variable bioturbation boundary.

Equations (42), (44) and (45) can now be consecutively applied for each of the dynamic biogeochemical zone boundaries (Fig. 3), starting at the bottom of the sediment column. 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 the boundary conditions at the sediment-water interface and the bottom of the sediments.

2.3.2 Abstracting out the bioturbation boundary

The bioturbation boundary affects the diffusion coefficient of the modelled solutes, as well as the conservation equation of organic matter (and thereby the exact form of each reaction-transport equation). This boundary is particularly inconvenient as it can, in principle, occur in the middle of any of the dynamically shifting biogeochemical zones and therefore generate multiple cases (Fig. 3). The GBCM algorithm described above is thus not only used to construct a piecewise solution of the whole sediment column, but also to abstract out the bioturbation boundary. For each biogeochemical zone the "bioturbation-status" is initially tested (i.e. fully bioturbated, fully non-bioturbated, or crossing the bioturbation boundary). Therefore, the upper and lower boundaries for the different zones (e.g. for the nitrogenous zone: $z_U = z_{\text{ox}}$, $z_L = z_{\text{NO}_3}$), as well as the respective reactive terms and diffusion coefficients (bioturbated and non-bioturbated) are passed over to the routine **zTOC.prepfg_l12** where the bioturbation-status is determined. In case the bioturbation depth is located within this zone (i.e. $z_U < z_{\text{bio}} < z_L$) a piecewise solution for this layer is constructed. Therefore, the reactive terms and diffusion coefficients are handed over to the routines **zTOC.calcfg_l1** and **zTOC.calcfg_l2**

which calculate the basis functions (E_U, F_U, G_U and E_L, F_L, G_L) and their derivatives for the bioturbated and the non-bioturbated part of this specific geochemical zone. The concentration and flux
 705 for both solutions at z_{bio} are matched and the coefficients $c_1, c_2, c_3, c_4, d_1, d_2$ (as in Eq. (42)) are calculated by the routine **benthic_utils.matchsoln**. These coefficients and the "bioturbation-status" of the layer are passed back to the main GBCM algorithm where they can be used by the routine **benthic_utils.xformsoln** to calculate the "transformed" basis functions ($E_U^*(z), F_U^*(z), G_U^*(z)$) such that both layers are expressed in the same basis (compare Eq. (43 - 45)).

710 For instance, in the case of sulfate, **zTOC.prepfg_I12** is called three times before the actual profile is calculated (once per zone: oxic, nitrogenous, sulfidic) and hands back the information about the "bioturbation-status" of the three layers and the coefficients $c_1, c_2, c_3, c_4, d_1, d_2$ for the biogeochemical zone including the bioturbation depth. When calculating the complete piecewise solution for the sediment column, this information is passed to the function **zTOC.calcfg_I12** which
 715 sorts out the correct solution type to use. The main GBCM algorithm therefore never needs to know whether it is dealing with a piecewise solution (i.e. matched across the bioturbation boundary) or a "simple" solution (i.e. the layer is fully bioturbated or fully non-bioturbated).

2.4 Model Parameters

The following section provides a summary of global relationships used to constrain reaction and
 720 transport parameters in OMEN-SED. Table 9 synthesises sediment and transport parameters, while Tab. 10 provides an overview of all biogeochemical parameters used in OMEN-SED.

2.4.1 Transport Parameters

The burial of sediments and pore water is directly related to the accumulation of new material on the seafloor (i.e. sedimentation, Burdige, 2006). This results in a downward advective flux of older
 725 sediment material and pore water 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 OMEN-SED uses the empirical global relationship between sediment accumulation rate (w in cm yr^{-1}) and seafloor depth (z in m) of Middelburg et al. (1997):

$$w = 3.3 \cdot 10^{-0.87478367 - 0.00043512 \cdot z}. \quad (46)$$

730 As an option we include the parameterisation of Burwicz et al. (2011)

$$w = \frac{w_1}{1 + (\frac{z}{z_1})^{c1}} + \frac{w_2}{1 + (\frac{z}{z_2})^{c2}} \quad (47)$$

with parameter values as found in the original study (i.e. $w_1 = 0.117 \text{ cm yr}^{-1}$, $w_2 = 0.006 \text{ cm yr}^{-1}$, $z_1 = 200 \text{ m}$, $z_2 = 4000 \text{ m}$, $c1 = 3$, $c2 = 10$). As mentioned before (Section 2.1), 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
 735 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):

$$D_{\text{bio}} = 5.2 \cdot 10^{0.76241122 - 0.00039724 \cdot z} \quad (48)$$

Observations indicate that bioturbation is largely restricted to the upper 10 cm of the sediments and is only marginally related to seafloor depth (e.g. Boudreau, 1998; Teal et al., 2010). Therefore,

740 OMEN-SED imposes a globally invariant bioturbation depth z_{bio} of 10 cm. In case the bottom water oxygen concentration is below 5 nmol cm⁻³ **REF for it???** **???** **email nils?** infaunal activity is assumed to cease and $z_{\text{bio}} = 0.01$ cm. We choose a low value unequal to zero in order to simplify the implementation of the model. This approach ensures that the sediment column always consists of a bioturbated (even though very small for the low oxygen condition) and a non-bioturbated zone, 745 thus the same GBCM algorithm can be used to solve the conservation equations. Furthermore, when OMEN-SED is coupled to an Earth system model the same method can be used to convert the POC depositional flux into a SWI concentration (i.e. the flux needs to be converted assuming bioturbation, see Section 4.1).

Bioirrigation (i.e the pumping activity by burrow-dwelling animals) exchanges burrow water 750 with overlying water and may enhance the SWI-flux of solutes (Aller, 1984, 1988). Several approaches exist to incorporate this into a 1-D diagenetic model, for instance as a non-local transport/exchange process (Boudreau, 1984; Emerson et al., 1984) or as an enhancement factor of the molecular diffusion coefficient (Devol and Christensen, 1993; Soetaert et al., 1996). In OMEN-SED the latter approach is applied and the apparent “bio-diffusion” coefficient is calculated as 755 $D_{i,0} = D_{\text{mol},i} \cdot f_{ir}$. Soetaert et al. (1996) derived an empirical relationship between f_{ir} and seafloor depth ($f_{ir} = \text{Min}\{1; 15.9 \cdot z^{-0.43}\}$) based on observations from Archer and Devol (1992) and Devol and Christensen (1993). As this relationship just varies for depth above ~623 m (with a maximum value of 3 at ~50 m) a constant value of $f_{ir} = 1$ is used in the default OMEN-SED configuration. The specific molecular diffusion coefficients $D_{\text{mol},i}$ are corrected for sediment porosity ϕ , tortuosity 760 F and are linearly interpolated for an ambient temperature T using zero-degree coefficients D_i^0 and temperature-dependent diffusion coefficients D_i^T (Soetaert et al., 1996):

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

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 $m = 3$ is used representing muddy 765 sediments with high porosity). Values for D_i^T and D_i^0 are summarised in Table 9 and are adapted from Li and Gregory (1974), Schulz (2006) and Gypens et al. (2008).

2.4.2 Stoichiometries and reaction parameters

The first-order organic matter degradation constants of compound class i , k_i (yr⁻¹), 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 770

Table 9. Sediment characteristics and transport parameters.

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
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
$D_{\text{O}_2}^T$	$\text{cm}^2 \text{yr}^{-1} \text{°C}^{-1}$	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
$D_{\text{NO}_3}^T$	$\text{cm}^2 \text{yr}^{-1} \text{°C}^{-1}$	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
$D_{\text{NH}_4}^T$	$\text{cm}^2 \text{yr}^{-1} \text{°C}^{-1}$	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
$D_{\text{SO}_4}^T$	$\text{cm}^2 \text{yr}^{-1} \text{°C}^{-1}$	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
$D_{\text{H}_2\text{S}}^T$	$\text{cm}^2 \text{yr}^{-1} \text{°C}^{-1}$	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
$D_{\text{PO}_4}^T$	$\text{cm}^2 \text{yr}^{-1} \text{°C}^{-1}$	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	$\text{cm}^2 \text{yr}^{-1} \text{°C}^{-1}$	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	$\text{cm}^2 \text{yr}^{-1} \text{°C}^{-1}$	7.93	Diffusion coefficient for linear temp. dependence of ALK
Note: DIC and ALK coefficients are the values of HCO_3^- from Schulz (2006).			

modelled profiles in Section 3.2) or related to a master variable provided by a coupled Earth system model (e.g. sedimentation rate, see Section 4.2). The partitioning of the bulk OM pool into reactivity classes (f_i) needs to be specified manually in the stand-alone version or can be provided by the ESM. Organic matter degradation releases N, P and DIC to the pore water using Redfield molar ratios (Redfield, 1963) and consumes TEA with specific stoichiometries (O_2C , NO_3C , SO_4C) as summarised in Table 10. Table 15 in the appendix provides a list of reactions and their stoichiometries as implemented in OMEN-SED. The effect of OM degradation and secondary redox reactions on total alkalinity is also accounted for via reaction specific stoichiometries representing the release of NH_4 , H_2S and P and is based on Jourabchi et al. (2005). In reality, the reoxidation of reduced substances produced during OM degradation may be incomplete. Yet, in OMEN-SED we have to assume their complete, instantaneous reoxidation at z_{ox} to allow for an analytical solution. In order to relax this assumption, for cases where it can be justified, we include a “switch” to allow part of the NH_4 , H_2S and CH_4 flux to escape reoxidation. The secondary redox parameters (i.e. γ_{NH_4} , γ_{H_2S} , γ_{CH_4}) therefore account for the fraction of reduced substances that are reoxidised and would be ideally parameterised for instance in relation to bottom water oxygen concentration or oxygen penetration depth (z_{ox}). Gypens et al. (2008) for example expressed γ_{NH_4} as a function of oxygen penetration depth ($\gamma_{NH_4} = 0.243 \cdot \ln(z_{ox}) + 1.8479$) based on a fitting exercises to a numerical model and showed that the fraction varies between 0.2 for $z_{ox} = 0.1\text{cm}$ and 1.0 for $z_{ox} > 3\text{cm}$. Due to mathematical constraints in OMEN-SED for finding an analytical solution to the model equations these fractions take constant values generally representing oxygenated deep sea conditions. The instantaneous equilibrium adsorption coefficients of NH_4 and PO_4 (K_{NH_4} , $K_{PO_4}^{ox}$, $K_{PO_4}^{anox}$) are based on Wang and Van Cappellen (1996) and Slomp et al. (1998), respectively. The first order rate constants for sorption of PO_4 to Fe oxides (k_s), release of PO_4 from Fe-bound P due to Fe-oxide reduction (k_m) and authigenic CFA precipitation (k_a), as well as 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 (FeP^∞) are taken from Slomp et al. (1996). See Table 10 for a complete summary of the parameters and their values.

3 Stand-alone sensitivity analysis and case studies

3.1 Sensitivity Analysis

800 3.1.1 Methodology

Model parameters implicitly account for processes that are not explicitly resolved. They are notoriously difficult to constrain and thus a primary source of uncertainty for numerical and analytical models - in particular on the global scale and/or in data-poor areas. A comprehensive sensitivity analysis can help quantify this uncertainty and identify the most sensitive parameters. More specif-

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

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 _{SO₄}
DICC ^{II}	mol/mol	0.5	DIC to carbon ratio below z _{SO₄}
O ₂ C	mol/mol	$\frac{x+2y}{x} = \frac{138}{106}$	Oxygen to carbon ratio
NO ₃ C	mol/mol	$\frac{4x+3y}{5x} = \frac{94.4}{106}$	Nitrate to carbon ratio
SO ₄ C	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 ^{H₂S}	mol/mol	-2	ALK from H ₂ S oxidation
ALK ^{AOM}	mol/mol	2	ALK from AOM
Secondary reaction parameters			
γ _{NH₄}	-	0.9	Fraction of NH ₄ that is nitrified
γ _{H₂S}	-	0.95	Fraction of H ₂ S that is oxidised
γ _{CH₄}	-	0.99	Fraction of CH ₄ that is oxidised
Adsorption coefficients (Wang and Van Cappellen, 1996; Slomp et al., 1998)			
K _{NH₄}	-	1.4	NH ₄ adsorption coefficient
K _{PO₄} ^{OX} , K _{PO₄} ^{ANOX}	-	200.0, 2.0	PO ₄ adsorption coefficient (oxic, anoxic)
P related parameters (Slomp et al., 1996)			
k _s	yr ⁻¹	94.9	Rate constant for PO ₄ sorption
k _m	yr ⁻¹	0.193	Rate constant for Fe-bound P release
k _a	yr ⁻¹	0.365	Rate constant for authigenic CFA precipitation
PO ₄ ^s	mol cm ⁻³	$1 \cdot 10^{-9}$	Equilibrium conc. for P sorption
FeP [∞]	mol cm ⁻³	$1.99 \cdot 10^{-10}$	Asymptotic concentration for Fe-bound P
PO ₄ ^a	mol cm ⁻³	$3.7 \cdot 10^{-9}$	Equilibrium conc. for authigenic P precipitation

805 ically, sensitivity analysis is used 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 the relative influence of parameter x_i on output y_j with a scalar $S_{i,j}$ (for $i \in \{1, \dots, M\}$ and $j \in \{1, \dots, N\}$), 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). The latter indices take values between zero and one ($S_{i,j} \in [0, 1]$), where zero indicates a non-influential parameter and a higher value a more influential parameter. Here, sensitivity analysis is used mainly to identify which parameters have the largest impact on the different model outputs and therefore require more careful calibration. As the probability density functions of our model outputs (i.e. the resulting SWI-fluxes) are generally

810 highly-skewed towards extreme organic matter degradation rates (not shown) variance-based sensitivity indices may not be a suitable proxy for output uncertainty (Pianosi et al., 2016). Hence, instead the density-based PAWN method by Pianosi and Wagener (2015) is employed which considers the entire conditional and unconditional Cumulative Distribution Function (CDF) of the model output rather than its variance only. The unconditional CDF, $F_y(y)$, of output y is obtained when all un-

815 certain parameters (x_1, \dots, x_M) are varied simultaneously, and the conditional CDFs, $F_{y|x_i}(y)$, are obtained when all inputs but the i -th parameter are varied (i.e. x_i is fixed to a so-called conditioning value). The sensitivity index of parameter i is measured by the distance between the two CDFs using the Kolmogorov-Smirnov statistic (Kolmogorov, 1933; Smirnov, 1939), i.e.:

$$S_i = \max_{x_i} \max_y |F_y(y) - F_{y|x_i}(y)|. \quad (49)$$

820 Since $F_{y|x_i}(y)$ accounts for what happens when the variability due to x_i is removed, the distance between the two CDFs provides a measure of the effects of x_i on the output y . Due to the model complexity it is impossible to compute the sensitivity indices analytically. Therefore, they are approximated from a Latin-Hypercube sampling of parameter inputs and calculated outputs. For a brief description of the methodology, see Fig. 4. For more details, we refer the interested reader to Pianosi and Wagener (2015).

The PAWN method, as implemented within the Sensitivity Analysis for Everyone (SAFE) matlab toolbox (Pianosi et al., 2015), is used to investigate $M = 11$ model parameters for ranges as specified in Table 11. 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 12) are calculated. We use $NU = 200$ samples

830 to estimate the unconditional CDF, $NC = 100$ samples to estimate the conditional CDFs and $n = 10$ conditioning points. Thus as $N_{eval} = 200 + 100 \cdot 10 \cdot 11$, 11200 model evaluations are performed for each sediment condition. The resulting indices are then translated into a color code and summarised in a pattern plot to simplify comparison (Fig. 5).

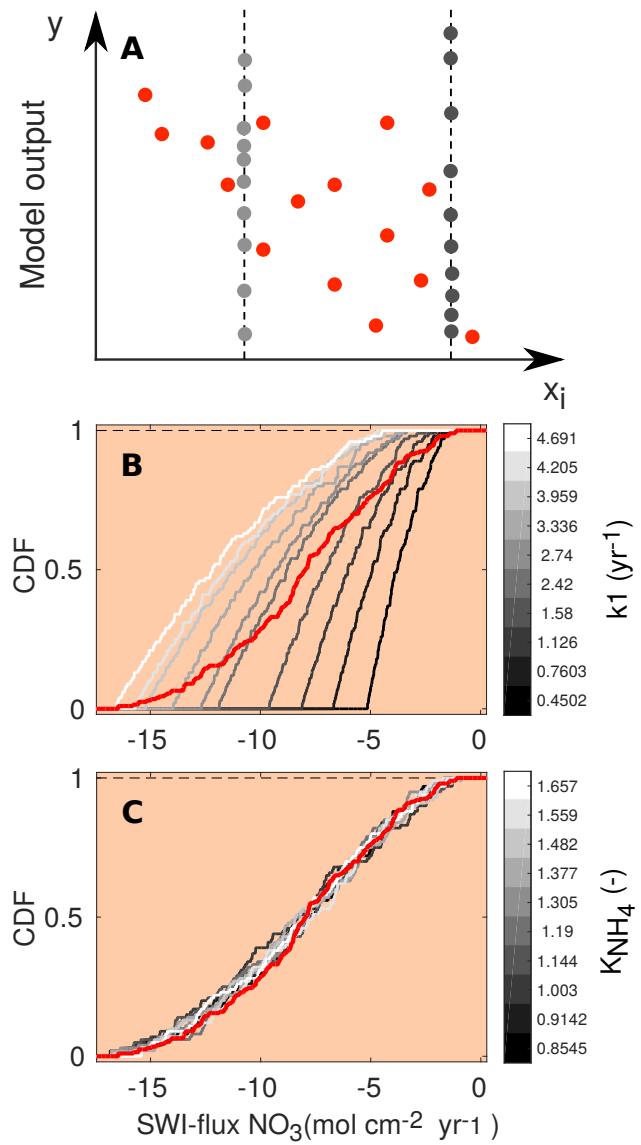


Figure 4. A: Schematic of the PAWN method, plotting an uncertain parameter (x_i) against a generic model output (y). Red dots represent points for calculating the unconditional CDF (NU, here 15), grey dots are points for calculating each conditional CDF (NC, here 10) with $n = 2$ conditioning points as an example. The user can change the values of NU, NC and n . The number of model evaluations equals $N_{\text{eval}} = \text{NU} + n \cdot \text{NC} \cdot M$, where M is the number of uncertain input parameters. B + C: Two examples of CDFs of the model calculated SWI-flux of NO_3 using NU = 200, NC = 100 and $n = 10$. The red lines are the unconditional distribution functions $F_y(\text{NO}_3)$ and the grey lines are the conditional distribution functions $F_{y|x_i}(\text{NO}_3)$ at different fixed values of the input parameters k_1 (B) and K_{NH_4} (C). As the maximal distance between conditional CDFs and unconditional CDF is greater for k_1 , this parameter is more influential for the model output (here SWI-flux of NO_3 , compare Fig. 5).

Table 11. 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 12. Model boundary conditions for the two idealised sediment conditions used for the sensitivity analysis (Fig. 5 and 6). All solute concentrations are in nmol 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

3.1.2 Results

- 840 Fig. 5 summarises results of the sensitivity analysis as a colour map. Results indicate that generally the most significant parameters for all model outputs are the degradation rate constant for the labile OM pool (k_1) and the fraction of this pool to the total OM stock (f_1). Other parameters play a minor role for the SWI-fluxes, with the exception of the secondary redox parameters (i.e. γ_{NH_4} , $\gamma_{\text{H}_2\text{S}}$) in the oxic scenario. Here, NH_4 , SO_4 and H_2S are very sensitive to changes in γ_{NH_4} and $\gamma_{\text{H}_2\text{S}}$, as 845 these parameters determine how much of the respective TEA is produced in situ via reoxidation, thus affecting the resulting SWI-fluxes. For the oxic scenario, the reoxidation of H_2S produced in the sulfidic layer also has a strong influence on alkalinity ($\gamma_{\text{H}_2\text{S}}$, Table 8 Eq. 5) as it decreases alkalinity by 2 moles per mole of S oxidized ($\text{ALK}^{\text{H}_2\text{S}}$, Table 10). However, these high sensitivities are partially caused by the wide range of allowed values ($\gamma_{\text{NH}_4}, \gamma_{\text{NH}_4} \in [0.5; 1.0]$). Yet, for oxic 850 deep sea conditions it is more likely that reduced substances are almost completely reoxidised (e.g. Hensen et al., 2006). For the anoxic scenario the secondary redox parameters are essentially non-influential as no O_2 is available for the reoxidation of reduced substances. Especially for the oxic

condition the PO₄ SWI-flux appears to be insensitive to P-related parameters (i.e. $K_{\text{PO}_4}^{\text{ox}}$, $K_{\text{PO}_4}^{\text{anox}}$, k_s , k_m , k_a) as the majority is absorbed to Fe-oxides. The sensitivities change if other PO₄ related equilibrium concentrations PO₄^s, PO₄^a and FeP[∞] are used (not shown). Overall the results of the sensitivity analysis are in line with what one would expect from a diagenetic model and thus provide ground to confirm that OMEN-SED provides sensible results. The parameterisation of the organic matter pools (f_1) and their degradation rate constants (k_1 , k_2) is critical especially when the model is used in a global Earth system model framework, as these parameters, as well as the γ -parameters, can have a very important influence on the flux of dissolved species through the SWI. At the same time these are the weakest constrained parameters. Thus, one should rather choose γ -values close to 1 and consider carefully where a relaxation of the “all reoxidised” assumption is appropriate. In contrast, the importance of the OM degradation rate constants can not be overemphasised. Therefore, much care should be given to how these are parameterised in coupled simulations and a range of different plausible scenarios should be tested to quantify uncertainty.

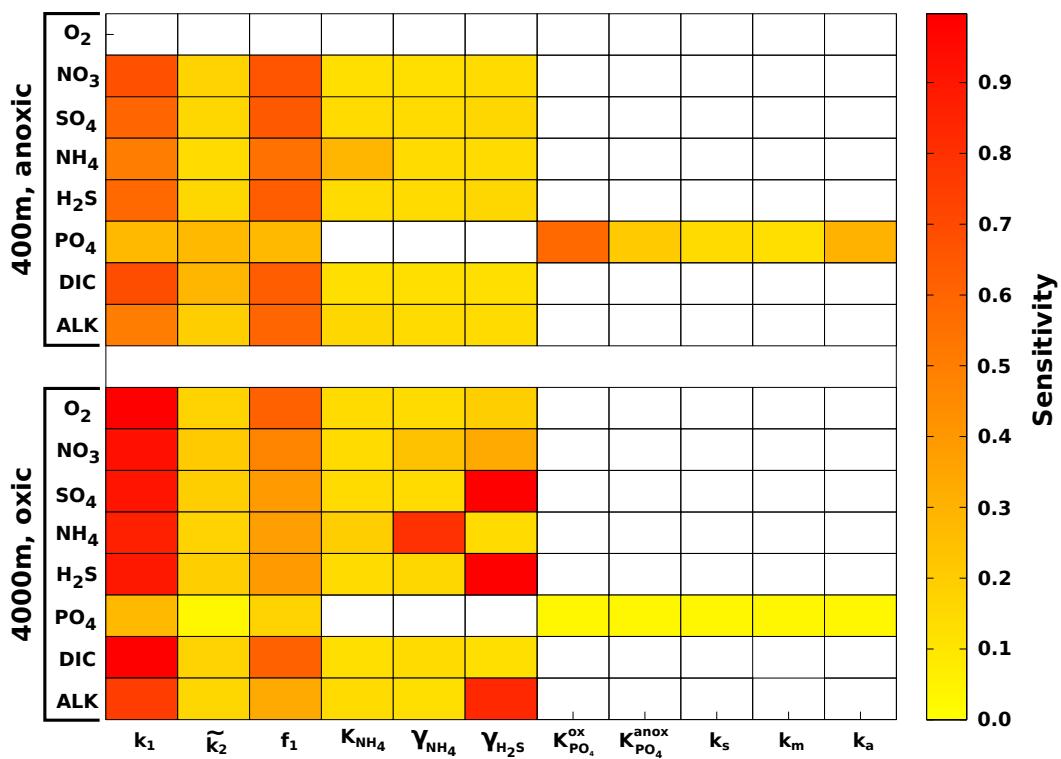


Figure 5. Pattern plot, showing the output sensitivity for each SWI flux (i.e. the chemical compounds on the vertical axis) and each input factor (i.e. the model parameters on the horizontal axis) for two idealised sediment cores. White patterns are assigned where the SWI flux is independent of the specific parameter.

Because of the strong sensitivity of model results on OM degradation rate parameters, we further explore the sensitivity of simulated sediment-water exchange fluxes to variations in organic matter degradation parameters by varying k_1 , f_1 and \tilde{k}_2 while all other model parameters are set to their default values (Tables 9 and 10). Minimum and maximum values for k_1 , \tilde{k}_2 and f_1 in the shallow ocean are as in Table 11. For the deep sea condition we account for the presence of more refractory OM by sampling $f_1 \in [0.02, 0.3]$, whereas the variation of k_1 and \tilde{k}_2 is as in the shallow ocean. The parameter space is sampled using another Latin-Hypercube approach with sample sizes of $N = 3500$ for each idealised sediment condition. Figure 6 summarises the results of the sensitivity study and the ranges of observed O_2 and NO_3 sediment-water interface fluxes extracted from a global database (Stolpovsky et al., 2015) are indicated on the colour scale. The colour patterns in Figure 6 A and B reveal the complex interplay between the amount of labile OM f_1 and its degradation rate k_1 for the resulting SWI-fluxes of NO_3 in anoxic sediments and O_2 in aerobic sediments. In general, a higher degradation rate in combination with more labile OM available leads to a higher SWI-flux. However, higher fluxes extend over a larger range of k_1 -values when the amount of labile OM f_1 is high. The absence of a colour pattern in Figure 6 C highlights the limited interaction of the two model parameters for NO_3 SWI-fluxes under oxic conditions. Figure 6 shows that SWI-fluxes can vary widely over the range of plausible organic matter degradation parameters and that simulated fluxes generally fall within the range of observed SWI-fluxes. However, a large number of different k-f combinations can result in SWI-fluxes that fall within the observed ranges reported by Stolpovsky et al. (2015) further emphasising the care that should be devoted to constraining OM degradation parameters.

3.2 Case study: Simulations of sediment cores

3.2.1 Methodology

In order to illustrate the capabilities of OMEN-SED, comprehensive datasets from the Santa Barbara Basin (Reimers et al., 1996), as well as from the Iberian margin and the Nazaré Canyon (Epping et al., 2002) are modelled. Modelled profiles are compared with measured pore water data from different depths including the continental shelf (108 m) and the lower slope (2213 m) located at the Iberian margin, the upper slope (585 m) from the Santa Barbara Basin, and a deep sea site (4298 m) in the Nazaré Canyon. The Santa Barbara Basin is characterised by anoxic bottom waters, high POC concentrations and varved sediments (Reimers et al., 1990), therefore the depth of bioturbation in OMEN-SED is restricted to the upper 0.01 cm. In the uppermost sediments iron(III) hydroxides are reduced, releasing Fe^{2+} which reacts with sulfide to form iron sulfides. Thus, the Fe cycle exerts a strong control on sulfide concentrations in the sediments of this basin (Reimers et al., 1996). In addition, the sediments are generally supersaturated with respect to carbonate fluorapatite by and below 2 cm (Reimers et al., 1996). The Iberian margin, situated in the northeastern Atlantic, generally

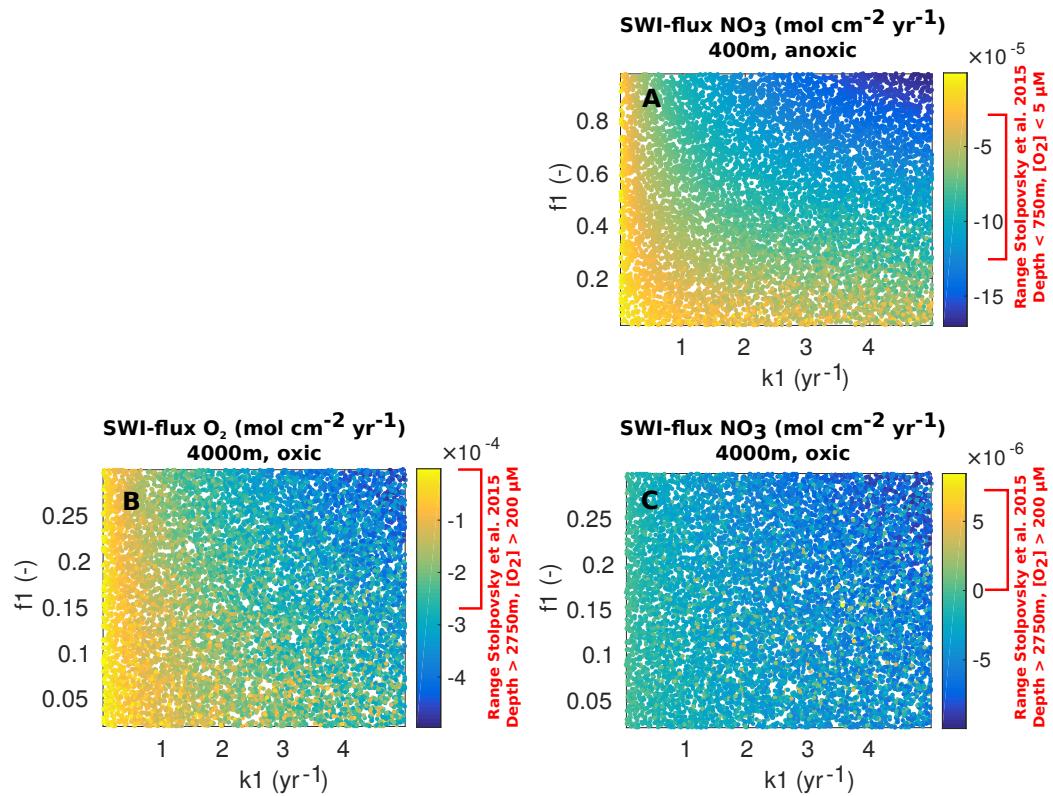


Figure 6. Scatter plots (k_1 vs f_1) of resulting OMEN-SED SWI-fluxes for the 400m anoxic (A: NO_3) and 4000m oxic (B: O_2 , C: NO_3) scenario. Negative values represent a flux from the water column into the sediments. Ranges indicated in red on the colour scale correspond to observed benthic fluxes as reported in the global database of Stolpovsky et al. (2015).

belongs to the more productive regions of the global ocean (Longhurst et al., 1995), however, seasonal changes in upwelling creates a strong temporal variability in primary productivity and organic carbon deposition. Submarine canyons in this area (like the Nazaré Canyon) may deliver organic carbon from the shelf to the ocean interior (van Weering et al., 2002; Epping et al., 2002). For a more 905 detailed description of the study areas and the experimental work, the interested reader is referred to the publications by Reimers et al. (1996) and Epping et al. (2002).

In OMEN-SED sediment characteristics and boundary conditions are set to the observed values where available (Table 13). Other sediment characteristics (e.g. sedimentation rate, porosity, density), stoichiometric factors and secondary reaction parameters are set to the default value (see 910 Tables 9 and 10). Organic matter is modelled as two fractions, with different first-order degradation rate constants. The POC and pore water profiles were manually fitted by optimizing the POC partitioning into the fast and slow degrading pool and their respective first-order degradation rate

Table 13. Model boundary conditions for the simulated sediment profiles in the Santa Barbara basin (108 and 2213 m) and Iberian margin (585 and 4298 m) reported in Figure 7. For all sites a DIC bottom water concentration of 2,400 nmols cm⁻³ is assumed.

Sediment characteristics:								
Depth (m)	Temp. (°C)	z_{bio} (cm)	D_{bio} (cm ² yr ⁻¹)	POC ₁ (wt%)	POC ₂ (wt%)	k_1 (yr ⁻¹)	k_2 (yr ⁻¹)	PO ₄ ^a (nmol cm ⁻³)
108	12.50	1.00	0.02	2.64	1.8	0.650	$1.0e^{-5}$	15.0
585	5.85	0.01	0.02	2.00	3.5	0.200	$8.0e^{-4}$	90.0
2213	3.20	10.00	0.17	0.45	0.5	0.100	$4.0e^{-4}$	5.0
4298	2.50	4.20	0.18	0.83	1.2	0.052	$1.0e^{-5}$	5.0

Bottom water concentrations of solutes (all in nmol cm ⁻³):							
Depth	O ₂	NO ₃	SO ₄	NH ₄	H ₂ S	PO ₄	Alkalinity
108	210.0	9.6	28,000	0.40	0.0	0.0	2,400
585	10.0	25.0	28,000	0.00	0.0	50.0	2,480
2213	250.0	25.0	28,000	0.60	0.0	0.0	2,400
4298	243.0	30.1	28,000	0.22	0.0	0.0	2,400

constants (priority is given to reproduce the POC and O₂ profiles). For phosphorus the equilibrium concentration for authigenic P formation (PO₄^a) was adjusted to fit the PO₄ concentration at z_{∞} .

915 3.2.2 Results

Fig. 7 compares modelled and observed sediment profiles for the Santa Barbara Basin and the Iberian margin. Results show that OMEN-SED is able to capture the main diagenetic features across a range of different environments without changing model parameters (other than the 4 we tuned, i.e. k_1 , k_2 , f_1 and PO₄^a) to site specific conditions. For the two open Iberian margin stations (108 and 2213 m) OMEN-SED fits all observations well. OMEN-SED does especially well at seafloor depth (SFD) 2213 m by reproducing the deep O₂ penetration and the subsurface maximum in NO₃ concentration due to the nitrification of NH₄ (note, that NH₄ is overestimated at this SFD). For the anoxic Santa Barbara Basin (585 m) the decrease in SO₄ and the increase in ALK concentration with sediment depth is well represented, indicating the importance of sulfate reduction as the primary pathway of OM degradation at this site (compare with Meysman et al., 2003). However, a misfit is observed for H₂S and PO₄ in the upper 20 cm of this sediment core. The discrepancy for H₂S can be explained by high iron(III) hydroxide concentrations, which is reduced to degrade organic matter (especially in the 2 – 4 cm depth interval), therefore placing the beginning of the sulfate reduction zone and the production of H₂S to the deeper sediments (Reimers et al., 1996). Iron processes are currently not dynamically represented in OMEN-SED. In addition, produced dissolved Fe reacts with H₂S to form iron sulfides (e.g. pyrite, FeS₂) and thus further inhibits the rise of H₂S (Reimers et al.,

1990). The iron cycle also plays a critical role for phosphorus, as the reduction of iron(III) hydroxides in the surface sediments releases sorbed phosphate, leading to pore waters around and below 2 cm which are supersaturated with respect to fluorapatite, thus initiating CFA precipitation. Reimers 935 et al. (1996) could even show that the accumulation of CFA is mainly restricted to the near-surface sediments (~ 5 cm) instead of throughout the sediment column. As OMEN-SED currently does not include an iron-cycle, and Fe-bound P and CFA processes are highly parameterised, the model is not able to capture these complex, non-steady state phosphorus dynamics at this specific site. For the Nazaré Canyon station (4298 m) satisfactory fits could be realised apart from NH_4 . However, also 940 Epping et al. (2002) could not obtain a better fit using a more complex diagenetic model. They suggested non-local solute exchange resulting from bioirrigation being responsible for the higher NH_4 concentrations at this site which is neglected in their model, as well as in OMEN-SED. Furthermore, the fractured POC profile (indicating episodic depositional events through the canyon) could have been approximated using a different partitioning of the bulk POC into labile and refractory pool with 945 different degradation rate constants, thus potentially leading to a better fit of the NH_4 profile. In general, better approximations of the data could have potentially been acquired by applying a sensitivity study using different NC-ratios (e.g. Epping et al., 2002, report different ratios from Redfield stoichiometry) and exploring the parameter space for the secondary reaction parameters (γ_{NH_4} , $\gamma_{\text{H}_2\text{S}}$). However, considering these generalisations and our assumption of steady-state, which might not be 950 valid, particularly for the complex Santa Barbara basin, the shallow core and the Nazaré Canyon, which are affected by seasonality and biology, OMEN-SED generally reproduces the observed pore water trends and hence captures the main diagenetic processes.

3.3 Case study: Stand-alone simulations of global ocean transect

3.3.1 Methodology

955 In this section we explore to what degree OMEN-SED is capable of capturing the dynamics of organic matter degradation pathways and related TEA-fluxes as simulated with a more complete and complex numerical diagenetic model (Thullner et al., 2009). Therefore, we reproduce the simulations of typical conditions along a global ocean hypsometry of Thullner et al. (2009) and compare our modelled TEA-fluxes with the results of the complex model as well as with observations from 960 Middelburg et al. (1996). To explore the global degradation of OM in the seafloor Thullner et al. (2009) quantified various diagenetic processes using the Biogeochemical Reaction Network Simulator (BRNS, Aguilera et al., 2005), a flexible simulation environment suitable for reactive transport simulations of complex biogeochemical problems (e.g. Jourabchi et al., 2005; Thullner et al., 2005). Thullner et al. (2009) used seafloor depth (SFD) as the master variable and calculated model parameters, such as w , D_{bio} and ϕ , from existing empirical relationships (e.g. Van Cappellen and Wang, 965 1995; Middelburg et al., 1997). Organic matter degradation was described with a 1G approach, thus

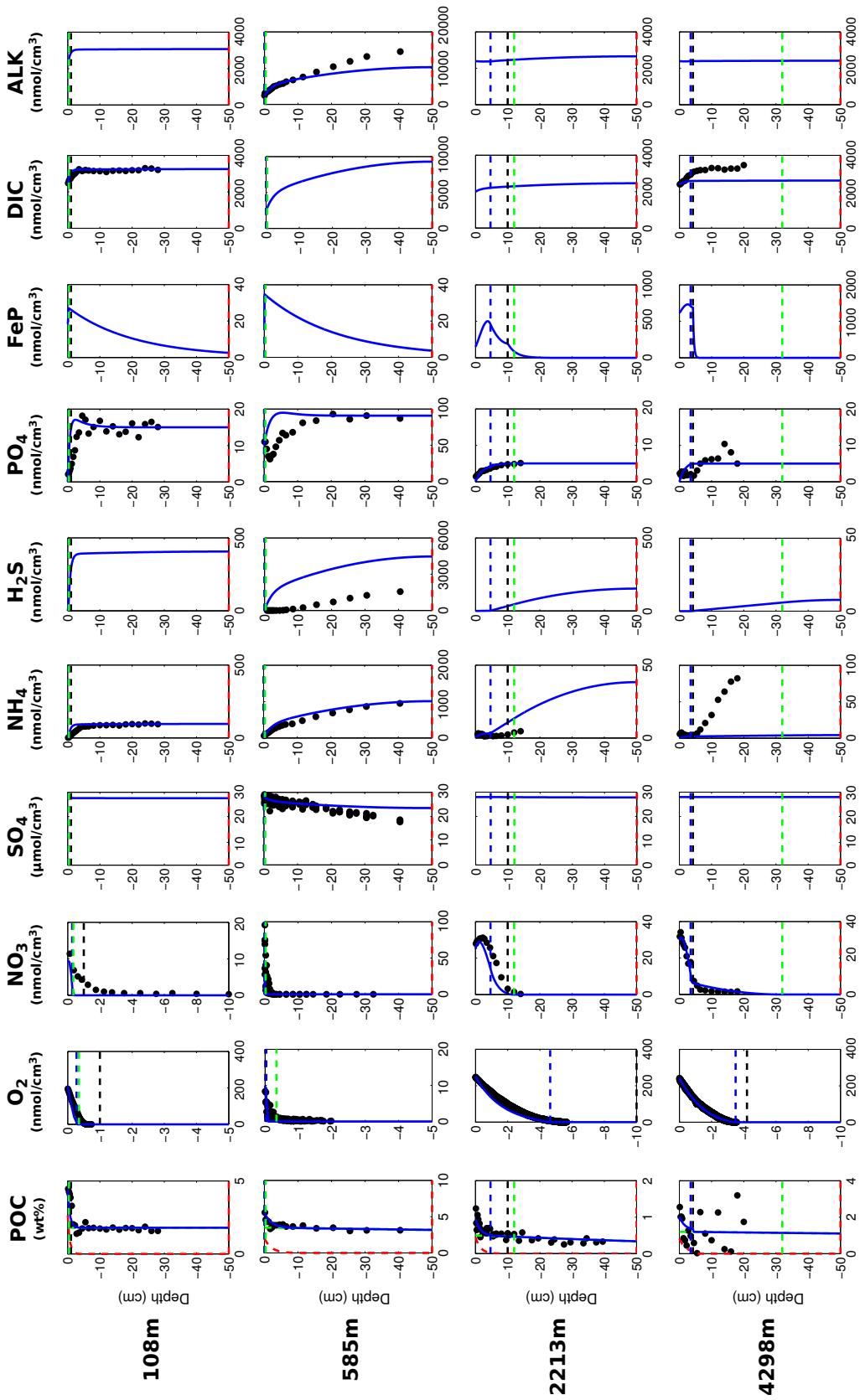


Figure 7. Modelled (curves) and measured (filled dots) solid phase and dissolved pore water profiles for four different sediment cores. Note that different scales are used for different stations. The blue POC curve represents the sum of the refractory (green) and labile (red) POC fraction. The horizontal dashed lines in each panel indicate the bioturbation depth (black) and the penetration depths of oxygen (blue), nitrate (green) and sulfate (red) as calculated by OMEN-SED.

assuming a single pool of organic matter of uniform reactivity. The first order rate constant was related to the burial velocity, w (cm year $^{-1}$), following the empirical relationship of Boudreau (1997):

$$970 \quad k = 0.38 \cdot w^{0.59}. \quad (50)$$

This rate constant can be assumed as the mean reactivity of the organic matter fractions which are degraded in the upper, bioturbated 10 – 20 cm of the sediments. Thus, more reactive fractions (degraded during days/weeks close to the SWI) and more refractory fractions (degraded on longer time scales deeper in the sediments) are not captured by this relationship (Boudreau, 1997). BRNS simulations were performed using boundary conditions and parameters for depths representative for shelf, slope and deep sea sediments (i.e. SFD of 100m, 200m, 500m, 1000m, 2000m, 3500m and 5000m). In order to reproduce these results, OMEN-SED is configured here as a 1G model and boundary conditions and model parameters are defined as in Thullner et al. (2009, see Table 14). As OMEN-SED assumes a fixed fraction (i.e. γ_{NH_4} , γ_{H_2S}) of reduced substances to be reoxidised, which exerts a large impact on the resulting SWI-fluxes (compare Section 3.1), two sets of simulations are performed in order to show the range of possible model outputs. In the first setup 95% of the reduced substances are reoxidised (i.e. $\gamma_{NH_4} = \gamma_{H_2S} = 0.95$) and in the second, less realistic case, only 5% are reoxidised (all other model parameters and boundary conditions are equal). **why not 0 and 1 to show the entire range??**

985 3.3.2 Results

Figure 8 compares simulated SWI-fluxes of TEAs (i.e. O₂, NO₃ and SO₄) along the global hypsometry using OMEN-SED (black lines) with the results of Thullner et al. (2009) (red lines). Observations for O₂ and NO₃ fluxes are taken from Middelburg et al. (1996). Due to the applied empirical relations organic matter flux to the seafloor decreases by 2 orders of magnitude from 100 to 5000 m and its degradation rate constant by 1 order of magnitude (Table 14). Therefore, the rate of organic matter degradation is about 50 times greater at 100 m than at 5000 m (compare Thullner et al., 2009), thus resulting in a decrease of TEA-fluxes along the hypsometry (Figure 8). The 95%-reoxidation experiments (dots) show proportionally higher O₂ in-fluxes than the the 5%-reoxidation experiments (triangles) because more O₂ is utilised for in situ production of NO₃ and SO₄ in the sediments. This is also mirrored by the increased NO₃ out-flux and decreased SO₄ in-flux for shallower SFDs. This is in line with the results of Thullner et al. (2009) which showed that in situ production is an important pathway of SO₄ supply in the sediment, which is responsible for ~80% of the total OM degradation at depths between 100 and 2000 m (in our results SO₄ is not used for OM degradation in OMEN-SED below 2000m). In general, Figure 8 shows that OMEN-SED captures the main trends in observed and numerically simulated TEA fluxes well. Results also confirm that higher γ -values better represent SWI-fluxes for most of the global hypsometry. A slight overestimation of shallow ocean SWI-fluxes (SFD < 200 m) for the high γ scenario indicates that slightly lower γ -

Table 14. Seafloor depth dependency of key model parameters and boundary conditions (adapted from Thullner et al., 2009).

	Seafloor depth					5000 m
	100 m	200 m	500 m	1000 m	2000 m	
Model parameters						
w^a (cm yr ⁻¹)	3.98 × 10 ⁻¹	3.60 × 10 ⁻¹	2.67 × 10 ⁻¹	1.62 × 10 ⁻¹	5.94 × 10 ⁻²	1.32 × 10 ⁻²
D_{bio}^a (cm ² yr ⁻¹)	27.5	25.1	19.0	12.1	4.83	1.23
ϕ^b	0.85	0.85	0.80	0.80	0.80	0.80
T ^c (°C)	10.3	9.7	8.1	5.8	3.0	1.5
ρ_{sed}^c (g cm ⁻³)	2.5	2.5	2.5	2.5	2.5	2.5
k^d (yr ⁻¹)	0.221	0.208	0.174	0.130	0.0718	0.0296
Upper boundary conditions						
POC _{flux} ^a ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$)	510	467	357	228	93.0	24.3
POC ^e (wt%)	0.79	0.78	0.55	0.50	0.42	0.32
O _{2,0} ^c (nmol cm ⁻³)	132	129	121	114	116	135
NO _{3,0} ^c (nmol cm ⁻³)	17.3	18.6	22.1	26.5	31.0	31.6
SO _{4,0} ^b (nmol cm ⁻³)	28,000	28,000	28,000	28,000	28,000	28,000

^a Derived from Middelburg et al. (1997).

^b Derived from Conkright et al. (2002).

^c Calculated with OMEN-SED from POC_{flux}.

^d Derived from Van Cappellen and Wang (1995).

^e Derived from Boudreau (1997).

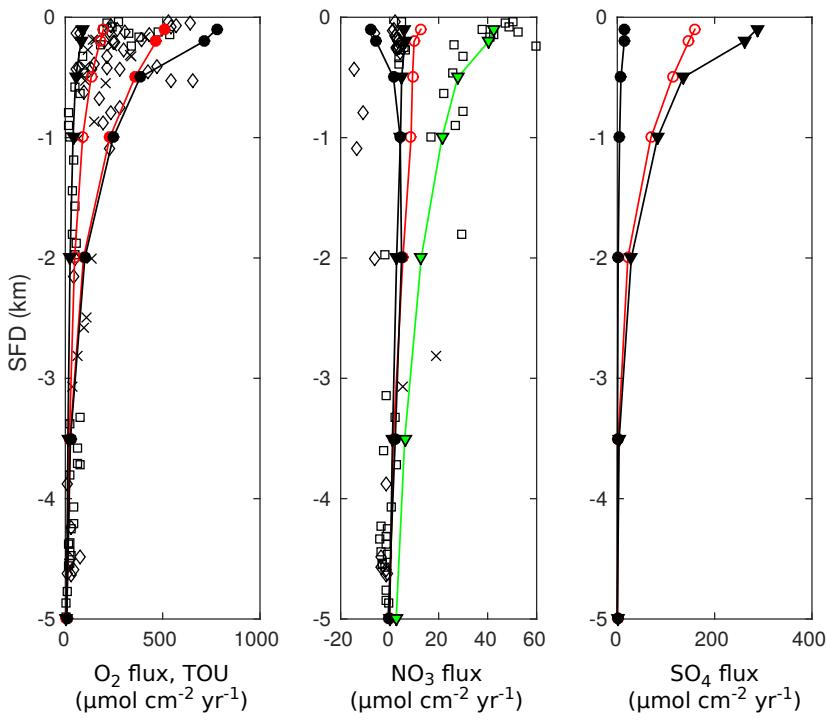


Figure 8. Fluxes of O₂, NO₃ and SO₄ to the sediment along the global hypsometry. Red lines (with open symbols) are modelled fluxes from Thullner et al. (2009) using BRNS; black lines are results from OMEN-SED (● : $\gamma_{NH_4} = \gamma_{H_2S} = 0.95$; ▼: $\gamma_{NH_4} = \gamma_{H_2S} = 0.05$). Observations 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. Positive fluxes are directed from the ocean into the sediments.

values would better capture SWI-fluxes in these areas, where rapid oxygen consumption favours the escape of reduced species across the SWI.

- 1005 In addition, observed O₂ fluxes in the upper 2000m are generally encompassed by our total range in predicted OMEN-SED fluxes. Oxygen fluxes for the deep-sea sediments, however, are slightly underestimated. These deviations can presumably be related to the assumed 1G 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.
- 1010 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

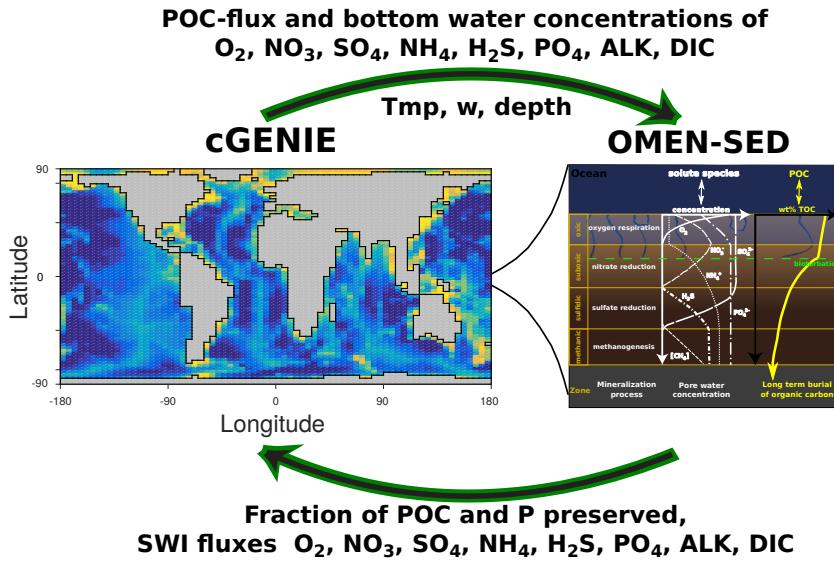


Figure 9. Schematic of the relationship between OMEN-SED and cGENIE. Arrows represent the information transferred between models.

higher flux of labile organic matter for their 2G model. By changing the boundary conditions and the N:C elemental 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). Bohlen et al. (2012) report that the elemental N:C ratio strongly deviates from Redfield stoichiometry (0.151) with specifically lower values for the East Pacific Ocean. The use of their globally averaged value of 0.067 allows reconciling modelled and observed values provided that bottom water conditions are also changed to the low oxygen/high nitrate levels more likely to be found in the shallow Pacific Ocean ($O_2 = 10 \text{ nmol cm}^{-3}$ and $NO_3 = 80 \text{ nmol cm}^{-3}$).

4 Coupled pre-industrial Earth system model simulations

4.1 Coupling to the cGENIE Earth system model

In a final step, we couple OMEN-SED to the carbon-centric version of the “GENIE” Earth system model (cGENIE, Ridgwell et al., 2007) in order to illustrate how a fully coupled ocean-sediment system can be configured and applied. We start by providing a brief description of cGENIE and the coupling procedure (Fig. 9).

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-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 (SEDGEM, Ridgwell and Hargreaves, 2007) and terrestrial weathering (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). A finer grid (72×72) is used for the sediments (see Fig. 11C and Ridgwell and Hargreaves, 2007) and OMEN-SED is called by SEDGEM for each wet ocean grid point. Depending on the configuration of the overlying biogeochemical ocean model, processes can be included or excluded in OMEN-SED and stoichiometric factors (Tab. 10) need to be matched between models to ensure preservation of mass. As nitrogen is not modelled explicitly in the employed cGENIE configuration, NC_i , ALK^{NIT} and ALK^{DEN} in OMEN-SED are set to zero. cGENIE, however, implicitly includes the effects of NH_4^+ release and its complete nitrification on alkalinity but neglects the impact of P release. Therefore, alkalinity stoichiometries for aerobic degradation, sulfate reduction and methanogenesis are changed to $\text{ALK}^{\text{OX}} = -16/106$, $\text{ALK}^{\text{SUL}} = 122/106$ and $\text{ALK}^{\text{MET}} = -16/106$, respectively (compare to default in Table 10).

Various biogeochemical tracers and parameters are transferred from SEDGEM to OMEN-SED (see Fig. 9) and are 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 $1.0 \text{ cm}^3 \text{ g}^{-1}$. Within the water column in cGENIE, POC is partitioned into two fractions with different degradation length scales of $\sim 590 \text{ m}$ and 1000000 m , respectively. The labile pool thus degrades while sinking through the water column, whereas the refractory pool is assumed relatively unreactive (Ridgwell et al., 2007). Thus, depending on seafloor depth, the partitioning of bulk POC reaching the sediments is different (Fig. 10A+B). This information is used by OMEN-SED to define the parameters f_1 and f_2 . Other parameters used from cGENIE are seafloor depth and local temperature. The advection/burial rate (w) is taken from the previous time-step of cGENIE, however, it is assured that w is not smaller than the detrital flux (Det_{flux}) to the sediments (e.g. $w < 0$ can occur if initially carbonate rich sediments are eroded during the spin-up of cGENIE). In case ($w \leq \text{Det}_{\text{flux}} \& \text{Det}_{\text{flux}} = 0.0$) all POC is remineralised at the ocean floor. Furthermore, a minimum value of $w = 0.4 \text{ cm kyr}^{-1}$ is imposed as OMEN-SED tends to be less stable for lower values. For comparison, this threshold is crossed for seafloor depths below 7000 m when applying the relationship between burial rate and water depth of Middelburg et al. (1997) and below 5200 m for the Burwicz et al. (2011) parameterisation. The bulk POC_{flux} is separated into the labile and refractory component and the routine to find the steady-state solution for POC is called. Here, the two POC depositional fluxes are first converted into SWI concentrations ($\text{POC}_i(z=0)$, in mol cm^{-3}) by solving the flux divergence equation:

$$\frac{\partial F}{\partial z} = -\frac{\partial}{\partial z} \left(-\xi D_i \frac{\partial \text{POC}_i}{\partial z} + \xi w \text{POC}_i \right) \quad (51)$$

for $z=0$. OMEN-SED then computes the fraction of POC preserved in the sediment (f_{POC} , see Eq. (5)) and subsequently calls the routines to find the steady-state solutions for the solute substances.

1070 Note, that in this initial coupling the calculated benthic uptake/return fluxes F_{C_i} of dissolved species C_i (compare Eq. (6)) are adjusted for the advective loss at the lower sediment boundary ($w \cdot C_i(z_\infty)$) to assure the conservation of mass in the coupled model:

$$F_{C_i} = \phi(0) \left(D_i \frac{\partial C_i(z)}{\partial z} \Big|_{z=0} - w [C_i(0) - C_i(z_\infty)] \right). \quad (52)$$

In case OMEN-SED computes unrealistic results for POC preservation (i.e. $f_{\text{POC}} < 0.0$ or $f_{\text{POC}} > 1.0$) we discard the results of OMEN-SED and all POC is remineralised at the ocean floor. For the modern ocean setup, using the adjustments for w described above, this has not occurred and is just installed as a safety check. Finally, f_{POC} and the SWI-fluxes of solutes (F_{C_i} , in $\text{mol cm}^{-2} \text{yr}^{-1}$) are returned to cGENIE. In case no POC is deposited on the seafloor (i.e. $\text{POC}_{\text{flux}} = 0$), OMEN-SED is not executed and f_{POC} and F_{C_i} for all i are set to zero. In order to reduce memory requirements, the sediment profiles (e.g. as shown in Fig. 7) are not calculated in the FORTRAN version of OMEN-SED, however, the boundary conditions are saved and sediment profiles for specific grid-cells, ocean basins and ocean transects can be plotted at the end of each experiment using the stand-alone MATLAB version of OMEN-SED.

4.2 Parameterising the OM degradation rate constants in a global model

1085 As shown in our sensitivity analysis (Section 3.1) and discussed by Arndt et al. (2013), the degradation rate constants for OM (k_i) are the most influential parameters and exert a dominant control on the SWI-flux of redox-sensitive elements as well as the preservation of organic matter. Yet, their spatial variability is unknown at the global scale and reported rate constants in the sediments can vary by about 10 orders of magnitude or more (Middelburg et al., 1993; Arndt et al., 2013). Furthermore,

1090 when OMEN-SED is coupled to cGENIE, very different timescales have to be considered for OM degradation in the sediments compared to the water column (Fig. 10A+B) and thus the diagenetic rate constants cannot be easily implied by the assumed water column POC flux profiles in cGENIE. To illustrate this, let's consider the degradation of fresh, marine organic matter as it is transported and degraded along the ocean-sediment continuum. The bulk material is composed of a complex

1095 mixture of different organic carbon compounds that can be described by a reactivity continuum. Microbes preferentially degrade the more reactive organic matter compounds first (Emerson and Hedges, 1988; Wakeham et al., 1997; Lee et al., 2000), resulting in the preferential preservation of more unreactive compounds, rendering the remaining mixture less and less reactive with time. Thus depending on the age of OM (or depth in the water and sediment column) the reactivity distribution

1100 of its compounds changes significantly (Fig. 10C) and the multi-G (2G in this case) approximation of this continuum has to take this shift into account. Fig. 10 illustrates these changes in the original reactivity distribution within a ocean-sediment framework. The reactivity distribution $t < 1$ year

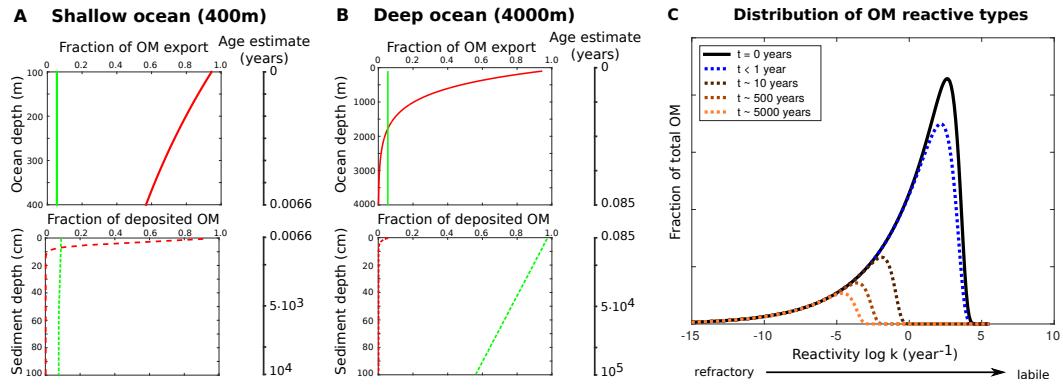


Figure 10. Idealised relationship of organic matter decomposition during remineralisation in the water column and the sediments. **A+B - Upper panels:** Water column development of the two organic matter fractions as represented in cGENIE for two ocean depths (red: labile OM with degradation length scale of 589m; green: refractory OM which is unreactive in the water column). The values are normalised to OM export at 100m. Age estimates for the OM since its export from the euphotic zone are calculated using a sinking velocity of 125m/day. **A+B - Lower panels:** Schematic representation of the development of the two OM fractions in the sediments (normalised to OM deposited on the seafloor). For the age estimates in the sediment column an advection rate of 0.01 and 0.001cm/yr is assumed, respectively. **C:** Idealised distribution functions of OM reactive types during remineralisation for different OM ages assuming a reactive continuum model for OM degradation. The initial distribution (at $t = 0$) represents fresh OM when it is exported from the euphotic zone (characterised by $a = 3e^{-4} \text{ yr}^{-1}$ and $\nu = 0.125$ Boudreau et al., 2008).

represents the organic matter mixture after it settled through the water column (Fig. 10C). Only the most reactive OM compounds are remineralised. This explains why the POC flux in the ocean can
 1105 be represented with a 1G or pseudo 2G degradation model. In the sediments, however, much longer timescales have to be considered and a wider range of more unreactive compounds are degraded. As a consequence, significant changes in the reactivity distribution already take place in the upper millimetres of the sediments ($t \sim 10$ years, Fig. 10C). Therefore, a broader range of OM reactive types must be represented by the degradation model to capture the reactivity spectrum of OM in surface
 1110 sediments, explaining why at least a pseudo 3G model (including two degradable and one refractory fraction Soetaert et al., 1996; Boudreau, 1997; Stolpovsky et al., 2015) is required. To complicate the situation even further, different sediment depths can represent very different timescales. For instance, half a meter of sediment can be deposited within a year in a coastal setting, while it will represent thousands of years (if not more) of sedimentation in a deep ocean setting. Therefore, residence times and thus degradation rate timescales (or OM age) are mainly controlled by advection
 1115 rates. For instance, assuming an advection rate of 0.01 cm/yr for the shallow ocean, OM at 5cm depth has been degraded for approximately 500 years, whereas a deep ocean advection rate of 0.001 cm/year allowed for OM degradation of approximately 1000 years at the same depth. As a

consequence, organic matter degradation in deep ocean sediments affects a much wider range of the
1120 reactivity continuum and our simple pseudo 3G approximation of the complex OM mixture needs to reflect this by allowing for different k and f values (Fig. 10C).

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
1125 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 (Toth and Lerman, 1977; Tromp et al., 1995; Boudreau, 1997; Stolpovsky et al., 2015). Nevertheless, these relationships are generally based and/or tested on limited data sets and their global applicability, especially under past
1130 or projected future environmental conditions is questionable (Arndt et al., 2013). We hence test several alternative schemes in the coupled OMEN-cGENIE framework. Our objective is not to perform and discuss a detailed calibration of the coupled models as this is beyond the scope of this sediment model development paper. Rather we want to showcase the feasibility of the model coupling, illustrate the range of results and thus information that can be generated with OMEN-SED and verify
1135 that model results capture the main observed global benthic biogeochemical features.

4.2.1 Methodology

In this section we compare modelled mean POC weight percentages (wt%) in the upper 5cm of the sediments ($\text{POC}_{5\text{cm}}$) to the global distribution pattern of POC content in surface sediments (< 5cm sediment depth) of Seiter et al. (2004) using different parameterisations for the degradation
1140 rate constants k_1 and k_2 . For our observational target we take the original POC distribution pattern in $1^\circ \times 1^\circ$ grid resolution (interpolated from > 5500 measurements, compare Seiter et al., 2004) and transform it onto the 72×72 SEDGEM grid (Figure 11). The regridding of the original POC distribution obviously affects the resolution of the data, especially for the continental margin, as some sites with higher POC wt% are lost in the regridding process (compare e.g. maximum values
1145 for the East Pacific and upwelling waters of the Namibian shelf, Figure 11A + B). The colour of the points in Figures 12 - 14 indicates the seafloor depth (SFD) of the respective cGENIE grid-cell. As the individual data-points are highly scattered and in order to see if a certain relation between k_1 and k_2 performs better for specific ocean depths, the data-points are binned into 6 uniform depth-classes of 1000m each (respective mean POC wt% and SFD are represented by the triangles). The regression
1150 line (and the corresponding R^2 -value) is calculated for the 6 bin-classes and included in the figures.

TODO Andy: Section describing the prescribed fields of solids (i.e. detrital, opal, CaCO_3) to the sediments!

To parameterise the reactivity of organic matter in OMEN-SED two different schemes are tested and compared. First, spatially uniform degradation rate constants k_1 and k_2 are assumed. By simu-

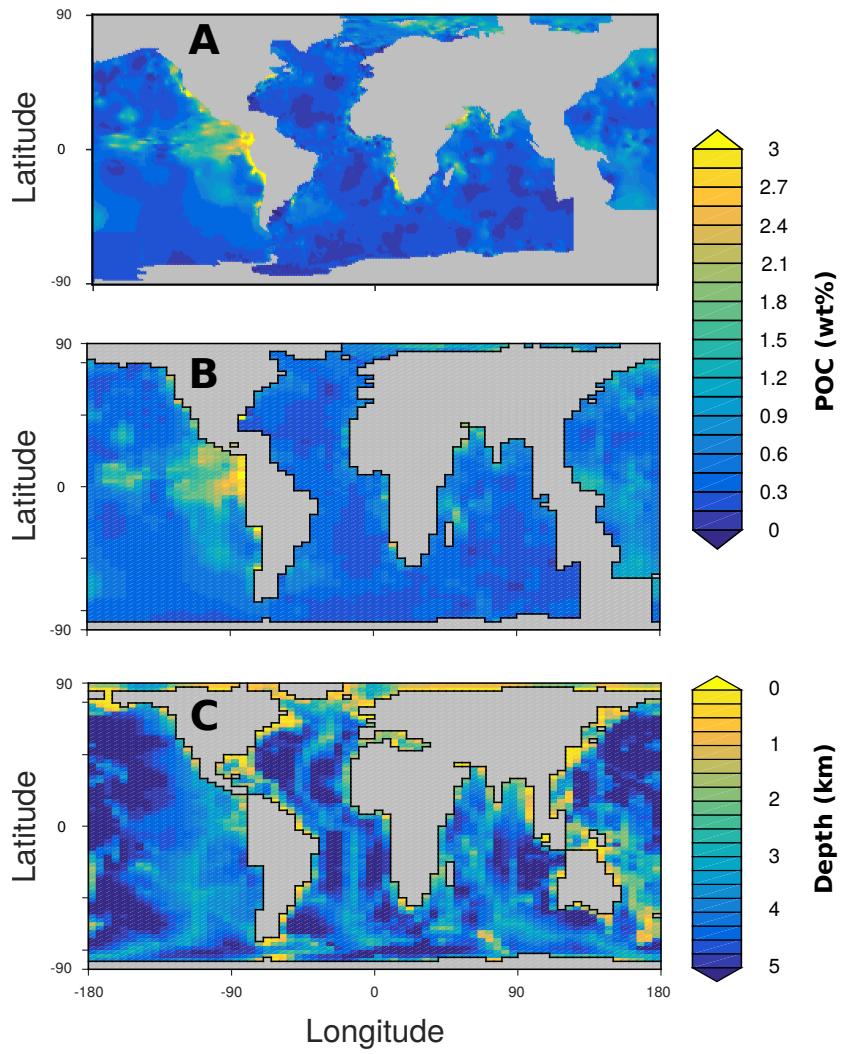


Figure 11. Observed distribution of sediment surface (< 5cm) POC wt% (A, B) and cGENIE bathymetry (C). (A) Original global distribution of POC wt% interpolated on a $1^\circ \times 1^\circ$ grid from more than 5500 individual data points (compare Seiter et al., 2004, for the interpolation procedure). (B) Observed POC wt% data transformed onto the 72×72 SEDGEM grid. Grid points without any observations are left blank (grey). (C) Gridded continental configuration and ocean bathymetry of the 16-level, 72×72 equal-area cGENIE grid.

1155 lating two different pools of POC in the water-column characterised by different degradation length scales (Ridgwell et al., 2007), cGENIE implicitly accounts for the decrease in mean POC reactivity with water-depth. The rate constants for the more refractory OM pool, k_2 , is systematically varied between 0.004 and 0.006 year $^{-1}$ and the more labile OM component, described by k_1 , is assumed to degrade a multiple times faster (i.e. $x \in \{1.1, 1.2, 1.3, 1.5, 2\}$). However, although accounting for
 1160 the decrease in mean POC reactivity with seafloor depth, this approach does not take into account the change in distribution of organic matter reactivity types caused by different burial velocities and thus different residence time scales in the sediments (Fig. 10). Therefore, the second approach uses the empirical relationship proposed by Boudreau (1997), which relates the apparent OM degradation rate constant in the upper sediments to the burial velocity, w (cm year $^{-1}$, see also Section 3.3):

$$1165 k_{app} = 0.38 \cdot w^{0.59}. \quad (53)$$

Following Boudreau (1997) and Stolpovsky et al. (2015) it can be assumed that k_{app} represents the mean OM reactivity within the upper 10-20cm of the sediments. The following assumptions are made in order to calculate the two degradation rate constants for OMEN-SED:

$$k_{app} = f_1 \cdot k_1 + f_2 \cdot k_2 \quad (54)$$

$$1170 k_1 = x \cdot k_2 \quad (55)$$

where x describes the relation between k_1 and k_2 and is subject to sensitivity experiments (with values of $x \in \{2, 5, 8, 10, 12, 15, 20, 25\}$). Note that the differences between k_1 and k_2 using this approach is significantly larger as in the globally uniform approach. As the fractions of labile and
 1175 refractory OM reaching the sediments (f_1, f_2) is known from cGENIE, k_1 and k_2 can be calculated independently for each grid-cell.

To simulate steady state sediment composition we configure the model as a “closed” system, i.e., one in which there is no loss of CaCO₃ through burial. The redox dependent P-cycle in OMEN-SED is not used in these experiments and all organic phosphorus is returned at the seafloor. To speed up
 1180 the calculation and to assure that ocean redox changes caused by OMEN-SED do not impact the sediment composition of CaCO₃, we use the prescribed solid fields as described earlier. Apart from the prescribed fields and the 72 × 72 sediment grid the model is configured as in Archer et al. (2009) and atmospheric CO₂ is restored to a pre-industrial value of 278 ppmv. First a 20,000 year spinup is performed without OMEN-SED being coupled. All presented coupled cGENIE-OMEN simulations
 1185 are run for 10,000 years to steady state from this spinup. 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.

4.2.2 Results

Figure 12 presents results for the spatially uniform degradation rate experiments. In general, using
 1190 spatially uniform degradation rate constants 5 of the 6 bin-classes are located closer to the 1:1 line

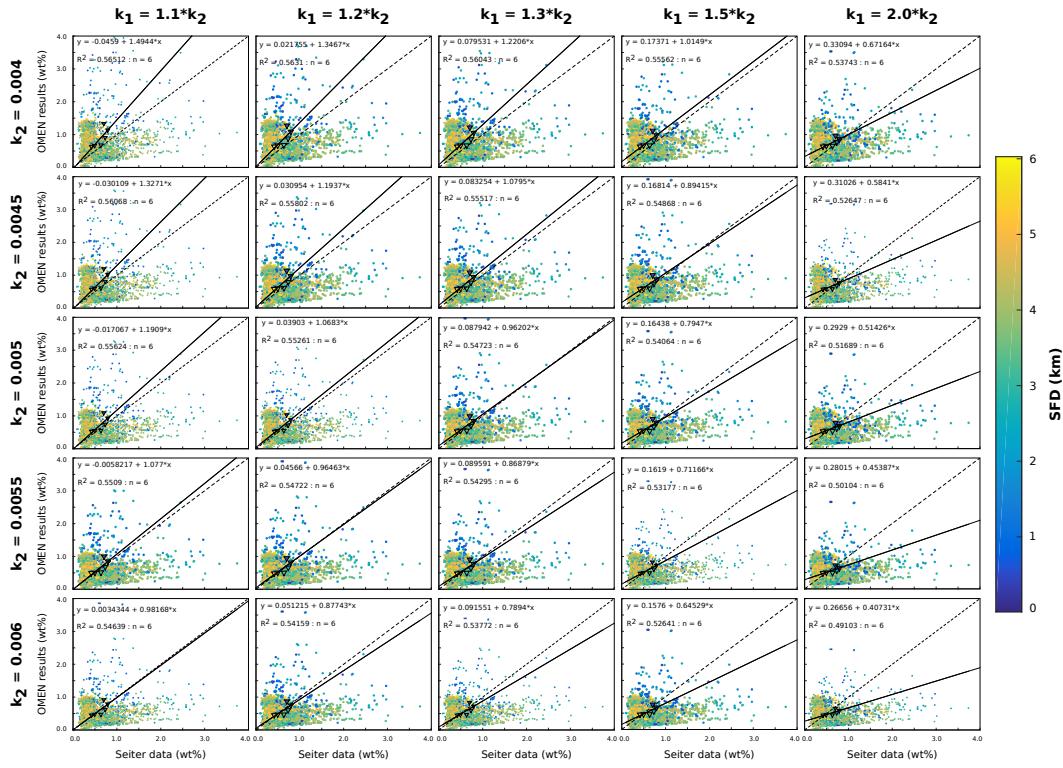


Figure 12. Crossplots comparing modelled and observed mean POC wt% in the upper 5 cm of the sediments using spatially uniform degradation rate constants k_1 and k_2 . Data-points are binned into 6 uniform depth-classes of 1000m as in Fig. 13, each class is represented by a triangle. Grid-points with more than 4.0 POC wt% are not shown.

as in the experiments using the Boudreau (1997) relation (Fig. 13). Also the slope of some regression lines is close to 1.0 (e.g. $(k_2, x) \in \{(0.004, 1.5), (0.0045, 1.3), (0.005, 1.2), (0.005, 1.3), (0.0055, 1.1), (0.0055, 1.2), (0.006, 1.1)\}$), indicating that the simpler parameterisation adequately captures the relationship between depth and observed POC wt% by bin-class. The reason for this is that BIOGEM provides a depth 1195 dependent POC flux and partitioning between the two fractions (Fig. 10). The shallowest bin-class (between 0 and 1000m) represents an exception, as OMEN-SED tends to overestimate POC preservation for this depth class. However, this could also be related to the regridding of the original POC distribution pattern of (Seiter et al., 2004) on to the SEDGEM grid, as some data grid-cells with 1200 higher POC wt% on the continental margin are lost due to the restricted SEDGEM resolution (compare Section 4.2). Overall, using this parameterisation, a relationship where the labile POC fraction degrades not more than 1.5 times faster than the refractory fraction fits the Seiter et al. (2004) data better than a larger spread between both POC pools (i.e. $x > 2.0$). We discuss later the implications of collapsing the k values in this specific calibration for long-term, geological carbon preservation.

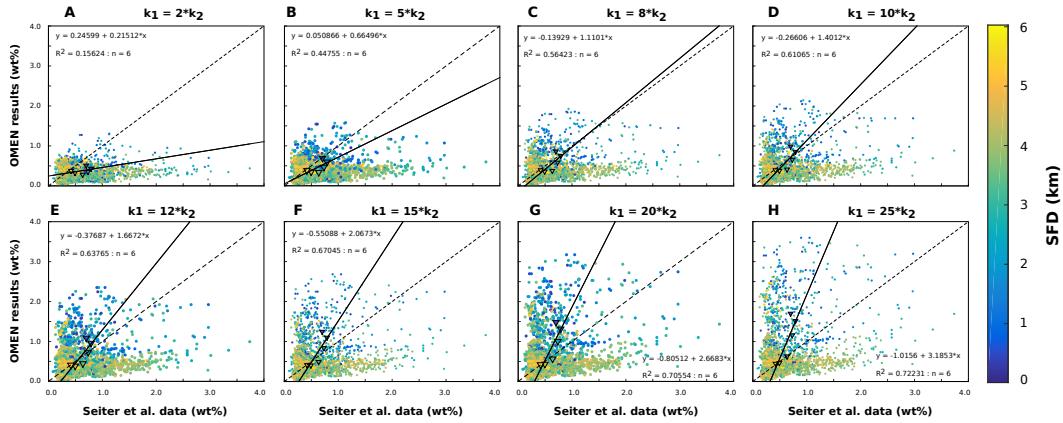


Figure 13. Crossplots comparing modelled and observed mean POC wt% in the upper 5 cm of the sediments using the relationship of Boudreau (1997) and the assumptions of Eq. (54) and (55) to calculate k_1 and k_2 . Data-points are binned into 6 uniform depth-classes of 1000m, each class is represented by a triangle. Grid-points with more than 4.0 POC wt% are not shown.

Next the relationship of Boudreau (1997) and the assumptions of Eq. (54) and (55) are used to 1205 calculate k_1 and k_2 . In Figure 13 (A-H) the relation between the two degradation rate constants (Eq. (55)) is changed globally, thus independent of the seafloor depth. The crossplots show that it is not possible to achieve a solution where all bin-classes fall onto, or close to, the 1:1 line. Also, the slope of the regression lines are generally much larger or smaller than 1.0 (with the exception of Figure 13C), indicating that the relationship between depth and observed POC wt% by bin-class 1210 is not adequately represented by the model. The R^2 values are strictly monotonically increasing for increasing x because a depth-dependency is artificially imposed for the modelled POC wt% through the relation between k_1 and k_2 . When looking at the individual bin-classes it can be seen that shallow ocean depths are better represented by smaller differences between k_1 and k_2 (e.g. $k_1 = 5 \cdot k_2$ for SFD < 1000m, Figure 13B), and the deep ocean by a larger spread (e.g. $k_1 = 25 \cdot k_2$ for SFD > 3000m, Figure 13H). These results reflect the preferential degradation of more reactive organic matter types (Wakeham et al., 1997; Lee et al., 2000) and thus the change in the distribution functions of OM reactive types for different OM ages (Fig. 10C). In the shallow ocean bulk POC consists of fresher organic matter types on average and is therefore generally more reactive overall (i.e. higher k_{app} due to higher w in the model) as in the deep ocean. In addition, OM at 5cm sediment depth in the deep 1215 ocean is generally older as in the shallow ocean due to lower burial rates, therefore more reactive types are affected by degradation and a larger spread between k-values is needed to capture these dynamics (compare Fig. 10C).

Departing from our theoretical considerations (see discussion of Fig. 10C), we use these observations to create a depth dependent relationship between the two degradation rate constants, where x in Eq. (55) is a function of SFD and takes values of $x = 5$ for SFD < 1000m, $x = 8$ for 1000m \leq 1220

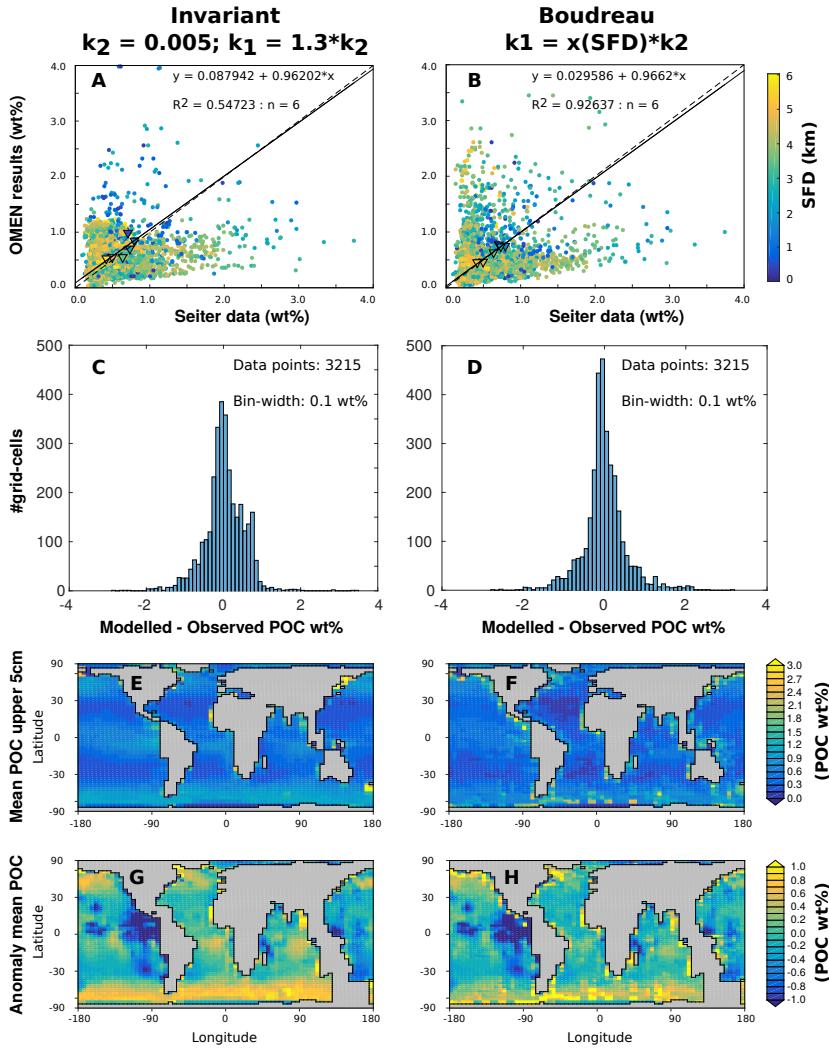


Figure 14. Mean POC concentrations in the upper 5cm of the sediments ($\text{POC}_{5\text{cm}}$) using the globally uniform model ($k_2 = 0.005$, $k_1 = 1.3 \cdot k_2$) and the depth dependent parameterisation $k_1 = x(\text{SFD}) \cdot k_2$ adapted from Boudreau (1997). A+B: Crossplots as shown before in Fig. 12 and 13. C+D: Histograms of the residuals of modelled minus observed $\text{POC}_{5\text{cm}}$. E+F: $\text{POC}_{5\text{cm}}$ as calculated with OMEN-SED. G+H: Difference map of $\text{POC}_{5\text{cm}}$ as calculated with OMEN-SED and interpolated data from Seiter et al. (2004).

SFD < 2000m, $x = 12$ for $2000m \leq SFD < 3000m$ and $x = 25$ for $SFD \geq 3000m$ for the 6 SFD bin-classes, respectively. In this depth dependent approach all bin-classes are close to the 1:1 line and the resulting regression model accounts for 92.6% of the variance of the modeled POC wt% around the observed mean of the bin-classes (Figure 14A). Furthermore, the slope of the regression line
1230 (0.9662) indicates that the relationship between depth and observed POC wt% for the bin-classes is well represented by the model. The histograms (Fig. 14C+D) visualize the difference between modelled and observed mean POC concentrations and demonstrate the high density of data points close to the 1:1 line. For the depth dependent approach, 92.5% of the cGENIE grid-cells show a difference between modelled and observed POC concentration of less than 1.0 POC wt%; in 79.9%
1235 of the grid-cells, the difference is less than 0.5 POC wt% (for the globally uniform approach the percentages are 95.37% and 70.95%, respectively).

Both experiments reproduce minimal POC concentrations in the subtropical gyres and generally higher concentrations along the continental margins (Fig. 14E+F). Both experiments, however, underestimate mean POC wt% in the surface sediments of the equatorial east Pacific and overestimate
1240 POC concentrations in the North Pacific and Southern Oceans (Fig. 14G+H). The depth dependent approach of Boudreau (1997) shows more spatial variability in POC preservation than the other parameterisation. In general, implementing lower, anaerobic degradation rate constants when bottom water oxygen concentrations fall below a threshold value could potentially improve the simulation of higher POC concentrations in areas with high POC input to the sediments (Palastanga et al., 2011).

1245 **can you quickly run the simulation with the new stopolsky set for me??? Not for this paper, but for illustration and potentially review?**

4.3 Modelled fluxes and sediment characteristics

why not plot the O2 observations from the global hypsometry figure and/or stopolsky as dots
on the map?? Or you could also show the Seiter ODU map for oxic degradation rates. I also
1250 have seen globals maps of O2 consumption- will try to digg this out. Should be quickly done as all the data is compiled.

For the spatially uniform experiment A ($(k_2, x) = (0.005, 1.3)$) modelled SWI-fluxes and sediment characteristics are shown in Figure 15. Modelled total POC degradation (POC_{degr}) rates in the upper sediments decrease from the shelves to the deep sea by up to 2 orders of magnitude (Fig. 15B).
1255 This is in agreement with data from the literature (e.g. Middelburg et al., 1993, 1997; Burdige, 2007) and other model results (e.g. Thullner et al., 2009) which indicate that the highest degradation rates in marine sediments are found in the coastal ocean ($SFD < 200m$). Oxygen fluxes into the sediments (Fig. 15C) range from 0.0 for the deep ocean and sites without OM deposition to values of about 300 $\mu\text{mol cm}^{-2}\text{yr}^{-1}$ for the shallow ocean with the highest POC degradation rates. Influx of SO_4^{2-} into the sediments is rather low (between 0.0 and 23.9 $\mu\text{mol cm}^{-2}\text{yr}^{-1}$) because in OMEN-SED
1260 95% of produced H_2S is reoxidised to SO_4^{2-} , therefore sulfate reduction is mainly driven by in situ

$$\text{Boudreau } k_1 = x(\text{SFD}) \cdot k_2$$

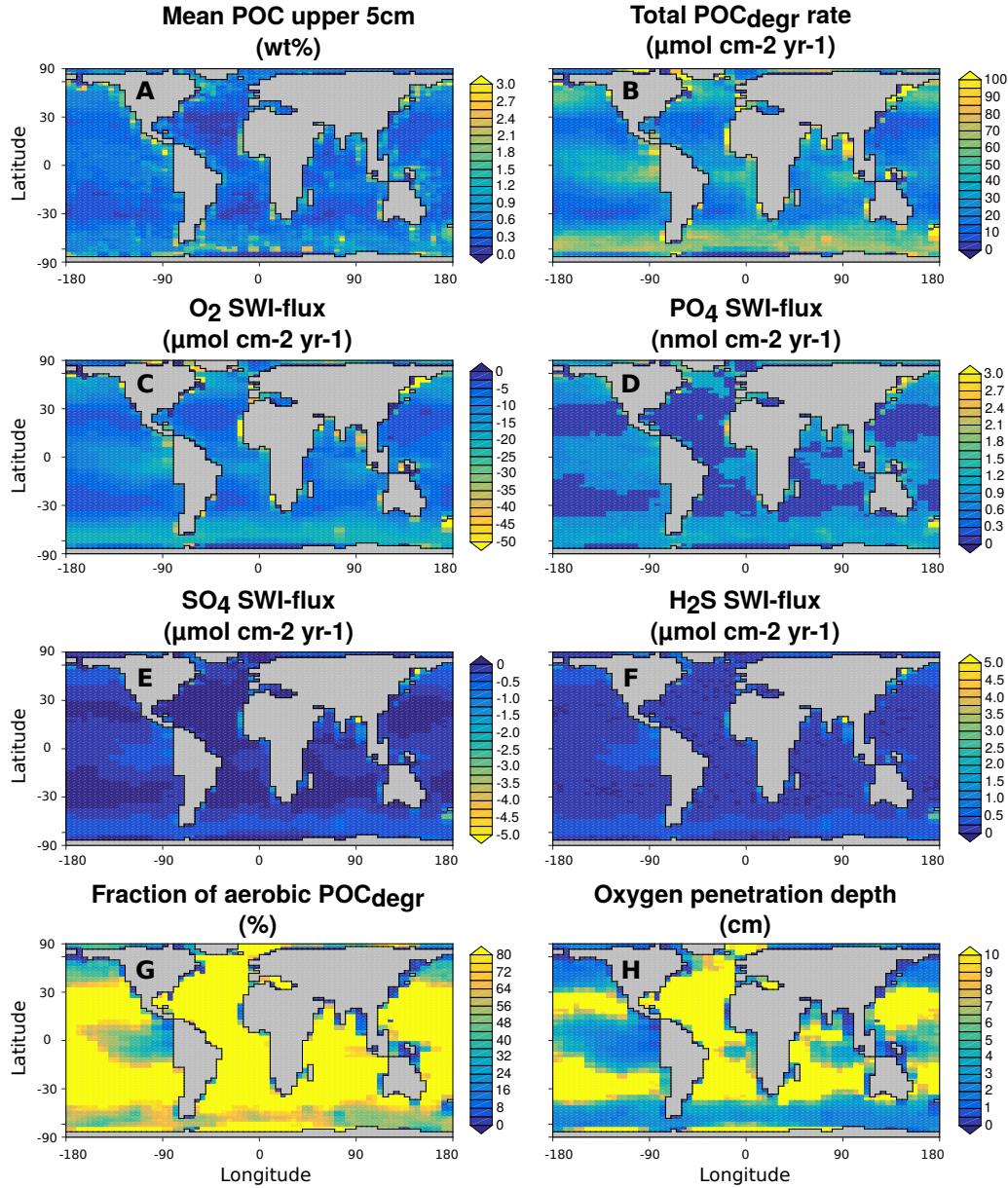


Figure 15. Sediment characteristics related to POC degradation and oxygen consumption for the depth dependent parameterisation after Boudreau (1997) with $k_1 = x(\text{SFD}) \cdot k_2$. Total POC_{degr} rate and fraction of aerobic POC_{degr} are the respective values for the first 5cm in the sediments.

sulfide oxidation. However, in general the coupled model fluxes fall well within the ranges predicted by the stand-alone global hypsometry experiments (O_2 between 0.0 and $800 \mu\text{mol cm}^{-2}\text{yr}^{-1}$ and SO_4 between 0.0 and about $300 \mu\text{mol cm}^{-2}\text{yr}^{-1}$, compare Section 3.3). In accordance with the total POC degradation rates the release of PO_4 shows a maximum value of $8.12 \text{ nmol cm}^{-2}\text{yr}^{-1}$ on the shelves (Fig. 15D). The relative contribution of aerobic POC degradation in the upper sediments increases from the shelves to the deep sea (Fig. 15G) which is also consistent with estimates from Thullner et al. (2009) who found that oxygen is responsible for less than 10% of POC_{degr} at 100m SFD and for more than 80% in the deep sea. The oxygen penetration depth in OMEN-SED increases from values below 1cm at the shelves to more than 10cm in the deep ocean (Fig. 15H and 16). Small oxygen penetration depths of a few millimetres are typical for bioturbated sediments in the coastal ocean (e.g. Wenzhöfer and Glud, 2002) and the oxygen penetration depth has been shown to increase rapidly with SFD to more than 10cm in the deep sea (Meile and Van Cappellen, 2003; Glud, 2008). Fischer et al. (2009) even found cores along a transect in the South Pacific gyre being oxygenated over their entire length (up to 8m) which is consistent with our model results (not shown). Simulated mean oxygen penetration depths for the 6 depth bin-classes also agree well with observations compiled by Meile and Van Cappellen (2003, Fig. 16).

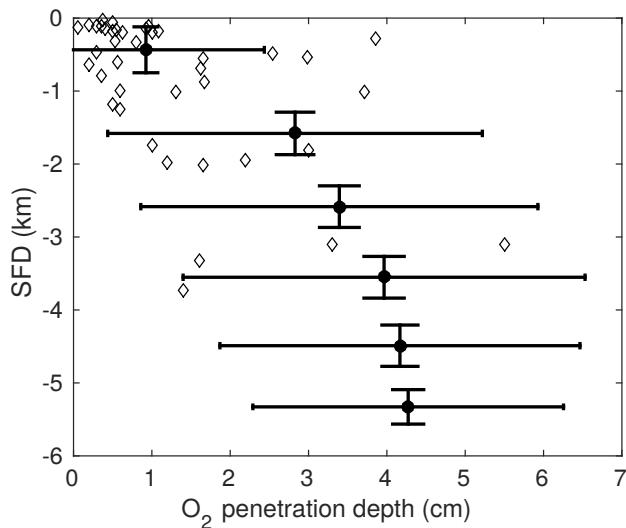


Figure 16. Seafloor depth versus O_2 penetration depth for the depth dependent parameterisation after Boudreau (1997) with $k_1 = x(\text{SFD}) \cdot k_2$. Diamonds represent the observations compiled by Meile and Van Cappellen (2003). Circles are the mean model results for the 6 SFD bin-classes (with standard deviations). Grid-cells where the entire sediment column is oxic (i.e. $z_{\text{ox}} = 100\text{cm}$) are not considered in these statistics (17, 32, 102, 300, 477 and 307 cells for the 6 bin-classes, respectively).

5 Scope of applicability and model limitations

State-of-the art numerical models representing the full complexity of the diagenetic processes typically perform well 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 to oxic degradation with a limited number of explicit pore water tracers. 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 practical and legitimate compromise 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 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 extreme climate events such as OAEs. **TODO: Sandra please check discussion of geological carbon burial:** Furthermore, as OMEN-SED models the concentration of organic matter until 1m sediment depth also questions concerning long-term, geological organic carbon burial can be addressed. Therefore, in order to preserve parts of the organic matter in the deeper sediments, the degradation rate constant for the refractory OM pool has to be scaled down. The resulting larger difference between degradation rate constants can be interpreted as being needed to capture the broader range of OM reactivities degraded over the entire sediment column (see Fig. 10). Instead, more collapsed degradation rate constants are needed to model OM preservation in the upper sediments, such as the first 5 centimetres as shown in Section 4.2.2.

On more regional scales OMEN-SED can be coupled to local models of 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

1315 oxygen and nutrient exchange fluxes are explicitly modelled and depend on reoxidation of reduced substances which causes a substantial part of oxygen consumption in these environments.

However, the model presented here, despite being more complete than previous analytical models, is inevitably 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
1320 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
1325 changes in boundary conditions such as input of OM or bottom water oxidation state on degradation and burial dynamics, for instance during OAEs. Yet, OMEN-SED is not able to predict the system response to short-term or seasonal variations of boundary conditions. In future versions, non-steady state conditions could be approximated by implementing a relaxation between different steady states, similar to the schemes used in Ruardij and Van Raaphorst (1995) and Arndt and Regnier (2007),
1330 thus enabling an application of the model to systems characterised by higher variability in boundary conditions. In addition, the unavoidable assumption of depth invariant porosity limits the correct calculation of the sediment-water interface flux of dissolved species as in reality porosity decreases with sediment depth.

Furthermore, the global parameterisation of the sensitive model parameters (OM degradation rate
1335 constants and secondary redox parameters) is not straight forward. A comparison between simulated OM contents and observations indicates that depth dependent k-f relationships provide the best fit (Section 4.2.2), confirming more theoretical considerations regarding the different time and reactivity scales that need to be considered (see Section 4.2). With respect to γ -values, model simulations along the global hypsometry (Section 3.3) have shown that high γ -values generally capture the main
1340 SWI-flux features, but have also highlighted that slightly lower γ -values would result in a better fit of SWI-fluxes to observations of the shallow ocean. In the future, fully formulated, multi-component diagenetic models could be used to derive transfer functions that would allow quantifying γ -values as a function of environmental forcings, such as organic matter degradation rates. Currently, no general theoretical framework exists to quantify these parameters on a global scale. As a consequence,
1345 attention should be devoted to choosing their values and sensitivity studies over plausible ranges are recommended.

Furthermore, the current version of OMEN-SED does not yet resolve the full range of important biogeochemical species, thus limiting its applicability. Manganese and iron dynamics are not included and as such OMEN-SED is not able to simulate all processes important in coastal marine
1350 environments and highly accumulating upwelling regions. In particular the lack of iron limits the scope of applicability of the model, especially in anoxic systems characterized by high Fe oxide

inputs, where redox driven iron dissolution-precipitation reactions induce a high internal recycling of the sedimentary Fe pool. This can cause problems when modelling H₂S and PO₄ profiles in such environments as their concentrations are affected by these metal ions (compare Section 3.2). Therefore, already planned future work will focus on an explicit description of iron. Finally, although the model also simulates DIC and alkalinity production and, thus, has the potential to predict pH profiles within the sediment, a major limitation at this stage is the lack of an explicit description for CaCO₃ precipitation/dissolution coupled to OM decomposition, which also controls the inorganic carbon system (Krumins et al., 2013).

1360 6 Conclusions

Andy didn't read. As seemed to be to long and repreton of previous discussion. He says, shorten by 25%.

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 analytical model to explicitly represent oxic degradation, denitrification, sulfate reduction and implicitly methanogenesis, as well as the reoxidation of reduced substances produced during organic matter degradation. Pore water tracers include O₂, NO₃, NH₄, SO₄, H₂S, DIC and ALK and the solid phase includes two degradable fractions of organic matter, Fe-bound P and authigenic Ca-P minerals.

An extensive sensitive analysis, based on the novel density-based PAWN method (Pianosi and Wagenner, 2015) emphasises the key role of OM degradation rate parameters and thus highlights the need for the development f for th are the most sensitive parameter. In addition, under anoxic conditions secondary redox parameters exert an important control on related SWI-fluxes of SO₄, H₂S, NH₄ and alkalinity. We have shown that the performance of OMEN-SED is similar to that of a fully formulated, multi-component numerical model and that the new analytical model is able to reproduce observed pore water profiles across very different depositional environments and captures observed large scale patterns of surface sediment organic matter contents Seiter et al. (2004) as well as SWI-fluxes, oxygen penetrateion depths and biogeochemical reaction rates. Furthermore, as the major parts of the global carbon cycle are included in the new model it is well suited to examine the role of sediments for global biogeochemical cycles and climate and for exploring feedbacks within the Earth system in response to a wide range of perturbations and over various timescales.

7 Code Availability

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

Acknowledgements. We thank Claire Reimers and Filip Meysman for supplying the dataset from the Santa Barbara Basin, as well as Martin Thullner and Jack Middelburg for making the BRNS results and observations included in Section 3.3 available. We are also grateful to Andy Dale for providing the global flux database used in Section 3.1 and acknowledge the British Oceanographic Data Centre for the OMEXDIA dataset used
1390 in Section 3.2. We are also grateful to Francesca Pianosi for helpful insights into sensitivity analysis. DH is supported by a graduate teaching studentship by the University of Bristol. SA is supported by funding from the European Unions Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 643052 (C-CASCADES). AR acknowledge funding from the EU grant ERC-2013-CoG-617313.

TODO: add for Stuart and Pierre!

1395 **Appendix A: Reaction Network**

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	$(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + \frac{(\text{4x}+3\text{y})}{5}\text{NO}_3^- \rightarrow \frac{(2\text{x}+\text{4y})}{5}\text{N}_2 + \frac{(\text{x}-3\text{y}-10\text{z})}{5}\text{CO}_2 + \frac{(\text{4x}-3\text{y}-10\text{z})}{5}\text{HCO}_3^- + \text{zHPO}_4^{2-} + \frac{(\text{3x}+3\text{y}+10\text{z})}{5}\text{H}_2\text{O}$
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	$\text{PO}_4^{2-} \xrightarrow{K_{\text{P}\text{O}_4}^{\text{I},\text{II}}} \text{PO}_4^{2-}(\text{ads}); \quad \text{PO}_4^{2-} \xrightarrow{k_s} \text{Fe-bound P} \xrightarrow{k_m} \text{PO}_4^{2-}$
CFA precipitation	$\text{PO}_4^{2-} \xrightarrow{k_a} \text{CFA}$

Appendix B: Sensitivity Analysis

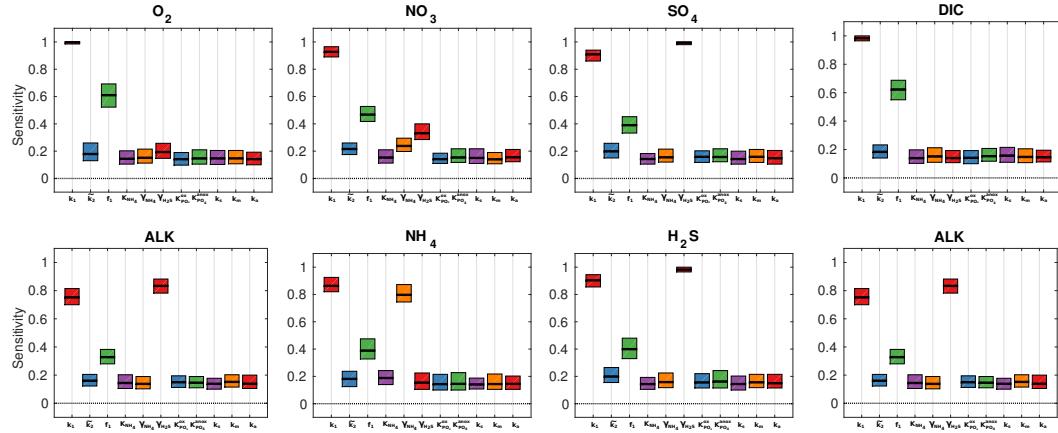


Figure 17. Move to Appendix Box plot of parameter sensitivities for the calculated SWI-fluxes for the 4000m oxic condition. Average sensitivities (black lines) and 90% confidence intervals using $N = 11200$ model evaluations and $N_{boot} = 100$ bootstrap resamples.

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