Replies to Anonymous Referee #1 on "OMEN-SED 0.9: A novel, numerically efficient organic matter sediment diagenesis module for coupling to Earth system models"

1. Comment:
Model formulation - The model assumes no overlap of mineralization reactions with different terminal electron acceptors, and assumes that secondary redox reactions can be collapsed onto the interfaces between different mineralization zones (p.9). This is probably ok in environments typically encountered at greater water depth, but there is ample evidence of 'overlapping' mineralization pathways in surficial sediments, in particular in permeable or bioturbated settings.

Response:
We agree with the reviewer that different biogeochemical zones can overlap. However, as stated in the text, OMEN-SED is designed for the coupling to ESMs and its formulation is thus first and foremost guided by achieving numerical efficiency while retaining biogeochemical reality. As summarized in the manuscript, there are essentially two approaches that can be used to describe biogeochemical processes in models. The first approach solves the general diagenetic equation numerically on a regular or irregular grid and biogeochemical zonation emerges in response to inhibition terms allowing a certain degree of overlap between biogeochemical zones. This approach is highly flexible and thus preferable. Yet, its excessive computational demand unfortunately renders its application within a three-dimensional Earth System Model framework impossible. On the other hand, analytical models that subdivide the sediment into distinct biogeochemical zones are computationally efficient and thus ideally suited to describe diagenetic dynamics in ESM.

By their very nature, analytical models do not allow for overlapping biogeochemical zones. As stated in the manuscript, this is a simplification. However, we disagree with the reviewer that this simplification would *per-se* prevent the application of such analytical approaches in shallower aquatic environments. In fact, OMEN-SED builds on a number of analytical models that were developed to investigate local, coupled nutrient and oxygen cycles in coastal sediments (e.g. Billen, 1982; Goloway and Bender, 1982; Jahnke et al., 1982; Slomp et al. 1996). Similar approaches were later successfully applied from oxic to anoxic sediments and at the regional coastal ocean scale (e.g. Ruardij and Van Raaphorst, 1995; Tromp et al., 1995; Gypens et al., 2008). In particular, Gypens et al., (2008) points out that accounting for secondary redox process in the boundary condition induces little error as: "Using a numerical model, Soetaert et al. (1996) showed that this re-oxidation mainly occurs at the oxic-anoxic transition interface."

Finally, the good agreement between OMEN-SED and the results obtained with a fully formulated numerical RTM (compare Section 3.3, allowing for overlapping TEA use) shows that this is not a critical limitation of OMEN-SED - even for shallow sediments.

We included a little paragraph on this in the limitation section (pg 54 lines 3-8):
"Furthermore, by their very nature, analytical models do not allow for overlapping biogeochemical zones or depth dependent porosity, which introduces a certain error to simulation results. However, the energy yield dependent sequence of oxidants is generally valid (e.g. Hensen et al., 2006) and the good agreement between OMEN-SED and the results obtained with a fully formulated numerical RTM (allowing for overlapping TEA use and depth dependent porosity, Section 3.3) shows that these are not critical limitations of OMEN-SED - even for shallow sediments."

2. Comment:

In the denitrification layer, all N goes to N2. However, in the suite of processes involved in the breakdown of organic matter, ammonium is produced as well, even if nitrate serves as TEA. Ammonium produced in the denitrification zone would need to be accounted for at the transition to the oxic zone as well, which may further reduced the O2 penetration depth.

Also, processes such as DNRA or anammox are not included, even though literature surveys (e.g. Dalsgaard et al. 2005) indicate that anammox is relevant at shallower water depth.

Response:

Anammox is implicitly included in the model. The organic nitrogen released during the denitrification process is assumed to be directly oxidized with nitrite to N_2 through a coupling between denitrification and anaerobic ammonium oxidation.

However, we would like to stress again that OMEN-SED is a benthic model designed for the coupling to ESMs. Most ESMs do not even explicitly resolve N-dynamics. In addition, OMEN-SED is a system/global scale model that aims to resolve the most pertinent biogeochemical dynamics on a global scale (including a paleoenvironmental context) and estimate the main SWI-fluxes and not a model that aims at resolving specific local scale dynamics. Even most local scale RTM applications do not resolve DNRA and anammox explicitly. However, OMEN-SED could be easily adapted to explicitly resolve these processes if the specific application requires their representation (e.g. coastal ocean).

We included a sentence on this in the Section 2.2.3 "Nitrate and Ammonium" (pg. 12, lines 22-24):
"*Anaerobic ammonium oxidation (anammox) is implicitly included in the model. The organic nitrogen released during denitrification is assumed to be directly oxidized with nitrite to N2 through a coupling between denitrification and anammox.*"

3. Comment:

Methane oxidation: All methane is assumed to be oxidized anaerobically. Is this done for simplicity? Is there no leakage term (gamma_CH4; comparable to incomplete sulfide and ammonium oxidation) because methane escaping from the anoxic zone is assumed to be removed by aerobic methane oxidation?

Response:

First, there is a leakage term γ_{CH4} comparable to incomplete sulfide and ammonium oxidation (see Table 10, SO_4 boundary conditions 5 and 8.2; H2S boundary conditions 5 and 9). Second, it can be safely assume that almost all CH4 is oxidized anaerobically in the sediments (e.g. Reeburgh (2007) and Hinrichs & Boetius (2002) estimated > 90%) - except for active (very localized) sites and slope failure, which can, in theory, be accounted for through the gamma term.

We included this sentence in the Section 2.2.4 "Sulfate and Sulfide" (pg. 14 line 10 – pg 15 line 1):
"*It can be safely assumed that almost all CH4 is oxidized anaerobically in the sediments (e.g. Reeburgh (2007) suggests up to 90%)- except for active (very localized) sites and slope failure, which can, in theory, be accounted for through the γ_{CH4} term.*"

4. Comment:

Methanogenesis: the 1/2 methane to DIC ratio seems to imply acetoclastic methanogenesis. What evidence is there to ignore hydrogenotrophic methanogenesis?

Response:
We thank the reviewer for this valid point. However, we are not aware of an approach that would allow splitting the two pathways in quantitative terms in a global context. Following the approach of Jourabchi et al. (2005), we assume a ½ methane to DIC ratio (i.e. the acetoclastic pathway). However, OMEN-SED could be easily adapted to represent hydrogenotrophic methanogenesis globally (i.e. by adapting the stoichiometric factor by a value depending on the specific pathway).

5. Comment:
For a globally applicable model, the lack of CaCO3 dissolution is an obvious issue. Thus, can you expand on what problems the modeling of CaCO3 dissolution would cause (page 18)? Is this linked to the calculation of pH? Why can pH (and then carbonate) not be estimated from DIC and alkalinity?

Response:
In general, the coupling between multiple reaction-transport equations (i.e. strongly coupled biogeochemical dynamics) make finding an analytical solution difficult or even impossible. Calcium carbonate dissolution is kinetically controlled by the amount of $CaCO_3$ and thermodynamically controlled by the porewater concentrations of calcium ion, Ca^{2+}, and carbonate ions, CO_3^{2-}. The reaction terms of the $CaCO_3$, (the Ca^{2+}), the DIC and balance equations would thus depend on the concentrations of $CaCO_3$, Ca^{2+} and CO_3^{2-} (DIC, pH/Alk). This set of strongly coupled equations does not have a simple analytical solution. Finding a solution to the problem requires some creativity and a number of assumptions that need to be independently tested and validated. This task thus requires some additional work and model development that go beyond the scope of this first model description paper centered on organic carbon and nutrients. However as pointed out in Section 5 "already planned future extensions of OMEN-SED include an explicit description of carbonate dissolution and iron."

6. Comment:
Is there no P sorption on iron oxides below the oxic zone? If so, why?

Response:
We here follow the approaches of Slomp et al. (1996) and Gypens et al. (2008) who both assume that HPO_4^{2-} is released due to the reduction of Fe oxides throughout the reduced sediment (i.e. starting at zox).

7. Comment:
Why does some of the ammonium created below the oxic zone escape oxidation, but oxidation of ammonium to nitrate is complete in the oxic zone?

Response:
This is a misunderstanding: There is also leakage term (γ_{NH4}) for ammonium to nitrate oxidation in the oxic zone (see Eqs. 12, 15 and 16).

8. Comment:
A fraction of the sulfide produced is assumed to escape complete oxidation. Does this mimicking the effect of precipitation with iron, rather than escape from the sediment?

Response:
In the reviewed version of OMEN-SED, this fraction mimicked the escape from the sediment.
However, in response to the first critical comment of reviewer 3 (K. Wallmann) we made the following
changes to OMEN-SED:
When coupled to an ESM the γ_{H2S} value (fraction of H2S that is oxidised) becomes dependent on the
bottom water oxygenation state. That is, γ_{H2S} = 1.0 for oxic bottom waters and a user defined value γ_{H2S}
<1.0 for anoxic bottom waters.
In addition, we introduce another parameter (γ_{FeS}) representing the fraction of sulfide that is
precipitated as pyrite (i.e. $0.0 <= \gamma_{FeS} < 1 - \gamma_{H2S}$) in the sulfate reduction zone. γ_{FeS} is an auxiliary
parameter used as a fix until iron is explicitly represented. We thus assume that a user-defined fraction
of the produced H2S precipitates as FeS(FeS2) in the sulfate reduction zone. If a user does not want to
make any assumptions about FeS precipitation – it can be set it to 0.

The text, tables and equations (for O_2, SO_4, H_2S and alkalinity) are changed accordingly. The presented
results have not been changed and we note that γ_{FeS} = 0.0 for all simulations, as we do not want to
make any assumptions. About FeS precipitation.

Changes made in:
2.2.2 Oxygen: Table 3 boundary condition 4.2 + Text pg. 12 lines 14-16:
" *It is assumed that respective fractions (γNH4 and γH2S) are directly reoxidised at the oxic/anoxic*
*interface and the remaining fraction escapes reoxidation **(or is precipitated as pyrite, γFeS)**.*"

2.2.4 Sulfate and Sulfide: Equations 23 + Table 5 boundary condition 5) + (pg. 14 lines 9-10):
"*In the sulfidic zone a defined fraction of sulfide, γFeS , can be precipitated as pyrite (in*
the presented simulations γFeS = 0.0 as we do not want to make any assumptions about pyrite
precipitation)."

2.2.7 Alkalinity: Table 8 boundary condition 5)
Text (pg. 20 lines 5-7):
" *In addition, the effect of secondary redox reactions, such as nitrification, sulfide and methane*
*oxidation**, as well as pyrite precipitation,** are implicitly accounted for in the boundary conditions. *"

Text (pg. 20 lines 21-23):
"*The decrease of alkalinity due to oxidation of reduced species produced in the anoxic zones **and due***
***to the precipitation of pyrite** (with stoichiometry ALK^{NIT} , ALK^{H2S} and **ALK^{FeS}**) is implicitly taken into*
*account through the flux boundary condition at zox (Table 8 Eq. 5). *"

2.4.2 Stoichiometries and reaction parameters: (pg. 27 lines 19-23):
"*However, when coupled to an ESM γH2S becomes dependent on the bottom water oxygenation state.*
That is, γH2 S = 1.0 for oxic bottom waters and a user defined value γH2S < 1.0 for anoxic bottom
waters. The parameter γFeS represents the fraction of sulfide that is precipitated as pyrite in the
sulfidic zone. The majority of H2S produced by sulfate reduction is reoxidised, but it is estimated
that ∼ 10 − 25% is eventually buried as pyrite (Bottrell and Newton, 2006). However, this fraction can
vary significantly over geological timescales (Berner, 1984). If a user does not want to make any
assumptions about pyrite precipitation – it can be set to 0 (as in the results presented here)."

We also added pyrite precipiation to Table 1 and A1 in the Appendix.

9. Comment:
Iron cycling is not represented explicitly but some of the effect of iron cycling is parameterised. With its effect on sulphur cycling, P sorption and C mineralization (metal reduction can be the main mineralization pathway, see e.g. Canfield et al. 1993), I don't fully understand the reason for doing so (apart from the added complexity when dealing with another solid phase).

Response:
OMEN-SED will be mainly applied on a system/global scale, coupled to an ESM, where iron reduction has been shown to play just a minor role (i.e. about 3% of the global carbon mineralization rate Thullner et al. (2009); or compare Archer et al. (2002) Fig. 9D). Also, Fe-dynamics are generally not explicitly resolved in ESMs. However, as stated in Section 5, "already planned future extensions of OMEN-SED include an explicit description of iron."

10. Comment:
transport processes: A 1D diffusion/bioturbation model clearly faces major challenges in the coastal ocean, where sediments one predominantly are permeable. And setting fir=1, implying no bioirrigation, is also a very strong assumption.

Response:
Most sediments on the globe are non-sandy, therefore we had decided to neglect sandy sediments. However, the bioirrigation coefficient has been changed and is now represented by the empirical relationship with seafloor depth derived by Soetaert et al. (1996): fir = Min{1; 15.9 · z−0.43 }. We also added to the limitations section that our approach might not be appropriate to simulate non-accumulating permeable sands.
The text has been changed to (pg. 25 lines 21-23):
"Soetaert et al. (1996) derived an empirical relationship between fir and seafloor depth (fir = Min{1; 15.9 · z −0.43 }) based on observations from Archer and Devol (1992) and Devol and Christensen (1993) which is used in OMEN-SED"
And in the limitations section (pg. 54 lines 17-18):
"Also note that our 1-D diffusion/bioturbation model might not be appropriate to simulate non-accumulating permeable sands of the coastal ocean."

11. Comment:
The 2G model is a sensible choice. Model parameterisation is a general concern (page 3, line 30), but I suggest to cite some promising new approaches to address this issues such as presented by https://www.biogeosciences-discuss.net/bg-2017-397

Response:
We added the suggested reference to the manuscript (Section 4.2 "Parameterising the OM degradation rate constants in a global model"). However, the suggested approach is based on empirical relationships derived from modern ocean data, as well as strong assumptions. Its applicability to past and future oceans is thus questionable and the problem of parameterizing organic matter reactivity remains for these applications.

Added sentence (page 45 lines 19-22):
"Stolpovsky et al. (2015, 2017) suggested empirically derived approaches to constrain degradation rate constants in a 2G model on a global scale. These approaches are derived from present-day observations and might help constrain parameters for present-day applications. However, the problem

*of constraining 2G degradation model parameters remains for largely different environmental
conditions encountered in the past that could also prevail in the future (Arndt et al., 2013)."*

12. Comment:
site comparison case studies: - Table 13: fix the depths for the SB and IM sites (SB is the 585m site ...).

Response:
Changed.

13. Comment:
site comparison case studies: - Why are the stoichiometric factors set to default values when
Epping et al. provide the C/N ratio of the surface sediment?

Response:
We intended to do as little site tuning as possible in order to test how the default model performs for
these sites and to be able to evaluate the performance of the model in data poor areas.

14. Comment:
site comparison case studies: - If a non-local exchange mechanism resulting from bioirrigation is
invoked for the Canyon site, what is the source of the high ammonium (and DIC) leading to the
observed increase in concentration at depth?

Response:
As suggested by the papers describing the study area (van Weering et al., 2002; Epping et al., 2002), we
assume it is a result of degradation of organic matter which has been delivered from the shelf to the
ocean interior.

15. Comment:
- global transect case study: I don't see the value of the 5% reoxidation case. This is simply unrealistic
for the conditions considered here. A possible explanation why lower gammas are giving better match
to the data in the shallow sites is that under those conditions, the conceptual model of a vertical
separation of reaction zones is more and more violated, so the gamma become a 'fudge-factor' to
account for this (see also above comments about the coastal ocean).

Response:
We agree with the reviewer, that gamma is a fudge factor. It accounts for all the processes that may
enhance escape from re-oxidation but are not explicitly resolved. However, we would reject the
comment that this is a problem with assuming strict zonation. We would argue that this reflects the
more intense dynamics in shallow ocean regions and that the increased escape is due to enhanced
macrofaunal activity.
We also want to stress again, that similar analytical approaches (with distinct redox zones) have given
good results for coastal/estuarine sediments (e.g. Billen, 1982; Goloway and Bender, 1982; Jahnke et
al., 1982; Ruardij and Van Raaphorst, 1995; Slomp et al., 1996; Gypens et al., 2008).

16. Comment:
- link to cGENIE: - on page 43, it says tha if fPOC is computed to be > 1 (more than 100% is preserved), then this is discarded and all POC is remineralized. Imposing constraints is fine, but what is the rationale for jumping from >100 to 0 % preservation?

Response:
The result fPOC > 1.0 does not imply that 100% preservation is a realistic result. It just means that the OMEN-SED solution does not provide sensitive values. Therefore, its results are discarded and a reflective boundary is assumed (a reflective boundary is a better choice than the conservative as in most cases the majority of OM is degraded during early diagenesis). However, this is just a safety measure and has not occurred in our experiments so far.

17. Comment:
- link to cGENIE. Page 44 discusses the challenges in applying the model in such a setting. In addition, deposition fluxes may change over time. At what point is the steady state assumption on the POC profile still valid under such settings? This is addressed summarily at of the bottom of page 54. However, I think it is important to lead with this, before interpreting the data-model comparison.

Response:
As suggested by the reviewer the steady-state assumption is addressed earlier in the text.
We added the following sentence to Section "4.2 Parameterising the OM degradation rate constants in a global model" (pg 45, lines 12-13):
"Furthermore, by assuming steady-state in OMEN-SED we assume that deposition fluxes of OM are constant over the characteristic timescales of the reaction-transport processes."

18. Comment:
On p.54 it says "In theory, its scope of applicability thus ranges from the regional to the global and from the seasonal to the millennial time-scale. " - in the following para-graph they recognize that "This steady-state assumption is only valid if the variability in boundary conditions and fluxes is generally longer than the characteristic timescales of the reaction-transport processes. "
I recommend to be a little more cautious in the application of the model, since I am not convinced that violations of assumptions underlying the conceptual model and non-steady state effects can be ignored. The model clearly requires substantial tuning. It is clear that the authors are aware of the shortcomings, and they discuss that the model may not be adequate to assess seasonal patterns (and one can think of additional set-tings, where fluxes vary over timescales intrinsic to the POC profile in the top 50cm of sediment modeled here). My concern is that they largely ignore them in their appli-cation, before acknowledging them in the discussion.

Response:
As stated in the manuscript, OMEN-SED is first and foremost designed for the coupling to ESMs. More specific tuning/adaptation is needed if OMEN-SED is used for specific, regional environments, e.g coastal environments.
However, we would like to re-emphasize that the current version of OMEN-SED performs well across different depositional environments ranging from the coastal to the deep ocean as evidenced by the

model-data and model-model comparison. As outlined in the "Scope of applicability and model limitations" section additional developments, such as adapting pseudo-transient dynamics will further facilitate the application of OMEN-SED to more dynamic environments. A number of benthic models specifically designed for coastal/estuarine environments (e.g. ERSEM Ruardij and Rapphorst et al., 1997; Arndt and Regnier, 2007) have successfully applied such an approach. We therefore maintain our point of view that, in theory, the scope of applicability of OMEN-SED also includes coupling to system-scale estuarine and/or coastal ocean models..

19. Comment:
I also suggest to tone down the finding that "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). " The age-reactivity relationship is pretty well established, without confirmation by this modeling effort.

Response:
This is a misunderstanding. We do not argue that model results "confirm" the reactivity-age link. We wanted to emphasize these results confirm that reducing the continuous distribution of organic matter reactivities into two distinct reactivity classes (2G Model) requires different k-f values for shallow vs deep ocean sediments because of the largely different reaction timescales involved (also see Fig. 10).

To clarify, we rephrased the sentence (pg 54 lines 22-25):
"A comparison between simulated OM contents and observations indicates that a depth dependent k-f relationship provides the best fit (Section 4.2.2). These results confirm that reducing the continuous distribution of organic matter reactivities into two distinct reactivity classes (2G Model) requires different k-f values for shallow vs deep ocean sediments because of the largely different reaction timescales involved (also see Fig. 10)."

OMEN-SED – cGENIE coupling
20. Comment:
The stated purpose of section 4 is …
… The validation of the coupled model requires more work, and I wonder whether this was not better done in a separate paper, in which the coupling to cGENIE and the parameterization of POC mineralization was explored in more detail.

Response:
As stated in the manuscript (page 45, lines 23-26):
"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 that model results capture the main observed global benthic biogeochemical features."

We think that demonstrating how OMEN-SED can be coupled to an ESM and illustrating the type of output/information generated by OMEN-SED within such a coupling is a central aspect of the model description paper.
However, we agree trimming down this section (as in the re-submitted version). We will discuss an

improved model-data analysis (also using observations of SWI-fluxes) in a follow-up publication (as also suggested by reviewer #3 K. Wallmann).
Specifically, the sensitivity analysis for the spatially uniform degradation rate constants (Figure 12) and it's discussion has been removed (compare pages 47-50).

21. Comment:
Figures 12 - 14: I gather the R2 values are for the bin averages. I don't see much value of that, as over- and underpredictions cancel each other out in the averaging. Why not compute statistics for the actual model results with the Seiter data directly?

Response:
Figure 12 has been deleted from the manuscript. As the statistics for the actual data are not helpful/misleading (see also comment 4 of reviewer #2) we decided to remove the R2 values in Figures 13 and 14 (as well as their discussion in the text). Compare changes on pages 47-50.

Minor comments:

22. Comment:
page 8/ line 1: It is said that all parameters in Eq. 1 may vary with depth, but above it is stated that porosity and burial rates are constant with depth.
Response:
We thank the reviewer for highlighting this. This has been changed in the revised manuscript to (pg 8 lines 1-2):
*"All parameters in Eq. (1)**, apart from porosity and burial rate,** may vary with **sediment** depth and many reaction rate expressions depend on the concentration of other species. "*

23. Comment:
- the fraction of POC buried is defined as the POC at z=0 relative to the POC at depth. Why is it not defined as the flux at z=0 vs. the flux at depth (it seems Eq. 5 ignores the diffusion flux)?
Response:
We decided to calculate the fraction of POC preserved dependent on the concentrations of POC at z=0 and z=zinf mainly because this information is required by cGENIE. Also POC at z=0 is calculated on the basis of the flux provided by cGENIE, therefore does include advection-diffusion-reaction.

24. Comment:
Related to that, page 10, line 18 refers to a concentration/flux boundary conditions at the SWI. The following equations and Table 2 only show a known concentration, not a flux condition. However, the latter would be useful when connecting the sediment model to a model of the water column. On page 43, Eq. 51 this is addressed - make this clear earlier.
Response:
We thank the reviewer for highlighting this. The text has been changed and a reference to Eq. 51 has been added (pg 10 lines 17-20):
*"For organic matter, OMEN-SED applies a known **concentration** at the sediment-water interface and assumes continuity across the bottom of the bioturbated zone, zbio. **When OMEN-SED is coupled to an ESM, the POC depositional flux from the coupled ocean model is converted to a concentration by**

solving the flux divergence equation (51)."

25. Comment:
Can lines 21-23 on page 21 be deleted?
Response:
We refer to both equations later in the text (pg 22 line 14 and 22), therefore we would like to keep them in.

26. Comment:
page 31, line 2: specify NH4, SO4 and H2S FLUXES
Response:
Text has been corrected as suggested (pg 29 line 33).

27. Comment:
Figure 3 did not help me much. Does the green dashed vertical arrow indicate possible locations of zbio?
Response:
Yes, it does indicate locations of zbio. We added this to the caption of Figure 3. However, we strongly believe that Figure 3 illustrates the bioturbation boundary problem in an efficient way and also highlights the integration constants and ODE solutions for the different sediment layers.
New caption:
"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 bioturbation boundary **(possible locations are indicated by the green vertical arrow)***."*