Date: July 8th, 2021

Subject: Response to Reviewer’s comments on BG-2021-4

Manuscript ID: gmd-2021-4 “OMEN-SED(-RCM) (v1.1): A pseudo reactive continuum representation of organic matter degradation dynamics for OMEN-SED”

Dear Bernard Boudreau,

On behalf of the co-authors, I want to thank you for the detailed and constructive review of our manuscript. In the following, we reply to each of the issues raised and explain how these will be addressed in the revised manuscript.

Sincerely yours,

Philip Pika and co-authors

This paper reports a means by which the OMEN-SED diagenesis program (Hülse et al., 2018, GMD 11), which uses 2-G organic matter (OM) decay kinetics, can be altered to approximate a reactive continuum decay model, instead. The interest in this modification lies in better approximating the observed decrease in OM reactivity with depth in sediments, which is a desirable goal. I do have four comments on the execution of this paper, one of which reflects one that I made on a recent related submission by some of these authors, i.e., Freitas et al. (2020, BG-2020-435).

Comment:

1) Equations (4) and (8) in the Introduction and on page 7 are strictly valid only in non-bioturbated sediments, where there is a simple relationship between time and depth, a point that is only briefly mentioned in the present manuscript. These equations are stated and applied without any serious caveat. The correct expression with bioturbation is given in Boudreau and Ruddick (1991), their Equation (49), and it is not in an easily implemented form, as needed here.
No one has adequately explored the effects of applying Equation (8) to a bioturbated sediment. In Table 1 of Boudreau and Ruddick (1991), there are 6 applications of Equation (8) to non-bioturbated or negligibly bioturbated sediments. These generate v values between 0.05 and 0.3; the Peru Margin sediments in that same table are almost certainly bioturbated and have associated v values closer to unity (0.8 and 0.91). This dichotomy of results may indicate the effects of improperly dealing with bioturbation, but I really cannot affirm this. I also recognize that the actual calculations are made with a discrete numerical approximation, which removes much of the mathematical challenge, but also assumes a v characteristic of a non-mixed sediment; this may create unintentional modifications to the calculated "a" value.
Further to this point, om(k,0) in Equation (7) is said to be the initial distribution of reactivities. In a non-mixed sediment, that distribution is exclusively altered by the decay of components with time. In a bioturbated sediment, "older" and "newer" organic matter components are mixed together, so that in leaving the mixed layer, the organic matter reactivity distribution is different than om(k,0) at the SWI. Thus, the mathematics get even more demanding.
Progress in global modelling is needed to meet the challenges of global change; I appreciate that; corners will be cut by necessity. However, explicitly recognizing and stating those shortcuts is not only desirable, bit is essential.

Response:
We really appreciate the points raised and agree that the method section needs further clarification and explanation. More specifically we will make the following points clearer:

Although, equations (4) and (8) are strictly valid only in non- bioturbated sediments, they, as well as other, empirical continuum models (Middelburg et al., 1989, Jørgensen et al., 2010) that use a similar expression to describe the depth evolution of apparent OM reactivity have been successfully applied across a wide range of depositional environments (see compilation of published studies in Arndt et al., 2013). However, like many other factors that are not explicitly accounted for (e.g. microbial community structure, temperature, thermodynamic inhibition, TEA availability, …) the effects of bioturbation (not only transport, but also priming, stabilization of OM, ...) will be implicitly accounted for in the parameter values, thus explaining the reported variability in model parameters.

In addition, as pointed out by the reviewer, we here use a discrete approximation of the continuum model that is merely constrained on the initial distribution om(k,0), but makes no assumptions about the evolution of bulk OM reactivity in the bioturbated zone or how *a*-*v* characteristics would relate to it.

Within this discrete approximation (i.e. the 500 G model), the evolution of the apparent bulk OM reactivity within the bioturbated zone (and below) is not only determined by the specific consumption rates of the 500 OM pools (G), but also by their transport via bioturbation and advection. The 500 G model approximation thus accounts for the mixing of "older" and "newer" organic matter components (as long as the assumed steady state conditions apply). In leaving the mixed layer, the organic matter reactivity distribution is thus indeed different than om(k,0) at the SWI and would be equivalent to om(k, t_apparent) with t_apparent being the apparent age of the OM that is determined by transport and degradation processes.

We will include a section that discusses the caveats, simplifications and limitations of our approach in more detail. Here we will also note that, in reality, the distribution of OM reactivities are likely to be more complex and that our choice of the specific mathematical approximation represents a necessary simplification in the first place (as has been noted by the reviewer before, e.g. in Boudreau & Ruddick, 1991). We will also revise the equations stated in our Introduction and Model Description (especially equations 4, 7 and 8) and adapt them so they reflect our specific discrete approximation of the continuum model better. In particular we will omit Equations (4) and (8) from the manuscript as they are not relevant for our approach.

Comment:

2) The methodology of this paper and of Hülse et al. (2018) is to create a diagenetic module that can be solved analytically and to calculate the resulting integration constants by fast linear matrix methods (see section 2.3.1 of Hülse et al., 2018). I am confused about this second part, as there is insufficient detail in either paper to see how the latter can be accomplished. Take sulfate in its reduction zone. The analytical solution will be a sum of exponentials, two of which will be multiplied by unknown integration constants. Boundary conditions at the top of the zone and at the base of the zone will allow calculation of the two constants, and these resulting equations will indeed be linear in the two integration constants. However, the position of the base of the sulfate reduction zone is a further unknown, a point that was extensively discussed in Boudreau and Westrich (1984, GCA 48, 2503-2516). A third boundary condition is needed to determine the unknown zSO4.

Hülse et al. (2018) do supply a third equation, and so it should be in the present paper too. What puzzles me is that this third equation, as in Boudreau and Westrich (1984), is a nonlinear function of zSO4. Thus, linear matrix methods cannot be employed to arrive at a solution. What have the authors done to avoid this problem, which seems fundamental to their paper?

Response:

The explanation for how to solve the dynamically changing penetration depth problem is explained in Hülse et al. (2018). However, it is actually included in the subsections for the specific terminal electron rather than in section 2.3.1.Briefly, taking the example of the reviewer, i.e. sulfate in its reduction zone (compare 2.2.4 of Hülse et al., 2018):

OMEN-SED iteratively solves for zSO4 by first testing if SO4 is still available at zmax (i.e. SO4 (zmax) > 0). In that case, zSO4 is not an unknown anymore (as zSO4 = zmax) and just the zero diffusive flux boundary condition at the lower boundary is sufficient to solve the diagenetic equation (compare (8.1) in Table 5 of Hülse et al., 2018). In the case zSO4 < zmax (i.e. zSO4 is unknown) an extra boundary condition is needed. Here, OMEN-SED requires (1) zero SO4 concentration at zSO4 and (2) the SO4 diffusive flux at zSO4 must equal the flux of methane from below that is reoxidized (compare 8.2 in Table 5 of Hülse et al., 2018). OMEN-SED then iteratively solves for zSO4.

We will include a specific reference (including page number) to the relevant section of the original OMEN-SED publication in a relevant section of the revised model description.

Comment:

3) I fail to agree that the model predictions and observations provided in Figure 6 "generally agree well with observations and capture also the widely observed increase in OPD with water depths (see Fig. 6)." The model in this paper generally overpredicts the OPD, more often by far more than an order of magnitude. The data appear to have an upper limit of 1000 mm with ocean depth, which is not present in the model predictions. The obvious discrepancies are not discussed in the paper. They really need to be. Is the "observed" 1000 mm limit an artifact or real? Why the common overprediction of the OPD? There is something valuable to be learned from negative results!

Response:

Also see response to Reviewer 1

We agree that the presented model generally overpredicts the observed OPD. We will discuss and address this shortcoming in the revised manuscript. The mismatch between model results and observations can be partly explained by

1) A bias in the observational data set towards shallower OPD

The upper limit of 1000mm in the observed OPD is likely an artefact of the data selected here, since oxygen is known to penetrate several meters (Glud, 2008), or even down to 60m (see D'Hondt et al., 2015; Roy et al., 2012), in the oligotrophic gyres of the South Pacific. The observational data set does not include these deep OPD of several meters to kilometers that have been observed in the central parts of the oceans (D'Hondt et al., 2015; Murray, J. W. & Grundmanis, 1980, Roy et al., 2012). We will update our database and/or discuss the bias in the revised text.

2) two simplifications/limitations in the model configuration and boundary conditions

First, the applied OM concentration at the sediment-water interface (SWI) (Seiter et al. (2004) is actually more representative for the mean OM concentration in the upper 5cm of the sediment. It thus represents a lower limit for the actual SWI concentration. Second, the applied a-w parameterization used to calculate the average life-time of the more reactive OM compounds represents only a weak relationship ($R^2 = 0.46$) as it is only based on a limited number of observations (see Fig. 15b of Arndt et al., 2013). The resulting a-values following the parameterization are in the range of 34 – 2239 yrs. with a mean value of 1240 yrs. ($\sigma = 955$ yrs.) and thus likely more representative for an OM mixture of lower reactivity. Both limitations result in lower OM degradation rates and thus an overestimation of the OPD.

We will include additional results in the revised manuscript using a rescaled a-w relationship that yields lower *a*-values, while still following the widely observed inverse trend between *a* and sediment accumulation rate (*w*) (e.g. Middelburg, 1989; Boudreau and Ruddick, 1991). The new results should agree better with the observations. We agree with the reviewer that there is something valuable to learn from the negative results, namely that the a-w parameterization generally results in rather low OM reactivities. This will be discussed in the revised manuscript alongside other limitations of this specific modeling exercise (i.e. the global maps of SWI TOC concentrations and sediment accumulation rates certainly have flaws, the distribution of OM compounds is certainly more complex in reality and site specific peculiarities are not represented in our approach). Thus some degree of mismatch is to be expected (while the reviewer is correct that our previous results generally overpredict the OPD).

The upper limit of 1000m in the observed OPD is likely an artefact of the data selected here, since oxygen is known to penetrate several meters (Glud, 2008), or even down to 60m (see D'Hondt et al., 2015; Murray & Grundmanis, 1980; Roy et al., 2012), in the oligotrophic gyres of the South Pacific. We will try to update our database and/or note the artefact in the revised text.

Comment:

4) Finally, as much as Equation (15) might prove valuable, it is repeated as Equation (17) with a discussion that is similar. Is this duplication needed or am I missing something?

Response:

Agreed with being a duplication and unnecessary, and will be removed and Equation (15) will then be referenced in the Global application (3.3).

Arndt, S., Jørgensen, B. B., LaRowe, D. E., Middelburg, J. J., Pancost, R. D., and Regnier, P. (2013). Quantifying the degradation of organic matter in marine sediments: A review and synthesis. Earth-Science Reviews, 123:53–86.

D'Hondt, S., Inagaki, F., Zarikian, C. A., Abrams, L. J., Dubois, N., Engelhardt, T., Evans, H., Ferdelman, T., Gribsholt, B., Harris, R. N., Hoppie, B. W., Hyun, J.-H., Kallmeyer, J., Kim, J., Lynch, J. E., McKinley, C. C., Mitsunobu, S., Morono, Y., Murray, R. W., Pockalny, R., Sauvage, J., Shimono, T., Shiraishi, F., Smith, D. C., Smith-Duque, C. E., Spivack, A. J., Steinsbu, B. O., Suzuki, Y., Szpak, M., Toffin, L., Uramoto, G., Yamaguchi, Y. T., Zhang, G.-l., Zhang, X.-H., and Ziebis, W. (2015). Presence of oxygen and aerobic communities from sea floor to basement in deep-sea sediments. Nature Geoscience, 8(4):299–304.

Murray, J. W., & Grundmanis, V. (1980). Oxygen consumption in pelagic marine sediments. Science, 209(4464), 1527-1530.

Glud, R. N. (2008). Oxygen dynamics of marine sediments. Marine Biology Research, 4(4):243– 289.

Roy, H., Kallmeyer, J., Adhikari, R. R., Pockalny, R., Jorgensen, B. B., and D'Hondt, S. (2012). Aerobic Microbial Respiration in 86-Million-Year-Old Deep-Sea Red Clay. Science, 336(6083):922– 925.