Biogeosciences Discussion



Dr Felipe Sales de Freitas School of Earth Sciences University of Bristol Wills Memorial Building, Queen's Road BS8 1RJ Bristol United Kingdom

Email: felipe.salesdefreitas@bristol.ac.uk

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Subject: Point-by-point reply to Reviewers' comments

Manuscript ID: BG-2020-435 "Advancing on large-scale trends on apparent organic matter reactivity in marine sediments and patterns of benthic carbon transformation"

Dear Associate Editor Marilaure Grégoire,

On behalf of all co-authors, I want to thank you for considering our responses to the comments made by the reviewers and for inviting us to submit a revised manuscript. We appreciate the constructive and detailed comments and the opportunity to improve our work. In the following, we provide detailed responses and indicate how we incorporated changes in the revised manuscript (text marked in purple). Additionally, I would like to point out a slight change in the manuscript title to "<u>New insights into</u> *large-scale trends on apparent organic matter reactivity in marine sediments and patterns of benthic carbon transformation*", which we believe better enunciates our work and findings.

Sincerely yours

Fellipe Jales de Fruitas

Felipe Sales de Freitas and co-authors

Reply to Reviewer 1 – Bernard Boudreau

We have revised the manuscript and clarified points to assure we do not intend to criticize nor discredit the work by Boudreau and Ruddick (1991). We emphasize that our assessments build that work, and thus on the early developments of the Reaction Continuum Model (RCM), which were instrumental for our analyses. However, we advocate for the inclusion of further constraints for the extraction of RCM parameters. Here, alongside total organic carbon (TOC) depth-profiles, we include porewater sulfate (and methane) profiles to improve the robustness of the model-data fit. We have clarified that issues inherent to inverse modeling (e.g., core top loss, steady state assumption, and uniqueness of fit) also affect our assessments. We have carefully revised the Inverse Modeling sections of both Model Description (Sect. 3.2.4, L. 232 onwards) and Results and Discussion (Sect. 4.1.1, L.326 onwards). Additionally, as mentioned, our work largely benefits from findings by Boudreau and Ruddick (1991). Furthermore, our findings confirm and consolidate the range of RCM parameters on a global scale (L. 648—656).

Our findings corroborate previous findings (Arndt et al., 2013; Boudreau and Ruddick, 1991; Forney and Rothman, 2012; Middelburg, 1989) that the RCM parameter v is globally relatively constant (v = 0.1-0.2). Exceptionally high v > 0.2 are often associated to deposition and burial of highly reactive phytoplankton debris in high productivity regions associated with well-established OMZs. In contrast, in agreement with previous findings, RCM parameter a can span several orders of magnitude at a global scale, suggesting that the parameter a exerts the main control on the variability of apparent OM reactivity. Consequently, future modelling efforts to quantify OM reactivity on a global scale could be reduced to one main reactivity variable. Based on our results and previous findings, we consolidate the range of predominant a distribution to 10^0-10^4 years. This is a valuable constraint when dealing with data poor regions and timescales (e.g., Hülse et al., 2018), since it excludes extreme values at both ends of the a-range.

Below we provide more details to specific comments and how they were incorporated to the revised manuscript.

A - The model presentation sections 3.2.1.2 and 3.2.1.3 are difficult to understand and, as a consequence, could be incorrect. I highlight the following points in the order they appear in the text:

The Model Description section was carefully revised <u>(Sect. 3.2, L. 148 onwards)</u>. As suggested by Reviewer 2 (see below), this section was shortened, and specific details were incorporated to the Electronic Supplementary Material (ESM, Sect. S2).

Aa) Equation (6), which is entirely equivalent to Eq (39B) of BR91, is valid only in non-bioturbated sediments; in that situation, the POC at any depth is only a function of parameters "a" and ν , as the sedimentation rate is used to convert depth into age. In bioturbated sediments (constant mixing and porosity), the appropriate form for POC (G) is given by Eq (49) of BR91,

$$G(\mathbf{x}) = \int_0^\infty \frac{\mathbf{g}(\mathbf{k}, 0)}{\left(1 - \frac{\mu}{\sigma} \, \mathbf{e}^{(\mu - \sigma)L}\right)} \left(\mathbf{e}^{\mu \mathbf{x}} - \frac{\mu}{\sigma} \, \mathbf{e}^{(\mu - \sigma)L} \mathbf{e}^{\sigma \mathbf{x}} \right) d\mathbf{k} \tag{49}$$

.

which cannot be reduced to a form like Eq (6) of the present paper. There is no caveat with regard to Eq (6) in this paper. This makes me wonder if ascribing all OM reactivity to parameters "a" and ν is really correct if the sediment is bioturbated. That may very well explain the lack of correlation later described in Figure 6 of the present paper. That point has not been considered.

Indeed, Eq. 6 (in the non-revised manuscript) is only valid for non-bioturbated sediments for the reasons you highlight. We highlight the limitations of the RCM in bioturbated sediments (L. 213–216, revised manuscript). Therefore, the above equation is never applied to bioturbated sediments. Instead, we use a multi-G approximation of the RCM in these mixed sediments (ESM, Sect. S2.3, L150 onwards).

For non-bioturbated sediments ($z > z_{bio}$) the burial age(z) can be calculated as a function of the burial velocity (Sect. S2.3). However, within the bioturbated upper sediment layers, the age distribution of reactive species is controlled by both sedimentation, bioturbation, and the reactivity *k* of reactive species (Meile and Van Cappellen, 2005). In such cases, we apply a multi-G approximation for the RCM in the bioturbated sediments (Sect. S2.3, Eq. S9–S18).

We are confident that results we later present on Fig. 6, which show a lack of significant correlation with single descriptors of depositional environments (e.g., water depth, sedimentation rates) are correct; further, the lack of correlations is explored on the context of additional existing datasets and our assessments highlight the complex and dynamic interplay of multiple environmental controls on organic matter reactivity (Sect. 4.1.4, L. 464 onwards).

Ab) To deal with bioturbated sediments, the authors bin the OM continuum by introducing Fi, which is the fraction of the total OM having reactivity between kj and kj+dkj.

For bioturbated sediments, we simply use a discrete (multi-G) approximation of the RCM, which can be solved analytically for steady-state conditions, constant mixing and porosity. However, we agree that the mathematical description of the approximation is not clear. A revised description of the multi-G approximation has been moved to the ESM (Sect. S2.3, L150 onwards).

In short, the PDF, which determines the fraction of organic matter with reactivity k at time t=0 is:

$$f(k,0) = \frac{a^{\nu} k^{\nu-1} e^{-ak}}{\Gamma(\nu)}$$

The corresponding CDF then gives the fraction of total organic matter with a reactivity less or equal than k at t=0:

$$F(k,0) = \frac{\Gamma(v,0,a\,k)}{\Gamma(v)}$$

We then separate the total organic matter into 200 different discrete fractions by calculating the fraction of organic matter with reactivity $k_i = 10^{i+1/2}$ y⁻¹ at t=0 (for a given *a* and *v* couple) with:

$$F_{i}(k_{i}, 0) = \frac{\Gamma(v, 0, a * k_{i+1}) - \Gamma(v, 0, a * k_{i})}{\Gamma(v)}$$

Ac) The symbols used in this manuscript are non-systematic, non-intuitive and idiosyncratic.

We revised the symbols used throughout and adhered to conventional symbols presented in the literature. To avoid inconsistencies and help guide the reader, we now provide a summary **<u>table (Table</u> <u>3</u>**, **revised manuscript)**.

B - On another point, the authors spend some time establishing the need for their approach by pointing out some shortcomings of the method in BR91. Specifically, the BR91 approach is "compromised" by loss of sediment at the top during coring, by assuming steady state over long periods in slope and coastal sediments, and by the supposed non-uniqueness of a and ν values (Meister et al., 2013).

We would like to point out that, as mentioned above and carefully revised in the manuscript <u>(Sect. 3.2.4 and Sect. 4.1.1)</u>, all the limitations listed here also apply to the statistical fitting of organic matter and sulfate (and methane) profiles and are in no way meant to discredit the work by Boudreau and Ruddick (1991). We have revised these points (see below Ba-Bc) to accurately deliver our main message, which is to highlight the general limitations of inverse modeling/profile fitting approaches (i.e., core top loss, non-steady state conditions, uniqueness of fit) and to advocate that including more information – ideally a full set of porewater depth profiles – provides further constraints. However, this does not mean that our work discredits the results presented in Boudreau and Ruddick (1991). We evidenced that by the comparison of our results to previous findings throughout the manuscript. As pointed out,

comprehensive observational sets are hard to come by and they only offer additional constraints that help rule out some of the limitations inherent to the fitting approach, but do not necessarily yield a statistically better fit.

Ba) Firstly, the method in BR91 does not require the concentration of OM at the sediment-water interface (SWI). It uses any data available and requires none at any specific depth. When sediment is lost, and the top of the core is erroneously set to depth zero. That depth error is translated into an error tin the ages of the samples in the core. The authors seem to think that only multicores can be used to avoid this. While piston cores are problematic, properly collected gravity cores are far less prone to this problem, and that represents most of the data in BR91.

In the revised manuscript, we highlight the core top loss as a general limitation of the used approach (L. 234–237), rather than as a specific limitation of Boudreau and Ruddick (1991). In fact, we acknowledge that core top loss likely also affects some of the data considered in this study (L. 345–347).

Multicores are indeed well suited to recover undisturbed core tops, thus preventing sediment loss. Nevertheless, as already mentioned here, gravity cores are also suitable when *properly* collected. Nevertheless, we do not intent to recommend or disregard sampling techniques (especially because global data sets are already limited). Our intention is rather to emphasize that profile fits might be affected by core loss and that including further constraints, e.g., sulfate (and methane) depth profiles for which bottom water values are usually well established might increase the confidence in derived estimates.

Bb) It is one thing to say that a non-steady state will affect calculated a and ν values and quite another to specifically show that the profiles used in BR91 are so afflicted by such effects that they cannot be trusted. The authors have not demonstrated that this is a problem in BR91. The cores used by the authors also have non-steady state effects (I can guarantee that), but they do not question their own use of a steady state model.

Again, we definitely do not think or advocate that the results from Boudreau and Ruddick (1991) are overly impacted by non-steady state effects and cannot be trusted, but rather highlight the steady state assumption as an additional limitation of all (steady state) profile fitting approaches. We emphasise that in the revised manuscript (L. 239–241 and L. 338–345).

Bc) The authors state that Meister et al. (2013) show that different a and ν pairs can produce the same OM profiles. My reading of that paper is that Meister et al. (2013) show nothing of the sort. These latter authors show that the depth of the sulfate-methane transition zone (SMT) is not unique to a and ν pairs.

That in no way shows that the associated POC profiles are the same; in fact, Meister et al. (2013) display no POC profiles whatsoever.

We agree that the study by Meister et al. (2013) focusses solely on the sulfate-methane transition zone (SMTZ) and the effect of a and v on STMZ depth and does not explicitly assess POC. However, it nicely illustrates how different pairs of a and v can result in similar SMTZ depths. In our initial tests and model assessments, we detected a similar issue when merely fitting organic matter profiles, i.e., some depth profiles could be equally well fitted by different a and v couples. By including additional constraints (e.g., sulfate profiles, SMTZ depth), we were able to exclude those pairs that only fitted organic matter profiles well. We have revised this statement to reflect the point we make here (L. 241–245; L. 268–274).

Finally, multiple parameter sets might fit the observations equally well. Because both a and v exert an influence on the apparent OM reactivity and its evolution with depth (see below, Eq. 7), they are not completely independent parameters. For instance, a decrease in v (decreasing reactivity) can be compensated by a simultaneous decrease in parameter a (increasing reactivity). Consequently, different a and v parameter couples, might result in equally statistically satisfying fits between the simulated and observed profile.

Thus, a combination of TOC, SO_4^{2-} , and CH_4 (if available to verify the depths of the SMTZ) depth profiles incorporates the information contained in the observed benthic sulfur and carbon dynamics and is sufficient to extract robust estimates of apparent OM reactivity and its evolution from the sediment-water interface down to the SMTZ. In addition, because changes in a-v exert different effects on TOC and SO_4^{2-} depth profiles (see Fig. S1 & S2), including these two species reduces the impact of the a-v correlation on the uniqueness of fit. Thus, here we perform a sitespecific data-model fit based on TOC and SO_4^{2-} (and CH_4) depth profiles.

B1) To shore up their claim that simply fitting Eq (6) to their POC data is inadequate ("compromised"), the authors create a synthetic data profile and then demonstrate that various curves generated by Eq(6) with different a and ν values resemble the data, i.e., their Fig. S1. Like the present paper, BR91 use a statistical fitting technique; if uniqueness was a problem, the BR91 approach would have failed to produce fits with high R2 values, i.e., R2 > 0.8 in every case, non-uniqueness does not seem to be a problem. What the authors have failed to do is: 1) to show that fitting Eq (6) to their own data below the mixed zone of sediments gives statistically different a and ν values than their method that takes into account sulfate and methane profiles.

We do fit Eq. 6 (or its discrete 200 bin approximation) to our data below the mixed zone. Sulfate (and methane) profiles just serve as additional constraints (see above). Additionally, we now provide a detailed description of the inverse modelling approach <u>(Sect. 3.2.4, revised manuscript)</u> and data <u>(Table 5, revised manuscript)</u> displaying quantitative assessments of our model-data fit based on Taylor diagram metrics (Taylor, 2001).

B2) Show that the BR91 a and ν values as a group are demonstrably different than the values generated with their new method. In fact, the opposite is true, as they state unequivocally in the conclusions (lines 900-901), their results for the ν parameter "corroborate previous findings (Arndt et al., 2013;

Boudreau and Ruddick, 1991) that the RCM parameter v is globally relatively constant (v = 0.1-0.2)." As for the a parameter, they state that based "on inverse model results, we narrowed the most plausible range of a to $10^{0}-10^{4}$ years." Reproduced below is Table 1 of the results in BR91. Note that the 7th column reports the a values. These values are in the range advocated by the present authors.

As mentioned earlier, we do not apply a *new method* and definitely do not argue that we should obtain largely different results. All the contrary – as you rightly point out here – our results further confirm the conclusions by Boudreau and Ruddick (1991). We have revised our conclusions (see above) to reflect the fact that with our new dataset we consolidate the plausible range of RCM parameters a and v in a global scale (L. 648–656).

B3) It is not necessary for the present paper to advance demonstrably questionable claims about BR91 in order to justify the development and use of their method. They need to show actual improved robustness of their method. And in situations where the abundant chemical data available to the authors is absent, then Eq (6) may be all one can do.

Again, it is definitely not our intention to discredit the study by Boudreau and Ruddick (1991), especially because we actually do not develop a new method; rather, we use the exact same approach used in Boudreau and Ruddick (1991). We totally agree with your statement "... and in situations where the abundant chemical data available to the authors is absent, the Eq. 6 may be all one can do.". However, we believe that is also important to define an ideal "minimal set" of benthic observations to derive robust RCM (or more generally speaking, organic matter degradation model) parameter estimates. We believe that organic matter and sulfate (and methane) depth profiles (see above) in combination with information about sedimentation rates and macrobenthic activity provide such a "minimal set" (L. 268–274).

C – The authors keep referring to the parameter a as the apparent reactivity of the organic matter. In non-mixed sediment the ratio ν/a is the apparent reactivity. And in mixed sediment, no study has established the form of the apparent reactivity. Maybe the authors need to attenuate their discussion to those facts.

We agree with this point. However, our results suggest that the variability of parameter a distributions exert the main controls on apparent OM reactivity variability on a global scale. Furthermore, we believe that we should aim at addressing a broad audience. Parameter a is very technical, while apparent reactivity is more meaningful to readers, albeit in a more simplistic way. Nevertheless, we have revised the manuscript where appropriate.

D – Lines 754-771. The discussion on the dominance of various oxidants seems isolated from previous work by many other authors. As an example, I reproduce Table 3 from Boudreau et al. (1998. JMR) that reports exactly the same thing for a number of other sites. Again, perhaps this other data should inform your discussion? You might want to search for other documents of this type in past publications.

We agree with this point. However, it is beyond our scope to establish comprehensive comparisons here. Additionally, due to distinct model formulations and assumptions, direct comparisons are not straightforward. Nevertheless, we have revised the manuscript to include a brief comparison and highlighting the challenges of making meaningful comparisons (L. 539–546).

The relative contributions quantified here are generally lower than previous estimates for coastal and shelf sediments (> 20%) (e.g., Long Island Sound, Mackin and Swider, 1989; Skagerrak, Canfield et al., 1993; Eastern Canadian continental margin, Boudreau et al., 1998; Barents Sea, Freitas et al., 2020; and Northern Gulf of Mexico, Owings et al., 2021). Additionally, estimates are consistently lower than values in deep-sea (> 70%) (e.g., Cape Hatteras continental rise, Heggie et al., 1987), as well as over the global-scale hypsometry (Thullner et al., 2009). However, the overall dynamic nature of the considered environments, which favours the dominance of organoclastic sulfate reduction (Bowles et al., 2014; Jørgensen and Kasten, 2006; Thullner et al., 2009), as well as the length of sediment column (1,000 cmbsf) considered here render a direct comparisons difficult.

Reply to Reviewer 2

General comments

"the text is not always easy to read. This is especially the case for its first paragraph, which is close to unreadable. Readers have to search for actual sentence parts among a plethora of citations—there are nearly sixty of them in thirty lines of text (are these really all necessary?). The rest of the paper is more readable but in general so wordy that one often loses the focus on what is actually important."

We have shortened the manuscript, in particular the model description section (see below), where possible without losing the essence of our work and findings.

We assume that Reviewer 2's comment on citations refers to line 65-75. This section discusses the interplay of different environmental controls on organic matter (OM) reactivity, and we prefer to refer to the original literature and topic specific review papers instead of merely citing a couple of more general review papers. However, to increase the readability, we created a table summarizing the main environmental factors controlling OM reactivity in marine sediments (Table 1, revised manuscript) and specific references to the original work that explores their respective influence on OM reactivity. As such, the revised manuscript now reads (L. 68–70):

In fact, OM reactivity is determined by the dynamic interplay of a plethora of different factors (Arndt et al., 2013; Burdige, 2006; Middelburg, 2019; LaRowe et al., 2020) (Table 1 and references therein).

Despite its central role in the study, the inversion method is described in a completely inadequate way. In its current form, that description does not allow to reproduce the results as critical details on the adopted algorithm are missing.

We extend the description of the inverse modelling approach <u>(Sect. 3.2.4, revised manuscript)</u>. See detailed answer to specific comments below.

The notation in the paper is not entirely consistent (the same symbols have different meanings or different symbols used for the same types of variables, or symbols that even change for one and the same variable) and at times unconventional which makes reading again unnecessarily difficult.

To avoid inconsistency and help guiding the reader, we included a summary table of the used symbols throughout the manuscript <u>(Table 3, revised manuscript)</u>. See detailed answer to specific comments below.

The conclusions are overdone, both in content and tone. They would benefit from a fair share nuance and precise contextualization (they are for an RC model with a particular choice of reactivity distribution, which is not necessarily the only possible choice, even if it is the most commonly adopted one) would do them good. It would be desirable to let the results speak for themselves so that there is no need to emphasize how important they are.

We have reviewed the conclusions (Sect. 5; L. 641 onwards). See detailed answer to specific comments below.

Finally, there are problems of more fundamental nature: there are no such things as Log(yr) units, central concepts are misnamed. More unfortunately still, the all too critical treatment of previously published results make the rationale adopted here end up in incoherences in some instances. I think it is not a referee's duty to raise these types of issues, which ought to be purged or fixed at an earlier stage.

We revised all figures for units and notations. See detailed answers to specific comments below.

We certainly did not intend to be overly critical with respect to previous results (see answer to Reviewer 1). We would like to clarify that the highlighted issues are inherent to all inverse modeling/model fitting approaches, including the one adopted here. Hence, we advocate for including additional constraints that can help alleviate some of these limitations (L. 268–274). After all, the findings of this study corroborate the findings of previous continuum model studies. See detailed answer to specific comments below.

In conclusion I cannot recommend this paper for publication in Biogeosciences unless it undergoes a major revision. Here are a series of points to consider for such a revision.

• The actually used inversion algorithm must be described in detail. As the study is presented as an inversion study, this is obviously a conditio sine qua non.

• Meaningful uncertainties and correlations between the determined values must be reported. This may possibly require to use another inversion method if the currently used one cannot provide this information.

• The paper would benefit from a substantial shortening (by one third to one half).

• Attention should be paid to precise language, consistent notation and fair treatment of the existing literature.

We have addressed all the above points. See detailed answers to specific comments below.

Specific comments

Model Description and Inverse Method

The description of the Biogeochemical Reaction Network Simulator (BRNS) comes with a great deal of details. Most of these can, however, be found elsewhere. This part could essentially be reduced to one half to one page at most and, for the readers' convenience, the current model description transferred to the Supplement.

We think that, in the context of this manuscript, it is important to provide a detailed model description, but agree that this could be moved to the supplementary information. Therefore, the revised manuscript now provides a short, more general model description (Sect. 3.2). Additionally, we include in the ESM a more detailed model description (Sect. S2).

On the other hand, the inverse method used is presented only very summarily and above all in very general terms. Nothing is said about the optimization algorithm or the inversion procedure, which makes me wonder if it does not reduce to a trial and error approach. This would then also explain why there are no uncertainties or correlations reported for the derived n and a values. We are only told that the adjustment is carried out with the TOC and pore water SO4 concentration profiles (and CH₄ where available) and that there is an exploration stage on a coarser grid of values (by the way a values above 10^4 are not evenconsidered—see conclusions) However, nothing is said about the applied metric (χ^2 ?) to quantify the misfit etc. nor about the criterion to select the results.

For an inversion study—and this study is announced as such—this is clearly insufficient.

We revised and extended the description of the inverse modelling approach in the revised manuscript (Sect. 3.2.4). Additionally, we also provided a table summarizing the statistical information for each of the best fit a - v couples (Table 5).

The Reactive Continuum Model

The presentation of the Reactive Continuum (RC) model is rather one-sided, especially when it comes to comparing it to n-G models with all their disadvantages.

Are reactive continuum models really that superior to the discrete models? Although they allow to describe the same phenomenon with fewer free parameters than, say, 3-G models, I do not think this comparison is completely fair. The shape of the chosen probability distribution easily substitutes for a number of parameters. The number of parameters for a 3-G model could also be reduced by prescribing the ratios of successive class sizes (i. e., by prescribing the shape of their distribution). RC models are certainly attractive, but is their predictive ability really superior to few-G models that are easier to understand? Mathematical complexity is not a compelling argument. Since the main purpose of this study is the derivation of a and n parameter values for the RC model in different settings, that RC model is actually a centerpiece of the paper and it should be discussed in a more adequate way,

We do not mean to discard discrete OM degradation models and fully acknowledge that they have been instrumental in making significant advances in our quantitative understanding of biogeochemical cycling in marine sediments. We also generally agree that RCM and multi-G models (generally 2G or 3G models) perform equally well in reproducing comprehensive local porewater and sediment depth profiles, as well as estimating biogeochemical reaction rates and recycling fluxes in the upper sediment layers (tens of centimeters). However, RCM are characterized by several advantages over discrete solutions:

• <u>RCM models are in better agreement with our current conceptual understanding of OM</u> reactivity and its evolution during burial.

They emphasize the notion that OM is continuously distributed over a wide spectrum of reactivities and resolve the widely observed continuous decrease in OM reactivity with burial depth. They are fully consistent with widely observed, continuous decrease in OM reactivity in soils, lacustrine and marine sediments (Middelburg, 1989; Boudreau and Ruddick, 1991; Forney and Rothman, 2012; Katsev and Crowe, 2015). In contrast, multi-G models divide the complex and dynamic OM mixture into a number (generally one to two and less often three) distinct pools and OM reactivity than converge to a constant, fixed reactivity at depth. Therefore, RCM models have a higher predictive ability and are a better choice for the representation of OM degradation dynamics in deeper sediments or on longer timescales.

• <u>They are less sensitive to noise in the data.</u>

RCM only require constraining two unknown parameters or, as indicated by previously published results and further corroborated by the results presented in this manuscript, one parameter (parameter a). Thus, they are simpler than multi-G representations as the dynamic information is contained in only two parameters. In contrast, discrete nG-Models require

identifying n*2 unknown parameters. Consequently, multi-G models are not robust to noise in the data and are over-parametrized (e.g., Jørgensen, 1978; Forney and Rothman, 2012; Middelburg, 1989, 2018). Therefore, RC approaches facilitate model parametrization in data poor area.

<u>They are the most suitable degradation model type to explore links between reactivity</u> parameters and environmental controls.
 Multi-G models are too over-parametrized to identify robust quantitative links between the plethora of environmental controls and OM reactivity (Forney and Rothman, 2012). Therefore, RC represent the most suitable choice for the study presented here.

It is beyond the scope of our work to provide an extensive discussion on the advantages and disadvantages of RCM and G-type models and this topic has already been extensively discussed in a number of previous articles (e.g., Manzoni et al., 2009; Forney and Rothman, 2012; Arndt et al., 2013; LaRowe et al., 2020). Therefore, we revised the manuscript to highlight our reasoning for adopting the RCM approach without making parallels with discreet models (L. 102–104).

OM degradation is formulated according to the Reactive Continuum Model (RCM) (Boudreau and Ruddick, 1991), which represent the most suitable degradation model type to explore links between reactivity parameters and environmental controls (see Sect. 3.2 for details).

also addressing shortcomings (only parallel reactions, no interaction between the different k-components, . . .).

We have addressed these points shortly in the revised manuscript (L. 200-206).

Due to the rapid depletion of the most reactive compounds, the reactivity of the bulk material decreases during degradation, reflecting the widely observed reactivity decrease with burial time/depth/age (Boudreau and Ruddick, 1991; Middelburg, 1989). This indicates that degradation of OM proceeds at different rates in parallel. Interactions between different compounds or transformations of compounds can change the reactivity of a given compound. While the RCM does not explicitly account for such interactions/transformations, the overall OM profiles take these interactions implicitly into account. Thus, OM compounds are continuously and dynamically distributed over a range of reactivities that captures the decrease in apparent reactivity with burial age/depth as the most reactive compounds are successively degraded.

The results for a are critically dependent on the completeness of the sediment data used for the inversion and it is therefore important to ask how reliable the results obtained here can be. From eqn. (39A) in Boudreau and Ruddick (1991), we have for two instants in time, t1 and t2,

$$G(t_1) = \frac{g_0}{(a+t_1)^{\nu}}$$
 and $G(t_2) = \frac{g_0}{(a+t_2)^{\nu}}$ (1)

and thus, assuming that $t^2 > t^1$

$$G(t_2) = G(t_1) \left(\frac{a+t_1}{a+t_1+\Delta t}\right)^{\nu} \text{ with } \Delta t = t_2 - t_1$$
(2)

which is a generalization of eqn. (39B) from Boudreau and Ruddick (1991), i. e., eqn. (6) in the manuscript. Hence due to "[...] the common loss of the upper few centimetres during sampling [...]" (lines 438–439), the core top may be missing and thus the critical fresh POC(0) (eqn. (6)) cannot be recovered. Instead, the organic matter at the assumed sediment water interface actually has already (an unknown) age t1 and not 0 as supposed.

The inversion procedure will thus provide an estimate for a+t1 instead of the expected a. Depending on t1, these two may be significantly different from each other. k(0) at the sediment water interface (eqn. (23)) incorrect.

As discussed in the manuscript and correctly pointed out here, core loss and/or the definition of the sediment-water interface in very dynamic settings is a common limitation of all inverse modeling/ model fitting studies. Including additional species depth profiles provides additional constraints and can alleviate this limitation <u>(see above; L. 268–274, revised manuscript)</u>. However, given that macrobenthic activity often efficiently mixes the upper layer (<10 cm) of the sediment, we expect that potential core top loss exerts a limited impact on bioturbated sediments. Its impact might become important at sites characterized by high sedimentation rates and/or an enhanced delivery of initially very reactive OM. In these cases, the inversely determined initial apparent reactivity might not be representative for the reactivity at the sediment-water interface <u>(although Eq. 23 remains correct; Eq. 8 in the revised manuscript)</u>. In the revised manuscript, we highlighted where these issues may impact our results <u>(Sect. 4.1.1, L. 333 onwards; also see above response to Reviewer 1)</u>.

Imprecisions, errors and incoherences

The text is very long, the language not always precise, and it unfortunately even contains a number of errors.

We have revised and addressed these issues. Also see detailed answer to specific comments below.

In the model description, we read that the sequence of terminal electron acceptors (TEAs) is "described by a combination of Michaelis-Menten and inhibition terms" (line 296). The description that follows suggests that these rate law formulations are the same as in Van Cappellen and Wang (1996). This gets confirmed later at lines 380ff, where part of the information is repeated and completed—it would be good to avoid such repetitions and give one complete description in a single place. Van Cappellen and Wang (1996) call their approach a modified Monod formulation or modified Monod kinetic formulation. Notwithstanding the debate whether Michaelis-Menten or Monod is the more appropriate denomination (see Boudreau and Westrich (1984) and references therein on this issue), the expressions used here correspond neither to the former nor the latter as both would imply a hyperbolic shape. Keeping the denomination from Van Cappellen and Wang (1996) would be just fine.

In the revised manuscript, the model description has been shortened. We now simply refer to previous model applications to describe the reaction network (L. 164–170).

Briefly, the implemented reaction network encompasses the most pertinent primary and secondary redox reactions found in the upper layers of marine sediments (e.g., Aguilera et al., 2005; Thullner et al., 2009; Van Cappellen and Wang, 1996;). It explicitly accounts for the heterotrophic degradation of OM coupled to the consumption of oxygen (aerobic OM degradation), nitrate (denitrification), sulfate (organoclastic sulfate reduction), as well as methanogenesis. Additionally, the reaction network accounts for secondary redox reactions, i.e., re-oxidation of reduced species produced during primary redox reactions. It explicitly resolves nitrification, sulfide re-oxidation by O_2 , anaerobic oxidation of methane coupled to sulfate reduction (AOM) and CH_4 reoxidation by O_2 .

The description of the multi-G approximation of the RC model in the bioturbated layer is impossible to understand.

A revised description of the multi-G approximation has been moved to the ESM (Sect. S2.3, L150 onwards) and the main text now reads (L. 214–216). For details, also see response to Reviewer 1 (see above).

However, within the bioturbated upper sediment layers, the age distribution of reactive species is controlled by both sedimentation, bioturbation, and the reactivity k of reactive species (Meile and Van Cappellen, 2005). In such cases, we apply a multi-G approximation for the RCM in the bioturbated sediments (Sect. S2.3, Eq. S9–S18).

Again, the notation is misleading, as the symbol f was previously used to denote inhibition terms. (...) Besides these, there are too many other errors in the details.

We have addressed these issues in the revised manuscript. We now provide a summary table <u>(Table 3, revised manuscript)</u> to assure consistency and help guiding the readers.

The incoherences between the treatment of previous studies and the approach adopted here are truly unfortunate. I am deeply annoyed to read on one hand that previous estimates of the RC model parameters were "compromised by several factors" (line 437) among which the steady-state assumption of OM deposition fluxes, and then see that same steady-state assumption being made here.

This is a misunderstanding and we have carefully revised the manuscript (see above response to Reviewer 1) to clarify this may issue affect both previous RCM applications and our own (Sect. 3.2.4 and Sect. 4.1.1). The limitations we discuss here may apply to all inverse model/model fitting approaches, including our work. The intention of this section was to emphasize that adding further constraints can alleviate some of these limitations. However, we also highlight that this is not always the case and discuss the potential effect of some of the mentioned limitations (i.e., core loss, non-steady state and uniqueness of fit) on our results. Furthermore, we certainly do not discard previous findings. Previously published parameter values (also including those from multi-G model studies) are an integral part of our discussion and we highlight how our model results further corroborate previous findings throughout the manuscript (Sect. 4.1.2, L. 360; Sect. 5, L. 641 onwards).

One furthermore reads that "multiple a and n pairs could potentially fit a given TOC profile" (lines 440–441), i. e., that the fitted values for these parameters are more or less strongly correlated, and then not even find a hint of a check for possible correlations between the values determined here. The extra constraint from the pore water sulfate profile may alleviate the degree of correlation between the two parameter values, but it is highly unlikely that the correlation between their values would go away.

As discussed above and in the revised manuscript, the adopted inverse modeling approach (four statistical measures, 2 species) alleviates the limitation induced by the correlation between parameter a and v (see discussion above). In addition, our best-fit parameter estimates do not reveal a correlation between a and v.



Figure 1. Model-derived a and v values for best fits determined in this study (extracted from Fig. 6 in the revised manuscript).

Accordingly, it does not make any sense to conclude that the whole story boils down in the end to determine solely a. In the absence of information about the correlation between a and n values, such a conclusion is simply unwarranted. Similarly, problems related to the difficulties "to quantify OM contents at the sediment-water interface (SWI) due to the common loss of the upper few centimetres during sampling [...]" (lines 438–439) are emphasized for the results of previous studies, but not even mentioned regarding the results presented here. The uncertainties on the a values derived here may thus possibly be significantly larger than one might think, as illustrated above.

We agree that model results are subject to the discussed limitations (non-steady state, core top loss, uniqueness of fit), and we further indicate that in the revised manuscript <u>(Sect. 4.1.1, L. 333 onwards;</u> <u>see above)</u>; however, we reiterate that adding additional constraints alleviates these limitations. In addition, as discussed in the manuscript, our conclusions are fully supported by:

- Several different, previously published RCM model studies, each using a different model structure, different observational data (degradation rates, pore water depth profiles, OM depth profiles) and spanning a wide range of different environments and timescales (Middelburg, 1989; Boudreau and Ruddick, 1991; Forney and Rothman, 2012; Katsev and Crowe, 2015; Jørgensen and Parkes, 2010; compilation by Arndt et al., 2013).
- Previously published, additional observational data from the respective sites (e.g., direct rate measurements, other model studies).
- Their consistency with our current understanding of the main controls of OM degradation in marine sediments (see discussion in Sect. 4.1.4).

Finally, in the conclusions readers are "[. . .] caution[ed] against the use of single environmental master variable such as water depth, sedimentation rate or organic matter deposition fluxes beyond the local scale" (lines 912-914) and yet the model simulations rely upon exactly this kind of master variable when it comes to determining the solids' burial rate, w(z), which is above all quite critical for the outcome of the paper. It is furthermore not entirely clear what is meant by "beyond the local scale." Does "local" stand for regional or for a given environmental setting, or does it stand for a given depth, deposition rate or some other chosen independent master variable? This should be stated more unambiguously.

We argue that the complex and dynamic set of environmental factors that control OM reactivity cannot be easily reduced to one single master variable such as water depth or sedimentation rate. This is supported by the lack of statistically significant relationships between the inversely determined OM reactivity parameters established here (as well as in previous studies, e.g., Arndt et al, 2013) and those single environmental master variables. However, we do observe – albeit weak – relationships between OM reactivity and water depths or sedimentation rate on the regional scale (i.e., under broadly similar environmental conditions). Furthermore, we acknowledge that water depth may be an acceptable proxy for OM reactivity in the absence of more suitable information (Sect. 4.1.4, L. 488–490; Sect. 5, L. 663–665).

However, Fig. 6b indicates that water depth seems to be a useful and easily accessible first-order proxy for this complex interplay of environmental controls on OM reactivity. Thus, it may serve as an acceptable predictor for first-order global reactivity patterns in the absence of more suitable information.

Yet, results show that, if no other information is available, water depth can serve as a useful proxy for the complex and dynamic interplay of environmental drivers and can be used to predict first-order, large scale OM reactivity patterns.

By local scale we refer to a specific, local depositional environment in contrast to multiple depositional

environments or the global scale. We have clarified this point in the revised manuscript (L. 37-39, L.

<u>475–476)</u>.

Thus, we caution against the simplifying use of a single environmental control for predicting apparent OM reactivity beyond a specific local environmental context (i.e., well defined geographic scale).

While these trends are extremely weak on a global scale, they are relatively more pronounced within a given geographical setting (i.e., on a local/regional scale).

We do make use of empirically derived global relationships that link water depth with sedimentation rates and bioturbation coefficients (Middelburg et al., 1997). However, in contrast to OM reactivity data, the compiled global observational data sets in Middelburg et al. (1997) reveal statistically significant relationships between sedimentation rate/ bioturbation coefficient and water depths that are further confirmed by additional global data (e.g., Burwicz et al., 2011; Solan et al., 2019). Additionally, the empirical water depth–sedimentation rate relationship is only applied to estimate sedimentation rates at sites for which no direct observational data was available (e.g., Severn estuary). For the majority of our sites, we apply observed sedimentation rates. Unfortunately, bioturbation rate estimations are often not available for the studied sites, thus we mostly rely on the empirical global relationship to estimate bioturbation coefficients.

Conclusions

As mentioned in the general appreciation of manuscript, I find that the conclusions are overdone. The authors claim that they "[...] narrowed the most plausible range of a to 10^0 – 10^4 years." (line 909),

from a range of 10^{-3} – 10^{7} derived from a global compilation. This reads impressive. However, upon inspection of the results on Fig. 4, one realizes that the size of "This study" is only about one quarter of the "Global compilation", and that more than 90% of the values for a from the "Global compilation" were already within 10^{0} – 10^{4} . As models with complex reaction networks are known to generally present a stable rather than a dynamic behavior when it comes to the sensitivity with respect to parameter value perturbations, the clustering of the model results around the mean or the median was thus to be expected. It is therefore not clear how significant and important this narrowing is in the end.

A reformulation of the conclusions in more modest terms would be appropriate.

The significance of our findings, alongside previous publications, is the consolidation of this information. As pointed out by previous studies, more data and consistent model approaches would be needed to confirm the observed parameter trends (e.g., Boudreau and Ruddick, 1991; Arndt et al., 2013). Previous model results have been obtained using different model structures and observational data sets of different comprehensiveness, questioning the direct comparability of these results. By gathering these data and confirming this window, we offer means for model parametrisation when dealing with data poor areas and timescales based on a robust and transferable dataset. We have revised the conclusions to make clear our point here, the consolidation of the RCM parameters dataset in a global scale (**L. 648–656**).

Our findings corroborate previous findings (Arndt et al., 2013; Boudreau and Ruddick, 1991; Forney and Rothman, 2012; Middelburg, 1989) that the RCM parameter v is globally relatively constant (v = 0.1-0.2). Exceptionally high v > 0.2 are often associated to deposition and burial of highly reactive phytoplankton debris in high productivity regions associated with well-established OMZs. In contrast, in agreement with previous findings, RCM parameter a can span several orders of magnitude at a global scale, suggesting that the parameter a is the main parameter describing the variability of apparent OM reactivity. Consequently, future modelling efforts to quantify OM reactivity on a global scale could be reduced to one main reactivity variable. Based on our results and previous findings, we consolidate range of predominant a distribution to 10^0-10^4 years. This is a valuable constraint when dealing with data poor regions and timescales (e.g., Hülse et al., 2018), since it excludes extreme values at both ends of the a-range.

Additionally, the model applied here, and certainly some of these applied previously, do not include complex reaction networks. We focus on OM dynamics mainly driven by organic carbon, sulfate, and methane interplay (ESM, Table S4).

Technical comments

Throughout the paper: as far as I know, the symbol used for "year" in Biogeosciences is not y but yr.

Corrected.

Throughout the paper: watch out for spurious points after equation numbers Corrected.

Line 247: "Findley" should read "Findlay"

Removed.

Line 264: "a Gamma function" should read "a gamma distribution" (the name is not capitalized; the gamma function and the gamma distribution are two completely different things— here it is the distribution that is relevant)

Corrected.

Lines 267 and 269: please use the standard notation for the gamma function which has been Γ for more than two centuries (and not τ ; also notice that "the Gamma function" should read "the gamma function"

Corrected.

Lines 267ff: before this line, the RC parameters were denoted by a and n. Now they become a and n and on line 477, it is switched back to a and $n \dots Eq. (5)$ here has both. Please chose one notation and use it throughout. Be aware that the irrigation parameter is also denoted by the symbol a.

Corrected.

Line 286: "the Gamma distribution" should read "the gamma distribution" Corrected.

Line 286: "the burial age (z = z - zbio)" is ambiguous/unclear

Corrected (L. 212). For non-bioturbated sediments ($z > z_{bio}$) the burial age(z)...

Line 296: "Michalis-Menten" should be "Michaelis-Menten" (but should be discarded anyway) Removed.

Lines 296–305: the style of this whole paragraph is very confusing and cannot be understood without a priori knowledge. Please rewrite and use precise language, starting by making a clear distinction between TEA and TEA concentrations.

Revised, see specific comments above.

Lines 303 and 305 (eqns. (8) and (9)): something is wrong here – neither j > Kj nor $j \le Kj$ make sense. Also: there is a spurious point after the equation number (9).

Removed.

Line 309: "biomolecular" should read "bi-molecular"

Removed.

Lines 319ff and eqn. (10): is this correct? What is ki? Is the numerator at the right-hand side of eqn. (10) correct? There is a spurious point after the equation number.

Removed.

Line 331: "incomplete Gamma function" should read "incomplete gamma function" Corrected.

Lines 333 and 335 (eqns. (12) and (13)): τ *should read* Γ *(four times)* Removed.

Line 361: φ^2 is certainly not tortuosity (symbol φ was previously used for porosity). . . Removed. Lines 370ff: please specify the units of the parameters and of the resulting Dbio

 z_{bio} is given in cm; D_{bio} is given in cm² yr⁻¹ (**Table 4**).

ine 411: should read "quadratically distributed for $\xi n >> \xi c$ and linearly distributed for $\xi n << \xi c$ " Removed.

Line 418 (eqn. (21):

Yes, the run time is dependent on the length of the model domain L, thus $runtime = L/\omega$. However, this equation has been removed from the revised model description.

Line 418: "where concentrations exceed mM": something must be missing here

Corrected (L. 263). where concentrations exceed millimolar levels.

Lines 486ff: here, F is used as a symbol for fluxes; elsewhere (section 3.2.1.3), F denotes fractions; a few lines below, the symbol for fluxes becomes by J. Please revise the notation scheme for the whole paper and chose a consistent one to improve readability. As far as possible, please stay close to schemes used elsewhere in the literature

All notations have been revised (see above; Table 3, revised manuscript).

Line 584: Not sure what the citation of Westrich and Berner (1984) has to do here as it is about (multi) G models, not about RC models.

The mentioned a value is derived from a fit to the data provided in *Westrich and Berner (1984)*. This might be misleading; thus, this reference was removed.

Line 1068: 137Cs should read ¹³⁷Cs

Corrected.

Table 1: this table runs over five (!) pages, with some pages having only two (!) lines. This is completely impractical. It would be better to present this information, if required, in an alternative form.

We shortened Table 1 (Table 2, revised manuscript) by removing the more descriptive column *Biological Parameters*. Such information has been incorporated to the ESM (Sect. S1, Table S1).

Table 4: character size too small (exponents essentially unreadable)

The font size of all tables was adjusted (10 pt) to improve readability.

Figure 4: the x-axis annotation for part b) is incorrect. There is no unit such as Log y. What is shown on the x axis is log(a/yr), i.e., the logarithm in base 10 of a expressed in years. Logarithms never have units and neither have their arguments.

Figs. 5, 6, 7, 8: same as for Fig. 4 (all units related to logarithmic axes are wrong).

All figures were revised for symbols and notations. Specifically, here the axes are now given in scientific notation (10^x) .

References

Aguilera, D. R., Jourabchi, P., Spiteri, C., and Regnier, P.: A knowledge-based reactive transport approach for the simulation of biogeochemical dynamics in Earth systems, Geochem. Geophys. Geosystems, 6, 1–18, https://doi.org/10.1029/2004GC000899, 2005.

Arndt, S., Jørgensen, B. B., LaRowe, D. E., Middelburg, J. J., Pancost, R. D., and Regnier, P.: Quantifying the degradation of organic matter in marine sediments: A review and synthesis, Earth-Sci. Rev., 123, 53–86, https://doi.org/laro, 2013.

Boudreau, B. P. and Ruddick, B. R.: On a reactive continuum representation of organic matter diagenesis, Am. J. Sci., 291, 507–538, https://doi.org/10.2475/ajs.291.5.507, 1991.

Boudreau, B. P., Mucci, A., Sundby, B., Luther, G. W., and Silverberg, N.: Comparative diagenesis at three sites on the Canadian continental margin, J. Mar. Res., 56, 1259–1284, https://doi.org/10.1357/002224098765093634, 1998.

Bowles, M. W., Mogollon, J. M., Kasten, S., Zabel, M., and Hinrichs, K.-U.: Global rates of marine sulfate reduction and implications for sub-sea-floor metabolic activities, Science, 344, 889–891, https://doi.org/10.1126/science.1249213, 2014.

Burdige, D. J.: Geochemistry of marine sediments, Princeton University Press, Princeton, NJ, 609 pp., 2006.

Burwicz, E. B., Rüpke, L. H., and Wallmann, K.: Estimation of the global amount of submarine gas hydrates formed via microbial methane formation based on numerical reaction-transport modeling and a novel parameterization of Holocene sedimentation, Geochim. Cosmochim. Acta, 75, 4562–4576, https://doi.org/10.1016/j.gca.2011.05.029, 2011.

Canfield, D. E., Jørgensen, B. B., Fossing, H., Glud, R., Gundersen, J., Ramsing, N. B., Thamdrup, B., Hansen, J. W., Nielsen, L. P., and Hall, P. O. J.: Pathways of organic carbon oxidation in three continental margin sediments, Mar. Geol., 113, 27–40, https://doi.org/10.1016/0025-3227(93)90147-N, 1993.

Forney, D. C. and Rothman, D. H.: Inverse method for estimating respiration rates from decay time series, Biogeosciences, 9, 3601–3612, https://doi.org/10.5194/bg-9-3601-2012, 2012.

Freitas, F. S., Hendry, K. R., Henley, S. F., Faust, J. C., Tessin, A. C., Stevenson, M. A., Abbott, G. D., März, C., and Arndt, S.: Benthic-pelagic coupling in the Barents Sea: an integrated data-model framework, Phil. Trans. R. Soc. A., 378, 1–15, http://dx.doi.org/10.1098/rsta.2019.0359, 2020.

Heggie, D., Maris, C., Hudson, A., Dymond, J., Beach, R., and Cullen, J.: Organic carbon oxidation and preservation in NW Atlantic continental margin sediments, Geol. Soc. Lond. Spec. Publ., 31, 215, https://doi.org/10.1144/GSL.SP.1987.031.01.15, 1987.

Hülse, D., Arndt, S., Daines, S., Regnier, P., and Ridgwell, A.: OMEN-SED 0.9: A novel, numerically efficient organic mattersediment diagenesis module for coupling to Earth system models, Climate and Earth System Modeling, https://doi.org/10.5194/gmd-2017-296, 2018.

Jørgensen, B. B.: A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments: II. Calculation from mathematical models, Geomicrobiol. J., 1, 29–47, https://doi.org/10.1080/01490457809377722, 1978.

Jørgensen, B. B. and Kasten, S.: Sulfur Cycling and Methane Oxidation, in: Marine Geochemistry, edited by: Schulz, H. D. and Zabel, M., Springer-Verlag, Berlin/Heidelberg, 271–309, https://doi.org/10.1007/3-540-32144-6_8, 2006.

Jørgensen, B. B. and Parkes, R. J.: Role of sulfate reduction and methane production by organic carbon degradation in eutrophic fjord sediments (Limfjorden, Denmark), Limnol. Oceanogr., 55, 1338–1352, https://doi.org/10.4319/lo.2010.55.3.1338, 2010.

Katsev, S. and Crowe, S. A.: Organic carbon burial efficiencies in sediments: The power law of mineralization revisited, Geology, 43, 607–610, https://doi.org/10.1130/G36626.1, 2015.

LaRowe, D. E., Arndt, S., Bradley, J. A., Estes, E. R., Hoarfrost, A., Lang, S. Q., Lloyd, K. G., Mahmoudi, N., Orsi, W. D., Shah Walter, S. R., Steen, A. D., and Zhao, R.: The fate of organic carbon

in marine sediments - New insights from recent data and analysis, Earth-Sci. Rev., 204, 103146, https://doi.org/10.1016/j.earscirev.2020.103146, 2020.

Mackin, J. E. and Swider, K. T.: Organic matter decomposition pathways and oxygen consumption in coastal marine sediments, J. Mar. Res., 47, 681–716, https://doi.org/10.1357/002224089785076154, 1989.

Manzoni, S., Katul, G. G., and Porporato, A.: Analysis of soil carbon transit times and age distributions using network theories, J. Geophys. Res. Biogeosciences, 114, https://doi.org/10.1029/2009JG001070, 2009.

Meile, C. and Van Cappellen, P.: Particle age distributions and O $_2$ exposure times: Timescales in bioturbated sediments, Glob. Biogeochem. Cycles, 19, 1–12, https://doi.org/10.1029/2004GB002371, 2005.

Meister, P., Liu, B., Ferdelman, T. G., Jørgensen, B. B., and Khalili, A.: Control of sulphate and methane distributions in marine sediments by organic matter reactivity, Geochim. Cosmochim. Acta, 104, 183–193, https://doi.org/10.1016/j.gca.2012.11.011, 2013.

Middelburg, J. J.: A simple rate model for organic matter decomposition in marine sediments, Geochim. Cosmochim. Acta, 53, 1577–1581, https://doi.org/10.1016/0016-7037(89)90239-1, 1989.

Middelburg, J. J.: Reviews and syntheses: to the bottom of carbon processing at the seafloor, Biogeosciences, 15, 413–427, https://doi.org/10.5194/bg-15-413-2018, 2018.

Middelburg, J. J.: Marine Carbon Biogeochemistry: A Primer for Earth System Scientists, Springer International Publishing, Cham, https://doi.org/10.1007/978-3-030-10822-9, 2019.

Middelburg, J. J., Soetaert, K., and Herman, P. M. J.: Empirical relationships for use in global diagenetic models, Deep Sea Res. Part Oceanogr. Res. Pap., 44, 327–344, https://doi.org/10.1016/S0967-0637(96)00101-X, 1997.

Owings, S. M., Bréthous, L., Eitel, E. M., Fields, B. P., Boever, A., Beckler, J. S., Bombled, B., Lansard, B., Metzger, E., Rabouille, C., and Taillefert, M.: Differential manganese and iron recycling and transport in continental margin sediments of the Northern Gulf of Mexico, Mar. Chem., 229, 103908, https://doi.org/10.1016/j.marchem.2020.103908, 2021.

Solan, M., Ward, E. R., White, E. L., Hibberd, E. E., Cassidy, C., Schuster, J. M., Hale, R., and Godbold, J. A.: Worldwide measurements of bioturbation intensity, ventilation rate, and the mixing depth of marine sediments, Sci. Data, 6, 58, https://doi.org/10.1038/s41597-019-0069-7, 2019.

Taylor, K. E.: Summarizing multiple aspects of model performance in a single diagram, J. Geophys. Res. Atmospheres, 106, 7183–7192, https://doi.org/10.1029/2000JD900719, 2001.

Thullner, M., Dale, A. W., and Regnier, P.: Global-scale quantification of mineralization pathways in marine sediments: A reaction-transport modeling approach, Geochem. Geophys. Geosystems, 10, 1–24, https://doi.org/10.1029/2009GC002484, 2009.

Van Cappellen, P. and Wang, Y.: Cycling of iron and manganese in surface sediments; a general theory for the coupled transport and reaction of carbon, oxygen, nitrogen, sulfur, iron, and manganese, Am. J. Sci., 296, 197–243, https://doi.org/10.2475/ajs.296.3.197, 1996.

Wang, Y. and Van Cappellen, P.: A multicomponent reactive transport model of early diagenesis: Application to redox cycling in coastal marine sediments, Geochim. Cosmochim. Acta, 60, 2993–3014, https://doi.org/10.1016/0016-7037(96)00140-8, 1996.

Wehrmann, L. M., Arndt, S., März, C., Ferdelman, T. G., and Brunner, B.: The evolution of early diagenetic signals in Bering Sea subseafloor sediments in response to varying organic carbon deposition over the last 4.3Ma, Geochim. Cosmochim. Acta, 109, 175–196, https://doi.org/10.1016/j.gca.2013.01.025, 2013.