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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 Bernard Boudreau (RC1),

On behalf of all co-authors, I want to thank you for revising our manuscript. We appreciate the set of very detailed and constructive comments you made on our work.

Firstly, I would like to stress that we have no intention to criticize the work by Boudreau and Ruddick (1991), hereafter BR91, nor to take credit for *developing a quite different approach*. We will carefully revise the manuscript to avoid this misunderstanding. In fact, we use the same approach as BR91 (i.e., statistical fitting of organic matter profiles). However, in our work, we approximate the Reactive-Continuum Model (RCM) in the bioturbated sediment to a multi-G approach to circumvent difficulties in determining the age distribution of reactive species within the bioturbated layer (L292-294), as well as extend the RCM by including SO<sub>4</sub> (and CH<sub>4</sub>) profiles into the fitting procedure as additional constraints (L462-464). I believe the misunderstanding might have partly arisen from our discussion (L434-442) of the limitations that are inherent to inverse modeling/profile fitting approaches (i.e., core top loss, non-steady state effects, uniqueness of solution). These limitations apply to all these

approaches (i.e., from comprehensive sets of profile data to single profiles, and including the ones presented here). I would like to stress that this discussion is definitely not intended to discredit the results presented in BR91, but rather to highlight limitations and justify the inclusion of additional constraints. Our study thus builds on BR91 and further extends the already existing RCM parameter estimates (from BR91 and others) with the aim of better constraining the parameter span across a range of different depositional environments, and thus ultimately advances our understanding of the environmental controls on apparent organic matter reactivity. Most importantly, as you point out in your last comment, the new parameter estimates in fact confirm the initial findings of BR91 (relatively constant  $\nu$  and similar  $a$  range) and, together, the extended data set thus serves as a guide for model parametrization in data poor areas.

Below we provide more detailed and specific comments to the issues you raised.

A) We will revise the presentation of Sections 3.2.1.2 and 3.2.1.3 for clarity.

Aa) You are correct regarding the application of Eq. 6. It is only valid for non-bioturbated sediments for the reasons you highlight. In our work, we make a similar observation (L292-294) on the limitations when dealing with bioturbated layer. Therefore, Eq. 6 is never applied to bioturbated sediments. We are confident that results we later present on Fig. 6 (L657 onwards), 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 (L662-665).

Ab) 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 very clear. We will improve this description in the revised manuscript. 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  $k_i = 10^{i+1/2} \text{ y}^{-1}$  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 symbol change of the Gamma function was non-intentional and must have occurred during the editing of the manuscript. Additionally, we agree that we should be more consistent in the use of symbols for organic matter and fluxes, as well as avoid double uses. We will revise the manuscript accordingly.

B) I would like to point out that, as mentioned throughout the manuscript, 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 BR91 results. Therefore, for clarity of the revised manuscript, we will restate our points in L437-441 (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 BR91. We evidenced that by the comparison of our results to BR91 results 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) In the manuscript, we highlight the core top loss as a general limitation of the used approach, rather than as a specific limitation of BR91. In fact, we acknowledge that core top loss likely also affects some of the data considered in this study. 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) Again, we definitely do not think or advocate that the BR91 results 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. In fact, our results for the Bering Sea site are influenced by non-steady state conditions (p 17, line 517-518).

Bc) 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 SMTZ 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 adding additional constraints (e.g., sulfate profiles, SMTZ depth), we were able to exclude those pairs that only fitted organic matter profiles well. We will rephrase the statement on L440-441.

B1) 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).

B2) 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 of BR91.

B3) Again, it is definitely not our intention to discredit the BR91 study, especially because we actually do not develop a new method; rather, we use the exact same approach used in BR91. 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 in combination with information about sedimentation rates and macrobenthic activity provide such a “minimal set”.

C) We agree with this point and will revise the manuscript accordingly.

D) We agree and will extend the discussion to include existing datasets.

Sincerely yours



Felipe Sales de Freitas and co-authors