Review of

Advancing on large-scale trends of apparent organic matter reactivity in marine sediments and patterns of benthic carbon transformation

submitted to *Biogeosciences*
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General comments

In this paper, Freitas and co-authors present model results obtained with the Biogeochemical Network Reaction Simulator (BRNS) configured to use a Reactive Continuum (RC) representation for organic matter degradation based upon a gamma distribution for the initial reactivity of organic matter and an inverse method to retrieve the characteristic RC parameters a and ν of the gamma distribution from TOC and pore water concentration profiles at fourteen different stations in five different depositional environments. The paper fits well the scope of *Biogeosciences*.

I found the study in itself quite interesting. The systematic investigation of the reactivity across very different environmental settings with a common approach and set of tools looks very promising to me. Unfortunately, the paper does not come up to my expectations. Despite the excellent English—I cannot remember having had to review a paper with so few English errors—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.

Besides these matters of style, the paper unfortunately presents several weaknesses and even errors. 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. 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.

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.

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.

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.

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.

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 ν and a values. We are only told that the adjustment is carried out with the TOC and pore water SO_4^{2-} concentration profiles (and CH_4 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 even considered—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.

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 ν 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, also addressing shortcomings (only parallel reactions, no interaction between the different k-components, . . .). 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, t_1 and t_2,

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

and thus, assuming that $t_2 > t_1$

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

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 t_1 and not 0 as supposed. The inversion procedure will thus provide an estimate for $a+t_1$ instead of the expected a. Depending on t_1, these two may be significantly different from each other. $k(0)$ at the sediment water interface (eqn. (23)) incorrect.

Imprecisions, errors and incoherences

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

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.

The description of the multi-G approximation of the RC model in the bioturbated layer is impossible to understand. There is a mixture of i and j subscripts that is not very transparent. The definition of the $F(k_j,0)$ is not given. Eqn. (11) suggests to me that $F(k_j,0)$ is probably the fraction of the initial OM, OM(0), for which $k \geq k_j$ and accordingly F_i would be that fraction of OM(0) that has $k_{j-1} \leq k \leq k_j$. This is, however, only a guess and it actually implies that eqn. (11) should read

$$F_i = F(k_{j-1},0) - F(k_j,0)$$

because $F(k_{j-1},0) > F(k_j,0)$ if $k_{j-1} < k_j$. A precise model description would not require such guesswork.

Eqns. (12) and (13) are also unclear and as they stand, they are not correct. First of all $f(k,0)$ has not been defined, but should most probably be $om(k,0)/POC(0)$, with $om(k,0)$ from eqn. (5). Again, the notation is misleading, as the symbol f was previously used to denote inhibition terms. Second, $f(k_1,0)$ and $f(k_{200},0)$ would be constant and both integrals thus infinite. It would make more sense to integrate $f(k,0)$. This would however mean that the definition for F_1 (eqn. (12)) cannot be correct, and should rather be

$$F_1 = \frac{1}{\Gamma(\nu)} \int_0^{k_1} a^\nu k^{\nu-1} \mathrm{e}^{-ak}\, dk = 1 - \frac{\Gamma(\nu, ak_1)}{\Gamma(\nu)}$$

because else, the fraction with $k < k_1$ would be lost. F_1 following eqn. (12) would actually be close to 1.

Besides these, there are too many other errors in the details: the grid description is incorrect, the run time definition looks as if run time was dependent on depth. . . (see technical notes below). I may have overlooked some more. Most of these errors can be easily fixed. They do, however, witness of a certain lack of care in the preparation and the proofreading of the manuscript before submission.

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. One furthermore reads that "multiple a and ν 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. 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 ν 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.

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, $\omega(z)$, 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.

Conclusions

A 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.

Technical comments

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

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

Line 247: "Findley" should read "Findlay"

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)

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"

Lines 267ff: before this line, the RC parameters were denoted by a and ν. Now they become α and ν and on line 477, it is switched back to a and ν ... 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.

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

Line 286: "the burial *age* ($z = z - z_{bio}$)" is ambiguous/unclear

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

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*.

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

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

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

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

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

Line 361: φ^2 is certainly not tortuosity (symbol φ was previously used for porosity)...

Lines 370ff: please specify the units of the parameters and of the resulting D_{bio}

Line 411: should read "quadratically distributed for $\xi_n \ll \xi_c$ and linearly distributed for $\xi_n \gg \xi_c$"

Line 418 (eqn. (21): does "$run\ time = 2\frac{z}{\omega}$" make sense as it would imply that *run time* is different for each depth? I guess this should rather be "$run\ time = 2\frac{L}{\omega_L}$" or "$run\ time = 2\frac{L}{\omega_\infty}$."

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

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

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.

Line 1068: 137Cs should read ^{137}Cs

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.

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

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 $\log(a/\mathrm{yr})$, 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).

References

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. and Westrich, J. T.: The dependence of bacterial sulfate reduction on sulfate concentration in marine sediments, Geochim. Cosmochim. Ac., 48, 2503–2516, https://doi.org/10.1016/0016-7037(84)90301-6, 1984.

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.