AUTHOR'S RESPONSE

Dear Editor,

Please find below our listing to changes in response to the reviewers' comments. We refer to our author comments at <u>https://doi.org/10.5194/gmd-2022-84-AC2</u> and <u>https://doi.org/10.5194/gmd-2022-84-AC3</u> for detailed responses. We also provide a tracked-change version of the manuscript highlighting the point-by-point insertions and deletions in the text alongside a revised manuscript. We hope these changes will address the reviewer's comments.

Best regards,

Stanley Nmor, on the behalf of the authors.

REVISIONS IN RESPONSE TO COMMENTS BY ANONYMOUS REFEREE #1

(1) Model description

It would be helpful if the authors can provide a short overview of model development relative to the previous and already published works/models. Current manuscript referred to these works, but what is exactly new is kind of obscure. Also, brief summary of the capacity/features of previous models from which the current model has been developed will be useful, including programing language, governing equations, and algorithms utilized for numerical solutions (finite difference/volume/element method for equation differencing and Newton iteration if adopted for solution seeking etc.). The current manuscript provides some of above information, but some information is still missing. And it is not 100% clear which part is new to the current model and which part is not new.

• We added a paragraph (section 1.0) to the introduction that briefly describes how FESDIA differs from its other published models. Furthermore, a new sub-section has been added to the materials and methods (section 2.2.9 in revised manuscript) detailing FESDIA's numeric solution methods.

(2) Definition of relaxation time

Eq. 22 describes the change rate of species concentration within sediment profile but does not necessarily define deviation from the pre-flood profile. Also, current manuscript lacks figures that directly compare the solute profile development relative to the pre-event profile. I think Figs. 4-8 need to be improved so that profile development relative to the pre-event profile is more visually obvious.

• We explained why the profiles shown in Figures 4–8 were chosen because our paper only attempted to provide an estimate of when the perturbation disappears and not necessarily "return to the old profile" (see section 2.2.10 and section 4.5). The former concept is easily

quantifiable, whereas the latter may be difficult to estimate for a complex dynamical system such as those found in coastal sediment.

(3) Description of model limitations and future development

Relevant to the above point, but limitations of model should be discussed more. There are several simplifying assumptions in the model but its influences on e.g., model validation, comparison with observation and estimation for relaxation time are not discussed. For instance, the authors assume that burial rate/porosity does not change with the flooding, but it is not discussed whether this assumption is defendable or close to what we observe. Model validation or comparison with the observed data is essentially based on solute profiles, which likely resulted from a good fit of TOC and may be achievable under different assumptions (those that allow changes of burial rate, porosity, bio-mixing and irrigation etc.). If this is the case, the relaxation time is likely quite different under different assumptions. While most of manuscript discussed how relaxation time is calculated under the specific assumption adopted for this study, it is not discussed how the relaxation time is affected by adopted assumptions.

• We have added a new section on model limitations, as well as where future development will be made to FESDIA (see section 4.4 in revised manuscript). There we discuss possible biogeochemical processes which might affect the relaxation estimate we calculated in line with the reviewer's comment.

SPECIFIC COMMENTS

L134. Three OM fractions? Thought the authors are using two.

• In the revised paper, this sentence has been clarified by emphasizing that FESDIA only considers TWO reactive modelled fractions with the inert fraction parameterized using an asymptotic refractory carbon as background to diagnose the total organic carbon (TOC) from the simulation.

L138. Froelich et al. (1979) rather than Froelich (1988) according to Bethke et al. (2011, AJS 311, 183)?

• We apologize for this. This have been corrected in the revised manuscript (see L150 in the revision).

L166. What does 'a coupled reaction formulation' mean?

• This statement has been rewritten in L179 in the revised manuscript.

Eqs. 6, 7. It does not make any sense to use/define 'maximum rates' when one is not using Monod or Michaelis-Menten type of equation.

• We have corrected for the text by correctly removing the "maximum" from the sentence.

Eq. 7. What is the definition of rH2Soxid?

• This is have removed as it was duplicated in the original text.

Eqs. 8, 9. What is the assumption behind the formulation of these equations? For instance, how do you obtain Eq. 9 for aqueous NH4+ with accounting for adsorbed NH4+? Can you track NH4+ adsorbed onto solid species along with OM and other solids or do you have to simplify that adsorption is depthindependent and/or time-independent? This can be important if solid materials with unoccupied exchange sites are flooded to sediment depocenter in a short period of time. If such case is possible, one would expect a large sink of NH4+ to the exchange sites? Related to this, do you model PO4 adsorption onto Fe hydroxides or you do not have to do this?

• The assumption underlying this formulation has been clarified in section 2.2.3 L195-199 of the revised manuscript. We did not discuss the effect of PO4 because the described model does not include it. However, we explain how adsorption affects NH4 diffusion.

L205. Does porosity 'decay'?

• We have changed the phrase according in revised manuscript in L224.

L209. According to Eq. 10, the authors seem to assume intraphase biodiffusion (Meysman et al., 2005, GCA 69, 3601). The statement here mentioning an interphase biodiffusion is inconsistent with Eq. 10.

• This mistake as used in this particular sentence have been corrected to "*interphase*" to reflect how bioturbation is modelled in FESDIA (in L228 of revised manuscript).

Eq. 14. Irrigation term is not found in the governing equation. Is it included as a reaction term?

• We have stated clearly where that the REAC term in Eq 8 – 9 includes the irrigation term in L191-194.

Section 2.2.5 & Section 2.2.6. More details are desirable as adding grid for implementing a deposition event must be an important addition to the previous modeling framework. For instance, how you define Zpert, e.g., number of grids and their geometry etc. Some examples, not only schematics may also be useful.

• We have explained how the vertical grid was created using other community tools for early diagenesis. There is a reference to those tools. The grid layer schematic is shown in the supplementary figure (Fig S1).

L276. 'maximum in the spring and minimum in fall and winter'. This line does not make sense to me.

• This ambiguity in our choice of word have been corrected in the reviewed manuscript (in L305 for revised manuscript).

Eq. 21. What is the units of TOC? Also, how do you derive Eq. 21? Is this simply analytical solution of the governing equation? In any case, it would be helpful if the authors can provide the procedure to obtain Eq. 21 somewhere.

• This part of section 2.2.8 have been rewritten to entail to the TOC calculation, unit and how it was derived.

L321. 'were utilizes the R programming language'. Correct English?

• We apologize for this grammatical mistake. It has been corrected in the revised manuscript.

Section 2.2.9. It would be helpful if the authors can make a short description of what part of "deSolve package" they used, not only directing the reader to the R-forge webpage. More specifically, how the authors numerically solve the governing equations, apart from "method-of-lines" methods? Use of any finite difference/volume/element method?

• We have added a new subsection (see section 2.2.9) to reflect this remark and the method used to solve the PDE (in L333 of revised manuscript).

How is the time-integration of governing equations made (time-implicitly or -explicitly)?

• New information on this is added in section 2.2.9 of the revised manuscript.

L331. What is a "slow" stationary state?

• We have clarified to the remark of the phrase above. This sentence has been paraphrased better (in L372).

Eq. 22. Not quite sure this is a legit mathematical expression. phi(tau) < threshold is what I thought is consistent with what the authors described.

• To aid comprehension and consistency with the textual explanation, we modified this equation block to explicitly include the threshold subscript (in L377 of the revised manuscript).

L334. "threshold (i.e given by the median over the entire time duration)." Do you mean that the run is finished when difference becomes less than the median value throughout the simulation and then tau is defined as the model time required for this?

• No change required. We provided answer our affirmative answer to the reviewer.

L340. I probably do not fully understand the ensemble of simulations here to estimate the uncertainty in tau. What parameter do you randomly re-sampled exactly? Median of the reference run through time? If so, the runs for determining the uncertainty in tau is conducted until (randomly-chosen) prescribed median is crossed? But this does not necessitate re-running of the model as the boundary conditions are not changed?

• This section 2.2.10 has been rewritten to better convey the nature of the ensemble run calculation for determining the uncertainty.

L383. "a thickness scale of 1 cm to 30 cm in 5 cm increments". This line does not make sense to me. What exactly did you use for thickness in sensitivity analysis?

• This line has been rewritten (in L434 in the revised manuscript).

L507. Please specify what "RiOmar" stands for.

• This is a common abbreviation used by researchers in this field. We expanded on this definition in the introduction, where it was first mentioned.

L621. above \rightarrow below?

• This word and its surrounding sentence have been changed (in L674 of the revised manuscript).

--- TECHNICAL COMMENTS ---

• The minor fix for the technical comments listed by the reviewer have been corrected accordingly in the revised manuscript.

REVISIONS IN RESPONSE TO COMMENTS BY ANONYMOUS REFEREE #2

GENERAL COMMENT

Rassmann et al. (2016 https://doi.org/10.5194/bg-13-5379-2016, 2020 https://doi.org/10.5194/bg-17-13-2020) described Rhône river delta sediments rich in calcium carbonates, and reported signs of the various reactions associated with calcium carbonates occurring in those sediments. If the focus here is Rhône river delta sediments, why not including any calcium carbonate species in the current model?

• In our response to the reviewer's comment we have address reasons why modelling the carbonate system wasn't modelled by FESDIA. We re-emphasis the primary goal of work presented here is to design a model to study the first order effects of flood deposition on the profiles (we argue that the effect of calcite formation is contribute <15% to the overall

variation in DIC profile which could help justify our choice), as well as to highlight the possibility of incorporating diagenesis changes in the sediment when including abrupt discontinuities. Given this computational demanding nature of incorporating carbonate chemistry as reflected in other model, we have omitted including such dynamics in the first working version of FESDIA. Effort are underway to bring this interesting carbonate calculation possibility to FESDIA. To that effect, we discuss this as some model limitation in section of 4.4 of the revised manuscript.

Section 2.2.6: this seems to be the most important section in terms of model development, but it is also the part I had the hardest time to follow. There are a lot of new terms introduced here and they are not well defined. The second paragraph starts to explain how post-flood organic carbon contents are derived, then mentions the solutes, then goes back to post-flood organic carbon content with Eq.(15)... I suggest putting more effort clarifying this section, defining terms with precise and consistent words, in order not to confuse the reader.

• This section has been rewritten to improve how FESDIA handled this depositional event calculation. A new table (see Table 1 in revised manuscript) has been added to the revised manuscript to assist in providing summary context to some of the symbols used in the FESDIA.

Specifically, what is the carbon enrichment factor (confac) exactly, and how does it differ from the proportionality constant (pfast)?

• We have clarified where the differences between in the concfac and pfast exist in L280 of section 2.2.6 in the revised manuscript. Briefly, "...This OC flux partitioning by pf ast occurs regardless of the event and it is related to the carbon flux received at the boundary, but the carbon enrichment factor occurs only during the event. The Carbon enrichment factor (α) can be viewed as a method of imposing a new initial condition only at the time of the event ...".

What is *Corg flood* and how does it differ from TOC (both are present in Eq. (15)? Is confactured for each simulation or is it constant? Is pfast tuned for each simulation or is it constant?

• We respond to the reviewer's observation. We included a glossary of the symbols used in the manuscript in the revised manuscript (see Table 1). Furthermore, the original manuscript states that only We respond to the reviewer's observation. We included a glossary of the symbols used in the manuscript in the revised manuscript (see Table 1). Furthermore, the original manuscript states that only alpha was changed in the sensitivity runs, with all other parameters remaining constant. This is added in section 2.2.11.1, in L427.

It is stated L187-188 that "For dynamic simulation, w can change as a function of time but in most cases, we assumed a constant value." In which cases exactly was w changing? Changing w in all cases seem like a necessity given that the novelty of the model is to simulate events in which the flux of deposited material (thus w) is strongly changing with time. How can a constant w be appropriate to simulate a flood? w also changes with sediment depth, because of chemical reactions occurring within the sediment (see Munhoven, 2021 https://doi.org/10.5194/gmd-14-3603-2021). Can the authors either better justify their choice of a non-changing w or update that in the model simulations?

• We have responded to the reviewer's comment. To summarize, we argue that because episodic flood deposition (~10-30cm/d of deposition in about 5 days depending on the extremity of the event) dominates the average background variation in sedimentation rate in the Rhône prodelta (where our benchmark was conducted) and this instantaneous deposited is treated separately in FESDIA, we can justify that the main variation in sedimentation is already accounted for. Furthermore, FESDIA has the option of including time-dependent sedimentation rates if such data are available (see section 4.4). We also mentioned that the current version of FESDIA does not take into account depth dependency change of w due to chemical diagenesis, and we explained why in our response to the reviewer's comment.

Section 2.2.7: in most O2 and pH microprofiles from the Rhône delta presented in Rassmann et al. (2016) we can see the influence of a diffusive boundary layer. Please discuss and justify the absence of diffusive boundary layer control on solutes as an upper boundary condition, or update the upper boundary condition accordingly to include this, as other models do in a simple manner (Boudreau et al., 1996 https://doi.org/10.1016/0098-3004(95)00115-8; Munhoven, 2021 https://doi.org/10.5194/gmd14-3603-2021; Sulpis et al., 2022 https://doi.org/10.5194/gmd-15-2105-2022)

• This is a significant omission in the current version of FESDIA, and we addressed it in our response to the reviewer. We made some simplifications and assumptions in the boundary condition, which are now covered in section 4.4 of the revised manuscript. Essentially, our conclusion for the relaxation times calculation does not drastically change with the inclusion of the DBL as the deviation of our simple calculation suggests that the relaxation times were within the confidence interval shown in this paper. However, we acknowledge that if oxygen fluxes are to be estimated, FESDIA in its current form will overestimate oxygen fluxes but less so for solutes such as DIC and SO₄. FESDIA will almost certainly include diffusive boundary layer dynamics in future versions. Section 4.5 of the revised article contains additional explanation (see L715).

SPECIFIC COMMENTS:

Shouldn't "Rhône" be spelled "Rhône", even in English language?

• The proper French spelling have been corrected in all instance within the manuscript.

L35: The use of the acronym RiOmar is not really needed, since only used once after. In general, avoid unnecessary acronyms.

L36: Although more commonly used, POC is also an unnecessary acronym here, since only used once after.

• We have corrected the text and removed redundant acronyms that were not used elsewhere in the manuscript.

L36-39: The sentence is unclear. "because it serves as a sink for particulate organic carbon and nutrients as well as an intense site of carbon and nutrient": what is the "it" referring to?

• The sentence has been rewritten to improve clarity (see L39 in the revised manuscript).

L40: I am not convinced that all the cited models have time-dependent capabilities, unlike several other, more recent models, published in this journal that explicitly do. Please update the list.

• An updated list of models has been added (see L42 in the revised manuscript).

L43: "massive episodic events" could refer to lots of processes, please be more specific

• The sentence has been modified (see L44).

L47-50: Sentence unclear. "Attempts to use mathematical models to understand perturbation-induced events on early diagenetic processes have resulted in a variety of approaches that incorporate this type of local phenomenon.": what is "this type of local phenomenon" referring to?

• The sentence has been changed to refer to the "phenomenon" (see L49).

L48-50: "As an example, previous research in deep-sea systems suggests that megafaunal perturbation can cause a 35% increase in silicic flux when compared to steady state estimates (Rabouille and Gaillard, 1990)" this is interesting but this level of precision seems unnecessary, what is the relevance for this study? Besides, what is a "silicic flux"? In which direction is the mentioned flux going?

• This entire sentence has been deleted because its omission has no effect on the overall narrative of the paragraph block.

L50: What is the "redox boundary"

L52-53: What does the "redistribution of solid-phase manganese with multiple peaks" mean?

• The sentence has been changed to explain what a "redox boundary" is and why "redistribution of solid-phase manganese with multiple peaks" could occur (see L50-54 in revised manuscript).

L62: "porewater species like oxygen (O2) can be restored after a few months": it is unclear. Do you mean that porewater concentrations can be restored to their pre-flood levels?

L66: what does "short-lived species" mean?

L67: DIC is a component, not a species.

• We have made correction to the text according (see L62, L67 -68).

Materials and methods

L93: "the organic matter delivered reflects the Rhône River inputs (Lansard et al., 2008; Cathalot et al., 2013)", in terms of what? Composition? Reactivity? Fig.1: I assume that the dashed and solid gray linings shown on the map depict bathymetry; it would be useful to precise it in a caption/legend.

• The sentence "organic matter delivered..." has been changed to reflect the origin and compositional nature. The map now has a caption (see L101 in the revised manuscript).

L107: what does "mode of behavior" mean?

L140: how exactly do "the reactivities decrease with depth" in the present model? From Table S1, it seems that the reactivities are constant.

L140: The sentence formulation is awkward: it is the degradation that would "cease", not its rate. Saying this also slightly exaggerated, degradation rates become indeed very small deep below the sedimentwater interface but they are never really equal to zero (e.g. Bradley et al., 2020 https://doi.org/10.1126/sciadv.aba0697).

Eq. (7): What are FeSpro and H2Soxid? Are they different from the FeS and the H2S produced by the reactions shown in Eq. (5)?

Why is one rate a capital R and the other a lower case r?

• In the revised manuscript, all points have been noted and changed. The word choice and syntax errors have been corrected.

Eq. (9): What is the value of kads and can you give some information on this aspect of the model?

• This information is provided in 2.2.3, and the kads value of 1.3 has been added to the main text and parameter table (see Table 3 and L197).

L216-220: How is irrigation implemented into the model, i.e., where does it appear in Eqs. (8 & 9)?

• We addressed this issue by stating that irrigation is included in Equations 8 and 9, and a comment on this has been added to the revised manuscript (see L205 and L235).

L236: What is a "time run"?

• This has been rewritten to be more understandable (see L255).

Eq. (15) Please precise here that TOCold is the TOC concentration at the old sedimentwater interface

• This distinction has been added to the text, and a table with a summary of the notation used has been provided (see Table 1 and L268).

L248: it would be good to have more information on confac (alpha): here it is tuned. How should it be used in future applications? Always to the same value? Does its value depends on type and magnitude of flood?

• This comment on the confac's flexibility can be found in sections 2.2.6 and 4.2 of the original text.

Fig.2: change "reactive Corg" for the notation "C (superscript)fast (subscript)org" for consistency

Table 2: the value for rslow is 0.0 d-1, but in the text it is indicated as 0.0031 d-1. Please clarify that

• Both have bee corrected and updated in the figure and table respectively (see Table 3).

Section 2.2.7: what about bottom boundary conditions? Is the concentration really set to 0 for all species, as indicated in Table S1? That would seem unjustified.

• This has been removed from the parameters list because all species have the same "zero flux boundary."

L289: By sedimentation rate do you mean solid burial velocity? Porewater burial velocity? Both should be different because porosity is not constant with depth.

• In our response to the reviewer, we addressed this question. FESDIA assumed that the advection rate is the same for both solid and solute, but that the diffusion effect is more dominant as transport for porewater species than for solute advection.

L289: Is w 0.027 or 0.03 cm per day? Be consistent between the text and tables.

• We have changed that and made both entry consistent (see L317 and Table 3).

L283: Why a different NC ratio for both organic matter fractions? How were the values of 0.14 and 0.1 obtained? Why are these values different from those shown in Table 2?

• In our response to the reviewer, we explain why the NC ratio for each fraction was different. The table value has been corrected.

L306: Can you provide details (i.e., show the formula) on how are equations 8-10 integrated?

L306: Please provide guidance on what dt values should users set depending on the simulation

• We provided this information in section 2.2.9 of the revised manuscript.

L313: First time the "mix" perturbation is mentioned. What is that?

• The "mix" phrase has been corrected.

Eq.(22) Why is it summed over the total number of grid points? Any perturbation following a flood should be the highest near the sediment-water interface, so wouldn't using data coming from deeper in the sediment to compute the relaxation time dilute the true signal and induce additional uncertainties?

• We provided our justification of why the whole grid was used for the calculation of the relaxation timescale in our response to the reviewer's comment.

Results

Fig4: what is the alpha value for the slow organic carbon fraction?

• The value of alpha has been included and updated in the Figure 4.

L409-412: Can the authors interpret the mismatch between modelled and observed SO4, DIC and NH4 values at depth? Wouldn't that argue for overestimated organic carbon reactivities at depth?

• We have provided a remark on the misfit, made an adjustment to a parameter (sedimentation rate - w) and updated the result accordingly.

Table 3: How can there be an oxygen flux to the sediment that is ten times smaller than a DIC flux from the sediment? Wouldn't a value closer to one be expected?

• No changes were made here. We have provided a response to this in our reply to the reviewer.

Fig.9: what is "degradable OM"? does that mean that the alpha value is the same for both fast- and slowdecay organic carbon? If so, precise it.

• This has been clarified in the revised manuscript with comment on the alpha value used have been mentioned previously (see L545).

L524: "mixing events" are again mentioned as something the model is able to simulate, but they are not described earlier, so it is unclear what they are.

• "These mixing events" have been removed and the text updated.

Section 4.4: to add to this discussion, and in reference to the mention earlier in the manuscript of a "perturbed trajectory frequently arbitrarily divided into a fast, transient phase and a slow, asymptotic

stage": should we instead think about relaxation time as the time necessary for most of, rather than all, changes to occur, similar to the concept of half-life in radioactivity?

• We have responded to the half-life concept alluded to by the reviewer in our reply.

Reference [Ait Ballagh et al., 2021] is missing from the list

• The reference has been updated.