Interactive comment on "BioRT-Flux-PIHM v1.0: a watershed biogeochemical reactive transport model" by Wei Zhi et al.

Anonymous Referee #1

Received and published: 17 August 2020

Dear authors, I am rather torn on this paper. On one hand, I strongly believe some of the results of the paper are significant and interesting and without a doubt worth publishing. On the other hand, I am fairly disappointed with the presentation of the manuscript.

Response: Thanks for comments. We apologize for the confusions in the earlier manuscript. We have thoroughly revised the manuscript for clarity. Specifically,

1) we have defined the scope in the Introduction to focus on the new advance in the model development. References are added for land surface and hydrological process description discussed in previous work.
2) we have shortened the Methodology section, and moved some equations (including the water equation and Monod rate laws) to the Supporting Information. We have also revised all equations for clarity and brevity in notations and their definitions.
3) we have added more model details, including the numerical scheme for solving the reactive transport equation, data needs for setting up spatially lumped and distributed domains, and how to calibrate the model
4) we have also shortened the three model examples such that the new model features stand out

Section 3 is poorly written. A lot of terms are not defined, and it seems that there are some inconsistencies. Notations are poor and make the equations hard to read. The structure of the paper is somehow chaotic. Section 5 includes a series of description of new processes, definition of parameters, rates... The most important associated issue is the fact that I do not see what motivated the choice of the content of section 3. The hydrology part could be summed up by one or two equations and adequate references (it's basically Darcy and Richards equation on which multiple pages focus). The reactive transport equation is fairly basic as well. And somehow, these fairly simple concepts are presented in a confusing way and most of the terms are poorly defined, and a lot of equations are redundant. I feel that that section could almost be entirely removed with adequate citations. On the other hand, it seems that a significant proportion of the methods are lacking description (and are included within section 5). Another problem to me is that it seems that some key processes (evapotranspiration) are barely discussed in

the modelling part), despite some modelling results showing a comparison between ET model and data.

Response: Thanks for these comments.

- we have shortened this section significantly by moving the repeated equations to SI and merged some reaction equations as suggested to improve the logic flow.
- we have revised all equations, notations, and their definitions for brevity and clarity.
- we did keep some of the reaction description there so that the readers (and users) know the types of reactions that the model can simulate. BioRT differs from other water quality models that often primarily target a few contaminants (e.g., N, P, metals). The framework of the code is flexible and the users can define their own types of reactions and solutes of interests. We believe it is important for readers to understand that aspect. Please see pages 9 - 16 for revised Section 3.

Line 131 – 136: "This paper introduces new developments in the BioRT model. The code has been verified against the widely used reactive transport code CrunchTope (Supporting Information, SI). This paper briefly overviews water and energy related processes incorporated in the model. Readers are referred to previous publications for more details of processes such as evapotranspiration (ET), hydrological flow, and abiotic reactions (Shi et al., 2013;Bao et al., 2017;Li et al., 2017a;Qu and Duffy, 2007)."

Line 243 – 245: "The ET is calculated by the Penman potential evaporation scheme and detailed equations can be found in Shi (2012). A similar set of water equations for the deep zone are in the SI (Eqn. S1 and S2)."

Line 291 - 294: "BioRT differs from general water quality models that often primarily target a few contaminants (e.g., N, P, metals). The framework of the code is flexible and the users can define their reactions and solutes of interests in the input files."

This work is obviously built within a collaborative effort but the paper fails to present what was actually done within this research. A good example is how all the complexity from figures 1, 2 and 4 are completely ignored within the model description.

Response: We have revised the manuscript to focus more on new model developments to suit the scope of the GMD journal, and discuss some but less in the Examples.

A last important issue regards how the objectives are stated. Reading the title, abstract and introduction and even the equation section really gives the feeling it is a modelling/numerical paper, while the results section goes into important and interesting details about these coupled multi-physics dynamics and predictive applications for large-scale field data. I feel that the first half of the paper does not constitute a proper description of what is coming next.

Response: Thanks for the comment, and apologies for trying to insert too much materials in one paper. We have decided to focus this manuscript mostly on the model development. As you can see from the revised manuscript, we have reorganized much of the model description and removed a large part of results and discussions, with the remaining figures mostly intended to show the model capability.

There are multiple good things about this very relevant work: - model results are interesting - model verification are good - interesting modelling approach - multi-scale - multi-physics problem, - ....and I'm confident this is worthy of a very nice publication. However, this paper, as is, is a poor representation of the work which was performed. In my opinion, an important work of structure has to be done. Considering how rich the results section is, i would maybe suggest to emphasize these very interesting features of the work as the main part of the article. I am sorry if my review sounds very negative. I was somehow upset by the quality disparity between the work itself and the paper writing. I guess it's better in this way.

Response: We agree and we appreciate the comment about directions for change. As stated earlier, we have done a major overhaul of the manuscript following these comments. We have revised the methodology for clarity and brevity but also emphasize more of the new features of the model in the examples.

In the attached files, you can find some detailed line by line comments. These are comments which occur to me "as i am reading", please forgive the tone within that text file. Hopefully, this can help you. Please also note the supplement to this comment: https://gmd.copernicus.org/preprints/gmd-2020-157/gmd-2020-157-RC1-supplement.pdf

Detailed comments in the attachment:

13: hydrology processes

Response: Changed as suggested.

32: spatially implicit: what this means is not clear.

Response: Revised to "spatially lumped".

- abstract: not clear whether the verification with Crunch is part of the paper

Response: We have added clarifications:

Lines 131 – 133: "The code has been verified against the widely used reactive transport code CrunchTope (Supporting Information, SI)."

Line 419 – 420: "The BioRT module had been verified against CrunchTope under different transport and reaction conditions (Figures S1 – S7 in SI)."

42: microbes?
Response: Changed.

42: more general than CO2: gases fluxes?
Response: Changed.

59-60: unclear sentence
Response: We have rephrased the long sentence.

Line 65 – 68: "The lack of understanding of mechanisms governing hydrological and biogeochemical interactions presents major roadblocks for forecasting water quality, including water issues such as eutrophication that persist worldwide".

38-64: there are other references which could be worth citing
Response: We have added multiple references in the Introduction.

64: remove "that"
Response: Removed.

65-69: this is a pretty long sentence.
Response: This long sentence has been rephrased to the following:

Line 73 – 78: "Hydrologic models focus on solving for water storage and fluxes at the watershed scale and beyond (Fatichi et al., 2016). Reactive transport models (RTMs) have traditionally centered on transport and multi-component biogeochemical reactions typically in groundwater systems, which often have limited interactions with climate and other surficial watershed processes (Steefel et al., 2015;Li et al., 2017b;Mayer et al., 2002)."

70: MacQuarrie and Mayer not sure this is the best citation in this sentence.
Response: Citation removed.

128: solar radiation?
Response: Yes, the model includes solar radiation processes as suggested in Figure 1.

- Figure 1: beautiful figure!
Response: Thanks.

- 144: kinetically controlled or at equilibrium

Response: Changed to “kinetically controlled” or “equilibrium-controlled”.

- 145: no eg for kinetically?

Response: added an example of “microbial redox reaction”.

Line 177 – 179: “The reactions can be kinetically controlled (e.g., microbial redox reaction) or equilibrium-controlled (e.g., ion exchange, surface complexation (sorption), and aqueous complexation).”

- Figure 2: resolution is not great. it may be due to the journal processing of the figures to generate this file. please be careful with resolution.

Response: We have re-generated the figure a 300 dpi resolution.

- eq (1) and (2): why is the porosity there? in the previous figure caption, it says "h" refers to "head", so i expect meters. in typical Richards equation, this would yield a specific storage coefficient, for example. but then in the paragraph, h is the water storage. What does that mean? what units? L of water/ L of porous medium?

Response: The “h” refers to water storage [m] and the fluxes in Eqn 1 and 2 are area-normalized fluxes in the unit of [m/s]. The storage h here is essentially the height of soil column with fully saturated water, not the height of the 100% water column. That is why the porosity term θ_i^{sl} [m^3 pore space/m^3 total volume] is there. We added the following to clarify:

Line 232 – 236: “Note that the storages h here are essentially the height of soil column with equivalent saturated water, not the height of the pure water (100% volume) column. That is why porosity is in the equation. For saturation zones, this height is needed to quantify the depths of water tables and determines the direction of water flow between neighboring grids.”

- need to be consistent between figure 2 caption and this equation.

Response: Revised both Figure 2 and Eqn 1 and 2 to be consistent. Thanks.

- please say where this reaction comes from and define the different terms clearly and properly with units. Looking at Li 2019 RiMG, the storage is defined in m of water, but the porosity does not appear.

Response: As discussed earlier, we have added some clarification about this. The Storage (S) equation (5) and (6) in Li (2019) is actually the same as ($\theta \times h$) here. The equations in Li 2019 were meant to represent the general water balance of the system so it is not necessary to represent the storage as ($\theta \times h$). In the specific code BioRT, we do

need to calculate the height of saturated water table in porous media to infer the direction of flow among neighboring grids so this soil water height calculation is needed.

- eq (2): sum ij to 1? this isn't clear. why is j <= 3? this notation is unclear. I'd rather have a sum over symbolic "neighbors" than not defining i, j properly and have a "sum up to 1"
- in every equation, "shallow", "lateral", and actual English words should not be in italic. \textrm or \mathrm in LaTeX, or straight formatting in word.

Response: We have changed the notation and added an explanation for it. We used a straight formatting in the built-in Equation in Word to be consistent.

Line 241 – 243: "N_{ij} (≤ 3) is the number of neighbor elements j. For a prismatic element i, a boundary cell could have one or two neighbors; a non-boundary cell has three neighbors."

- 190: this should not be a new paragraph.

Response: Changed.

- Eq (3) and (4): this suggests that q has units of m3/s. In equations (1) and (2), if h is in the units of meters, q should have units of m/s. Anyway, there are inconsistencies between the equations. This could be dealt with simply by removing "A" from the equation (and in the text).

Response: Apologies for the mistake. Area A has been removed from Eqn. 3 and 4 to be consistent in flux (m/s). Thanks for the catch.

- 191: K_infil ^shallow: this is an infiltration? from the form of equation (3), it looks like a hydraulic conductivity.

Response: This is the hydraulic conductivity of the infiltration layer, which is the top 0.1 m of the subsurface and is considered to have different conductivity from the rest of subsurface. We modified the text.

Line 253 – 255: "$K_{i,inf}$ [m/s] is the hydraulic conductivity of the infiltration layer, the top 0.1 m of the subsurface and is considered to have different conductivity from the rest of subsurface;"

- 192: in the vertical direction? this suggests some kind of anisotropy: is this the case?

Response: Correct, hydraulic conductivity often differs in horizontal (K_H) and vertical (K_V) direction. The users have the option to set up the different conductivity in different directions.

- all the notations with sub and superscripts are really not clear. this should be significantly improved for readability. maybe call q_rechg with a new symbol R, not write "shallow" on every single term, ...

Response: Thanks for the suggestion. We have changed the subscript and superscript of the notations. We would like to keep the q to be consistent with all other flow but have revised the definitions for clarity. In addition, “R” and “r” have been used for total and specific reaction rates (see Eqn. 6, 7). Please sees Eqn. 1 – 5 and relevant description for water equations.

- 198: K_eff H_ij ^shallow --> very heavhy notation again. why the need of H_ij. I guess it could simply be written as K_ij (every other K has ^shallow), i don't see why a distinction is required for the "effective".

Response: We have followed the suggestions and revised all notations and removed “eff” in K.

Line 255 – 256: “$K_{i,V}^{sl}$ [m/s] is the hydraulic conductivity in the vertical direction (i.e., weighted average of macropore $K_{i,macV}$ and soil matrix $K_{i,satV}$, Eqn. S7); ”

- 199: now the subscript H is used to denote horizontal. I would suggest simply K_ij to say averaging between two adjacent cells. and if there is some anisotropy, maybe just distinguish using subscripts z, or x, to avoid confusion between all these symbols.

Response: Thanks for the suggestion. We have removed “H” and simplified as suggested. See our revised Eqn.2 and 5 and relevant descriptions.

Eqn. 2:

$$\theta_i^{sl}\frac{dh_{i,s}^{sl}}{dt} = q_{i,u2s}^{sl} - q_{i,rechg} - e_{i,s}^{sl} + \sum_{1}^{N_{ij}} q_{ij}^{sl} \quad (2)$$

Eqn. 5:

$$q_{ij}^{sl} = K_{ij}^{sl}\frac{H_{i,s}^{sl} - H_{j,s}^{sl}}{d_{ij}} \quad (5)$$

- eq (7): similar problem. subscript "i" is not defined. these equations all adopt some form of discretization and are written for a volume "i". maybe some of the notation and clarity issues would be diminished if they were not written in a discretized fashion, hence removing all the "i" and "j" from the equations. Because in theory, a subscript "i" should be added to every other variable to be consistent.

Response: We have added subscript “i” to all equations. Thanks.

- also if there are indeed written in a discretized fashion, somehow volumes and surfaces should appear. they don't. or they're hidden within the variables. but it's hard to say as almost no units are given and variables are not clearly established.
Response: The governing equations are in the ordinary differential form (in terms of time). In the water equation, all fluxes with volume units have been normalized by surface/area to be in the unit of [m/s], to be consistent with what is typically done in hydrologic literature. Volume is implicit there if we time the q terms with corresponding area. The volume and surfaces are in the reactive transport equation (Eqn. 6).

- eq (8): same as equation (5). Typical Darcy's law, it could be given once, and text could specify where it is used (if needed).
Response: We agree. This has been moved to Supporting Information.

- eq (9) --> please explain the denominator
Response: Explanation added in the SI.

SI, *Line 24 – 25: "*$0.5\ [H_{i,s}^{sl} + (d_i^{dp} - H_{i,s}^{dp})]$ *is the distance between the center of shallow saturated zone and the center of the deep unsaturated zone (i.e.,* $d_i^{dp} - H_{i,s}^{dp}$*)."*

- line 235: why area fraction instead of volume fraction?
Response: Because the hydraulic conductivity depends on how much area in the direction vertical to the flow is macropore and how much is soil or rock matrix. Added in SI:

SI, Line 51 – 53: "The conductivity depends on area fraction instead of volume fraction, because the hydraulic conductivity depends on how much area in the direction vertical to the flow is macropore and how much is soil or rock matrix."

- 238: infiltration hydraulic conductivity --> please change this denomination. hydraulic conductivity of a certain porous media, but not infiltration.
Response: Changed.

- section 3.1 should be significantly improved. this section does not introduce many new concepts, but somehow is surprisingly unclear, due to very heavy notations, repetitions, ...
Response: We have shortened the section. Water equations in the deep zone have been moved to SI. All equations and notations (e.g., subscript and superscript) have been revised for clarity. Thanks.

- section 3.2 here in equation (14), the discretization factors (Vi and Aij) do appear. Why not in the previous ones?

Response: The water equations (e.g., Eqn. 1 – 5) were all written in fluxes terms [m/s] because if we use volume / time, the equations will need to involve two types of areas, one is the land area in the horizontal direction, the other is the area between neighboring prismatic grids, which can become confusing. If the reviewer thinks this is essential, we can change the equations to forms that involve volume in the next revision.

For reactive transport equations (Eqn. 6), since they are mass balance equations, it is much easier to have volume, because all concentrations are related to volume. Mathematically we can normalize everything by land area but then the units will become confusing. So, for now we are keeping the current forms.

- (14) the indices around the sum symbol are pretty heavy. maybe just put sum over j (neighbours), and explain in the text than j refers to the neighbors of cell i. but N_i,1 to N_i,x is confusing.

Response: We have revised the equation to the following:

Line 273: " $V_i \frac{d(S_{w,i}\theta_i C_{m,i})}{dt} = \sum_1^{N_{ij}} \left(A_{ij} D_{ij} \frac{C_{m,j} - C_{m,i}}{d_{ij}} - q_{ij} A_{ij} C_{m,j} \right) + R_{m,i},\ m = 1, \dots, nm \quad (6)$"

Line 276 – 280: "N_{ij} *is the number of fluxes from neighbor element* j *for element* i*,* N_{ij} *is 2 for the unsaturated zone (infiltration, recharge) with only vertical flows and 5 for saturated zone with flux from (or to) the unsaturated zone, from (or to) the deeper zone, and fluxes between* i *and three neighbor elements* j *in lateral flow directions for non-boundary grids;"*

- (14)/256: all units of distance within gradients have been expressed with "d" or "D" and here it's l_ij. maybe some consistency could be appreciated.

Response: We have changed all distance notation to "d".

- 250: + gas volume, i guess (or simply remove the parenthesis, i don't think it's important).

Response: Removed.

- 250: put the m^3 in [] somewhere else, like where Vi [m^3] is the total volume of grid cell i.

Response: Changed as suggested.

- 252: index of elements sharing surfaces --> it's unclear and i don't think it adds anything

Response: We have revised the indexes:

Line 276 – 280: "N_{ij} *is the number of fluxes from neighbor element* j *for element* i*,* N_{ij} *is 2 for the unsaturated zone (infiltration, recharge) with only vertical flows and 5 for saturated zone with flux from (or to) the unsaturated zone, from (or to) the deeper zone,*

and fluxes between i and three neighbor elements j in lateral flow directions for non-boundary grids;"

- 255: "combined". for consistency i would suggest to stick with "mean" as was done for hydraulic conductivities (is it harmonic?)

Response: We have changed the sentence.

Line 281 – 283: "D_{ij} [m^2/s] is the hydrodynamic dispersion coefficient (i.e., sum of mechanical dispersion and effective diffusion coefficient) normal to the shared surface A_{ij};"

- 257: agree that here, q has m^3/s, because Aij has been incorporated. Be careful about consistency with previous section and equations where it seemed to me that q was m/s (but again, it was not very clear).

Response: Area A_{ij} has been added to the q_{ij} term (Eqn. 6). All fluxes (e.g., Eqn. 1 – 5) are now in the unit of [m/s] for consistency.

Line 273: " $V_i \frac{d(S_{w,i}\theta_i C_{m,i})}{dt} = \sum_1^{N_{ij}} \left(A_{ij} D_{ij} \frac{C_{m,j} - C_{m,i}}{d_{ij}} - q_{ij} A_{ij} C_{m,j} \right) + R_{m,i},\ m = 1, \dots, nm \quad (6)$"

- 261: microbes

Response: Changed.

- 265: precipitate as carbonate materials?

Response: We have rephrased the sentence.

Line 301 – 302: "With coexisting cations (e.g., Ca, Mg), DIC can often precipitate and become carbonate minerals (e.g., $CaCO_3$)."

- 265: transition between sentences can be improved. "it can oxidize into CO_2. or it can precipitate. hence it can release CO_2". It would make more sense, i think, if it was grouped differently: "oxidize into CO2 which can be released back to the atmosphere or surface water. or it can precipitate".

Response: We have re-organized the sentence.

Line 297 – 301: "SOM can be decomposed partially into organic molecules that dissolve in water (Wieder et al., 2015), i.e., DOC, or it can be oxidized completely into CO2 that is released back to the atmosphere as a gas (Davidson, 2006) or surface water in the form of dissolved inorganic carbon (DIC)."

- 266: chnage CO2 level (not changes, i think).

Response: This part has been deleted due to rephrase.

- Figure 3 resolution is not great again. But nice illustrating figure, it is helpful.
Response: Thanks. We have made sure all the upload figures are in 300 dpi resolution.

- 276: maybe give chemical form of ammonia. why is NO_2^- within parentheses?
Response: Changed.

Line 309 – 310: "OM decomposition releases organic nitrogen (R-NH_2), which can further react to become NH_4^+, and other nitrogen forms (N_2, N_2O, NO, NO_2^-, NO_2) (Figure 3)."

- It is weird that these paragraphs are part of a section called "equations". Maybe another section after line 258 "Biogechoemical processes"? a first "paragraph" about description, then the "paragraph" describing kinetics (294) (And maybe section 3 should be modified to governing equations and processes?)
Response: Changed as suggested. Now this section is named as "*3.3 Biogeochemical processes and reaction kinetics*".

- eq (15)/ line 303: why the subscript "C5H7O2N" and not simply microorganisms?
Response: Good point. we have changed all to "B_{micro}" to represent biomass of microorganisms in relevant equations.

- can you give an example of D and A (electron donor and acceptor)? are they linked to the three pools, A and D being the intermediate stages?
Response: Electron donors are typically dissolved organic carbon (DOC) that can be oxidized and become inorganic carbon, and electron acceptors are chemicals that can be reduced. In the denitrification example, the electron donor is DOC and the electron acceptor is nitrate. They are the reactants.

SI, Line 74 – 80: "The denitrification rates can be represented by:

$$r_{NO_3^-} = \mu_{max,NO_3^-} B_{micro} \frac{C_D}{K_{m,D} + C_D} \frac{C_{NO_3^-}}{K_{m,A} + C_{NO_3^-}} \frac{K_{I,O_2}}{K_{I,O_2} + C_{O_2}} \quad (S11)$$

Here C_D is the concentration of electron donor such as organic matter or carbon (Di Capua et al., 2019); $C_{NO_3^-}$ is the concentration of electron acceptor nitrate; K_{I,O_2} is the inhibition coefficient of O_2, or the O_2 concentration at which it inhibits denitrification."

- line 307: espectively; "they are the concentrations at which half of the maximum rates are reached for the electron donor and acceptor respectively" i think this can be omitted. it's part of the reference and is fairly well understood or self-explanatory.
Response: Omitted as suggested.

- equation (16) could be summed up in one equation with one symbolic term like (Product)_inhibiteurs K_inh / (K_inh + C_inh) and then in the text examples could be given.

Response: Thanks for the suggestion. Changed to the following:

$$r = \mu_{max} B_{micro} \frac{C_D}{K_{m,D} + C_D} \frac{C_A}{K_{m,A} + C_A} \prod \frac{K_{I,H}}{K_{I,H} + C_H} \quad (S10)$$

- 334-336: with little pore space for air. I'm not a big fan of this terminology. and the overall paragraph is not very clear. I would simplify like important under conditions where electron donors and acceptors are limited, e.g. anoxic conditions for O2. Under conditions org carb and o2 are abundant, SOM rate loaw ... eq(19) and the following.

Response: We have re-organized the paragraph. The two conditions have been separately as suggested.

Line 327 – 330: "For example, in shallow oxic soils where organic carbon and O_2 are often abundant, the rate law for carbon decomposition can be simplified to the following form assuming microorganism concentrations are relatively constant.

$$r = kAf(T)f(S_w)f(Z_w) \quad (7)$$

SI, Line 56 – 59: "Under conditions where electron donors and acceptors are limited, especially anoxic conditions, the kinetics of microbe-mediated reactions can be described by the general dual Monod rate law (Monod, 1949):

$$r = \mu_{max} B_{micro} \frac{C_D}{K_{m,D} + C_D} \frac{C_A}{K_{m,A} + C_A} \quad (S9)$$

- eq (19) and 340. need to change notation for μ_max. it's not the same unit, it does not bear the same meaning.

Response: Changed to rate constant k [mol/m^2/s] in *Line 330 – 331.*

- eq (19): which surface area? m2 of what?

Response: A lumped parameter to represents SOM content and biomass abundance. It could be estimated based on experimental surface area measurement of SOM or biomass.

Line 331 – 333: "the surface area A [m^2] is a lumped parameter that quantitatively represents SOM content and biomass abundance,"

- 348: if it is often used, i guess you could include some citations here :)

Response: References added.

Line 351 – 353: "A typical n value is 2 (Yan et al., 2018) with a range between 1.2 and 3.0 (Hamamoto et al., 2010), depending on soil structure and texture."

- 351: accounted for
Response: Changed.

- eq 20: i would suggest to merge equations 19 and 20.
Response: Merged as suggested, now as Eqn. 7.
Line 330: $r = kAf(T)f(S_w)f(Z_w) \quad (7)$

- eq 20: bm is the declining coefficient? It's simply a characteristic depth. "declining coefficient" is a weird denomination.
Response: changed to "depth coefficient". Thanks.

361: CVODE? what do the CV stand for?
Response: CVODE is short for C-language Variable-coefficients ODE solver. So "CV" stands for C-language Variable-coefficients.
Line 410 – 411: "solved in CVODE (short for C-language Variable-coefficients ODE solver, https://computing.llnl.gov/projects/sundials/cvode),"

- you do not specify how you solve set of equations 14 (reactive transport) which are arguably the most complicated to solve.
Response: A few sentences added for the reactive transport equation.
Line 413 – 417: "In BioRT, the transport step is first solved with water by the preconditioned Krylov (iterative) method and the Generalized Minimal Residual Method (Saad and Schultz, 1986). In the following reaction step, all primary species in each finite volume are assembled in a local matrix and then solved iteratively by the Crank-Nicolson and Newton-Raphson method in CVODE (Bao et al., 2017)."

- 374: at a range of reaction complexity levels? "a variety of transport conditions" is a bit overselling what has been done in the SI. In my understanding, there is only one transport condition and 3 investigated reaction networks.
Response: There are two different transport conditions (Table S1) plus three reaction scenarios. We have rephrased the sentence as following:
Line 419 – 420: "The BioRT module had been verified against CrunchTope under different transport and reaction conditions (Figures S1 – S7 in SI)."

- there are 2 sections "4"?
Response: Thanks for the catch. Corrected.

- 398: I'd rather say something like "negligible, as the associated evolution of hydrological parameters".

Response: We have rephrased the sentence.

Line 439 – 442: "At the time scale of months to years that are typical for BioRT-Flux-PIHM simulations, alterations in solid phase properties, including, porosity, permeability, and reactive surface area, are considered negligible such that hydrological parameters remain constant with time."

- fig 4: you mention a lot of things which were not discussed in the model section. for example, thermal effects (evapotranspiration, solar radiation, air temperature) --> how do they impact what has been discussed. Basically, most of the complexity from figure 1 and figure 4 was absolutely not addressed in the model section. are there some missing references?

Response: Sorry for the confusion. This paper is to introduce BioRT-Flux-PIHM focusing on recent new developments. So some of the complexity in Figure 1 or Figure 4 regarding land surface, hydrological, and reactive transport processes have been described and explored in previous papers (Bao et al., 2017;Shi et al., 2013). For example, ET is a core process in the land-surface and hydrological model (Flux-PIHM) and its interactions with soil temperature, sensible and latent heat fluxes (surface energy balance) have been explored in Shi et al. (2013). As mentioned earlier, we also revised the intro to better define the scope.

Line 113 – 136: "This paper introduces new developments in the BioRT model. The code has been verified against the widely used reactive transport code CrunchTope (Supporting Information, SI). This paper briefly overviews water and energy related processes incorporated in the model. Readers are referred to previous publications for more details of processes such as evapotranspiration (ET), hydrological flow, and abiotic reactions (Shi et al., 2013;Bao et al., 2017;Li et al., 2017a;Qu and Duffy, 2007)."

We also added the following in the caption of Figure 5 to clarify the scope,

Line 474 – 477: "This paper focuses on the BioRT component. The land-surface, hydrological processes, and abiotic reactive transport processes have been described in previous papers (Bao et al., 2017;Shi et al., 2013). Discussions on how air temperature and ET influence stream chemistry can be found in Li (2019)."

- temperature effects: how do they impact thermodynamic constants, evaporation, - ET: how do you compute that?

Response: The ET process is coded in the Flux-PIHM and calculated by the Penman potential evaporation scheme. We have added one sentence in the text with reference.

Line 243 – 244: "The ET is calculated by the Penman potential evaporation scheme and detailed equations can be found in Shi (2012)."

We also added more detailed description (*Line 339 – 368*) and Figure 4 of rate dependence on T and soil moisture in the manuscript.

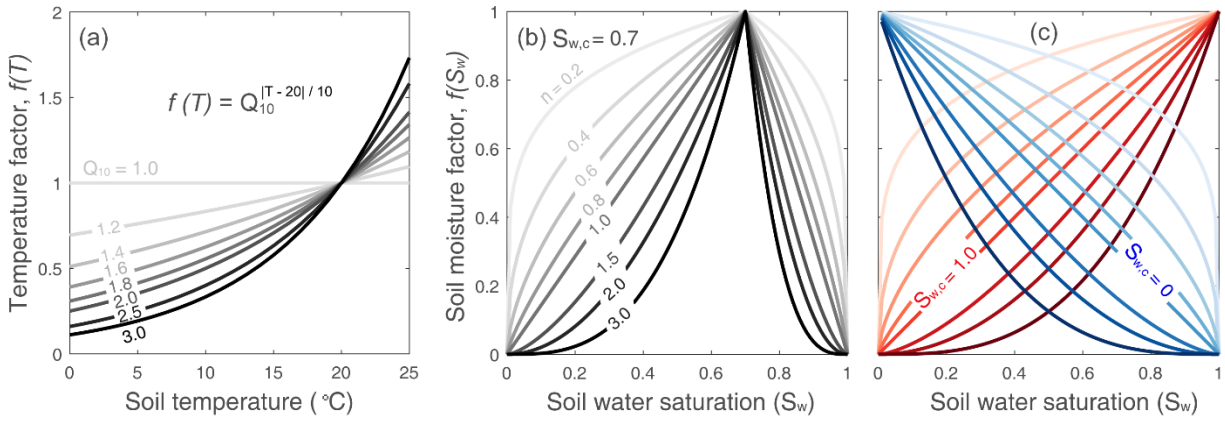

Figure 4*. (a) Function form of soil temperature dependence and (b, c) soil moisture dependence for reaction rates. The temperature factor $f(T)$ is a function of the Q_{10} (defined by users) and soil temperature. The soil moisture factor $f(S_w)$ is a function of two user-defined parameters $S_{w,c}$ and n and soil water saturation S_w. The soil moisture function can represent three types of behaviors: the threshold behavior (b, $0 < S_{w,c} < 1$), increase behavior (red in (c), $S_{w,c} = 1$), and decrease behavior (blue in (c), $S_{w,c} = 0$). Values of n = 1 leads to a linear threshold dependence of S_w while $n < 1$ and $n > 1$ lead to concave and convex dependences, respectively.*

- Nash Sutcliffe efficiency? can you explain what that is? or refer to some work regarding that?

Response: Deleted as we have shortened the three examples.

- 560: issue within the chemical species

Response: Corrected as the following:

Line 579 – 585: "Here this process was modeled by the Monod rate law with DOC as the electron donor (Di Capua et al., 2019), NO_3^- as the electron acceptor, and with an inhibition term $f(O_2)$ (Eqn. S13). The reaction rate: $r_{denitrification} = kA\frac{C_{DOC}}{K_{m,DOC}+C_{DOC}}\frac{C_{NO_3^-}}{K_{m,NO_3^-}+C_{NO_3^-}}f(O_2)f(T)f(S_w)$, where k = 10^{-10} [mol/m^2/s] is the denitrification rate constant (Regnier and Steefel, 1999), half-saturation constants $K_{m,DOC} = 15\ [uM]$ and $K_{m,NO_3^-} = 45\ [uM]$ (Regnier and Steefel, 1999;Billen, 1977)."

- eq 25-26: some references are needed

Response: References added. Thanks.

- structure of the paper needs to be revised. a huge amount of new variables and information are given within the applications.

Response: This Example 2 has been rearranged, with most of the reaction rate related description in method in main text or SI.

- results: generally nice figures and results. but the leadup to here does not give the results the credit they deserve.

Response: Now we have defined the scope of this work in the Introduction and shortened the methodology part (especially the water equation part moved to SI) to focus on new developments in the BioRT model. We have organized the results to focus more on the modeling capabilities. We appreciate the reviewer's careful reading and detailed comments.

---------- SUPPLEMENTARY

Table S2: given rates are surface rates, but no surface area are discussed and the kinetic law is missing.

Response: We have added the TST rate law with the surface area terms.

SI, Line 141 – 146: "The apatite dissolution rate is based on the Transition State Theory (TST) (Helgeson et al., 1984), as described by the following:

$$r_{TST} = Ak(1 - \frac{IAP}{K_{eq}}) \quad (S15)$$

Where r_{TST} [mol/s] is the mineral dissolution rate, A [m^2] is the mineral surface area, k [mol/m^2/s] is the rate constant, IAP is the ion activity product, K_{eq} is the equilibrium constant.

- it would be nice to add the Saturation index of the initial solution and boundary condition solution with respect to apatite.

Response: added.

SI, Line 146 – 147: "The initial and boundary saturation index (i.e., $log_{10}(IAP/K_{eq})$) is -28.9 and -20.9, respectively."

- figure S2c: looking at h+ concentration on (a) after 1 residence time, it looks like it at 1e-8 mol/L (and going down). in figure s2c, downstream h+ concentration looks higher. as its probably in equilibrium with apatite, it's surprising that this value is higher than in figure S2(a). can you comment?

Response: thanks for the catch. We have corrected the "1 residence time" to be 0.5 residence time.

SI, Line 161: "… spatial pattern plotted at 0.5 residence time (c, d)."
SI, Line 221: "… at 0.5 residence time (b)."
SI, Line 257: "… at 0.5 residence time (b)."

- table S3: - units of rate constant. - what is X_mio? - what is CH2O(s)? s for solid? how do you define their concentrations? what does it represent? I would understand if it represented a surface area but this seems odd.
Response: We have updated the reaction rate expression in Table S3 and S5 for consistency with microbial equation (Eqn. S9 – S11). The rate and microbial terms are described in *Line 52 – 89*.

S12 --> what about flow/transport setup in this simulation? same as for the first? should be indicated
Response: transport conditions have added.
SI, Line 188 – 189: "The carbon case was tested under the full transport condition with advection, diffusion, and dispersion."
SI, Line 230 – 231: "soil nitrogen verification was performed under the full transport condition with advection, diffusion, and dispersion."

line 128: i think the reference is Figure S6. - same transport than previously?
Response: Corrected to Figure S6. Yes, same transport as the previous carbon case.
SI, Line 230 – 231: "soil nitrogen verification was performed under the full transport condition with advection, diffusion, and dispersion."

table S5: same comments than for table S3
Response: We have updated the reaction rate expression in Table S3 and S5 for consistency with microbial equation (Eqn. S9 – S11). The rate and microbial terms are described in the section of S2 (*Line 52 – 89)*.

S2. what's the exponential factor?
Response: The exponential factor is a fitted equation (or parameters) to account for the exponentially declining rooting density at Shale Hills (Hasenmueller et al., 2017), which is also common in the forested watershed (López et al., 2001).
Line 399 – 404: "

$$f_{root}(d_w) = \exp((-d_w + \delta)/\lambda) \quad (14)$$

Where $f_{root}(d_w)$ is the normalized rooting density term in the range of 0 to 1 as a function of water depth to the groundwater (d_w). The rooting term (Eqn. 14) was exponentially

fitted (δ= 0.013, λ = 0.20) based on field measurements of root distribution along depth (Hasenmueller et al., 2017).”

Figure S9: (a) it's really not clear what is observed. precipitation is the grey on the top, I guess. Could you write "precipitation" in gray then?
Please include evapotranspiration (ET) in the caption. The word "precipitation" in the middle of the frame is surprising.
- Figure S9 (c): there is more water in the unsaturated than in the saturated part?
Response: We have removed Figure S9 in SI as it does not pertain to the new model development in this paper.