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# *Interactive comment on* "On the relationships between Michaelis–Menten kinetics, reverse Michaelis–Menten kinetics, Equilibrium Chemistry Approximation kinetics and quadratic kinetics" *by* J. Y. Tang

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**Overall comments**: *J.Y. Tang in this paper show the relationship between the recently introduced Equilibrium Chemistry Approximation (ECA) kinetics with commonly used other formulation of substrate kinetics. This is an important topic and valuable to the modelling community, as this substrate kinetics is central to soil organic matter modeling.*

*While I strongly suggest publishing the paper, I give some constructively meant cri-*



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*tiques that hopefully help to convey the message of the paper better to the reader.*

**Response**: I sincerely appreciate your positive comments. I addressed your comments point by point in the following.

**Comment 1**: *Note that GM journal also addresses readers that do not have a very strong mathematical background. Please, give some more aid, so that the readers can follow the derivations (Some suggestion are given in the specific section below)*

**Response**: I revised the manuscript by following your specific suggestions below.

**Comment 2**:*Both the abstract and the main part of the paper present a mathematical treatment without sufficient user-aid on how to interpret the results. Why are the parametric sensitivities important? What does it mean for modelling the processes?*

**Response**: Correct parametric sensitivity is important for both model calibration and model interpretation. All calibration techniques (either explicitly or implicitly) rely on the parametric sensitivity to adjust parameter values and wrong parametric sensitivity would mislead empirical measurements to do incorrect measurements. I added this discussion in the revised manuscript.

**Comment 3**: *Beware of confounding the concepts of microbial uptake and enzyme kinetics (e.g. p. 7680 ll line 14). The ECA, as I understood it, deals with enzymatic breakdown of soil organic matter (SOM) into smaller compounds. The Monod-Description of microbial uptake of these components has a different more empirical background. While with the assumption of enzymatic breakdown to be the limiting step, models can apply ECA also for microbial growth, the two concepts should be kept clear.*

**Response**: Sorry I missed some nuance for this part in the paper. As described in Tang and Riley (2013), ECA is derived for generic purposes including, but are not limited to, enzymatic breakdown of SOM, microbial growth and predator-prey relationships, with appropriate setting up of the stage. The use of enzymatic reaction in the paper is just for a convenience of presentation. I clarified this nuance in the revised manuscript.



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**Comment 4**: *ECA are based on total concentrations including the enzyme-substrate complex. Most SOM models are formulated on a more abstract level. How to deal with this practically? What are the consequences when total concentrations would be replaced by modelled pure concentrations or by pools in mass units? Under which conditions is this is viable?*

**Response**: I added more detailed explanation to this technical nuance. In most applications, the total substrate concentration is equivalent to the free substrate concentration as used in the Monod kinetics. However, as I explained in the paper, when free substrate concentration is very low, application of the Monod kinetics or the MM kinetics violates their condition of validity. When total concentrations are replaced by modelled pure concentrations or by pools in mass units, the ECA kinetics only requires all units of substrates, affinity parameters and enzymes (or microbes) are consistently defined. The major difference (between ECA and MM) occurs when one applies ECA for modeling microbial DOC uptake in presence of mineral surface adsorption. In ECA, the total DOC concentration means the total of adsorbed and free DOC, whereas in the MM kinetics, only free DOC is used. As shown in Tang and Riley (2013; Figure 6), this difference in treatment would lead the MM kinetics to predict very inaccurate decomposition dynamics.

**Comment 5**: *The introduction is written well, and the importance becomes clear. The main message of the paper to me is that ECA for one substrate-one enzyme is a mass-balanced approximation of the general QSS (quasi steady state) solution and that generalizes both MM and RMM. The derivation (from eq. 11 to 12), however, is too condensed to understand without more mathematical efforts. Did you generate the Taylor series at E=0 and S=0? Did you truncate second order terms of E and S? What does it mean to truncate for* $\epsilon$*?*

**Response**: ECA is a mass-balanced approximation for arbitrary number of enzymes (or competitors in general) and substrates, and this paper focuses on the one-substrate-one-enzyme example to analytically tease apart the differences and con-



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nections between ECA, MM and RMM because such analytical analysis is not possible for the most general case involving many substrates and many enzymes. However, numerical results did indicate ECA is superior to MM kinetics for the general case. In the derivation, the Taylor expansion is performed with respect to $\epsilon$, and the first order approximation is defined with respect to $\epsilon$.

**Comment 6**: *Can you, please, extend the explanation of the points at the end of section 2.1? To what and how is Eq. 12 applied? Is eq. 13 not just a re-statement of eq. 5? In what way does this form the tQSSA?*

**Response**: I did my best in the revised manuscript to clarify this. To put it simple, the QSSA means taking the temporal derivative of Eq. (4) to zero. The total substrate concentration means adding together the free substrate and enzyme-substrate complex. Therefore, tQSSA means adding Eq. (3) and Eq. (4) together. Mathematically, Eq.(13) is equivalent to a restatement of Eq. (5), yet, they mean different things. A more detailed analysis of such difference warrants the perturbation analysis of tQSSA, however, that is very lengthy and involved, though (if interested) the paper by Borghans et al. (1996) and some references they cited explained it very well.

**Comment 7**: *Maybe also move the equations of the parametric sensitivity analysis to the appendix and focus in the main text on the figures and their interpretation for modelling. Why were the sensitivities normalized? Especially why multiplied by the rates? How are these normalized sensitivities interpreted?*

**Response**: I too have struggled in deciding where I should put those equations, but I finally decided to include them in the main text to please both readers who enjoy mathematical rigorousness and readers who are less math-oriented. The normalization follows the tradition in analyzing chemical kinetics. Such normalization assures that all parametric sensitivities are not unit-dependent. Mathematically, the normalized parametric sensitivity indicates the relative change in dependent variable (reaction velocity here) in response to a relative change in the free parameter.



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**Comment 8**: *Section 3.2. can be shortened by noting that the sensitivities are 1- the sensitivities of 3.1. I could not follow derivation from eq. B2 to B3. When I insert vECA and KES in the second term on the right of B3, I arrived at a result different from B2. (to editor: I did not check Taylor expansion of eq. 10 nor Appendix A)*

**Response**: As for the length of section 3.2 and section 3.1., I decide to put them as they are, so readers can understand both without referring to each other. For mathematical derivation, I double-checked the math, it is correct.

**Comment 9**:*P.7670 L.1: suggest aid: By inserting [E] solved from (7) and [S] from (8) into (6) one arrives at the following quadratic equation.*

**Response**: Per your suggestion, I added these manipulation details in the revised manuscript.

**Comment 10**: *P.7670 L.9, L12: Some more details are required.*

**Response**: I made it clear that the Taylor expansion is done with respect to $\epsilon$. I also added a reference to help readers understand the mathematics, although the details for more general case can be found in Tang and Riley (2013).

**Comment 11**: *P. 7671: L15: What does the error in parametric sensitivities mean for modeling?*

**Response**: They could either mean the model will fail in calibration (see example of litter decomposition in Tang and Riley (2013)) or the model interpretation will be incorrect.

**Comment 12**: *P.7675 L.8: term predictions refer to sensitivities or reaction rates?*

**Response**: They refer to sensitivity. I removed this ambiguity in the revision.

**Comment 13**:*P.7675 L.14: Color scale in Fig. 1 goes to -9% instead of 5% in the text. What is the difference?*



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**Response**: Note -0.09 is the value normalized with respect to the sum of parametric sensitivity from both the ECA approximation and exact solution; therefore 5% is about (half of 9%) the actual relative difference.

**Comment 14**:*Figs (1-3d) are hard to understand. Why do you apply log in single variables in the derivatives instead of log(sensitivity). Also with so much overplotting the figure is obscured. Where does the spread come from?*

**Response**: I was comparing the parametric sensitivity calculated by the three approximations to the true parametric sensitivity as calculated from the exact solution (the definition of parametric sensitivity is explained in the response to comment 7). This comparison tells how well the MM, RMM and ECA kinetics approximate the exact solution. The spread comes from the poor performances of the MM and RMM kinetics. I also have redrawn the plots to have a clearer visual.

**Comment 15**:*Two Typos after eq. B3 (Then, refer to eq. B3 instead of B2)*

**Response**: Typos corrected.

**Comment 16**: *P.7680 L.13. Important sentence, but very long. Can be broken up.*

**Response**: I broke it up.

**Reference**

Tang, J. Y., and W. J. Riley (2013), A total quasi-steady-state formulation of substrate uptake kinetics in complex networks and an example application to microbial litter decomposition, Biogeosciences, 10(12), 8329-8351.

Borghans, J. A. M., R. J. DeBoer, and L. A. Segel (1996), Extending the quasi-steady state approximation by changing variables, B Math Biol, 58, 43-63, doi: 10.1007/Bf02458281.

Interactive comment on Geosci. Model Dev. Discuss., 8, 7663, 2015.