

## Response to reviewer 1

**Comments:** This is an elegant mathematical formulation of a generalized model that can be applied to a broad range of physico-chemical reactions. I enjoyed the thoroughness of the stepwise progress through the derivations needed to reject alternative approaches and develop the final SUPECA format. I also appreciate the applications, which demonstrate proof-of-concept. Nonetheless, I don't think many soil scientists will be convinced to use it or find it very useful, for several reasons (below).

**Response:** We sincerely thank the reviewer's appreciation of our work. We below address the reviewer's specific comments with the hope to alleviate some of his/her concerns regarding whether others will find it useful. In this regard, we note that the ideas based on the Equilibrium Chemistry Approximation are being currently applied (admittedly by us, so far) to evaluate site-level nutrient interactions (Zhu et al. 2016a,b; Zhu et al. 2017) and to develop the global land model (ALM) integrated in the Earth System Model ACME (Tang and Riley submitted).

**Comments:** From a soil ecology standpoint, some of assumptions were very constraining, while others were unrealistic. For example, the assumption that multiple substrate relationships with a single consumer do not have interactions (pg 11) is not realistic for either microbial-substrate interactions or enzyme-substrate interactions (e.g., pg 15).

**Response:** While we agree with the reviewer's concern, we contend that the assumptions we made are even less restrictive than assumptions leading to the Dual Monod or multi-Monod kinetics that have been widely used for decades. For example, in almost every existing modeling study of aerobic oxidation of a certain substrate, say  $\text{CH}_2\text{O}$ , whether  $\text{O}_2$  is taken up before or after  $\text{CH}_2\text{O}$  is assumed not to affect the oxidation of  $\text{CH}_2\text{O}$  into  $\text{CO}_2$ . It is possible that some enzymes need to first bind one substrate to be activated before binding a second substrate. Such is the case for photosynthesis, where the Rubisco enzyme needs to be activated by  $\text{CO}_2$  and magnesium before it is able to bind  $\text{O}_2$  and  $\text{CO}_2$  to carry out photosynthesis. However, existing photosynthesis models are every successful without accounting for such details (Von Caemmerer, 2000). Therefore while it is possible that representing such details may be valuable in some contexts, we leave them for future work in our current attempt at developing concepts for representing soil biogeochemistry. Further, our analysis in this study indicates that, compared with Monod kinetics, the SU and SUPECA kinetics are built on less restrictive assumptions of the kinetic parameters (e.g., our discussion of the kinetic parameters in P14). Therefore, given these goals, we contend our assumptions here are programmatically reasonable.

**Comments:** Alternatively, although true, it is not likely that earlier applications of the SU model have often been unreasonable because consumer abundances approached infinity. Some of these theoretical scenarios present real mathematical contradictions, but exist only when the basic equation is used in isolation from other system controls. In reality, consumers are unlikely to reach infinity for reasons apart from the SU equation, which other models variously attempt to capture.

**Response:** We should have clarified that the test of consumers approaching infinity is in a relative sense (i.e., compared to other state variables in the model), which is a common

practice to derive approximate solutions and evaluate edge cases (Feynman et al., 1963). For instance, when both mineral surfaces and microbes are modeled using the MM-type equations, the mineral surface, as compared to microbes and DOC, becomes very large, effectively approaching infinity in the context of a biogeochemical model. Our treatment will therefore theoretically better handle substrate-limited conditions. As shown in Tang (2015), this testing will also avoid the difficulty associated with choosing among forward and reverse Michaelis-Menten kinetics. And in this study, we further (in section 4) showed that our SUPECA kinetics would avoid the dilemma whether the equilibrium Langmuir adsorption should be applied before or after applying the substrate kinetics, therefore achieving a better numerical accuracy in approximating the equilibrium chemistry approximation.

**Comments:** By page 18, I became convinced that the matrix formulation would necessarily include many zeros for kinetic coefficients in a microbial-enzyme-substrate system, which also addresses a point made several times: whereas a superabundance of a substrate would eliminate a particular substrate-consumer interaction term, so would a  $K=0$ .

**Response:** Effectively, when a substrate-consumer interaction term is to be eliminated,  $K$  should be a very large number compared to substrate concentrations, for pragmatic calculations. The matrix formulation is a way to visualize the relationships between substrates and consumers, and in application we can easily screen those inactive entries off. We also made this point clear by revising the captions of Figure 2.

**Comments:** Other hierarchical interactions are ignored. Do the authors imagine other sets of functions and matrices of coefficients that could be used to capture controls exerted by other environmental conditions on these kinetic coefficients, such as pH, stoichiometry, CUE, etc.? This model rapidly becomes unwieldy.

**Response:** We contend that the SUPECA kinetics proposed here is only one component necessary to build a comprehensive soil biogeochemical model to resolve the variability of CUE, stoichiometry, and other environmental variables. There are models, such as ECOSYS (Grant et al., 2015; 2016), that have made such an attempt, but our approach will enable an alternative that is theoretically more consistently formulated from substrate uptake to CUE control. In our published study (Tang and Riley, 2015) that considers the non-oxygen limited aerobic decomposition, we show that ECA kinetics allows the derivation of realistic mineral-organic matter interactions. Together with the simple examples shown here and in Tang and Riley (2013), we contend that our extension of the Monod kinetics has the potential to produce more robust and accurate results than existing models.

**Comments:** The specific applications of this model demonstrated some utility. However, I am not convinced that the model is necessarily superior to other more common formulations that have been used in these ways despite SUPECA's analytical elegance. I suggest more effort to demonstrate the utility of this model as something more than a really elegant mathematical exercise. For example, the statement on line 21 page 29 is that SUPECA can scale reaction networks without changing mathematical formulation. Is this a utilitarian or theoretical accomplishment?

**Response:** We believe part of SUPECA's analytical elegance is its ability to scale reaction networks with a consistent formulation, and that this capability will lead to more rigorously defensible biogeochemical models. In that regard, we do think our new approach is both utilitarian and a theoretical accomplishment, and that this combination is lacking in current model formulations. We agree that more demonstrations of the approach can be valuable, but the paper is already very long, and we have provided an example that indicates the power of the approach and will present more applications elsewhere.

## References

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