Response Letter

Comments to the Authors from the Editor
Two new referee reports have now been submitted. One gives an excellent appraisal and the other quite skeptical on the merits and usefulness of the manuscript. Therefore, after 4 referee reports only one has fully rejected this work, with Report #1 requiring substantial improvement of the text. Please read the reviews thoroughly and make the required changes. I will then assess your manuscript on re-submission.
Response: We first thank you for handling this complex paper. We now have thoroughly addressed the comments from Reviewer #1. Specifically, we made the following changes, on which we expand in the following section:

1) In the Abstract, Introduction (P4: L12-22), and Methods (P13: L6-9; P25: L18-21) sections, we clarify that our intent is not to replace existing biogeochemical (BGC) representations in earth system models (ESMs), but rather for the SUPECA kinetics to extend the spectrum of approaches for analyzing these complex interactions. In this regard, the SUPECA fills a specific, and we think important, niche among BGC representations. In particular, compared to the widely used SU and Monod family kinetics, SUPECA better resolves plant-microbial competition under limited soil nutrient conditions, a feature that characterizes many natural ecosystems (Schimel and Bennett, 2004; Vitousek et al., 2010). We also note that SUPECA is an extension of the published ECA kinetics, which we have shown to be very useful for biogeochemical modeling (Tang, 2015; Tang and Riley, 2015; Zhu et al. 2016a,b, 2017) and currently forms the basis for representing nutrient and carbon interactions in the Department of Energy's ACME ESM land model (ALM; Zhu and Riley, 2015; Zhu et al. in prep, Tang and Riley, 2016; in review).
2) We included one popular response function approach in our soil respiration modeling comparison (Figure 5; also see Figure 2 in this response). We also reviewed current literature and found that the form of response function applied varies widely across studies (P28: L19-22, P29: L1-2 of the revised text, and the discussion of Figure 1 in this response). This wide variation in functional forms, each of which are likely derived from individual field site observations, further motivates our attempt here to develop a mechanistic treatment for the processes underlying these emergent responses.
3) We also carefully revised the English and clarified sections, which Reviewer #1 indicated, might be difficult to follow for readers with less mathematical training.

With these changes, we sincerely hope that the manuscript has been sufficiently improved and is ready for acceptance.

Reviewer 1

Tang and Riley: The SUPECA kinetics for scaling redox reactions in networks of mixed substrates and consumers and an example application to aerobic soil respiration.

Comment 1:

This is a revision of this paper. The initial reviews were mixed, with reviewer #1 admiring the conceptual elegance of the model, but feeling that the nature of the assumptions meant that it wouldn't likely be taken up and used by many biogeochemists—this reviewer stated "From a soil ecology standpoint, some of assumptions were very constraining, while others were unrealistic." Reviewer #2 was much more critical but the authors argue that this reviewer "largely misunderstood our development and analyses."

Frankly, I can't blame reviewer #2 for misunderstanding major aspects of the paper. The math is complex, and I'll have to take the authors' and other reviewers' evaluations of the derivations. But much of the English description is largely inexplicable. I'm not a mathematician, but I have worked with biogeochemical models and chemical kinetics, and when I read statements like: "This contrasting requirement on parameters, as we will show later, fails the DM kinetics to achieve a consistent scaling of substrate-consumer interactions for generic biogeochemical modeling" I'm really at a loss for understanding what it's supposed to mean.

Response:

First, we sincerely thank the reviewer for taking the time to comment on our work. We understand that the work we are presenting is mathematically complex (as was pointed out by the reviewer and reflected in the contrasting evaluations we received through the two rounds of review), so we appreciate the opportunity to revise the manuscript based on the reviewers' comments, and hope it is now more understandable for a broad range of readers. We have carefully revised the manuscript and done our best to clarify statements like the example provided by the reviewer.

Second, we would like to stress that we do not intend for the SUPECA approach to supersede other modeling approaches of soil organic matter decomposition. Rather, we are attempting to introduce an explicit mechanistic treatment of BGC processes to expand the current spectrum of approaches. We do feel that our field will benefit from more mechanistic treatments of biogeochemistry, but demonstrating that the SUPECA approach should replace other approaches is not our goal here. As a proof-of-concept example of the potential value of the SUPECA approach, we applied it here to mechanistically explain the measured dependence of soil respiration on soil moisture, which is not possible from the response function approach typically applied in soil BGC models (we explained this in detail in both the revised manuscript (P28: L3-22; P29: L1-4) and the response to comment 3 below).

Third, we have clarified our discussion of conditions under which consumer abundances may approach large magnitudes compared to substrate abundances (which is implied as unrealistic by the reviewers). Such conditions are corroborated by the often-observed nutrient limitations in natural ecosystems (e.g., Vitousek, 1982; Schimel and Bennett, 2004; Vitousek et al., 2010), and methods to represent nutrient limitations under these conditions is a topic of substantial interest in current ESM development (Wieder et al., 2015; Achat et al., 2016; Niu et al., 2016). In this regard, our SUPECA approach demonstrated significant improvement over the popular SU method (see Figure 4 in the revision), and we show it to be more robust than Monod kinetics in representing plant and microbial competition for limited soil nutrients (Tang and Riley, 2013; Tang, 2015).

Fourth, the SUPECA approach is applicable to a wide range of biogeochemical processes. For instance, in the discussion paper (P3: L20-23; P4: L1-L13), we stated that SUPECA is presented to improve modeling of substrate-consumer interactions involved in microbial decomposition of soil organic matter and plant microbial competition for nutrients. SUPECA is an extension of ECA theory, which has been demonstrated to effectively model terrestrial nutrient and carbon cycles (Zhu and Riley, 2015; Zhu et al, 2016a, 2016b; 2017), and organo-mineral interactions (Tang and Riley, 2015). We believe that the SUPECA approach will enable researchers to explore mechanisms and dynamics not possible with some current representations and thereby improve modeling of ecosystem biogeochemistry.

To help readers who may be less math-oriented to better appreciate why we present this complex development, we revised our text to include more background information (P4: L12-22), and highlight that, because of its better numerical accuracy and theoretical scaling consistency, our method will significantly improve representation of plant-microbial competition under limited soil nutrient conditions (P8: L7-10; P9: L7-10; P10: L14-18; P17: L19, P18: L1-5; P25: L10-15; P32: L8-11).

Comment 2:

At a conceptual level, I can clearly see the value of this work. Soils are a complex network of chemical reactions that we usually treat as an aggregate mix, rather than as a network of separate independent chemical reactions. This approach takes a conceptually appealing approach to treat soil organic matter turnover as a network. By the author's arguments, this approach is better, more robust and more accurate than other approaches to formulating multi-reaction networks of organic matter reactions.

However, the paper suffers terribly from a lack of connection to real data to show us that all of this elaborate math really does offer an improvement over other approaches. There is limited comparison to other model approaches to show how it works. Yes, it compares it to the ES and simple SU approaches, but these are both complex conceptual approaches as well. There is no comparison to more traditional approaches, or evaluation of whether adding a suite of additional variables and parameters really creates a more statistically robust approach. I see no mention of real materials or real reactions in the paper. The model is parameterized with "dissolvable organic carbon" as the substrate and honestly, I consider this a major weakness—why go to this vast level of mathematical complexity but to still use a chemically undefined substrate? I don't know what dissolvable organic carbon is! It's not just what's in solution and since if you extract a soil multiple time you keep getting more dissolved material out—hence I don't even know how I'd measure it.

Response: First, we thank the reviewer's appreciation that it is a useful idea to characterize soil biogeochemistry as a network of chemical reactions. However, we would like to clarify that this is not an idea that we invented in this paper. Rather, this approach has been extensively applied in the literature for decades and is well supported by modeling results and comparison with observations. For instance, the *ecosys* model is built upon this concept and has been applied in dozens of studies since the 1990's (e.g., Grant et al., 1993a, 1993b; Grant, 2001; Grant et al., 2016).

Second, our presentation of the SUPECA approach here was not intended to only provide a more mechanistic treatment of soil organic matter decomposition. Rather, as we stated, many new land models are beginning to explicitly represent microbes and plant-microbe interactions to improve their subsurface biogeochemistry representations, and our SUPECA approach is an attempt to formulate the mathematics representing these dynamics in a coherent and robust way. The EC and SU approaches are published methods demonstrated to have value for soil biochemistry modeling (e.g., Brandt et al., 2003; Jennings et al., 1982; Steefel et al., 2009). Since the SUPECA approach is based on the EC approach, it is naturally suitable for soil biogeochemical modeling.

Third, the ECA approach, which is the reduced version of SUPECA, has been shown to be very useful in biogeochemical modeling and has significant benefits over existing methods when confronted with observations (e.g., Tang and Riley, 2013, 2015; Zhu and Riley, 2015; Zhu et al., 2016a, 2016b, 2017). Therefore, we felt that it is valuable here to provide a detailed mathematical derivation of SUPECA and apply it using a proof-of-concept example to demonstrate its potential.

Fourth, in our model, we define DOC as dissolvable organic carbon, which includes adsorbed and dissolved components, and the two can be partitioned using empirically derived adsorption isotherms (Mayes et al., 2012). We chose this term intentionally to acknowledge exactly what the reviewer mentioned: multiple extractions can continue to produce more dissolved material as organic compounds move from mineral-associated phases to the aqueous phase. The SUPECA approach attempts to represent these multi-phase dynamics. We note that some models have attempted to more explicitly represent the chemical complexity of OC, including our own (BAMS1; Riley et al. 2014), where we divided dissolvable organic carbon into seven functional groups. Although we found that approach valuable for the questions we addressed in that paper, our subsequent work has shown that for some analyses a single functional group is sufficient (Dwivedi et al., 2017). Therefore, DOC is a precise concept in our model and is relevant to observations. We have added discussion on this point in the revised manuscript to clarify this point (P40: L14-18).

Fifth, following the reviewer's request of a comparison of our method to more traditional methods (see the revised Figure 5 and Figure 2 of this response), we included one popular response function approach in our evaluation of the soil moisture effect on decomposition and found it overestimated the soil respiration at high soil moisture content. The SUPECA approach mechanistically demonstrates that diffusion limitation is a key factor in the observed moisture response curves, but the simpler response function approaches cannot provide such mechanistic insights.

Finally, the SUPECA approach allows explicit kinetic links between plants and microbes (e.g., Zhu et al., 2016a, 2016b, 2017), which are difficult to represent with existing approaches. We therefore feel that the potential mechanistic understanding and insights provided by our new approach outweigh its complexity. Time (and more analysis) will tell, of course.

Comment 3:

Additionally, the authors compare the model to one experimental data set, and *argue that it fits the data well, but honestly, it really doesn't. Yes, the model kind of matches the observed data, but I have two issues. First, I have to take my glasses off to convince myself that the model lines match the data well (and my vision without glasses is pretty terrible). Is this better than you would get with other modeling approaches? Is it really better than applying a response function to a Century-type model? And second, actually, the match doesn't seem very good anyhow—the data seem flatter than the model lines; higher at low relative saturation and slightly lower than the model predictions at high relative saturation. The scatter in the data makes that less than perfectly clear, but that's what I'm seeing. So if I had to ask whether the model did a great job of capturing the data, at best I'd have to be pretty equivocal. All this work and we still have a relationship that is going to misrepresent respiration at low water contents?*

Response: We did not intend to say that the predictions from our proof-of-concept model fit the data perfectly. Rather, we intended to show that our new approach could reasonably capture the variability in soil respiration as a function of soil moisture. The statement that our approach has value beyond that provided by the response function approach as applied in CENTURY-type models is based on several arguments. First, in Tang and Riley (2015), we showed that the response function approach failed to capture the complex dynamics of how soil respiration responds to changes in temperature, and ignoring that additional variability not captured by the temperature response function may potentially result in very significant model bias. Since moisture and temperature are almost always intertwined in soil biogeochemistry, we hypothesize that the response function approach may equally miss a lot of the dynamics of how soil respiration responds to concurrent changes in moisture and temperature.

Second, the response function approach gives no mechanistic insights as to *why* soil moisture causes the changes in decomposition, while the SUPECA approach does, as discussed above.

Third, our approach has less arbitrariness than the response function approach, for which there is no widely accepted form. For instance, Sierra et al. (2015) identified 9 different response functions to represent the moisture effect on soil respiration, each of which might fit well with the data that are used to derive the specific response function, but among them, the divergence is very large (see Figure 1 below). Further, with the data that we used in this study, the response function approach based on the parabolic function (one of the often adopted forms; Sierra et al., 2015) over-predicted soil respiration at high soil moisture content, even though its R^2 coefficient of determination is high (0.84 compared to 0.82, 0.81, and 0.77 for the SUPECA approach). We hypothesize (but do not show) that the SUPECA approach will be easier to extrapolate to other soils, since it is more closely linked to fundamental processes and soil properties.

Again, we emphasize that we are not arguing that the SUPECA approach should replace existing models, but rather that it is a valuable tool to mechanistically and numerically robustly analyze the complex web of interactions in soil biogeochemistry. Finally, we stress that the approach and comparison with observations we present here is a proof-of-concept demonstration, rather than presentation of a fully completed soil BGC model.

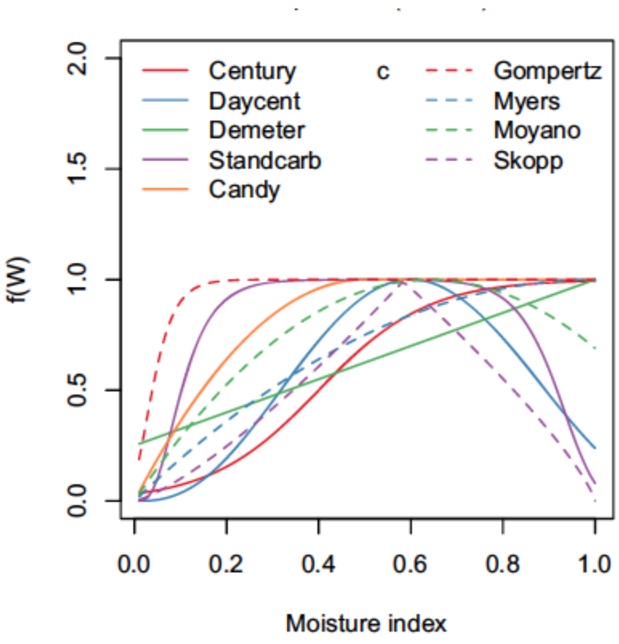

Figure 1. The divergence among the 9 moisture response functions as surveyed in Sierra et al. (2015). The figure is extracted from their Figure 4.

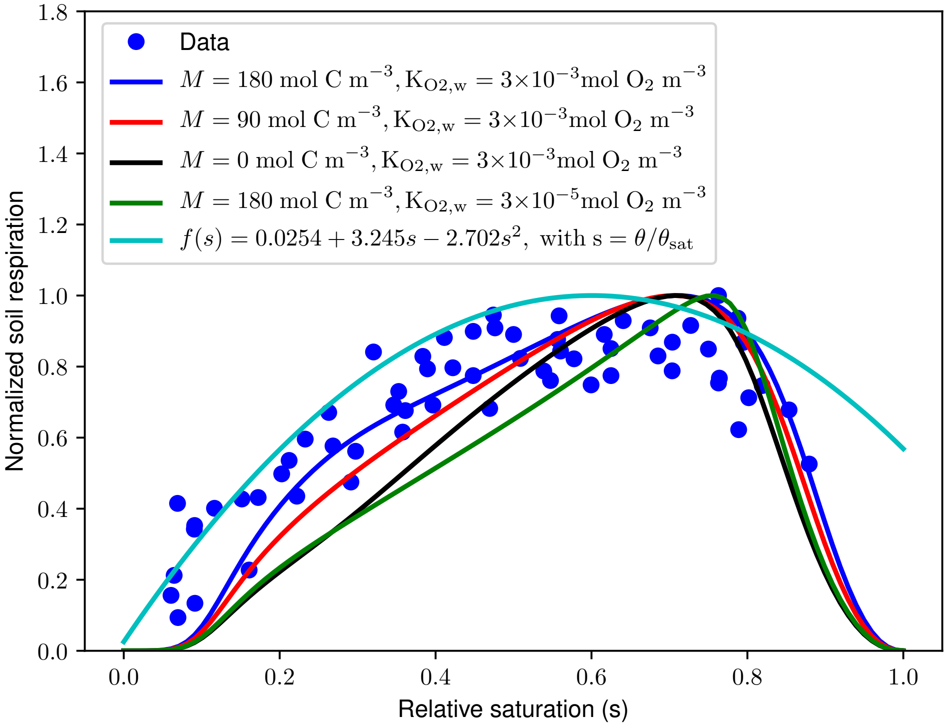

Figure 2. Comparison between the response function approach and the SUPECA based predictions. The response function over-predicted the respiration at high soil moisture content, which we explain using the SUPECA approach. More discussions are in the main text of the manuscript (P27: L10-22; P28: L1-22; P29: L1-4).

Comment 4:

And that leaves me wondering again whether this is really better than simpler model approaches? This model approach involves huge complexity and heavy parameterization—could a less complex model do as good a job of matching the data? The authors don't show that and hence I am left wondering about the real value of this enormous exercise. Reviewer #1 was impressed with the mathematical exercise but worried whether this model had a chance of ever being picked up and used by a broader community that just Tang and Riley (who presumably understand it).

Response: The mathematical complexity is a consequence of the system complexity and the basic assumption (i.e., law of mass action) that we used to represent the network-based conceptualization of soil biogeochemistry. There exist several successful numerical models with complex approaches to representing soil processes, published for ecosystem dynamics (e.g., *ecosys*; see Grant, 2001) and subsurface biogeochemistry (e.g., TOUGH-REACT (Xu et al., 2014; Riley et al., 2014; Dwivedi et al., 2017), CRUCHFLOW (Steefel, 2009)). Our goal here was to improve the mathematical consistency of these BGC process representations, describe them carefully and thoroughly in the peer-reviewed literature, and perhaps inspire further work on this end of the model complexity spectrum (which we believe is missing in our field, to the community's detriment). We acknowledge that the reviewer may be correct in stating that this added complexity may not lead to improved predictability. However, that point has not been demonstrated in the literature, and in the absence of a numerically robust and mechanistically realistic model, cannot be demonstrated.

As a side note, in atmospheric chemistry (a field with many analogous problems to those in soil biogeochemistry) researchers have applied a spectrum of modeling approaches, from lumped schemes to very sophisticated mechanistic descriptions (e.g., Wang et al., 1998). This range of model complexity provides a more complete analysis and predictive capability that are clearly of value to the atmospheric chemistry field.

Comment 5:

So I'm left with a conundrum in what I should recommend as a reviewer. A) I don't have the expertise to fully evaluate the math or derivations. I know Tang and Riley's skills so I feel comfortable in trusting that they performed the math reliably. But I remain thoroughly unconvinced by the paper that the exercise was really worth the effort or that it has substantial value to the broader biogeochemical modeling community. The paper doesn't do an adequate job of showing me how I would apply this model in "the real world" and the one comparison to data isn't very impressive—it doesn't convince me that the effort was worth it. How do I apply this to real soil and real substrates? I agree with reviewer #1 that the model makes some assumptions that are either excessively constraining or perhaps unrealistic. How do we apply it?

Response: We first thank the reviewer for trusting our mathematical skills and derivation; both Tang and Riley have thoroughly checked the mathematical derivations, and reviewer #2 only found a typo (which was corrected in the revision). Second, we emphasize that we have made our best effort to revise the manuscript to help readers appreciate why our approach could be valuable to them, e.g., providing more mechanistic insights into soil biogeochemical processes and providing numerically robust simplifications to the full chemical kinetics appropriate for microbial and enzymatic dynamics, particularly for modeling plant-microbial competition for soil nutrients.

Finally, we acknowledge that, as models take more mechanistic details into account, special expertise is needed to ensure numerically robust and mechanistically realistic representations are available. We do not contend to have developed a model structure that will answer all questions for everyone, but we do believe that the SUPECA approach has value and can move the field of soil biogeochemistry forward.

Specific Comments:

Comment 6:

9: I could accuse CENTURY of "explicitly representing microbial processes"! The processes are explicitly microbial, even if the model formulations don't explicitly include microbes as drivers.

Response: We revised the word "microbial processes" into "microbial dynamics" to make the statement more balanced and less ambiguous.

Comment 7:

4: 1-4: we contend that readers should not misunderstand our discussion of scaling below as an attempt to do ecological aggregation (e.g., Iwasa et al., 1987; 1989). Rather we are presenting a methodology to improve the consistency in formulating the microdynamics for ecological aggregation. Is this supposed to be clear? If so it fails. Perhaps because I'm not a mathematician, I don't know the ins and outs of "ecological aggregation" and so this section derails the development for me. The distinction between "ecological aggregation" and "the microdynamics for ecological aggregation" is unclear to me and suffers from a major case of "curse of knowledge": you have to know a lot to capture the half described nuance here. Inserting this to defend against a reviewer who you argue completely misunderstood the work seems a poor idea. Additionally negative arguments are almost always challenging. Don't tell us what this is not—instead just tell us what it is, and do it clearly enough that it is obvious what it isn't.

Response: We sincerely thank the reviewer for making this important suggestion, and, in our revision, we made our best effort to remove potential "curse of knowledge" and focus on what we are presenting rather than on what we are not presenting.

Comment 8:

5: 7 & 9: You don't need "the" in front of "two substrate" and "multi-substrate."

Response: We corrected this English error.

Comment 9:

6: 1: You do need a "the" in front of "consumer-substrate complex." I'm now getting annoyed. I understand that Jim Tang may not speak English as a native, but Riley does and I can only conclude that you didn't read this carefully enough.

Response: We corrected this error, and carefully checked the language throughout the revised manuscript. Also, Jim Tang is not the author of this manuscript, so he should not be blamed for this problem.

Comment 10:

6: 15: "which are mathematically identical"

6: 15: Oh, come on: "is mathematically identical" is then followed by "and they"? Why has this not been adequately proofread for English?
Response: We revised the text to avoid such confusion.

Comment 11*:*

24:8: Langmuir isotherm. I'm uncomfortable with having to do this. But that is the authors' point—for SU kinetics it appears necessary. Hence the problem with SU kinetic modeling. This is mixing equilibrium and non-equilibrium processes. The very reason for developing a kinetic model is because soil is a wildly non-equilibrium system. Extracting the "free substrate" concentration by assuming its in equilibrium via the Langmuir and then applying kinetic modeling seems questionable to me. Will the SUPECA approach avoid this problem?
Response: This is an approach widely adopted in modeling processes whose dynamics are characterized with multiple time scales. The fast processes are assumed in equilibrium within a numerical time step, and through the temporal integration, the whole system is de facto integrated as non-equilibrium. The SUPECA approach is more robust (than the SU kinetics) because it allows explicit incorporation of the quasi-equilibrium processes (e.g., Langmuir isotherm) into the substrate-consumer interactions, which the SU approach fails to achieve. This explicit incorporation of quasi-equilibrium processes is one advantage that leads to better numerical accuracy of the SUPECA kinetics; in Tang and Riley (2013) we showed that such an advantage makes the resultant model numerically more robust.

Comment 12:

23: 15: "We evaluated the accuracy of SUPECA" How do you evaluate the "accuracy" of a model when it is only being run with theoretical values? Doesn't "accuracy" imply that there is a real, defined target that you are trying to match? This shows up on the page 24 where the authors state "The SUPECA kinetics is more accurate in terms of both goodness of linear fitting and RMSE." In analytical chemistry, accuracy is defined by how close you come to the actual value of an analyte, while precision is the tightness of fit of your different replicates, regardless of whether they are accurate or not. So this seems closer to an estimate of precision than of accuracy in a chemical sense. I guess that the measure of "accuracy" is really that the SUPECA model much more closely matches the EC model prediction—but there is no absolute target here. This is still all theory and so there is no defined "correct" here to measure accuracy, is there?
Response: First, we should clarify that SUPECA is an analytical approximation to the EC formulation of a class of problems; which in our case is the network of mixed single substrate and redox reactions. Therefore, SUPECA is not a model (and we indicated clearly in the revision that substrate kinetics are mathematical tools for developing various mechanistic models; see P1: L13, P2: L9-13; P13: P6-9); and it is justified to evaluate SUPECA's numerical accuracy against the corresponding EC problem. In the revision, we further stressed that the accuracy is really the "numerical accuracy" and is evaluated against the predictions from the EC approach, which is the theoretically correct representation of a given biogeochemical system (which is of course an assumption that

we have to make like many others have in their use of the method (e.g., Pedersen et al., 2008); P25: L13-15). Therefore, in this context, our evaluation is standard practice and is as sound as any other exercise in evaluating the numerical accuracy of a newly developed numerical approximation. For instance, in numerical analyses of the diffusion equation, one always evaluates the numerical scheme against analytical solutions or a known numerical solution to quantify the accuracy of a new numerical scheme (Atkinson, 1989). When confronted with observed chemistry data, whether SUPECA can make accurate predictions will be dependent on whether the law of mass action (and further the EC formulation) is a good theoretical representation of the chemical system. However, such an analysis is beyond the scope of this study.

Comment 13:

25: 14: "uniformly distributed across the soil pores" Well, how likely is that? This seems one of the questionable assumptions mentioned by Reviewer #1.

Response: This is a very common approximation to facilitate construction of BGC models. The same assumption has been adopted in many other models of soil respiration, e.g., the conventional CENTURY-type model (like those in CMIP5 ESMs) represents only the topsoil, which various from 5 to 20 cm and the RothC model by Coleman and Jenkinson (1999) used an even cruder assumption (i.e., a homogeneous 23 cm thick topsoil). In our case, the choice of 10 cm is consistent with the 0-10 cm soils used by Franzluebbers (1999) to conduct his incubation experiment.

Comment 14:

25:13: Is DOC "dissolvable" or "dissolved" organic C? The normal is to consider it "dissolved"—i.e. in solution. There is much C that can be dissolved but which may not be in solution. In classic studies, Jerry Qualls showed that if you extracted a soil sample multiple times, you kept getting more and more C out. So what is DOC? By the standard definition, it would only be what is in solution; by this terminology, it could be all of that potentially extractable material.

Response: Please see our response to comment 2 on this topic.

Comment 15:

27: 5: Is "prognosed" a technical term in modeling or is it just a really weird word choice? Since this is the first time in my life I can remember seeing it used as a verb, instead of the original noun form of "prognosis" from medicine, I find it unclear and jarring.

Response: The second dictionary definition of "prognose" is "forecast". In modeling, the term is often used to distinguish a solution that explicitly accounts for dynamic evolution considering a mass, momentum, or energy balance, as distinguished from "diagnose", which does not. However, for clarity for readers with a variety of backgrounds, we replaced "prognosed" with "simulated" in the revision.

Comment 16:

27:23: "Such a result strongly contrasts with the popular approach in existing *soil BGC models (e.g., Koven et al., 2013; Tang et al.,2013), which apply a soil moisture response function as a multiplier on an unstressed rate." I don't understand this concern. I would argue that many response functions in 1st order BGC models actually represent emergent functions that reflect an integration of biotic and abiotic factors. So how is this criticism different from anything else?*

Response: This sentence was intended to highlight that hysteresis cannot be predicted with existing soil BGC model approaches to representing water stress (e.g., Koven et al., 2013; Tang et al., 2013). To clarify this statement, the revised text now reads (P28: L16-22; P29: L1-2) "we conclude that because the soil moisture response function emerges from interactions between biotic and abiotic factors that co-regulate soil organic carbon decomposition (Manzoni et al., 2016), its functional shape is not deterministic. This result contradicts the popular approach used in many soil BGC models (including our own, e.g., Koven et al., 2013; Tang et al., 2013; and others, e.g., Sierra et al., 2015), where a deterministic soil moisture response function is applied to the moisture-unstressed decomposition rate. We also note that there are many different functional forms for the soil moisture response function used in soil BGC models (Sierra et al. 2015)".

Comment 17:

28: 9: "Figures 6 and 7 demonstrate that soil aggregates may have profound influence on soil carbon decomposition rates." I think we already knew that.

Response: We agree that many in the community already knew this fact from measurements. However, demonstrating it using a mechanistic model is valuable and indicates our approach is mechanistically reasonable.

Comment 18:

Fig. 4 caption. It would be nice if the caption identified what the graph showed—there is no mention of which reaction system this applies to. I'm also concerned that the approaches give concentration ranges that differ by a full order-of-magnitude. It's also notable that the SUPECA approach doesn't fix the scatter above the line (thought it reshapes it and the scatter is greater in the middle of the range, rather than growing with EC prediction). Notably, the SUPECA approach seems more to put a lower limit on the scatter—it can't go much below the EC prediction but can go way above.

Response: First we note that in the revision, this figure now becomes Figure 3. Second, we are not able to put all the details of the reactions in the figure caption, because that will make the figure unreadable. However, in addition to the numerical method of fixed-point iteration, we now graphically described the reactions in the supplemental material. We acknowledge (here and in the manuscript; P25: L10-15) that SUPECA is not a perfect approximation to the EC prediction, but it nevertheless approximates the EC prediction more accurately than the SU approach (this point is clarified in the new Figure 3 and 4, where SU demonstrated significant overestimation compared to SUPECA). We also note that (in the new Figure 3 and 4) the scales of the differences in the comparison between SUPECA and EC predictions on the right are exaggerated compared to those between SU and EC predictions on the left. Therefore, considering that the reduced version of SUPECA (i.e., ECA) is also more accurate than the SU approach (which is *de facto* the Michaelis-Menten kinetics) in approximating the EC prediction for single substrate Monod type reactions (e.g., Tang and Riley, 2013; Tang, 2015); we contend that

SUPECA is an overall good candidate for practical use.

Reviewer 2:

I appreciate reading this important contribution to biogeochemical modeling by developing a more comprehensive reaction kinetics (i.e., SUPECA) based on their previous ECA kinetics. I respect the authors' careful derivation of a series of equations, where I only found a typo in Eq (26): should be kB+ before each [B].

For the first time, I am surprised to see that the soil moisture response function could be mechanistically predicted by a kinetics modeling, which may solve the dilemma how to choose an empirical moisture response function for a specific reaction. I expect to see, in the future, different soil moisture response functions for sophisticated reaction networks could be predicted in this way.

Another significance is that the authors demonstrate the robustness of SUPECA when more substrates and consumers are included in the system, indicating its applicability to the trait-based modeling.

Altogether, I would like to see this important work to be published.

Response:

We thank the reviewer's appreciation of our work. We have corrected the typo as identified above and hope the paper could be accepted for publication after addressing the other reviewer's comments.

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SUPECA kinetics for scaling redox reactions in networks of mixed substrates and consumers and an example application to aerobic soil respiration

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Abstract. Several land biogeochemical models used for studying carbon-climate feedbacks have begun explicitly representing microbial dynamics. However, to our knowledge, there has been no theoretical work on how to achieve a consistent scaling of the complex biogeochemical reactions from microbial individuals to populations, communities, and interactions with plants and mineral soils. We focus here on developing a mathematical formulation of the substrate-consumer relationships for consumer mediated redox reactions of the form $A+B\xrightarrow{E}products$, where products could be, e.g., microbial biomass or bio-products. Under the quasi-steady-state approximation, these substrate-consumer relationships can be formulated as the computationally difficult full Equilibrium Chemistry problem or approximated analytically with the Dual Monod (DM) or Synthesizing Unit (SU) kinetics. We find that DM kinetics are scaling inconsistent for reaction networks because: (1) substrate limitations are not considered, (2) contradictory assumptions are made regarding the substrate processing rate when transitioning from single- to multi-substrate redox reactions, and (3) the product generation rate cannot be scaled from one to multiple substrates. In contrast, SU kinetics consistently scale the product generation rate from one to multiple substrates, but predict unrealistic results as consumer abundances reach large values with respect to their substrates. We attribute this deficit to SU's failure to incorporate substrate limitation in its derivation. To address these issues, we propose SUPECA (SU Plus Equilibrium Chemistry Approximation) kinetics, which consistently impose substrate and consumer mass balance constraints. We show that SUPECA kinetics satisfy the partition principle, i.e., scaling invariance across a network of an arbitrary number of reactions (e.g., as in Newton's Law of motion and Dalton's law of partial pressures). We tested SUPECA kinetics with the equilibrium chemistry solution for some simple problems and found SUPECA outperformed SU kinetics. As an example application, we show that a steady-state SUPECA-based approach predicted an aerobic soil respiration moisture response function that agreed well with laboratory observations. We conclude that, as an extension to SU and ECA kinetics, SUPECA provides a robust mathematical representation of complex soil substrate-consumer interactions and can be applied to improve ESM land models.

Keywords: Dual-Monod kinetics, Synthesizing Unit, SUPECA kinetics, soil respiration, trait-based modeling

1. Introduction

Near surface soils holds more than twice the carbon in the current atmosphere; therefore a small change in land carbon dynamics can imply significant feedbacks to the ongoing climate warming (Ciais et al., 2013). This sensitivity has motivated research to better understanding Earth's land biogeochemical cycles, both for prediction and assessing the efficacy of climate mitigation and adaptation strategies. To date, however, soil biogeochemical models suffer from high uncertainty (e.g., Arora et al., 2013; Bouskill et al. 2014; Friedlingstein et al., 2014; He et al. 2016). For instance, eight CMIP5 Earth System Models (ESMs) predicted that net land carbon uptake varies from 22 to 456 Pg C for the 2006-2100 period under the Representative Concentration Pathway 4.5 (RCP4.5; Shao et al., 2013). Similarly, Todd-Brown et al. (2013) estimated that 16 CMIP5 ESMs predicted contemporary global soil carbon stocks ranging from 510 to 3040 Pg C to 1 m depth, while the most recent empirical estimation is 1408±154 Pg C to 1 m depth and 2060±217 Pg C to 2 m depth (Batjes, 2016).

The predictive power of existing land biogeochemical models is diminished by uncertainties from structural design, numerical implementation, model parameterization, initial conditions, and forcing data (Tang and Zhuang, 2008; Tang et al., 2010; Luo et al., 2015; Wieder et al., 2015a; Blanke et al., 2016; Tang and Riley, 2016). Among these, developing better model structures and mathematical formulations have been identified as priorities. One proposed structural improvement is to include explicit microbial dynamics (Wieder et al., 2015b), which may enable better predictions of global soil carbon stocks (Wieder et al., 2013), priming effects (Sulman et al., 2014), vertical soil carbon profiles (Riley et al., 2014; Dwivedi et al., 2017), and respiratory temperature sensitivity (Tang and Riley, 2015). A second proposal is to explicitly resolve ecosystem nutrient cycles, following the hypothesis that the potential for increasing land ecosystem carbon uptake from atmospheric CO_2 fertilization could be limited by nutrient availability (Vitousek, 1982; Shi et al., 2015; Wieder et al., 2015c).

A common feature that underlies these two proposed model structural improvements are substrate-consumer interactions, which affect microbial substrate decomposition (Grant et al., 1993; Tang and Riley, 2013a; Riley et al., 2014; Le Roux et al., 2016), mineral soil interactions with adsorptive substrates (Smith, 1979; Grant et al., 1993; Resat et al., 2011; Tang and Riley, 2015; Dwivedi et al., 2017), and plant-microbe competition for nutrients (Grant, 2013; Zhu et al., 2016a, 2016b, 2017). In soil, because there are many consumers competing for many substrates in different places at different times, soil biogeochemical models must be able to scale consistently across space, time, and processes. Scaling across spatial and temporal dimensions is achieved through spatial and temporal discretization and integration, which has been intensively studied elsewhere (e.g., Kolditz et al., 1998; Mao et al., 2006). Here we examine scaling along the less studied third dimension (process), focusing on development of a consistent mathematical formulation of substrate-consumer interactions.

Previously, we studied a simple configuration of this consumer-substrate interaction, i.e., the network of single-substrate Monod type reactions (discussed later), and developed a scaling method, the Equilibrium Chemistry Approximation (ECA) kinetics (Tang and Riley, 2013a). ECA kinetics significantly improved the modeling of plant-microbial nutrient competition in the ACME land biogeochemical model (Zhu and Riley, 2015; Zhu et al., 2016a, 2016b, 2017), and was recently cited as one of the most promising methods to improve representation of nutrient competition in ESMs (Achat et al., 2016; Niu et al., 2016). The ECA method also successfully explained why organo-mineral interactions can slow soil organic matter decomposition rates and how lignin-cellulose ratios (Melillo et al., 1989) can be stabilized during litter decomposition (Tang and Riley, 2013a, 2015).

Following Tang and Riley (2013a), we start our analysis here by assuming a certain homogeneous space-time-process unit in soil, within which there are generally three types of substrate-consumer relationships: (1) single-substrate Monod type (aka A-E type) reactions in the form of $A\overset{E}{\rightarrow}products$; (2) two-substrate (aka AB-E type) redox reactions in the form of $A+B\overset{E}{\rightarrow}products$, where substrate A and B are called complementary because they both are required for the redox reaction to proceed; and (3) multi-substrate (>2) reactions $\sum_i A_i\overset{E}{\rightarrow}products$. The scaling of single-substrate Monod type reactions has been extensively discussed in Tang and Riley (2013a), and is resolved with ECA kinetics (more discussion on ECA kinetics for process scaling will be provided in later sections when discussing SUPECA kinetics). Further, because many multi-substrate reactions can be separated into a combination of single-substrate reactions and redox-reactions, our discussion below focuses on achieving a consistent kinetic scaling from a single redox reaction to many reactions in a network.

Mathematically, the problem can be addressed with an explicit formulation of all kinetic processes using ordinary differential equations accounting for all substrates and consumers (Chellaboina et al., 2009). However, such a formulation would require too many parameters and would be numerically very difficult to solve because of its multi-temporal scale nature. By making the quasi-steady-state-approximation (QSSA), i.e., assuming that product generation from the consumer-substrate complex is much slower than equilibration between consumers, substrates, and consumer-substrate complexes (Briggs and Haldane, 1925; Pedersen et al., 2008), the full kinetic problem is reduced to the simpler Equilibrium Chemistry (EC) form (e.g., Chellaboina et al., 2009). However, the EC formulation is also usually very difficult to solve numerically. Therefore, analytical approximations to the EC formulation are generally made.

Two classic analytical approximations for modeling redox-reactions are Dual Monod (DM) kinetics (e.g., Yeh et al., 2001) and Synthesizing Unit (SU) approach (Kooijman, 1998; Brandt et al., 2003). Although both of these are special cases of the EC formulation (Kooijman, 2010; Tang and Riley, 2013a), they make different assumptions regarding the relative magnitudes of involved kinetic parameters. For this, Kooijman (2010) has shown that DM kinetics require the consumer-substrate complex dissociation rate to be much larger than the product generation rate from the complexes. In contrast, single-substrate Monod kinetics (Monod, 1949) or Michaelis-Menten (MM) kinetics (Michaelis and Menten, 1913; which is mathematically identical to the empirical Monod kinetics) do not impose this requirement on its parameters. Moreover, in applications to r-K scaling (e.g., Tilman, 1982; Litchman and Klausmeier, 2008), single-substrate Monod kinetics require the product-generation rate to be faster than the dissociation rate of consumer-substrate complexes. This contrasting requirement on the relative magnitudes of parameters, as we will show later, implies that DM kinetics cannot achieve consistent scaling of substrate-consumer interactions for generic biogeochemical modeling.

We define a kinetic formulation to have consistent process scaling when the formulated substrate-consumer relationship: (1) can seamlessly transition from a single substrate-consumer pair to a network of many substrate-consumer pairs without changing its mathematical form (aka the partition principle as in Newton's second Law of motion, Feynman et al., 1963) and (2) does not predict any singularity over the range of substrate and consumer concentrations (aka the non-singular principle, e.g., Schnell and Maini, 2000; Tang, 2015). The full kinetics and EC formulations both satisfy these two criteria, which can be explained using the following example network of consumer-substrate relationships:

$$S_i + E_j \overset{k^+_{1,ij}}{\underset{k^-_{1,ij}}{\leftrightarrow}} E_jS_i \overset{k^+_{2,ij}}{\rightarrow} P_{ij} + E_j \tag{1}$$

where substrate S_i complexes with consumer E_j to form complex E_jS_i, which is then degraded into product P_{ij} and free consumer. Throughout this study, forward and backward kinetic parameters are indicated with superscript "+" and "−", respectively. Unless an ambiguity needs clarification, we assume all variable units are consistently defined.

The full kinetic formulation for the network of equation (1) is:

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$$\frac{d[S_i]}{dt} = -[S_i]\sum_j\left(k^+_{1,ij}[E_j]\right) + \sum_j\left(k^-_{1,ij}[E_jS_i]\right) \tag{2}$$

$$\frac{d[E_jS_i]}{dt} = k^+_{1,ij}[S_i][E_j] - \left(k^-_{1,ij} + k^+_{2,ij}\right)[E_jS_i] \tag{3}$$

$$\frac{d[E_j]}{dt} = -[E_j]\sum_i\left(k^+_{1,ij}[S_i]\right) + \sum_i\left(\left(k^-_{1,ij} + k^+_{2,ij}\right)[E_jS_i]\right) \tag{4}$$

where $[x]$ indicates the concentration of x.

The first summation in equations (2) and (4) satisfies the partition principle. For instance, for equation (4), by defining an appropriate mean specific substrate affinity $k^+_{1,j}$, the summation $\sum_i\left(k^+_{1,ij}[S_i]\right)$ can be recast as $k^+_{1,j}[S]$, in which $[S] = \sum_i [S_i]$ resembles

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Dalton's law of partial pressures (and many other similar relationships in physics, e.g., Newton's second law of motion (Feynman et al., 1963)).

Meanwhile, that the full kinetic formulation satisfies the nonsingular principle can be verified by noting that, at any time:

$$[S_i]+\sum_j [E_jS_i]=[S_i]_T \qquad (5)$$

and that consumption of S_i is through generation of product from $[E_jS_i]$. Therefore, by combining equations (2), (3), and (5), the overall consumption rate of S_i (i.e., $\sum_j k^+_{2,ij}[E_jS_i]$) is always smaller than $[S_i]_T \sum_j k^+_{2,ij}$, even when consumers have high abundances relative to their substrates, a common situation in *in vivo* cells (Sols and Marco, 1970) and in plant-microbial competition for limited soil nutrients (Vitousek, 1982; Schimel and Bennett, 2004; Vitousek et al., 2010).

Since the EC formulation is obtained by applying the QSSA to the full kinetic formulation (i.e., $d[E_jS_i]/dt \approx 0$ for equation (3)), it automatically satisfies the two criteria for consistent process scaling. However, Monod kinetics is scaling inconsistent when it is applied, for example, to single-substrate competition by multiple populations, or to multi-substrate consumption by a single population (e.g., Williams, 1973; Schnell and Mendoza, 2000; Tang et al., 2010; Riley et al., 2011, 2014; Allison, 2012; Bouskill et al., 2012; Wieder et al., 2013, 2014). Specifically, that Monod kinetics violates the partition principle can be shown from the following inequality:

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$$F_j=\left[E_j\right]\sum_i \frac{k_{2,ij}^{+}\left[S_i\right]}{K_{ij}+\left[S_i\right]} \neq \left[E_j\right]\frac{\sum_i k_{2,ij}^{+}\left[S_i\right]/K_{ij}}{1+\sum_i \left[S_i\right]/K_{ij}} \tag{6}$$

Here F_j describes the uptake of all substrates S_i by consumer E_j. The left hand side of the inequality is the uptake computed by directly applying Monod kinetics, while the right hand side is obtained by applying competitive Monod kinetics (e.g., Litchman and Klausmeier, 2008). Inequality (6) is even true when K_{ij} is independent of i. Besides being inconsistent with the partition principle, Monod kinetics also violates the non-singular principle, which can be demonstrated by observing that, as $\left[E_j\right]$ approaches very large values, so does F_j. This linear dependence of F_j on $\left[E_j\right]$ results in large biases of predicted parametric sensitivities under high ratios of $\left[E_j\right]$ with respect to substrates (Schnell and Maini, 2000; Tang and Riley, 2013a; Tang, 2015), and is inconsistent with the non-singularity implied in equation (5).

For competitive Monod kinetics on the right hand side of inequality (6), we may define $K_j=\left[S\right]\Big/\left(\sum_i\left[S_i\right]/K_{ij}\right)$ (e.g., Murdoch, 1973), resulting in:

$$F_j=\left[E_j\right]\frac{k_{2,j}^{+}\left(\sum_i\left[S_i\right]\right)\Big/K_j}{1+\left(\sum_i\left[S_i\right]\right)\Big/K_j}=\left[E_j\right]\frac{k_{2,j}^{+}\left[S\right]/K_j}{1+\left[S\right]/K_j} \tag{7}$$

where $\left[S\right]=\sum_i\left[S_i\right]$ designates the total free concentrations of all substrates. Equation (7) therefore carries the same partition principle implied in the first summation in

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equation (4) of the full kinetic formulation, suggesting that competitive Monod kinetics satisfy the partition principle for consistent scaling of substrate-consumer relationships. Nevertheless, because competitive Monod kinetics are linear in $\left[E_j\right]$, as are classic Monod kinetics, they still violate the non-singular principle for consistent scaling.

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In Tang (2015) (and also in Borghans et al. (1996) and Tang and Riley (2013a)), it was shown that the linear dependence of F_j on $\left[E_j\right]$ as predicted by Monod kinetics and similarly by competitive Monod kinetics is due to their failure to impose the substrate mass (or surface area) balance in deriving their mathematical formulations. This problem has been rectified in ECA kinetics (Tang and Riley, 2013a), which was shown to predict much more accurate parametric sensitivity than Monod kinetics when compared with analytical solutions (Tang, 2015). Since the success of all model calibrations relies on the accuracy of modeled response variables' sensitivity to model parameters (e.g., Wang et al., 2001; Williams et al, 2005; Tang and Zhuang, 2009; van Werkhoven et al., 2009; Qian et al., 2015), and plant-microbial competitions of nutrients often occur under high consumer abundances with respect to their substrates (as corroborated by the nitrogen and phosphorus limitations that are commonly observed in natural ecosystems; e.g., Vitousek et al. (2010)), developing robust biogeochemical models requires substrate kinetics that give accurate parametric sensitivities under a wide range of parameter values.

We therefore ask the question: how should we achieve a consistent scaling from the simplest redox reaction $A+B\xrightarrow{E}products$ (i.e., AB-E type) to a network that mixes many redox reactions and even single substrate Monod-type reactions? Aside from the two criteria (i.e., the partition principle and non-singularity) discussed above, we suggest a third criterion that a consistent scaling of substrate-consumer relationships should seamlessly transition from a single substrate A-E Monod-type reaction to the AB-E type redox reaction without making contradictory assumptions of the parameters in its theoretical derivation.

In the following, we address the above process-scaling question by first presenting the step-by-step derivation of DM kinetics and SU kinetics from the EC formulation of the redox reaction $A+B\xrightarrow{E}products$. Conceptually, DM kinetics can be viewed as a direct application of chemical kinetics that the reaction rate of substrates A and B with consumer E is determined by the product of A and B's binding probability to E (which in Monod form is $[A]/(K_A+[A])$ for substrate A, and $[B]/(K_B+[B])$ for substrate B). Kooijman (1998) was the first to derive SU kinetics using queue theory (e.g., Gross et al., 2011) and Brandt et al. (2003) discussed its use for AB-E type redox reactions. The following derivation stresses scaling-inconsistencies implied in DM and SU kinetics, and we will show that DM kinetics cannot be extended for consistent process scaling of substrate-consumer relationships. We then present SUPECA kinetics, which remedies the inconsistencies in SU kinetics. We demonstrate the benefits of using SUPECA kinetics in terms of numerical accuracy and present a proof-of-concept example by modeling the moisture control of aerobic soil respiration. Finally, we discuss how one can apply SUPECA kinetics to trait-based modeling approaches in various biogeochemical systems (e.g., Bouskill et al., 2012; Follows et al., 2007; Litchman and Klausmeier, 2008).

2. Derivation of ECA kinetics for AB-E type redox reaction $A+B\xrightarrow{E}products$

2.1 Governing equations

We schematically represent the enzymatic redox reaction network as

$$\begin{array}{ccccccccc}
E & + & A & \overset{k_A^+}{\underset{k_A^-}{\leftrightarrow}} & EA & & & & \\
+ & & & & + & & & & \\
B & & & & B & & & & \\
k_B^- \updownarrow k_B^+ & & & & k_B^- \updownarrow k_B^+ & & & & \\
EB & + & A & \overset{k_A^+}{\underset{k_A^-}{\leftrightarrow}} & EAB & \overset{k_2^+}{\rightarrow} & E & + & P
\end{array} \tag{8}$$

where it is assumed that the order of substrates *A* and *B* binding to consumer *E* does not affect the kinetic coefficients, as is done in most modeling studies (e.g., Yeh et al., 2001).

By law of mass action and the total QSSA (tQSSA; e.g., see Borghans et al., 1996; Tang and Riley, 2013a), we have the governing equations (appendix A):

$$\frac{d\left[A\right]_T}{dt}=-k_2^+\left[EAB\right] \tag{9}$$

$$\frac{d\left[B\right]_T}{dt}=-k_2^+\left[EAB\right] \tag{10}$$

$$k_A^+\left[E\right]\left[A\right]+k_B^-\left[EAB\right]=\left(k_A^-+k_B^+\left[B\right]\right)\left[EA\right] \tag{11}$$

$$k_B^+\left[E\right]\left[B\right]+k_A^-\left[EAB\right]=\left(k_B^-+k_A^+\left[A\right]\right)\left[EB\right] \tag{12}$$

$$k_A^+\left[EB\right]\left[A\right]+k_B^+\left[EA\right]\left[B\right]=\left(k_A^-+k_B^-+k_2^+\right)\left[EAB\right] \tag{13}$$

where

$$\left[A\right]_T=\left[A\right]+\left[EA\right]+\left[EAB\right] \tag{14}$$

$$\left[B\right]_T=\left[B\right]+\left[EB\right]+\left[EAB\right] \tag{15}$$

$$\left[E\right]_T=\left[E\right]+\left[EA\right]+\left[EB\right]+\left[EAB\right] \tag{16}$$

The derivation of substrate kinetics is therefore equivalent to solving for $\left[EAB\right]$ from the EC problem defined by equations (11)-(16). However, because this set of equations is non-linear, and no analytical solutions are available (to our knowledge), some linearization is warranted to obtain analytical approximations. As we describe below, linearization with different assumptions lead to DM, SU, and SUPECA kinetics.

To clarify, we note that obtaining the substrate kinetics only requires solving equations (11)-(16); various production and destruction terms can be added to equations (9) and (10) to form a full dynamic model (e.g., Maggi and Riley, 2009) without affecting our derivation below.

2.2 **Dual Monod kinetics and synthesizing unit kinetics**

One method to linearize equations (11)-(16) is to assume that concentrations of consumer-substrate complexes are so small that free substrate concentrations are effectively equal to bulk concentrations (e.g., for substrate A: $\left[A\right]_T=\left[A\right]$). This approach, when combined with different assumptions on the relative magnitudes of kinetic parameters, leads to the popular DM kinetics and the two-substrate SU kinetics.

2.2.1 Dual Monod kinetics

We now derive DM kinetics. Adopting the equilibrium approximation that forward binding between consumer and substrate is in rapid equilibrium with backward dissociation of consumer-substrate complex (e.g., Michaelis and Menten, 1913; Pyun, 1971), we have the following

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$$[EA][B]=\frac{k_B^-}{k_B^+}[EAB]=K_B[EAB] \tag{17}$$

$$[EB][A]=\frac{k_A^-}{k_A^+}[EAB]=K_A[EAB] \tag{18}$$

which then transforms equations (11) and (12) into

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$$[E][A]=\frac{k_A^-}{k_A^+}[EA]=K_A[EA] \tag{19}$$

$$[E][B]=\frac{k_B^-}{k_B^+}[EB]=K_B[EB] \tag{20}$$

By solving for $[EAB]$ from equations (14)-(16) using equations (17)-(20), we obtain the consumer-substrate complex for DM kinetics (see Appendix B)

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$$\frac{d[A]_T}{dt}=-k_2^+[E]_T\frac{[A]}{K_A+[A]}\frac{[B]}{K_B+[B]} \tag{21}$$

As one substrate, e.g., $[A]$, becomes unlimited, equation (21) can be reduced to the classical MM kinetics

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$$\frac{d[A]_T}{dt}=-k_2^+\frac{[E]_T[B]}{K_B+[B]} \tag{22}$$

We note that the half saturation coefficient $K_B=k_B^-/k_B^+$ in equation (22) is different from its usual definition (i.e., $K_B=\left(k_2^++k_B^-\right)/k_B^+$) if one derives MM kinetics rigorously starting from a single substrate and single consumer system (e.g., Tang, 2015). For this reason, we assert that DM kinetics cannot achieve a self-consistent scaling from one-

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substrate reaction to multiple-substrate reactions. More specifically, by substituting equations (17) and (18) into equation (13), one obtains $k_2^+ = 0$, or at least $k_2^+ \ll \max\left(k_A^-, k_B^-\right)$, which states that the consumer is very inefficient in processing the substrate. However, MM kinetics does not require the dissociation rate to be much higher than the product generation rate from the consumer-substrate complex, i.e. $k_2^+ \ll \max\left(k_A^-, k_B^-\right)$ (e.g., Briggs and Haldane, 1925). Nor do the high dissociation rates of $\left[EA\right]$, $\left[EB\right]$, and $\left[EAB\right]$ favor the consumer's assimilation of substrates under usual substrate concentrations (e.g., Van Slyke and Cullen, 1914), even though a high dissociation rate of the enzyme-substrate complexes may possess some theoretical advantage under high substrate concentrations when the consumer is a single enzyme (Reuveni et al., 2014). To the contrary, most existing applications tend to assume $k_2^+ \gg k_A^-$ and $k_2^+ \gg k_B^-$ (e.g., Holling, 1959, 1966; Aksnes and Egge, 1991; Armstrong, 2008; Bonachela et al., 2011), such that $K_B \approx k_2^+ / k_B^+$ for MM kinetics and r-K selection can be explained by linking k_2^+ with growth rate, and k_A^+ and k_B^+ with substrate competitive ability (e.g., Litchman and Klausmeier, 2008). Therefore, for biogeochemical modeling, DM and MM (or Monod) kinetics are based on different assumptions of the relative magnitudes of kinetic parameters, and no smooth transition from single- (MM) to multi-substrate (DM) kinetics exists.

2.2.2 Synthesizing unit kinetics

In deriving SU kinetics for the redox reaction network represented in equation (8), consumer E is viewed as a generalized enzyme that generates bio-products by processing

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substrates A and B. SU computes the specific reaction rate per unit concentration of E as the product generation rate k_2^+ times the probability that E binds with both substrates A and B (which is $\left[EAB\right]/\left[E\right]_T$). SU kinetics requires the sufficient flux condition $k_A^+\left[A\right]\gg k_B^-$ and $k_B^+\left[B\right]\gg k_A^-$ (Kooijman, 2010). Defining $\tilde{k}_2^+ = k_A^- + k_B^- + k_2^+$, equations (11)-(13) become

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$$k_A^+\left[E\right]\left[A\right]=k_B^+\left[B\right]\left[EA\right] \qquad (23)$$

$$k_B^+\left[E\right]\left[B\right]=k_A^+\left[A\right]\left[EB\right] \qquad (24)$$

$$k_A^+\left[EB\right]\left[A\right]+k_B^+\left[EA\right]\left[B\right]=\tilde{k}_2^+\left[EAB\right] \qquad (25)$$

From equations (23)-(25), we obtain (see Appendix C)

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$$\frac{d\left[A\right]_T}{dt}=-\frac{k_2^+\left[E\right]_T/\tilde{k}_2^+}{\frac{1}{\tilde{k}_2^+}+\frac{1}{k_A^+\left[A\right]}+\frac{1}{k_B^+\left[B\right]}-\frac{1}{k_A^+\left[A\right]+k_B^+\left[B\right]}} \qquad (26)$$

The two-substrate SU kinetics (equation (26)) can also be viewed as a special case of the general SU kinetics for any number of complementary substrates, which was first derived by Kooijman (1998) based on queue theory (e.g., Gross et al., 2011). Kooijman (1998) assumed that consumers act like synthesizing units, which process substrates in two steps: binding and production. He then assumed that all flux rates (including production rates k_2^+ and substrate binding rates $k_A^+\left[A\right]$ and $k_B^+\left[B\right]$) are of Poisson distributions, and calculated the overall specific substrate consumption rate as the reciprocal of the expected total processing time (i.e., the denominator of equation (26)). The last term in the denominator of equation (26) comes from the assumption of parallel

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binding of substrates A and B to E, which disappears if sequential binding is assumed (e.g., Brandt et al., 2003).

As one substrate, e.g., A, becomes unlimited, single-substrate Monod kinetics is recovered from equation (26):

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$$\frac{d\left[A\right]_T}{dt}=-\frac{k_2^+\left[E\right]_T}{1+\frac{\tilde{k}_2^+}{k_B^+\left[B\right]}}=-\frac{k_2^+\left[E\right]_T\left[B\right]}{\frac{\tilde{k}_2^+}{k_B^+}+\left[B\right]} \tag{27}$$

which has a half saturation coefficient similar to what would be derived for a single substrate, single consumer reaction (e.g., Tang, 2015). By assuming Poisson distribution of the kinetic parameters, it can also be shown for a single enzyme molecule that MM kinetics represent the statistical mean of the fluctuating activity of the enzyme (English et al., 2006; Reuveni et al., 2014). That kinetics of both single-substrate reactions and two-substrate redox reactions can be similarly derived using statistical theory and that equations (26) and (27) can be obtained from the EC formulation using consistent assumptions of the relative magnitudes of kinetic parameters indicates, in contrast to DM kinetics, that SU kinetics is able to scale consistently between one- and two-substrate redox reactions.

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2.3. SUPECA kinetics

In Tang and Riley (2013a) and Tang (2015), it was shown that the derivation of MM kinetics ignores the substrate mass balance constraint, resulting in MM kinetics predicting inaccurate parametric sensitivity over the wide range of substrate to consumer ratios (e.g., Figure 1 in Tang (2015)). This problem is particularly acute when consumer abundances are high with respect to their substrates, a situation that may occur in *in vivo* conditions (Sols and Marco, 1970; Schnell and Maini, 2000) or when consumers interact with mineral surfaces, such as microbial decomposition of soil organic matter or plant-microbial competition for soil nutrients (Schimel and Bennett, 2004; Vitousek et al., 2010; Resat et al., 2011; Tang and Riley, 2015; Zhu et al., 2016a). In the above, we also note that the substrates' mass balance constraints (equations (14) and (15)) are not used in deriving DM and SU kinetics, suggesting that both DM and SU kinetics may suffer from the same deficiency as MM kinetics. Further, since DM kinetics fail to consistently scale from a single to two substrates, we below focus on combining SU and ECA kinetics into SUPECA kinetics to achieve a scalable and non-singular formulation of redox reactions.

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As implied in equations (9)-(16), the derivation of substrate kinetics requires solving for $\left[EAB\right]$ from nonlinear equations (11)-(16), whose analytical solutions are not available. To obtain improved solutions as compared to SU kinetics, we applied a first order closure approach (appendix D; which is the perturbation method truncated to first order accuracy that describes the first order term using appropriate mean states (e.g., Shankar, 1994; Tang et al., 2007)) to the system formed by equations (11)-(16), leading to SUPECA kinetics:

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$$\begin{aligned}\frac{d\left[A\right]_T}{dt}&=-\frac{\left[E\right]_T}{\dfrac{1}{k_2^+}\dfrac{\bar{f}_A\bar{f}_B f_{AB}}{f_A f_B \bar{f}_{AB}}+\dfrac{1}{f_A}+\dfrac{1}{f_B}-\dfrac{f_A\bar{f}_B+\bar{f}_A f_B-\bar{f}_A\bar{f}_B}{f_A f_B \bar{f}_{AB}}}\\&=-\frac{k_2^+\left[E\right]_T\left(f_A/k_2^+\right)\left(f_B/k_2^+\right)}{\dfrac{\bar{f}_A\bar{f}_B}{k_2^+\bar{f}_{AB}}\dfrac{f_{AB}}{k_2^+}+\dfrac{f_{AB}}{k_2^+}-\dfrac{f_A\bar{f}_B+\bar{f}_A f_B-\bar{f}_A\bar{f}_B}{k_2^+\bar{f}_{AB}}}\end{aligned} \tag{28}$$

where $f_A = k_A^+ \left[A\right]_T$, $f_B = k_B^+ \left[B\right]_T$, $\overline{f}_A = f_A + k_A^+ \left[E\right]_T$, $\overline{f}_B = f_B + k_B^+ \left[E\right]_T$, $f_{AB} = f_A + f_B$, and $\overline{f}_{AB} = \overline{f}_A + \overline{f}_B$. In equation (28), we assumed $k_2^+ \gg k_A^-$ and $k_2^+ \gg k_B^-$, so that $k_2^+ \approx \tilde{k}_2^+$ (this relationship will be used throughout the remainder of this paper). It can then be verified that if $\left[E\right]_T \ll \left[A\right]_T$ and $\left[E\right]_T \ll \left[B\right]_T$, SUPECA kinetics as represented in equation (28) becomes SU kinetics in equation (26). Further, if one of the two substrates, say $\left[B\right]_T$, becomes unlimited, equation (28) is reduced to

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$$\frac{d\left[A\right]_T}{dt} = -\frac{\left[E\right]_T}{\frac{1}{k_2^+}\frac{\overline{f}_A}{f_A} + \frac{1}{f_A}} = -\frac{f_A\left[E\right]_T}{1 + \frac{\overline{f}_A}{k_2^+}} \tag{29}$$

which, by using the definition of f_A and $\overline{f}_A$, becomes the single substrate ECA kinetics equation (Tang, 2015).

3. SUPECA kinetics for a network of reactions

In actual biogeochemical systems, it is more common for many substrates to be processed by many consumers concurrently (and such an assumption is implicitly assumed in the space-time-process unit of any biogeochemical model). To consistently handle such situations, Tang and Riley (2013a) derived ECA kinetics (see Figure 1 for a graphic demonstration) for calculating the consumption of a substrate S_i by a consumer E_j in a network of single substrate reactions $A \xrightarrow{E} products$:

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$$\frac{d\left[S_i\right]_{T,j}}{dt}=-\frac{k_{2,ij}^{+}\left[E_j\right]_T\left(\left[S_i\right]_T/K_{ij}\right)}{1+\sum_{l=1}^{l=I}\left(\left[S_l\right]_T/K_{lj}\right)+\sum_{l=1}^{l=J}\left(\left[E_l\right]_T/K_{il}\right)} \qquad (30)$$

By defining the normalized substrate flux (with subscript "*c*" designating that the summation is over a column of the graph in Figure 1)

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$$F_{c,j}=\sum_{l=1}^{l=I}\left(\left[S_l\right]_T/K_{lj}\right)=\sum_{l=1}^{l=I}F_{c,j}^{\{l\}} \qquad (31)$$

and its conjugate (with subscript "*r*" designating that the summation is over a row of the graph in Figure 1)

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$$F_{r,i}=\sum_{l=1}^{l=J}\left(\left[E_l\right]_T/K_{il}\right)=\sum_{l=1}^{l=J}F_{r,i}^{\{l\}} \qquad (32)$$

equation (30) can then be rewritten as

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$$\frac{d\left[S_i\right]_{T,j}}{dt}=-k_{2,ij}^{+}\left[E_j\right]_T\left(\frac{F_{c,j}^{\{i\}}}{1+F_{r,i}+F_{c,j}}\right)=-k_{2,ij}^{+}\left[S_i\right]_T\left(\frac{F_{r,i}^{\{j\}}}{1+F_{r,i}+F_{c,j}}\right) \qquad (33)$$

The normalized substrate flux as defined in equation (31) and its conjugate in equation (32) implies that the consumption of substrate S_i by consumer E_j as described by ECA kinetics in equation (33) may be interpreted as either (i) the potential substrate processing rate of E_j (i.e., $k_{2,ij}^{+}\left[E_j\right]$) weighted by the relevant importance of the reaction pathway $S_i \xrightarrow{E_j} products$ (i.e., $F_{c,j}^{\{i\}}$) under the influence of all competing substrate fluxes $F_{c,j}^{\{l\}}$

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(towards consumer E_j) and all competing agents' demands $F_{r,i}^{\{l\}}$ (towards substrate S_i) or (ii) the linear decay potential of S_i (i.e., $k_{2,ij}^{+}\left[S_i\right]_T$) weighted by the relevant importance of $F_{r,i}^{\{j\}}$ under the influence of all competing substrate fluxes and competing agents' demands.

We note that equations (31) and (32) define some very interesting scaling relationships. For instance, from equation (31), we can define the effective substrate affinity for the bulk substrates ($\left[\bar{S}\right]_T$, defined as the total of all substrates) that are accessible for consumer E_j as

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$$K_{E,j}=\left(\sum_{l=1}^{l=I}\left[S_l\right]_T\right)\Big/F_{c,j}=\left[\bar{S}\right]_T\Big/F_{c,j} \qquad (34)$$

Similarly, we can define the effective affinity for substrate S_i resulting from all competing agents as

$$K_{S,i}=\left(\sum_{l=1}^{l=J}\left[E_l\right]_T\right)\Big/F_{r,i}=\left[\bar{E}\right]_T\Big/F_{r,i} \qquad (35)$$

Then by substituting equations (34) and (35) into equation (33), we obtain

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$$\begin{aligned}\frac{d\left[S_i\right]_{T,j}}{dt}&=-\frac{k_{2,ij}^{+}\left[E_j\right]_T\left(\left[\bar{S}\right]_T/K_{E,j}\right)}{1+\left[\bar{S}\right]_T/K_{E,j}+\left[\bar{E}\right]_T/K_{S,i}}\frac{F_{c,j}^{\{i\}}}{F_{c,j}}\\&=-\frac{k_{2,ij}^{+}\left[S_i\right]_T\left(\left[\bar{E}\right]_T/K_{S,i}\right)}{1+\left[\bar{S}\right]_T/K_{E,j}+\left[\bar{E}\right]_T/K_{S,i}}\frac{F_{r,i}^{\{j\}}}{F_{r,i}}\end{aligned} \qquad (36)$$

which again shows the linear partition in terms of $F^{\{i\}}_{c,j}\big/F_{c,j}$ and $F^{\{j\}}_{r,i}\big/F_{r,i}$.

By applying the above two scaling relationships and the three consistent scaling criteria (as we proposed in the introduction section) to SUPECA kinetics in equation (28), we obtain (in appendix E) the network form of SUPECA kinetics:

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$$\frac{d\left[A_i\right]_{T,jk}}{dt}=-\frac{k^{+}_{2,ijk}\left[E_k\right]_T F^{\{i\}}_{c,A,k}F^{\{j\}}_{c,B,k}}{\frac{G_{A,ik}G_{B,jk}}{G_{AB,ijk}}F_{c,AB,k}+F_{c,AB,k}-\frac{F_{c,A,k}G_{B,jk}+G_{A,ik}F_{c,B,k}-G_{A,ik}G_{B,jk}}{G_{AB,ijk}}} \tag{37}$$

where

$$F_{c,A,k}=\sum_l F^{\{l\}}_{c,A,k}=\sum_l\left[A_l\right]_T\big/K_{A,lk} \tag{38}$$

$$F_{c,B,k}=\sum_l F^{\{l\}}_{c,B,k}=\sum_l\left[B_l\right]_T\big/K_{B,lk} \tag{39}$$

$$F_{c,AB,k}=F_{c,A,k}+F_{c,B,k} \tag{40}$$

$$F_{r,A,i}=\sum_l\left[E_l\right]_T\big/K_{A,il} \tag{41}$$

$$F_{r,B,j}=\sum_l\left[E_l\right]_T\big/K_{B,jl} \tag{42}$$

$$G_{A,ik}=F_{c,A,k}+F_{r,A,i} \tag{43}$$

$$G_{B,jk}=F_{c,B,k}+F_{r,B,j} \tag{44}$$

$$G_{AB,ijk}=G_{A,ik}+G_{B,jk} \tag{45}$$

For equation (37), one can verify that if $F_{c,B,k}$ (or $F_{c,A,k}$) goes to very large values, SUPECA kinetics is reduced to ECA kinetics (equation (33)). Therefore, SUPECA kinetics as formulated in equation (37) are an extension of SU and ECA kinetics, and SUPECA is applicable for consistent scaling of substrate-consumer networks involving both single-substrate reactions and redox-reactions (a visual demonstration of SUPECA kinetics is in Figure 2).

4. Numerical accuracy of SUPECA kinetics

Following Tang and Riley (2013a), we assume that the EC formulation is a good approximation to the law of mass action and use it to evaluate the numerical accuracy of SUPECA kinetics. Because of numerical complexity, we restricted the comparison to the AB-E problem as formulated by equations (11)-(16) with the assumption of $k_A^- = k_B^- = 0$ and included a substrate sorbent to mimic a class of biogeochemistry problems in soil, such as aerobic soil ammonium nitrification and aerobic soil organic carbon decomposition (formulated in appendix F; a graphic representation is available in supplemental material).

We evaluated the numerical accuracy of SUPECA (equation (37)) and SU (equation (26)) over a wide range of parameter values. We fixed both substrates at a nominal value of 40 mol m^{-3}, and k_2^+, the maximum substrate processing rate at 48 s^{-1}. Then we sampled the affinity parameters exponentially over the range $\left[0,1000\right]$ mol m^{-3}

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and the microbe and sorbent concentrations uniformly over the range $\left[0,1000\right]$ mol m^{-3}. Using a total of 1000 sets of randomly paired parameters, we compared how close SUPECA and SU approximations are to the EC solution in terms of root mean square error (RMSE) and goodness of linear fit. Because SU kinetics do not allow a direct integration of the Langmuir adsorption into the calculation of microbe-substrate complexes, we followed Resat et al. (2011) and first solved the Langmuir isotherm to obtain the free substrate concentrations and then entered these free substrate concentrations into SU to obtain the microbe-substrate complex. This artificial ordering in calculation (as needed by the SU approach) suggests that the SU implementation may lead to significant numerical errors (similar numerical difficulties are associated with the popular MM kinetics (Resat et al., 2011; Tang and Riley, 2013a)).

Our comparison (Figure 3 and Figure 4) indicates that SUPECA kinetics are superior to SU kinetics in computing the microbe-substrate complex in the presence of substrate binding competition between microbes and sorbent. SUPECA predictions are more accurate than SU predictions in terms of goodness of linear fitting and RMSE (for which the linear regressions are shown as black solid lines in the Figure 3). In magnitude, the RMSEs of SUPECA predictions are less than 10% of that of SU predictions (and also note that the y-axis ranges for SU predictions are 20 times of those for SUPECA predictions). The slope of linear fitting from SUPECA predictions is also much closer to the ideal value 1.0, whereas that from SU predictions is far greater than 1.0, suggesting that SU kinetics significantly overestimate microbe-substrate complexes under a wide range of conditions. When the model predictions are evaluated as a function of the relative abundances of consumers and substrates (Figure 4), SU overestimates are found

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under high ratios of consumer abundances with respect to substrates (Figure 4a, c). In contrast, SUPECA predictions agree well with EC predictions over the whole range of relative abundances (Figure 4b, d). This very large overestimation by SU calculations is explained by the linear dependence of the consumer-substrate complexes on microbial abundances in deriving SU kinetics (equation (26)). Therefore, combined with the better numerical performance of ECA (Tang and Riley, 2013a; Tang, 2015) than MM kinetics, we contend that SUPECA kinetics are numerically more convenient and more accurate than SU kinetics in calculating the microbe-substrate complexes for situations involving microbes, enzymes, substrates, and soil minerals (e.g., Tang and Riley, 2015). In particular, because nutrient limitations tend to occur under high relative consumer abundances with respect to their substrates, the larger prediction bias of SU than SUPECA suggests that SUPECA should be preferred for soil biogeochemical modeling. However, for applications to real problems, the validity of SUPECA kinetics depends on the EC formulation and the tQSSA, and there are situations where even the EC formulation might fail (e.g., Maggi and Riley, 2009; Pedersen et al., 2008).

5. Example application to modeling aerobic heterotrophic respiration

As a proof-of-concept example, we applied SUPECA kinetics to predict the moisture stress on aerobic soil respiration. We note that we are not suggesting that SUPECA kinetics replace existing soil BGC models, but rather that mechanistic analysis using a SUPECA-based model can inform process understanding and thereby improve such models. Following the CENTURY-like models' approach in modeling topsoil soil carbon dynamics (Coleman and Jenkinson, 1999; Parton and Rasmussen, 1994) and the set up of Franzluebbers' (1999) soil incubation experiments (from which the data were

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used for our model evaluation), this example (Appendix G) considers a homogenous 10 cm thick topsoil with 2.0 mol C m^{-3} microbes and 3.0 mol C m^{-3} DOC (i.e., dissolvable organic carbon; different DOC values affected our results negligibly as long as they were larger than 0.5 mol C m^{-3}). We conceptualize transport of substrates (i.e., oxygen and DOC) in soil as a two-stage diffusion process (e.g., Grant, 1991) with the first stage from the bulk soil matrix to the water film covering the microbial microsites and the second stage from the water film to the microbial transporters where substrates are processed. The diffusion processes in soil are calculated based on soil moisture status and the hydraulic properties of a hypothesized soil with a texture of 40% clay and 30% sand. The pedotransfer functions used for calculating soil hydraulic properties are from CLM4.5 (Oleson et al., 2013).

Our approach assumes that the inter-microsite (or aggregates) transport dominates intra-aggregate transport, consistent with pore scale simulations (Yang et al., 2014). The model is solved to steady state by assuming that the microbes, atmospheric oxygen, and DOC are in balance under the influence of Langmuir type DOC sorption by soil minerals. Calculations are conducted for three levels of soil minerals (with adsorption capacities at 0, 90, and 180 mol C m^{-3}) and two levels of microbial oxygen affinity (with default $K_{O2,w}=3\times10^{-5}$ mol m^{-3} and elevated $K_{O2,w}=3\times10^{-3}$ mol m^{-3}; Figure 5 and Figure 6).

The calculation with elevated $K_{O2,w}$ (compared to the default $K_{O2,w}$) indicates the effect of soil aggregates on moisture control of decomposition (see also Appendix G). We evaluated: (1) how close our predicted moisture response function is to incubation data from Franzluebbers (1999) and (2) how soil mineral DOC adsorption would affect the

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soil moisture response function. We also tested a widely used response function approach (e.g., Sierra et al., 2015) for comparison.

When the respiration curves are normalized, we found that all curves have the same pattern that soil respiration first increases from dry soil with increasing moisture and then levels off after reaching a peak value (where the respiration is co-limited by oxygen and DOC bioavailability). The curve with the highest mineral soil carbon adsorption capacity (180 mol C m^{-3}) and elevated $K_{O2,w}$ value best approximates the incubation data from Franzluebbers (1999). As the sorption capacity becomes smaller, the moisture response function becomes sharper.

When the oxygen affinity parameter is reduced to its default value (while keeping the adsorption capacity at 180 mol C m^{-3}; see explanation in Appendix G), the soil moisture response function becomes the sharpest with the highest threshold moisture where the respiration peaks (see green line in Figure 5). Unlike Kausch and Pallud (2013) and Yang et al. (2014), we have not explicitly simulated the oxygen distribution inside the aggregates. Since the apparent oxygen affinity parameter (which we use here) generally increases with aggregate size (Griffin, 1968), the poorer agreement between data and predictions using the default oxygen affinity parameter indicates that soil aggregates may play an important role in controlling microbes' response to soil moisture stress. Indeed, Franzluebbers (1999) indicated in his Figure 1 that there are many aggregates in his incubated soil. Moreover, the higher moisture threshold (where respiration peaks) with the default apparent oxygen affinity parameter is consistent with measurements that aggregates may facilitate anaerobic processes under well-ventilated

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conditions (by increasing the range of soil moisture conditions where oxygen limits aerobic processes; Renault and Stengel, 1994; Keiluweit et al., 2016).

When the moisture response function is evaluated, we found a higher R^2 (0.84) than those predicted from SUPECA based methods, which (from top to bottom as in the legends) are 0.82, 0.81, 0.77 and 0.71 for the blue, red, black and green lines respectively. However, the response function approach overestimated the observed aerobic soil respiration rate at high soil moisture contents. This example illustrates that a higher overall R^2 from the empirical response function can mask an important feature of soil respiration's dependence on soil moisture.

Higher adsorption capacity resulted in significantly lower soil respiration (Figure 6), consistent with results for temperature sensitivity described in Tang and Riley (2015). Combining results from Figure 5 and Figure 6, we conclude that because the soil moisture response function emerges from interactions between biotic and abiotic factors that co-regulate soil organic carbon decomposition (Manzoni et al., 2016), its functional shape is not deterministic. This result contradicts the popular approach used in many soil BGC models (including our own, e.g., Koven et al., 2013; Tang et al., 2013; and others, e.g., Sierra et al., 2015), where a deterministic soil moisture response function is applied to the moisture-unstressed decomposition rate. We also note that there are many different functional forms for the soil moisture response function used in soil BGC models (Sierra et al. 2015).

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At the default oxygen affinity value (3×10^{-5} mol O_2 m^{-3}), the derived soil moisture response function is essentially insensitive to mineral soil carbon adsorption capacity (not shown). Since the oxygen affinity parameter reflects the impacts of aggregates, these results demonstrate how soil aggregates may influence soil carbon decomposition rates, an insight that cannot be obtained by fitting response functions to a single dataset.

6. Potential applications of SUPECA kinetics for trait-based biogeochemical modeling

Besides the example application above, SUPECA kinetics could be a powerful tool for trait-based modeling in various biogeochemical systems (e.g., Follows et al., 2007; Bouskill et al., 2012; Litchman and Klausmeier, 2008; Merico et al., 2009). As we show above and below, SUPECA kinetics will enable more robust predictions with better numerical consistency and smaller parametric sensitivities than the popular family of Monod kinetics, and SUPECA will be applicable for any biogeochemical system that involves substrate-consumer binding and binding competition (of the AB-E or A-E type).

The assertion of smaller parametric sensitivity as predicted by SUPECA (than by Monod kinetics) can be verified using the single-substrate reaction network as an example. In this case, SUPECA is reduced to ECA kinetics, and for some substrate S_i in the reaction network, ECA kinetics predict the sensitivity of its consumption by consumer $\left[E_j\right]$ with respect to the maximum processing rate $k_{2,ij}^{+}$ as

$$\left|\frac{\partial}{\partial k_{2,ij}^{+}}\left(\frac{d\left[S_i\right]_{T,j}}{dt}\right)\right| = \underbrace{\frac{\left[E_j\right]_T F_{c,j}^{\{i\}}}{1+F_{r,i}+F_{c,j}}}_{\text{ECA}} < \underbrace{\frac{\left[E_j\right]_T F_{c,j}^{\{i\}}}{1+F_{c,j}}}_{\text{Competitive Monod}} < \underbrace{\frac{\left[E_j\right]_T F_{c,j}^{\{i\}}}{1+F_{c,j}^{\{i\}}}}_{\text{Monod}} \quad (46)$$

where the term after the first "<" is prediction by competitive Monod kinetics and that after the second "<" is by Monod kinetics, suggesting that models using Monod kinetics for substrate competition are more sensitive to parameters and therefore more difficult to calibrate (e.g., Tang and Riley, 2013a).

To quantitatively evaluate our assertion that SUPECA kinetics predict lower parametric sensitivity, we applied equation (46) to 100 competing substrate fluxes of equal magnitude. We then have $F_{c,j} = 100F_{c,j}^{\{i\}}$. Meanwhile, if $F_{c,j}^{\{i\}} > 1$, then the sensitivity predicted by competitive Monod kinetics is less than 1% of that by Monod kinetics. Further, if the competing efforts from all agents is comparable to the overall substrate fluxes, i.e., $F_{r,i} \approx F_{c,j}$, then the parametric sensitivity predicted by ECA is about 50% of that by competitive Monod kinetics. Therefore, ECA (and by extension, SUPECA) prediction is much less sensitive with respect to $k_{2,ij}^{+}$ than that by competitive Monod kinetics and Monod kinetics. Moreover, with equations (30) and (37), one can verify that the more substrates and consumers represented in the system, the smaller the resulting sensitivity predicted by ECA (and SUPECA) kinetics for each $k_{2,ij}^{+}$. One can also verify lower SUPECA uncertainty for other parameters, including substrates and consumer abundances. That including more substrates and consumers will lead to more robust

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model predictions is a premise underlying trait-based modeling (e.g., Follows et al., 2007; Bouskill et al., 2012), and SUPECA kinetics explicitly integrates this presumption in its formulation.

The assertion of wide applicability with SUPECA kinetics has been demonstrated by a number of successful applications that we have published with ECA kinetics. In a series of studies (Zhu and Riley, 2015; Zhu et al., 2016a, 2016b, 2017), we showed that ECA kinetics significantly improved the modeling of nutrient competition between plants, microbes, and mineral soils. In Tang and Riley (2013a), where ECA kinetics was first proposed, lignin decomposition dynamics were accurately captured without *a priori* imposing a target lignocellulose index. In Tang and Riley (2013a, 2015) and this study, ECA kinetics were able to seamlessly incorporate Langmuir type substrate adsorption without invoking an ad hoc numerical order that is prerequisite to MM (or Monod) kinetics for modeling mineral, microbe, and substrate interactions.

Finally, we expect SUPECA kinetics will provide a robust approach to resolve the redox ladder in soil biogeochemistry. Existing approaches have imposed the redox ladder following some specific order, e.g., $O_2\left(H_2O\right)$, $NO_3^-\left(N_2\right)$, $MnO_2\left(Mn^{2+}\right)$, $Fe\left(OH\right)_3\left(Fe^{2+}\right)$, $SO_4^{2-}\left(H_2S\right)$, $CO_2\left(CH_4\right)$, and $H_2O\left(H_2\right)$ (e.g., Grant, 2001). In contrast, SUPECA kinetics will allow all these redox-couples to operate concurrently (in any space-time-process unit), a situation that is more consistent with natural soils. Such a feature will also allow microbial biogeochemistry models (most of which are considered to be valid at pore scale) to be valid at the scale of well-mixed bulk soils (~cm^3).

7. Conclusions

In this study, we showed that the popular Monod family kinetics and synthesizing unit (SU) kinetics are not scaling consistent for a reaction network involving mixed $A\overset{E}{\rightarrow}products$ type and $A+B\overset{E}{\rightarrow}products$ type reactions. SUPECA kinetics, by accounting for mass balance constraints of substrates and consumers, is able to represent an arbitrary number of substrates and consumers without changing mathematical formulation. Our numerical tests indicate that SUPECA kinetics is superior to SU kinetics both in numerical accuracy and numerical robustness, particularly under high relative abundances of consumers with respect to substrates (a typical feature in plant-microbial competition for limited soil nutrients; Schimel and Bennett, 2004; Vitousek et al., 2010). SUPECA kinetics were also able to predict the moisture response function of aerobic soil respiration, providing mechanistic insights not available from the response function approach. Finally, because SUPECA kinetics represents measurable microbial traits and the mechanisms by which they affect soil biogeochemical dynamics, we conclude that this approach can benefit interpretation of observed dynamics and thereby improve soil BGC models.

8. Code and data availability

The source code and data used in this manuscript are available upon request to the corresponding author.

Appendix A: Deriving the governing equations

The law of mass action formulation of the redox reaction (8) is

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$$\frac{d\left[EA\right]}{dt}=k_A^+\left[E\right]\left[A\right]+k_B^-\left[EAB\right]-\left(k_A^-+k_B^+\left[B\right]\right)\left[EA\right] \tag{A1}$$

$$\frac{d\left[EB\right]}{dt}=k_B^+\left[E\right]\left[B\right]+k_A^-\left[EAB\right]-\left(k_B^-+k_A^+\left[A\right]\right)\left[EB\right] \tag{A2}$$

$$\frac{d\left[EAB\right]}{dt}=k_A^+\left[EB\right]\left[A\right]+k_B^+\left[EA\right]\left[B\right]-\left(k_A^-+k_B^-+k_2^+\right)\left[EAB\right] \tag{A3}$$

$$\frac{d\left[P\right]}{dt}=k_2^+\left[EAB\right] \tag{A4}$$

$$\frac{d\left[A\right]}{dt}=-k_A^+\left(\left[E\right]+\left[EB\right]\right)\left[A\right]+k_A^-\left(\left[EA\right]+\left[EAB\right]\right) \tag{A5}$$

$$\frac{d\left[B\right]}{dt}=-k_B^+\left(\left[E\right]+\left[EA\right]\right)\left[B\right]+k_B^-\left(\left[EB\right]+\left[EAB\right]\right) \tag{A6}$$

We now apply the total quasi-steady-state approximation (e.g., Borghans et al., 1996) to obtain the Equilibrium Chemistry formulation of the system. Specifically, we obtain equations (11)-(13) by respectively setting the time derivatives of equations (A1)-(A3) to zero. Equation (9) is obtained by adding together equations (A1), (A3) and (A5), and using the definition of $\left[A\right]_T$ by equation (14). Equation (10) is obtained by adding together equations (A2), (A3) and (A6) with the definition of $\left[B\right]_T$ by equation (15).

Appendix B: Deriving the dual Monod kinetics in equation (21)

Replacing $\left[EA\right]$ in equation (17) with that obtained from equation (19), we obtain

$$\left[EAB\right]=\frac{\left[A\right]}{K_A}\frac{\left[B\right]}{K_B}\left[E\right] \tag{B-1}$$

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By solving $[EA]$ from equation (19), $[EB]$ from equation (20) and combining these with equation (B-1) into equation (16), we find

$$[E]_T=\left(1+\frac{[A]}{K_A}\right)\left(1+\frac{[B]}{K_B}\right)[E] \tag{B-2}$$

Now solve $[E]$ from (B-2) and enter the result into equation (B-1), we then get

$$[EAB]=\left(\frac{[A]}{K_A+[A]}\right)\left(\frac{[B]}{K_A+[B]}\right)[E]_T \tag{B-3}$$

We thence obtain dual Monod kinetics by entering equation (B-3) into equation (9).

Appendix C: Deriving the synthesizing unit kinetics in equation (26)

Since SU kinetics assumes that substrates are not limiting the biogeochemical reaction, we then, from equations (23) and (24), obtain

$$[EA]=\frac{k_A^+[A]}{k_B^+[B]}[E] \tag{C-1}$$

$$[EB]=\frac{k_B^+[B]}{k_A^+[A]}[E] \tag{C-2}$$

By entering equations (C-1) and (C-2) into equation (13), and solving for $[EAB]$, we find

$$[EAB]=\frac{[E]}{k_2^++k_A^-+k_B^-}\left(k_A^+[A]+k_B^+[B]\right)=\frac{[E]}{\tilde{k}_2^+}\left(k_A^+[A]+k_B^+[B]\right) \tag{C-3}$$

Now if we combine equations (C-1)-(C-3) with equation (16), we get

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$$\begin{aligned}[E] &= \frac{[E]_T}{1+\frac{k_A^+[A]}{k_B^+[B]}+\frac{k_B^+[B]}{k_A^+[A]}+\frac{k_A^+[A]+k_B^+[B]}{\tilde{k}_2^+}} \\ &= \frac{[E]_T}{\frac{\left(k_A^+[A]+k_B^+[B]\right)^2}{\left(k_A^+[A]\right)\left(k_B^+[B]\right)}+\frac{k_A^+[A]+k_B^+[B]}{\tilde{k}_2^+}-1}\end{aligned} \qquad \text{(C-4)}$$

which, when combined with equation (C-3), leads to

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$$\begin{aligned}[EAB] &= \frac{k_A^+[A]+k_B^+[B]}{\tilde{k}_2^+}\frac{[E]_T}{\frac{\left(k_A^+[A]+k_B^+[B]\right)^2}{\left(k_A^+[A]\right)\left(k_B^+[B]\right)}+\frac{k_A^+[A]+k_B^+[B]}{\tilde{k}_2^+}-1} \\ &= \frac{[E]_T/\tilde{k}_2^+}{\frac{1}{\tilde{k}_2^+}+\frac{k_A^+[A]+k_B^+[B]}{\left(k_A^+[A]\right)\left(k_B^+[B]\right)}-\frac{1}{k_A^+[A]+k_B^+[B]}} \\ &= \frac{[E]_T/\tilde{k}_2^+}{\frac{1}{\tilde{k}_2^+}+\frac{1}{k_A^+[A]}+\frac{1}{k_B^+[B]}-\frac{1}{k_A^+[A]+k_B^+[B]}}\end{aligned} \qquad \text{(C-5)}$$

When $[EAB]$ from equation of (C-5) is entered into equation (9), we then obtain equation (26).

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Appendix D: Deriving SUPECA kinetics equation (28)

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We first derive the set of linear equations using the first order closure approach (i.e., the perturbation method truncated to first order accuracy; Shankar, 1994; Tang et al., 2007). By entering equations (14)-(16) into equation (23), we have

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$$k_B^+[EA]\left([B]_T-[EB]-[EAB]\right)=k_A^+\left([A]_T-[EA]-[EAB]\right)\times\left([E]_T-[EA]-[EB]-[EAB]\right) \tag{D-1}$$

Now if we expand equation (D-1), and keep only the 0th and 1st order terms of $[EA]$, $[EB]$ and $[EAB]$, we obtain

$$k_B^+[B]_T[EA]=k_A^+[E]_T\left([A]_T-[EA]-[EAB]\right)-k_A^+[A]_T\left([EA]+[EB]+[EAB]\right) \tag{D-2}$$

which after some rearrangement becomes

$$\left(k_A^+[A]_T+k_A^+[E]_T+k_B^+[B]_T\right)[EA]+k_A^+[A]_T[EB]+k_A^+\left([A]_T+[E]_T\right)[EAB]=k_A^+[A]_T[E]_T \tag{D-3}$$

Using the definitions of $f_A=k_A^+[A]_T$, $f_B=k_B^+[B]_T$ and $\bar{f}_A=f_A+k_A^+[E]_T$, we may rewrite equation (D-3) as

$$\left(\bar{f}_A+f_B\right)[EA]+f_A[EB]+\bar{f}_A[EAB]=f_A[E]_T \tag{D-4}$$

Because substrates A and B are symmetric in forming the consumer substrate complexes, a similar linear equation can be derived by switching A and B in equation (D-4) (or by repeating procedures to the derivation of equation (D-4) but using equations (14)-(16) and (24))

$$f_B[EA]+\left(f_A+\bar{f}_B\right)[EB]+\bar{f}_B[EAB]=f_B[E]_T \tag{D-5}$$

Now substitute equations (14)-(16), (23) and (24) into equation (25) and assume $\tilde{k}_2^+\approx k_2^+$ (i.e., unbinding is much smaller compared to the product genesis rate), we have

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$$\begin{aligned}&\left\{k_A^+\left([A]_T-[EA]-[EAB]\right)+k_B^+\left([B]_T-[EB]-[EAB]\right)\right\}\\&\times\left([E]_T-[EA]-[EB]-[EAB]\right)=k_2^+[EAB]\end{aligned} \tag{D-6}$$

Once again, by dropping the second and higher order terms of the consumer-substrate complexes, equation (D-6) can be reduced to

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$$\begin{aligned}&\left(k_A^+[A]_T+k_B^+[B]_T\right)[E]_T=\left(k_A^+[A]_T+k_B^+[B]_T\right)\\&\times\left([EA]+[EB]+[EAB]\right)+k_A^+[E]_T\left([EA]+[EAB]\right)\\&+k_B^+[E]_T\left([EB]+[EAB]\right)+k_2^+[EAB]\end{aligned} \tag{D-7}$$

which by aid of $f_A=k_A^+[A]_T$, $f_B=k_B^+[B]_T$, $\overline{f}_A=f_A+k_A^+[E]_T$, $\overline{f}_B=f_B+k_B^+[E]_T$, $f_{AB}=f_A+f_B$, and $\overline{f}_{AB}=\overline{f}_A+\overline{f}_B$ becomes

$$\left(\overline{f}_A+f_B\right)[EA]+\left(f_A+\overline{f}_B\right)[EB]+\left(k_2^++\overline{f}_{AB}\right)[EAB]=f_{AB}[E]_T \tag{D-8}$$

Now we solve for $[EAB]$ from the set of linear equations (D-4), (D-5) and (D-8) using Cramer's rule (e.g., Habgood and Arel, 2012), and find the denominator as

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$$\det\left(M_d\right)=\begin{vmatrix}\overline{f}_A+f_B & f_A & \overline{f}_A\\ f_B & f_A+\overline{f}_B & \overline{f}_B\\ \overline{f}_A+f_B & f_A+\overline{f}_B & k_2^++\overline{f}_{AB}\end{vmatrix} \tag{D-9}$$

and the numerator as

$$\det\left(M_n\right)=[E]_T\begin{vmatrix}\overline{f}_A+f_B & f_A & f_A\\ f_B & f_A+\overline{f}_B & f_B\\ \overline{f}_A+f_B & f_A+\overline{f}_B & f_{AB}\end{vmatrix} \tag{D-10}$$

Equations (D-9) and (D-10) together lead to

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\begin{aligned}
\left[EAB\right]&=\frac{\det\left(M_n\right)}{\det\left(M_d\right)}=\frac{f_A f_B \overline{f}_{AB}\left[E\right]_T}{k_2^+\left(f_A\overline{f}_A+f_B\overline{f}_B+\overline{f}_A\overline{f}_B\right)+\overline{f}_A\overline{f}_B f_{AB}}\\
&=\frac{f_A f_B \overline{f}_{AB}\left[E\right]_T}{k_2^+\left(f_{AB}\overline{f}_{AB}-f_A\overline{f}_B-\overline{f}_A f_B+\overline{f}_A\overline{f}_B\right)+\overline{f}_A\overline{f}_B f_{AB}}\\
&=\frac{\left[E\right]_T}{k_2^+\left(\dfrac{f_{AB}}{f_A f_B}-\dfrac{f_A\overline{f}_B+\overline{f}_A f_B-\overline{f}_A\overline{f}_B}{f_A f_B\overline{f}_{AB}}\right)+\dfrac{\overline{f}_A\overline{f}_B f_{AB}}{f_A f_B\overline{f}_{AB}}}\\
&=\frac{\left[E\right]_T\big/k_2^+}{\dfrac{1}{k_2^+}\dfrac{\overline{f}_A\overline{f}_B f_{AB}}{f_A f_B\overline{f}_{AB}}+\left(\dfrac{1}{f_A}+\dfrac{1}{f_B}-\dfrac{f_A\overline{f}_B+\overline{f}_A f_B-\overline{f}_A\overline{f}_B}{f_A f_B\overline{f}_{AB}}\right)}
\end{aligned}
\qquad \text{(D-11)}
$$

which, when entered into equation (9), leads to equation (28).

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Appendix E: Deriving SUPECA for a network of substrates and consumers

In the second equation of equations (33), we show that the consumption of a certain substrate as represented in ECA kinetics is determined by the consumer reaction potential $k_{2,ij}^+\left[E_j\right]_T$ multiplied with the relative contribution of the specific consumption pathway with respect to all competing pathways ($F_{c,j}^{\{r\}}\big/\left(1+F_{r,j}+F_{c,j}\right)$). Since SUPECA kinetics is a compatible extension of ECA kinetics, SUPECA kinetics should have its numerator indicating the potential reaction rate of the specific pathway, and its denominator indicating the efforts of all interacting pathways. Bearing this partition equivalence in mind, therefore, we assert that $\overline{f}_A\big/k_2^+$ in equation (29) should be equivalent to $F_{r,i}+F_{c,j}$ in equation (33). This assertion then leads to equations (38), (41) and (43) for A substrates. Similarly, equations (39), (42) and (44) are for B substrates. With the definitions of $f_A\big/k_2^+$, $f_B\big/k_2^+$, $\overline{f}_A\big/k_2^+$ and $\overline{f}_B\big/k_2^+$, using the partition

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equivalence, we can easily define the network form of f_{AB} in equation (40), and the network form of $\overline{f}_{AB}$ in equation (45). Further, we observe that the denominator of the last equation in equation (28) could be rewritten as

$$\frac{\left(\overline{f}_A/k_2^+\right)\left(\overline{f}_B/k_2^+\right)\left(f_{AB}/k_2^+\right)}{\left(\overline{f}_{AB}/k_2^+\right)}+\left(f_{AB}/k_2^+\right)-\frac{\left(f_A/k_2^+\right)\left(\overline{f}_B/k_2^+\right)+\left(\overline{f}_A/k_2^+\right)\left(f_B/k_2^+\right)-\left(\overline{f}_A/k_2^+\right)\left(\overline{f}_B/k_2^+\right)}{\left(\overline{f}_{AB}/k_2^+\right)}$$

which, after replacing f_A/k_2^+, f_B/k_2^+, $\overline{f}_A/k_2^+$, $\overline{f}_B/k_2^+$, f_{AB}/k_2^+ and $\overline{f}_{AB}/k_2^+$ with their corresponding network forms (i.e. equations (38)-(45)), leads to SUPECA kinetics equation (37).

Appendix F: Formulation of the kinetics-benchmarking problem

Following equations (23)-(25), the Equilibrium Chemistry (EC) problem used to benchmark synthesizing unit (SU) and SUPECA predictions is defined as

$$k_{BS1}\left[B\right]\left[S_1\right]=k_{BS2}\left[S_2\right]\left[BS_1\right] \tag{F-1}$$

$$k_{BS2}\left[B\right]\left[S_2\right]=k_{BS1}\left[S_1\right]\left[BS_2\right] \tag{F-2}$$

$$k_{BS1}\left[BS_2\right]\left[S_1\right]+k_{BS2}\left[BS_1\right]\left[S_2\right]=k_2^+\left[BS_1S_2\right] \tag{F-3}$$

$$K_{MS1}\left[MS_1\right]=\left[M\right]\left[S_1\right] \tag{F-4}$$

which are subject to the constraints

$$\left[S_1\right]_T=\left[S_1\right]+\left[MS_1\right]+\left[BS_1\right]+\left[BS_1S_2\right] \tag{F-5}$$

$$\left[S_2\right]_T=\left[S_2\right]+\left[BS_2\right]+\left[BS_1S_2\right] \tag{F-6}$$

$$\left[B\right]_T=\left[B\right]+\left[BS_1\right]+\left[BS_2\right]+\left[BS_1S_2\right] \tag{F-7}$$

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$$\left[M\right]_T = \left[M\right] + \left[MS_1\right] \tag{F-8}$$

To relate these equations to a dynamic system, S_1 and S_2 are substrates, B is microbial population, and M is some sorbent that can reversibly adsorb substrate S_1. The corresponding graphic representation of the problem is available in the supplemental material.

For benchmarking, $\left[BS_1S_2\right]$ is solved from equations (F-1)-(F-8) using a fixed-point iteration algorithm (see supplemental materials) for each set of parameters. Unlike the Newton-Raphson iteration, the fixed-point iteration ensures positive mass of all variables, and mass balance relationships from (F-5)-(F-8) are automatically satisfied by the numerical solution.

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Appendix G: Derivation of relevant kinetic parameters for the steady state aerobic respiration problem

The aerobic respiration problem is formulated as

$$\frac{d\left[\mathrm{O}_2\right]_{g,s}}{dt} = \frac{\left(\left[\mathrm{O}_2\right]_a - \left[\mathrm{O}_2\right]_{g,s}\right)}{\left(R_a + R_s\right)Z} - F\left(B,\left[\mathrm{O}_2\right]_{g,s},S,M\right) \tag{G-1}$$

where $\left[O_2\right]_{g,s}$ is gaseous oxygen concentration in bulk soil. $\left[O_2\right]_a$ is atmospheric oxygen concentration (set to 8.45 mol m^{-3}), S is dissolvable organic carbon (DOC) concentration (set to 3 mol m^{-3}; we note that SUPECA is able to accommodate more specific carbon compounds (like in Riley et al (2014)), yet our recent analysis (Dwivedi et al., 2017) suggests that a lumped DOC is sufficient for simple applications like the one we present here), and M is soil mineral sorbent concentration (with variable values). All concentrations are defined with units (mol m^{-3}). R_a is aerodynamic resistance, which is set to 50 s m^{-1}. R_s is soil resistance (s m^{-1}) calculated using the approach in Tang and Riley (2013b). Z is soil depth (set to 10 cm, following the incubation set up of Franzluebbers (1999)). $F\left(B,\left[O_2\right]_{g,s},S,M\right)$ is the oxygen consumption rate calculated using SUPECA kinetics, whose kinetic parameters are derived as following. The steady-state problem is solved by setting the temporal derivative of equation (G-1) to zero, and solved for $\left[O_2\right]_{g,s}$ through iterations. The shape of the flux $F\left(B,\left[O_2\right]_{g,s},S,M\right)$ is then compared to that derived from incubation studies in Franzluebbers (1999).

In this aerobic respiration problem, microbes are assumed to form microsites sitting uniformly inside pores of the bulk soil. O_2 approaches the microsites through both aqueous and gaseous diffusion, and only the aqueous phase is used for microbial respiration. These assumptions lead to the relationship between near cell aqueous O_2 concentration and the diffusive flux:

$$v_m \frac{d\left[\mathrm{O}_2\right]_{w,0}}{dt} = -k_{02,w,1}\left[X\right]\left[\mathrm{O}_2\right]_{w,0} + \kappa_{O2}\left(\left[\mathrm{O}_2\right]_w - \left[\mathrm{O}_2\right]_0\right) \qquad \text{(G-2)}$$

where the conductance κ_{O2} is

$$\left(\frac{\kappa_{O2}}{4\pi}\right)^{-1} = \frac{\delta}{D_{w,02}r_m\left(r_m+\delta\right)} + \frac{1}{D_{02}\left(r_m+\delta\right)} \qquad \text{(G-3)}$$

and r_m is the radius of the microsite (or aggregate), δ is thickness of the water film that covers the microsite (Grant and Rochette, 1994), v_m is the microsite volume (m^3 site^{-1}),

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and $\left[\mathrm{O}_2\right]$ is the aqueous oxygen concentration in the bulk soil matrix. $\left[X\right]$ is the cell density (mol cell site^{-1}). The unit of $k_{02,1}$ is then m^3 (mol cell)$^{-1}$ s^{-1}.

The bulk aqueous diffusivity in equation (G-3) is

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$$D_{02} = \theta D_{02,w} + \frac{\varepsilon}{\alpha_{02}} D_{02,g} \tag{G-4}$$

Now if we assume steady state (aka $d\left[O_2\right]_0 / dt \approx 0$) of equation (G-2), we obtain

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$$\left[\mathrm{O}_2\right]_{w,0} = \frac{\left[\mathrm{O}_2\right]_w}{1+\frac{k_{02,w,1}\left[X\right]}{\kappa_{02}}} \tag{G-5}$$

which leads to the revised affinity parameter:

$$\tilde{K}_{02} = \frac{k_2}{k_{02,w,1}}\left(1+\frac{k_{02,w,1}\left[X\right]_T}{\kappa_{02}}\right) \tag{G-6}$$

where the zero order approximation is made by taking $\left[X\right] \approx \left[X\right]_T$.

Now assume that the ball-like microbe is covered with N disc-like transporters, whose mean radius is r_p. Assuming that the binding is limited by diffusion, then using the chemoreception theory by Berg and Purcell (1977), we have

$$k_{02,w,1} = 4\pi D_{02,w,0} r_c \frac{Nr_p}{Nr_p + \pi r_c} \text{cell}^{-1} \tag{G-7}$$

where the term $Nr_p / \left(Nr_p + \pi r_c\right)$ accounts for the interference between different transporters of a cell. Thus assuming $\left[X\right]_T = m$ cell site^{-1}, we get

$$\tilde{K}_{\mathrm{O2}}=\frac{k_2}{k_{\mathrm{O2},w,1}}\left(1+\frac{k_{\mathrm{O2},1}\left[X\right]_T}{\kappa_{\mathrm{O2}}}\right)=K_{\mathrm{O2,w}}\left(1+\frac{Nr_p}{Nr_p+\pi r_c}\frac{mr_c}{r_m+\delta}\left(\frac{\delta}{r_m}+\frac{D_{\mathrm{O2},w,0}}{D_{O2}}\right)\right) \quad \text{(G-8)}$$

With similar procedure, for DOC we have the following

$$\tilde{K}_{\mathrm{DOC}}=\frac{k_2}{k_{\mathrm{DOC},w,1}}\left(1+\frac{k_{\mathrm{DOC},w,1}\left[X\right]_T}{\kappa_{DOC}}\right)=K_{\mathrm{DOC}}\left(1+\frac{Nr_p}{Nr_p+\pi r_c}\frac{mr_c}{r_m+\delta}\left(\frac{\delta}{r_m}+\frac{D_{DOC,w,0}}{D_{DOC}}\right)\right) \quad \text{(G-9)}$$

and

$$k_{\mathrm{DOC},w,1}=4\pi D_{\mathrm{DOC},w,0}r_c N_A\frac{Nr_p}{Nr_p+\pi r_c}\left(\mathrm{mol}\cdot\mathrm{cell}\right)^{-1} \quad \text{(G-10)}$$

where $N_A=6.02\times10^{23}\mathrm{mol}^{-1}$.

Below we provide some estimates for the parameters to support the above model of moisture dependence of microbial decomposition. The microbial cell radius r_c is on the order of 10^{-6} m, and r_p/r_c is about 10^{-3}. At 25 °C, the aqueous diffusivity of O_2 is about 2.9×10^{-9} m^2 s^{-1}, therefore, assuming $N=3000$ transporters per cell (which covers only 0.3% of the cell's surface area), we have $k_{\mathrm{O2},w,1}=1.0\times10^{10}$ m^3 $\left(\mathrm{mol\ cell}\right)^{-1}\mathrm{s}^{-1}$. Similarly, since the aqueous diffusivity of DOC is about 10^{-9} m^2 s^{-1}, assuming $N=3000$ transporters per cell, we have $k_{\mathrm{DOC},w,1}=3.7\times10^{9}$ m^3 $\left(\mathrm{mol\ cell}\right)^{-1}\mathrm{s}^{-1}$. Suppose the respiration is bottlenecked by a single respiratory enzyme, and since the enzyme activity varies on the order of 10~1000 s^{-1} (English et al., 2006), then by taking $k_2=100N\ \mathrm{s}^{-1}=3\times10^{5}\mathrm{s}^{-1}$ per cell, we have $K_{\mathrm{O2,w}}=3\times10^{-5}$ mol m^{-3}, which agrees well with parameters reported for microbes in aqueous solutions in Button (1985). However, Grant (1991) estimated $K_{\mathrm{O2,w}}=3.0\times10^{-3}$ mol m^{-3}; Borden and Bedient (1986) estimated

$K_{\mathrm{O2,w}} = 3.1\times10^{-3}$ mol m^{-3} for application in soil. We therefore elevated the numerical value to $K_{\mathrm{O2,w}} = 3.0\times10^{-3}$ mol m^{-3}. According to equations (G-7) and (G-8), such elevation could occur either by increasing the maximum substrate processing rate k_2 or decreasing the diffusion $k_{\mathrm{O2},w,1}$ controlled parameter (through the formation of micro-pores in aggregates; e.g., Kausch and Pallud, 2013; Yang et al., 2014). Based on similar magnitude analysis, we obtain $K_{\mathrm{DOC,w}} = 8.1\times10^{-5}\mathrm{mol\ m}^{-3}$, which falls to the lower end of the values reported for many hydrocarbon compounds as reported in Button (1985). We did not elevate the value of $K_{\mathrm{DOC,w}}$ because it could vary over four orders of magnitudes (Button, 1985), and our number leads to a good fit between model predictions and data.

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Taking all these numbers together, we have

$$\begin{aligned}\tilde{K}_{\mathrm{O2,w}} &= K_{\mathrm{O2,w}}\left(1+0.48\times\frac{mr_c}{r_m+\delta}\left(\frac{\delta}{r_m}+\frac{D_{\mathrm{O2,w,0}}}{D_{\mathrm{O2}}}\right)\right)\\ &= 3\times10^{-3}\left(1+0.48\times\frac{mr_c}{r_m+\delta}\left(\frac{\delta}{r_m}+\frac{D_{\mathrm{O2,w,0}}}{D_{\mathrm{O2}}}\right)\right)\end{aligned} \qquad \text{(G-11)}$$

$$\begin{aligned}\tilde{K}_{\mathrm{DOC}} &= K_{\mathrm{DOC}}\left(1+0.48\times\frac{mr_c}{r_m+\delta}\left(\frac{\delta}{r_m}+\frac{D_{\mathrm{DOC,w,0}}}{D_{\mathrm{DOC}}}\right)\right)\\ &= 8.1\times10^{-5}\left(1+0.48\times\frac{mr_c}{r_m+\delta}\left(\frac{\delta}{r_m}+\frac{D_{\mathrm{DOC,w,0}}}{D_{\mathrm{DOC}}}\right)\right)\end{aligned} \qquad \text{(G-12)}$$

Since at 25 °C, the Bunsen solubility coefficient of oxygen is 0.032, we have

$$\tilde{K}_{\mathrm{O2,g}} = \frac{\tilde{K}_{\mathrm{O2},w}}{0.032} = 9.4\times10^{-2}\left(1+0.48\times\frac{mr_c}{r_m+\delta}\left(\frac{\delta}{r_m}+\frac{D_{\mathrm{O2,w,0}}}{D_{\mathrm{O2}}}\right)\right) \qquad \text{(G-13)}$$

The water film thickness is a function of soil water potential (Tokunaga, 2009) and we calculate it using the approach in ECOSYS (Grant, 2001), which is

$$\delta = \max\left(10^{-6}, \exp\left(-13.65 - 0.857\log\left(-\psi\right)\right)\right) \tag{G-14}$$

where the soil matric potential is of unit m, and water film thickness is restricted to at least 1 μm.

For model applications, microbes are often in the unit of mol C m^{-3}. Bratbak and Dundas (1984) reported that the wet biomass density of bacteria is over the range 1.1~1.2 g cm^{-3}, of which about 40% is dry biomass, and about 50% of dry biomass is carbon. Therefore, with the medium cell density 1.15 g cm^{-3}, 1 mol C m^{-3} microbial biomass is about 52.17 cm^{3}, by further taking $r_c = 10^{-6}$ m=10^{-4} cm, the cell number density is 2.1×10^{-11} mol cell m^{-3}. Therefore, for $k_2 = 100$ s^{-1} per porter, given each cell has 3000 transporters, the maximum respiration rate is 6.3×10^{-6} s^{-1} for 1 mol C m^{-3} dry microbial biomass, which was then elevated to 3.8×10^{-4} s^{-1} to obtain a better fitting between data and model prediction. This required elevation in maximum respiration rate indicates that the data as obtained (after 24 days of incubation) in Franzluebbers (1999) are representative of fast growing microbes.

Author Contributions

J.Y. Tang designed the theory and conducted the analysis. J.Y. Tang and W.J. Riley discussed the results and wrote the paper.

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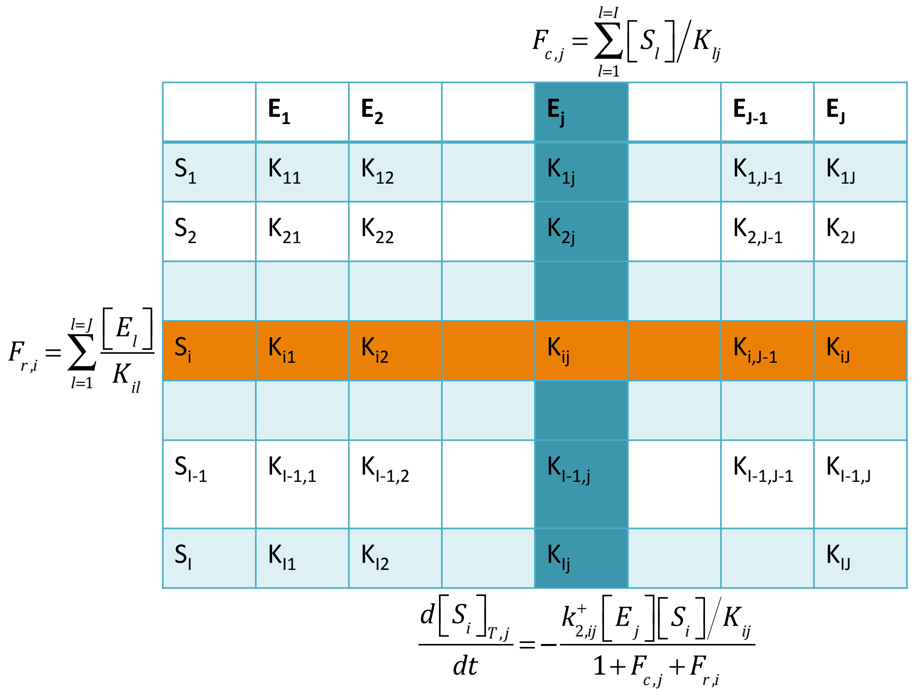

$$F_{c,j}=\sum_{l=1}^{l=I}\left[S_l\right]/K_{lj}$$

	E_1	**E_2**		**E_j**		**E_{J-1}**	**E_J**
S_1	K_{11}	K_{12}		K_{1j}		$K_{1,J-1}$	K_{1J}
S_2	K_{21}	K_{22}		K_{2j}		$K_{2,J-1}$	K_{2J}
S_i	K_{i1}	K_{i2}		K_{ij}		$K_{i,J-1}$	K_{iJ}
S_{I-1}	$K_{I-1,1}$	$K_{I-1,2}$		$K_{I-1,j}$		$K_{I-1,J-1}$	$K_{I-1,J}$
S_I	K_{I1}	K_{I2}		K_{Ij}			K_{IJ}

$$F_{r,i}=\sum_{l=1}^{l=J}\frac{\left[E_l\right]}{K_{il}}$$

$$\frac{d\left[S_i\right]_{T,j}}{dt}=-\frac{k_{2,ij}^{+}\left[E_j\right]\left[S_i\right]/K_{ij}}{1+F_{c,j}+F_{r,i}}$$

Figure 1. Graphical representation of ECA kinetics as derived in Tang and Riley (2013a). The equation below the table shows the uptake of substrate S_i by consumer E_j as a function the normalized substrate flux $F_{c,j}$ and its conjugate flux $F_{r,i}$. Subscript "c" designates column, and "r" designates row. When K_{ij} is very large compared to other entries in the matrix, the interaction between substrate S_i and consumer E_j can be ignored.

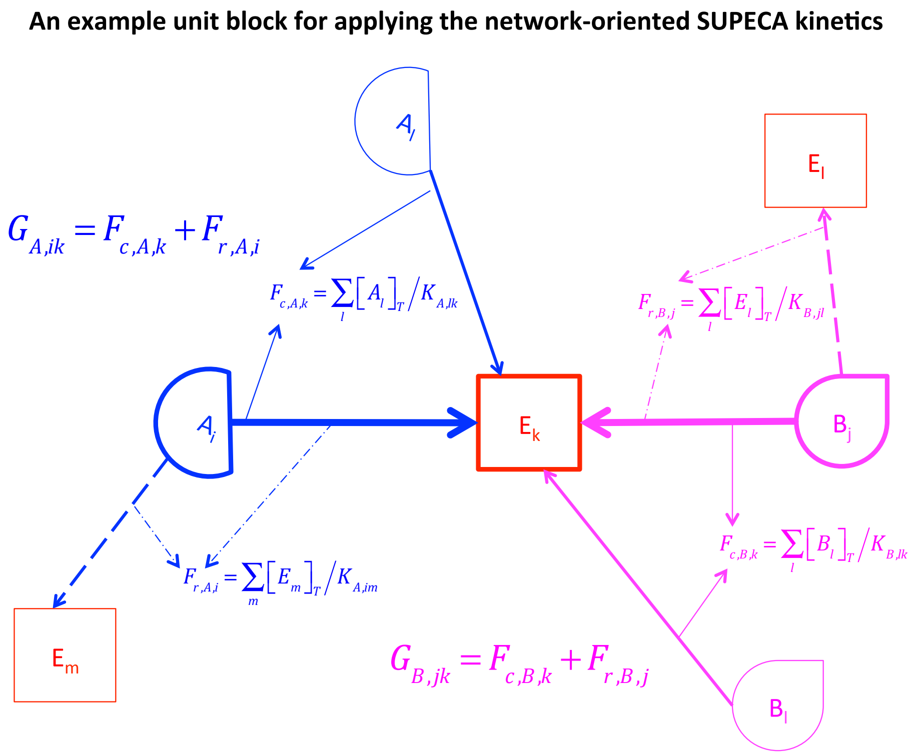

Figure 2. Graphic representation for the relationships between substrates, consumers, and normalized fluxes and their conjugates for a block unit of a large substrate-consumer network.

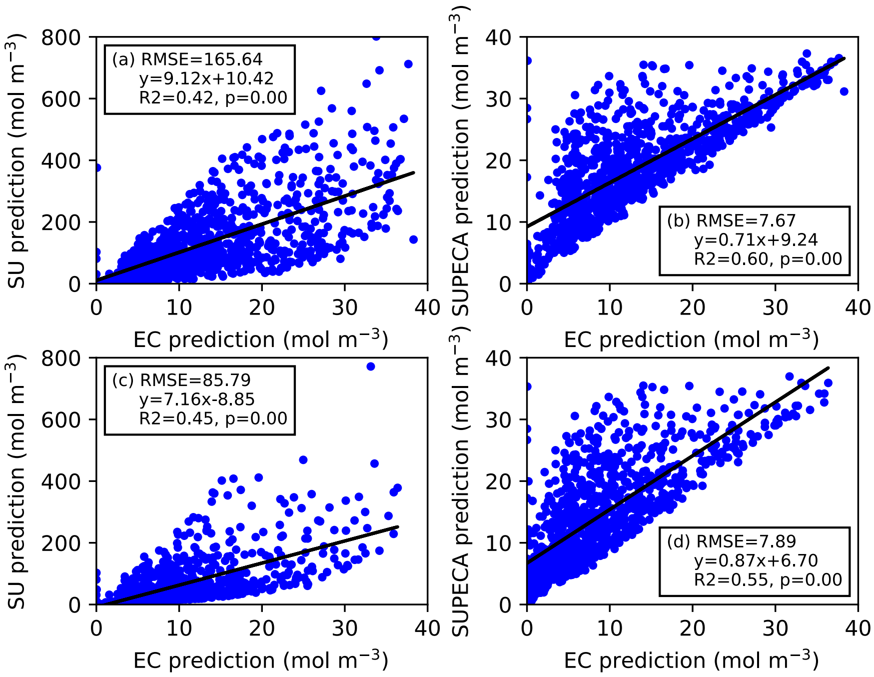

Figure 3. Benchmark of the SU (left column) and SUPECA (right column) predictions against those by the full EC formulation. We note that the y-axes of the left panels are of much larger scale than those on the right. The problem is formulated in Appendix F. Panels (a) and (b) are for the case when $M = 0$; panels (c) and (d) are for uniformly distributed $M > 0$. The black solid lines are the linear regression of SU or SUPECA predictions with respect to the EC solution, whose statistics are shown on the figure. The related distributions of parameters are in Figure S1 of the supplemental material.

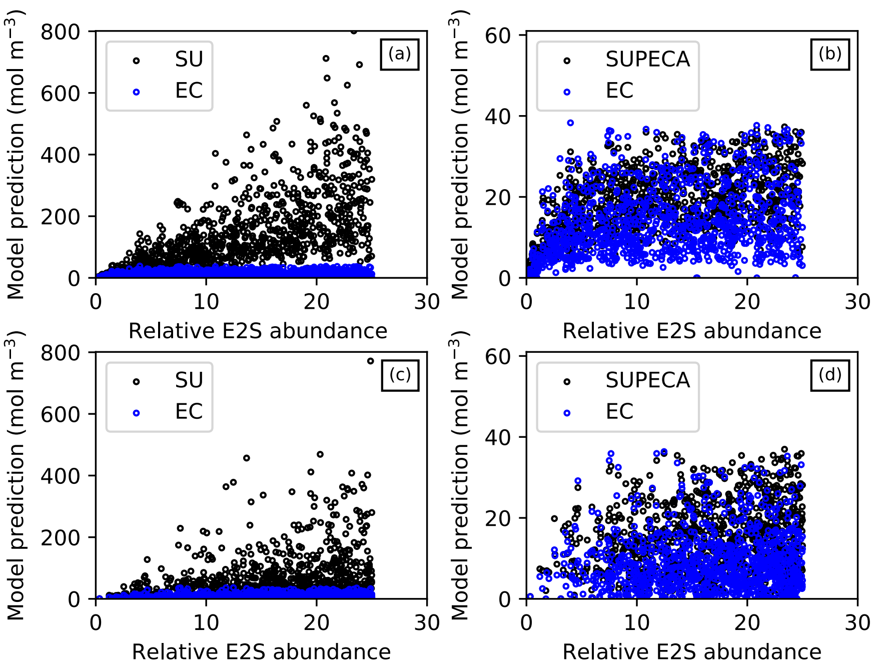

Figure 4. Model predicted consumer-substrate complexes as a function of the relative abundance of consumers with respect to substrates. Corresponding to Figure 3, panels (a) and (b) are for the case when $M = 0$; panels (c) and (d) are for uniformly distributed $M > 0$.

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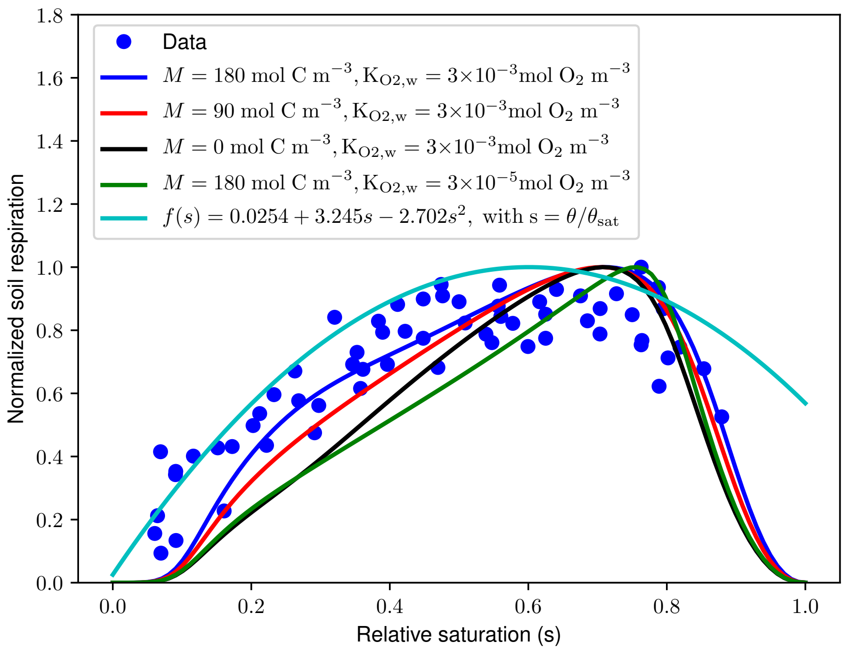

Figure 5. Comparison of predicted normalized soil moisture response functions to that derived from incubation data from Franzluebbers (1999). All response functions are normalized with their respective peak respiration. The R-squared coefficients of determination for the different response function curves from top to bottom are, respectively, 0.82, 0.81, 0.77, 0.71 and 0.84. Note that the curve of $f\left(s\right)$ has been normalized to set its maximum value at 1, making it slightly above the majority of the data points.

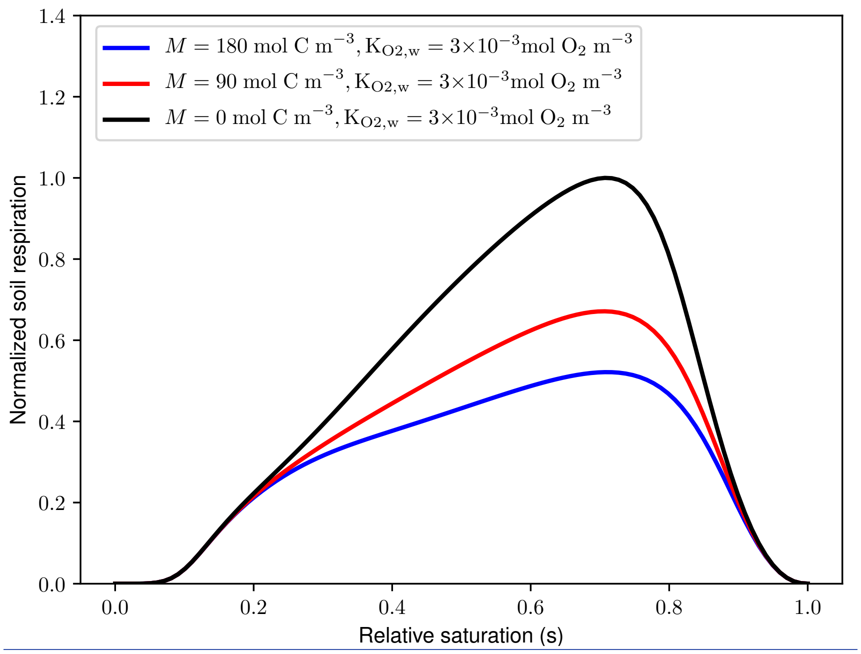

Figure 6. Simulated moisture response functions using elevated affinity parameter for O_2. The respiration data are normalized with the peak value from the case with zero soil minerals (i.e., black line in Figure).