May 18, 2017

Geoscientific Model Development

Dear Editors Jason Williams and Astrid Kerkweg,

We appreciate your editorial handling of our submitted paper “The SUPECA kinetics for scaling redox reactions in networks of mixed substrates and consumers and an example application to aerobic soil respiration”. We gladly accept the constructive criticisms from the 1st anonymous reviewer, which have led to improvements in the manuscript.

However, we found the criticisms from the 2nd reviewer to consist largely of misunderstandings, fundamentally incorrect criticisms, and poorly constructed suggestions for improving the manuscript. We did, however, respond to each point in the attached document. Our experience indicates that it is unlikely that such a reviewer, who rejects a manuscript based on fundamental misunderstanding and mischaracterizations will be able to change his/her mind. We therefore request a third reviewer’s opinion of our manuscript to ensure a fair peer review of our work.

We sincerely appreciate your understanding and patience in handling this situation. Please don’t hesitate to contact us with questions or concerns about our request.

Best regards.

Sincerely

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Response to reviewer 1

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

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

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

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

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

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

Comments: By page 18, I became convinced that the matrix formulation would necessarily include many zeros for kinetic coefficients in a microbial-enzyme-substrate system, which also addresses a point made several times: whereas a superabundance of a substrate would eliminate a particular substrate-consumer interaction term, so would a K=0.
Response: Effectively, when a substrate-consumer interaction term is to be eliminated, K should be a very large number compared to substrate concentrations, for pragmatic calculations. The matrix formulation is a way to visualize the relationships between substrates and consumers, and in application we can easily screen those inactive entries off. We also made this point clear by revising the captions of Figure 2.

Comments: Other hierarchical interactions are ignored. Do the authors imagine other sets of functions and matrices of coefficients that could be used to capture controls exerted by other environmental conditions on these kinetic coefficients, such as pH, stoichiometry, CUE, etc.? This model rapidly becomes unwieldy.
Response: We contend that the SUPECA kinetics proposed here is only one component necessary to build a comprehensive soil biogeochemical model to resolve the variability of CUE, stoichiometry, and other environmental variables. There are models, such as ECOSYS (Grant et al., 2015; 2016), that have made such an attempt, but our approach will enable an alternative that is theoretically more consistently formulated from substrate uptake to CUE control. In our published study (Tang and Riley, 2015) that considers the non-oxygen limited aerobic decomposition, we show that ECA kinetics allows the derivation of realistic mineral-organic matter interactions. Together with the simple examples shown here and in Tang and Riley (2013), we contend that our extension of the Monod kinetics has the potential to produce more robust and accurate results than existing models.

Comments: The specific applications of this model demonstrated some utility. However, I am not convinced that the model is necessarily superior to other more common formulations that have been used in these ways despite SUPECA’s analytical elegance. I suggest more effort to demonstrate the utility of this model as something more than a really elegant mathematical exercise. For example, the statement on line 21 page 29 is that SUPECA can scale reaction networks without changing mathematical formulation. Is this a utilitarian or theoretical accomplishment?
Response: We believe part of SUPECA’s analytical elegance is its ability to scale reaction networks with a consistent formulation, and that this capability will lead to more rigorously defensible biogeochemical models. In that regard, we do think our new approach is both utilitarian and a theoretical accomplishment, and that this combination is lacking in current model formulations. We agree that more demonstrations of the approach can be valuable, but the paper is already very long, and we have provided an example that indicates the power of the approach and will present more applications elsewhere.

References

Response to Reviewer # 2

Overall response

First, we thank Reviewer #2 for taking his/her time to read through our paper. However, we are disappointed that Reviewer #2 largely misunderstood our development and analyses, while Reviewer #1 has grasped the important concepts and agrees with their relevance and importance. Below we respond to Reviewer #2’s comments. However, given Reviewer #2’s (1) large number of misunderstandings of our work; (2) fundamentally incorrect criticisms, and (3) poorly constructed suggestions for improving the manuscript, we request an alternative reviewer to evaluate our paper and responses.

Among other problems described below, Reviewer #2 misclassified our work into the category of ecological “aggregation” of “micro-dynamics” into “macro-dynamics”, a topic well trodden by previous researchers in ecology. We are very aware of the studies mentioned without citation by the reviewer. Briefly, the so-called “aggregation” approach, as studied in ecology (and also in theoretical economics), is a mathematical technique of dimensional reduction. This approach assumes that the micro-dynamics is available for “aggregation” so that the resultant macro-dynamics retains as much of the micro-dynamical functional responses as possible. Such work falls broadly in the category of “reduced order modeling”, a topic on which we have recently published a number of papers (e.g., Liu et al., 2016; Pau et al., 2014, 2016). In stark contrast, the study we present here describes an approach to formulate the micro-dynamics in a physically consistent manner. Therefore, the reviewer’s primary summary criticisms are irrelevant to our study. Further, the reviewer’s comments contain several blatant errors, which we detail below.

Comment: In this paper, the authors go through many different formulations of enzyme kinetics in an attempt to ‘scale’ kinetics from a single enzyme system to a metabolic network consisting of 10’s to 100’s of reactions. The paper doesn’t have a good introduction and there is little motivation for why it’s so critical to be able to ‘scale’ enzyme reaction kinetics other than it’s computationally intensive to simulation a bunch of equations instead of one. Reducing dimensionality will always make life easier, but it’s not clear that anyone in a real world modeling situation would even be in a position to try to translate kinetics for 10’s to 100’s of reactions for soil organic matter decomposition to reduced set of reactions. In a real network, there will be feedbacks between reactions but all are considered independent in this manuscript.

Response: Given reasonable space constraints for journal articles, we did not detail the huge literature on enzyme kinetics relevant to soil biogeochemistry. However, we included sufficient references (Allison, 2012; Bouskill et al., 2012, Grant et al., 2016; Riley et al., 2014; Sulman et al., 2014; Tang, 2015; Tang and Riley, 2013, 2015; Wieder, 2013, 2014) on the topic to indicate that soil biogeochemical models are now in a position to include a wide range of biogeochemical reactions, which may very well exceed 100 reactions. For instance, the soil biogeochemistry module of the site- to regional-scale ecosystem model ecosys (e.g., Grant et al., 2015, 2016; Mekonnen et al. 2016) represents a wide range of microbes, including heterotrophic aerobic bacteria and fungi, methanogens, methanotrophs, autotrophic ammonia oxidizers, autotrophic nitrate oxidizers, acetogen fermenters, and autotrophic and heterotrophic nitrogen fixers. The model also represents the aqueous chemistry of phosphorus dynamics that involves iron,
calcium, carbonate, etc. We also never stated that our goal was to reduce the reaction network. Rather, we emphasized the need for formulation consistency between the many reactions in describing the substrate-consumer relationship, which is the first step in modeling soil biogeochemistry (as indicated in the title, abstract P1: L12-13, and throughout the main text). If formulation reductions were proposed, they should only be applied to substitutable substrates (as discussed in section 3 and also in Tang and Riley, 2013). For example, aerobic heterotrophic bacteria can feed on proteins, cellulose, carbohydrates, and starch; if the specific evolution of those chemical compounds is not of interest, we can regard them all as carbon substrates, which is the fundamental assumption that has been widely applied in the development of many soil BGC models (e.g., RothC model (Coleman and Jenkinson, 1996), CENTURY model (Parton et al., 1998)). A similar problem involving enzyme interactions with many substrates was also studied in Schnell and Mendoza (2000). Given soil microbes are competing and collaborating with each other to consume the many chemical substrates, our study is definitely relevant to modeling complex soil BGC networks. We also acknowledged that feedbacks between reactions are critical components of the soil BGC network (e.g., on P4: L13-17, we acknowledged that there are temporal and spatial scaling methods to cover those feedbacks). Overall, our formulation attempts to better resolve the interactions and feedbacks between reactions at the microbial uptake stage (i.e., the consumer-substrate interactions), which is a misunderstood or ignored topic in the literature (see the long review in Tang and Riley, 2013). Therefore, this reviewer’s comment both misses the point of our manuscript and mischaracterizes its relevance. To ensure readers who’re unfamiliar with soil biogeochemical modeling not to confuse our study with dimension reduction through so-called “aggregation”, we added a new paragraph in page 4 in the revision to state specifically that we’re attempting to improve the microdynamics.

**Comment:** The authors quickly jump into kinetic equation after equation with no clear goal and minimal to non-existent links between models/equations.  
**Response:** These comments are somewhat shocking given the manuscript’s theoretical development goals are given in the Title, Abstract (P1: L11-15), and Introduction (P4: L6-18, P10: L13-22, P11: L1-6). Clearly, we are proposing the SUPECA kinetics to (1) scale redox reactions in networks of mixed substrates and consumers; (2) consistently address the interactions between substrates and microbes at the substrate uptake stage in modeling soil biogeochemistry; and (3) demonstrate its applicability using a simple aerobic soil respiration problem.

**Comment:** The authors never even clearly articulate why what they are presenting is better than anything else. The manuscript is incredibly hard to follow as well. It may be possible for the authors to distill some of this down into a coherent compelling message, but in its current form it’s not publishable.  
**Response:** This comment is again strange, given our substantial discussion in the Abstract (P1: L15-23, P2: L1-11), Introduction (P5-10), and sections 3, 4, and 5. Throughout our discussion, we also highlighted problems with the current formulations of soil BGC kinetics.
For the editor and reviewer’s information, and to put the value of this work in context (i.e., “why it may be better than anything else”), the formulation we described in this paper follows the work described in Tang and Riley (2013), where we originally described the Equilibrium Chemistry Approximation. In this context, we note that Jinyun Tang received the Ecological Society of America’s Honorable Mention for the Gene E. Likens Award for this paper (indicating it, at least, may have value compared to other approaches). Further, the ECA concepts are actively being applied in site to global-scale modeling efforts (Zhu and Riley 2015; Zhu et al., 2016a,b; 2017), which we cite in the manuscript. We therefore believe these reviewer’s comments indicate a misunderstanding of our paper and the broader modern literature on numerical model representations of biogeochemical processes.

Comments: Pg. 7, line 12: This doesn’t make sense. The whole idea is to consider a network of interactions, each with their own kinetics. Gardner, O’Neill, and Iwasa, among other did seminal work on aggregating model dynamics and establish good rules of thumb for when aggregation is reasonable. The problem the authors of this manuscript are trying to address is one of aggregation, not scaling. Furthermore, their expressions are incorrect. A sum can be expressed as the number of terms in the sum multiplied by the mean of the sum. In their case, each term is a product of a rate constant and a concentration, which means that impossible to make their substitution. At a given instant, it can work, but a soon as concentrations change their expression is invalid.

Response: This comment is again a misreading of our work. First, we are addressing the substrate-consumer relationship, an important component in formulating the microdynamics; whereas the works by Gardner, O’Neill, Iwasa (see our listed reference on aggregation) and others are on aggregating the microdynamics when the latter is given. Second, we did not indicate that we are averaging nonlinear terms. Even when we sum (and average) the terms in equation (7), we state clearly that the kinetic parameters must be equal for such a summation (P9: L6). Throughout the paper, we used the summation and average rules according to standard practices widely used in mathematics and physics, and therefore this criticism appears baseless.

Comments: Furthermore, there’s no way to average the nonlinear interaction between enzyme and substrate for multiple reactions. I tried looking up the partition principle and didn’t find anything, and the analogies with Dalton’s and Newton’s laws don’t make any sense.

Response: First, we did not contend that we are averaging the nonlinear interactions between enzymes and substrates for multiple reactions. Second, we introduced and defined the “partition principle” on page 6, line 16. The concept is widely used in deriving macroscopic representations of complex phenomena in physics (e.g., Dalton’s law of partial pressures; superposition principle of electrostatic forces, angular moment etc.; Feynman et al, 1963), and we argue in this manuscript that it should be applied in developing representations of soil BGC dynamics. Third, we only apply averaging when the relationship is linear and there is a good conceptual understanding to support it (e.g., equation (7)). For instance, as we explained above, some models of soil organic matter decomposition aggregate different organic matter constituents (e.g., protein, cellulose, carbohydrates) into a single carbon pool, and still provide important scientific insights to
the soil carbon cycle.

**Comment:** Pg. 3, line 23: Wieder, not wider  
**Response:** Thanks for pointing this out. We corrected it in the revision.

**Comment:** Pg. 6, line 2: dissociation  
**Response:** Thanks for pointing this out. We corrected it in the revision.

**Comment:** Pg. 6 line 7: r-K selection is only briefly mentioned in the Klausmeier and Litchman (2008) paper.  
**Response:** Yes, we agree, so we added a citation to Tilman’s work (Tilman, 1982) for readers interested in this topic.

**Comment:** Pg. 7, eq. 2: Both terms are negative but dissociation should be positive  
**Response:** We think there is a misreading of equation 2. Only the first term is negative, the second term is positive and describes dissociation.

**Comment:** Pg. 8, line 1: I have no idea what the nonsingularity principle is, and again, searching for it gave no results. The expression is really conservation of mass anyway.  
**Response:** We apologize that we did not originally provide a citation for this concept on page 8 (it is mentioned on Page 9, lines 1-3 and the singularity is defined in P2: L1-L3); we have now added references on the concept at the first appearance of the term in the revision (Schnell and Maini, 2000; Tang and Riley, 2013; Tang, 2015).

**Comment:** Pg. 8, line 12: I don’t know what this means. Furthermore, the only difference between the two sides of the equation is that the r.h.s. just moves the half saturation constant around. They appear equal and there is no basis for why they wouldn’t be.  
**Response:** No, in equation (6) the term after the first equal sign is not equal to the term after the second equal sign, as we show below:

Suppose there are two substrates, S1 and S2, with concentrations of 1 and 2 units, respectively; and half saturation constants of 1 and 2, respectively. Then, assuming all other parameters are of numerical value 1, the value after the first equal sign is 1/(1+1)+2/(2+2)=1. However, the value after the second equal sign is (1/1+2/2)/(1+(1/1+2/2))=2/3. Therefore, they are not equal (i.e., 1 ≠ 2/3). Such a case will occur, for instance, in situations when both NH3 and NO3− are taken up by a microbe or plant to synthesize biomass. Only the term after the second equal sign will describe this uptake process consistently. A similar situation is discussed in detail in Schnell and Mendoza (2000).

**Comment:** Litchman and Klausmeier (2008) don’t even mention Monod kinetics. It is unacceptable to incorrectly use references to justify assumptions or manipulations.  
**Response:** It seems the reviewer misunderstood the reference to Litchman and Klausmeier (2008). In their page 620, the second equation, which we copy below, is the Monod kinetics:
uptake = \( v(R) = \frac{v_{\text{max}} R}{K + R} \)

with \( R \) is the substrate and \( K \) is the half saturation constant.

Even though Litchman and Klausmeier (2008) did not use the term “Monod kinetics”, they are clearly applying that approach. As the reviewer may be aware, Monod kinetics and Michaelis-Menten (MM) kinetics were proposed based on different empirical evidences. The Monod kinetics is purely empirical (Monod, 1949) and MM kinetics can be derived mechanistically (Briggs and Haldane, 1925). In soil biogeochemical modeling, the Monod and MM kinetics are used for modeling microbial substrate uptake, and under the assumption of no substrate-storage in microbial cells (which is valid under some restrictive conditions), the Monod kinetics and MM kinetics (or any substrate kinetics such as the SUPECA we present here) can reasonably represent microbial growth (Monod, 1949; Wieder et al., 2013, 2014; Tang and Riley, 2015).

Comment: Pg. 9, line 3: When is it even reasonable to enzyme concentration approach infinity?
Response: It is a common practice in deriving macroscopic representations of complex phenomena to ensure that the solutions are robust across a range of conditions. The term “approach infinity” is widely used in scientific literature to imply “as a state becomes large compared to another state” (e.g., see chapters on oscillators and electrostatics in Feynman et al., 1963). In biogeochemistry, for example, such a situation exists in vivo conditions inside an organisms’ cell (e.g., Schnell and Maini, 2000), or when mineral surface interactions are represented analogously to enzyme kinetics (e.g., adsorption is of Langmuir type). In such situations, the ratio of enzyme and substrate concentrations becomes very large (i.e., approaches infinity).

Comment: Pg. 9, line 5: There is no paper that I can find that matches the Murdock reference, and one published in the same year is completely unrelated. This is a very disturbing pattern of misrepresentation of the literature. I basically can’t follow the rest of page 9 and I have no idea what parametric sensitivity is.
Response: It appears the reviewer was searching for a citation by “Murdock”, when the paper we cited is by “Murdoch”. The reviewer’s assertion of a “disturbing pattern of misrepresentation of the literature” is ridiculous and unprofessional, considering that he/she could have simply gone to the reference list at the end of our manuscript and found the citation.

In 1973, William W. Murdoch published two papers, one is “The functional response of predators”, and the other is “Predation by Coccinellid Beetles: Experiments on Switching” which he co-authored with J.R. Marks. The first paper is the one we cited (and is listed in the references).

The term “parametric sensitivity” is a widely used term in numerical modeling, and we cited a recent paper on the topic in the original manuscript. However, there are many other recent publications applying this term; we have therefore added some of those citations (e.g., Qian et al., 2015; van Werkhoven et al., 2009).

Comment: Starting in section two, the ‘derivations’ seem to be ok, but they are trivial algebra. It’s easy to start with any reaction diagram, assume quasi steady state and derive
equations. However, they still seem to retaining more dynamics that is typical because the substrates/reactants A and B are changing over time.

**Response:** Our careful derivation attempts to present nuances to readers, and indicate clearly where critical assumptions are being made. Since one of our clearly stated goals is to formulate a consistent set of reaction kinetics for soil BGC, we believe having a consistent derivation formulated in the peer-reviewed literature is important. Further, we used this derivation to describe possible problems with other approaches in characterizing biogeochemical kinetics, such as dual-Monod kinetics and synthesizing unit kinetics. Therefore, our derivation will help readers to understand the uncertainties behind using those kinetic formulations for their modeling analyses. In the same spirit, throughout the paper, we have clearly reported that our new approach is only a better approximation to the law of mass action (e.g., section 4 and also see Tang, 2015), and should not be regarded as accurate for all conditions (a situation that is discussed in detail by Pedersen et al., 2008, which we have cited in the revision).

**Comment:** Pg. 17, lines 2-3: I have no idea what this sentence means.

**Response:** The phrase “MM kinetics ignores the mass balance constraint of substrate” simply means: in the derivation of MM kinetics, no constraint is placed on the substrate mass balance. Tang (2015) described this condition and discussed its implications, as have others (Borghans et al., 1996; Tang and Riley, 2013; Maggi and Riley, 2015). We have added these other citations to the revised manuscript to buttress this point. However, as the subsequent sentences explain, our point is that a similar problem may be happening in Dual Monod and Synthesizing Unit kinetics formulations.

**Comment:** Pg. 17, line 15 (and appendix): I have no idea what their ‘first order closure approach’ is. The appendix isn’t really a help here.

**Response:** In the revision, we added some explanation to the “first order closure approach” and a citation to Tang and Riley (2013) where the approach was first applied to enzymatic chemical kinetics. We also note that the first order closure approach has been applied in many other fields, and have added citations (Shankar, 1994; Tang et al., 2007) to the revised manuscript.

**Comment:** Pg. 19: The problem with trying to average over a bunch of nonlinear interactions seems to render this derivation incorrect.

**Response:** As we discussed above, we are not trying to “average over a bunch of nonlinear interactions”. Given that Reviewer #1 understood this important point, we are at something of a loss to address Reviewer #2’s misunderstanding. Nowhere in the manuscript did we state we are “trying to average over a bunch of nonlinear interactions”, so it is not clear where he/she developed that perception.

**Comment:** Data examples and figures: By this point, I am totally lost and quite skeptical of whether their derivations are correct. The comparisons with data are poorly motivated and described so it’s not possible to even know what we should be taking away from the exercise and why.

**Response:** Although we appreciate the reviewer’s taking his/her time to read through our manuscript, we believe that this reviewer is an inappropriate choice, given his/her (1)
large number of misunderstandings, (2) fundamentally incorrect criticisms, and (3) poorly constructed suggestions for improving the manuscript. In other contexts we would be happy to discuss the details of the approach with the reviewer, but given that this is a manuscript review, we request the editor to find another reviewer who’s more familiar with biogeochemistry and approaches to develop conceptual and numerical models of complex reaction networks.

References

Works on aggregation

Works on reduced order model

Works on soil biogeochemical modeling cited in the first submission


**Other references**


The 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 processes. 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 here study this scaling
problem by focusing on the substrate-consumer relationships for consumer mediated
redox reactions of the form $A + B \rightarrow \text{products}$, where products could be microbial
biomass and different bio-products. Under the quasi-steady-state approximation, these
substrate-consumer relationships can be formulated as the computationally difficult full
Equilibrium Chemistry problem, which is then usually approximated analytically with the
popular Dual Monod (DM) kinetics and Synthesizing Unit (SU) kinetics. However, we
found that the DM kinetics is scaling inconsistent for reaction networks because it (1)
does not incorporate substrate limitation in its derivation, (2) invokes contradictory
assumptions regarding the substrate processing rate when transitioning from single
substrate reactions to two-substrate redox reactions, and (3) cannot scale the product
generation rate from one to multiple substrates. In contrast, the SU kinetics can
consistently scale the product generation rate from one to multiple substrates, but suffers
from the deficit that as the consumer abundance approaches infinity, it predicts singular
infinite reaction rates even for limited substrates. We attribute this deficit to SU’s failure
to incorporate the substrate limitation in its derivation and remedy SU with the proposed
SUPECA (SU Plus Equilibrium Chemistry Approximation) kinetics, which consistently
imposes the mass balance constraints from both substrates and consumers on consumer-
substrate interactions in calculating redox reaction rates. Moreover, we show the
SUPECA kinetics satisfies the partition principle as in theories like Newton’s Law of
motion and Dalton’s law of partial pressures, such that its mathematical manifestation is
scaling invariant when transitioning from an individual reaction to a network of many
reactions. We benchmarked the SUPECA kinetics with the equilibrium chemistry
solution for some simple problem configurations and found SUPECA outperformed the
SU kinetics. In applying the SUPECA kinetics to aerobic soil respiration, we found that
SUPECA predicted consistent but variable moisture response functions that agreed well
to those derived from incubation data. We finally discuss how the SUPECA kinetics
could help Earth System Models consistently incorporate more biogeochemical reactions
to improve their biogeochemical modules.

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

Land holds more than twice the carbon that is in atmosphere; therefore a small change in land carbon dynamics can imply significant feedbacks to the ongoing climate warming (Ciais et al., 2013). This has motivated intense research towards better understanding of Earth’s land biogeochemical cycles, both for prediction and assessing the efficacy of climate mitigation and adaptation strategies. To date, however, soil biogeochemical models are suffering 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 the net land carbon uptake varies from 22 to 456 PgC for the 2006-2100 period under the Representative Concentration Pathway 4.5 (RCP4.5; Shao et al., 2013). Similarly, the 16 CMIP5 ESM simulations analyzed in Todd-Brown et al. (2013) estimated the contemporary global soil carbon stocks ranging from 510 to 3040 PgC to 1 m depth, while the most recent empirical estimation is 1408±154 PgC to 1 m depth and 2060±217 Pg C to 2 m depth (Batjes, 2016). Therefore, it is urgent to improve our models’ predictive power.

The predictive power of existing land biogeochemical models is plagued 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 them, developing better model structure and formulation has been identified as a priority. One proposed structural improvement is to include explicit microbial processes (Wieder et al., 2015b), which has recently been shown to 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), and respiratory temperature sensitivity (Tang and Riley, 2015). A second major proposal is to explicitly resolve the ecosystem nutrient cycle, which aligns with the hypothesis that the potential for increasing land ecosystem carbon uptake resulting from the effect of atmospheric CO₂ fertilization could be limited by nutrient availability (Vitousek, 1982; Shi et al., 2015; Wieder et al., 2015c).

A common process that underlies both of these two proposed structural improvements is the substrate-consumer interaction, which is fundamental for modeling microbial decomposition of substrates (Tang and Riley, 2013a; Riley et al., 2014; Le Roux et al., 2016), mineral soil interaction with adsorptive substrates (Tang and Riley, 2015), and plant-microbe competition for nutrients (Zhu et al., 2016a, 2016b, 2017). In soil, because there are many consumers competing for many substrates in different places at different times, the biogeochemical models being developed must be able to scale the many biogeochemical processes consistently across space, time, and processes. Of the three dimensions that call for scaling (Figure 1), scaling across the 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), so here we study the scaling along the less studied third dimension—process—with a focus on substrate-consumer interactions.

The substrate-consumer relationship is the first step in formulating biogeochemical models, and is formulated with the so-called substrate kinetics that is a function of consumer and substrate abundance under the influence of various environmental factors, such as soil mineralogy, temperature and moisture (see Tang and Riley (2013a) for a review). Since substrate-consumer kinetics only accounts for how
substrates are taken up by organisms, 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.

Within a certain homogeneous space-time-process unit in soil (Figure 1), there are generally three types of substrate-consumer relationships: (1) single-substrate Monod type reactions in the form of \( A \rightarrow \text{products} \) ; (2) the two-substrate redox reactions in the form of \( A + B \rightarrow \text{products} \), where substrate \( A \) and \( B \) are called complementary because they both are required to proceed the redox reaction; and (3) the multi-substrate (\( >2 \)) reactions \( \sum_{i} A_i \rightarrow \text{products} \). The scaling of the single-substrate Monod type reaction has been extensively discussed in Tang and Riley (2013a), and is resolved with the Equilibrium Chemistry Approximation (ECA) kinetics (and more discussion on the ECA kinetics for process scaling will be provided in later sections when discussing the 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 should be addressed with 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 to drive the model and is numerically very difficult to solve because of its multi-temporal scale nature. By making the quasi-steady-state-approximation (QSSA),
i.e., assuming that the product generation from consumer-substrate complex is much
slower than the equilibration between consumers, substrates, and consumer-substrate
complexes (Briggs and Haldane, 1925), the full kinetic problem is reduced to the simpler
Equilibrium Chemistry (EC) form (e.g., Chellaboina et al., 2009). However, the EC form
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 the Dual
Monod (DM) kinetics (Kooijman, 1998; Brandt et al., 2003). Although both of them are a special case of the EC
formulation (Kooijman, 2010; Tang and Riley, 2013a), they make different assumptions
of the relative magnitudes of the involved kinetic parameters. For this, Kooijman (2010)
has shown that the DM kinetics inevitably requires the dissociation rate to be much larger
than the product-generation rate from the consumer-substrate complexes. In contrast, to
apply the single-substrate Monod kinetics (Monod, 1949) or Michaelis-Menten (MM)
kinetics (Michaelis and Menten, 1913; which is mathematically identical to the empirical
Monod kinetics and they two will be used interchangeably hereafter) does not impose this
requirement on its parameters. Moreover, in applications to r-K scaling (e.g., Tilman,
1982; Litchman and Klausmeier, 2008), the single-substrate Monod kinetics even
requires the product-generation rate to be faster than the dissociation rate of the
consumer-substrate complexes. 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.
We define a kinetic formulation to have consistent 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 forms (aka the partition principle) and (2) does not predict any singularity
over the whole range of substrate and consumer concentrations (aka the non-
singular principle which says that the predicted reaction rate won’t increase to infinity as the
consumer concentration approaches infinity (e.g., Schnell and Maini, 2000; Tang, 2015)).
The full kinetics formulation and its EC formulation both satisfy these two criteria, which
can be explained using the following example network of consumer-substrate
relationships:

\[
S_i + E_j \underset{k_{-1}}{\overset{k_{+1}}{\leftrightarrow}} E_jS_i \longrightarrow P_{ij} + E_j
\]  

(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 the free consumer. In equation (1) (and throughout this
study), the forward kinetic parameters are indicated with superscript “+”, while the
backward kinetic parameters are with superscript “−”. Here and below we assume that the
units of all variables are consistently defined, and they are only put forward explicitly
when it is necessary to resolve an ambiguity.

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

\[
\frac{d[S_i]}{dt} = -[S_i]\sum_j\left(k_{+1}E_j[S_i] + k_{-1}E_jS_i\right)
\]  

(2)
\[
\begin{align*}
\frac{d[E_iS_j]}{dt} &= k_{i,j}^+ [S_i][E_j] - (k_{i,j}^- + k_{j,i}^-) [E_iS_j] \\
\frac{d[E_j]}{dt} &= -[E_j] \sum_i (k_{i,j}^- [S_i]) + \sum_j ((k_{i,j}^+ + k_{j,i}^+) [E_jS_i])
\end{align*}
\]

(3)

(4)

where, and also throughout this study, we use \([x]\) to indicate the concentration of \(x\).

That the full kinetic formulation is consistent with the partition principle is manifested in the first summation in equations (2) and (4). Particularly for equation (4), by defining an appropriate mean specific substrate affinity \(k_{1,j}^+\), the summation

\[
\sum_i (k_{1,j}^+ [S_i])
\]

can be recast into the form

\[
\sum_i k_{i,j}^+ [S_i] = k_{1,j}^+ [S],
\]

in which \([S] = \sum_i [S_i]\)

resembles 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)) and is clearly partition consistent.

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

\[
[S_i] + \sum_j [E_jS_i] = [S_i],
\]

(5)

and that the consumption of \(S_i\) is through the generation of product from \([E_jS_i]\).

Therefore, by combining equations (2), (3), and (5), the overall consumption rate of \(S_i\) (i.e., \(\sum_j k_{1,j}^+ [E_jS_i]\)) is always smaller than \([S_i] \sum_j k_{1,j}^+\).

Since the EC formulation is obtained by applying QSSA to the full kinetic formulation (i.e., \(d[E_jS_j]/dt = 0\) for equation (3)), it automatically satisfies the two
criteria for consistent process scaling. However, the Monod kinetics is scaling inconsistent when it is applied, for example, to the single-substrate competition by multiple populations, or to the 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, the Monod kinetics violates the partition principle, which can be shown from the following inequality:

\[
F_j = \left[ E_j \sum_i k_{ji} \left( \frac{S_i}{K_{ji}} + \frac{S_i}{K_{ji}} \right) \right] \neq \left[ E_j \sum_i k_{ji} \left( \frac{S_i}{K_{ji}} \right) / K_j \right] / \left( 1 + \sum_i S_i / K_{ji} \right)
\]  

(6)

Here \( F_j \) describes the uptake of all substrates \( S_i \) by population \( E_j \). The left hand side of the inequality is the uptake computed by directly applying the Monod kinetics, while the right hand side of the inequality is by applying the competitive Monod kinetics (e.g., Litchman and Klausmeier, 2008). The inequality (6) is even true when \( K_{ji} \) is independent of \( i \). Besides being inconsistent with the partitioning principle, the Monod kinetics also violates the non-singular principle, which can be demonstrated by observing that, as \( [E_j] \) approaches infinity, so does \( F_j \).

For the competitive Monod kinetics on the right hand side of the inequality in equation (6), (e.g., Murdoch, 1973), if all substrates have the same affinity parameter (i.e., \( K_j = K_j \)), we have the following
where $[S] = \sum_i [S_i]$ designates the total free concentrations of all substrates. Equation (7) therefore suggests that the competitive Monod kinetics satisfies the partition principle for consistent scaling of substrate-consumer relationships. Nevertheless, because the competitive Monod kinetics is linear in $[E_j]$, like the classic Monod kinetics, it still violates the non-singular principle for consistent scaling.

In Tang (2015) (and also in Borghans et al. (1996), Tang and Riley (2013a)), it was shown that the linear dependence of $F_j$ on $[E_j]$ as predicted by the Monod kinetics and similarly by the 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 the Equilibrium Chemistry Approximation kinetics (Tang and Riley, 2013a), which was shown to predict much more accurate parametric sensitivity than the Monod kinetics in comparing with analytical solutions (Tang, 2015).

Since the success of all model calibrations rely on the sensitivity of model predicted responses with respect 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), ensuring that the substrate kinetics predicts accurate parametric sensitivity is essential for developing robust biogeochemical models.
We therefore ask the question: how should we achieve a consistent scaling from the simplest redox reaction $A + B \rightarrow \text{products}$ (i.e., AB-E type) to a network that mixes many redox reactions and even single substrate Monod-type reactions (a situation found commonly in nature)? 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 be able to seamlessly transition from a single substrate Monod-type reaction to the AB-E type redox reaction without making contradictory assumptions in its theoretical derivation.

In the following, we address the above question by first presenting the step-by-step derivation of the DM kinetics and the SU kinetics from the EC formulation of the redox reaction $A + B \rightarrow \text{products}$. Conceptually, DM kinetics can be viewed as a direct application of chemical kinetics that the reaction rate of substrates $A$ and $B$ over consumer $E$ is determined by the product of $A$ and $B$’s binding probability to $E$ (which in Monod form is $\frac{[A]}{[K_A + [A]]}$ for substrate $A$, and $\frac{[B]}{[K_B + [B]]}$ for substrate $B$).

Kooijman (1998) was the first to derive the SU kinetics using the 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 will stress on exposing the scaling-inconsistencies implied in the DM kinetics and SU kinetics, and, in particular, we will show that DM kinetics cannot be extended for consistent process scaling of the substrate-consumer relationship. We then present the SUPECA kinetics that remedies the inconsistencies of the SU kinetics. We demonstrate the benefits of SUPECA in terms of its numerical accuracy and present an example application of modeling the moisture control of aerobic
soil respiration. Finally, we discuss how one can apply the SUPECA kinetics to trait-based modeling approaches in various biogeochemical systems.

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

2.1 Governing equations

We schematically represent the enzymatic redox reaction network as

$$E + A \xrightleftharpoons[k_i^-]{k_i^+] EA$$

where it is assumed that the order of substrates $A$ and $B$’s 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 (see appendix A for derivations) as follows:

$$\frac{d[ A ]}{dt} = -k_i^+[EAB]$$

(9)

$$\frac{d[ B ]}{dt} = -k_i^+[EAB]$$

(10)

$$k_i^+[E][A] + k_i^-[EAB] = (k_i^- + k_i^+)[B][EA]$$

(11)

$$k_i^+[E][B] + k_i^-[EAB] = (k_i^- + k_i^+)[A][EB]$$

(12)

$$k_i^+[EB][A] + k_i^-[EA][B] = (k_i^- + k_i^+)[EAB]$$

(13)
where
\[
\begin{align*}
[A]_r & = [A] + [EA] + [EAB] \quad (14) \\
[B]_r & = [B] + [EB] + [EAB] \quad (15) \\
[E]_r & = [E] + [EA] + [EB] + [EAB] \quad (16)
\end{align*}
\]

The derivation of substrate kinetics is therefore equivalent to solving for \([EAB]\) 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. And as we describe below, linearization with different assumptions lead respectively to the DM, SU, and SUPECA kinetics.

To avoid confusions for readers that are not familiar with substrate-kinetics, we also note that because obtaining the substrate kinetics is just to solve equations (11)-(16), various production and destruction terms can be added to equations (9) and (10) 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 the concentration of consumer-substrate complexes are so small that the free substrate concentrations are equal to the bulk concentrations (e.g., for substrate A, it holds \([A]_r = [A]\)). This approach when combined with different assumptions on the relative magnitudes of the kinetic parameters then leads to the popular DM kinetics and the two-substrate SU kinetics.

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

\[
[EA] = \frac{k^-}{K_d}[EAB] = K_d[EAB] \tag{17}
\]

\[
[EB] = \frac{k^-}{K_d}[EAB] = K_d[EAB] \tag{18}
\]

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

\[
[E_A] = \frac{k^-}{K_d}[EA] = K_d[EA] \tag{19}
\]

\[
[E_B] = \frac{k^-}{K_d}[EB] = K_d[EB] \tag{20}
\]

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

\[
\frac{d[A]}{dt} = -k^- \frac{[E_A][A][B]}{K_d + [A][B]} \tag{21}
\]

Although as one substrate, e.g., \([A]\), approaches infinity, equations (21) can be reduced to the classical MM kinetics:

\[
\frac{d[A]}{dt} = -k^- \frac{[E_A][B]}{K_d + [B]} \tag{22}
\]
we note that the half saturation coefficient $K_B = k^-_B / k^+_B$ in equation (22) is different from its usual definition, which should be $K_B = (k^+_2 + k^-_B) / k^+_B$, if one derives the MM kinetics rigorously starting from a single substrate and single consumer system (e.g., Tang, 2015). For this reason, we assert that the DM kinetics cannot achieve a self-consistent scaling from one-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 $k^+_2 \ll k^-_B$, 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. $k^+_2 \ll \max(k^-_x, k^-_B)$ (e.g., Briggs and Haldane, 1925). Nor do the high dissociation rates of $[EA]$, $[EB]$, and $[EAB]$ favor the consumer’s assimilation of substrates under usual substrate concentrations (e.g., Van Slyke and Cullen, 1914), even though a high dissociation rate 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 $K_B = k^-_B / k^+_B$ for MM kinetics and the 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 kinetic parameters, and the smooth
transition from DM to single substrate Monod kinetics is only ostensible.

2.2.2 Synthesizing unit kinetics

In deriving the 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 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 together with both substrates \( A \) and \( B \) (which is \( \frac{[EAB]}{[E]} \)). Mathematically, SU kinetics requires the sufficient flux condition \( k_{-}^2 [A] \gg k_{-}^2 \) and \( k_{-}^2 [B] \gg k_{-}^2 \) (Kooijman, 2010). Define \( \tilde{k}_{+}^2 = k_{-}^2 + k_{-}^2 + k_{-}^2 \), equations (11)-(13) become

\[
\begin{align*}
 k_{+}^2 [EA][A] & = k_{+}^2 [B][EA] \quad (23) \\
 k_{+}^2 [EB][B] & = k_{+}^2 [A][EB] \quad (24) \\
 k_{+}^2 [EB][A] + k_{+}^2 [EA][B] & = \tilde{k}_{+}^2 [EAB] \quad (25)
\end{align*}
\]

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

\[
\frac{d[A]}{dt} = \frac{k_{+}^2 [E][A] / \tilde{k}_{+}^2}{\frac{1}{k_{+}^2} + \frac{1}{k_{+}^2} + \frac{1}{k_{+}^2}} - \frac{1}{k_{+}^2} [A] + \frac{1}{k_{+}^2} [B] \quad (26)
\]

The two-substrate SU kinetics as indicated by equation (26) can be viewed alternatively as a special case of the general SU kinetics for any number of complementary substrates, which was derived by Kooijman (1998) based on the queue theory (e.g., Gross et al., 2011). Kooijman (1998) assumed that the consumers act like
synthesizing units, which process the substrates in two steps: binding and production. He then assumed that all flux rates (including production rates $k'_a$ and substrate binding rates $k'_3[A]$ and $k'_6[B]$) 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 binding of substrates $A$ and $B$ to $E$, and it disappears if sequential binding is assumed.

As one substrate, e.g., $A$, approaches infinity, the single-substrate Monod kinetics is recovered from equation (26):

$$\frac{d[A]}{dt} = \frac{k'_3[E]B}{1 + \frac{k'_3}{k'_6[B]}} - \frac{k'_6[E]B}{k'_6} = \frac{k'_3[E]B}{k'_6 + [B]}$$  \hspace{1cm} (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 represents the statistical mean of the fluctuating activity of the enzyme (English et al., 2006; Reuveni et al., 2014). That the kinetics of both single-substrate reaction and two-substrate redox reaction can be similarly derived using statistical theory and that equations (26) and (27) could be obtained from EC formulation using consistent assumptions of the kinetic parameters indicate, in contrast to DM kinetics, that SU kinetics is able to scale consistently between one-substrate and two-substrate redox reactions.
2.3. SUPECA kinetics

In Tang (2015), it was shown that the derivation of MM kinetics ignores the mass balance constraint of substrate, resulting in the MM kinetics to predict inaccurate parametric sensitivity over the wide range of substrate to consumer ratios (e.g., Figure 1 in Tang (2015)). In the above, we also noticed that the substrates mass balance constraints as indicated by equations (14) and (15) are not used in deriving the DM and SU kinetics, suggesting that both the DM and SU kinetics may suffer from the same deficit as the MM kinetics. Further, since the DM kinetics fails to consistently scale from a single substrate to two complementary substrates, we below only remedy the SU kinetics into the SUPECA kinetics to achieve a scalable and non-singular formulation of the redox reactions.

As implied in equations (9)-(16), the derivation of substrate kinetics requires solving for \([EAB]\) 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 the 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 the SUPECA kinetics:
\[
\frac{d[A]}{dt} = -\frac{1}{k_2} \left( f_A + \frac{1}{f_A} \right) - E \left( f_A / k_2^* \right)
\]

(28)

where \( f_A = k_A \left[ A \right] \), \( f_B = k_B \left[ B \right] \), \( \bar{f}_A = f_A + k_A^* \left[ E \right] \), \( \bar{f}_B = f_B + k_B^* \left[ E \right] \), \( f_{AB} = f_A + f_B \),

and \( \bar{f}_{AB} = \bar{f}_A + \bar{f}_B \). In equation (28), we assumed \( k_2^* \gg k_2^* \) and \( k_2^* \gg k_2^- \), so that \( k_2^* = \bar{k}_2^* \).

(we note that this relationship will be used throughout the remainder of this paper). It can then be verified that if \( \left[ E \right] \ll \left[ A \right] \) and \( \left[ E \right] \ll \left[ B \right] \), the SUPECA kinetics as represented in equation (28) becomes the SU kinetics in equation (26). Further, if one of the two substrates, say \( \left[ B \right] \), approaches infinity, equation (28) is reduced to

\[
\frac{d[A]}{dt} = -f_A \left[ E \right] \left( f_A / k_2^* \right)
\]

(29)

which by using the definition of \( f_A \) and \( \bar{f}_A \) can be reduced to 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 the ECA kinetics (see Figure 2) 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 $A \rightarrow \text{products}$ as

$$
\frac{d[S_{i,j}]}{dt} = -k_{2,i,j} \left[ E_j \right] \frac{\left[ S_i \right] / K_{ii}}{1 + \sum_{I=1}^{J} \left( \left[ S_i \right] / K_{ii} \right) + \sum_{j=1}^{I} \left( \left[ E_j \right] / K_{jj} \right)} 
$$

(30)

By defining the normalized substrate flux (with subscript “c” designating that the summation is over a column of the graph in Figure 2)

$$
F_{c,j} = \sum_{I=1}^{J} \left( \left[ S_i \right] / K_{ii} \right) = \sum_{I=1}^{J} F_{c,i}^{[I]} 
$$

(31)

and its conjugate (with subscript “r” designating that the summation is over a row of the graph in Figure 2)

$$
F_{r,i} = \sum_{j=1}^{I} \left( \left[ E_j \right] / K_{jj} \right) = \sum_{j=1}^{I} F_{r,j}^{[I]} 
$$

(32)

equation (30) can then be rewritten as

$$
\frac{d[S_{i,j}]}{dt} = -k_{2,i,j} \left[ E_j \right] \frac{F_{c,j}^{[I]} F_{r,i}^{[I]} / \left( 1 + F_{r,j} + F_{c,j} \right)}{1 + F_{r,j} + F_{c,j}} 
$$

(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 the ECA kinetics in equation (33) may be interpreted as either (i) the potential substrate

20
processing rate of $E_j$ (aka $k_{E_j}^i \left[ E_j \right]$) weighted by the relevant importance of the reaction

during pathway $S_i \rightarrow \text{products}$ (aka $F_{c,j}^{(l)}$) under the influence of all competing substrate fluxes
$F_{c,j}^{(l)}$ (towards consumer $E_j$) and all competing agents' efforts $F_{r,i}^{(l)}$ (towards substrate $S_i$)
or (ii) the linear decay potential of $S_i$ (aka $k_{S_i}^r \left[ S_i \right]$) weighted by relevant importance of
$F_{r,i}^{(l)}$ under the influence of all competing substrate fluxes and competing agents' efforts.

We further 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 ($\left[ S \right]$ defined as the total of all substrates) that are
accessible for consumer $E_j$ as

$$K_{E_j} = \left( \sum_{l=1}^{L} \left[ S_i \right]_l \right) / F_{c,j} = \left[ S \right] / F_{c,j}$$

(34)

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

$$K_{S_i} = \left( \sum_{l=1}^{L} \left[ E_j \right]_l \right) / F_{r,i} = \left[ E \right] / F_{r,i}$$

(35)

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

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

$$K_{E_j} = \left( \sum_{l=1}^{L} \left[ S_i \right]_l \right) / F_{c,j} = \left[ S \right] / F_{c,j}$$

(34)

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

$$K_{S_i} = \left( \sum_{l=1}^{L} \left[ E_j \right]_l \right) / F_{r,i} = \left[ E \right] / F_{r,i}$$

(35)

Then by substituting equations (34) and (35) into equation (33), we obtain
\[
\frac{d [S]_{i,j}}{dt} = \frac{k_{ij}^* \left(E_j \right) \left([S]_{i,j}/K_{E,i,j} \right)}{1 + \left[S\right]_{i,j}/K_{E,i,j} + \left[E\right]_{i,j}/K_{E,i,j} F_{i,j}} \tag{36}
\]

which again shows the linear partition in terms of \( F_{i,j}/F_{c,i} \) and \( F_{i,j}/F_{c,j} \).

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

\[
\frac{d [A]_{i,j,h}}{dt} = -\frac{k_{ij}^* \left(E_j \right) F_{i,j}^{|} F_{i,j}^{|}}{G_{AB,i,h} + F_{AB,i,h}} - \frac{F_{c,a,k} G_{B,B,k} + G_{A,B,k} F_{c,B,k} - G_{A,B,k} G_{B,B,k}}{G_{AB,i,h}} \tag{37}
\]

where

\[
F_{c,A,k} = \sum_j F_{c,A,k}^{|} = \sum_j \left[A\right]_{i,j,h}/K_{A,B,h} \tag{38}
\]

\[
F_{c,B,k} = \sum_j F_{c,B,k}^{|} = \sum_j \left[B\right]_{i,j,h}/K_{B,B,h} \tag{39}
\]

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

\[
F_{r,A,h} = \sum_j \left[E\right]_{i,j,h}/K_{A,H} \tag{41}
\]

\[
F_{r,B,h} = \sum_j \left[E\right]_{i,j,h}/K_{B,H} \tag{42}
\]
\[ G_{A,k} = F_{c,A,k} + F_{r,A,j} \]  \hspace{1cm} (43)

\[ G_{B,jk} = F_{c,B,j} + F_{r,B,j} \]  \hspace{1cm} (44)

\[ G_{AB,jk} = G_{A,j} + G_{B,jk} \]  \hspace{1cm} (45)

For equation (37), it is straightforward to verify that if \( F_{c,A,k} \) \((or F_{c,A,k})\) goes to infinity, then SUPECA kinetics is reduced to the ECA kinetics in equation (33). Therefore, the SUPECA kinetics as formulated in equation (37) is an extension of both the SU and ECA kinetics, and SUPECA is applicable for consistent scaling of substrate-consumer networks involving both single-substrate reactions and redox-reactions (a visually more appealing demonstration of the SUPECA kinetics is in Figure 3).

4. Accuracy of the SUPECA kinetics

Following Tang and Riley (2013a), we below evaluate the numerical accuracy of the SUPECA kinetics by comparing its solution against that obtained from solving the equilibrium chemistry problem. However, 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 include 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).

We evaluated the accuracy of SUPECA (equation (37)) and SU (equation (26)) over a wide range of parameter values. Specifically, we fixed both substrates at a nominal
value of 40 mol m$^{-3}$, and the maximum substrate processing rate at 48 s$^{-1}$. Then we
sampled the affinity parameters exponentially over the range of $[0,1000]$ mol m$^{-3}$ and
the microbe and sorbent concentrations uniformly over the range of $[0,1000]$ mol m$^{-3}$.
With a total of 1000 sets of randomly paired parameters, we compared how close the
SUPECA and SU approximations are to the EC solution in terms of root mean square
error (RMSE) and goodness of linear fit. Because the SU kinetics does 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. Apparently, such an
artificial ordering in calculation (as needed by the SU approach) suggests that the
implementation of SU is numerically cumbersome (and similar numerical difficulties are
also associated with the popular MM kinetics (Resat et al., 2011; Tang and Riley,
2013a)).

Our comparison (Figure 4) clearly indicates that the SUPECA kinetics is superior
to the SU kinetics in computing the microbe-substrate complex in presence of the
substrate binding competition between microbes and sorbent. The SUPECA kinetics is
more accurate in terms of both goodness of linear fitting and RMSE. In magnitude, the
RMSE of SUPECA predictions is less than 10% of that of SU calculations. The slope of
linear fitting from SUPECA calculations is also much closer to the ideal value 1.0,
whereas that from SU calculations is far greater than 1.0, suggesting that SU kinetics
significantly overestimates microbe-substrate complexes under a wide range of
conditions. This very large slope from SU calculations is also consistent with the
singularity at infinite microbial abundances as implied by the linear dependence on
microbial abundances in deriving the 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 is both numerically more convenient
and more accurate than SU kinetics (which becomes the MM kinetics for one-substrate
reactions; see equation (27)) in calculating the microbe-substrate complexes for situations
involving microbes, enzymes, substrates and soil minerals (e.g., Tang and Riley, 2015).

5. Example application to modeling aerobic heterotrophic respiration

As an example application, we applied the SUPECA kinetics to model the
moisture stress on aerobic soil respiration. In our formulation of the problem (Appendix
G), we consider a homogenous 10 cm thick soil with 2.0 mol C m\(^{-3}\) microbes and 3.0 mol
C m\(^{-3}\) dissolvable organic carbon (different DOC values affected our results negligibly as
long as they are larger than 0.5 mol C m\(^{-3}\)) uniformly distributed across the soil pores. We
conceptualize the 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 the 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 conceptual model assumes that the inter microsites (or aggregates) transport dominates the intra-aggregate transport, which is 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 $K_{O_2,w} = 3 \times 10^{-5}$ mol m$^{-3}$ and elevated $K_{O_2,w} = 3 \times 10^{-2}$ mol m$^{-3}$; Figure 5, Figure 6 and Figure 7). The calculation with elevated $K_{O_2,w}$ (when compared to the default $K_{O_2,w}$) indicates the effect of soil aggregates on determining microbes’ moisture response (see explanations below and in Appendix G). We evaluated (1) how close our predicted moisture response function is to the incubation data from Franzluebbers (1999) and (2) how soil mineral adsorption of DOC would affect the shape of the soil moisture response function.

When the respiration curves are normalized to the range of $[0,1]$, we found that all curves have the 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 $K_{O_2,w}$ value best approximates the incubation data from Franzluebbers (1999) and as the sorption capacity becomes smaller, the sharper the moisture response function becomes.
When the affinity parameter of oxygen is reduced to its default value (while keeping the adsorption capacity to 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 here have not explicitly prognosed 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 of the data with respect to the prediction 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 significant amount of aggregates in his incubated soil. Moreover, the higher moisture threshold (where respiration peaks) with the default apparent oxygen affinity parameter is also consistent with measurements that aggregates may facilitate anaerobic processes under well-ventilated conditions (by increasing the range of soil moisture conditions where oxygen limits aerobic processes; Renault and Stengel, 1994).

When the effect of different mineral soil carbon adsorption capacity is evaluated against the normalized respiration (Figure 6), we found, being consistent with results described in Tang and Riley (2015), that higher adsorption capacity results in significantly lower soil respiration. Therefore, when the results from Figure 5 and Figure 6 are taken together, we contend that, like the soil temperature effect discussed in Tang and Riley (2015), the soil moisture response function is an emergent response resulting from the interactions between biotic and abiotic factors that co-regulate soil organic carbon decomposition (Manzoni et al., 2016). 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. We therefore suspect that treating moisture stress as a multiplier in modeling soil C
decomposition could also significantly bias existing soil biogeochemical model
predictions. We will explore such biases in other studies.

When the default oxygen affinity parameter was used in analyzing the effects of
different mineral soil carbon adsorption capacities, all the respiration moisture response
functions are essentially the same (Figure 7). Since the oxygen affinity parameter reflects
the impacts of aggregates at the cm$^3$ scale, Figures 6 and 7 demonstrate that soil
aggregates may have profound influence on soil carbon decomposition rates.

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

Besides the example application above, we expect that the SUPECA kinetics will
be a unique and powerful tool for trait-based modeling in various biogeochemical
systems. As we show above and below, the 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.

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 predicts the sensitivity of its consumption by

consumer \( [E_j] \) with respect to the maximum processing rate \( k_{2j}^* \) as

\[
\frac{\partial}{\partial k_{2j}^*} \left( \frac{d [S_{i, j}]}{dt} \right) = \frac{[E_j] F_{c,j}^{(i)}}{1 + F_{r,j} + F_{c,j}} < \frac{[E_j] F_{r,j}^{(i)}}{1 + F_{r,j}} + \frac{[E_j] F_{c,j}^{(i)}}{1 + F_{c,j}}
\]

(46)

where the term after the first “<” is prediction by the competitive Monod kinetics and that after the second “<” is by the Monod kinetics, suggesting that models using Monod kinetics for substrate competition is most sensitive to parameters and least robust to calibrate (e.g., Tang and Riley, 2013a).

To quantitatively evaluate our assertion that SUPECA kinetics predicts lower parametric sensitivity, we, for instance, apply equation (46) to 100 competing substrate fluxes of equal magnitude. We then have \( F_{c,j} = 100 F_{c,j}^{(i)} \). 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., \( F_{r,j} = F_{c,j} \), then the parametric sensitivity predicted by ECA is about 50% of that by competitive Monod kinetics. Therefore, the ECA (and by extension, SUPECA) prediction is much less sensitive with respect to \( k_{2j}^* \) than that predicted by competitive Monod kinetics and Monod kinetics. Moreover, with equations (30) and (37), one can verify that the more substrates and consumers are represented in the system, the smaller the parametric sensitivity will be predicted by the ECA (and SUPECA) kinetics. One can also verify that such robustness is true for other parameters in the SUPECA kinetics, including the substrates and consumer abundances. That including more
substrates and consumers will lead to more robust model predictions is the fundamental premise that underlines the proposal of trait-based modeling (e.g., Bouskill et al., 2012), and SUPECA is the only kinetics that explicitly contains 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 the ECA kinetics. In a series of studies (Zhu and Riley, 2015; Zhu et al., 2016a, 2016b, 2017), we show that ECA kinetics was able to significantly improve the modeling of nutrient competition between plants, microbes, and mineral soils. In Tang and Riley (2013a), where the ECA kinetics was first proposed, the lignin decomposition dynamics was correctly captured without a priori imposing a target lignocellulose index. In Tang and Riley (2013a, 2015) and this study, the ECA kinetics was able to seamlessly incorporate the Langmuir type substrate adsorption into its numerical implementation without invoking the ad hoc numerical order that is prerequisite to MM (or Monod) kinetics for modeling mineral, microbe, and substrate interactions.

Finally, we expect the SUPECA kinetics will provide a robust approach to resolve the redox ladder in soil biogeochemistry. Existing approaches have imposed the redox ladder rigorously following some specific order, e.g.

- $O_2 \left( H_2O \right)$
- $NO_3^- \left( N_2 \right)$
- $MnO_2 \left( Mn^{2+} \right)$
- $Fe(OH)_3 \left( Fe^{3+} \right)$
- $SO_4^{2-} \left( H_2S \right)$
- $CO_2 \left( CH_4 \right)$

and

- $H_2O \left( H_2 \right)$ (e.g., Grant, 2001). In contrast, the 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 the 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$^3$). We are now building such a model and
will describe it elsewhere.

7. Conclusion

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
$A \rightarrow$ $E$ type and $A + B \rightarrow$ $E$ type reactions. The SUPECA kinetics, by
properly accounting for mass balance constraints of both substrates and consumers, is
able to scale such reaction networks without changing its mathematical formulation. Our
numerical tests indicate that SUPECA kinetics is superior to SU kinetics both in
numerical accuracy and numerical robustness and SUPECA kinetics is able to
satisfyingly predict the moisture response function of aerobic soil respiration. Moreover,
because SUPECA kinetics intrinsically represents specific microbial traits that can be
measured, we expect many more novel modeling applications will be plausible to
improve predictions of a wide range of biogeochemical systems.

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
\[ \frac{d[EA]}{dt} = k_a^*[E][A] + k_b^*[EB] - (k_a^* + k_b^*[B])[EA] \]  
\( \text{(A1)} \)

\[ \frac{d[EB]}{dt} = k_a^*[E][B] + k_b^*[EAB] - (k_a^* + k_b^*[A])[EB] \]  
\( \text{(A2)} \)

\[ \frac{d[EAB]}{dt} = k_a^*[EB][A] + k_b^*[EA][B] - (k_a^* + k_b^* + k_3^*)[EAB] \]  
\( \text{(A3)} \)

\[ \frac{d[P]}{dt} = k_3^*[EAB] \]  
\( \text{(A4)} \)

\[ \frac{d[A]}{dt} = -k_a^*[E][A] + k_b^*[EB] + k_3^*[EA][EB] \]  
\( \text{(A5)} \)

\[ \frac{d[B]}{dt} = -k_b^*[B][A] + k_3^*[EB][EAB] \]  
\( \text{(A6)} \)

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 \( (11) \) to \( (13) \) by respectively setting the time derivatives of equations \( (A1) \) to \( (A3) \) to zero. Equation \( (9) \) is obtained by adding together equations \( (A1) \), \( (A3) \) and \( (A5) \), and using the definition of \( [A] \), by equation \( (14) \), Equation \( (10) \) is obtained by adding together equations \( (A2) \), \( (A3) \) and \( (A6) \) with the definition of \( [B] \), by equation \( (15) \).

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

Replacing \( [E] \) in equation \( (17) \) with that obtained from equation \( (19) \), we obtain

\[ [EAB] = \frac{[A][B]}{K_A K_B} [E] \]  
\( \text{(B-1)} \)
By solving $[EA]$ from equation (19), $[EB]$ from equation (20) and combining these with equation (B-1) into equation (16), we find

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

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

$$[EAB] = \left(\frac{[A]}{K_A} + \frac{[B]}{K_B}\right)[E]_r \quad \text{(B-3)}$$

We hence obtain the 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

$$[EA] = \frac{k_s A}{k_s + B}[E] \quad \text{(C-1)}$$

$$[EB] = \frac{k_s B}{k_s A}[E] \quad \text{(C-2)}$$

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

$$[EAB] = \frac{[E]}{k_s + k_s + k_g} \left(\frac{k_s A}{k_s A + k_g B} + \frac{[E]}{k_s A + k_g B}\right) \quad \text{(C-3)}$$

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

\[
\begin{bmatrix}
\bar{E}
\end{bmatrix} = \begin{bmatrix}
\frac{k_2^* [A] + k_3^* [B]}{k_2^*} \\
\frac{k_4^* [A] + k_5^* [B]}{k_2^*}
\end{bmatrix}
\]

When \( \bar{E} \) from equation of (C-5) is entered into equation (9), we then obtain equation (26).

**Appendix D: Deriving the SUPECA kinetics equation**

We first derive the set of linear equations using the first order closure approach (Shankar, 1994; Tang et al., 2007). By entering equations (14)–(16) into equation (23), we have

\[
\begin{bmatrix}
\bar{E}
\end{bmatrix} = \begin{bmatrix}
\frac{k_2^* [A] + k_3^* [B]}{k_2^*} \\
\frac{k_4^* [A] + k_5^* [B]}{k_2^*}
\end{bmatrix}
\]

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

\[
\begin{bmatrix}
E_{AB}
\end{bmatrix} = \frac{k_2^* [A] + k_3^* [B]}{k_2^*} \left( \frac{k_2^* \bar{E}}{k_2^*} \right) + \frac{k_4^* [A] + k_5^* [B]}{k_2^*} - 1
\]

\[
\begin{bmatrix}
E_{AB}
\end{bmatrix} = \frac{1}{k_2^*} \left( \frac{k_2^* \bar{E}}{k_2^*} \right) + \frac{1}{k_2^*} \left( \frac{k_4^* [A] + k_5^* [B]}{k_2^*} \right) - 1
\]
Now if we expand equation (D-1), and keep only the zero and the first order term of

\begin{align*}
k'_i \left[ EA \right] \left[ B \right] & - \left[ EB \right] - [EAB] = k'_i \left[ A \right] \left[ EA \right] - [EAB] \\
	imes \left[ E \right] & - \left[ EB \right] - [EAB]
\end{align*}

we obtain

\begin{align}
& k'_i \left[ B \right] \left[ EA \right] = k'_i \left[ E \right] \left[ A \right] - E \left[ EA \right] - [EAB] \\
& - k'_i \left[ A \right] \left[ EA \right] + \left[ EB \right] + [EAB] \tag{D-2}
\end{align}

which after some rearrangement becomes

\begin{align}
& \left( k'_i + k'_i \left[ B \right] \right) \left[ EA \right] + k'_i \left[ A \right] \left[ EB \right] \\
& + k'_i \left[ A \right] \left[ E \right] \left[ EAB \right] - k'_i \left[ A \right] \left[ E \right] \tag{D-3}
\end{align}

Using the definitions of \( f_A = k'_i \left[ A \right] \), \( f_B = k'_i \left[ B \right] \), and \( T_A = f_A + k'_i \left[ E \right] \), we may rewrite equation (D-3) as

\begin{align}
& \left( T_A + f_B \right) \left[ EA \right] + f_A \left[ EB \right] + \left[ EA \right] \left[ EAB \right] = f_A \left[ E \right] \tag{D-4}
\end{align}

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),

\begin{align}
& f_B \left[ EA \right] + \left( f_A + T_A \right) \left[ EB \right] + f_A \left[ EAB \right] = f_B \left[ E \right] \tag{D-5}
\end{align}

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

\[ 35 \]
\[
\frac{\left[ k_1 \left[ \{A\} - [EA] - [EAB] \right] + k_2 \left[ \{B\} - [EB] - [EAB] \right]\right]}{\left[ E \right] - [EA] - [EB] - [EAB]} = k_1 \left[ EAB \right]
\]  
(D-6)

Once again, by dropping the second and higher order terms of the consumer-

substrate complexes, equation (D-6) can be reduced to

\[
\frac{\left( k_1 \left[ \{A\} + k_2 \left[ \{B\} \right] \right) \left[ E \right]}{\left[ E \right] - [EA] - [EB] - [EAB]} = \left( k_1 \left[ \{A\} + k_2 \left[ \{B\} \right] \right) \right)
\]  
(D-7)

which by aid of \( f_a = k_1 \{A\}, \ f_b = k_2 \{B\} \), \( \bar{f}_a = f_a + k_2 \{E\}, \ \bar{f}_b = f_b + k_2 \{E\} \),

\[
f_{ab} = f_a + f_b, \text{ and } \bar{f}_{ab} = f_a + f_b \text{ becomes}
\]

\[
\left( \bar{f}_a + \bar{f}_b \right) \left[ EA \right] + \left( f_a + f_b \right) \left[ EB \right] + \left( k_1 + f_{ab} \right) \left[ EAB \right] = f_{ab} \left[ E \right]
\]  
(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

\[
\det(M_a) = \begin{vmatrix}
\bar{f}_a + f_b & f_a & \bar{f}_a \\
f_b & f_a + \bar{f}_b & \bar{f}_b \\
\bar{f}_a + f_b & f_a + \bar{f}_b & k_1 + \bar{f}_{ab}
\end{vmatrix}
\]  
(D-9)

and the numerator as

\[
\det(M_a) = \begin{vmatrix}
\bar{f}_a + f_b & f_a & f_a \\
f_b & f_a + \bar{f}_b & f_b \\
\bar{f}_a + f_b & f_a + \bar{f}_b & f_{ab}
\end{vmatrix}
\]  
(D-10)

Equations (D-9) and (D-10) together lead to
With the definitions of $E_{AB}$ equivalent to $|E_{AB}|$, indicating the efforts of all interacting pathways. Bearing this in mind, therefore, we assert that $\frac{k_1}{k_2} |E_{AB}|$ multiplied with the relative contribution of the specific consumption of a certain substrate as represented in ECA kinetics is determined by the consumer reaction potential $k_2 |E_{AB}|$ multiplied with the relative contribution of the specific consumption pathway with respect to all competing pathways ($F_{ij}^{[r]} / (1 + F_{ij} + F_{ij})$). Since SUPECA kinetics is a compatible extension of the 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 $\frac{T_A}{k_2}$ in equation (29) should be equivalent to $F_{ij} + F_{ij}$ 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 $f_A/k_2$, $f_B/k_2$, $\bar{T}_A/k_2$ and $\bar{T}_B/k_2$, using the partition...
equivalence, we can easily define the network form of $f_{ab}$ in equation (40), and the
network form of $\tilde{f}_{ab}$ in equation (45). Further, we observe that the denominator of the
last equation in equation (28) could be rewritten as

$$\frac{(f_a/k'_2)(f_a/k'_2)(f_{ab}/k'_2)}{(f_{ab}/k'_2)} + \frac{(f_a/k'_2)(f_{ab}/k'_2)}{(f_{ab}/k'_2)}$$

which, after replacing $f_a/k'_2$, $f_{ab}/k'_2$, $\tilde{f}_a/k'_2$, $\tilde{f}_{ab}/k'_2$ and $f_{ab}/k'_2$ 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

$$k_{r01}[B][S_1] = k_{r02}[S_2][BS_1] \quad \text{(F-1)}$$

$$k_{r02}[B][S_2] = k_{r01}[S_1][BS_2] \quad \text{(F-2)}$$

$$k_{r01}[BS_1][S_1] + k_{r02}[BS_2][S_1] = k_{f1} [BS_1 S_2] \quad \text{(F-3)}$$

$$K_{M01}[M S_1] = [M][S_1] \quad \text{(F-4)}$$

which are subject to the constraints

$$[S_1] = [S_1] + [MS_1] + [BS_1] + [BS S_1] \quad \text{(F-5)}$$

$$[S_2] = [S_2] + [BS_2] + [BS S_1] \quad \text{(F-6)}$$

$$[B] = [B] + [BS_1] + [BS_2] + [BS S_2] \quad \text{(F-7)}$$
\[ [M]_{\text{eq}} = [M]_0 + [MS_1] \]  

To relate these equations to a dynamic system, \( S_1 \) and \( S_2 \) are substrates, \( B \) is a microbial population, and \( M \) is some sorbent that can reversibly adsorb substrate \( S_1 \).

For benchmarking, \([BS_1S_2]\) 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.

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

The aerobic respiration problem is formulated as

\[
\frac{d[O_2]_{g,s}}{dt} = \left( \frac{[O_2]_a - [O_2]_{g,s}}{R_a + R_s} \right) - F(B_s[O_2]_{g,s}, S, M) \quad \text{(G-1)}
\]

where \([O_2]_{g,s}\) is gaseous oxygen concentration in bulk soil. \([O_2]_a\) is atmospheric oxygen concentration (set to 8.45 mol m\(^{-3}\)). \( S \) is dissolvable organic carbon concentration (set to 3 mol m\(^{-3}\)), and \( M \) is soil mineral sorbent concentration (with variable values). All concentrations are defined with unit 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). \( F(B_s[O_2]_{g,s}, S, M) \) is the oxygen consumption rate calculated using the 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 \([O_2]_{w,b}\) through iterations. The shape of the flux \(F(B,O_2,S,M)\) 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 aqueous phase is used for microbial respiration. This leads to the relationship between near cell aqueous \(O_2\) concentration and the diffusive flux as

\[
\nu_m \frac{d[O_2]_{w,b}}{dt} = -k_{O_2,1} \left[X\right][O_2]_{w,b} + \kappa_{O_2} \left([O_2]_{w,b} - [O_2]_0\right) \tag{G-2}
\]

where the conductance \(\kappa_{O_2}\) is

\[
\left(\frac{\kappa_{O_2}}{4\pi}\right)^{-1} = \frac{\delta}{D_{O_2}} \frac{1}{r_m + \delta} + \frac{1}{D_{O_2}} \frac{r_m + \delta}{r_m + \delta} \tag{G-3}
\]

where \(r_m\) is the radius of the microsite (or aggregate), \(\delta\) is thickness of the water film that covers the microsite (Grant and Rochette, 1994), \(\nu_m\) is the microsite volume \((m^3\text{ site}^{-1})\), and \([O_2]\) is the aqueous oxygen concentration in the bulk soil matrix. \([X]\) is the cell density \((\text{mol cell site}^{-1})\). The unit of \(k_{O_2,1}\) is then \(m^3\text{ (mol cell)}^{-1}\text{ s}^{-1}\).

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

\[
D_{O_2} = \theta D_{O_2,m} + \frac{\epsilon}{\alpha_{O_2}} D_{O_2,b} \tag{G-4}
\]
Now if we assume steady state (aka $d[O_2]/dt = 0$) of equation (G-2), we then obtain

$$[O_2]_{w,0} = \frac{[O_2]_w}{1 + \frac{k_{O_2,w,1}[X]}{\kappa_{O_2}}}$$  \hspace{1cm} \text{(G-5)}$$

which leads to the revised affinity parameter as

$$\tilde{K}_{O_2} = \frac{k_2}{k_{O_2,w,1}} \left( 1 + \frac{k_{O_2,w,1}[X]}{\kappa_{O_2}} \right)$$  \hspace{1cm} \text{(G-6)}$$

where the zero order approximation is made by taking $[X]_w = [X]_w^{T}$.

Now assume that the ball-like microbe is covered with $N$ disc-like porters, 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

$$k_{O_2,w,1} = 4\pi D_{O_2,w,0} r_c \frac{N r_p}{N r_p + \pi r_c} \text{cell}^{-1}$$  \hspace{1cm} \text{(G-7)}$$

where the term $N r_p / (N r_p + \pi r_c)$ accounts for the interference between different porters of a cell. Thus assuming $[X]_w = m$ cell$^{-1}$, we get

$$\tilde{K}_{O_2} = \frac{k_2}{k_{O_2,w,1}} \left( 1 + \frac{k_{O_2,w,1}[X]}{\kappa_{O_2}} \right) = K_{O_2,w,1} \left( 1 + \frac{N r_p}{N r_p + \pi r_c} \frac{m r_c}{r_m} \left( \frac{\delta}{r_m} + \frac{D_{O_2,w,0}}{D_{O_2}} \right) \right)$$  \hspace{1cm} \text{(G-8)}$$

10 With similar procedure, for DOC we have the following

$$\tilde{K}_{DOC} = \frac{k_2}{k_{DOC,w,1}} \left( 1 + \frac{k_{DOC,w,1}[X]}{\kappa_{DOC}} \right) = K_{DOC} \left( 1 + \frac{N r_p}{N r_p + \pi r_c} \frac{m r_c}{r_m} \left( \frac{\delta}{r_m} + \frac{D_{DOC,w,0}}{D_{DOC}} \right) \right)$$  \hspace{1cm} \text{(G-9)}$$
and

\[ k_{\text{DOC},w,1} = 4\pi D_{\text{DOC},w} r_c N_a \frac{N_T}{N_T + \pi r_c} (\text{mol} \cdot \text{cell})^{-1} \]  \hspace{1cm} (G-10)

where \( N_a = 6.02 \times 10^{23} \text{mol}^{-1} \).

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 \( 10^{-6} \text{ m} \), and \( r_p / r_c \) is about \( 10^{-3} \). At 25 °C, the aqueous diffusivity of \( \text{O}_2 \) is about \( 2.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \), therefore, assuming \( N = 3000 \) porters per cell (which covers only 0.3% of the cell’s surface area), we have \( k_{\text{O}_2,w,1} = 1.0 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1} \text{ cell}^{-1} \text{ s}^{-1} \).

Similarly, since the aqueous diffusivity of \( \text{DOC} \) is about \( 10^{-9} \text{ m}^2 \text{ s}^{-1} \), assuming \( N = 3000 \) porters per cell, we have \( k_{\text{DOC},w,1} = 3.7 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1} \text{ cell}^{-1} \text{ s}^{-1} \). Suppose the respiration is bottlenecked by a single respiratory enzyme, and since the enzyme activity varies on the order of \( 10^{-1000} \text{ s}^{-1} \) (English et al., 2006), then by taking \( k_z = 100N \text{ s}^{-1} = 3 \times 10^8 \text{ s}^{-1} \) per cell, we have \( K_{\text{O}_2,w} = 3 \times 10^{-5} \text{ mol} \text{ m}^{-3} \), which agrees well with parameters reported for microbes in aqueous solutions in Button (1985). However, Grant (1991) estimated \( K_{\text{O}_2,w} = 3.0 \times 10^{-3} \text{ mol} \text{ m}^{-3} \); Borden and Bedient (1986) estimated \( K_{\text{O}_2,w} = 3.1 \times 10^{-3} \text{ mol} \text{ m}^{-3} \) for application in soil. We therefore elevated the numerical value to \( K_{\text{O}_2,w} = 3.0 \times 10^{-3} \text{ mol} \text{ m}^{-3} \). According to equations \((G-7)\) and \((G-8)\), such elevation could occur either by increasing the maximum substrate processing rate \( k_z \) or...
decreasing the diffusion $k_{O_2,w,3}$ 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 $K_{DOC,w} = 8.1 \times 10^{-5}$ 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 $K_{DOC,w}$ because it could vary over four orders of magnitudes

(Button, 1985), and our number leads to a good fit between model predictions and data.

Taking all these numbers together, we have

$$\tilde{K}_{O_2,w} = K_{O_2,w} \left(1 + 0.48 \times \frac{mr}{r_m + \delta \left(\frac{r_m}{D_{O_2}} \right)} \right)$$

$$= 3 \times 10^{-3} \left(1 + 0.48 \times \frac{mr}{r_m + \delta \left(\frac{r_m}{D_{O_2}} \right)} \right) \quad \text{(G-11)}$$

$$\tilde{K}_{DOC} = K_{DOC} \left(1 + 0.48 \times \frac{mr}{r_m + \delta \left(\frac{r_m}{D_{DOC}} \right)} \right)$$

$$= 8.1 \times 10^{-5} \left(1 + 0.48 \times \frac{mr}{r_m + \delta \left(\frac{r_m}{D_{DOC}} \right)} \right) \quad \text{(G-12)}$$

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

$$\tilde{K}_{O_2,g} = \frac{\tilde{K}_{O_2,w}}{0.032} = 9.4 \times 10^{-2} \left(1 + 0.48 \times \frac{mr}{r_m + \delta \left(\frac{r_m}{D_{O_2}} \right)} \right) \quad \text{(G-13)}$$

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

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

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

least 1 µm.
For model applications, the 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 $k_z = 100$ s$^{-1}$ per porter, given each cell has 3000 porters, 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 Franzulebbers (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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Figure 1. Relationships of the three dimensions involved in the scaling exercise for numerical modeling of biogeochemical systems. In general, as one scales the Space-Time-Process unit from small scales into large scales, the resultant macroscale equations may appear simpler than the microscale equations.
Figure 2. Graph representation of the ECA kinetics as derived in Tang and Riley (2013a). The equation in blue shows the uptake of substrate $S_i$ by consumer $E_j$ as a function of the normalized substrate flux $F_{c,j}$ and its conjugate flux $F_{r,i}$. Here subscript “c” designates column, and “r” designates row. When $K_{ij}$ is infinity or a very large number compared to other entries in the matrix, the interaction between substrate $S_i$ and consumer $E_j$ can be ignored.

\[ F_{c,j} = \sum_{i=1}^{I} \frac{[S_i]}{K_{ij}} \]

\[ F_{r,i} = \sum_{j=1}^{J} \frac{[E_j]}{K_{ij}} \]

\[ \frac{d[S_{i,j}]}{dt} = \frac{k_{ij}^c [E_j] [S_i]}{1 + F_{c,j} + F_{r,j}} \]
An example unit block for applying the network-oriented SUPECA kinetics

\[ G_{A,j,k} = F_{c,A,k} + F_{r,A,j} \]

\[ F_{c,k} = \sum [A_{j,l}] / K_{A,k} \]

\[ F_{r,j} = \sum [E_{c,l}] / K_{B,b} \]

\[ G_{B,j,k} = F_{c,B,k} + F_{r,B,j} \]

\[ F_{c,k} = \sum [A_{j,l}] / K_{A,k} \]

\[ F_{r,j} = \sum [E_{c,l}] / K_{B,b} \]

Figure 3. Graph representation for the relationships between substrates, consumers, and normalized fluxes and their conjugates for a block unit of a large substrate-consumer network.
Figure 4. 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 related distributions of parameters are in Figure S1 of the supplemental material.
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.
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).
Figure 7. Simulated moisture response functions using default affinity parameter for O₂. The respiration data are normalized with the peak value from the case with zero soil minerals (i.e., black line in Figure). Note here all three lines overlap each other almost perfectly.