1	SUPECA kinetics for scaling redox reactions in networks of mixed substrates and
2	consumers and an example application to aerobic soil respiration
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8	Abstract. Several land biogeochemical models used for studying carbon-climate
9	feedbacks have begun explicitly representing microbial dynamics. However, to our
10	knowledge, there has been no theoretical work on how to achieve a consistent scaling of
11	the complex biogeochemical reactions from microbial individuals to populations,
12	communities, and interactions with plants and mineral soils. We focus here on developing
13	a mathematical formulation of the substrate-consumer relationships for consumer
14	mediated redox reactions of the form $A+B \rightarrow products$, where products could be, e.g.,
15	microbial biomass or bio-products. Under the quasi-steady-state approximation, these
16	substrate-consumer relationships can be formulated as the computationally difficult full
17	Equilibrium Chemistry problem or approximated analytically with the Dual Monod (DM)
18	or Synthesizing Unit (SU) kinetics. We find that DM kinetics are scaling inconsistent for
19	reaction networks because: (1) substrate limitations are not considered, (2) contradictory
20	assumptions are made regarding the substrate processing rate when transitioning from
21	single- to multi-substrate redox reactions, and (3) the product generation rate cannot be
22	scaled from one to multiple substrates. In contrast, SU kinetics consistently scale the
23	product generation rate from one to multiple substrates, but predict unrealistic results as

1	consumer abundances reach large values with respect to their substrates. We attribute this
2	deficit to SU's failure to incorporate substrate limitation in its derivation. To address
3	these issues, we propose SUPECA (SU Plus Equilibrium Chemistry Approximation)
4	kinetics, which consistently impose substrate and consumer mass balance constraints. We
5	show that SUPECA kinetics satisfy the partition principle, i.e., scaling invariance across a
6	network of an arbitrary number of reactions (e.g., as in Newton's Law of motion and
7	Dalton's law of partial pressures). We tested SUPECA kinetics with the equilibrium
8	chemistry solution for some simple problems and found SUPECA outperformed SU
9	kinetics. As an example application, we show that a steady-state SUPECA-based
10	approach predicted an aerobic soil respiration moisture response function that agreed well
11	with laboratory observations. We conclude that, as an extension to SU and ECA kinetics,
12	SUPECA provides a robust mathematical representation of complex soil substrate-
13	consumer interactions and can be applied to improve ESM land models.
14	
15	Keywords: Dual-Monod kinetics, Synthesizing Unit, SUPECA kinetics, soil respiration,
16	trait-based modeling
17	
18	1. Introduction
19	Near surface soils holds more than twice the carbon in the current atmosphere;
20	therefore a small change in land carbon dynamics can imply significant feedbacks to the
21	ongoing climate warming (Ciais et al., 2013). This sensitivity has motivated research to
22	better understanding Earth's land biogeochemical cycles, both for prediction and
23	assessing the efficacy of climate mitigation and adaptation strategies. To date, however,

1	soil biogeochemical models suffer from high uncertainty (e.g., Arora et al., 2013;
2	Bouskill et al. 2014; Friedlingstein et al., 2014; He et al. 2016). For instance, eight
3	CMIP5 Earth System Models (ESMs) predicted that net land carbon uptake varies from
4	22 to 456 Pg C for the 2006-2100 period under the Representative Concentration
5	Pathway 4.5 (RCP4.5; Shao et al., 2013). Similarly, Todd-Brown et al. (2013) estimated
6	that 16 CMIP5 ESMs predicted contemporary global soil carbon stocks ranging from 510
7	to 3040 Pg C to 1 m depth, while the most recent empirical estimation is 1408 ± 154 Pg C
8	to 1 m depth and 2060±217 Pg C to 2 m depth (Batjes, 2016).
9	The predictive power of existing land biogeochemical models is diminished by
10	uncertainties from structural design, numerical implementation, model parameterization,
11	initial conditions, and forcing data (Tang and Zhuang, 2008; Tang et al., 2010; Luo et al.,
12	2015; Wieder et al., 2015a; Blanke et al., 2016; Tang and Riley, 2016). Among these,
13	developing better model structures and mathematical formulations have been identified as
14	priorities. One proposed structural improvement is to include explicit microbial dynamics
15	(Wieder et al., 2015b), which may enable better predictions of global soil carbon stocks
16	(Wieder et al., 2013), priming effects (Sulman et al., 2014), vertical soil carbon profiles
17	(Riley et al., 2014; Dwivedi et al., 2017), and respiratory temperature sensitivity (Tang
18	and Riley, 2015). A second proposal is to explicitly resolve ecosystem nutrient cycles,
19	following the hypothesis that the potential for increasing land ecosystem carbon uptake
20	from atmospheric CO ₂ fertilization could be limited by nutrient availability (Vitousek,
21	1982; Shi et al., 2015; Wieder et al., 2015c).
22	A common feature that underlies these two proposed model structural
23	improvements are substrate-consumer interactions, which affect microbial substrate

1	decomposition (Grant et al., 1993; Tang and Riley, 2013a; Riley et al., 2014; Le Roux et
2	al., 2016), mineral soil interactions with adsorptive substrates (Smith, 1979; Grant et al.,
3	1993; Resat et al., 2011; Tang and Riley, 2015; Dwivedi et al., 2017), and plant-microbe
4	competition for nutrients (Grant, 2013; Zhu et al., 2016a, 2016b, 2017). In soil, because
5	there are many consumers competing for many substrates in different places at different
6	times, soil biogeochemical models must be able to scale consistently across space, time,
7	and processes. Scaling across spatial and temporal dimensions is achieved through spatial
8	and temporal discretization and integration, which has been intensively studied elsewhere
9	(e.g., Kolditz et al., 1998; Mao et al., 2006). Here we examine scaling along the less
10	studied third dimension (process), focusing on development of a consistent mathematical
11	formulation of substrate-consumer interactions.
12	Previously, we studied a simple configuration of this consumer-substrate
13	interaction, i.e., the network of single-substrate Monod type reactions (discussed later),
14	and developed a scaling method, the Equilibrium Chemistry Approximation (ECA)
15	kinetics (Tang and Riley, 2013a). ECA kinetics significantly improved the modeling of
16	plant-microbial nutrient competition in the ACME land biogeochemical model (Zhu and
17	Riley, 2015; Zhu et al., 2016a, 2016b, 2017), and was recently cited as one of the most
18	promising methods to improve representation of nutrient competition in ESMs (Achat et
19	al., 2016; Niu et al., 2016). The ECA method also successfully explained why organo-
20	mineral interactions can slow soil organic matter decomposition rates and how lignin-
21	cellulose ratios (Melillo et al., 1989) can be stabilized during litter decomposition (Tang
22	and Riley 2013a 2015)

1	Following Tang and Riley (2013a), we start our analysis here by assuming a
2	certain homogeneous space-time-process unit in soil, within which there are generally
3	three types of substrate-consumer relationships: (1) single-substrate Monod type (aka A-
4	E type) reactions in the form of $A \rightarrow products$; (2) two-substrate (aka AB-E type) redox
5	reactions in the form of $A+B \rightarrow products$, where substrate A and B are called
6	complementary because they both are required for the redox reaction to proceed; and (3)
7	multi-substrate (>2) reactions $\sum_{i} A_{i} \xrightarrow{E} products$. The scaling of single-substrate Monod
8	type reactions has been extensively discussed in Tang and Riley (2013a), and is resolved
9	with ECA kinetics (more discussion on ECA kinetics for process scaling will be provided
10	in later sections when discussing SUPECA kinetics). Further, because many multi-
11	substrate reactions can be separated into a combination of single-substrate reactions and
12	redox-reactions, our discussion below focuses on achieving a consistent kinetic scaling
13	from a single redox reaction to many reactions in a network.
14	Mathematically, the problem can be addressed with an explicit formulation of all
15	kinetic processes using ordinary differential equations accounting for all substrates and
16	consumers (Chellaboina et al., 2009). However, such a formulation would require too
17	many parameters and would be numerically very difficult to solve because of its multi-
18	temporal scale nature. By making the quasi-steady-state-approximation (QSSA), i.e.,
19	assuming that product generation from the consumer-substrate complex is much slower
20	than equilibration between consumers, substrates, and consumer-substrate complexes

- 21 (Briggs and Haldane, 1925; Pedersen et al., 2008), the full kinetic problem is reduced to
- 22 the simpler Equilibrium Chemistry (EC) form (e.g., Chellaboina et al., 2009). However,

1 the EC formulation is also usually very difficult to solve numerically. Therefore,

analytical approximations to the EC formulation are generally made.

2

3 Two classic analytical approximations for modeling redox-reactions are Dual 4 Monod (DM) kinetics (e.g., Yeh et al., 2001) and Synthesizing Unit (SU) approach 5 (Kooijman, 1998; Brandt et al., 2003). Although both of these are special cases of the EC 6 formulation (Kooijman, 2010; Tang and Riley, 2013a), they make different assumptions 7 regarding the relative magnitudes of involved kinetic parameters. For this, Kooijman 8 (2010) has shown that DM kinetics require the consumer-substrate complex dissociation 9 rate to be much larger than the product generation rate from the complexes. In contrast, 10 single-substrate Monod kinetics (Monod, 1949) or Michaelis-Menten (MM) kinetics 11 (Michaelis and Menten, 1913; which is mathematically identical to the empirical Monod 12 kinetics) do not impose this requirement on its parameters. Moreover, in applications to r-13 K scaling (e.g., Tilman, 1982; Litchman and Klausmeier, 2008), single-substrate Monod 14 kinetics require the product-generation rate to be faster than the dissociation rate of 15 consumer-substrate complexes. This contrasting requirement on the relative magnitudes 16 of parameters, as we will show later, implies that DM kinetics cannot achieve consistent 17 scaling of substrate-consumer interactions for generic biogeochemical modeling.

We define a kinetic formulation to have consistent process scaling when the formulated substrate-consumer relationship: (1) can seamlessly transition from a single substrate-consumer pair to a network of many substrate-consumer pairs without changing its mathematical form (aka the partition principle as in Newton's second Law of motion, Feynman et al., 1963) and (2) does not predict any singularity over the range of substrate and consumer concentrations (aka the non-singular principle, e.g., Schnell and Maini,

2000; Tang, 2015). The full kinetics and EC formulations both satisfy these two criteria,
 which can be explained using the following example network of consumer-substrate

3 relationships:

$$S_{i} + E_{j} \underset{k_{1,j}}{\overset{k_{1,j}^{*}}{\longleftrightarrow}} E_{j} S_{i} \xrightarrow{k_{2,j}^{*}} P_{ij} + E_{j}$$

$$\tag{1}$$

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

9

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

$$\frac{d\left[S_{i}\right]}{dt} = -\left[S_{i}\right]\sum_{j}\left(k_{1,ij}^{+}\left[E_{j}\right]\right) + \sum_{j}\left(k_{1,ij}^{-}\left[E_{j}S_{i}\right]\right)$$
(2)

$$\frac{d\left[E_{j}S_{i}\right]}{dt} = k_{1,ij}^{+}\left[S_{i}\right]\left[E_{j}\right] - \left(k_{1,ij}^{-} + k_{2,ij}^{+}\right)\left[E_{j}S_{i}\right]$$
(3)

$$\frac{d\left[E_{j}\right]}{dt} = -\left[E_{j}\right]\sum_{i}\left(k_{1,ij}^{+}\left[S_{i}\right]\right) + \sum_{i}\left(\left(k_{1,ij}^{-} + k_{2,ij}^{+}\right)\left[E_{j}S_{i}\right]\right)$$
(4)

10 where $\begin{bmatrix} x \end{bmatrix}$ indicates the concentration of x.

11 The first summation in equations (2) and (4) satisfies the partition principle. For 12 instance, for equation (4), by defining an appropriate mean specific substrate affinity $k_{1,j}^+$,

13 the summation
$$\sum_{i} \left(k_{1,ij}^{+} \left[S_{i} \right] \right)$$
 can be recast as $k_{1,ij}^{+} \left[S \right]$, in which $\left[S \right] = \sum_{i} \left[S_{i} \right]$ resembles

- 1 Dalton's law of partial pressures (and many other similar relationships in physics, e.g.,
- 2 Newton's second law of motion (Feynman et al., 1963)).
- 3 Meanwhile, that the full kinetic formulation satisfies the nonsingular principle can
 4 be verified by noting that, at any time:

$$\begin{bmatrix} S_i \end{bmatrix} + \sum_j \begin{bmatrix} E_j S_i \end{bmatrix} = \begin{bmatrix} S_i \end{bmatrix}_T$$
(5)

- and that consumption of S_i is through generation of product from $[E_j S_i]$. Therefore, by combining equations (2), (3), and (5), the overall consumption rate of S_i (i.e.,
- 7 $\sum_{j} k_{2,ij}^+ \left[E_j S_i \right] \right)$ is always smaller than $\left[S_i \right]_T \sum_{j} k_{2,ij}^+$, even when consumers have high
- 8 abundances relative to their substrates, a common situation in *in vivo* cells (Sols and
 9 Marco, 1970) and in plant-microbial competition for limited soil nutrients (Vitousek,
- 10 1982; Schimel and Bennett, 2004; Vitousek et al., 2010).
- 11 Since the EC formulation is obtained by applying the QSSA to the full kinetic formulation (i.e., $d\left[E_{j}S_{i}\right]/dt \approx 0$ for equation (3)), it automatically satisfies the two 12 13 criteria for consistent process scaling. However, Monod kinetics is scaling inconsistent 14 when it is applied, for example, to single-substrate competition by multiple populations, 15 or to multi-substrate consumption by a single population (e.g., Williams, 1973; Schnell 16 and Mendoza, 2000; Tang et al., 2010; Riley et al., 2011, 2014; Allison, 2012; Bouskill et 17 al., 2012; Wieder et al., 2013, 2014). Specifically, that Monod kinetics violates the 18 partition principle can be shown from the following inequality:

$$F_{j} = \left[E_{j}\right] \sum_{i} \frac{k_{2,ij}^{+} \left[S_{i}\right]}{K_{ij} + \left[S_{i}\right]} \neq \left[E_{j}\right] \frac{\sum_{i} k_{2,ij}^{+} \left[S_{i}\right] / K_{ij}}{1 + \sum_{i} \left[S_{i}\right] / K_{ij}}$$
(6)

Here F_i describes the uptake of all substrates S_i by consumer E_j . The left hand side of 1 2 the inequality is the uptake computed by directly applying Monod kinetics, while the 3 right hand side is obtained by applying competitive Monod kinetics (e.g., Litchman and 4 Klausmeier, 2008). Inequality (6) is even true when K_{ij} is independent of *i*. Besides 5 being inconsistent with the partition principle, Monod kinetics also violates the nonsingular principle, which can be demonstrated by observing that, as $\begin{bmatrix} E_j \end{bmatrix}$ approaches 6 very large values, so does F_j . This linear dependence of F_j on $\begin{bmatrix} E_j \end{bmatrix}$ results in large 7 biases of predicted parametric sensitivities under high ratios of $\begin{bmatrix} E_i \end{bmatrix}$ with respect to 8 9 substrates (Schnell and Maini, 2000; Tang and Riley, 2013a; Tang, 2015), and is 10 inconsistent with the non-singularity implied in equation (5).

11 For competitive Monod kinetics on the right hand side of inequality (6), we may 12 define $K_j = \left[S\right] / \left(\sum_i \left[S_i\right] / K_{ij}\right)$ (e.g., Murdoch, 1973), resulting in:

$$F_{j} = \left[E_{j}\right] \frac{k_{2,j}^{+}\left(\sum_{i}\left[S_{i}\right]\right)/K_{j}}{1 + \left(\sum_{i}\left[S_{i}\right]\right)/K_{j}} = \left[E_{j}\right] \frac{k_{2,j}^{+}\left[S\right]/K_{j}}{1 + \left[S\right]/K_{j}}$$

$$(7)$$

13 where $[S] = \sum_{i} [S_i]$ designates the total free concentrations of all substrates. Equation 14 (7) therefore carries the same partition principle implied in the first summation in 15 equation (4) of the full kinetic formulation, suggesting that competitive Monod kinetics

1	satisfy the partition principle for consistent scaling of substrate-consumer relationships.
2	Nevertheless, because competitive Monod kinetics are linear in $\begin{bmatrix} E_j \end{bmatrix}$, as are classic
3	Monod kinetics, they still violate the non-singular principle for consistent scaling.
4	In Tang (2015) (and also in Borghans et al. (1996) and Tang and Riley (2013a)),
5	it was shown that the linear dependence of F_j on $\begin{bmatrix} E_j \end{bmatrix}$ as predicted by Monod kinetics
6	and similarly by competitive Monod kinetics is due to their failure to impose the substrate
7	mass (or surface area) balance in deriving their mathematical formulations. This problem
8	has been rectified in ECA kinetics (Tang and Riley, 2013a), which was shown to predict
9	much more accurate parametric sensitivity than Monod kinetics when compared with
10	analytical solutions (Tang, 2015). Since the success of all model calibrations relies on the
11	accuracy of modeled response variables' sensitivity to model parameters (e.g., Wang et
12	al., 2001; Williams et al, 2005; Tang and Zhuang, 2009; van Werkhoven et al., 2009;
13	Qian et al., 2015), and plant-microbial competitions of nutrients often occur under high
14	consumer abundances with respect to their substrates (as corroborated by the nitrogen and
15	phosphorus limitations that are commonly observed in natural ecosystems; e.g., Vitousek
16	et al. (2010)), developing robust biogeochemical models requires substrate kinetics that
17	give accurate parametric sensitivities under a wide range of parameter values.
18	We therefore ask the question: how should we achieve a consistent scaling from
19	the simplest redox reaction $A+B \rightarrow products$ (i.e., AB-E type) to a network that mixes
20	many redox reactions and even single substrate Monod-type reactions? Aside from the
21	two criteria (i.e., the partition principle and non-singularity) discussed above, we suggest
22	a third criterion that a consistent scaling of substrate-consumer relationships should

seamlessly transition from a single substrate A-E Monod-type reaction to the AB-E type
 redox reaction without making contradictory assumptions of the parameters in its
 theoretical derivation.

4 In the following, we address the above process-scaling question by first 5 presenting the step-by-step derivation of DM kinetics and SU kinetics from the EC formulation of the redox reaction $A+B \rightarrow products$. Conceptually, DM kinetics can be 6 7 viewed as a direct application of chemical kinetics that the reaction rate of substrates A 8 and B with consumer E is determined by the product of A and B's binding probability to *E* (which in Monod form is $[A]/(K_A + [A])$ for substrate *A*, and $[B]/(K_B + [B])$ for 9 10 substrate B). Kooijman (1998) was the first to derive SU kinetics using queue theory 11 (e.g., Gross et al., 2011) and Brandt et al. (2003) discussed its use for AB-E type redox 12 reactions. The following derivation stresses scaling-inconsistencies implied in DM and 13 SU kinetics, and we will show that DM kinetics cannot be extended for consistent 14 process scaling of substrate-consumer relationships. We then present SUPECA kinetics, 15 which remedies the inconsistencies in SU kinetics. We demonstrate the benefits of using 16 SUPECA kinetics in terms of numerical accuracy and present a proof-of-concept 17 example by modeling the moisture control of aerobic soil respiration. Finally, we discuss 18 how one can apply SUPECA kinetics to trait-based modeling approaches in various 19 biogeochemical systems (e.g., Bouskill et al., 2012; Follows et al., 2007; Litchman and 20 Klausmeier, 2008).

21 2. Derivation of ECA kinetics for AB-E type redox reaction A+B→products 22 2.1 Governing equations

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

1

By law of mass action and the total QSSA (tQSSA; e.g., see Borghans et al.,

5 1996; Tang and Riley, 2013a), we have the governing equations (appendix A):

$$\frac{d\left[A\right]_{T}}{dt} = -k_{2}^{+}\left[EAB\right]$$
⁽⁹⁾

$$\frac{d\left[B\right]_{T}}{dt} = -k_{2}^{+}\left[EAB\right]$$
(10)

$$k_{A}^{+} \begin{bmatrix} E \end{bmatrix} \begin{bmatrix} A \end{bmatrix} + k_{B}^{-} \begin{bmatrix} EAB \end{bmatrix} = \left(k_{A}^{-} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}\right) \begin{bmatrix} EA \end{bmatrix}$$
(11)

$$k_{B}^{+}\left[E\right]\left[B\right] + k_{A}^{-}\left[EAB\right] = \left(k_{B}^{-} + k_{A}^{+}\left[A\right]\right)\left[EB\right]$$

$$(12)$$

$$k_{A}^{+} \begin{bmatrix} EB \end{bmatrix} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} EA \end{bmatrix} \begin{bmatrix} B \end{bmatrix} = \left(k_{A}^{-} + k_{B}^{-} + k_{2}^{+}\right) \begin{bmatrix} EAB \end{bmatrix}$$
(13)

6 where

$$\begin{bmatrix} A \end{bmatrix}_{T} = \begin{bmatrix} A \end{bmatrix} + \begin{bmatrix} EA \end{bmatrix} + \begin{bmatrix} EAB \end{bmatrix}$$
(14)

$$\begin{bmatrix} B \end{bmatrix}_{T} = \begin{bmatrix} B \end{bmatrix} + \begin{bmatrix} EB \end{bmatrix} + \begin{bmatrix} EAB \end{bmatrix}$$
(15)

$$\begin{bmatrix} E \end{bmatrix}_{T} = \begin{bmatrix} E \end{bmatrix} + \begin{bmatrix} EA \end{bmatrix} + \begin{bmatrix} EB \end{bmatrix} + \begin{bmatrix} EAB \end{bmatrix}$$
(16)

The derivation of substrate kinetics is therefore equivalent to solving for $\begin{bmatrix} EAB \end{bmatrix}$ from the 1 2 EC problem defined by equations (11)-(16). However, because this set of equations is 3 non-linear, and no analytical solutions are available (to our knowledge), some 4 linearization is warranted to obtain analytical approximations. As we describe below, 5 linearization with different assumptions lead to DM, SU, and SUPECA kinetics. 6 To clarify, we note that obtaining the substrate kinetics only requires solving 7 equations (11)-(16); various production and destruction terms can be added to equations 8 (9) and (10) to form a full dynamic model (e.g., Maggi and Riley, 2009) without affecting 9 our derivation below. 10 2.2 Dual Monod kinetics and synthesizing unit kinetics 11 One method to linearize equations (11)-(16) is to assume that concentrations of 12 consumer-substrate complexes are so small that free substrate concentrations are effectively equal to bulk concentrations (e.g., for substrate A: $\begin{bmatrix} A \end{bmatrix}_T = \begin{bmatrix} A \end{bmatrix}$). This 13 14 approach, when combined with different assumptions on the relative magnitudes of 15 kinetic parameters, leads to the popular DM kinetics and the two-substrate SU kinetics. 16 2.2.1 Dual Monod kinetics 17 We now derive DM kinetics. Adopting the equilibrium approximation that 18 forward binding between consumer and substrate is in rapid equilibrium with backward

- 19 dissociation of consumer-substrate complex (e.g., Michaelis and Menten, 1913; Pyun,
- 20 1971), we have the following

$$\begin{bmatrix} EA \end{bmatrix} \begin{bmatrix} B \end{bmatrix} = \frac{k_B^-}{k_B^+} \begin{bmatrix} EAB \end{bmatrix} = K_B \begin{bmatrix} EAB \end{bmatrix}$$
(17)

$$\begin{bmatrix} EB \end{bmatrix} \begin{bmatrix} A \end{bmatrix} = \frac{k_A^-}{k_A^+} \begin{bmatrix} EAB \end{bmatrix} = K_A \begin{bmatrix} EAB \end{bmatrix}$$
(18)

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

$$\begin{bmatrix} E \end{bmatrix} \begin{bmatrix} A \end{bmatrix} = \frac{k_A^-}{k_A^+} \begin{bmatrix} EA \end{bmatrix} = K_A \begin{bmatrix} EA \end{bmatrix}$$
(19)

$$\begin{bmatrix} E \end{bmatrix} \begin{bmatrix} B \end{bmatrix} = \frac{k_B^-}{k_B^+} \begin{bmatrix} EB \end{bmatrix} = K_B \begin{bmatrix} EB \end{bmatrix}$$
(20)

2 By solving for [EAB] from equations (14)-(16) using equations (17)-(20), we

3 obtain the consumer-substrate complex for DM kinetics (see Appendix B)

$$\frac{d\left[A\right]_{T}}{dt} = -k_{2}^{+}\left[E\right]_{T}\frac{\left[A\right]}{K_{A}} + \left[A\right]\frac{\left[B\right]}{K_{B}} + \left[B\right]}$$
(21)

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

$$\frac{d\left[A\right]_{T}}{dt} = -k_{2}^{+} \frac{\left[E\right]_{T} \left[B\right]}{K_{B} + \left[B\right]}$$
(22)

6 We note that the half saturation coefficient $K_B = k_B^-/k_B^+$ in equation (22) is different from 7 its usual definition (i.e., $K_B = (k_2^+ + k_B^-)/k_B^+$) if one derives MM kinetics rigorously 8 starting from a single substrate and single consumer system (e.g., Tang, 2015). For this 9 reason, we assert that DM kinetics cannot achieve a self-consistent scaling from one-10 substrate reaction to multiple-substrate reactions. More specifically, by substituting 11 equations (17) and (18) into equation (13), one obtains $k_2^+ = 0$, or at least

1	$k_2^+ \ll \max(k_A^-, k_B^-)$, which states that the consumer is very inefficient in processing the
2	substrate. However, MM kinetics does not require the dissociation rate to be much higher
3	than the product generation rate from the consumer-substrate complex, i.e.
4	$k_2^+ \ll \max(k_A^-, k_B^-)$ (e.g., Briggs and Haldane, 1925). Nor do the high dissociation rates of
5	[EA], $[EB]$, and $[EAB]$ favor the consumer's assimilation of substrates under usual
6	substrate concentrations (e.g., Van Slyke and Cullen, 1914), even though a high
7	dissociation rate of the enzyme-substrate complexes may possess some theoretical
8	advantage under high substrate concentrations when the consumer is a single enzyme
9	(Reuveni et al., 2014). To the contrary, most existing applications tend to assume
10	$k_2^+ \gg k_A^-$ and $k_2^+ \gg k_B^-$ (e.g., Holling, 1959, 1966; Aksnes and Egge, 1991; Armstrong,
11	2008; Bonachela et al., 2011), such that $K_B \approx k_2^+ / k_B^+$ for MM kinetics and r-K selection
12	can be explained by linking k_2^+ with growth rate, and k_A^+ and k_B^+ with substrate
13	competitive ability (e.g., Litchman and Klausmeier, 2008). Therefore, for biogeochemical
14	modeling, DM and MM (or Monod) kinetics are based on different assumptions of the
15	relative magnitudes of kinetic parameters, and no smooth transition from single- (MM) to
16	multi-substrate (DM) kinetics exists.

2.2.2 Synthesizing unit kinetics

18 In deriving SU kinetics for the redox reaction network represented in equation (8), 19 consumer E is viewed as a generalized enzyme that generates bio-products by processing 20 substrates A and B. SU computes the specific reaction rate per unit concentration of E as the product generation rate k_2^+ times the probability that E binds with both substrates A 21

- 1 and B (which is $[EAB]/[E]_T$). SU kinetics requires the sufficient flux condition
- 2 $k_A^+ [A] \gg k_B^-$ and $k_B^+ [B] \gg k_A^-$ (Kooijman, 2010). Defining $\tilde{k}_2^+ = k_A^- + k_B^- + k_2^+$, equations
- 3 (11)-(13) become

$$k_{A}^{+}\left[E\right]\left[A\right] = k_{B}^{+}\left[B\right]\left[EA\right]$$
(23)

$$k_{B}^{+}\left[E\right]\left[B\right] = k_{A}^{+}\left[A\right]\left[EB\right]$$
(24)

$$k_{A}^{+} \begin{bmatrix} EB \end{bmatrix} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} EA \end{bmatrix} \begin{bmatrix} B \end{bmatrix} = \tilde{k}_{2}^{+} \begin{bmatrix} EAB \end{bmatrix}$$
(25)

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

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

5 The two-substrate SU kinetics (equation (26)) can also be viewed as a special case 6 of the general SU kinetics for any number of complementary substrates, which was first 7 derived by Kooijman (1998) based on queue theory (e.g., Gross et al., 2011). Kooijman 8 (1998) assumed that consumers act like synthesizing units, which process substrates in 9 two steps: binding and production. He then assumed that all flux rates (including production rates k_2^+ and substrate binding rates $k_A^+[A]$ and $k_B^+[B]$) are of Poisson 10 11 distributions, and calculated the overall specific substrate consumption rate as the 12 reciprocal of the expected total processing time (i.e., the denominator of equation (26)). 13 The last term in the denominator of equation (26) comes from the assumption of parallel binding of substrates A and B to E, which disappears if sequential binding is assumed 14 15 (e.g., Brandt et al., 2003).

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

$$\frac{d\left[A\right]_{T}}{dt} = -\frac{k_{2}^{+}\left[E\right]_{T}}{1 + \frac{\tilde{k}_{2}^{+}}{k_{B}^{+}\left[B\right]}} = -\frac{k_{2}^{+}\left[E\right]_{T}\left[B\right]}{\frac{\tilde{k}_{2}^{+}}{k_{B}^{+}} + \left[B\right]}$$
(27)

3 which has a half saturation coefficient similar to what would be derived for a single 4 substrate, single consumer reaction (e.g., Tang, 2015). By assuming Poisson distribution 5 of the kinetic parameters, it can also be shown for a single enzyme molecule that MM 6 kinetics represent the statistical mean of the fluctuating activity of the enzyme (English et 7 al., 2006; Reuveni et al., 2014). That kinetics of both single-substrate reactions and two-8 substrate redox reactions can be similarly derived using statistical theory and that 9 equations (26) and (27) can be obtained from the EC formulation using consistent 10 assumptions of the relative magnitudes of kinetic parameters indicates, in contrast to DM 11 kinetics, that SU kinetics is able to scale consistently between one- and two-substrate 12 redox reactions.

13 2.3. SUPECA kinetics

In Tang and Riley (2013a) and Tang (2015), it was shown that the derivation of MM kinetics ignores the substrate mass balance constraint, resulting in MM kinetics predicting inaccurate parametric sensitivity over the wide range of substrate to consumer ratios (e.g., Figure 1 in Tang (2015)). This problem is particularly acute when consumer abundances are high with respect to their substrates, a situation that may occur in *in vivo* conditions (Sols and Marco, 1970; Schnell and Maini, 2000) or when consumers interact

1	with mineral surfaces, such as microbial decomposition of soil organic matter or plant-
2	microbial competition for soil nutrients (Schimel and Bennett, 2004; Vitousek et al.,
3	2010; Resat et al., 2011; Tang and Riley, 2015; Zhu et al., 2016a). In the above, we also
4	note that the substrates' mass balance constraints (equations (14) and (15)) are not used in
5	deriving DM and SU kinetics, suggesting that both DM and SU kinetics may suffer from
6	the same deficiency as MM kinetics. Further, since DM kinetics fail to consistently scale
7	from a single to two substrates, we below focus on combining SU and ECA kinetics into
8	SUPECA kinetics to achieve a scalable and non-singular formulation of redox reactions.
9	As implied in equations (9)-(16), the derivation of substrate kinetics requires
10	solving for $[EAB]$ from nonlinear equations (11)-(16), whose analytical solutions are not
11	available. To obtain improved solutions as compared to SU kinetics, we applied a first
12	order closure approach (appendix D; which is the perturbation method truncated to first
13	order accuracy that describes the first order term using appropriate mean states (e.g.,
14	Shankar, 1994; Tang et al., 2007)) to the system formed by equations (11)-(16), leading
15	to SUPECA kinetics:

$$\frac{d\left[A\right]_{T}}{dt} = -\frac{\left[E\right]_{T}}{\frac{1}{k_{2}^{+}}\frac{\overline{f}_{A}\overline{f}_{B}f_{AB}}{f_{A}f_{B}\overline{f}_{AB}} + \frac{1}{f_{A}} + \frac{1}{f_{B}} - \frac{f_{A}\overline{f}_{B} + \overline{f}_{A}f_{B} - \overline{f}_{A}\overline{f}_{B}}{f_{A}f_{B}\overline{f}_{AB}}} = -\frac{k_{2}^{+}\left[E\right]_{T}\left(f_{A}/k_{2}^{+}\right)\left(f_{B}/k_{2}^{+}\right)}{\frac{\overline{f}_{A}\overline{f}_{B}}{k_{2}^{+}}\frac{f_{AB}}{k_{2}^{+}} + \frac{f_{AB}}{k_{2}^{+}} - \frac{f_{A}\overline{f}_{B} + \overline{f}_{A}f_{B} - \overline{f}_{A}\overline{f}_{B}}{k_{2}^{+}\overline{f}_{AB}}} \tag{28}$$

16 where
$$f_A = k_A^+ [A]_T$$
, $f_B = k_B^+ [B]_T$, $\overline{f}_A = f_A + k_A^+ [E]_T$, $\overline{f}_B = f_B + k_B^+ [E]_T$, $f_{AB} = f_A + f_B$,

17 and
$$\overline{f}_{AB} = \overline{f}_A + \overline{f}_B$$
. In equation (28), we assumed $k_2^+ \gg k_A^-$ and $k_2^+ \gg k_B^-$, so that $k_2^+ \approx \tilde{k}_2^+$

1 (this relationship will be used throughout the remainder of this paper). It can then be 2 verified that if $[E]_T \ll [A]_T$ and $[E]_T \ll [B]_T$, SUPECA kinetics as represented in 3 equation (28) becomes SU kinetics in equation (26). Further, if one of the two substrates,

4 say $[B]_{T}$, becomes unlimited, equation (28) is reduced to

$$\frac{d\left[A\right]_{T}}{dt} = -\frac{\left[E\right]_{T}}{\frac{1}{k_{2}^{+}}\frac{\overline{f}_{A}}{f_{A}} + \frac{1}{f_{A}}} = -\frac{f_{A}\left[E\right]_{T}}{1 + \frac{\overline{f}_{A}}{k_{2}^{+}}}$$
(29)

5 which, by using the definition of f_A and \overline{f}_A , becomes the single substrate ECA kinetics 6 equation (Tang, 2015).

7 **3. SUPECA kinetics for a network of reactions**

8 In actual biogeochemical systems, it is more common for many substrates to be 9 processed by many consumers concurrently (and such an assumption is implicitly 10 assumed in the space-time-process unit of any biogeochemical model). To consistently 11 handle such situations, Tang and Riley (2013a) derived ECA kinetics (see Figure 1 for a 12 graphic demonstration) for calculating the consumption of a substrate S_i by a consumer

13 E_j in a network of single substrate reactions $A \rightarrow products$:

$$\frac{d\left[S_{i}\right]_{T,j}}{dt} = -\frac{k_{2,ij}^{+}\left[E_{j}\right]_{T}\left(\left[S_{i}\right]_{T}/K_{ij}\right)}{1 + \sum_{l=1}^{l=l}\left(\left[S_{l}\right]_{T}/K_{lj}\right) + \sum_{l=1}^{l=l}\left(\left[E_{l}\right]_{T}/K_{il}\right)}$$
(30)

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

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

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

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

5 equation (30) can then be rewritten as

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

6 The normalized substrate flux as defined in equation (31) and its conjugate in equation
7 (32) implies that the consumption of substrate
$$S_i$$
 by consumer E_j as described by ECA
8 kinetics in equation (33) may be interpreted as either (i) the potential substrate processing
9 rate of E_j (i.e., $k_{2,ij}^+ [E_j]$) weighted by the relevant importance of the reaction pathway
10 $S_i \stackrel{E_j}{\rightarrow} products$ (i.e., $F_{c,j}^{\{i\}}$) under the influence of all competing substrate fluxes $F_{c,j}^{\{l\}}$
11 (towards consumer E_j) and all competing agents' demands $F_{r,i}^{\{l\}}$ (towards substrate S_i) or

- 12 (ii) the linear decay potential of S_i (i.e., $k_{2,ij}^+ \begin{bmatrix} S_i \end{bmatrix}_T$) weighted by the relevant importance

of F^{j}_{r,i} under the influence of all competing substrate fluxes and competing agents'
 demands.

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

6 accessible for consumer E_j as

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

7

8

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

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

9

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

$$\frac{d\left[S_{i}\right]_{T,j}}{dt} = -\frac{k_{2,ij}^{+}\left[E_{j}\right]_{T}\left(\left[\overline{S}\right]_{T}/K_{E,j}\right)}{1 + \left[\overline{S}\right]_{T}/K_{E,j} + \left[\overline{E}\right]_{T}/K_{S,i}} \frac{F_{c,j}^{\{i\}}}{F_{c,j}} = -\frac{k_{2,ij}^{+}\left[S_{i}\right]_{T}\left(\left[\overline{E}\right]_{T}/K_{S,i}\right)}{1 + \left[\overline{S}\right]_{T}/K_{E,j} + \left[\overline{E}\right]_{T}/K_{S,i}} \frac{F_{r,i}^{\{j\}}}{F_{r,i}} \qquad (36)$$

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

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

$$\frac{d\left[A_{i}\right]_{T,jk}}{dt} = -\frac{k_{2,jjk}^{+}\left[E_{k}\right]_{T}F_{c,A,k}^{\{i\}}F_{c,B,k}^{\{j\}}}{\frac{G_{A,ik}G_{B,jk}}{G_{AB,jjk}}F_{c,AB,k} + F_{c,AB,k} - \frac{F_{c,A,k}G_{B,jk} + G_{A,ik}F_{c,B,k} - G_{A,ik}G_{B,jk}}{G_{AB,jjk}}}$$
(37)

4 where

$$F_{c,A,k} = \sum_{l} F_{c,A,k}^{\{l\}} = \sum_{l} \left[A_{l} \right]_{T} / K_{A,lk}$$
(38)

$$F_{c,B,k} = \sum_{l} F_{c,B,k}^{\{l\}} = \sum_{l} \left[B_{l} \right]_{T} / K_{B,lk}$$
(39)

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

$$F_{r,A,i} = \sum_{l} \left[E_{l} \right]_{T} / K_{A,il}$$
(41)

$$F_{r,B,j} = \sum_{l} \left[E_{l} \right]_{T} / K_{B,jl}$$
(42)

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

$$G_{B,jk} = F_{c,B,k} + F_{r,B,j}$$
(44)

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

1 For equation (37), one can verify that if $F_{c,B,k}$ (or $F_{c,A,k}$) goes to very large values,

SUPECA kinetics is reduced to ECA kinetics (equation (33)). Therefore, SUPECA
kinetics as formulated in equation (37) are an extension of SU and ECA kinetics, and
SUPECA is applicable for consistent scaling of substrate-consumer networks involving
both single-substrate reactions and redox-reactions (a visual demonstration of SUPECA
kinetics is in Figure 2).

7 4. Numerical accuracy of SUPECA kinetics

8 Following Tang and Riley (2013a), we assume that the EC formulation is a good 9 approximation to the law of mass action and use it to evaluate the numerical accuracy of 10 SUPECA kinetics. Because of numerical complexity, we restricted the comparison to the AB-E problem as formulated by equations (11)-(16) with the assumption of $k_A^- = k_B^- = 0$ 11 12 and included a substrate sorbent to mimic a class of biogeochemistry problems in soil, 13 such as aerobic soil ammonium nitrification and aerobic soil organic carbon 14 decomposition (formulated in appendix F; a graphic representation is available in 15 supplemental material). 16 We evaluated the numerical accuracy of SUPECA (equation (37)) and SU 17 (equation (26)) over a wide range of parameter values. We fixed both substrates at a nominal value of 40 mol m⁻³, and k_2^+ , the maximum substrate processing rate at 48 s⁻¹. 18 Then we sampled the affinity parameters exponentially over the range [0,1000] mol m⁻³ 19 and the microbe and sorbent concentrations uniformly over the range [0,1000] mol m⁻³. 20

21 Using a total of 1000 sets of randomly paired parameters, we compared how close

1	SUPECA and SU approximations are to the EC solution in terms of root mean square
2	error (RMSE) and goodness of linear fit. Because SU kinetics do not allow a direct
3	integration of the Langmuir adsorption into the calculation of microbe-substrate
4	complexes, we followed Resat et al. (2011) and first solved the Langmuir isotherm to
5	obtain the free substrate concentrations and then entered these free substrate
6	concentrations into SU to obtain the microbe-substrate complex. This artificial ordering
7	in calculation (as needed by the SU approach) suggests that the SU implementation may
8	lead to significant numerical errors (similar numerical difficulties are associated with the
9	popular MM kinetics (Resat et al., 2011; Tang and Riley, 2013a)).
10	Our comparison (Figure 3 and Figure 4) indicates that SUPECA kinetics are
11	superior to SU kinetics in computing the microbe-substrate complex in the presence of
12	substrate binding competition between microbes and sorbent. SUPECA predictions are
13	more accurate than SU predictions in terms of goodness of linear fitting and RMSE (for
14	which the linear regressions are shown as black solid lines in the Figure 3). In magnitude,
15	the RMSEs of SUPECA predictions are less than 10% of that of SU predictions (and also
16	note that the y-axis ranges for SU predictions are 20 times of those for SUPECA
17	predictions). The slope of linear fitting from SUPECA predictions is also much closer to
18	the ideal value 1.0, whereas that from SU predictions is far greater than 1.0, suggesting
19	that SU kinetics significantly overestimate microbe-substrate complexes under a wide
20	range of conditions. When the model predictions are evaluated as a function of the
21	relative abundances of consumers and substrates (Figure 4), SU overestimates are found
22	under high ratios of consumer abundances with respect to substrates (Figure 4a, c). In
23	contrast, SUPECA predictions agree well with EC predictions over the whole range of

1	relative abundances (Figure 4b, d). This very large overestimation by SU calculations is
2	explained by the linear dependence of the consumer-substrate complexes on microbial
3	abundances in deriving SU kinetics (equation (26)). Therefore, combined with the better
4	numerical performance of ECA (Tang and Riley, 2013a; Tang, 2015) than MM kinetics,
5	we contend that SUPECA kinetics are numerically more convenient and more accurate
6	than SU kinetics in calculating the microbe-substrate complexes for situations involving
7	microbes, enzymes, substrates, and soil minerals (e.g., Tang and Riley, 2015). In
8	particular, because nutrient limitations tend to occur under high relative consumer
9	abundances with respect to their substrates, the larger prediction bias of SU than
10	SUPECA suggests that SUPECA should be preferred for soil biogeochemical modeling.
11	However, for applications to real problems, the validity of SUPECA kinetics depends on
12	the EC formulation and the tQSSA, and there are situations where even the EC
13	formulation might fail (e.g., Maggi and Riley, 2009; Pedersen et al., 2008).
14	5. Example application to modeling aerobic heterotrophic respiration
15	As a proof-of-concept example, we applied SUPECA kinetics to predict the
16	moisture stress on aerobic soil respiration. We note that we are not suggesting that
17	SUPECA kinetics replace existing soil BGC models, but rather that mechanistic analysis
18	using a SUPECA-based model can inform process understanding and thereby improve
19	such models. Following the CENTURY-like models' approach in modeling topsoil soil
20	carbon dynamics (Coleman and Jenkinson, 1999; Parton and Rasmussen, 1994) and the
21	set up of Franzluebbers' (1999) soil incubation experiments (from which the data were
22	used for our model evaluation), this example (Appendix G) considers a homogenous 10
23	cm thick topsoil with 2.0 mol C m ⁻³ microbes and 3.0 mol C m ⁻³ DOC (i.e., dissolvable
23	en mer opson win 2.0 more in merodes and 5.0 more in DOC (i.e., dissorvable

1 organic carbon; different DOC values affected our results negligibly as long as they were 2 larger than 0.5 mol C m⁻³). We conceptualize transport of substrates (i.e., oxygen and 3 DOC) in soil as a two-stage diffusion process (e.g., Grant, 1991) with the first stage from 4 the bulk soil matrix to the water film covering the microbial microsites and the second 5 stage from the water film to the microbial transporters where substrates are processed. 6 The diffusion processes in soil are calculated based on soil moisture status and the 7 hydraulic properties of a hypothesized soil with a texture of 40% clay and 30% sand. The 8 pedotransfer functions used for calculating soil hydraulic properties are from CLM4.5 9 (Oleson et al., 2013).

Our approach assumes that the inter-microsite (or aggregates) transport dominates intra-aggregate transport, consistent with pore scale simulations (Yang et al., 2014). The model is solved to steady state by assuming that the microbes, atmospheric oxygen, and DOC are in balance under the influence of Langmuir type DOC sorption by soil minerals. Calculations are conducted for three levels of soil minerals (with adsorption capacities at 0, 90, and 180 mol C m⁻³) and two levels of microbial oxygen affinity (with default $K_{o2,w} = 3 \times 10^{-5}$ mol m⁻³ and elevated $K_{o2,w} = 3 \times 10^{-3}$ mol m⁻³; Figure 5 and Figure 6).

17	The calculation with elevated $K_{02,w}$ (compared to the default $K_{02,w}$) indicates the
18	effect of soil aggregates on moisture control of decomposition (see also Appendix G). We
19	evaluated: (1) how close our predicted moisture response function is to incubation data
20	from Franzluebbers (1999) and (2) how soil mineral DOC adsorption would affect the
21	soil moisture response function. We also tested a widely used response function approach
22	(e.g., Sierra et al., 2015) for comparison.

1	When the respiration curves are normalized, we found that all curves have the
2	same pattern that soil respiration first increases from dry soil with increasing moisture
3	and then levels off after reaching a peak value (where the respiration is co-limited by
4	oxygen and DOC bioavailability). The curve with the highest mineral soil carbon
5	adsorption capacity (180 mol C m ⁻³) and elevated $K_{02,w}$ value best approximates the
6	incubation data from Franzluebbers (1999). As the sorption capacity becomes smaller,
7	the moisture response function becomes sharper.

8 When the oxygen affinity parameter is reduced to its default value (while keeping the adsorption capacity at 180 mol C m⁻³; see explanation in Appendix G), the soil 9 10 moisture response function becomes the sharpest with the highest threshold moisture 11 where the respiration peaks (see green line in Figure 5). Unlike Kausch and Pallud (2013) and Yang et al. (2014), we have not explicitly simulated the oxygen distribution inside 12 13 the aggregates. Since the apparent oxygen affinity parameter (which we use here) 14 generally increases with aggregate size (Griffin, 1968), the poorer agreement between 15 data and predictions using the default oxygen affinity parameter indicates that soil 16 aggregates may play an important role in controlling microbes' response to soil moisture 17 stress. Indeed, Franzluebbers (1999) indicated in his Figure 1 that there are many 18 aggregates in his incubated soil. Moreover, the higher moisture threshold (where 19 respiration peaks) with the default apparent oxygen affinity parameter is consistent with 20 measurements that aggregates may facilitate anaerobic processes under well-ventilated 21 conditions (by increasing the range of soil moisture conditions where oxygen limits 22 aerobic processes; Renault and Stengel, 1994; Keiluweit et al., 2016).

When the moisture response function is evaluated, we found a higher R² (0.84) than those predicted from SUPECA based methods, which (from top to bottom as in the legends) are 0.82, 0.81, 0.77 and 0.71 for the blue, red, black and green lines respectively. However, the response function approach overestimated the observed aerobic soil respiration rate at high soil moisture contents. This example illustrates that a higher overall R² from the empirical response function can mask an important feature of soil respiration's dependence on soil moisture.

8 Higher adsorption capacity resulted in significantly lower soil respiration (Figure 9 6), consistent with results for temperature sensitivity described in Tang and Riley (2015). 10 Combining results from Figure 5 and Figure 6, we conclude that because the soil 11 moisture response function emerges from interactions between biotic and abiotic factors 12 that co-regulate soil organic carbon decomposition (Manzoni et al., 2016), its functional 13 shape is not deterministic. This result contradicts the popular approach used in many soil 14 BGC models (including our own, e.g., Koven et al., 2013; Tang et al., 2013; and others, 15 e.g., Sierra et al., 2015), where a deterministic soil moisture response function is applied 16 to the moisture-unstressed decomposition rate. We also note that there are many different 17 functional forms for the soil moisture response function used in soil BGC models (Sierra 18 et al. 2015).

19 At the default oxygen affinity value $(3 \times 10^{-5} \text{ mol O}_2 \text{ m}^{-3})$, the derived soil 20 moisture response function is essentially insensitive to mineral soil carbon adsorption 21 capacity (not shown). Since the oxygen affinity parameter reflects the impacts of 22 aggregates, these results demonstrate how soil aggregates may influence soil carbon

decomposition rates, an insight that cannot be obtained by fitting response functions to a
 single dataset.

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

4 modeling

5 Besides the example application above, SUPECA kinetics could be a powerful 6 tool for trait-based modeling in various biogeochemical systems (e.g., Follows et al., 7 2007; Bouskill et al., 2012; Litchman and Klausmeier, 2008; Merico et al., 2009). As we 8 show above and below, SUPECA kinetics will enable more robust predictions with better 9 numerical consistency and smaller parametric sensitivities than the popular family of 10 Monod kinetics, and SUPECA will be applicable for any biogeochemical system that 11 involves substrate-consumer binding and binding competition (of the AB-E or A-E type). 12 The assertion of smaller parametric sensitivity as predicted by SUPECA (than by

13 Monod kinetics) can be verified using the single-substrate reaction network as an

14 example. In this case, SUPECA is reduced to ECA kinetics, and for some substrate S_i in

15 the reaction network, ECA kinetics predict the sensitivity of its consumption by

16 consumer $\begin{bmatrix} E_j \end{bmatrix}$ with respect to the maximum processing rate $k_{2,ij}^+$ as

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

$$ECA \qquad Competitive \qquad Monod$$

$$Monod$$

$$(46)$$

1	where the term after the first "<" is prediction by competitive Monod kinetics and that
2	after the second "<" is by Monod kinetics, suggesting that models using Monod kinetics
3	for substrate competition are more sensitive to parameters and therefore more difficult to
4	calibrate (e.g., Tang and Riley, 2013a).
5	To quantitatively evaluate our assertion that SUPECA kinetics predict lower
6	parametric sensitivity, we applied equation (46) to 100 competing substrate fluxes of
7	equal magnitude. We then have $F_{c,j} = 100F_{c,j}^{\{i\}}$. Meanwhile, if $F_{c,j}^{\{i\}} > 1$, then the sensitivity
8	predicted by competitive Monod kinetics is less than 1% of that by Monod kinetics.
9	Further, if the competing efforts from all agents is comparable to the overall substrate
10	fluxes, i.e., $F_{r,i} \approx F_{c,j}$, then the parametric sensitivity predicted by ECA is about 50% of
11	that by competitive Monod kinetics. Therefore, ECA (and by extension, SUPECA)
12	prediction is much less sensitive with respect to $k_{2,ij}^+$ than that by competitive Monod
13	kinetics and Monod kinetics. Moreover, with equations (30) and (37), one can verify that
14	the more substrates and consumers represented in the system, the smaller the resulting
15	sensitivity predicted by ECA (and SUPECA) kinetics for each $k_{2,ij}^+$. One can also verify
16	lower SUPECA uncertainty for other parameters, including substrates and consumer
17	abundances. That including more substrates and consumers will lead to more robust
18	model predictions is a premise underlying trait-based modeling (e.g., Follows et al.,
19	2007; Bouskill et al., 2012), and SUPECA kinetics explicitly integrates this presumption
20	in its formulation.

1	The assertion of wide applicability with SUPECA kinetics has been demonstrated
2	by a number of successful applications that we have published with ECA kinetics. In a
3	series of studies (Zhu and Riley, 2015; Zhu et al., 2016a, 2016b, 2017), we showed that
4	ECA kinetics significantly improved the modeling of nutrient competition between
5	plants, microbes, and mineral soils. In Tang and Riley (2013a), where ECA kinetics was
6	first proposed, lignin decomposition dynamics were accurately captured without a priori
7	imposing a target lignocellulose index. In Tang and Riley (2013a, 2015) and this study,
8	ECA kinetics were able to seamlessly incorporate Langmuir type substrate adsorption
9	without invoking an ad hoc numerical order that is prerequisite to MM (or Monod)
10	kinetics for modeling mineral, microbe, and substrate interactions.
11	Finally, we expect SUPECA kinetics will provide a robust approach to resolve the
12	redox ladder in soil biogeochemistry. Existing approaches have imposed the redox ladder
13	following some specific order, e.g.,
14	$O_2(H_2O), NO_3(N_2), MnO_2(Mn^{2+}), Fe(OH)_3(Fe^{2+}), SO_4^{2-}(H_2S), CO_2(CH_4), and$
15	$H_2O(H_2)$ (e.g., Grant, 2001). In contrast, SUPECA kinetics will allow all these redox-
16	couples to operate concurrently (in any space-time-process unit), a situation that is more
17	consistent with natural soils. Such a feature will also allow microbial biogeochemistry
18	models (most of which are considered to be valid at pore scale) to be valid at the scale of
19	well-mixed bulk soils ($\sim cm^3$).

20 7. Conclusions

1	In this study, we showed that the popular Monod family kinetics and synthesizing
2	unit (SU) kinetics are not scaling consistent for a reaction network involving mixed
3	$A \rightarrow products$ type and $A + B \rightarrow products$ type reactions. SUPECA kinetics, by
4	accounting for mass balance constraints of substrates and consumers, is able to represent
5	an arbitrary number of substrates and consumers without changing mathematical
6	formulation. Our numerical tests indicate that SUPECA kinetics is superior to SU
7	kinetics both in numerical accuracy and numerical robustness, particularly under high
8	relative abundances of consumers with respect to substrates (a typical feature in plant-
9	microbial competition for limited soil nutrients; Schimel and Bennett, 2004; Vitousek et
10	al., 2010). SUPECA kinetics were also able to predict the moisture response function of
11	aerobic soil respiration, providing mechanistic insights not available from the response
12	function approach. Finally, because SUPECA kinetics represents measurable microbial
13	traits and the mechanisms by which they affect soil biogeochemical dynamics, we
14	conclude that this approach can benefit interpretation of observed dynamics and thereby
15	improve soil BGC models.

16 8. Code and data availability

17 The source code and data used in this manuscript are available upon request to the18 corresponding author.

19 Appendix A: Deriving the governing equations

20

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

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

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

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

$$\frac{d[P]}{dt} = k_2^+ [EAB]$$
(A4)

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

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

1 We now apply the total quasi-steady-state approximation (e.g., Borghans et al., 1996) to

2 obtain the Equilibrium Chemistry formulation of the system. Specifically, we obtain

3 equations (11)-(13) by respectively setting the time derivatives of equations (A1)-(A3) to

4 zero. Equation (9) is obtained by adding together equations (A1), (A3) and (A5), and

- 5 using the definition of $[A]_T$ by equation (14). Equation (10) is obtained by adding
- 6 together equations (A2), (A3) and (A6) with the definition of $\begin{bmatrix} B \end{bmatrix}_T$ by equation (15).
- 7

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

8

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

$$\begin{bmatrix} EAB \end{bmatrix} = \frac{\begin{bmatrix} A \end{bmatrix} \begin{bmatrix} B \end{bmatrix}}{K_A} \begin{bmatrix} E \end{bmatrix}$$
(B-1)

1 By solving $\begin{bmatrix} EA \end{bmatrix}$ from equation (19), $\begin{bmatrix} EB \end{bmatrix}$ from equation (20) and combining

2 these with equation (B-1) into equation (16), we find

$$\begin{bmatrix} E \end{bmatrix}_{T} = \left(1 + \frac{\begin{bmatrix} A \end{bmatrix}}{K_{A}}\right) \left(1 + \frac{\begin{bmatrix} B \end{bmatrix}}{K_{B}}\right) \begin{bmatrix} E \end{bmatrix}$$
(B-2)

3

Now solve $\begin{bmatrix} E \end{bmatrix}$ from (B-2) and enter the result into equation (B-1), we then get

$$\begin{bmatrix} EAB \end{bmatrix} = \left(\frac{\begin{bmatrix} A \end{bmatrix}}{K_A + \begin{bmatrix} A \end{bmatrix}}\right) \left(\frac{\begin{bmatrix} B \end{bmatrix}}{K_A + \begin{bmatrix} B \end{bmatrix}}\right) \begin{bmatrix} E \end{bmatrix}_T$$
(B-3)

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

5 (9).

7

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

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

$$\begin{bmatrix} EA \end{bmatrix} = \frac{k_A^+ \begin{bmatrix} A \end{bmatrix}}{k_B^+ \begin{bmatrix} B \end{bmatrix}} \begin{bmatrix} E \end{bmatrix}$$
(C-1)

$$\begin{bmatrix} EB \end{bmatrix} = \frac{k_B^+ \begin{bmatrix} B \end{bmatrix}}{k_A^+ \begin{bmatrix} A \end{bmatrix}} \begin{bmatrix} E \end{bmatrix}$$
(C-2)

9

11

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

10 we find

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

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

$$\begin{bmatrix} E \end{bmatrix} = \frac{\begin{bmatrix} E \end{bmatrix}_{T}}{1 + \frac{k_{A}^{+} \begin{bmatrix} A \end{bmatrix}}{k_{B}^{+} \begin{bmatrix} B \end{bmatrix}} + \frac{k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}{k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}}{\tilde{k}_{2}^{+}}$$

$$= \frac{\begin{bmatrix} E \end{bmatrix}_{T}}{\frac{\left(k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}\right)^{2}}{\left(k_{A}^{+} \begin{bmatrix} A \end{bmatrix}\right)\left(k_{B}^{+} \begin{bmatrix} B \end{bmatrix}\right)} + \frac{k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}{\tilde{k}_{2}^{+}} - 1}$$
(C-4)

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

$$\begin{bmatrix} EAB \end{bmatrix} = \frac{k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}{\tilde{k}_{2}^{+}} \frac{\begin{bmatrix} E \end{bmatrix}_{T}}{\frac{\left(k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}\right)^{2}}{\left(k_{A}^{+} \begin{bmatrix} A \end{bmatrix}\right) \left(k_{B}^{+} \begin{bmatrix} B \end{bmatrix}\right)^{2}} + \frac{k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}{\tilde{k}_{2}^{+}} - 1}$$

$$= \frac{\begin{bmatrix} E \end{bmatrix}_{T} / \tilde{k}_{2}^{+}}{\frac{1}{\tilde{k}_{2}^{+}} + \frac{k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}{\left(k_{A}^{+} \begin{bmatrix} A \end{bmatrix}\right) \left(k_{B}^{+} \begin{bmatrix} B \end{bmatrix}\right)} - \frac{1}{k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}{k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}$$

$$= \frac{\begin{bmatrix} E \end{bmatrix}_{T} / \tilde{k}_{2}^{+}}{\frac{1}{\tilde{k}_{2}^{+}} + \frac{1}{k_{A}^{+} \begin{bmatrix} A \end{bmatrix}} + \frac{1}{k_{B}^{+} \begin{bmatrix} B \end{bmatrix}} - \frac{1}{k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}{k_{A}^{+} \begin{bmatrix} A \end{bmatrix} + k_{B}^{+} \begin{bmatrix} B \end{bmatrix}}}$$
(C-5)

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

4 Appendix D: Deriving SUPECA kinetics equation (28)

5 We first derive the set of linear equations using the first order closure approach
6 (i.e., the perturbation method truncated to first order accuracy; Shankar, 1994; Tang et

7 al., 2007). By entering equations (14)-(16) into equation (23), we have

$$k_{B}^{+} \begin{bmatrix} EA \end{bmatrix} \left(\begin{bmatrix} B \end{bmatrix}_{T} - \begin{bmatrix} EB \end{bmatrix} - \begin{bmatrix} EAB \end{bmatrix} \right) = k_{A}^{+} \left(\begin{bmatrix} A \end{bmatrix}_{T} - \begin{bmatrix} EA \end{bmatrix} - \begin{bmatrix} EAB \end{bmatrix} \right)$$

$$\times \left(\begin{bmatrix} E \end{bmatrix}_{T} - \begin{bmatrix} EA \end{bmatrix} - \begin{bmatrix} EB \end{bmatrix} - \begin{bmatrix} EAB \end{bmatrix} \right)$$
 (D-1)

- 1 Now if we expand equation (D-1), and keep only the 0^{th} and 1^{st} order terms of [EA],
- 2 $\begin{bmatrix} EB \end{bmatrix}$ and $\begin{bmatrix} EAB \end{bmatrix}$, we obtain

$$k_{B}^{+} \begin{bmatrix} B \end{bmatrix}_{T} \begin{bmatrix} EA \end{bmatrix} = k_{A}^{+} \begin{bmatrix} E \end{bmatrix}_{T} \left(\begin{bmatrix} A \end{bmatrix}_{T} - \begin{bmatrix} EA \end{bmatrix} - \begin{bmatrix} EAB \end{bmatrix} \right)$$

$$-k_{A}^{+} \begin{bmatrix} A \end{bmatrix}_{T} \left(\begin{bmatrix} EA \end{bmatrix} + \begin{bmatrix} EB \end{bmatrix} + \begin{bmatrix} EAB \end{bmatrix} \right)$$
 (D-2)

3 which after some rearrangement becomes

$$\begin{pmatrix} k_A^+ \begin{bmatrix} A \end{bmatrix}_T + k_A^+ \begin{bmatrix} E \end{bmatrix}_T + k_B^+ \begin{bmatrix} B \end{bmatrix}_T \end{pmatrix} \begin{bmatrix} EA \end{bmatrix} + k_A^+ \begin{bmatrix} A \end{bmatrix}_T \begin{bmatrix} EB \end{bmatrix}$$

+ $k_A^+ \begin{pmatrix} \begin{bmatrix} A \end{bmatrix}_T + \begin{bmatrix} E \end{bmatrix}_T \end{pmatrix} \begin{bmatrix} EAB \end{bmatrix} = k_A^+ \begin{bmatrix} A \end{bmatrix}_T \begin{bmatrix} E \end{bmatrix}_T$ (D-3)

4 Using the definitions of
$$f_A = k_A^+ \begin{bmatrix} A \end{bmatrix}_T$$
, $f_B = k_B^+ \begin{bmatrix} B \end{bmatrix}_T$ and $\overline{f}_A = f_A + k_A^+ \begin{bmatrix} E \end{bmatrix}_T$, we may

5 rewrite equation (D-3) as

$$\left(\overline{f}_{A} + f_{B}\right)\left[EA\right] + f_{A}\left[EB\right] + \overline{f}_{A}\left[EAB\right] = f_{A}\left[E\right]_{T}$$
(D-4)

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

$$f_{B}\left[EA\right] + \left(f_{A} + \overline{f}_{B}\right)\left[EB\right] + \overline{f}_{B}\left[EAB\right] = f_{B}\left[E\right]_{T}$$
(D-5)

10 Now substitute equations (14)-(16), (23) and (24) into equation (25) and assume 11 $\tilde{k}_2^+ \approx k_2^+$ (i.e., unbinding is much smaller compared to the product genesis rate), we have

$$\left\{ k_A^+ \left(\begin{bmatrix} A \end{bmatrix}_T - \begin{bmatrix} EA \end{bmatrix} - \begin{bmatrix} EA B \end{bmatrix} \right) + k_B^+ \left(\begin{bmatrix} B \end{bmatrix}_T - \begin{bmatrix} EB \end{bmatrix} - \begin{bmatrix} EA B \end{bmatrix} \right) \right\}$$

$$\times \left(\begin{bmatrix} E \end{bmatrix}_T - \begin{bmatrix} EA \end{bmatrix} - \begin{bmatrix} EB \end{bmatrix} - \begin{bmatrix} EA B \end{bmatrix} \right) = k_2^+ \begin{bmatrix} EA B \end{bmatrix}$$
 (D-6)

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

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

$$\begin{pmatrix} k_A^+ \begin{bmatrix} A \end{bmatrix}_T + k_B^+ \begin{bmatrix} B \end{bmatrix}_T \end{pmatrix} \begin{bmatrix} E \end{bmatrix}_T = \begin{pmatrix} k_A^+ \begin{bmatrix} A \end{bmatrix}_T + k_B^+ \begin{bmatrix} B \end{bmatrix}_T \end{pmatrix}$$

$$\times \begin{pmatrix} \begin{bmatrix} EA \end{bmatrix}_T + \begin{bmatrix} EB \end{bmatrix}_T + \begin{bmatrix} EAB \end{bmatrix} \end{pmatrix} + k_A^+ \begin{bmatrix} E \end{bmatrix}_T \begin{pmatrix} \begin{bmatrix} EA \end{bmatrix}_T + \begin{bmatrix} EAB \end{bmatrix})$$

$$+ k_B^+ \begin{bmatrix} E \end{bmatrix}_T \begin{pmatrix} \begin{bmatrix} EB \end{bmatrix}_T + \begin{bmatrix} EAB \end{bmatrix}) + k_2^+ \begin{bmatrix} EAB \end{bmatrix}$$

$$(D-7)$$

3 which by aid of $f_A = k_A^+ \begin{bmatrix} A \end{bmatrix}_T$, $f_B = k_B^+ \begin{bmatrix} B \end{bmatrix}_T$, $\overline{f}_A = f_A + k_A^+ \begin{bmatrix} E \end{bmatrix}_T$, $\overline{f}_B = f_B + k_B^+ \begin{bmatrix} E \end{bmatrix}_T$,

4
$$f_{AB} = f_A + f_B$$
, and $\overline{f}_{AB} = \overline{f}_A + \overline{f}_B$ becomes

$$\left(\overline{f}_{A} + f_{B}\right)\left[EA\right] + \left(f_{A} + \overline{f}_{B}\right)\left[EB\right] + \left(k_{2}^{+} + \overline{f}_{AB}\right)\left[EAB\right] = f_{AB}\left[E\right]_{T}$$
(D-8)

5 Now we solve for [EAB] from the set of linear equations (D-4), (D-5) and (D-8)

6 using Cramer's rule (e.g., Habgood and Arel, 2012), and find the denominator as

$$\det(M_{d}) = \begin{vmatrix} \overline{f}_{A} + f_{B} & f_{A} & \overline{f}_{A} \\ f_{B} & f_{A} + \overline{f}_{B} & \overline{f}_{B} \\ \overline{f}_{A} + f_{B} & f_{A} + \overline{f}_{B} & k_{2}^{+} + \overline{f}_{AB} \end{vmatrix}$$
(D-9)

7 and the numerator as

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

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

$$\begin{bmatrix} EAB \end{bmatrix} = \frac{\det(M_n)}{\det(M_d)} = \frac{f_A f_B \overline{f}_{AB} [E]_T}{k_2^+ (f_A \overline{f}_A + f_B \overline{f}_B + \overline{f}_A \overline{f}_B) + \overline{f}_A \overline{f}_B f_{AB}} \\ = \frac{f_A f_B \overline{f}_{AB} [E]_T}{k_2^+ (f_{AB} \overline{f}_{AB} - f_A \overline{f}_B - \overline{f}_A f_B + \overline{f}_A \overline{f}_B) + \overline{f}_A \overline{f}_B f_{AB}} \\ = \frac{[E]_T}{k_2^+ (\frac{f_{AB}}{f_A f_B} - \frac{f_A \overline{f}_B + \overline{f}_A f_B - \overline{f}_A \overline{f}_B}{f_A f_B \overline{f}_{AB}}) + \frac{\overline{f}_A \overline{f}_B f_{AB}}{f_A f_B \overline{f}_{AB}}}$$
(D-11)
$$= \frac{[E]_T / k_2^+}{\frac{1}{k_2^+} \frac{\overline{f}_A \overline{f}_B f_{AB}}{f_A f_B \overline{f}_{AB}} + (\frac{1}{f_A} + \frac{1}{f_B} - \frac{f_A \overline{f}_B + \overline{f}_A f_B - \overline{f}_A \overline{f}_B}{f_A f_B \overline{f}_{AB}})}$$

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

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

3 In the second equation of equations (33), we show that the consumption of a 4 certain substrate as represented in ECA kinetics is determined by the consumer reaction potential $k_{2,ij}^+ \begin{bmatrix} E_j \end{bmatrix}_T$ multiplied with the relative contribution of the specific consumption 5 pathway with respect to all competing pathways $(F_{c,j}^{\{r\}}/(1+F_{r,j}+F_{c,j}))$. Since SUPECA 6 7 kinetics is a compatible extension of ECA kinetics, SUPECA kinetics should have its 8 numerator indicating the potential reaction rate of the specific pathway, and its 9 denominator indicating the efforts of all interacting pathways. Bearing this partition equivalence in mind, therefore, we assert that \overline{f}_A/k_2^+ in equation (29) should be 10 equivalent to $F_{r,i} + F_{c,j}$ in equation (33). This assertion then leads to equations (38), (41) 11 12 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^+ , \overline{f}_A/k_2^+ and \overline{f}_B/k_2^+ , using the partition 13

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

$$4 \quad \frac{\left(\overline{f}_{A}/k_{2}^{+}\right)\left(\overline{f}_{B}/k_{2}^{+}\right)\left(f_{AB}/k_{2}^{+}\right)}{\left(\overline{f}_{AB}/k_{2}^{+}\right)} + \left(f_{AB}/k_{2}^{+}\right) - \frac{\left(f_{A}/k_{2}^{+}\right)\left(\overline{f}_{B}/k_{2}^{+}\right) + \left(\overline{f}_{A}/k_{2}^{+}\right)\left(f_{B}/k_{2}^{+}\right) - \left(\overline{f}_{A}/k_{2}^{+}\right)\left(\overline{f}_{B}/k_{2}^{+}\right)}{\left(\overline{f}_{AB}/k_{2}^{+}\right)}$$

5 which, after replacing f_A/k_2^+ , f_B/k_2^+ , \overline{f}_A/k_2^+ , \overline{f}_B/k_2^+ , f_{AB}/k_2^+ and \overline{f}_{AB}/k_2^+ with their 6 corresponding network forms (i.e. equations (38)-(45)), leads to SUPECA kinetics

7 equation (37).

8 Appendix F: Formulation of the kinetics-benchmarking problem

9

Following equations (23)-(25), the Equilibrium Chemistry (EC) problem used to

10 benchmark synthesizing unit (SU) and SUPECA predictions is defined as

$$k_{BS1} \begin{bmatrix} B \end{bmatrix} \begin{bmatrix} S_1 \end{bmatrix} = k_{BS2} \begin{bmatrix} S_2 \end{bmatrix} \begin{bmatrix} BS_1 \end{bmatrix}$$
(F-1)

$$k_{BS2} \begin{bmatrix} B \end{bmatrix} \begin{bmatrix} S_2 \end{bmatrix} = k_{BS1} \begin{bmatrix} S_1 \end{bmatrix} \begin{bmatrix} BS_2 \end{bmatrix}$$
(F-2)

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

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

11 which are subject to the constraints

$$\begin{bmatrix} S_1 \end{bmatrix}_T = \begin{bmatrix} S_1 \end{bmatrix} + \begin{bmatrix} MS_1 \end{bmatrix} + \begin{bmatrix} BS_1 \end{bmatrix} + \begin{bmatrix} BS_1S_2 \end{bmatrix}$$
(F-5)

$$\begin{bmatrix} S_2 \end{bmatrix}_T = \begin{bmatrix} S_2 \end{bmatrix} + \begin{bmatrix} BS_2 \end{bmatrix} + \begin{bmatrix} BS_1 S_2 \end{bmatrix}$$
(F-6)

$$\begin{bmatrix} B \end{bmatrix}_{T} = \begin{bmatrix} B \end{bmatrix} + \begin{bmatrix} BS_{1} \end{bmatrix} + \begin{bmatrix} BS_{2} \end{bmatrix} + \begin{bmatrix} BS_{1}S_{2} \end{bmatrix}$$
(F-7)

$$\begin{bmatrix} M \end{bmatrix}_T = \begin{bmatrix} M \end{bmatrix} + \begin{bmatrix} MS_1 \end{bmatrix}$$
(F-8)

1 To relate these equations to a dynamic system, S_1 and S_2 are substrates, B is 2 microbial population, and M is some sorbent that can reversibly adsorb substrate S_1 . The 3 corresponding graphic representation of the problem is available in the supplemental 4 material.

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.

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

- 11 respiration problem
- 12

The aerobic respiration problem is formulated as

$$\frac{d\left[O_{2}\right]_{g,s}}{dt} = \frac{\left(\left[O_{2}\right]_{a} - \left[O_{2}\right]_{g,s}\right)}{\left(R_{a} + R_{s}\right)Z} - F\left(B, \left[O_{2}\right]_{g,s}, S, M\right)$$
(G-1)

13 where $\begin{bmatrix} O_2 \end{bmatrix}_{g,s}$ is gaseous oxygen concentration in bulk soil. $\begin{bmatrix} O_2 \end{bmatrix}_a$ is atmospheric oxygen 14 concentration (set to 8.45 mol m⁻³), *S* is dissolvable organic carbon (DOC) concentration 15 (set to 3 mol m⁻³; we note that SUPECA is able to accommodate more specific carbon 16 compounds (like in Riley et al (2014)), yet our recent analysis (Dwivedi et al., 2017) 17 suggests that a lumped DOC is sufficient for simple applications like the one we present 18 here), and *M* is soil mineral sorbent concentration (with variable values). All

concentrations are defined with units (mol m⁻³). R_a is aerodynamic resistance, which is 1 set to 50 s m⁻¹. R_s is soil resistance (s m⁻¹) calculated using the approach in Tang and 2 3 Riley (2013b). Z is soil depth (set to 10 cm, following the incubation set up of Franzluebbers (1999)). $F(B, [O_2]_{a,s}, S, M)$ is the oxygen consumption rate calculated 4 5 using SUPECA kinetics, whose kinetic parameters are derived as following. The steady-6 state problem is solved by setting the temporal derivative of equation (G-1) to zero, and solved for $[O_2]_{q,s}$ through iterations. The shape of the flux $F(B, [O_2]_{q,s}, S, M)$ is then 7 8 compared to that derived from incubation studies in Franzluebbers (1999). 9 In this aerobic respiration problem, microbes are assumed to form microsites 10 sitting uniformly inside pores of the bulk soil. O_2 approaches the microsites through both 11 aqueous and gaseous diffusion, and only the aqueous phase is used for microbial 12 respiration. These assumptions lead to the relationship between near cell aqueous O₂ 13 concentration and the diffusive flux:

$$v_m \frac{d\left\lfloor O_2 \right\rfloor_{w,0}}{dt} = -k_{02,w,1} \left[X \right] \left[O_2 \right]_{w,0} + \kappa_{02} \left(\left[O_2 \right]_w - \left[O_2 \right]_0 \right)$$
(G-2)

14 where the conductance κ_{02} is

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

15 and r_m is the radius of the microsite (or aggregate), δ is thickness of the water film that 16 covers the microsite (Grant and Rochette, 1994), v_m is the microsite volume (m³ site⁻¹), 1 and $\begin{bmatrix} 0_2 \end{bmatrix}$ is the aqueous oxygen concentration in the bulk soil matrix. $\begin{bmatrix} X \end{bmatrix}$ is the cell 2 density (mol cell site⁻¹). The unit of $k_{02,1}$ is then m³ (mol cell)⁻¹ s⁻¹.

3

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

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

4

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

$$\begin{bmatrix} 0_2 \end{bmatrix}_{w,0} = \frac{\begin{bmatrix} 0_2 \end{bmatrix}_w}{1 + \frac{k_{02,w,1} \begin{bmatrix} X \end{bmatrix}}{\kappa_{02}}}$$
(G-5)

5 which leads to the revised affinity parameter:

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

6 where the zero order approximation is made by taking $\begin{bmatrix} X \end{bmatrix} \approx \begin{bmatrix} X \end{bmatrix}_r$.

7 Now assume that the ball-like microbe is covered with N disc-like transporters,

8 whose mean radius is r_p . Assuming that the binding is limited by diffusion, then using

9 the chemoreception theory by Berg and Purcell (1977), we have

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

10 where the term $Nr_p / (Nr_p + \pi r_c)$ accounts for the interference between different

11 transporters of a cell. Thus assuming $\begin{bmatrix} X \end{bmatrix}_T = m$ cell site⁻¹, we get

$$\tilde{K}_{02} = \frac{k_2}{k_{02,w,1}} \left(1 + \frac{k_{02,1} \left[X \right]_T}{\kappa_{02}} \right) = K_{02,w} \left(1 + \frac{Nr_p}{Nr_p + \pi r_c} \frac{mr_c}{r_m + \delta} \left(\frac{\delta}{r_m} + \frac{D_{02,w,0}}{D_{02}} \right) \right)$$
(G-8)

With similar procedure, for DOC we have the following

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

2 and

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

3 where
$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$
.

4 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 5 the order of 10⁻⁶ m, and r_p/r_c is about 10⁻³. At 25 °C, the aqueous diffusivity of O₂ is 6 about 2.9×10^{-9} m² s⁻¹, therefore, assuming N = 3000 transporters per cell (which covers 7 only 0.3% of the cell's surface area), we have $k_{02,w,1} = 1.0 \times 10^{10} \text{ m}^3 (\text{mol cell})^{-1} \text{ s}^{-1}$. 8 Similarly, since the aqueous diffusivity of DOC is about 10^{-9} m² s⁻¹, assuming N = 30009 transporters per cell, we have $k_{\text{DOC},w,1} = 3.7 \times 10^9 \text{ m}^3 \text{ (mol cell)}^{-1} \text{ s}^{-1}$. Suppose the 10 respiration is bottlenecked by a single respiratory enzyme, and since the enzyme activity 11 varies on the order of 10~1000 s⁻¹ (English et al., 2006), then by taking 12 $k_2 = 100N \text{ s}^{-1} = 3 \times 10^5 \text{ s}^{-1}$ per cell, we have $K_{02,w} = 3 \times 10^{-5} \text{ mol m}^{-3}$, which agrees well 13 with parameters reported for microbes in aqueous solutions in Button (1985). However, 14 Grant (1991) estimated $K_{02,w} = 3.0 \times 10^{-3}$ mol m⁻³; Borden and Bedient (1986) estimated 15

1	$K_{02,w} = 3.1 \times 10^{-3}$ mol m ⁻³ for application in soil. We therefore elevated the numerical
2	value to $K_{02,w} = 3.0 \times 10^{-3} \text{ mol m}^{-3}$. According to equations (G-7) and (G-8), such
3	elevation could occur either by increasing the maximum substrate processing rate k_2 or
4	decreasing the diffusion $k_{02,w,1}$ controlled parameter (through the formation of micro-
5	pores in aggregates; e.g., Kausch and Pallud, 2013; Yang et al., 2014). Based on similar
6	magnitude analysis, we obtain $K_{\text{DOC,w}} = 8.1 \times 10^{-5} \text{ mol m}^{-3}$, which falls to the lower end of
7	the values reported for many hydrocarbon compounds as reported in Button (1985). We
8	did not elevate the value of $K_{\text{DOC,w}}$ because it could vary over four orders of magnitudes
9	(Button, 1985), and our number leads to a good fit between model predictions and data.
10	Taking all these numbers together, we have

$$\tilde{K}_{02,w} = K_{02,w} \left(1 + 0.48 \times \frac{mr_c}{r_m + \delta} \left(\frac{\delta}{r_m} + \frac{D_{02,w,0}}{D_{02}} \right) \right)$$

$$= 3 \times 10^{-3} \left(1 + 0.48 \times \frac{mr_c}{r_m + \delta} \left(\frac{\delta}{r_m} + \frac{D_{02,w,0}}{D_{02}} \right) \right)$$
(G-11)

$$\tilde{K}_{\text{DOC}} = K_{\text{DOC}} \left(1 + 0.48 \times \frac{mr_c}{r_m + \delta} \left(\frac{\delta}{r_m} + \frac{D_{\text{DOC,w,0}}}{D_{\text{DOC}}} \right) \right)$$

$$= 8.1 \times 10^{-5} \left(1 + 0.48 \times \frac{mr_c}{r_m + \delta} \left(\frac{\delta}{r_m} + \frac{D_{\text{DOC,w,0}}}{D_{\text{DOC}}} \right) \right)$$
(G-12)

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

$$\tilde{K}_{02,g} = \frac{\tilde{K}_{02,w}}{0.032} = 9.4 \times 10^{-2} \left(1 + 0.48 \times \frac{mr_c}{r_m + \delta} \left(\frac{\delta}{r_m} + \frac{D_{02,w,0}}{D_{02}} \right) \right)$$
(G-13)

The water film thickness is a function of soil water potential (Tokunaga, 2009)

2 and we calculate it using the approach in ECOSYS (Grant, 2001), which is

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

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

For model applications, microbes are often in the unit of mol C m⁻³. Bratbak and 5 6 Dundas (1984) reported that the wet biomass density of bacteria is over the range 1.1~1.2 $g \text{ cm}^{-3}$, of which about 40% is dry biomass, and about 50% of dry biomass is carbon. 7 Therefore, with the medium cell density 1.15 g cm⁻³, 1 mol C m⁻³ microbial biomass is 8 about 52.17 cm³, by further taking $r_c = 10^{-6}$ m= 10^{-4} cm, the cell number density is 9 2.1×10^{-11} mol cell m⁻³. Therefore, for $k_2 = 100$ s⁻¹ per porter, given each cell has 3000 10 transporters, the maximum respiration rate is 6.3×10^{-6} s⁻¹ for 1 mol C m⁻³ dry microbial 11 biomass, which was then elevated to $3.8 \times 10^{-4} \text{ s}^{-1}$ to obtain a better fitting between data 12 13 and model prediction. This required elevation in maximum respiration rate indicates that 14 the data as obtained (after 24 days of incubation) in Franzluebbers (1999) are 15 representative of fast growing microbes.

16 Author Contributions

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

19 Acknowledgements

20 This research was supported by the Director, Office of Science, Office of Biological and

21 Environmental Research of the US Department of Energy under contract No. DE-AC02-

- 1 05CH11231 as part of the Accelerated Climate Model for Energy in the Earth system
- 2 Modeling program and the Next Generation Ecosystem Experiment-Arctic project.
- 3 Financial support does not constitute an endorsement by the Department of Energy of the
- 4 views expressed in this study.

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2 Figure 1. Graphical representation of ECA kinetics as derived in Tang and Riley (2013a).

3 The equation below the table shows the uptake of substrate S_i by consumer E_j as a

4 function the normalized substrate flux $F_{c,j}$ and its conjugate flux $F_{r,i}$. Subscript "c"

5 designates column, and "r" designates row. When K_{ij} is very large compared to other

6 entries in the matrix, the interaction between substrate S_i and consumer E_j can be 7 ignored.

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An example unit block for applying the network-oriented SUPECA kinetics



2 Figure 2. Graphic representation for the relationships between substrates, consumers, and

normalized fluxes and their conjugates for a block unit of a large substrate-consumer
 network.



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



2

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





derived from incubation data from Franzluebbers (1999). All response functions are

normalized with their respective peak respiration. The R-squared coefficients of

determination for the different response function curves from top to bottom are,

respectively, 0.82, 0.81, 0.77, 0.71 and 0.84. Note that the curve of f(s) has been

normalized to set its maximum value at 1, making it slightly above the majority of the data points.





2 Figure 6. Simulated moisture response functions using elevated 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).