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Interactive Comment

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

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Overall comments: *In this paper, Tang has followed up on his earlier work assessing the nature of microbial kinetics to use in microbially explicit biogeochemical models. The earlier generations of microbially implicit models assumed first-order kinetics for substrate movement from a source pool to a sink pool (dC/dt = k*C). The models (e.g. CENTURY) are powerful and simple, but they have limitations that researchers have been trying to overcome with newer models that treat microbes as actual drivers of processes, drivers whose population and characteristics can change dynamically and*

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so must be represented explicitly.

The challenge Tang notes is that authors have used different kinetic expressions in such models, depending on whether the model assumes that substrates are mobile and can saturate the enzyme active site (leading to Michaelis-Menten kinetics) or whether substrates are immobile and enzymes can saturate potential reaction sites (leading to reverse Michaelis-Menten kinetics). In an earlier paper, Tang and Riley had shown that these two formulations were really end members of a more general model which can shift between those states and doesn't require an assumption of either enzymes or substrates being a functionally immobile entity. That is the ECA model. In this paper, they further develop the analysis of these different approaches to modeling microbial kinetics. This is unquestionably a useful activity. I really appreciate developing a single integrated expression that isn't as constrained as any of the equations that place greater constraints in the assumptions.

Response: Many thanks for your positive comments. We'll keep doing the good work.

Comment 1: *Despite that, I have some questions as to the utility of getting deeply mechanistic in the derivation of fundamental chemical kinetics for these expressions.*

Response: I addressed you comments point by point below, and some of those discussions are integrated into the revised manuscript.

Comment 2: *First, classical kinetics deals in activities, not concentrations, and assumes that the activity of any material that is not dissolved is equal to 1. Yet, many of the decomposition reactions involving exo-enzymes are likely mixed phase, in which the substrate is not in solution, the enzyme may be, and the products certainly are. So at least for applying to a real-world situation, does the shift between single phase (dissolved or vapor) and mixed phase (some in solution, some not) change how we should view the real mechanistic interpretation of these expressions? It should, I think, as it converts a true mechanistic model into an empirical approximation of one in which we can use concentration terms that are per gram soil, for example.*

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Response: Thanks for raising this question and I will take this opportunity to clarify the goal of my manuscript. Yes, classical kinetics deals with activities, not concentration; however, the substrate uptake process as we are dealing with in soil biogeochemical modeling can be conceptualized as analogues to the predator-prey relationship, or, more generally, the resource competition problem. This generalization allows us to directly deal with the concentrations even though such generalization does make the solution to the problem slightly more empirical. Specifically, the prey-searching rate and prey-attacking rate together establish a dynamic equilibrium between prey and predator concentrations. This is analogous to the binding process between substrates and enzymes, and could be achieved without referring to the phase of existence for either the enzymes or substrates. Therefore, mathematically, as we discussed in the ECA paper (Tang and Riley, 2013), the problem can be formulated into the equilibrium chemistry form. Such analogy is also supported by the derivation of MM kinetics even for a single molecule enzyme (where substrate is unlimited and the definition of phase for enzyme becomes ill-defined; English et al., 2006). Because of the equilibrium binding as implied behind the conceptual model, we can establish the relationships between MM, RMM and ECA kinetics as I attempted in this manuscript.

Comment 3: *Second, in a physically constrained, diffusion-limited system, are these simple concentration-defined rate expressions accurate or appropriate? I suspect that they all "work" to capture the overall dynamics of major organic matter components in soil and plant litter (using bulk concentration), but maybe not because they meet the assumptions of the actual chemical models.*

Response: As I explained in the response to comment 2, when diffusion is unlimited, the adoption of the equilibrium binding is eligible. When diffusion limitation comes into place, the control of diffusivity can be incorporated accordingly to derive a revised kinetics (e.g., Tang and Riley, 2013). Application of such revised kinetics in marine ecosystems has indicated very successful results (Bonachela et al., 2011).

Comment 4: *That latter issue underlies a slight misrepresentation of the Schimel and*

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*Weintraub model's development of reverse M-M kinetics (page 7665, line 21). The author's statement that Schimel and Weintraub explored straight M-M kinetics is inaccurate (though unimportant). SW didn't get that far! Rather they explored linear kinetics and noted that if the reaction rate expression was linear on enzyme concentration (dC/dt = k * [Enz] * [Substrate]) the system was inherently unstable and would always either explode or crash.*

Response: Sorry for this misinterpretation, I corrected it in the revision.

Comment 5: *They proposed reverse-MM kinetics because it offered a mathematically simple equation to generate an asymptotic response; calling it reverse-MM kinetics gave a plausible rationale for using the equation, but the important thing was to get the needed general asymptotic shape. There was no fundamental chemical mechanism suggested in their use of the equation (even if one can be derived). With any mechanism to produce a system in which, as the enzyme pool increases, the activity per unit enzyme decreases, the system becomes potentially stable as it avoids the problem that if an enzyme returns more C over it's lifetime than it cost to produce the enzyme then the enzyme pool would continue to grow and accelerate decomposition (and vice versa as if the enzyme never paid for itself, it would run down). There must be a variable marginal return on investment, but there can be multiple mechanisms that produce that pattern. It could be that as there are more enzymes, microbes become more likely to target them as a substrate, it may involve increased growth of "cheaters" as enzyme activities increase and the bioavailable substrate pool grows, it may even involve increasing diffusion path lengths and so slowing the link between enzyme production and substrate recovery. The model imperative of non-linear kinetics need not, in fact, ever involve the explicit reverse M-M assumption of enzymes competing for binding to potential reaction sites on substrates (and so may not have a real Kes term in the sense implied by Tang's ECA model). In fact, multiple specific mechanisms may well be involved in creating the overall non-linearity that is required for model (and actual system) stability.*

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Response: Thanks for this detailed explanation of how RMM was motivated. Interestingly, the motivation that "it [RMM] avoids the problem that if an enzyme returns more C over it's lifetime than it cost to produce the enzyme then the enzyme pool would continue to grow and accelerate decomposition" clearly points to the deficit of the MM kinetics resulting from its incomplete consideration of the substrate limitation as I discussed in the manuscript (which implies that if enzymes have a small turnover, the system will become unstable as enzyme concentration increases). Therefore, it seems that the mechanism, which works, for enzyme-substrate system could be (conceptually) scaled up to the overall system of carbons and microbes, indicating the scaling power of ECA as a first-principle based mathematical theory. This scaling property also seems to support the hypothesis that a single rate limiting "master reaction" controls the overall response of microbial activity (Johnson and Lewin, 1946), which is implied in the Monod kinetics. Therefore, considering the benefit from process scaling, I suggest approaches such as that used in deriving ECA should be preferred, even though the parameters in the derived equations are up-scaled versions of those measured in a tube.

Comment 6: *Such phenomena leave me uncertain just how useful a pure chemical kinetic derivation of these equations really is as they may describe the rough behavior of the system that is produced by several mechanisms working in parallel (or at odds with each other), such that the parameters that drive the equations are not clean chemical rate or equilibrium constants, but empirical terms to give the right rough shape to the overall responses. To some degree this is analogous to the difference between Michaelis-Menten enzyme kinetics and Monod microbial growth kinetics. The equations have identical structures but are fundamentally different: M-M kinetics is derived from 1st principles, while Monod growth has no such basis. The half-saturation constant in Monod growth is purely empirical. Would that be the case with the Kes term in Equation 12 in the ECA model if it were integrated into a soil C model? I think so. Might that make it a more difficult term to consider and apply? Maybe because to use the model in a biogeochemical model, it would have to be the empirically derived term*

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rather than a real "affinity constant" that could be evaluated in a test-tube. But because it is an interaction term for the enzyme-substrate reaction it might be more sensitive to whether the non-linearity is being driven by substrate movement to the enzyme or to enzyme movement to the substrate. Please note, I'm not saying that would necessarily be the case (at least to within the bounds of experimental variation) but it remains a possibility. Such issues should be addressed more clearly by the authors, who I think somewhere should note the difference between a rate expression that is derived from fundamental chemical kinetics and one that may look the same but is only as an empirical approximation to force the model system to behave in reasonable, non-linear, patterns. I don't think that any such discussion need be long or involved, but I think it should be present.

Response: I share your sympathy towards the complexity of the soil organic carbon decomposition problem that we are trying to model. However, I think adopting an approach as close as possible to the first principles is more valuable than a more empirical approach, although they both require significant level of genius to work appropriately and sometimes may even appear similar (such as the MM kinetics and Monod kinetics). Compared to the empirical approach, the first-principle based approach would allow a more consistent and probably more mechanistic explanation to how the complexity of SOM decomposition could be scaled up and resolved by incrementally adding new identifiable processes one after another. For instance, the ECA approach would allow a consistent combination of microbe-substrate binding and substrate-mineral surface binding, such that it would naturally predict that k-strategist would be favored over the r-strategist with the increase of mineral adsorption, therefore both modelers and experimentalists could have a better clue to explain the measurements. Similarly, as we showed in Tang and Riley (2015), such combination enabled our model to explain many behaviors that are empirically observed, but otherwise require significant recalibration of the empirical approach for different experimental configurations or sometimes call for additional ad hoc parameterizations (e.g., the CENTURY-BGC module as we implemented in CLM4.5 requires a parameterization of decreasing decomposition rate

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with depth, which however will become ridiculous that by simply putting the same soil at different depth under same soil physical conditions will produce different respiration rates). Further, even it is arguable that the assumption underlines both the MM kinetics and Langmuir isotherm, or more generally, the law of mass action, are empirical, they all can be organized with a single statement, that there are two processes involved in the substrate uptake by consumers, i.e. find (or bind) the substrate and assimilate it. This simple assumption allows the consistent scaling of all mechanisms that are contributing to the SOM decomposition dynamics, therefore avoiding the necessity to propose a new empirical relationship when something new fails the model, such as replacing the MM kinetics with the RMM kinetics for enzyme degradation of SOM, because RMM is asymptotically more stable.

Minor points: *7665, 16: This may be a linguistic battle I'll lose, but "uptake" is not a verb. Microbes take up a substrate.*

7677, 6: "normalized" there's a typo

7679, 15: "very critical"? I'd delete "very." Response: Thanks for your careful examination. I corrected these issues.

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