Geosci. Model Dev. Discuss., 8, C2276–C2280, 2015
www.geosci-model-dev-discuss.net/8/C2276/2015/

Geoscientific Model Development Discussions

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

J. Schimel (Referee)

josh.schimel@lifesci.ucsb.edu

Received and published: 29 September 2015

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 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.

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

That latter issue underlies a slight misrepresentation of the Schimel and 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). S&W 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. 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 stableâĂŤit 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 versaâĂŤif 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 is more enzyme, 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 pathlengths 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.

Such phenomena leave me uncertain just how useful a pure chemical kinetic derivation of these equations really isâĂŤthey may describe the rough behavior of the sys-

tem 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? MaybeâĂŤbecause to use the model in a biogeochemical model, it would have to be the empirically derived term 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.

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."

Interactive comment on Geosci. Model Dev. Discuss., 8, 7663, 2015.