Comments from Referee #1

This paper extends the analytical solution approach of Chen et al (2012a, cited in draft) to develop an analytical solution to 1D advective-dispersive transport of solutes undergoing both kinetically-controlled reversible linear sorption and first-order decay lead into a chain of daughter products. The method derivation is detailed and is compared to a Laplace-transform numerical solution for cross-validation. The focal point of the paper is that kinetically-controlled sorption renders fate and transport differently than does equilibrium sorption, and that simulations using the equilibrium sorption assumption erroneously will be wrong, which is not really a novelty or a surprize. It seems to me that the real value is the solution itself. The solution is developed for the case of degradation or decay occurring exclusively in the aqueous (mobile) phase. This is I think critical for the mathematics because otherwise there could be the path C1 -> S1 -> S-2 -> C2, that is, sorption of the parent solution leading S1 which decays to S2 which could then desorb as C2. This path would complicate things mathematically and is not allowed here. The critical reader would prefer to see a justification of this assumption. The authors have not in my view delved into that topic enough here; however, I think that with some reviewing of the literature that they could find cases where sorption blocks decay, specifically for reduction or oxidation of TCE or other chlorinated solvents. Some places to begin looking include Yang et al, J. Contaminant Hydrology vol 211, Yu et al., Env. Science and Tech 2018 ("diffusion-coupled degradation ..."), Seyedabbasi et al., J. Contaminant Hydrology 2012. None of these directly answer the question of whether or not decay of sorbed species is significant or not but with a but more searching one should be able to find more supporting literature. At any rate this assumption requires more support because the entirety of the paper is based upon it. It may also be instructive to return to the
equilibrium sorption case to see what happens when (and when not) the sorbed species undergoes decay. In the "not" case one gets the usual retardation coefficient and in the yes case one gets something more complicated, although it would seem keeping track of time spent sorbed may be useful. Finally the authors may look into generalizing their sorption model to a memory function form, such as used for multirate mass transfer. It may be the case that their developments here would translate smoothly to such a generalization, which would be quite powerful. In summary this paper clearly articulates an extension of analytical solution approaches to the case specified, and is a nice contribution. Tim Ginn, Washington State University.

**Author's response**

The authors sincerely thank Prof. Tim Ginn for his extensive and constructive comments and suggestions which will substantially improve the quality of this paper. This paper develops an analytical model for multispecies transport subject to rate-limited sorption with an assumption of degradation or decay occurring exclusively in the dissolved phase. We fully accept that justifying the validity of the assumption is required for more reasonably and accurately simulating the transport behavior using our derived analytical model. Degradation or decay is a fundamental attenuation process that significantly governs the transport and fate of contaminant in the surface environment. Many modeling studies took into consideration of the decay of radionuclides in the sorbed phase, whereas the degradation of organic contaminants in the sorbed phase was frequently neglected in modeling approaches. For example, Clement et al. (2004) modeled DNAPL-dissolution, rate-limited sorption and biodegradation reactions in groundwater systems using the three-dimensional code RT3D (Clement, 1997) with exclusively degradation occurring in the dissolved phase.
Similar modeling approach were also adopted by Haggerty and Gorelick (1994). Currently, limited data were provided to justify the validity of the assumption. The degradation rate constants for the dissolved and sorbed phases are very site specific and should differ as a function of many factors involved in the complex interactions among microorganisms, contaminants and constituents of solid particles (Jury et al., 1987). It is generally accepted that sorption can block the degradation of organic contaminants. Earlier experimental work from many studies showed the evidence of the negative dependence of degradation on sorption for a variety of contaminants. Researchers postulated that the contaminants in the sorbed phase are less accessible to microorganisms that utilize exclusively or preferentially contaminants in the dissolved phase. Nevertheless, inverse dependence of sorption on degradation does not necessarily mean that degradation of contaminants in the sorbed phase should be negligible. Guo et al. (2000) presented a nonequilibrium model to quantitatively characterize the effect of sorption on degradation of 2, 4-D and to examine the role of nonequilibrium sorption plays in degradation kinetics. In combined use of batch sorption and incubation experiments, they estimated the degradation rate constant of 0.157 and 0.00243 day\(^{-1}\) for the dissolved and sorbed phases, respectively, differing by a factor of 65. For this case, it seems the degradation in the sorbed phase can be safely neglected in the modeling approach because the degradation rate in the sorbed phase is much faster than that in the sorbed phase. Although the simpler model that the degradation in the sorbed phase is neglected developed in this study seems to suffice for modeling a case with a small degradation rate constant in the sorbed phase. However, the more refined model that considers degradation in both the dissolved and sorbed phases is much more useful and necessary in accurately evaluating all the decaying and degradable contaminants, especially when the decay or degradation simultaneously
occurring in the dissolved and sorbed phases.

We also degenerate the more refined rate-limited model with simultaneous degradations in both the dissolved and sorbed phases into the simplified equilibrium model. Based on symbols used in our original manuscript, the governing equations for describing one-dimensional transport of decaying or degradable contaminants involving an arbitrary number of species undergoing a series of first-order decay/degradation reactions in the dissolved phase and first-order reversible kinetic sorption reaction between the dissolved and sorbed phases are

\[
D \frac{\partial^2 C_1(x,t)}{\partial x^2} - v \frac{\partial C_1(x,t)}{\partial x} - \lambda_1 C_1(x,t) - \frac{\beta_1}{\theta} \left( C_1(x,t) - \frac{S_1(x,t)}{K_1} \right) = \frac{\partial C_1(x,t)}{\partial t} \quad (1a)
\]

\[
D \frac{\partial^2 C_i(x,t)}{\partial x^2} - v \frac{\partial C_i(x,t)}{\partial x} - \lambda_i C_i(x,t) + \lambda_{i-1} C_{i-1}(x,t) - \frac{\beta_i}{\theta} \left( C_i(x,t) - \frac{S_i(x,t)}{K_i} \right) = \frac{\partial C_i(x,t)}{\partial t} \quad i = 2, ..., N \quad (1b)
\]

\[
\rho_b \frac{\partial S_i(x,t)}{\partial t} = \beta_i \left( C_i(x,t) - \frac{S_i(x,t)}{K_i} \right) \quad i = 1, ..., N \quad (2)
\]

It is noted that the degradation or decay reaction in the sorbed phase is neglected in Eq. (2).

If we consider the degradation reaction in the sorbed phase, Eq. (2) can be modified as

\[
\rho_b \frac{\partial S_1(x,t)}{\partial t} = \beta_1 \left( C_1(x,t) - \frac{S_1(x,t)}{K_1} \right) - \rho_b \gamma_1 S_1(x,t) \quad (3a)
\]

\[
\rho_b \frac{\partial S_i(x,t)}{\partial t} = \beta_i \left( C_i(x,t) - \frac{S_i(x,t)}{K_i} \right) - \rho_b \gamma_i S_i(x,t) + \rho_b \gamma_{i-1} S_{i-1}(x,t) \quad i = 2, ..., N \quad (3b)
\]
where \( \gamma_i \) is the first-order decay rate constant in the sorbed phase.

Eqs. (3a) and (3b) can be also expressed as

\[
\rho_b \frac{\partial S_1(x,t)}{\partial t} + \rho_b \gamma_1 S_1(x,t) = \beta_i \left( C_1(x,t) - \frac{S_1(x,t)}{K_1} \right)
\]

(4a)

\[
\rho_b \frac{\partial S_i(x,t)}{\partial t} + \rho_b \gamma_i S_i(x,t) - \rho_b \gamma_{i-1} S_{i-1}(x,t) = \beta_i \left( C_i(x,t) - \frac{S_i(x,t)}{K_i} \right)
\]

(4b)

Through substitution of the relations in Eqs. (4a) and (4b) into Eq. (1a) and (1b) and rearrangement of terms, we have

\[
D \frac{\partial^2 C_1(x,t)}{\partial x^2} - \nu \frac{\partial C_1(x,t)}{\partial x} - \lambda_i C_1(x,t)
\]

\[\] - \frac{\rho_b}{\theta} \gamma_1 S_1(x,t) = \frac{\partial C_1(x,t)}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S_1(x,t)}{\partial t}

(5a)

\[
D \frac{\partial^2 C_i(x,t)}{\partial x^2} - \nu \frac{\partial C_i(x,t)}{\partial x} - \lambda_i C_i(x,t) + \lambda_{i-1} C_{i-1}(x,t)
\]

\[\] - \frac{\rho_b}{\theta} \gamma_i S_i(x,t) + \frac{\rho_b}{\theta} \gamma_{i-1} S_{i-1}(x,t) = \frac{\partial C_i(x,t)}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S_i(x,t)}{\partial t}

(5b)

If a linear equilibrium-controlled sorption isotherm \( C_i(x,t) = \frac{S_i(x,t)}{K_i} \) is assumed, Eqs. (5a) and (5b) can be simplified as follows:

\[
D \frac{\partial^2 C_1(x,t)}{\partial x^2} - \nu \frac{\partial C_1(x,t)}{\partial x} - \left( \lambda_i + \frac{K_1 \rho_b}{\theta} \right) C_1(x,t)
\]

\[=\] \left( 1 + \frac{K_1 \rho_b}{\theta} \right) \frac{\partial C_1(x,t)}{\partial t}

(6a)

\[
D \frac{\partial^2 C_i(x,t)}{\partial x^2} - \nu \frac{\partial C_i(x,t)}{\partial x} - \left( \lambda_i + \frac{\rho_b K_i}{\theta} \gamma_i \right) C_i(x,t) + \left( \lambda_{i-1} + \frac{\rho_b K_{i-1}}{\theta} \gamma_{i-1} \right) C_{i-1}(x,t)
\]

\[=\] \left( 1 + \frac{\rho_b K_i}{\theta} \right) \frac{\partial C_i(x,t)}{\partial t}

(6b)

If we compare Eqs. (6a) and (6b) with the governing equations used in
BIOCHLOR, we can find the third term in Eq. (6a) and third and fourth terms in Eq. (6b) are replaced with $-\lambda_i C_1(x,t)$, $-\lambda_i C_1(x,t)$ and $+\lambda_i \gamma_{i-1} C_{i-1}(x,t)$. This implies that the degradation in the sorbed phase is neglected in BIOCHLOR.

Assuming that the sorption coefficient is the same in both the dissolved and sorbed phases ($\lambda_i = \gamma_i$), one gets

$$D \frac{\partial^2 C_1(x,t)}{\partial x^2} - v \frac{\partial C_1(x,t)}{\partial x} = R_1 \frac{\partial C_1(x,t)}{\partial t}$$

$$= R_1 \frac{\partial C_1(x,t)}{\partial t}$$

(7a)

$$D \frac{\partial^2 C_i(x,t)}{\partial x^2} - v \frac{\partial C_i(x,t)}{\partial x} = \left(\lambda_i + \frac{\rho_b K_i}{\theta} \gamma_i\right) C_i(x,t) + \left(\lambda_{i-1} + \frac{\rho_b K_{i-1}}{\theta} \gamma_{i-1}\right) C_{i-1}(x,t)$$

$$= R_i \frac{\partial C_i(x,t)}{\partial t}$$

(7b)

where $R_i = 1 + \frac{K_i \rho_b}{\theta}$.

Ultimately, we thank the very helpful suggestion that improve our rate-limited sorption model into the more generalized multiple-rate mass transfer model (Haggaery and Gorelick, 1995) that would be very useful in the realistic field condition. Such task will be proceeded in the near future.

References


Clement, T. P.: Generalized solution to multispecies transport equations coupled with


**Author's changes in manuscript.**

1. We have elaborated on the neglect of the degradation in the sorbed phase in the revised manuscript.

2. We have added a discussion regarding the advancement of our rate-limited sorption model to the more generalized multiple-rate mass transfer model (Haggaerty and Gorelick, 1995) in the revised manuscript.