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Considering the utility of backward-in-time simulations of multi-component reactive transport in porous media

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ABSTRACT

Indirect inversion has been the predominant method for matching models and data in geochemical systems, typically using observations of chemical concentrations as calibration targets. This reserves the data with the highest confidence (observed concentrations) for the final comparison but does little to constrain the initial state of the system on which the indirect inversion is based. An alternative approach to inverse modeling is to start with the observations to reconstruct a concentration field, but it is unclear if this is feasible for reactive transport in heterogeneous systems. The purpose of this article is to consider the applicability of backward-in-time (BIT) techniques as tools for simulating reactive transport in porous media. A multi-component reaction system is considered in a variety of systems of increasing complexity and we show that complex, non-linear systems can be simulated backward in time, given a sufficiently robust integration scheme. Recent advances in reactive random walk particle tracking are employed to investigate simple flow systems with spatially variable reactions, as well as 2-d heterogeneous flows, and we show that some level of time reversibility exists in both cases. Under a uniform injection scheme, the total masses generated in forward and backward simulations of the 2-d models were all within 3.5% of each other for all the species considered, indicating good overall agreement between the models. This suggests that BIT techniques may have yet unrealized applications to inverse modeling; however, further research on the sensitivity of the approach to measurement errors and on how to efficiently apply BIT methods to transient problems is needed.

1. Introduction

Reactive transport problems involve immense complexities existing at multiple temporal and spatial scales (Atchley et al., 2014; Dentz et al., 2011). A common approach to understanding the behavior of such systems starts by collecting and analyzing geochemical data at monitoring points, then using a lumped-parameter or distributed model to discover the physical implications or context of the observations for predictive modeling or other applications. At its core, this workflow is an application of indirect inverse modeling to reactive transport: the parameters, boundary conditions, and initial conditions of a forward model are specified, the simulation result is compared to the data, and then the model is revised accordingly until satisfactory agreement with observations is reached. Distributed parameter models (e.g. Appelo and Rolle, 2010; Beisman et al., 2015) are common tools for simulating reactive transport because of their ability to solve problems with spatially variable parameters, as opposed to lumped parameter models; however, these models also further complicate the problem because of their immense computational expense, which can require hours, days, or weeks for a single simulation (e.g. Mills et al., 2007). A key point about these models is that each forward simulation implicitly assumes that the specified initial and boundary conditions are correct and that the hydrologic and geochemical properties of the system will be able to approach the observed values, but this is far from guaranteed considering the uncertainty of the problem. Essentially, this approach relies on specifying something that we do not (or cannot) know – the initial condition – and uses this "guess" to try and recreate observations. This can be an effective strategy, but the enormous computational costs can limit its applicability to those with supercomputers at their disposal, making it impractical for many real-world problems. Inverse modeling can be sped up by adopting simplified forward models but this comes at the expense of accuracy since excessive simplifications will inevitably lead to inaccurate predictions, particularly regarding nonlinear processes. Clearly, a major challenge of any reactive transport model is identifying the starting state of the system, regardless of the simplicity or complexity of the forward model. With this in mind, it may be possible to improve the process of inverse modeling if the system can be solved in a way that begins with known data, as opposed to comparing to it in the end. This would then provide plausible estimates of the unknown initial conditions that are conditional to the observations, which are the component of the inverse problem that is known with the highest confidence. The

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main question is: How to incorporate the observations most effectively in the inverse model? Many ways of conditioning to chemical data exist, but one possibility that has seen little attention is simulating the full reactive transport system with time reversed.

Forward-in-time (FIT) models are widespread across hydrology, but the most common example of a backward-in-time (BIT), or adjoint, model is capture zone analysis, which is often associated with simulations of travel time. From a strictly mathematical perspective, there is nothing preventing integration of a system of ordinary differential equations (ODEs) in an arbitrary direction. The simplest case to consider to illustrate this point is a single analytical function, such as f with derivative $df/dx = 2x$. Given a known function value anywhere on the curve, say $f(x = 2) = 2$, one can determine the value at any other location, and the same is true for a system of equations as long as a starting point for each equation is known. However, Eulerian solutions of a system of partial differential equations in arbitrary directions (FIT or BIT) introduce complexities in the boundary conditions (see Neupauer and Wilson, 1999; 2002) and the stability of the problem is not guaranteed (Appendix B). Lagrangian approaches to the backward problem (De Rooij et al., 2013; Eberts et al., 2012) offer a conceptually simpler approach, at least mathematically, and they are adopted here for this reason.

The most common Lagrangian approach in hydrology is random walk particle tracking (RWPT). A simple form of the RW equation for a FIT model is:

$$\boldsymbol{X}_i(t + \Delta t) = \boldsymbol{X}_i(t) + \boldsymbol{v}(\boldsymbol{X}_i(t), t) + \sqrt{2D\Delta t}\boldsymbol{\xi}, \tag{1}$$

where $\boldsymbol{X}_i(t)$ $[L]$ is the position vector of the ith particle at time t, moving according to the velocity field $\boldsymbol{v}(x, t)$ $[L/T]$ and diffusing at rate D $[L^2/T]$, with n-dimensional Gaussian random noise included via $\boldsymbol{\xi}$, over time step Δt. In the continuum limit (*i.e.* for a large ensemble of particles), it is well known that this models an advection-dispersion process. We expect that many readers are at least conceptually familiar with the RW model so a more general form and more detail on the approach are reserved for Appendix A. The key point is that Lagrangian methods discretize the mass whereas Eulerian methods discretize space. Contemporary versions of the RW approach can now assign an arbitrary number of species to each particle (Bolster et al., 2016), allow inter-particle interactions (Benson and Meerschaert, 2008; Rahbaralam et al., 2015), and incorporate complex reactions (Engdahl et al., 2017), while avoiding numerical oscillations and numerical dispersion. The random walk BIT approach for advection is conceptually simple and differs from the FIT model only in the sign of the time step $\Delta t \rightarrow (-\Delta t)$ in (1), which can also be accomplished by reversing the sign of the velocity field. More details on advection are given in Appendix A, but it simply traces streamlines backwards instead of forwards. The diffusion operator is "self-adjoint," and this means that its forward and backward forms are identical; it remains a spreading operation in both cases, proportional in magnitude to $\sqrt{|\Delta t|}$. Backward-in-time dispersion due to sub-grid velocity heterogeneity incorporates some of the elements of the advection and diffusion operators and interested readers are referred to Uffink (1990) for details. It is important to note that, since diffusion is simulated as a random process, the forward and backward paths of an individual particle will differ unless the exact same jumps are used in both simulations.

Conceptually, a BIT model places particles at their terminus and sends them back to their source allowing for advection and random dispersive motion along the way. One interpretation of this approach is that it aims to identify the distribution of source locations conditional to the sampling location(s), whereas a FIT model does the opposite. The BIT approach has seen widespread use in source zone identification and simulations of residence time distributions (e.g. Engdahl and Maxwell, 2015), but it has also been used to reconstruct concentration histories of environmental tracers. Reactions have been simulated on particles in previous applications of BIT models, but these have been limited to simple reactions that do not require particles to interact, such as first order decay (e.g. McCallum et al., 2014). When more complex reactions are considered, the validity of BIT methods is not as clear because the combined impacts of advection, spreading, and reactions in the presence of a heterogeneous velocity field may have unanticipated effects. This also raises some basic questions. For example, are the same flow paths sampled when spreading occurs in a reversed velocity field? However, in order to assess whether or not source zone concentrations can be reconstructed using BIT methods, we must first address the issue of whether or not reactive transport can be simulated in backward time.

The purpose of this article is to investigate whether or not BIT simulations are possible for nonlinear reactive transport systems in an operational sense. The approach taken here applies recent advances in particle-based simulations of complex reactions to the backward problem and we provide several examples that evaluate the equivalency of the forward and backward models under different transport conditions. A single article cannot address all of the possible reaction systems, initial conditions, and boundary conditions, nor the infinite combinations of other factors that can influence reactive transport. Consequently, we focus on a few generic, steady-state problems and avoid making generalizations at this stage until more supporting research can be completed. However, the examples establish the general time-reversibility of reaction networks in a batch reactor and the equivalency of FIT and BIT models in 1-D domains under homogeneous and spatially variable reaction rates, and demonstrate some of the challenges presented by 2-D heterogeneous flows. The body of the article focuses on numerical analysis but two appendices are included that discuss theoretical considerations of backward-in-time models (Appendix A) and the numerical stability of the FIT and BIT models (Appendix B). Addressing this collection of basic questions is seen as a necessary prerequisite for future investigations of the potential applications of BIT simulations, such as in inverse problems and uncertainty reduction.

2. Reaction system

Simple, first-order reactions are trivial to reconstruct, and this is the basis of many environmental tracer analyses to determine water ages from tracers like Krypton-85 or Tritium. Our first task is to show that this "time reversibility" can also apply to more complex reaction networks. The reaction network we consider here is based on the competitive decay chain example found in Engdahl et al. (2017), which involves a combination of equilibrium and kinetic reactions:

$$pA + qB \rightarrow C \tag{2a}$$

$$C + E \rightleftharpoons F \tag{2b}$$

$$E \rightarrow \emptyset \tag{2c}$$

where p and q are stoichiometric coefficients, and the uppercase letters represent chemical species. These aqueous-phase reactions only affect solutes and involve no precipitation, dissolution, or surface complexation reactions; these processes can be included, but are omitted here for simplicity. Eqs. (2a) and (2c) are irreversible kinetic reactions with rate constants k_f and λ, respectively, and Eq. (2b) is an equilibrium, reversible reaction with equilibrium constant $k_{eq} = [C][E]/[F]$. We assume unit stoichiometry for (2b). Arbitrary chemical species are used for generality but this can represent a wide variety of processes. The system has a natural shift in its balance over time because F temporarily sequesters E, which causes it to stay in the system longer than if decay alone acted on E. In a transport system, this allows competition between mixing limitations and the direction of the equilibrium reaction to be simulated, while still being of manageable complexity.