Toward efficiency in heterogeneous multispecies reactive transport modeling: A particle-tracking solution for first-order network reactions

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Modeling multi-species reactive transport in natural systems with strong heterogeneities and complex biochemical reactions is a major challenge for assessing groundwater polluted sites with organic and inorganic contaminants. A large variety of these contaminants react according to serial-parallel reaction networks commonly simplified by a combination of first-order kinetic reactions. In this context, a random-walk particle tracking method is presented. This method is capable of efficiently simulating the motion of particles affected by first-order network reactions in three-dimensional systems, which are represented by spatially variable physical and biochemical coefficients described at high resolution. The approach is based on the development of transition probabilities that describe the likelihood that particles belonging to a given species and location at a given time will be transformed into and moved to another species and location afterwards. These probabilities are derived from the solution matrix of the spatial moments governing equations. The method is fully coupled with reactions, free of numerical dispersion and overcomes the inherent numerical problems stemming from the incorporation of heterogeneities to reactive transport codes. In doing this, we demonstrate that the motion of particles follows a standard random walk with time-dependent effective retardation and dispersion parameters that depend on the initial and final chemical state of the particle. The behavior of effective parameters develops as a result of differential retardation effects among species. Moreover, explicit analytic solutions of the transition probability matrix and related particle motions are provided for serial reactions. An example of the effect of heterogeneity on the dechlorination of organic solvents in a three-dimensional random porous media shows that the power-law behavior typically observed in conservative tracers breakthrough curves can be largely compromised by the effect of biochemical reactions.