Calculation of reaction parameter sensitivity coefficients in multicomponent subsurface transport models

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Abstract

A significant source of uncertainty in multicomponent transport models is due to reaction parameter estimation error. In this paper, two codes are developed to compute reaction parameter sensitivity coefficients, which provide a quantitative measure of the impact of this uncertainty. One of the codes solves the full coupled system of sensitivity equations, while the other applies the operator splitting approach to decouple the sensitivity equations for each chemical component. CPU time comparisons demonstrate that operator splitting significantly reduces the simulation time for solving both the state and sensitivity equations. These comparisons also confirm that solution of the sensitivity equations is more efficient than a traditional direct perturbation sensitivity analysis. Sensitivity calculations for an example transport problem with cobalt and nitrilotriacetate (NTA) are used to gain insight into the relative significance of reaction processes and to rank individual reaction parameters in terms of importance. In this example, speciation reactions cause an indirect linking of the NTA biodegradation and the cobalt sorption reactions, making the NTA concentration nearly as sensitive to the sorption parameters as to the degradation parameters. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Sensitivity analysis; Groundwater; Contaminant transport; Mathematical modeling; Operator splitting; Sorption; Biodegradation

Notation

- [A] combined advection–dispersion matrix; square matrix of order $N_a(N_c + N_m)$
- [A]_j advection–dispersion matrix for component j; square matrix of order $N_a$
- $a_{ij}$ stoichiometric coefficient giving the number of moles of component j in complex i
- b first-order microbial decay coefficient (h$^{-1}$)
- $c_j$ uncomplexed concentration of aqueous component j (moles/l)
- $C_j$ total concentration of aqueous component j (moles/l)
- $D_{xx}, D_{xy}, D_{yx}, D_{yy}$ elements of hydrodynamic dispersion
- $D_{jk}, D_{xy}$ coefficient tensor (m$^2$/h)
- $\varepsilon$ time-weighting factor between n and $n + 1$
- $H_{jq}$ hybrid sensitivity coefficient of component j with respect to parameter q (moles/l or moles/g)
- [J] combined Jacobian matrix; square matrix of order $N_a(N_c + N_m)$
- [J]_i Jacobian matrix for node i; square matrix of order $N_c + N_m$
- $K_A$ half-maximum-rate concentration for electron acceptor (moles/l)
- $K_d$ distribution coefficient for sorption (l/g)
- $K_{eq,j}$ formation constant for complex i
- $K_m$ sorption mass transfer coefficient (h$^{-1}$)
- $K_S$ half-maximum-rate concentration for electron donor (moles/l)
- L( ) advection–dispersion operator
- [M] combined mass matrix; square matrix of order $N_a(N_c + N_m)$
- $m_k$ concentration of immobile component k (moles/g)
- $N_c$ number of aqueous components

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Tanks. Contaminant plumes migrate through the subsurface environment. Pollutants from landfills, and leaking underground storage tanks. Common sources of groundwater contamination include: interactions between freshwater supplies [1].

1. Introduction

One of the most important environmental problems of today is the contamination of groundwater resources, which make up about 95% of the earth’s utilizable freshwater supplies [1]. Common sources of groundwater contamination include: interactions between groundwater and buried waste, downward migration of pollutants from chemical spills, infiltration of pesticides and fertilizers from agricultural lands, leaching of pollutants from landfills, and leaking underground storage tanks. Contaminant plumes migrate through the subsurface under the influence of physical flow processes and reaction mechanisms, which may modify the form of the contaminant species. The transport of a given contaminant species may be significantly affected by interactions with other dissolved species, mineral surfaces, and microorganisms; therefore, a contaminant transport model must be able to simulate the important chemical and biological reaction processes, as well as the physical processes of advection and dispersion. In recent years, a number of numerical models have been developed to simulate the reactive transport of contaminants in groundwater (e.g., [2–10]). These models are used to assess the risk of groundwater contamination and to predict the success of remediation alternatives in the subsurface environment.

In a reactive transport model, the fundamental reaction processes affecting the migration of groundwater contaminants are represented with an appropriate mathematical expression and a corresponding set of reaction parameters. The mathematical representation of each reaction process must be derived from field studies or laboratory batch and column experiments. Parameter values obtained in these investigations are subject to uncertainty due to measurement error as well as the spatial variability of properties in the subsurface environment. The quantification of the effects of parameter uncertainty on the state of the system is the objective of a parameter sensitivity analysis.

Brandstetter and Buxton [11] define a sensitivity analysis as a study that “determines the effects of variation(s) in one or more parameters on the performance of a system or some part of it”. In the case of reactive transport modeling, the state of the system is characterized by a set of concentrations, and the set of system parameters include both flow (e.g., hydraulic conductivity and dispersion coefficients) and reaction parameters. In the groundwater modeling literature, sensitivity analyses have been performed to examine the influence of physical flow parameters and retardation coefficients (e.g., [12–14]); however, the case of general reaction parameters has yet to be considered. In the chemical engineering literature, reaction parameter sensitivity has been examined in batch and one and two-dimensional plug flow systems in the context of chemical reactor design (e.g., [15–17]). Reaction parameter sensitivity analyses have also been used to examine photochemical reactions in well-mixed batch systems in the atmospheric literature (e.g., [18–20]).

The numerous approaches to sensitivity analysis have been reviewed by several authors [21–23]. The methods can broadly be divided into two groups: local sensitivity methods and global sensitivity methods. The local sensitivity measure represents the system response to infinitesimal, independent variations of the system parameters. Global sensitivity methods measure the system response to finite, simultaneous changes in the
system parameters. In general, the computational demand of the global methods is much larger than that of the local methods. Global sensitivity methods require the assumption that parameter values are randomly distributed according to a given probability density function (pdf). Because of the difficulty in assigning a pdf to each parameter, only local sensitivity methods will be considered in this analysis.

The objective of a local sensitivity analysis is to calculate a set of coefficients that quantify the effects of independently perturbing each of the system parameters by an infinitesimal amount. The local sensitivity coefficient is defined as the partial derivative of a state variable ($\phi$) with respect to a given system parameter ($\Delta a$). Higher order sensitivity coefficients may also be computed; however, this analysis will be confined to first-order sensitivity coefficients.

The most elementary local sensitivity method is the direct perturbation method (a.k.a. the finite difference method or the brute-force method). In the direct perturbation method, the local sensitivity coefficients are estimated by a difference formula, for example

$$\frac{\partial \phi}{\partial a} \approx \frac{\phi(a + \Delta a) - \phi(a)}{\Delta a},$$

where $\phi$ is a state variable and $a$ is a parameter. This method is computationally costly; specifically, for a system with $N_r$ reaction parameters, the direct perturbation method requires one solution of the governing equation to obtain the original state and an additional $N_r$ solutions of the governing equations to determine the effects of perturbing each parameter. Another disadvantage of the direct perturbation approach is that the size of the parameter perturbation ($\Delta a$) must be optimally selected to minimize the truncation error (due to nonlinear dependence of $\phi$ on $a$) and to simultaneously avoid excessive round-off error in the calculation of sensitivity coefficients [24].

Sensitivity coefficients can be computed more efficiently and accurately using the direct method [24,25]. In this method, the original governing equation is differentiated with respect to the parameter of interest. For reactive transport, the governing state equation consists of a nonlinear partial differential equation (PDE), and the resulting sensitivity equation takes the form of a linear PDE. After solving the state equations to obtain the spatial distribution of concentration at a given time level, the sensitivity coefficients are calculated by solving a linear system of equations for each reaction parameter in the system. The computational demand of solving the sensitivity equations is significantly lower than that of solving the state equations, since the nonlinearity of the state equations necessitates the use of an iterative solution method.

In the adjoint method, the direct sensitivity equations are manipulated to obtain an efficient algorithm for the calculation of the sensitivity of a set of performance functions with respect to each of the system parameters [24,25]. In this context, a performance function may be any arbitrary function of the state variables and the system parameters [14,26]. If sensitivity coefficients are to be computed for each of the chemical species at all spatial locations, then the number of performance functions is equal to the number of chemical species ($N_c$) multiplied by the number of nodes ($N_n$). The adjoint method is more efficient than the direct method of sensitivity calculations for problems in which the number of parameter values is larger than the number of performance functions [26]. In this analysis, we confine our attention to problems in which the reaction parameters are spatially uniform; therefore, the number of parameter values is generally much smaller than the number of performance functions. One advantage of the adjoint method is that it is possible to formulate the method to selectively calculate the sensitivity coefficients at critical locations in the problem domain; however, this approach necessitates the storage of the state variables calculated at all time steps prior to and including the time level(s) at which the selected sensitivity coefficients are needed. In this formulation, the sensitivity coefficients are computed using the adjoining state vectors, which are calculated by solving the adjoint problem “backwards in time” from the current time level to the starting time of the simulation [21,26,27]. The interested reader is referred to more rigorous derivations of the adjoint method of sensitivity calculations for groundwater flow [26,27], reactive transport [28,29], and design sensitivity analysis [24]. The excessive amount of runtime storage required for this formulation is generally prohibitive for reactive transport problems [28,29].

We have explored several algorithms for the direct calculation of the sensitivity of a reactive transport model to uncertainty in the reaction parameters [28,29]. These algorithms include the solution of the full system of sensitivity equations coupled among all of the chemical components (implemented in SIA1FULL) and the application of the operator splitting approach to uncouple the component sensitivity equations (implemented in OPSPLITSS). These two algorithms are described in Section 2. The accuracy and efficiency of these algorithms have been compared for a series of example problems [28,29]. The third section of this paper describes a one-dimensional transport problem involving cobalt ($Co^{2+}$) and nitrilotriacetate (NTA$^{3-}$). The reactive processes in this example problem include equilibrium aqueous speciation, linear kinetic sorption and nonlinear kinetic biodegradation reactions.

Applications for reaction parameter sensitivity coefficients include inverse modeling and the estimation of uncertainty in the results of a numerical model. In reactive transport modeling, a sensitivity analysis can also be used to simplify the reaction model and to
identify the most sensitive parameters that should be measured with greater accuracy. If the state of the system is susceptible to uncertainty in a particular reaction model, it may be necessary to expend more time and effort to obtain a more accurate model of this reactive process. On the other hand, the system may be relatively unaffected by variations in a particular reaction parameter. In this case, it is not necessary to consume valuable resources to conduct experiments in order to determine the value of the reaction parameter; a best-estimate from the literature will suffice. If the species concentrations are found to be insensitive to the reaction parameter(s) of a particular reaction, it is not necessary to include this reaction in a numerical model of the system. Finally, as the example application in Section 3 demonstrates, parameter sensitivity coefficients provide a great deal of insight into the relative importance of individual reactions within a suite of coupled reactive processes that govern the state of the system.

2. Governing equations and numerical solution methods

2.1. State equations

Numerous chemical and microbiological reaction processes can affect the mobility of contaminants in the subsurface. These reaction processes can generally be classified as either homogeneous aqueous-phase reactions or heterogeneous interphase reactions involving mass transfer between the aqueous and immobile phases in the groundwater system [30]. By convention, we treat all heterogeneous reactions with a kinetic approach. In contrast, most aqueous speciation reactions (including complexation and acid–base reactions) are treated as if they proceed instantaneously to thermodynamic equilibrium in our conceptual model. With the exception of aqueous redox reactions, aqueous speciation reactions are generally characterized by rapid rates, especially in comparison to the relatively slow rate of groundwater flow; therefore, in groundwater modeling, it is usually valid to treat aqueous speciation reactions as if they proceed instantaneously to thermodynamic equilibrium [31].

The equilibrium approach leads to the concept of a set of component species which form the basic building blocks of the aqueous system [32]. The total aqueous concentration of a component consists of both the uncomplexed form of the component and the aqueous complexes that are produced when the component reacts with other components. The total aqueous concentration of some component \( j \) \( (C_j) \) is defined as

\[
C_j = c_j + \sum_{i=1}^{N_c} a_{ij} x_i,
\]

where \( N_c \) is the number of complexes, \( c_j \) (moles/l) is the uncomplexed concentration of component \( j \), \( x_i \) (moles/l) is the concentration of aqueous complex \( i \), and \( a_{ij} \) is a stoichiometric coefficient giving the number of moles of component \( j \) in complex \( i \). At equilibrium, the activities of the component and complex species are related according to the law of mass action. Neglecting ionic strength corrections, the aqueous species are equal to its concentration, and the law of mass action can be written in the following form:

\[
x_i = K_{eq,i} \prod_{j=1}^{N_c} c_j^{a_{ij}},
\]

where \( K_{eq,i} \) is the equilibrium constant for the formation of complex \( i \).

In order to model the transport of \( N_c \) aqueous components, it is necessary to solve a set of \( N_c \) reactive transport equations. Assuming that the porosity is constant, the governing equation for the transport of aqueous component \( j \) through saturated porous media is given by

\[
\frac{\partial C_j}{\partial t} + L(C_j) = R_j \quad j = 1, \ldots, N_c,
\]

where \( N_c \) is the number of aqueous components, \( L(C_j) \) is the advection–dispersion operator, and \( R_j \) is a source term representing the effects of kinetic reaction processes [3,33]. SIA1FULL and OPSPLTSS are capable of simulating two-dimensional transport of contaminants through a saturated aquifer of unit thickness with constant porosity. For two-dimensional saturated groundwater flow, the advection–dispersion operator is given by

\[
L(C_j) = \frac{\partial}{\partial x} \left( v_x C_j - D_{xx} \frac{\partial C_j}{\partial x} - D_{xy} \frac{\partial C_j}{\partial y} \right) + \frac{\partial}{\partial y} \left( v_y C_j - D_{yx} \frac{\partial C_j}{\partial x} - D_{yy} \frac{\partial C_j}{\partial y} \right),
\]

where \( v_x \) and \( v_y \) are the steady-state average linear velocity components in the \( x \) and \( y \) directions, respectively, and \( D_{xx}, D_{xy}, D_{yx}, \) and \( D_{yy} \) are the coefficients of hydrodynamic dispersion. The advection–dispersion operator for aqueous component \( j \) is linear in \( C_j \) and independent of any of the other components; however, the set of \( N_c \) partial differential equations (PDEs) in (4) are coupled to one another through the kinetic reaction source/sink terms.

In addition to the aqueous components, it is necessary to include immobile components in a model of the subsurface environment. The mass balance equation for these components is given by

\[
\frac{dm_k}{dt} = R_{k+N_c} \quad k = 1, \ldots, N_m,
\]
where $m_k$ is the concentration of immobile component $k$ (moles/g), $N_m$ the number of immobile components, and $R_{j+k}$ equals the rate of accumulation of immobile component $k$ due to kinetic reactions. While there are no spatial derivatives in (6), the reaction rate term couples these ODEs to each other and to the spatially varying PDEs in (4). If Eq. (6) is decoupled from (4), the ODEs can be solved as a batch problem at each spatial location.

The reaction rate terms in Eqs. (4) and (6) are complex nonlinear functions involving any of the aqueous or immobile species in the system. Therefore, Eqs. (4) and (6) present a system of $N_c + N_m$ nonlinear coupled PDEs and ODEs. The solution of a linear PDE is relatively straightforward; there are a number of efficient numerical methods available to solve this type of equation. In order to avoid solving a nonlinear coupled system of PDEs, it is often advantageous to decouple the calculation of the nonlinear rate terms from the solution of the transport equation. The practice of separately solving the transport and reaction rate equations has been referred to as the two-step solution method in the literature [5,6,34].

The two-step solution method allows for the efficient incorporation of both equilibrium and kinetic reactions into the reactive transport equations. In our scheme, speciation reactions among the aqueous species are generally treated with an equilibrium approach, while all other reactions are represented by a kinetic rate expression. These kinetically controlled processes include all reactions that occur across the aqueous/immobile phase boundary and all reactions that are confined to the immobile phase. Reactions which are governed by thermodynamic equilibrium are mathematically represented by a system of nonlinear algebraic equations, which is obtained by combining Eqs. (2) and (3). The form of this system of equations and an appropriate solution technique are described elsewhere [28,29,32,35–37]. The kinetic reactions are represented by rate terms, which constitute source/sink terms in the governing partial differential equations (4) and (6). The kinetic rate terms can be functions of the dependent variables in Eqs. (4) and (6) and/or the concentrations of the individual aqueous species (components and complexes) that result from the equilibrium speciation reactions. Because of the possible dependence of the rate terms on the concentrations of individual aqueous species, the equilibrium speciation problem is solved prior to the evaluation of kinetic rate terms.

Numerous codes have been developed using some type of two-step solution approach to incorporate the effects of chemical or microbiological reactions in the transport equations (e.g., [2–6]). The two-step solution algorithms can generally be divided into two groups, based on whether the reactive and transport steps are coupled sequentially or iteratively. The technique of sequentially solving the transport and reactive portions of the reactive-transport equation is known as operator splitting. Alternatively, iterative methods, such as Newton–Raphson or the sequential iterative approach (SIA), involve repetitively solving a linearized form of the reactive transport equation until convergence is attained. It should be noted that at least one model [34] has been developed which combines the operator splitting and iterative approaches.

In operator splitting, the reactive-transport equation is integrated over an arbitrary time interval $[n, n + 1]$ in two stages. In the first stage, an intermediate solution is calculated from the nonreactive portion of the transport equation, $L(C_j)$. In the second stage, the desired solution at the new time level is obtained by integrating the reaction operator ($R_j$) over the interval $\Delta t$, using the intermediate solution as the initial condition. The operator splitting algorithm is represented by the following two steps:

$$
\frac{C_j^n - C_j^0}{\Delta t} + L(C_j) = 0, \quad j = 1, \ldots, N_c, \quad (7)
$$

$$
\frac{U_{\ell}^{n+1} - U_{\ell}^n}{\Delta M} = R_{\ell}, \quad \ell = 1, \ldots, N_c + N_m, \quad (8)
$$

where $C_j^0$ is an intermediate solution for the concentration of aqueous component $j$, and $\epsilon$ is a time-weighting factor varying between $n$ and $n + 1$. For aqueous components, $U_{\ell}^n$ refers to the intermediate solution, $C_j^0$; for immobile components, $U_{\ell}^n$ refers to the solution at the previous time level, $m_{\ell}^0$. The application of the operator splitting approach to the reactive transport Eqs. (4) and (6) leads to a spatial decoupling of the components. The $N_c$ equations in (7) are linear and decoupled from each other. After spatial discretization of the problem domain into $N_n$ nodes, the first operator splitting step entails solving $N_c$ systems of $N_n$ equations in $N_n$ unknowns. Eq. (8) contains no spatial derivatives; therefore, after spatial discretization of the domain, the second operator splitting step requires the solution of $N_n$ independent systems of $N_c + N_m$ coupled nonlinear equations.

At each node, the integration of the reactive portion of the transport Eq. (8) can be performed with standard solution techniques for systems of nonlinear ODEs. If the rates of the kinetic reactions vary over several orders of magnitude, a stiff [34,38] system of equations may result. Since the reaction step may take the form of a stiff system of equations, it is necessary to use an implicit time-weighting scheme, in which case Eq. (8) is solved iteratively. The Newton–Raphson method is obtained by approximating the rate term at time level $n + 1$ with a first-order Taylor Series expansion, as follows:

$$
R_{\ell}^{n+1,p+1} \approx R_{\ell}^{n+1} + \sum_{k=1}^{N_c+N_m} \left( \frac{\partial R_{\ell}}{\partial U_k} \right)^{n+1,p} (U_k^{n+1,p+1} - U_k^{n+1,p}), \quad (9)
$$
where the superscript $p$ refers to the iteration level. Using this approximation, Eq. (8) becomes a system of coupled linear algebraic equations that must be solved simultaneously. Alternatively, the rate term can be approximated with a truncated first-order Taylor series expansion, in which only the derivative of $R_j$ with respect to the concentration of component $\ell$ itself is retained. This approximation results in a set of linear algebraic equations that are decoupled from one another. Because this set of equations does not include coupling between components, the method may require more iterations to converge to the solution than the Newton–Raphson method [28,29]. In our implementation of the operator splitting algorithm, the user has the option of solving the reaction step using either the Newton–Raphson method or the truncated first-order method.

The operator splitting approach has been reported to be associated with mass-balance errors and numerical diffusion [39–41]. In particular, Valocchi and Malmstead [39] found the mass balance errors to increase as the reaction rate increased. These type of numerical errors can generally be reduced by using a smaller time-step; however, the computational burden of the problem increases as the time-step decreases. The numerical errors associated with the standard operator splitting method can also be reduced by using an alternative splitting algorithm, such as Strang splitting [40–42]. This paper considers only the standard operator splitting method.

For problems with fast kinetic reactions, the SIA often provides a more accurate and efficient solution method than operator splitting. The SIA has been described extensively in the literature by several authors [3,33,34,42,43]. Each SIA iteration consists of two parts: (1) estimation of the reaction source/sink terms from a trial solution, and (2) solution of the mass balance Eqs. (4) and (6) with the constant reaction source/sink term estimated in the first step.

The convergence behavior of the standard SIA can be improved by estimating the reaction rate term with additional terms from the Taylor Series expansion of the rate term [37]. In order to improve upon the computational performance of the standard SIA, while maintaining the decoupled nature of the equations, the rate term is approximated with a truncated first-order Taylor Series. The solution algorithm that arises from this approximation is known as the first-order sequential iterative approach (SIA-1) [37]. Applying a fully-implicit time discretization, the SIA-1 scheme is given by

$$\frac{C_{j,t}^{n+1,p+1} - C_{j,t}^{n}}{\Delta t} + L(C_{j,t}^{n+1,p+1})$$

$$= R_j^{n+1,p} + \left( \frac{\partial R_j}{\partial C_j} \right)^{n+1,p} (C_{j,t}^{n+1,p+1} - C_{j,t}^{n+1,p}).$$

Note that a similar time-discretized approximation is made for the immobile-phase mass balance equations (6). During each SIA iteration, the reaction rate term in Eq. (10) is estimated based on the trial solution from the previous iteration. Since the rate term is no longer a function of the concentrations at the present iteration level, Eq. (10) becomes a linear PDE, and the equations for each component become decoupled from one another.

The SIA method is said to have converged when the change in the total concentration of each aqueous and immobile component is small in both the absolute and relative sense. The relative convergence check ensures that the relative change in the concentration of each component is smaller than a user-specified tolerance, where the relative change in concentration is defined as the change in the concentration of a given component divided by the concentration of the component at the previous iteration level. Similarly, the absolute convergence check ensures that the change in the concentration of each component is smaller than a user-specified tolerance during the last iteration of every time step. The relative convergence check is generally more restrictive than the absolute convergence check; however the absolute convergence check may become important for regions in which the concentration is changing rapidly. If there are steep concentration gradients at any location in the problem domain, the absolute convergence check ensures that an extra SIA-1 iteration is performed.

Regardless of the coupling method used (operator splitting, standard SIA or SIA-1), the reactive transport equations must be solved on a spatially discretized domain at each time step. After the reaction source/sink terms are evaluated, the spatial derivatives arising from the advection and dispersion terms of the transport equation are approximated using standard finite element (FEM) techniques on regular rectangular elements [44]. The structure of the resulting matrix equation and the details of the SIA-1 solution procedure are described elsewhere [37].

2.2. Sensitivity equations

The state equations (4) and (6) can be differentiated with respect to a given reaction parameter to obtain a system of equations for the corresponding sensitivity coefficients. For a kinetic reaction parameter $x_q$, the sensitivity coefficients are defined as

$$S_{q,j} = \frac{\partial U_j}{\partial x_q}, \quad j = 1, \ldots, N_c + N_m,$$

where

$$U_j = \begin{cases} C_j, & j = 1, \ldots, N_c, \\ m_j, & j = N_c + 1, \ldots, N_c + N_m. \end{cases}$$
For parameter $q$, the sensitivity equations for aqueous components are given by the following system of coupled linear PDEs:

\[
\frac{\partial S_{jq}}{\partial t} + L(S_{jq}) = \frac{\partial R_j}{\partial x_q} + \sum_{i=1}^{N_c+N_m} \frac{\partial R_j}{\partial U_i} S_{iq}, \quad j = 1, \ldots, N_c.
\]

(13)

Since there is only a temporal derivative of the dependent variable in the state equations for immobile components, the sensitivity equations for immobile components take the form of linear ODEs

\[
\frac{dS_{jq}}{dt} = \frac{\partial R_j}{\partial x_q} + \sum_{i=1}^{N_c+N_m} \frac{\partial R_j}{\partial U_i} S_{iq}, \quad j = N_c+1, \ldots, N_c+N_m.
\]

(14)

Note that Eqs. (13) and (14) are coupled together by the second term on the right-hand-side of each equation. The quantities $R_j$ and $U_i$ are known at the current time level from the solution of the state equations. Eqs. (13) and (14) show the form of the sensitivity equations for kinetic reaction parameters; however, the set of reaction parameters may also include equilibrium constants in a problem with mixed kinetic and equilibrium reactions. The sensitivity equations for equilibrium constants are similar, except that the partial derivative of the rate with respect to the parameter value has a slightly different form. It can be shown that the sensitivity equations for equilibrium constant $K_i$ are obtained by replacing the first term on the right-hand sides of Eqs. (13) and (14) with the following term:

\[
\frac{\partial R_j}{\partial x_i} \frac{x_i}{K_i} \sum_{i=1}^{N_c+N_m} \frac{\partial R_j}{\partial C_{i}} d_{it}.
\]

(15)

Sections 2.2.1 and 2.2.2 present algorithms for solving Eqs. (13) and (14); minor modifications are necessary to solve the sensitivity equations for equilibrium constants.

It should be noted that the units of the absolute sensitivity coefficients $S_{jq}$ and $S_{iq}$ in Eqs. (13) and (14) depend upon the units of parameter $x_q$. In order to compare the sensitivity coefficients for a number of different reaction parameters, it is convenient to define a dimensionless relative sensitivity coefficient

\[
Z_{jq} = \frac{\partial \ln U_j}{\partial \ln x_q} = \frac{x_q}{U_j} \frac{\partial U_j}{\partial x_q} = \frac{x_q}{U_j} S_{jq},
\]

(16)

where $U_j$ refers to the total concentration of either an aqueous or immobile component. For sensitivity calculations in reactive transport problems, the computation of relative sensitivity coefficients may result in anomalous spikes in regions of extremely low concentration due to roundoff error; therefore, it is convenient to define a third type of sensitivity coefficient as follows:

\[
H_{jq} = \frac{\partial U_j}{\partial x_q} = x_q S_{jq},
\]

(17)

where $U_j$ is the total concentration of component $j$, which may be aqueous or immobile. The hybrid sensitivity coefficient defined in (17) has units of concentration, allowing for comparison of sensitivity coefficients for parameters with different units.

### 2.2.1. Direction solution

In Eq. (13), the advection–dispersion operator, $L$, is applied to the sensitivity coefficients of the aqueous component concentrations. Since the aqueous and immobile sensitivity equations are coupled together, the full system of sensitivity equations must be solved simultaneously on a discretized spatial domain. For a domain with $N_c$ nodes, a linear system of $N_c(N_c + N_m)$ algebraic equations must be solved for an equivalent number of unknowns at each time step for each parameter of concern. In comparison, the solution of the state equations using one of the two-step methods described in the previous section requires the solution of a linear system of $N_c$ algebraic equations for each of the $N_c$ aqueous components at every time step (or iteration level).

In order to calculate the sensitivity coefficients in reactive transport problems, Eqs. (13) and (14) are discretized in time and space, and the standard FEM approach is applied to form a sparse, nonsymmetric system of equations. For implicit time weighting, this system of equations is given by

\[
\frac{1}{N_c} [\mathbf{M}] (Z_{jq}^{n+1} - Z_{jq}^{n}) + [\mathbf{A}] (Z_{jq}^{n+1}) = \frac{\partial R_j}{\partial x_q} + [\mathbf{J}] Z_{jq}^{n+1},
\]

(18)

where $Z_{jq}^{n}$ is a vector containing the component sensitivity coefficients at each node for parameter $q$ and $R_j$ is a vector containing the rate of production of each component at each node. In (18), the combined mass matrix, $[\mathbf{M}]$, the combined advection–dispersion matrix, $[\mathbf{A}]$, and the combined Jacobian matrix, $[\mathbf{J}]$, are banded matrices of order $N_c(N_c + N_m)$. Assuming that the sensitivity coefficient array $Z_{jq}$ is numbered so that the sensitivity coefficients at a given node are grouped together, $[\mathbf{J}]$ is defined as follows:

\[
J_{jm} = \eta(i,e) \frac{\partial R_j}{\partial U_i} |_{\text{node } i},
\]

(19)

where $j = (e - 1)N_c + k$ and $m = (i - 1)N_c + \ell$. The term $\eta(i,e)$ is a weighting factor that results from the FEM discretization; it expresses the contribution from node $i$ on the calculations at node $e$. Each row or column of $[\mathbf{M}]$ that corresponds to an immobile component contains a one along the diagonal and zeros for all other entries. For a two-dimensional domain discretized into regular rectangular elements, $[\mathbf{A}]$ is a nine-diagonal matrix. In the rows and columns of $[\mathbf{A}]$ that correspond to immobile components, all entries are equal to zero.
Rearranging Eq. (18) so that the unknowns are on the left-hand-side gives the following matrix equation:

\[
\frac{1}{\Delta t} [M] + [A] = [J]^{n+1},
\]

\[
S_{eq}^{n+1} = \frac{\partial R_{eq}^{n+1}}{\partial x_q} + \frac{1}{\Delta t} [M] S_{eq}^{n+1}.
\]

At every time step, Eq. (20) is solved once for each parameter, \(x_q\), of interest; however, it is only necessary to decompose the left-hand-side matrix once per time step.

The system of equations defined in (20) has a bandwidth of \((N_y + 2)(N_c + N_m) - 1\), where \(N_y\) is the number of nodes in the \(y\)-direction and the assumption is made that the nodes are ordered sequentially by column (i.e., in the \(y\)-direction). This bandwidth was calculated for the case when \(S_{eq}\) is numbered so that the sensitivity coefficients at a given node are grouped together. In comparison, grouping the equations by component number rather than node number increases the bandwidth to \(N_y(N_c + N_m) + N_c + 1\). Eq. (20) can be expressed in matrix form as \([G] S_{eq} = b\), where the matrix \([G]\) is assembled from \([M], [A]\), and \([J]\). The structure of \([G]\) is shown in Fig. 1 for a two-dimensional domain discretized into regular rectangular elements. Each submatrix in \([G]\) is associated with a particular spatial node and is a square matrix of order \(N_c + N_m\). Since the two-dimensional domain is discretized into rectangular elements, each node is coupled to eight surrounding nodes, and the number of diagonals in \([G]\) is equal to \(9(N_c + N_m) + 3(N_c + N_m - 1)\).

The bandwidth and number of diagonals in \([G]\) can be further reduced by lumping the derivative rate terms. Lumping refers to the technique of approximating a specific term in the PDE by averaging its value over the element, rather than computing the element matrix for the term after approximating the solution variable with the standard interpolation function [44]. Using this technique, the off-diagonal elements in the off-diagonal submatrices in \([G]\) are eliminated. In this case, the bandwidth is \((N_y + 1)(N_c + N_m)\), and the number of diagonals is \(2(N_c + N_m) + 7\). In the lumped formulation, all of the off-diagonal submatrices in \([J]\) are zero matrices.

2.2.2. Operator splitting

The excessive computational demand of the sensitivity calculations suggests that the system of equations should be solved with an approximate method. One possible approximate solution method for the sensitivity equations is obtained by applying the operator splitting approach to the sensitivity calculations. The left-hand-side of Eq. (13) is split into two parts, one representing advection–dispersion and the other, reaction kinetics. In the first step, the advection–dispersion operator in (13) is integrated over the discretized domain using the finite element method. The first step is represented by the following matrix equation:

\[
\left( \frac{1}{\Delta t} [M] + [A] \right) S_{eq}^n = \frac{1}{\Delta t} [M] S_{eq}^{n+1},
\]

where the superscript \(\ast\) refers to an intermediate solution, and \(S_{eq}^n\) is the nodal vector of sensitivity coefficients of the concentration of the \(j\)th aqueous component with respect to parameter \(x_q\). The mass matrix, \([M]\), will be identical for all components. The subscript on the advection–dispersion matrix, \([A]_j\), reflects the fact that the entries in the matrix may vary if the dispersion coefficient has a different value for each aqueous component. The system of \(N_y\) equations given in (21) is solved once for each aqueous component and each parameter, \(x_q\), of interest. In the second step of the operator splitting method, the reactive portion of the sensitivity equations is integrated over the time step, by solving the equations as a batch system at each node. Approximating the time derivative with an implicit difference, the second step consists of solving the following matrix equation at each node \(i\):

\[
\left( \frac{1}{\Delta t} [I] - [J]_i^{n+1} \right) S_{eq,i}^{n+1} = \frac{\partial R_{eq,i}^{n+1}}{\partial x_q} + \frac{1}{\Delta t} S_{eq,i}^{n+1},
\]

where \(S_{eq,i}\) is a vector of length \(N_c + N_m\) containing the sensitivity coefficients for parameter \(x_q\) at node \(i\), \([J]\_i\) is the nodal Jacobian matrix for node \(i\), and \(R_{eq,i}\) is a vector containing the rate of production of each component at node \(i\). \(S_{eq,i}^n\) and \(S_{eq,i}^{n+1}\) are derived by dividing \(S_{eq}^n\) and \(R_{eq,i}\), respectively, into \(N_y\) vectors, each corresponding to a particular node \(i\). For each aqueous component, the initial conditions in this second step (\(S_{eq}^n\)) are given by the intermediate solution \((S_{eq,i}^n)\) calculated from (21). For each immobile component, the initial conditions are given by the sensitivity coefficients at the previous time level. Eq. (22) must be solved \(N_y\) times; however, it is only necessary to decompose the left-hand-side matrix once per time step at each node. It should be noted that

![Fig. 1. Structure of [G] for consistent formulation.](Image 48x72 to 284x280)
it is necessary to use a small time step in the operator splitting method, since the numerical error is proportional to $\Delta t$ [39,40]. However, if the operator splitting approach is used to solve the state equations, the time step will be already be limited to reduce the numerical error in solving for the concentrations at each time step.

2.3. Implementation of solution approaches for state and sensitivity calculations

The SIA1FULL code uses the SIA-1 method to solve the reactive transport equations and the direct solution method to solve the reaction parameter sensitivity equations. The operator splitting approach is applied to solve the state and sensitivity equations in the OPSPLTSS code. In both codes, reaction models are included for equilibrium aqueous speciation, linear kinetic sorption, Langmuir kinetic sorption, biodegradation with Monod kinetics, and a general reversible reaction with forward and reverse rate constants. Absolute, relative or hybrid sensitivity coefficients can be calculated for any of the kinetic reaction parameters or equilibrium constants.

An iterative solver based on the GMRES [45] algorithm is used to solve the state and sensitivity equations in SIA1FULL and to solve the transport portion of the state and sensitivity equations in OPSPLTSS. In SIA1FULL, the user has the option of lumping the mass and derivative rate terms in solving the state and sensitivity equations; in OPSPLTSS, the lumping option applies only to the mass matrix. OPSPLTSS allows the user to select whether to use the Newton–Raphson method or the truncated first-order method (resulting from the approximation in (9)) to solve the system of non-linear state equations in (8) describing the batch reactive system at each node. In OPSPLTSS, the system of linear sensitivity equations in (21) is solved by LU-decomposition followed by forward substitution and backsubstitution using routines from LAPACK [46].

Table 1

<table>
<thead>
<tr>
<th>Physical parameters for the cobalt-NTA transport problem</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of column</td>
</tr>
<tr>
<td>Grid spacing ($\Delta x$)</td>
</tr>
<tr>
<td>Porosity</td>
</tr>
<tr>
<td>Bulk density</td>
</tr>
<tr>
<td>Pore water velocity</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
</tr>
</tbody>
</table>

column. After 20 h, the fluid injected at the entrance has the same composition as the original background solution in the column.

The chemical system consists of seven aqueous components and two immobile components. Table 2 lists the component species and provides the initial conditions and the total concentrations of each component in the injected fluid. The pH and the total concentrations of the aqueous and immobile component species are allowed to vary under the influence of linear kinetic sorption and biodegradation reactions. The aqueous components undergo equilibrium speciation reactions to form 14 complex species. Table 3 gives the formation constants for each complex in the system.

The total concentration of NTA will decrease over time due to the aerobic biodegradation of the complex HNTA$^{2-}$. The biodegradation reaction is represented as follows [50]:

$$\text{HNTA}^{2-} + 1.620O_2 + 1.272H_2O + 2.424H^+ \rightarrow 0.576C_6H_7O_7N + 3.120H_2CO_3^2- + 0.424NH_4^+.$$  (23)

The rate of substrate degradation ($R_{\text{HNTA}}$) is modeled with multiplicative-Monod kinetics

$$R_{\text{HNTA}^{2-}} = -q_mX_m \frac{[\text{HNTA}^{2-}]}{K_S + [\text{HNTA}^{2-}]} \frac{[O_2]}{K_A + [O_2]}.$$  (24)

where $X_m$ is the biomass concentration, $[\text{HNTA}^{2-}]$ is the concentration of HNTA$^{2-}$ and $[O_2]$ is the concentration of oxygen. The parameters used in Eq. (24) are defined in Table 4. The rates of change in the concentration of $O_2$, $H^+$, $H_2CO_3^2-$, and $NH_4^+$ are proportional to the rate of substrate degradation. Using the stoichiometry of reaction (23), the appropriate rate expression are:

$$R_{O_2} = 1.620R_{\text{HNTA}^{2-}}, \quad R_{H^+} = 2.424R_{\text{HNTA}^{2-}},$$
$$R_{H_2CO_3^2-} = -3.120R_{\text{HNTA}^{2-}}, \quad R_{NH_4^+} = -0.424R_{\text{HNTA}^{2-}}.$$  

The net rate of microbial growth ($R_{\text{cells}}$) is given by the synthesis rate (which is equal to the rate of degradation of the substrate multiplied by a yield coefficient) minus a first-order decay rate

$$R_{\text{cells}} = -YR_{\text{HNTA}^{2-}} - bX_m.$$  (25)

where $Y$ is the yield coefficient and $b$ is the decay coefficient.

A set of experiments were conducted at Pacific Northwest National Laboratory (PNNL) to examine
the experimental results for metal-NTA systems with CCBATCH model produced very good agreement with the only degradable NTA species. Specifically, the biodegradation rate parameters for the cobalt-NTA transport problem were taken from a separate study of NTA degradation in activated sludge systems [51]; however, the possible formation of intermediates was not included in the reaction model for this sensitivity analysis. In this problem, uncomplexed cobalt (Co$^{2+}$) is retarded due to the process of adsorption. All other species are assumed to be unaffected by sorption. The sorption reaction is represented by a linear kinetic model, which is given by the following rate expression:

$$R_{Co^{2+}} = \frac{d[Co^{2+}]}{dt} = -k_m \left( [Co^{2+}] - \frac{Co_{(ads)}}{K_d} \right), \quad (26)$$

where $[Co^{2+}]$ denotes the aqueous concentration of cobalt in moles/l, $Co_{(ads)}$ denotes the adsorbed concentration of cobalt in moles/g, $k_m$ (h$^{-1}$) is the mass transfer coefficient, and $K_d$ (g/l) is the distribution coefficient for linear equilibrium adsorption. Eq. (26) is used to calculate the rate of change in the aqueous concentration of cobalt due to sorption. The rate of change in the sorbed concentration of cobalt is equal to the negative of the rate of change in the aqueous concentration of cobalt multiplied by a units conversion factor given by the porosity divided by the bulk rock density. The mass transfer coefficient is arbitrarily set equal to 1 h$^{-1}$ and the distribution coefficient is equal to $5.07 \times 10^{-3}$ l/g. This distribution coefficient was selected to give an approximate retardation factor of 20 for uncomplexed cobalt. For this problem, equilibrium sorption is not included in the reaction model for this sensitivity analysis.

In this problem, uncomplexed cobalt (Co$^{2+}$) is retarded due to the process of adsorption. All other species are assumed to be unaffected by sorption. The sorption reaction is represented by a linear kinetic model, which is given by the following rate expression:

$$R_{Co^{2+}} = \frac{d[Co^{2+}]}{dt} = -k_m \left( [Co^{2+}] - \frac{Co_{(ads)}}{K_d} \right), \quad (26)$$

where $[Co^{2+}]$ denotes the aqueous concentration of cobalt in moles/l, $Co_{(ads)}$ denotes the adsorbed concentration of cobalt in moles/g, $k_m$ (h$^{-1}$) is the mass transfer coefficient, and $K_d$ (g/l) is the distribution coefficient for linear equilibrium adsorption. Eq. (26) is used to calculate the rate of change in the aqueous concentration of cobalt due to sorption. The rate of change in the sorbed concentration of cobalt is equal to the negative of the rate of change in the aqueous concentration of cobalt multiplied by a units conversion factor given by the porosity divided by the bulk rock density. The mass transfer coefficient is arbitrarily set equal to 1 h$^{-1}$ and the distribution coefficient is equal to $5.07 \times 10^{-3}$ l/g. This distribution coefficient was selected to give an approximate retardation factor of 20 for uncomplexed cobalt. For this problem, equilibrium sorption is
approximated when \( k_m \) is at least two orders of magnitude larger than \( 1 \ h^{-1} \); therefore, kinetic mass transfer effects will affect the sorption process in these simulations.

The linear kinetic sorption model defined by (26) assumes that the rate of sorption is solely a function of the aqueous and sorbed concentrations of the sorbing species. Experimental evidence shows that the rate of sorption is often affected by the concentration of other species in solution (e.g., \( H^+ \)) or by the limited availability of surface sites [56,57]. In order to model these effects, a surface complexation sorption model is more appropriate than the linear kinetic model. In this example, sorption is modeled with a linear kinetic model because of the limited availability of experimental data on cobalt surface complexation reactions.

The top half of Fig. 2 shows the breakthrough of selected aqueous species at the end of the 10 m column. The results in Fig. 2 were obtained with time step of 0.01 h. This time step was selected based on a comparison of the results obtained with time steps of 0.005, 0.01, 0.1 and 0.5 h. The results of simulations with time steps of 0.01 and 0.005 h were indistinguishable; however, the concentration profiles for simulations with time steps of 0.1 and 0.5 showed significant numerical dispersion.

In Fig. 2, essentially all of the NTA is present as either \( \text{CoNTA}^- \) or \( \text{HNTA}^2^- \), and cobalt exists primarily as \( \text{CoNTA}^- \) or in the uncomplexed form. Throughout the simulation, the pH is approximately constant at a value of 6 because of the presence of the buffer in solution. Fig. 2 shows that most of the NTA elutes out of the 10 m column between 10 and 30 h. The observed breakthrough of the NTA pulse can be explained by the
fact that none of the NTA species are retarded; therefore, NTA would be expected to migrate with the pore water at a velocity of 1 m/h. The uncomplexed cobalt cation \((\text{Co}^{2+})\), with a retardation factor of 20) continues to elute out of the column long after the NTA pulse has passed through the column. At the end of the 50-h simulation, the trailing edge of the cobalt front has yet to emerge at the end of the column.

Between 12 and 27 h, the total NTA concentration decreases and the total aqueous concentration of cobalt gradually increases. The consumption of \(\text{HNTA}^{2-}\) during biodegradation causes the decrease in the amount of NTA in the system. The increase in the total aqueous concentration of cobalt can be attributed to the slow breakthrough of the uncomplexed form of cobalt. The shift in the total aqueous concentration of NTA relative to that of cobalt causes a shift in the distribution of species in solution. At a time of 10 h, the numerical data show that approximately 68% of the NTA is in the form of \(\text{CoNTA}^{-}\), and another 32% is in the form of \(\text{HNTA}^{2-}\). By 30 h, the NTA species distribution has shifted so that 83% of the NTA is in the form of \(\text{CoNTA}^{-}\), and the remaining 17% is in the form of \(\text{HNTA}^{2-}\).

### 3.2. Sensitivity analysis of the cobalt-NTA example problem

Figs. 3–6 show the results of the reaction parameter sensitivity analysis of this system. Each figure shows the time history of the hybrid parameter sensitivity coefficients for the total aqueous concentrations of cobalt and NTA at the end of the 10-m column. A comparison of the vertical scales in each of the figures reveals that the magnitudes of the sensitivity coefficients vary considerably. For convenience, Tables 5 and 6 rank the peak magnitudes of the sensitivity coefficients of the total aqueous concentrations of NTA and cobalt, respectively. The fourth column in each table lists the corresponding relative sensitivity coefficients, which were calculated by dividing the hybrid sensitivity by the appropriate total aqueous component concentration at the time at which the peak occurred. The relative sensitivity coefficient represents the fractional change in concentration that would result from a fractional change in the parameter value. Similarly, the hybrid sensitivity coefficient can be thought of as the absolute change in concentration that would result from a fractional change in the parameter value. Table 5 indicates that NTA is most sensitive to the maximum specific rate of substrate utilization, \(q_m\). The value of the hybrid sensitivity of NTA with respect to \(q_m\) implies that the total aqueous concentration of NTA would decrease by \(1.36 \times 10^{-8}\) moles/l if the value of \(q_m\) increased by 1%. The corresponding relative sensitivity coefficient is \(-0.34\), indicating that this change in concentration corresponds to a decrease of about 0.34% in the total aqueous concentration of NTA. NTA is also relatively sensitive to the half-maximum-rate concentration for the electron donor \((K_S)\), the yield coefficient \((Y)\), and the equilibrium constants \(K_{eq\text{NTA}}\) and \(K_{eq\text{CoNTA}}\). The parameters to which cobalt is most sensitive are the mass transfer coefficient of the sorption reaction \(k_m\), \(K_{eq\text{CoNTA}}\), \(K_{eq\text{NTA}}\), and \(q_m\). Tables 5 and 6 show that cobalt and NTA are relatively insensitive to the equilibrium constant of \(\text{H}_2\text{NTA}^{-}\) and the stoichiometric coefficients of \(\text{O}_2\), \(\text{H}_2\text{CO}_3\) and \(\text{H}^+\) in the biodegradation reaction (23); therefore, the sensitivity coefficient plots in Figs. 3–6 do not include profiles for these parameters.

Fig. 3 shows that the sensitivity of NTA is positive with respect to \(K_S\) and negative with respect to \(q_m\), reflecting the fact that the rate of biodegradation of NTA will decrease as \(K_S\) increases and will increase as \(q_m\) increases. During the period in which NTA is present at the end of the column, the sensitivity of cobalt is also positive with respect to \(K_S\) and negative with respect to \(q_m\). This trend indicates that the total aqueous concentration of cobalt will decrease as the biodegradation rate of NTA increases. As \(\text{HNTA}^{2-}\) is degraded, some of the complex \(\text{CoNTA}^{-}\) will dissociate into uncomplexed cobalt \((\text{Co}^{2+})\) and NTA \(^{3-}\) in order to satisfy chemical equilibrium. The speciation reactions then distribute the NTA in solution among the various protonated NTA species given in Table 3. This redistribution of species in solution causes more of the cobalt to exist as \(\text{Co}^{2+}\), which has a strong tendency to sorb to the mineral surfaces in the column. The sorption of \(\text{Co}^{2+}\) will result in a decrease in the total aqueous concentration of cobalt.

In Fig. 3 the total aqueous concentrations of cobalt and NTA first become sensitive to \(q_m\) and \(K_S\) as the NTA pulse breaks through at the end of the column. The sensitivity coefficients for \(q_m\) and \(K_S\) increase in magnitude up to a time of 27 h. This corresponds to the period during which the cell mass at the end of the column increases linearly. As is clear from Eq. (25), the rate of cell growth is directly proportional to the rate of biodegradation, which is in turn proportional to the cell concentration.

After the NTA pulse passes through the column, the sensitivity of NTA becomes zero and the sensitivity of cobalt plateaus at a small positive value for \(q_m\) and a small negative value for \(K_S\). This indicates that an increase in the rate of biodegradation causes a net increase in the total aqueous concentration of cobalt near the end of the simulation. As explained above, while the NTA pulse is passing through the column, an increase in the rate of biodegradation of NTA will cause an increase in the sorbed concentration of cobalt. This extra sorbed cobalt will remain in the column after the NTA pulse has passed through. As clean water is injected into the column, \(\text{Co}^{2+}\) will desorb from the mineral surfaces;
therefore, an increase in the amount of sorption while NTA is present will result in a small increase in the aqueous concentration of cobalt after the NTA has passed through the column.

In Fig. 4, the sensitivity coefficients of the total aqueous concentrations of cobalt and NTA are plotted versus time for the half-maximum-rate concentration for the electron acceptor ($K_A$) the yield coefficient ($Y$), and the decay coefficient ($b$). The vertical scale of the sensitivity plots in this figure is about three times smaller than the vertical scale in Fig. 3. The results indicate that the total aqueous component concentrations of cobalt and NTA are relatively insensitive to $b$; however the concentrations of cobalt and NTA are somewhat sensitive to $K_A$ and $Y$. At 28 h, the total aqueous concentration of NTA is about $4 \times 10^{-6}$ moles/l, and the sensitivity of NTA with respect to $K_A$ is about $3 \times 10^{-7}$ moles/l indicating that an order of magnitude increase in the value of $K_A$ will result in an increase of almost 8% in the total aqueous concentration of NTA. The sensitivity profiles for $K_A$ show similar behavior to the sensitivity profiles for $K_S$, which are plotted in Fig. 3. The

![Fig. 3. Hybrid sensitivity vs. time plots at the end of the 10-m column showing the sensitivity of the total aqueous concentrations of cobalt and NTA with respect to $q_m$ and $K_s$.](image-url)
sensitivity coefficients for $Y$ increase from 10 h to a time of about 28 h, then decrease to approximately zero by a time of about 33 h.

Large values for the $k_m$ sensitivity coefficient indicate the conditions under which kinetic effects are important for the sorption reaction. When the sorption reaction is far from equilibrium, the term in brackets in Eq. (26) will be large; therefore, the derivative of the sorption reaction rate with respect to $k_m$ will be large in magnitude. In Fig. 5, the $k_m$ sensitivity plots show that the cobalt sorption reaction is far from equilibrium while the NTA pulse is passing through the column.

Fig. 5 also contains plots of the sensitivity of the total aqueous concentrations of cobalt and NTA with respect to the distribution coefficient ($K_d$) for the cobalt sorption reaction. The sensitivity coefficients of cobalt and NTA are negative with respect to $K_d$, indicating that an increase in the value of $K_d$ will cause a decrease in the total aqueous concentration of both components. It is clear from Eq. (26) that increasing the value of $K_d$ will
increase the relative amount of cobalt in the sorbed form. The fact that NTA is sensitive to the value of $K_d$ demonstrates the coupling between the biodegradation and sorption processes in this system. An increase in the amount of cobalt sorption and, therefore, a decrease in the total aqueous concentration of cobalt will decrease the relative amount of NTA present in the form of the CoNTA$^-$ complex. The resulting increase in the amount of NTA present in the degradable form of HNTA$^{2-}$ will cause a net decrease in the total concentration of NTA in the column.

Fig. 6 contains plots of the sensitivity of the total aqueous concentrations of cobalt and NTA with respect to the equilibrium constants for HNTA$^{2-}$ and CoNTA$^-$. While the NTA pulse is passing through the column, the sensitivity coefficients of cobalt and NTA are negative for $K_{eq,HNTA}$ and positive for $K_{eq,CoNTA}$. This indicates that an increase in the value of $K_{eq,HNTA}$ or a decrease in the value of $K_{eq,CoNTA}$ will cause a decrease in the total aqueous concentration of both components. An increase in $K_{eq,HNTA}$ or a decrease in $K_{eq,CoNTA}$ will shift the distribution of NTA species in solution so that the concentration of HNTA$^{2-}$ will increase relative to that of CoNTA$^-$. Since HNTA$^{2-}$ is the biodegradable form of NTA, this redistribution of NTA in solution will enhance the degradation of NTA in the column. Additionally, an increase in $K_{eq,HNTA}$ or a decrease in $K_{eq,CoNTA}$ will shift the distribution of
species in solution so that more of the aqueous cobalt will be present as uncomplexed cobalt, Co\(^{2+}\), rather than the CoNTA\(^{-}\) complex. Increasing the concentration of Co\(^{2+}\) relative to that of CoNTA\(^{-}\) causes an increase in the amount of cobalt sorbed to the mineral surfaces and, therefore, a decrease in the total aqueous concentration of cobalt.

The preceding analysis of the temporal variation in the sensitivity coefficients at the end of the column provides a great deal of insight into the coupling among the biodegradation, sorption, and speciation reactions in the cobalt-NTA system. Although HNTA\(^{2-}\) is the only species that is biodegradable, Table 6 and Figs. 3 and 4 indicate that the total aqueous concentration of cobalt is

Table 5

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Time of peak (hours)</th>
<th>Hybrid sensitivity (moles/L)</th>
<th>Relative sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q_m)</td>
<td>27.83</td>
<td>(-1.36 \times 10^{-6})</td>
<td>(-0.339)</td>
</tr>
<tr>
<td>(k_S)</td>
<td>28.11</td>
<td>(7.69 \times 10^{-7})</td>
<td>0.195</td>
</tr>
<tr>
<td>(Y)</td>
<td>28.19</td>
<td>(-5.60 \times 10^{-7})</td>
<td>(-0.143)</td>
</tr>
<tr>
<td>(K_{eq,HNTA})</td>
<td>28.20</td>
<td>(-4.83 \times 10^{-7})</td>
<td>(-0.123)</td>
</tr>
<tr>
<td>(K_{eq,CoNTA})</td>
<td>28.20</td>
<td>(4.83 \times 10^{-7})</td>
<td>0.123</td>
</tr>
<tr>
<td>(K_A)</td>
<td>27.83</td>
<td>(2.79 \times 10^{-7})</td>
<td>0.0695</td>
</tr>
<tr>
<td>(K_b)</td>
<td>28.95</td>
<td>(-2.23 \times 10^{-7})</td>
<td>(-0.0665)</td>
</tr>
<tr>
<td>(k_m)</td>
<td>27.16</td>
<td>(-2.10 \times 10^{-7})</td>
<td>(-0.0514)</td>
</tr>
<tr>
<td>(b)</td>
<td>28.16</td>
<td>(4.19 \times 10^{-8})</td>
<td>0.0107</td>
</tr>
<tr>
<td>(v_{H2O})</td>
<td>27.64</td>
<td>(5.74 \times 10^{-9})</td>
<td>0.00142</td>
</tr>
<tr>
<td>(v_{H})</td>
<td>28.24</td>
<td>(3.12 \times 10^{-9})</td>
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<tr>
<td>(v_{H,CO3})</td>
<td>28.24</td>
<td>(-8.83 \times 10^{-10})</td>
<td>(-0.000227)</td>
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<tr>
<td>(K_{eq,H2NTA})</td>
<td>27.90</td>
<td>(2.32 \times 10^{-10})</td>
<td>0.0000579</td>
</tr>
</tbody>
</table>
quite sensitive to some of the biodegradation parameters. Similarly, although none of the NTA species sorb, the total aqueous concentration of NTA exhibits sensitivity to the values of $k_m$ and $K_d$ for the cobalt sorption reaction, as is shown in Fig. 5 and Table 5. Fig. 7 shows a schematic of the relationship between the biodegradation process (outlined in the short-dashed line) and the sorption reaction (outlined in the long-dashed line). For each reversible reaction process in the figure, the larger arrow shows the direction in which the reaction will proceed in response to an increase in the rate of biodegradation or the rate of sorption. While cobalt and NTA do not react with each other in any kinetic process, they do interact through equilibrium speciation reactions. Both the biodegradation of NTA and the sorption of cobalt result in a redistribution of species in solution. It is this redistribution of species in solution that causes cobalt to be sensitive to the biodegradation parameters and NTA to be sensitive to the sorption parameters. The importance of the speciation reactions is also reflected in the relatively high sensitivity of the total aqueous concentrations of cobalt and NTA with respect to the equilibrium constants of CoNTA$^{\cdot-}$ and HNTA$^{2-}$, as is shown in Fig. 6 and Tables 5 and 6.

The calculated sensitivity coefficients in Figs. 3–6 were verified by direct perturbation. The details of these calculations are provided elsewhere [28,29]. For each of the kinetic reaction parameters and equilibrium constants, the sensitivity coefficients using a time step of 0.01 h were indistinguishable from the direct perturbation results.

### 4. Computational performance and programming issues

#### 4.1. Computational performance of SIA1FULL and OPSPLTSS

In the cobalt-NTA example, sensitivity coefficients were computed for ten kinetic parameters and three equilibrium constants. The system contains seven aqueous components and two immobile components, and the domain is discretized into 202 nodes. At each time step, SIA1FULL solves 13 systems of 1818 equations in 1818 unknowns for the sensitivity coefficient calculations. To integrate the transport portion of the sensitivity equations at each time step, the operator splitting code solves 91 systems of 202 equations in 202 unknowns. To integrate the reactive portion of the sensitivity equations at each time step, the operator splitting code decomposes 202 systems of 9 equations in 9 unknowns. After decomposing each matrix, OPSPLTSS performs 13 forward/backward substitutions at each of the 202 nodes. The number of operations performed by SIA1FULL and OPSPLTSS is summarized in Table 7. Table 7 also compares the CPU times of SIA1FULL and OPSPLTSS. To solve both the state and sensitivity equations in this example, the operator splitting code requires less than half of the total CPU time of SIA1FULL. In Table 7, the simulations were performed with implicit time weighting, and OPSPLTSS used the Newton–Raphson method to solve the state equations for the batch reaction problem at each node. Note that the CPU times will vary depending on the...
convergence tolerance used for the SIA-1 iterations in SIA1FULL and for the Newton–Raphson iterations to solve the second operator splitting step in OPSPLTSS. For these simulations, a strict convergence tolerance was used for both the absolute tolerance (10^{-8} moles/l for cobalt and NTA) and the relative tolerance (10^{-8} for cobalt and NTA).

Table 7 summarizes the CPU times required for the solution of both the state and sensitivity equations for the cobalt-NTA example. For solution of the state equations only, SIA1FULL requires approximately 1223 CPU s, and OPSPLTSS requires about 934 CPU s. In order to calculate the sensitivity coefficients by direct perturbation, it is necessary to solve the state equations a total of 14 times, since there are 13 parameters in this example. If SIA-1 is used to solve the state equations, the direct perturbation approach will require about 17122 CPU s of simulation time, which is more than three times larger than the total CPU time (5290 CPU s) for the direct calculation of the sensitivity coefficients by SIA1FULL. If the operator splitting approach is used to solve the state equations, the direct perturbation approach will require about 13,076 CPU s of simulation time, which is more than six times larger than the total CPU time (2038 CPU s) for the calculation of the sensitivity coefficients by OPSPLTSS. These CPU time comparisons clearly illustrate the fact that direct calculation of the sensitivity coefficients is considerably more efficient than the direct perturbation approach.

The performance of SIA1FULL and OPSPLTSS were also compared for a set of example problems in which uranium (VI) sorbs onto a quartz surface according to a nonelectrostatic surface complexation model [57]; however, the details of these examples are given elsewhere [28,29]. For the uranium-quartz example problems, the domain is discretized into 842 nodes, and the system contains three aqueous components. The number of immobile surface site types varies between five and seven, and the number of parameters varies between eight and ten. The CPU time comparisons for the uranium-quartz example problems confirmed that the calculation of sensitivity coefficients with SIA1FULL or OPSPLTSS is much more efficient than the direct perturbation approach. These comparisons demonstrated that the CPU time for the calculation of the sensitivity coefficients by OPSPLTSS was three times smaller than the simulation time for direct perturbation with operator splitting for solution of the state equations.

For the cobalt-NTA example problem, SIA1FULL and OPSPLTSS had approximately the same level of accuracy with time step of 0.01 h. In contrast, for the uranium-quartz problems, it was necessary to run the operator splitting code with a time step of 0.002 h to obtain roughly the same accuracy as SIA1FULL with a time step of 0.01 h. Although the OPSPLTSS runs were performed with a time step five times smaller than that used in SIA1FULL, the operator splitting code still required about 30% less CPU time than SIA1FULL for solution of the state and sensitivity equations. However, the reduction in the size of the time step caused the operator splitting code to be less efficient than SIA1FULL for solution of the state equations alone. This result is confirmed by the CPU time summary in Table 7, which shows that the practice of operator splitting results in a larger reduction in CPU time for the sensitivity calculations than for the solution of the state equations. Operator splitting is a very efficient method for the calculation of sensitivity coefficients since the large system of sensitivity equations is divided into smaller systems of equations; however, the size of the system of state equations is the same for operator splitting and SIA-1.

### 4.2. Programming issues

The CPU time comparisons in Section 4.1 demonstrate a significant savings in computational time over the direct-perturbation approach when SIA1FULL or OPSPLTSS are used to solve the sensitivity equations. Furthermore, the reported CPU times for direct-perturbation do not include the additional time the user must spend to manually change the program input file(s) or to create a batch file to perform the file manipula-

<table>
<thead>
<tr>
<th>Code/equation</th>
<th>Step</th>
<th>Order of matrix</th>
<th># iterative matrix solves</th>
<th># matrix decompositions</th>
<th># r.h.s. vectors per decomposition</th>
<th>CPU time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIA1FULL/state</td>
<td>–</td>
<td>202</td>
<td>7 \cdot N_{\text{SIA}}</td>
<td>–</td>
<td>–</td>
<td>1223</td>
</tr>
<tr>
<td>SIA1FULL/sensitivity</td>
<td>–</td>
<td>1818</td>
<td>13</td>
<td>–</td>
<td>–</td>
<td>4067</td>
</tr>
<tr>
<td>OPSPLTSS/state</td>
<td>1</td>
<td>202</td>
<td>7</td>
<td>–</td>
<td>–</td>
<td>934</td>
</tr>
<tr>
<td>OPSPLTSS/sensitivity</td>
<td>2</td>
<td>202</td>
<td>91</td>
<td>202 \cdot N_{\text{N-R}}</td>
<td>1</td>
<td>1104</td>
</tr>
</tbody>
</table>

$a_{\text{SIA}}$ is the number of SIA-1 iterations; and $N_{\text{N-R}}$ is the number of Newton–Raphson iterations during the second operator splitting step.

$b$ Simulations were run on a Hewlett Packard workstation (model C160), and the CPU time was determined using the gprof profiling tool. Each program was compiled with HP Fortran 10.20 using level two optimization.
tions. On the other hand, the obvious advantage of the
direct-perturbation approach is the fact that the method
requires only minimal programmer time to calculate
sensitivity coefficients. (The only additional program-
ing requirement for direct-perturbation is a short
program to compute the sensitivity coefficients by a
difference formula, as in Eq. (1).)

In considering the merits of calculating reaction pa-
rameter sensitivity coefficients by solution of the sen-
itivity equations, it is important to account for the
programmer time needed to add this capability to an
existing reactive transport code. Subroutines must be
added to the code to control input and output and to
solve Eq. (20) if the full system of sensitivity equations is
solved simultaneously or Eqs. (21) and (22) if the op-
erator splitting solution approach is implemented. The
solution algorithm involves assembling the appropriate
matrices, calculating right-hand-side vectors, and calling
a solver. Comparing the sensitivity equations in (13) and
(14) to the state equations defined in Eqs. (4) and (6), it
is obvious that the left-hand sides of the sensitivity
equations have the same form as the corresponding left-
hand sides of the state equations. Because of this simi-
larity, some of the subroutines (e.g., for the purpose of
assembling the mass and advection–dispersion matrices)
in the original reactive transport code can be adopted or
slightly modified to perform the sensitivity calculations.

In order to add sensitivity calculations to an existing
reactive transport code, the most significant program-
ning modification will generally be the addition of
subroutines to calculate the derivative terms on the
right-hand sides of Eqs. (13) and (14). The programmer
time necessary to implement sensitivity coefficient cal-
culations depends to some extent on the type of method
used to solve the state equations in the reactive transport
code. If a global implicit approach [42] is used to solve
the state equations (i.e., the Newton–Raphson method
is applied to solve Eqs. (4) and (6)), then the original
code will already contain subroutines to calculate the deriva-
tives of the rates with respect to the concentrations of
each component. Similarly, if the operator splitting ap-
proach is applied to solve the state equations and the
Newton–Raphson method is used in the second step
(given by Eq. (8)), then subroutines are already available
to evaluate the Jacobian matrix needed for the sen-
sitivity calculations in Eq. (22). If the state equations are
solved with the SIA-1 method, then the reactive trans-
port code contains subroutines to compute the deriv-
aives of the rates of production of each component with
respect to the concentration of the component itself, and
the framework is in place to calculate the remaining
rate-concentration derivatives.

The modification of a reactive transport code to solve
the sensitivity Eqs. (13) and (14) will also result in a
significant increase in run-time storage requirements.
Both SIA1FULL and OPSPLTSS contain an array of
length $N_p N_c (N_c + N_m)$ which is used for storage of the
sensitivity coefficients. For SIA1FULL, the largest
block of memory is devoted to the left-hand-side matrix
in Eq. (20) which has $N_c (N_c + N_m)$ rows and 12
$(N_c + N_m) - 3$ diagonals. SIA1FULL also contains an
array of length $N_c (N_c + N_m)$ for the right-hand-side
vector in Eq. (20). Setting the time weighting factor ($\varepsilon$)
to a number less than one (e.g., for Crank–Nicolson
time stepping) results in greater run-time storage re-
quirements, since it is necessary to store the left-hand-
side matrix and the right-hand-side vectors from the
previous time step.

5. Summary and conclusions

Two codes have been developed to calculate reaction
parameter sensitivity coefficients in a numerical model
of subsurface contaminant transport. Each code was
designed to simulate the coupled effects of two-dimen-
sional steady-state groundwater flow, equilibrium
aqueous speciation reactions, and kinetically controlled
interphase reactions. Kinetic reaction models were in-
cluded for linear kinetic sorption, Langmuir kinetic
sorption, biodegradation with Monod kinetics, and a
general reversible reaction with forward and reverse rate
constants. The code SIA1FULL applies the first-order
sequential iterative approach (SIA-1) to solve the state
equations and solves the entire coupled system of sen-
sitivity equations. OPSPLTSS uses the operator splitting
approach to solve both the state and sensitivity
equations.

In this paper, reaction parameter sensitivity co-
efficients have primarily been used to interpret the complex
interactions between species in systems with coupled
reactive processes. Sensitivity coefficients were used to
gain insight into the relative significance of the reaction
processes and to rank the individual reaction parameters
in terms of importance. Reaction parameter sensitivity
coefficients were calculated with SIA1FULL and OPS-
PLTSS for an example cobalt-NTA transport problem
with linear kinetic sorption and biodegradation. For the
cobalt-NTA problem, coefficients were calculated to
quantify the sensitivity of the concentrations of nine
components with respect to 13 reaction parameters. This
set of parameters included three equilibrium constants,
two kinetic parameters for the cobalt sorption reaction,
and eight kinetic parameters for the biodegradation of
HNTA$^\text{2-}$. Although cobalt was not directly involved in
the NTA biodegradation reaction, the sensitivity coef-
ficients of cobalt and NTA with respect to the bio-
degradation parameters were similar in magnitude.
Similarly, although NTA was not involved in the sorp-
tion reaction, the sensitivity coefficients of cobalt and
NTA with respect to the sorption parameters were
similar in magnitude. Therefore, the sensitivity analysis
demonstrated that although cobalt and NTA did not interact in any kinetic reaction process, there was a strong degree of coupling between the total aqueous concentrations of these two components. The quantification of the coupling between components is an especially useful application of reaction parameter sensitivity coefficients.

CPU time comparisons for the sensitivity analysis of several example reactive transport problems indicated that the calculation of sensitivity coefficients using SIA1FULL or OPSPLTSS is much more efficient than the calculation of sensitivity coefficients by direct perturbation. These CPU comparisons also demonstrated that the operator splitting approach resulted in a significant reduction in simulation time. In general, the concentrations and sensitivity coefficients calculated with the operator splitting codes were comparable to the results obtained with SIA1FULL; however, for one of the example systems, it was necessary to reduce the size of the time step in OPSPLTSS to obtain an accurate solution. The CPU time comparisons for this example problem indicated that the reduction in the size of the time step causes the operator splitting approach to be less efficient than SIA-1 for the solution of the state equations alone; however, the operator splitting code was still more efficient than SIA1FULL for the solution of both the state and sensitivity equations.

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