

A compartmentalized solute transport model for redox zones in contaminated aquifers

1. Theory and development

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Abstract. This paper, the first of two parts [see *Abrams and Loague*, this issue], takes the compartmentalized approach for the geochemical evolution of redox zones presented by *Abrams et al.* [1998] and embeds it within a solute transport framework. In this paper the compartmentalized approach is generalized to facilitate the description of its incorporation into a solute transport simulator. An equivalent formulation is developed which removes any discontinuities that may occur when switching compartments. Rate-limited redox reactions are modeled with a modified Monod relationship that allows either the organic substrate or the electron acceptor to be the rate-limiting reactant. Thermodynamic constraints are used to inhibit lower-energy redox reactions from occurring under infeasible geochemical conditions without imposing equilibrium on the lower-energy reactions. The procedure used allows any redox reaction to be simulated as being kinetically limited or thermodynamically limited, depending on local geochemical conditions. Empirical reaction inhibition methods are not needed. The sequential iteration approach (SIA), a technique which allows the number of solute transport equations to be reduced, is adopted to solve the coupled geochemical/solute transport problem. When the compartmentalized approach is embedded within the SIA, with the total analytical concentration of each component as the dependent variable in the transport equation, it is possible to reduce the number of transport equations even further than with the unmodified SIA. A one-dimensional, coupled geochemical/solute transport simulation is presented in which redox zones evolve dynamically in time and space. The compartmentalized solute transport (COMPTRAN) model described in this paper enables the development of redox zones to be simulated under both kinetic and thermodynamic constraints. The modular design of COMPTRAN facilitates the use of many different, preexisting solute transport and geochemical codes. The companion paper [*Abrams and Loague*, this issue] presents examples of the application of COMPTRAN to field-scale problems.

1. Introduction

Aquifers that become contaminated with organic carbon have the potential to develop zones within the contaminant plume in which the groundwater chemistry is drastically different than in surrounding zones. Often, the major differences between zones are the concentrations of redox-sensitive compounds, also known as electron acceptors and donors, such as dissolved oxygen, nitrate, and dissolved manganese and iron. In such cases these areas are termed redox zones. Redox zones arise because the oxidation of dissolved organic carbon (DOC) occurs via sequential, microbially mediated redox reactions that differ widely in the amount of energy liberated by the reactions. Because the energy yields differ so greatly, the microbial consortia that can mediate a higher-energy reaction will greatly dominate over other consortia. For example, aerobic biodegradation will take place until essentially all the dissolved oxygen is depleted, leading to the formation of suboxic and/or anoxic zones. The sequential process continues, with each

stage utilizing successively less energetic reactions, until all the available DOC or electron acceptors are depleted.

Since methods such as pump-and-treat or capture-and-containment are frequently insufficient to remediate many contaminated aquifers, a significant amount of research has recently focused on the ability of bacteria to degrade organic compounds. As highlighted by the *National Research Council* [NRC, 1994], the ability to biodegrade many hazardous compounds is dependent on the redox conditions of the contaminated subsurface. For example, naphthalene biodegrades under aerobic conditions but does not degrade, or degrades very slowly, under anaerobic conditions. It is necessary therefore to know the redox conditions within a flow field to ensure that bioremediation will be successful.

The transport of heavy metals is also dependent on redox conditions. Nearly all metals of interest in groundwater problems are influenced by redox conditions [*Freeze and Cherry*, 1979]. Small changes in redox conditions can have drastic effects on the sorptive properties and toxicity of metals. For example, under reducing conditions, chromium exists in the plus three (Cr(III)) oxidation state, which can be irreversibly sorbed to aquifer solids; in contrast, under oxidizing conditions, chromium exists in the plus six (Cr(VI)) oxidation state and is mobile [*Kent et al.*, 1994]. Moreover, Cr(VI) is very toxic,

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while Cr(III) is less so [NRC, 1994]. Arsenic toxicity is also dependent on oxidation state; As(III) is more toxic than As(V) [NRC, 1994]. Thus an ability to characterize and predict the extent of multiple redox zones is necessary for a process-based understanding of the fate and transport of many chemical substances currently recognized as hazardous.

1.1. Simulation Approaches

1.1.1. Microbiologically based. Of the many models that have been developed in an effort to characterize and simulate solute transport coupled with biodegradation and/or redox processes, most have focused on the microbiological aspects of the problem [e.g., see *Essaid et al.*, 1995]. With models of this type, when more than one substrate or more than one biogeochemical process is involved, an empirical inhibition factor [Kindred and Celia, 1989; *Essaid et al.*, 1995; *Waddill and Widdowson*, 1998], a switching function [Kinzelbach *et al.*, 1991; *Schäfer and Therrien*, 1995; *Hunter et al.*, 1998], or an indicator coefficient [Smith and Jaffé, 1998] is needed. These parameters inhibit a reaction that yields a lower free energy change from occurring in the presence of a reaction that yields a higher free energy change. For example, denitrification is inhibited by the presence of appreciable dissolved oxygen.

Even though the energy released by biogeochemical reactions can be quantified using thermodynamics, the microbiologically based simulation approaches do not use this information to control reaction feasibility. The microbial populations and the chemical reactions that dominate in a given situation are functions of the amount of Gibbs free energy that can be liberated via chemical reactions. The more free energy released by a reaction, the higher the substrate consumption efficiency of the microbial population catalyzing the reaction. Geochemically based modeling approaches take advantage of this information to decide automatically which redox reactions should occur under which geochemical conditions. In this manner they can avoid empirical methods of reaction inhibition.

1.1.2. Geochemically based. Some previous efforts that exploited the thermodynamic information to avoid empirical reaction inhibition restricted the kinetic treatment to certain classes of reactions. For example, *Liu and Narasimhan* [1989a, b] presented a model that simulated multiple-species reactive transport, including redox reactions. The formulation described by Liu and Narasimhan required the use of a “redox parameter,” such as pE , and the kinetic formulation was limited to zero-order expressions for mineral dissolution. Following the work of *Liu and Narasimhan* [1989a, b], *McNab and Narasimhan* [1994] described a model of reactive transport that handled the first-order degradation of organic compounds, but also utilized thermodynamics in conjunction with a “quasi-expert system” to decide reaction feasibility. In the McNab and Narasimhan model, all inorganic reactions were considered to be at equilibrium. The decision parameter for the expert system in the McNab and Narasimhan model was the equilibrium pE of the system, which was calculated only from the inorganic species.

Other geochemically based modeling efforts allowed for a more general approach to reaction kinetics but still treated all chemical species as being at equilibrium with each other. *Keating* [1995] and *Keating and Bahr* [1998] presented a quasi-kinetic model that could remove redox reactions from the reaction network when the concentrations of the reactants became limiting. The rate-limited nature of the redox reactions in the Keating and Bahr model was simulated by using an

internal, time-dependent source of electrons. *Parkhurst* [1995] and *Parkhurst and Appelo* [1997] developed a model that could accommodate any user-specified kinetic formulation. For instance, the Parkhurst and Appelo model could stoichiometrically “titrate” DOC into a geochemical system, which is controlled by thermodynamic equilibrium, as a function of time according to user-specified rate expressions. The rate expressions in the Parkhurst and Appelo model could be designated to operate over user-specified concentration ranges.

Yeh et al. [1993, 1998] developed a general model that could solve mixed kinetic and equilibrium problems in a batch system; any type and number of reactions could be defined as kinetic or equilibrium, but the kinetic formulation was restricted to mass-action-based expressions. *Yeh and Salvage* [1995] incorporated the Yeh *et al.* model into a solute transport simulator. The Yeh *et al.* and Yeh and Salvage models provide no mechanism for the inhibition of a lower-energy kinetic reaction in the presence of a higher-energy kinetic reaction, such as denitrification in the presence of appreciable dissolved oxygen.

1.1.3. Numerical issues. When using thermodynamic constraints to control reaction feasibility, severe numerical problems can occur because the large range in free energy changes for the different redox reactions translates to equilibrium constants that span tens of orders of magnitude. This, in turn, leads to a range of concentrations which also spans tens of orders of magnitude. The large differences in concentrations lead to extremely ill-conditioned Jacobian matrices when the commonly used Newton-Raphson numerical scheme is employed. It should be noted that this problem is avoided in the microbiological approach because empirical reaction inhibition is used instead of thermodynamics to decide reaction feasibility.

Most geochemical codes do not solve for the concentration of complexed species (i.e., noncomponent species) within the Newton-Raphson solver. Instead, complexed species can be calculated simply as a function of a component set. The only requirement for a component set is that it is linearly independent. Techniques such as basis switching [e.g., *Lichtner*, 1992; *Bethke*, 1996; *Steeffel and Yabusaki*, 1996] can be used to eliminate some of the numerical problems. Basis switching works by eliminating components whose concentrations become very small. When a component is eliminated, a new component must be added to form a different linearly independent set of components. A new component set means that the chemical reactions that form the species set must be rewritten in terms of the new components.

While basis switching is not difficult to do computationally, there is a major drawback of this technique when the geochemical code is coupled to a solute transport code. A common procedure for reducing the number of transport equations required for a given problem is to define some form of the components (i.e., total analytical concentration or total aqueous concentration) as the dependent variable in the solute transport equations. If basis switching is to be used, however, each and every chemical species must have its own transport equation because it is impossible to define a static component set. The number of chemical species in a typical field problem can become quite large, easily exceeding 50 or more species.

If basis switching is not used (i.e., the component set remains fixed), then it is possible to greatly reduce the number of solute transport equations needed to simulate a particular system by making the components the dependent variables in the trans-

Table 1. Summary of Redox Models in Which Chemical Reactions Were Coupled With Mass Transport, Highlighting Key Differences Between Previous Efforts and COMPTRAN

Reference	Organic-Inorganic Link	Redox Variable Used	Kinetic Treatment (Primary Reactions)	Spatial Dimensions	Lower-Energy Redox Reactions Treated As Kinetic or Equilibrium	Thermodynamic Reaction Inhibition (With Kinetics)
<i>László and Székely</i> [1989]		X	none	2		
<i>Liu and Narasimhan</i> [1989a, b]		X	solids only	2		
<i>Postma et al.</i> [1991]		X	none	1		
<i>Yeh and Tripathi</i> [1990, 1991]		X	none	2		
<i>Engesgaard and Kipp</i> [1992]		X	none	1		
<i>Lensing et al.</i> [1994]	X		Monod	1		
<i>McNab and Narasimhan</i> [1994]	X	X	first order	2		
<i>Walter et al.</i> [1994a, b]		X	none	2		
<i>Schäfer and Therrien</i> [1995]	X		Monod	3		
<i>Yeh and Salvage</i> [1995]		X	mass action	2		
<i>Furrer et al.</i> [1996]	X		power function	1		
<i>Van Cappellen and Gaillard</i> [1996]	X		Monod	1		
<i>Wunderly et al.</i> [1996]		X	diffusion only	2		
<i>Parkhurst and Appelo</i> [1997]	X	X	user defined	1		
<i>Keating and Bahr</i> [1998]		X	quasi	2		
<i>Hunter et al.</i> [1998]	X		first order	1		
<i>Salvage and Yeh</i> [1998]	X	X	Monod or mass action	1		
COMPTRAN	X		Monod no growth	2	X	X

port equations, rather than each chemical species. The concentration of the equilibrium species can be easily calculated outside of the solute transport simulator, since they are simply functions of the component set.

1.1.4. Development of COMPTRAN. This paper links the geochemical compartmentalized approach described by *Abrams et al.* [1998] with solute transport. The resulting new model, COMPTRAN (compartmentalized solute transport model), can accommodate any number of kinetic reactions that compete for dissolved organic carbon, without the use of empirical reaction inhibition. Each reaction can have its own rate parameters and different kinetic formulations. COMPTRAN facilitates the use of a fixed component set by using reaction networks that do not contain insignificant reactions. Competing redox reactions can be either thermodynamically or kinetically limited, including lower-energy redox reactions that lose the thermodynamic competition with higher-energy redox reactions. COMPTRAN allows disequilibrium to exist among chemical species while still using thermodynamic constraints to select feasible redox reactions. The modular design of COMPTRAN facilitates the incorporation of many preexisting solute transport and geochemical codes. COMPTRAN is the set of protocols which links these preexisting models together to simulate the development of redox zones under thermodynamic and kinetic constraints. Table 1 provides a summary of previous redox models that have coupled chemical reactions with solute transport simulators and illustrates the key differences between them and the simulation protocols developed for this study. The companion paper [*Abrams and Loague*, this issue] presents two examples in which COMPTRAN was applied to field-scale problems that were based on data from the U.S. Geological Survey's Cape Cod research site.

2. Theory

2.1. Geochemistry

2.1.1. Definitions. In this paper the terms component and species are used in the same manner as in the work of

Westall et al. [1976]. Components do not necessarily equate to the thermodynamic concept as used in the phase rule; rather, they are defined in the sense that *Rubin* [1983] defined tenads. Components are chemical entities whose global mass is reaction-invariant. Only physical processes can change the global mass of a component, i.e., advection and dispersion. The most direct comparison is to the basis from linear algebra. Components constitute an independent basis set such that all species are formed from linear combinations of the components and no component can be represented by components other than itself. The free component itself is considered a species. The solution to a geochemical problem consists of a concentration value for each species. The solution for an equilibrium problem is obtained by solving a system of nonlinear mass action equations (one for each noncomponent species) and linear mass balance equations (one for each component). For a problem that includes kinetic reactions, rate expressions replace the appropriate mass action equation. The total mass for each component is referred to as the total analytical concentration. The total analytical concentration of a particular component is the sum of the concentrations of all species that contain the component, weighted by their stoichiometric coefficients. Since the concentrations of all species are unknown at the outset, the system of equations is closed by specifying a value for the total analytical concentration for each component. Borrowing terminology from *Morel and Hering* [1993], recipe items are defined as chemical entities that one might glean from a chemical analysis (e.g., alkalinity, total carbon dioxide, dissolved oxygen). The recipe items, which provide the value of the total analytical concentration for each component, are written in terms of the chosen component set as

$$T_j = \sum_{i=1}^M s_{ij}x_i = \sum_{i=1}^R a_{ij}y_i \quad j = 1, N_c, \quad (1)$$

where T_j is the total analytical concentration of component j ($M L^{-3}$), M is the number of chemical species, including free components, s_{ij} is the stoichiometric coefficient of component

Table 2. Reaction Network Used to Develop COMPTRAN

Reaction	log K^*
<i>Redox</i>	
(R1) $O_2(aq) + \text{“CH}_2\text{O”} = CO_3^{2-} + 2H^+$	68.38
(R2) $2NO_3^- + \frac{5}{2}\text{“CH}_2\text{O”} = N_2(aq) + \frac{5}{2}CO_3^{2-} + 3H^+$	163.5
(R3) $MnO_2(s) + \frac{1}{2}\text{“CH}_2\text{O”} + H^+ = Mn^{2+} + \frac{1}{2}CO_3^{2-}$	32.84
(R4) $Fe(OH)_3(s) = +\frac{1}{4}\text{“CH}_2\text{O”} + \frac{3}{2}H^+ = Fe^{2+} + \frac{1}{4}CO_3^{2-}$	11.92
<i>pH Buffering</i>	
$H_2O = H^+ + OH^-$	-13.99
$H_2CO_3 = CO_3^{2-} + 2H^+$	-16.67
$HCO_3^- = CO_3^{2-} + H^+$	-10.32
<i>Aqueous Speciation</i>	
$MnOH^+ + H^+ = Mn^{2+} + H_2O$	10.0
$MnHCO_3^+ = Mn^{2+} + CO_3^{2-} + H^+$	-12.1
$Fe(OH)_2^+ + 2H^+ = Fe^{2+} + 2H_2O$	20.57
$Fe(OH)^+ + H^+ = Fe^{2+} + H_2O$	9.5

Reactions (1) and (2) are the redox reactions in compartment 1 (oxic); reactions (2) and (3) are the redox reactions in compartment 2 (suboxic); and reactions (3) and (4) are the redox reactions in compartment 3 (anoxic).

*[Morel and Hering, 1993].

j in species i , x_i is the concentration of species i ($M L^{-3}$), R is the number of recipe items, a_{ij} is the stoichiometric coefficient of component j in recipe item i , y_i is the concentration of recipe item i ($M L^{-3}$), and N_c is the number of components.

2.1.2. Compartmentalized approach. The compartmentalized approach operates on the premise that some redox reactions dominate over others, allowing less significant reactions to be dropped from the reaction network while new reactions are added, as described by *Abrams et al.* [1998]. The compartments themselves have no spatial context. They are a function of reaction progress only. The switch from one compartment to the next is governed by a user-specified cutoff criterion that is based on concentration ratios of key redox constituents. In general, each “compartmentalized” reaction network uses at least some different components and species. The mass balance information (i.e., the total analytical concentration) must therefore be passed from one reaction network to the next so that the initial conditions in the new compartment match the final conditions in the previous compartment.

To facilitate describing the compartmentalized approach, “driving” and “nondriving” components are defined differently. In general, any number of different organic compounds can be included in the reaction networks. For the redox system of interest in this paper, all reactive dissolved organic carbon is lumped together and defined as the component “CH₂O,” which is considered to be the driving component. All chemical changes in the system are driven by reactions with “CH₂O.” For example, in the work of *Abrams et al.* [1998], small increments of “CH₂O” were added to the simulated equilibrium system to drive the development of redox zones. In this paper all other components are considered to be nondriving.

As *Abrams et al.* [1998] show, two redox reactions are present in each compartment. The sequence of reactions and compartments is determined by the energy yields of the redox reactions under consideration. The reactions are ordered from highest to lowest energy. There is always overlap of reactions

between compartments; that is, the lower-energy reaction in one compartment is the higher-energy reaction in the next compartment.

The compartmentalized approach for the development of redox zones can be generalized as follows:

$$T_j^n = \sum_{i=1}^{R_n} a_{ij} y_i^n + A_j \quad n = 1, k; j = 1, N_c, \quad (2)$$

$$A_j = \sum_{i=1}^{n-1} s_{(n-i)j}^h |x_{n-i}^{h,s} - x_{n-i}^h| \quad (3)$$

if j is a nondriving component,

$$A_j = s_{(n-1)j}^l |x_{n-1}^{l,s} - x_{n-1}^l| - s_{(n-1)j}^h |x_{n-1}^{h,s} - x_{n-1}^h| \quad (4)$$

if j is the driving component,

where n is the compartment number, R_n is the number of recipe items in compartment n , y_i^n is the concentration of recipe item i in compartment n , k is the number of compartments, s and x are defined the same as in (1) except the superscript h denotes the higher-energy redox species in n , the superscript l denotes the lower-energy redox species in n , and the superscript degree symbol denotes the initial concentration. For example, consider the reaction network for compartment 2 shown in Tables 2 and 3. The components are H^+ , CO_3^{2-} , NO_3^- , Mn^{2+} , and “CH₂O.” The respective redox reactions are denitrification and manganese reduction. Equations (2)–(4) are expanded as

$$T_{H^+}^2 = -ALK + 2[CO_2]_T - [MnO_2(s)]_T + A_{H^+}, \quad (5)$$

$$T_{CO_3^{2-}}^2 = [CO_2]_T + 0.5[MnO_2(s)]_T + A_{CO_3^{2-}}, \quad (6)$$

$$T_{NO_3^-}^2 = [NO_3]_T + A_{NO_3^-}, \quad (7)$$

$$T_{Mn^{2+}}^2 = [MnO_2(s)]_T + A_{Mn^{2+}}, \quad (8)$$

$$T_{\text{“CH}_2\text{O”}}^2 = [\text{“CH}_2\text{O”}]_T - 0.5[MnO_2(s)]_T + A_{\text{“CH}_2\text{O”}}, \quad (9)$$

$$A_{H^+} = 2([O_2(aq)]^\circ - [O_2(aq)]), \quad (10)$$

$$A_{CO_3^{2-}} = [O_2(aq)]^\circ - [O_2(aq)], \quad (11)$$

$$A_{NO_3^-} = 0, \quad (12)$$

$$A_{Mn^{2+}} = 0, \quad (13)$$

$$A_{\text{“CH}_2\text{O”}} = 1.25([NO_3^-]^\circ - [NO_3^-]) - [O_2(aq)]. \quad (14)$$

For the above example the redox reactions are treated as equilibrium reactions, as in the model evaluation shown by *Abrams et al.* [1998]. When the redox reactions are specified as kinetic reactions, which allows the assumption of an excess of the driving component, then (4) can be set to zero. If (4) is set to zero, then it follows that (14) becomes zero.

It is assumed here that the redox reactions are mediated by microbes and that the overall result of the oxidation of organic carbon can be represented by the four redox reactions shown in Table 2. Since the redox reactions represent biogeochemical processes, it is assumed that they are rate-limited processes, and they are simulated as kinetic reactions. *Bekins et al.* [1998] have shown that biogeochemical reactions, over a range of concentrations, are best represented by a hyperbolic rate ex-

pression, such as the Monod expression. If the concentration of microbes is assumed to be constant, the Monod expression can be written without a term for the concentration of microbes. It is intuitive that the rate of reaction should be a function of the concentrations of the electron acceptor and the organic substrate. Thus a modified Monod no-growth relationship was adopted [Bailey and Ollis, 1977; Molz *et al.*, 1986]:

$$\frac{dC}{dt} = -k \left(\frac{C}{k_c + C} \right) \left(\frac{S}{k_s + S} \right), \quad (15)$$

where C is the concentration of an electron acceptor ($M L^{-3}$), t is time (T), k is the maximum reaction rate ($M L^{-3} T^{-1}$), k_c is half-saturation constant associated with electron acceptor ($M L^{-3}$), S is the concentration of organic substrate ($M L^{-3}$), and k_s is the half-saturation constant associated with the organic substrate ($M L^{-3}$). This formulation allows either the organic substrate or the electron acceptor to limit the reaction rate, if either of their concentrations are low. For example, when $S \ll k_s$, the organic substrate term on the right-hand side of (15) becomes small and limits the overall reaction rate.

The various microbial communities that mediate the redox reactions shown in Table 2 compete for whatever organic carbon is available. The geochemical portion of COMPTRAN utilizes two redox reactions in each compartment, plus aqueous pH buffering reactions and appropriate aqueous speciation reactions for that compartment. In a given compartment, simulations in which both electron acceptors and organic substrate are present in excess will show that both reaction rates have finite, positive values. In currently available models, both electron acceptors would be consumed unless empirical reaction inhibition is used. In COMPTRAN, however, thermodynamic constraints dictate which reactions should actually occur.

2.1.3. Thermodynamic reaction inhibition. The same procedure described by Abrams *et al.* [1998] is used to determine reaction feasibility and the amount of dissolved organic carbon that should be partitioned to each reaction. No empirical reaction inhibition is used in COMPTRAN. The two-step procedure employed is schematically illustrated in Figure 1. First, a kinetic step is taken (Figure 1a) without using any form of reaction inhibition. This step results in the reduction of both redox reactants in the active compartment. Figure 1b shows an analogous thermodynamic step that checks if the concentration of the low-energy redox reactant that was determined in the kinetic step violated any thermodynamic constraints. The check is accomplished by adding to the reaction system enough of the driving component (e.g., “CH₂O” or DOC) so that the concentration of the high-energy redox reactant equals the concentration of the high-energy redox reactant that was determined in the kinetic step. When the two concentrations are equal, the reaction system has been advanced to equivalent states in terms of the dominant reaction.

When the reaction system has been advanced to equivalent

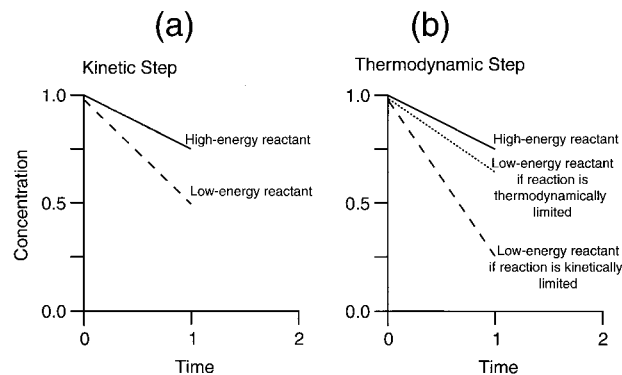


Figure 1. Schematic illustration of how COMPTRAN checks if the progress of kinetic reactions violated thermodynamic constraints. In the kinetic step, (a) preliminary concentrations of both redox reactants are obtained within a given compartment. In the thermodynamic step, (b) the concentration of the low-energy redox reactant is compared with its concentration from the kinetic step to ensure that thermodynamic constraints are obeyed. If the concentration of the low-energy reactant is higher in the thermodynamic step, the reaction is thermodynamically limited; if it is lower, the reaction is kinetically limited. This procedure eliminates the need for empirical methods of reaction inhibition.

states, the concentration of the low-energy redox reactant is compared between the kinetic and the thermodynamic steps: (1) If the concentration of the low-energy redox reactant is lower in the thermodynamic step, as illustrated in Figure 1b by the dashed line, then the results indicate that the rate limitation placed on the low-energy redox reaction did not violate any thermodynamic constraints; the low-energy reaction was approaching equilibrium, but kinetic constraints prevented it from attaining equilibrium. In this case, the low-energy redox reaction is kinetically limited. (2) If the concentration of the low-energy redox reactant is higher in the thermodynamic step, as illustrated by the dotted line in Figure 1b, then the results indicate that thermodynamic constraints were violated in the kinetic step; the kinetic step permitted the low-energy redox reaction to proceed beyond the state allowed by thermodynamic constraints. In this case, the low-energy redox reaction is thermodynamically limited.

2.2. Solute Transport

2.2.1. Computational strategy. Transport of conservative solutes is usually described by linear partial differential equations, with one written for each solute. Many different schemes have been proposed to couple equilibrium geochemical reactions with solute transport simulators. Yeh and Tripathi [1989] reviewed the three general approaches that have been taken and evaluated them in terms of their flexibility, practicality

Table 3. Components and Recipe Items Used in Each Compartment for the Development of COMPTRAN

Compartment	Components	Recipe Items
1	H ⁺ , CO ₃ ²⁻ , NO ₃ ⁻ , “CH ₂ O”	ALK, [CO ₂] _T , [O ₂] _T , [NO ₃ ⁻] _T , [“CH ₂ O”] _T
2	H ⁺ , CO ₃ ²⁻ , NO ₃ ⁻ , “CH ₂ O”, Mn ²⁺	ALK, [CO ₂] _T , [O ₂] _T , [NO ₃ ⁻] _T , [“CH ₂ O”] _T , [MnO ₂ (s)] _T
3	H ⁺ , CO ₃ ²⁻ , “CH ₂ O”, Mn ²⁺ , Fe ²⁺	ALK, [CO ₂] _T , [O ₂] _T , [“CH ₂ O”] _T , [MnO ₂ (s)] _T , [Fe(OH) ₃ (s)] _T

ALK is the carbonate alkalinity. The subscript T refers to the total concentration that would be gleaned from a chemical analysis.

(i.e., CPU time and memory usage), and the ease with which kinetic reactions can be included.

The three approaches described by *Yeh and Tripathi* [1989] differ by the manner in which the equations describing geochemical reactions are coupled to the solute transport equations. The approaches Yeh and Tripathi reviewed either (1) solve simultaneously a mixed system of differential and algebraic equations, (2) solve simultaneously a system of nonlinear partial differential equations, or (3) iterate sequentially between linear partial differential equations and nonlinear algebraic equations (\pm ordinary differential equations for kinetics). Yeh and Tripathi concluded that the latter approach, the sequential iteration approach (SIA), holds the most promise for solving a wide range of practical problems. One advantage of the SIA is that the nonlinearities caused by the geochemical equations are removed from the partial differential equations, making the task of solving the solute transport equations much simpler. Another advantage of the SIA is that it is relatively straightforward to utilize the wide range of already available geochemical codes.

The SIA can be subdivided. For example, one could use the concentration of each dissolved species as the dependent variable in the solute transport equations. To apply this method, one needs a separate solute transport equation for each dissolved species, a number that can become quite large. Alternatively, one could solve for the total dissolved concentration of each aqueous component in the transport equation [*Theis et al.*, 1982; *Kirkner et al.*, 1984, 1985; *Engesgaard and Kipp*, 1992; *Tebes-Stevens et al.*, 1998]. Both of these methods calculate the chemical speciation in a separate chemical module of the computer code, but for the latter approach, the solute transport equations have no direct knowledge of the individual chemical species. Clearly, such a method has the potential to reduce significantly the number of solute transport equations needed.

A third variant of the SIA employs the total analytical concentration of each component as the dependent variable in each transport equation. With this method, all forms of the component (i.e., total dissolved, total sorbed, and total precipitated) are summed and used as the dependent variable in the solute transport equations. Again, the chemical speciation is calculated in a separate chemical module. This method is very convenient because, as described above, the known value of the total analytical concentration for each component provides closure for the geochemical system of equations. Furthermore, it is very easy to include precipitated species and kinetic species with this variant of the SIA [*Yeh and Tripathi*, 1989].

The SIA was employed for the current version of COMPTRAN, with the total analytical concentration of each component as the dependent variable in the solute transport equations. HYDROGEOCHEM 2.1 [*Yeh and Salvage*, 1995] was modified to include no-growth Monod kinetics (i.e., equation (15)) and then combined with the compartmentalized approach [*Abrams et al.*, 1998] to create the current version of COMPTRAN. The flexible design of COMPTRAN is such that many multispecies transport codes (and geochemical codes) can be incorporated within it.

In the unmodified HYDROGEOCHEM 2.1, transport of equilibrium species is achieved by solving the relevant mass-action equations at each time step and then utilizing (1) to calculate the total analytical concentration of each component, which is then solved for at the next time step with the advection-dispersion equation, given as

$$\frac{\partial T_j}{\partial t} = -\nabla \cdot (\bar{v}C_j) + \nabla \cdot (\mathbf{D} \cdot \nabla C_j) \quad j = 1, N_c, \quad (16)$$

$$C_j = T_j - P_j, \quad (17)$$

where C_j is the total dissolved concentration of component j ($M L^{-3}$), P_j is the total precipitated concentration of component j ($M L^{-3}$), \bar{v} is the average linear velocity vector ($L T^{-1}$), and \mathbf{D} is the dispersion coefficient tensor ($L^2 T^{-1}$). Since the T_j values are functions of the C_j values, functional relationships need to be defined to link them. These functional relationships are the mass-action and mass-balance equations discussed above.

2.2.2. Kinetic species. *Tebes-Stevens et al.* [1998] recently reported a variant of the SIA in which all kinetic species that affect the concentration of a particular component are lumped together in a single term that represents the rate of production of that component. In the formulation of Tebes-Stevens et al. the rate-of-production term is included in equations of the form of (16), where the dependent variable is the total aqueous concentration of the component instead of the total analytical concentration. The traditional form of the SIA, however, which is employed by HYDROGEOCHEM 2.1, requires that each aqueous kinetic species have its own solute transport equation:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot (\bar{v}c_i) + \nabla \cdot (\mathbf{D} \cdot \nabla c_i) + r_i \quad i = 1, N_k, \quad (18)$$

where c_i is the concentration of the i th aqueous kinetic species ($M L^{-3}$), r_i is the rate of production of the i th aqueous kinetic species ($M L^{-3} T$), and N_k is the number of aqueous kinetic species. The contribution of the kinetic species to the total analytical concentration of each relevant component is accounted for with (1) before (16) and (17) are solved. As pointed out by *Tebes-Stevens et al.* [1998], the most efficient method of incorporating kinetic species into a solute transport framework is problem-dependent.

Equation (18) indicates that there is one transport equation for each aqueous kinetic species. Because the number of such species may be different in different compartments, a decision must be made regarding boundary conditions before the compartmentalized approach can be applied. For example, if one were to drop the kinetic species O_2 from the reaction network upon switching from compartment 1 to compartment 2 (i.e., oxic to suboxic), a discontinuity in (18) would be created. Moving boundaries would thus be needed for (18). The moving boundaries would separate the regions of an aquifer which are in the compartment-1 stage of reaction progress from those that are in different compartments.

The approach used in the current version of COMPTRAN is to retain the aqueous kinetic species from previous compartments so that no discontinuity develops and moving boundaries are not needed. This may seem to contradict the original premise of the compartmentalized approach, but it does not. A chief advantage of the compartmentalized approach is the ease with which thermodynamic feasibility can be decided. This is not affected by retaining insignificant kinetic reactions. When checking for thermodynamic feasibility, the insignificant reactions are still ignored; that is, thermodynamic calculations are not performed for species that are not part of the compartment in question. Furthermore, the numerical difficulties associated with calculating concentrations from insignificant reactions occur only in the thermodynamic computations. The kinetic spe-

cies are retained solely for the purpose of preventing discontinuities in (18). Moreover, when an insignificant kinetic species is retained, the concentration of that species is small, due to the cutoff criteria. Thus the contribution of the retained kinetic species to changes in chemical speciation is small, and the rate of reaction at this point is quite slow because of (15).

There are two precipitated kinetic species ($\text{Fe}(\text{OH})_3(s)$ and $\text{MnO}_2(s)$) associated with the reaction network used in this effort (see Table 2). Since the precipitated species are immobile, they do not need a transport equation. However, the precipitated species may be composed of components that are not present in all compartments (see Table 3). In this paper the component Mn is only present in compartments 2 and 3 (for $\text{MnO}_2(s)$ and associated aqueous complexes), and the component Fe is only present in compartment 3 (for $\text{Fe}(\text{OH})_3(s)$ and associated aqueous complexes). Again, there is the potential for discontinuities in transport equations that could be handled with moving boundaries. This time, however, it is (16) that could encounter a discontinuity at compartment boundaries, because the transported entities (i.e., dissolved Mn and Fe) are components, not kinetic species. A strategy similar to that used for aqueous kinetic species is employed. Since the incoming water is pristine (i.e., in compartment 1), Mn and Fe are defined as having a dissolved concentration of zero at the upstream boundary but an initial condition throughout the spatial domain that consists solely of precipitated concentration. This allows T_{Mn} and T_{Fe} to be continuous across the spatial domain because of (17).

2.2.3. Linkage. Inspection of (2) and (3) reveals that there is yet another potential for discontinuities in T_j during the course of redox zone development. This type of discontinuity cannot be handled in a manner similar to the kinetic species because it occurs with components that are present in all compartments. The cause of this discontinuity is that some components may experience a large change in value at compartmental boundaries. Clearly, such discontinuities would wreak havoc on most numerical methods for solute transport. An alternative formulation for the compartmentalized approach that circumvents this problem is

$$T_j^n = T_j^1 + \sum_{i=1}^{R_n} a_{ij} y_i^n |y_i^n \neq y_i^1| - \sum_{i=1}^{n-1} s_{(n-1)i}^h r_{n-1}^h \quad (19)$$

$$n = 1, k; j = 1, N_c.$$

When simulating perturbed redox systems, it can usually be assumed that the dissolved redox species are either initially zero or initially the maximum value for that particular setting. For these conditions, it can be shown that (19) is equivalent to (2) through (4). As an example, consider the reaction network outlined in Table 2. Expanding (2) and (3) for the total analytical concentration of H^+ in compartment 2 yields

$$T_{\text{H}^+}^2 = -\text{ALK} + 2[\text{CO}_2]_{\text{T}} - [\text{MnO}_2(s)]_{\text{T}} + 2[\text{O}_2(aq)]^\circ - 2[\text{O}_2(aq)]. \quad (20)$$

Expanding (19) for the total analytical concentration for H^+ in compartment 2 yields

$$T_{\text{H}^+}^2 = -\text{ALK} + 2[\text{CO}_2]_{\text{T}} + 2[\text{O}_2]_{\text{T}} - [\text{MnO}_2(s)]_{\text{T}} - 2[\text{O}_2(aq)]. \quad (21)$$

Since $[\text{O}_2(aq)]^\circ = [\text{O}_2]_{\text{T}}$, (20) and (21) are equivalent.

When (19) is used to account for compartmental switching, one simply transports only T_j^1 for components subject to large changes between compartments (in this paper H^+ and CO_3^{2-}). This alternative formulation for the compartmentalized approach eliminates the discontinuities associated with (2)–(4); T_j^n is calculated from (19) and then passed to the chemical module.

2.2.4. Flowchart of COMPTRAN. COMPTRAN was constructed with extensively modified versions of the geochemical code KEMOD [Yeh *et al.*, 1993, 1998] and the coupled solute transport/geochemical code HYDROGEOCHEM 2.1 [Yeh and Salvage, 1995]. HYDRAQL [Papelis *et al.*, 1988] was incorporated within COMPTRAN to perform the equilibrium calculations.

All of the solute transport simulations performed in this effort were conducted with COMPTRAN. The flowchart in Figure 2 illustrates how COMPTRAN operates. Only the major subroutines are shown in Figure 2. It should be pointed out that each one of the subroutines shown in Figure 2 (except for truth.f) contains calls to other subroutines to perform various tasks related to the primary purpose of the calling routine. The new routines that were developed and the HYDROGEOCHEM 2.1 routines that were modified for this study are represented, respectively, by the dark gray and light gray rectangles in Figure 2.

In addition to performing geochemical and solute transport calculations, COMPTRAN essentially works by making two key decisions. The first decision to be made is to assign each node to the correct compartment. This decision is made by the subroutine switch.f (Figure 2a). The sequence of operations that is followed each time ocsplit.f is called by gm2d.f is illustrated in the flowchart in Figure 2b. The subroutine ocsplit.f loops over the entire set of nodes in the boundary value problem and calculates a “batch” geochemical solution at each node. The second major decision is made within the geochemical sequence of operations. A decision is made within the subroutine truth.f as to whether the lower-energy redox reaction within a given compartment is behaving in a kinetically limited or thermodynamically limited manner. This decision is made by determining whether the concentration of the lower-energy redox product is lower in the kinetic step or in the thermodynamic step (see Figure 1): (1) If the concentration of the lower-energy redox product is lower in the kinetic step, then the reaction is kinetically limited. (2) If the concentration of the lower-energy redox product is lower in the thermodynamic step, then the reaction is being limited by free energy constraints.

2.3. Elimination of Transport Equations

Depending on how the geochemical problem is formulated, it may not be necessary to write a transport equation (i.e., equation (16)) for each component. Recall that the global mass of a component is reaction-invariant and is also independent of other components. The compartmentalized approach allows the definition of at least one reaction network in which the total analytical concentration (i.e., T_j) of some components does not change. If a particular T_j does not change in time and space, the transport equation for that T_j can be dropped from the system of equations under consideration.

Consider a pristine aquifer governed by oxic compartment conditions, in which the components are H^+ , CO_3^{2-} , NO_3^- , and “ CH_2O ” and oxygen reduction and denitrification are the only redox reactions. By definition, these reactions cannot change

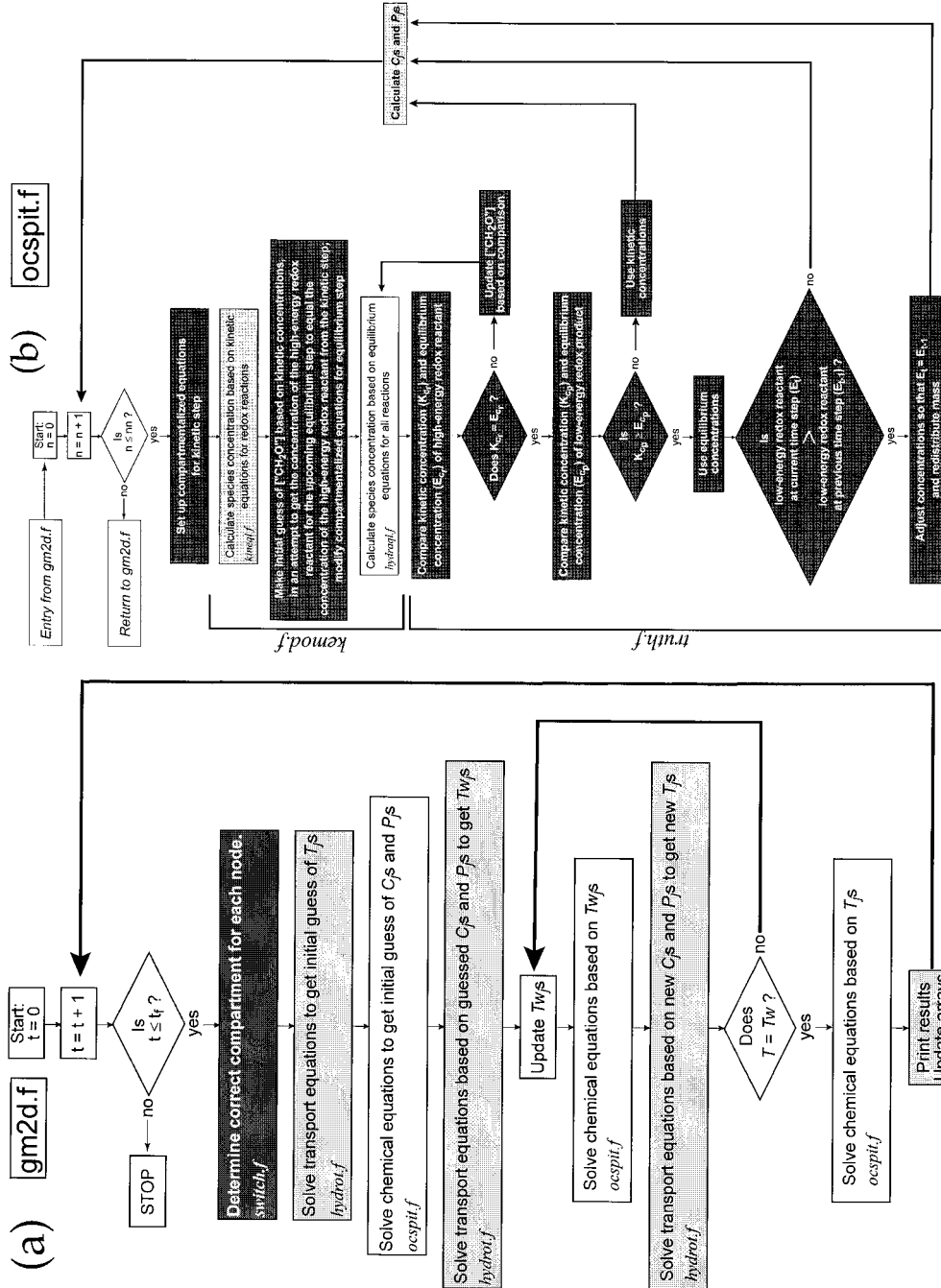


Figure 2. Two-part flowchart illustrating how COMPTAN operates. HYDROGEOCHEM 2.1 [Yeh and Sabage, 1995] was used as a framework in this study. Many of the routines from HYDROGEOCHEM 2.1 were not modified for use in COMPTAN (i.e., items with no shading). The new routines developed for COMPTAN are shown in dark gray. The existing HYDROGEOCHEM 2.1 routines that were modified, to varying degrees, are shown in light gray. Variables are as follows: t is time, t_f is the final time step, T_w is the iterate of T , n is the node number, m is the total number of nodes. All other variables are either defined on the flowchart or are the same as already defined elsewhere in this paper. (a) gm2d is the major “controlling” subroutine of HYDROGEOCHEM 2.1. (b) ocspit is the HYDROGEOCHEM 2.1 subroutine that loops over all nodes to calculate the concentrations of all species.

$T_{\text{H}^+}^1$ or $T_{\text{CO}_3^{2-}}^1$. The contaminants $T_{\text{NO}_3}^1$ and $T_{\text{CH}_2\text{O}}^1$ are initially infinitesimal in the aquifer. The upgradient boundary is set to allow the influx of pristine groundwater (plus unreacted contaminants) which is also governed by oxic compartment conditions. Hence the upstream boundary conditions for H^+ and CO_3^{2-} are equal to the initial conditions for H^+ and CO_3^{2-} , respectively. Thus advection and dispersion cannot change $T_{\text{H}^+}^1$ or $T_{\text{CO}_3^{2-}}^1$.

H^+ and CO_3^{2-} are components in each compartment (see Table 3). Solid phases present in later compartments can change the total analytical concentrations of H^+ and CO_3^{2-} due to advection and dispersion. Since only T_j^1 would be transported for H^+ or CO_3^{2-} , (16) is not needed for these components because $T_{\text{H}^+}^1$ and $T_{\text{CO}_3^{2-}}^1$ do not change in time or space. One simply specifies that $T_{\text{H}^+}^1$ and $T_{\text{CO}_3^{2-}}^1$ remain fixed in value. The chemistry is computed correctly because (19) is used to calculate $T_{\text{H}^+}^n$ and $T_{\text{CO}_3^{2-}}^n$ before passing them to the chemistry module. For the problem at hand, this reduces the total number of transport equations (i.e., equations (16) and (18)) from 8 to 6.

3. Testing of COMPTRAN

3.1. Problem Setup

Development of COMPTRAN consisted of coding (15) and (19) and the necessary associated modifications into HYDROGEOCHEM 2.1 [Yeh and Salvage, 1995], incorporating HYDRAQL [Papelis *et al.*, 1988], debugging, and testing. To test COMPTRAN, a one-dimensional solute transport problem was devised. The spatial domain can be conceptualized as a sand-filled laboratory column that is 1 m in length. The flux of water into the column was set to $7 \times 10^{-5} \text{ m d}^{-1}$. The porosity of the sand was assumed to be 0.3, which yields an average linear velocity of $2.3 \times 10^{-4} \text{ m d}^{-1}$. The dispersivity was set to 0.025 m (i.e., the same as Δx). The cutoff criteria used for switching between compartments 1 and 2 and 2 and 3 were 7×10^{-4} and 1×10^{-2} , respectively. Abrams *et al.* [1998] described the switching criteria in detail. The evaluation of these two cutoff values is given by Abrams and Loague [this issue].

The initial conditions, shown in Figure 3a, were designed to approximate pristine groundwater; dissolved oxygen (DO) of $2.5 \times 10^{-4} \text{ M}$, alkalinity of 0.06 meq L^{-1} , and total inorganic carbon of $5 \times 10^{-4} \text{ M}$. These parameters yield an initial $p\text{H}$ of 5.51. Two solid phases, $\text{MnO}_2(s)$ and $\text{Fe}(\text{OH})_3(s)$, were initially present at 10^{-5} and 10^{-3} M , respectively. These two solids were conceptually considered to be weathering coatings on aquifer solids. The rate parameters for the simulation are given in Table 4.

To simulate contamination of the column, a flux boundary condition was used at the inflow boundary:

$$qC_j = qC_j^B - D_L \frac{\partial C_j}{\partial x} \quad j = 1, N_c, \quad (22)$$

where q is the specific discharge ($L T^{-1}$) and D_L is the longitudinal dispersion coefficient. The concentration of the incoming flux C_j^B was 2.3×10^{-4} , 2.5×10^{-4} and $3.1 \times 10^{-3} \text{ M}$ for nitrate, DO, and dissolved organic carbon (DOC), respectively. The influx of nitrate and DOC represents the contamination of this hypothetical laboratory column.

3.2. Results

Figure 3a shows results after 1 year of simulated time. Even though DO flowed continuously across the upstream boundary

at the same concentration as the initial condition, DO began to disappear because of kinetic reactions with the incoming DOC. Nitrate was transported conservatively in the region where oxygen reduction occurred because thermodynamic constraints prevented denitrification from occurring. The $p\text{H}$ decreased because hydrogen ions were produced by oxygen reduction. Alkalinity did not change since oxygen reduction was the only major redox reaction that occurred.

As seen in Figure 3a, after 3 years of simulated time, consumption of DOC caused the DO concentration to decrease enough to allow denitrification to commence. Accordingly, the nitrate profile exhibits a region of "missing mass" where denitrification has occurred. Also, the $p\text{H}$ increased because of the consumption of hydrogen ions via denitrification. A very small amount of manganese reduction occurred in the denitrification region because the thermodynamic calculation indicated that manganese reduction was not quite completely inhibited, although it was nearly so. The concentration of dissolved manganese is too low to be seen on Figure 3a at 3 years of simulated time.

After 3.5 years of simulated time (Figure 3b), the zone of denitrification had grown to cover $\sim 0.15 \text{ m}$ of the column. The concentration of dissolved manganese increased enough via kinetic reductive dissolution of $\text{MnO}_2(s)$ to just appear on the plot ($\sim 3 \mu\text{M}$). The $p\text{H}$ had almost reached 5.9, and the alkalinity continued to increase.

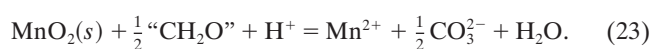
By 5 years of simulated time (Figure 3b), an iron zone had formed due to the reduction of $\text{Fe}(\text{OH})_3(s)$. This final redox reaction was thermodynamically feasible after the available $\text{MnO}_2(s)$ had been exhausted in this area. The peak dissolved manganese concentration in Figure 3b is $\sim 20 \mu\text{M}$. The $p\text{H}$ values reached about 6.6 in the zone of iron reduction. Denitrification was still thermodynamically inhibited in the first 0.2 m due to the constant influx of DO.

The test simulation illustrated in Figure 3 was stopped at 6 years. As more and more $\text{MnO}_2(s)$ was depleted, the iron-reducing zone continued to expand in length. The peak dissolved iron concentration after 6 years was $\sim 400 \mu\text{M}$, and the $p\text{H}$ had reached a value of ~ 8 . The last remaining high concentrations of oxygen left over from the initial condition had almost been swept from the problem domain.

3.3. Implications of the Thermodynamic Inhibition Mechanism

A chief advantage of the compartmentalized approach is that kinetic constraints are embedded within a thermodynamic framework. This allows a redox reaction that yields sufficiently lower energy to be inhibited automatically in the presence of a higher-energy reaction. The compartmentalized approach therefore does not need empirical or ad hoc approaches to reaction inhibition.

A disadvantage of the compartmentalized approach is that redox reactions are considered to be equilibrium reactions for a part of each time step. This is done to check the thermodynamic feasibility of the lower-energy redox reaction in a given compartment and to compute the amount of reaction inhibition but not necessarily to control reaction progress (see Abrams *et al.* [1998] and Figures 1 and 2). The implication is that it is possible to misinterpret a reaction as reversible. For example, consider the manganese reduction reaction



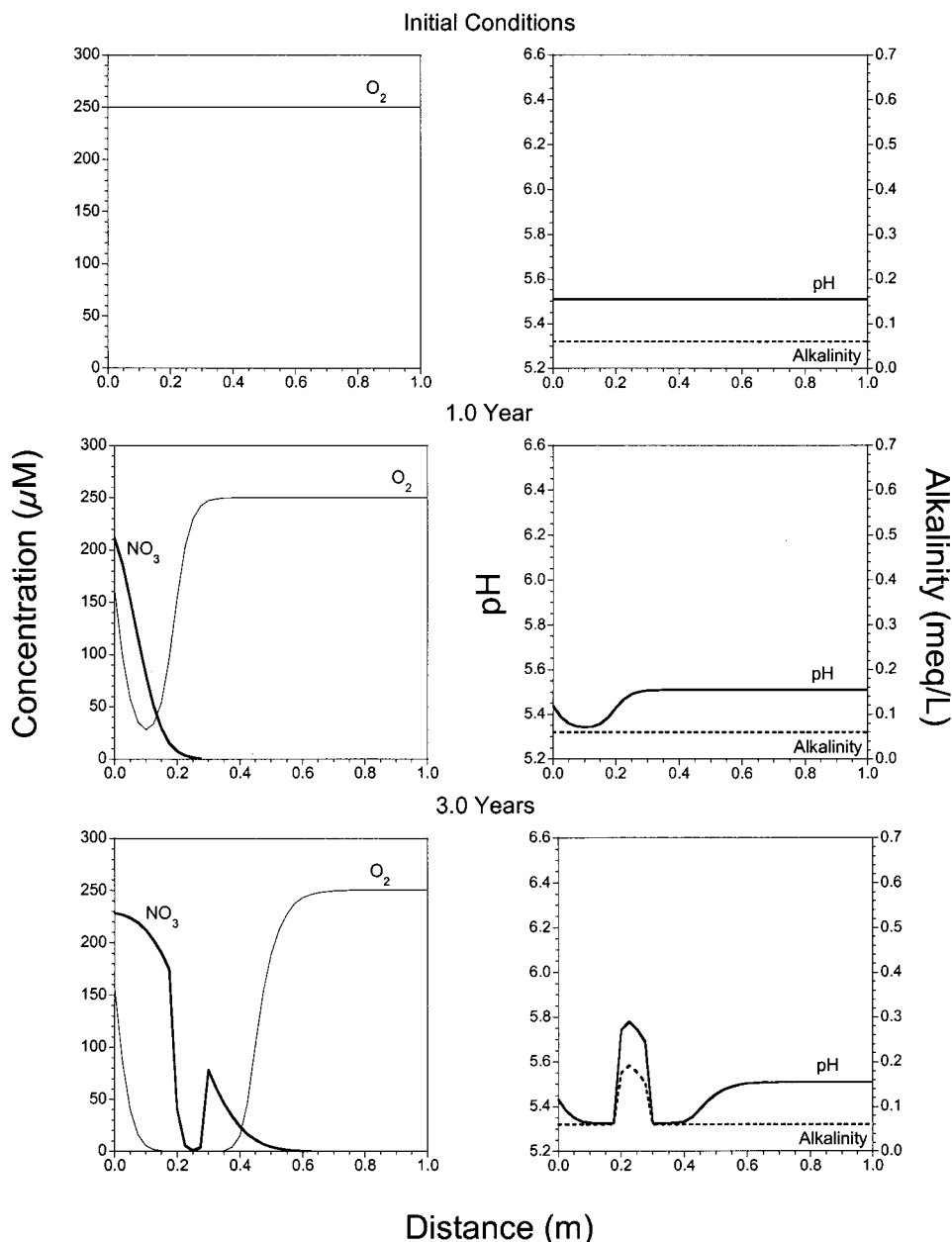


Figure 3a. Concentration profiles for the one-dimensional test simulation showing the initial conditions and results for 1.0 and 3.0 years.

If it is allowed to be reversible, $\text{MnO}_2(s)$ could precipitate from a combination of Mn^{2+} , CO_3^{2-} , and H_2O . This could occur if some dissolved manganese is transported downgradient to a location where no or very little manganese reduction has occurred. In this case, the total analytical concentration of manganese would be greater than the initial condition because the precipitated phase would still be at the initial concentration. Under geochemical conditions in which manganese reduction is not favored, the thermodynamic calculation would force the total precipitated concentration of manganese to equal the total analytical concentration of manganese via (23) and (17). Reaction (23) would also produce DOC. Clearly, this would be incorrect, since organic carbon is not intended to be produced by any reaction under consideration. Thus it is necessary to ensure that COMPTAN does not allow the amount

of redox-sensitive reactants to increase due to chemical reactions. This is accomplished by preventing the concentration of the redox reactant from increasing from one time step to the next due to chemical reactions (see flowchart in Figure 2). Conceptually, this is particularly important for precipitated species because chemical reactions are the only way that it is possible for the amount of a solid to increase in the system under consideration (i.e., solids are immobile).

4. Conclusions

Incorporating the compartmentalized approach of *Abrams et al.* [1998] into a solute transport framework (COMPTAN) facilitates the simulation of the development of redox zones under thermodynamic and kinetic constraints. Lower-energy

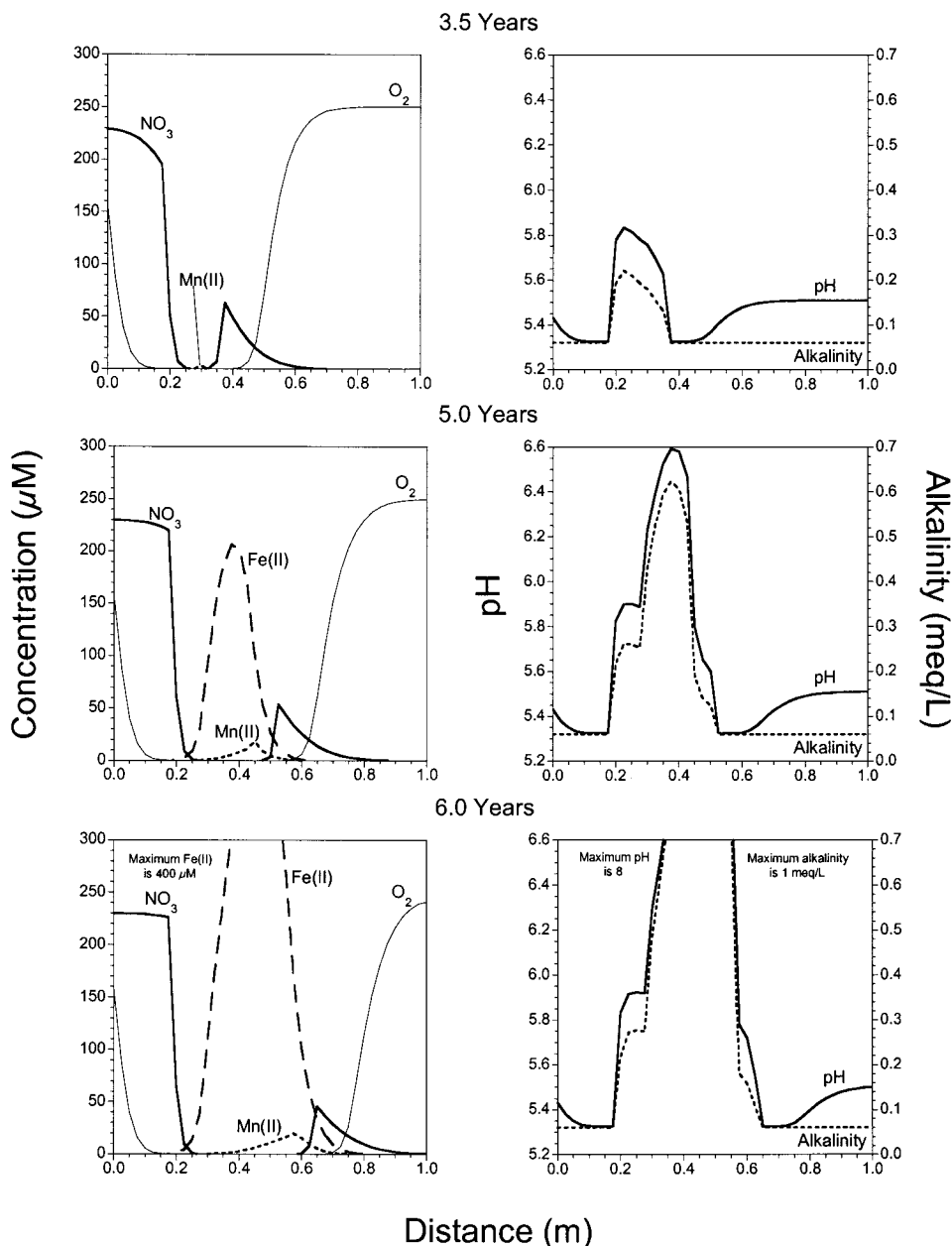


Figure 3b. Same as Figure 3a, except showing results for 3.5, 5.0, and 6.0 years.

redox reactions can be either thermodynamically or kinetically limited, depending on local geochemical conditions. The number of solute transport equations needed to simulate a particular system can be reduced due to the fact that the reaction networks are decoupled. The solute transport portions of the

Table 4. Rate Parameters for the One-Dimensional Simulation Used to Test COMPTRAN

	k (mole L ⁻¹ d ⁻¹)	k_c (mole L ⁻¹)	k_s (mole L ⁻¹)
Oxygen reduction	1.26×10^{-6}	5.01×10^{-5}	1.00×10^{-5}
Denitrification	1.26×10^{-6}	2.51×10^{-5}	1.00×10^{-5}
Manganese reduction	4.47×10^{-7}	3.98×10^{-7}	1.00×10^{-5}
Iron reduction	7.94×10^{-7}	6.31×10^{-5}	1.00×10^{-5}

See equation (15) for definitions and kinetic expression.

model are treated in a process-based manner by explicitly considering advection and dispersion.

The compartmentalized approach facilitates the use of a fixed component set by using reaction networks that do not contain insignificant reactions (i.e., basis-switching techniques are not needed to improve numerical stability). A fixed component set makes it possible to greatly reduce the number of solute transport equations by making the total analytical concentration of the components (i.e., the tenads) the dependent variables, rather than the individual chemical species. The concentrations of the equilibrium species can then be calculated outside of the solute transport simulator, since they are simply functions of the component set.

When a kinetic framework is imposed on the compartmentalized approach, the development of redox zones can be simulated as a function of time while still being constrained by

thermodynamics. Empirical reaction inhibition is not required for redox reactions that compete for available organic carbon. Any kinetic formulation to constrain reaction progress can be used, while still using thermodynamics to prevent reactions from occurring under infeasible conditions.

Since COMPTRAN employs the sequential iteration approach to simulate solute transport, the number of transport equations needed can be greatly reduced. Furthermore, a wide variety of currently available solute transport and geochemical codes can be used within COMPTRAN because most of these codes use the total (analytical or dissolved) concentration of components as the primary known quantities. When the compartmentalized approach is implemented with the total analytical concentration as the primary dependent variable, it is possible to reduce the number of transport equations required to simulate solute transport coupled with geochemical reactions even further. This can be done because reaction networks for widely different geochemical conditions can be effectively decoupled.

The ability of COMPTRAN to apply either a kinetically limited or thermodynamically limited solution is a distinct advantage over other currently available reactive transport codes. No currently available model that we are aware of is capable of simulating multiple, competitive kinetic reactions that are subject to thermodynamic constraints. Other models that use thermodynamics calculate the competition between redox reactions on the basis of equilibrium relationships only. The question that is not asked with these codes is if the lower-energy reaction (i.e., the loser in the thermodynamic competition) is rate-limited. COMPTRAN allows for this flexibility. The procedure used in the compartmentalized approach can easily check that the progress of kinetic reactions does not violate thermodynamic constraints.

In the companion paper [Abrams and Loague, this issue], COMPTRAN is applied to simulate the field-scale development of redox zones using boundary-value problems based on the U.S. Geological Survey's Cape Cod research site.

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