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Modeling of biologically mediated redox processes in the subsurface

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Abstract

To model bacterially catalyzed redox processes a multicomponent transport reaction model is presented. The transport part of the model solves the transient convection dispersion differential equations. The pure chemical submodel is conceptually similar to conventional thermodynamic equilibrium models. The kinetic submodel describes the heterotrophic metabolisms of several groups of microorganisms. To model a complete redox sequence (aerobic carbonaceous oxidation, denitrification, Fe(III)-reduction, Mn(IV)-reduction, and sulfate reduction) four functional bacterial groups are defined. Their growth and metabolisms are formulated in terms of Monod equations. As in other biofilm models, diffusion-limited exchange between the different phases (mobile pore water, biophase, and aquifer material) is also considered in this approach. The submodels are coupled by the equations of the microbially mediated redox reactions. This numerical technique permits direct mechanistic modeling of the influence of microbially catalyzed redox reactions on the chemical milieu of an aquifer. A two-step method is applied to solve the coupled transport and biochemical reaction equations. The numerical model was applied to field data of a natural subsurface flow path.

1. Introduction

Seventy per cent of the drinking water supply in Germany is provided by groundwater. Generally, groundwater has been considered a pristine source, but recent evidence indicates that many sites are contaminated, especially in urban and industrial areas. Because of the long groundwater residence time, there is a delay in the appearance of man-made pollution. The dominating factors are nitrate and fertilizer input by intensive agriculture, mineral oil accidents and leaks, and the

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extensive use of volatile chlorinated hydrocarbons. Monitoring to determine the location, extent, and source of contamination of groundwater is also much more difficult and expensive than the analysis of surface waters (McCarty et al., 1981). Hence, this has led to a demand on transport models for the integral assessment of local measurements to identify pollution risk and to predict the effect of biochemical remediation.

Redox reactions play an important role in environmental processes. A mechanistic description of natural aquatic systems must include parameters that characterize the influence of electrons on the environment (Stumm and Morgan, 1981). In a similar way to acids and bases being discussed as proton donors and proton acceptors, reductans and oxidants are defined as electron donors and electron acceptors. Because there are no free electrons, every oxidation is directly accompanied by a reduction and vice versa. Each redox reaction is composed by an oxidation and reduction half step. For a detailed introduction to redox reactions, see Stumm and Morgan (1981). Redox reactions determine the concentrations of aqueous forms of biologically important elements such as carbon, nitrogen, and sulfur (Table 1).

In a closed aqueous system containing organic material the oxidation of organic matter is paralleled by a sequence of reduction reactions (Table 1). Fig. 1 shows the 'Island Hengsen', which is part of the water supply system of the city of Dortmund (Germany). The percolation zone (Transect I) was intensively studied in the main research program of the German Research Foundation (DFG): 'Pollutants in Groundwater'. The water flows from the storage reservoir to the river via a subsurface flow path. The redox state of the aquifer is mainly influenced by microbially mediated redox reactions. In the subsurface flow path the following sequence of processes can be observed: aerobic respiration, denitrification, Mn(IV)-, Fe(III)-reduction, and sulfate reduction. Further observations of such complete redox sequences in groundwater area are described by Golwer et al. (1976), Edmunds et al. (1984), Lee (1985), Leuchs (1988), Lee and Strickland (1988). The identification of relevant governing redox processes is important, because

Table 1
Sequence of microbially mediated redox processes

Aerobic respiration
$CH_2O + O_{2(g)} \Rightarrow CO_{2(g)} + H_2O$

Denitrification
$CH_2O + \frac{4}{5}NO_3^- + \frac{4}{5}H^+ \Rightarrow CO_{2(g)} + \frac{2}{5}N_{2(g)} + \frac{7}{5}H_2O$

Mn(IV)-reduction
$CH_2O + 2\,MnO_{2(s)} \Rightarrow 2\,Mn^{2+} + 3\,H_2O + CO_{2(g)}$

Fe(III)-reduction
$CH_2O + 8\,H^+ + 4\,Fe(OH)_{3(s)} \Rightarrow 4\,Fe^{2+} + 11\,H_2O + CO_{2(g)}$

Sulfate-reduction
$CH_2O + \frac{1}{2}SO_4^{2-} + \frac{1}{2}H^+ \Rightarrow CO_{2(g)} + \frac{1}{2}HS^- + H_2O$

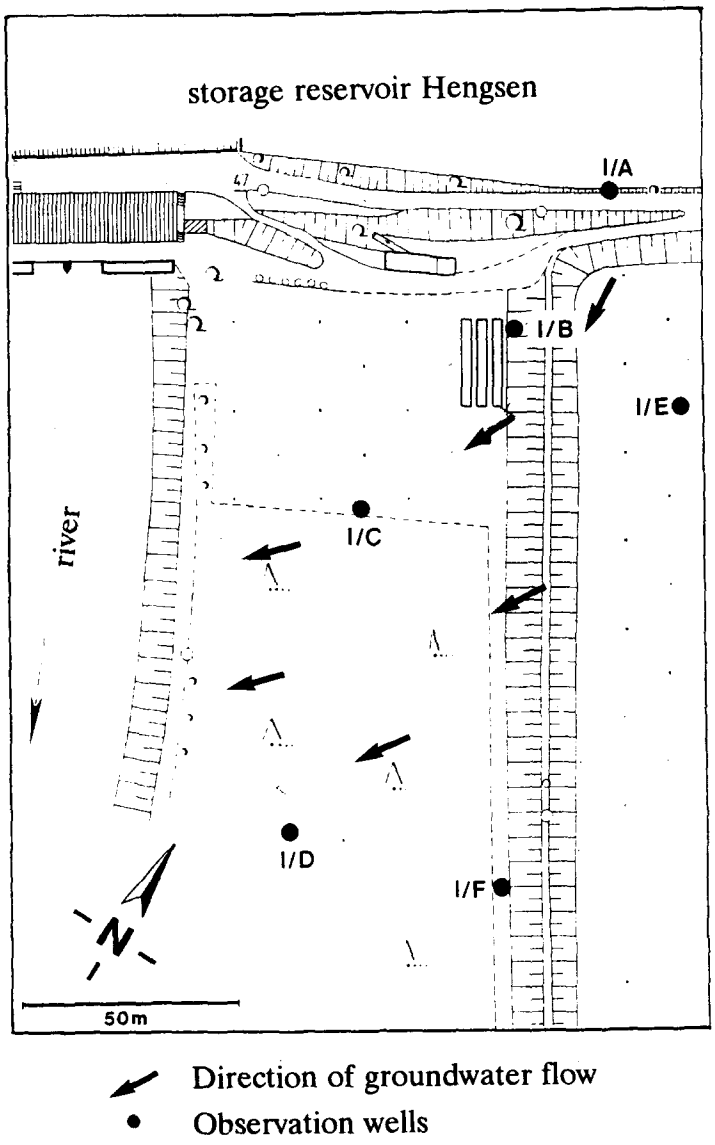

Fig. 1. Infiltration area.

the environmental compatibility and toxicity of organic contaminants and some heavy metals are determined by the redox state of the aquatic system (e.g. McCarty et al., 1981; Bouwer and McCarty, 1983a,b; Liu and Narasimhan, 1989).

In recent years different computer models have been developed for the simulation of transport processes of several interacting chemical species, which are involved in geochemical reaction processes. Liu and Narasimhan (1989) have grouped the existing different approaches to the modeling of the redox reactions into four classes. The

effective internal approach (Parkhurst et al., 1980), the external approach and the oxygen fugacity approach (Wolery, 1983) are all based on the assumption of thermodynamic equilibrium in the aquatic system. Redox potential (Eh) measurements reflect mixed potential measurements with little thermodynamic significance and also groundwater is mostly characterized by stable disequilibrium (Berner, 1981; Lindberg and Runnels, 1984). Many of the species which are involved in important groundwater oxidation–reduction reactions (e.g. SO_4^{2-}, NO_3^-, N_2, NH_4^+, HCO_3^-, CH_4) do not react with the platinum or gold electrodes used to measure Eh (Berner, 1981; Sigg and Stumm, 1989). The measured electrode potential generally does not agree with the value of Eh calculated from thermodynamic data and independent measurements (Berner, 1981). Therefore, several authors use the measurement of dissolved gases (e.g. O_2, H_2S, CH_4, H_2) for the characterization of the redox state of natural waters (Berner, 1981; Stumm, 1984). The fourth concept, called the redox couple approach, separates the redox couple (e.g. Fe^{3+}/Fe^{2+}) into two master species with independent mass balance equations. After the complete calculation of chemical speciation, the resulting specific redox potential is computed (Liu and Narasimhan, 1989). This technique is also unsuitable for modeling redox reactions, because the different redox couples in groundwater differ widely (Lindberg and Runnels, 1984) and so the transfer of the computed value to the other redox couples must be negated. Thus, these conventional thermodynamic equilibrium models are unsuitable to simulate slow, bacterially mediated changes of the redox state of an aquifer in a mechanistic way. The flow velocity of groundwater does not allow the assumption of equilibrium for the relevant redox reactions, unlike acid-based reactions.

The complexity of natural groundwater systems has prevented the identification of relevant processes and the development of kinetic approaches to model redox reactions (Liu and Narasimhan, 1989). Kinetic approaches depend on the availability of kinetic data for the redox reactions. Stumm and Morgan (1981) pointed out that most redox processes encountered in natural aquatic systems need biological mediation. In the flow path described, the observed, slow redox reactions are always catalyzed by several microorganisms. The chemical reactions are paralleled by an ecological sequence of microorganisms. The extent and velocity of these redox reactions are strictly correlated with growth and the metabolism of several microorganisms. The treatment of redox reactions as biological processes delivers the required data for kinetic approaches to model redox reactions in groundwater systems. The understanding and mathematical formulation of bacterially catalyzed redox reactions could be a further step in the development of 'deterministic multicomponent transport reaction models'.

2. Introduction to the simulation model

2.1. Transport

The transport part of the combined model (Fig. 2) solves the two-dimensional transient convection dispersion differential equation for each chemical component

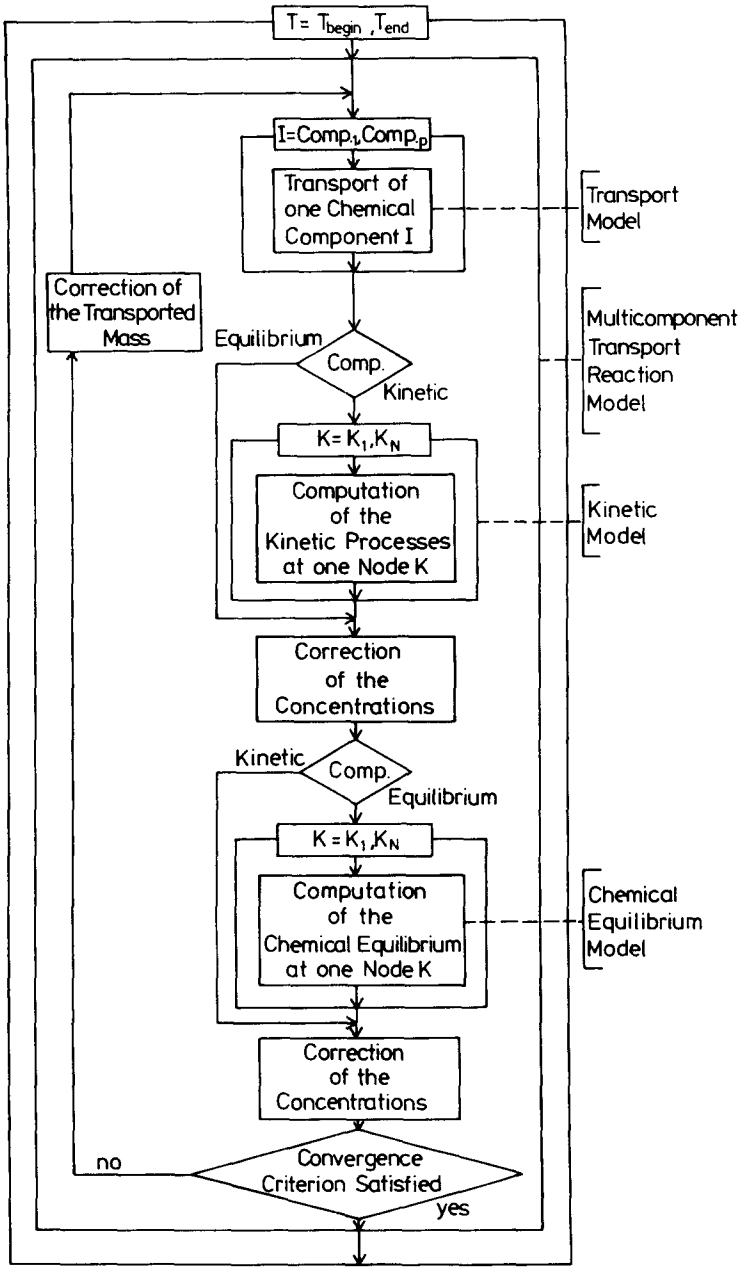

Fig. 2. Scheme of the multicomponent transport reaction model.

Table 2
Master species considered in both submodels

Master species of the chemical equilibrium submodel
Na^+, K^+, Mg^{2+}, Ca^+, Mn^{2+}, Fe^{3+}, Fe^{2+}, NH_4^+, H_2CO_3, HCO_3^-, CO_3^{2-}, H_2S, HS^-, S^{2-}, H^+, NO_3^-, SO_4^{2-}, Cl^-, H_4SiO_4, Al^{3+}
Master species of the kinetic submodel
$O_{2\,mob}$, $NO_{3\,mob}^-$, $SO_{4\,mob}^{2-}$, $CO_{2\,mob}$, H_2S_{mob}, Fe_{mob}^{2+}, Mn_{mob}^{2+}, $C_{org\,mob}$ (mobile species)
X1, X3, X4, X5, $O_{2\,im}$, $NO_{3\,im}^-$, $SO_{4\,im}^{2-}$, $Fe(OH)_{3\,im}$, $MnO_{4\,im}$, $CO_{2\,im}$, H_2S_{im}, Fe_{im}^{2+}, Mn_{im}^{2+}, $C_{org\,im}$ (immobile species)
$Fe(OH)_{3\,mat}$, $MnO_{4\,mat}$, $C_{org\,mat}$ (matrix species)

in two dimensions

$$\frac{\partial}{\partial t}(nc_{\mathrm{mob}}) + \frac{\partial}{\partial x_i} v_i c_{\mathrm{mob}} - \frac{\partial}{\partial x_i}\left(nD_{ij}\frac{\partial c_{\mathrm{mob}}}{\partial x_j}\right) - S_{c_{\mathrm{mob}}} = 0 \tag{1}$$

For the integration in space the finite-element method is applied. The integration in time is done by a weighted finite-difference method. The weighting factors are chosen according to the Leismann-scheme (Leismann and Frind, 1989), which results in a symmetric coefficient matrix. A comprehensive introduction to the transport part of the model is given by Vogt (1991).

2.2. Chemical equilibrium

The chemical equilibrium part of the model incorporates all reactions for which chemical equilibrium can be assumed. For the case study 'Transect I, Waterwork Hengsen' the master species considered are summarized in Table 2. Each primary variable requires an equation. The equations are constructed by mass balances, the charge balance for hydrogen and species equilibrium calculation. The formulations of all other chemical species are written in terms of the primary variables (Table 3). For each mineral phase an additional equation is implemented to solve the equation system in the equilibrium calculation. The mineral phases (Table 4) are automatically activated when their saturation index is reached and then the new chemical equilibrium is computed. The chemical equilibrium part of the combined model is conceptually similar to conventional equilibrium models. (For details see e.g. Ball et al., 1980; Liu and Narasimhan, 1989.) The equilibrium coefficients taken from WATEQ (Ball et al., 1980) undergo a temperature correction using the Van't Hoff differential equation. The formulation of the equilibrium equations results in a highly non-linear algebraic equation system, which is solved by a modified Newton Raphson procedure. The activity coefficients are calculated from the Davies equation in each iteration step. The chemical equilibrium calculations are carried out only for the mobile pore water.

Table 3
Chemical species considered in the chemical equilibrium submodel

$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$
$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+$
$Fe^{2+} + 3H_2O \rightleftharpoons Fe(OH)_3^- + 3H^+$
$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+$
$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$
$Fe^{3+} + 2Cl^- \rightleftharpoons FeCl_2^+$
$Fe^{3+} + 3Cl^- \rightleftharpoons FeCl_3^0$
$Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4$
$H_4SiO_4^0 \rightleftharpoons H_3SiO_4^- + H^+$
$H_4SiO_4^0 \rightleftharpoons 2H^- + H_2SiO_4^{2-}$
$Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4^0$
$Mg^{2+} + OH^- \rightleftharpoons MgOH$
$Na^+ + SO_3^{2-} \rightleftharpoons NaCO_3^-$
$Na^+ + HCO_3^- \rightleftharpoons NaHCO_3^0$
$Na^+ + SO_4^{2-} \rightleftharpoons NaSO_4^-$
$K^+ + SO_4^{2-} \rightleftharpoons KSO_4^-$
$Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3^0$
$Mg^{2+} + HCO_3^- \rightleftharpoons MgHCO_3^+$
$Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4^0$
$Ca^{2+} + OH^- \rightleftharpoons CaOH^+$
$Ca^{2+} + HCO_3^- \rightleftharpoons CaHCO_3^+$
$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$
$2Na^+ + CO_3^{2-} \rightleftharpoons Na_2CO_3$
$Al^{3+} + OH^- \rightleftharpoons AlOH^{2+}$
$Al^{3+} + 2OH^- \rightleftharpoons Al(OH)_2^+$
$Al^{3+} + 4OH^- \rightleftharpoons Al(OH)_4^-$
$Al^{3+} + SO_4^{2-} \rightleftharpoons AlSO_4^+$
$Al^{3+} + 2SO_4^{2-} \rightleftharpoons Al(SO_4)_2^-$
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$
$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+$
$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3^0 + 3H^+$
$Fe^{3+} + 4H_2O \rightleftharpoons Fe(OH)_4^- + 4H^+$
$Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2^0 + 2H^+$
$NH_4^+ + SO_4^{2-} \rightleftharpoons NH_4SO_4^-$
$H_2O \rightleftharpoons H^+ + OH^-$
$Mn^{2+} + Cl^- \rightleftharpoons MnCl^+$
$Mn^{2+} + 2Cl^- \rightleftharpoons MnCl_2^0$
$Mn^{2+} + 3Cl^- \rightleftharpoons MnCl_3^-$
$Mn^{2+} + H_2O \rightleftharpoons MnOH^+ + H^+$
$Mn^{2+} + 3H_2O \rightleftharpoons Mn(OH)_3^- + 3H^+$
$Fe^{3+} + 2SO_4^{2-} \rightleftharpoons Fe(SO_4)_2^-$
$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3^0 + 3H^+$

2.3. Bacterial growth

Heterotrophic activities of several bacterial groups dominate the chemical milieu of the subsurface flow path. Microbial growth is usually formulated in terms of Monod-type kinetics (e.g. Molz et al., 1986; Kindred and Celia, 1989). Besides pure microbial growth kinetics, the kinetics of substrate and nutrient transport from aqueous phase

Table 4
Mineral phases implemented in the chemical equilibrium submodel

$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3\,OH^-$
$FeOOH + 3\,H^+ \rightleftharpoons Fe^{3+} + 2\,H_2O$
$FeCO_3 \rightleftharpoons Fe^{2+} + CO_3^{2-}$
$MgCO_3 \rightleftharpoons Mg^{2+} + CO_3^{2-}$
$MgCa(CO_3)_2 \rightleftharpoons Mg^{2+} + Ca^{2+} + 2\,CO_3^{2-}$
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$
$MnSO_4 \rightleftharpoons Mn^{2+} + SO_4^{2-}$
$CaSO_4 \cdot 2\,H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2\,H_2O$
$FeS + H^+ \rightleftharpoons Fe^{2+} + HS^-$
$SiO_2 + 2\,H_2O \rightleftharpoons H_4SiO_4$
$MnCO_3 \rightleftharpoons Mn^{2+} + CO_3^{2-}$
$FeOOH + H_2O \rightleftharpoons Fe^{3+} + 3\,OH^-$
$Fe(OH)_3 + 3\,H^+ \rightleftharpoons Fe^{3+} + 3\,H_2O$
$MnS + H^+ \rightleftharpoons Mn^{2+} + HS^-$

to the microorganisms must also be considered (Bouwer and Cobb, 1987; Kinzelbach et al., 1991). Several field studies have suggested that a diffusion-limited exchange between the different phase of the aquatic system controls the microbial activity.

In recent years, an increasing number of mathematical models describing the concurrent growth of bacteria and transport of biodegradable substrates in aquifers has been developed, based on three different conceptual frameworks (Baveye and Valocchi, 1989). The first concept assumes that the aquifer material is covered uniformly by a biofilm in which consumption of substrate and electron acceptors takes place (Rittman et al., 1980; Bouwer and Cobb, 1987). The second framework considers that bacteria grow in small discrete microcolonies attached to the solid phases of the aquifer. The third group of models is characterized by the absence of any assumption concerning the distribution of the microorganisms at the pore scale. Based on the evaluation of the three model concepts mentioned (Baveye and Valocchi, 1989) and the work of Kinzelbach et al. (1991), the kinetic submodel is constructed as described below.

Metabolism and growth of the microorganisms are formulated in terms of Monod-type kinetics. Additionally, the water phase is divided into the mobile pore water and the stagnant biophase. Thus, besides the convection dispersion equation, a second differential equation for the immobile biophase is set up for all species which are considered in the kinetic model

$$\frac{\partial c_{\mathrm{im}}}{\partial t} = S_{c_{\mathrm{im}}} \tag{2}$$

The biophase is conceptualized as an operative means to easily include diffusion-limited exchange processes between the mobile pore water and bacteria (Kinzelbach et al., 1991). The microscopic definition of the distribution of the microorganisms in the pore space is not necessary for the macroscopic description of their growth and metabolism (Baveye and Valocchi, 1989). The exchange between mobile pore water and immobile biophase is assumed to be governed by a first-order expression with a

constant interphase transfer coefficient, which is the same for all species

$$S_{c_{\mathrm{mob}}} = -\alpha(c_{\mathrm{mob}} - c_{\mathrm{im}}) \tag{3}$$

The microorganisms are considered in the model only in the immobile biophase. Attached bacteria have an advantage over suspended bacteria and dominate the heterotrophic degradation of dissolved organic carbon (Bouwer and Cobb, 1987). Their uptake of substrate and electron acceptors takes place only via the immobile water phase. Though existing in real aquifers, mobile bacteria are not considered in the model. To guarantee the option of microbial growth in the model, a small number of bacteria is always conserved.

The microorganisms use only dissolved organic carbon (DOC) chemically defined as CH_2O and the utilizable portion of dead bacteria of 90% as their substrate. The interaction between the dissolved organic carbon in the mobile pore-water and the organic carbon absorbed to the aquifer matrix is formulated by a first-order expression. The complex redox sequence of Transect I requires the consideration of a variety of substrates, including organic compounds, molecular oxygen, nitrate, Fe(III), Mn(IV), and sulfate. In addition, since each mode of energy metabolism is associated with a different functional bacterial group, the growth of each group must be also considered in the model (Kindred and Celia, 1989). In the following equations describing the growth of several bacterial groups the index im (immobile) is ignored for convenience.

In aerobic parts of aquifers, the microbial population is dominated by heterotrophic bacteria which use dissolved organic carbon as energy and carbon source and molecular oxygen as electron acceptor. Further heterotrophic metabolisms using other electron acceptors are suppressed by the presence of oxygen. Some aerobic bacteria are capable of nitrate-reducing metabolism. The necessary enzymes are not maintained and are induced by low oxygen concentrations (Gottschalk, 1986; Bouwer and Cobb, 1987). Thus, in the model the bacterial group X1 uses, under aerobic conditions (aer), molecular oxygen and, under anaerobic conditions (den), nitrate as electron acceptor

$$\left[\frac{\partial \mathrm{X1}}{\partial t}\right]_{\mathrm{aer}} = v_{\mathrm{max_{X1}}}^{\mathrm{aer}}[1 - F(\mathrm{O_2})]\ \frac{[\mathrm{C_{org}}]}{K_{\mathrm{C_{org}}} + [\mathrm{C_{org}}]}\ \frac{[\mathrm{O_2}]}{K_{\mathrm{O_2}} + [\mathrm{O_2}]}\ \mathrm{X1}$$

$$\left[\frac{\partial \mathrm{X1}}{\partial t}\right]_{\mathrm{den}} = v_{\mathrm{max_{X1}}}^{\mathrm{den}} F(\mathrm{O_2})\ \frac{[\mathrm{C_{org}}]}{K_{\mathrm{C_{org}}} + [\mathrm{C_{org}}]}\ \frac{[\mathrm{NO_3}]}{K_{\mathrm{NO_3}} + [\mathrm{NO_3}]}\ \mathrm{X1}$$

$$\left[\frac{\partial \mathrm{X1}}{\partial t}\right]_{\mathrm{dec}} = v_{\mathrm{dec_{X1}}}\ \mathrm{X1}$$

$$S_{\mathrm{X1}} = \left[\frac{\partial \mathrm{X1}}{\partial t}\right]_{\mathrm{aer}} + \left[\frac{\partial \mathrm{X1}}{\partial t}\right]_{\mathrm{den}} - \left[\frac{\partial \mathrm{X1}}{\partial t}\right]_{\mathrm{dec_{X1}}} \tag{4}$$

The switching between aerobic and denitrifying growth conditions is based on the assumption of a non-competitive inhibition and is realized by a weighting function $F(O_2)$ dependent on the oxygen concentration, which was developed and tested by Kinzelbach et al. (1991). In fact, most heterotrophic denitrifiers known are optionally anaerobic (Deutscher Verband für Wasserwirtschaft und Kulturbau (DVWK), 1988). It is also assumed that the functional bacterial group X1 reduces nitrate quantitatively to N_2 under anaerobic conditions.

Anaerobic fermentative conditions are also encountered in subsurface environments. After the depletion of oxygen and nitrate in the immobile water phase, degradation of complex organic compounds is accomplished by consortia of symbiotic microorganisms (Beeftink and Staugaard, 1986; Dubourgier et al., 1988). The consortia of fermentative bacteria, obligate H_2-producing acetogens and H_2-consuming bacteria are attached mostly to the aquifer surface. Methanogenesis and sulfate reduction can occur simultaneously, if high concentrations of organic carbon are available. Sulfate-reducing bacteria have a higher affinity for hydrogen and acetate than methanogenic bacteria. At low DOC concentrations, sulfate-reducing bacteria outcompete methanogens and dominate the final degradation step within the consortia described. Thus, the bacterial group X3 oxidizes DOC and reduces sulfate in the model

$$S_{X3} = \frac{\partial X3}{\partial t} = v_{max_{X3}} \frac{[C_{org}]}{K^{X3}_{C_{org}} + [C_{org}]} \frac{[SO_4]}{K_{SO_4} + [SO_4]} X3 - v_{dec_{X3}} X3 \tag{5}$$

The complex degradation process of organic carbon to CO_2 is modeled as a single-step process. For highly contaminated areas, acidogens can produce measurable concentrations of volatile fatty acids. In this case the reaction rates of the several bacterial groups within the consortia differ and further bacterial groups must be defined in the model.

The saturation indices of iron hydroxides are very low and so iron concentrations are surely not sufficient for growth and metabolism of Fe(III)-reducing bacteria. Free Mn(IV) is unstable under conditions of natural aquifers. Fe(III)- and Mn(IV)-reducers receive their electron acceptors by exoenzymes (Schlegel, 1985; DVWK, 1988). These active processes are quite complex and are not completely understood. Therefore, a concentration-dependent exchange for $Fe(OH)_3$ and MnO_4 is assumed between the immobile biophase and the aquifer material formulated by a first-order expression, here shown for $Fe(OH)_3$

$$\frac{\partial [Fe(OH)_3]_s}{\partial t} = -\gamma \{k\ [Fe(OH)_3]_s - [Fe(OH)_3]_{im}\} \tag{6}$$

The bacterial group X4 reduces MnO_2; its growth is formulated by the following function

$$S_{X4} = \frac{\partial X4}{\partial t} = v_{max_{X4}} \frac{[C_{org}]}{K^{X4}_{C_{org}} + [C_{org}]} \frac{[MnO_2]}{K_{MnO_2} + [MnO_2]} X4 - v_{dec_{X4}} X4 \tag{7}$$

The bacterial group X5 uses $Fe(OH)_3$ as electron acceptor for the oxidation of dissolved organic carbon in the model

$$S_{X5} = \frac{\partial X5}{\partial t} = v_{max_{X5}} \frac{[C_{org}]}{K^{X5}_{C_{org}} + [C_{org}]} \frac{[Fe(OH)_3]}{K_{Fe(OH)_3} + [Fe(OH)_3]} X5 - v_{dec_{X5}} X5 \quad (8)$$

The non-competitive inhibition of the bacterial groups X3, X4, and X5 by oxygen and nitrate is carried out with terms employed by Kindred and Celia (1989).

For the application of biodegradation models, a central problem is the appointment of the specific microbiological data. Yield coefficients and maximum growth rates for the bacterial group X1 are fixed in accordance with Kinzelbach et al. (1991). The maximum potential energy yield of microorganisms is related to the free energy released by the redox species used for growth and metabolism (Stumm and Morgan, 1981). Thus, the required data for the bacterial groups X3, X4, and X5 are linearly extrapolated to the different energy yields of the several redox reactions (Table 1) starting from the values of bacterial group X1.

For the modeling of the complete redox reactions, the microbial decomposition products of the four bacterial groups defined are taken into account. The functions required are given by the equations of the microbially mediated redox reactions (Table 1). The master species considered are summarized in Table 2. The mathematical formulation of the kinetic reactions leads to a system of ordinary differential equations, which is solved by a Newton Raphson procedure. In addition, the computed concentration corrections of the chemically reacting species are considered in the chemical equilibrium calculation. Therewith, both submodels are coupled through the equations describing the biologically catalyzed exergonic redox reactions. This numerical technique permits direct mechanistic modeling of the influence of the heterotrophic activities on the chemical milieu of the aquifer.

Two solution strategies exist for the combined model (Miller and Benson, 1983). In the one-step method, the partial differential equations for transport and biochemical reaction equations are solved simultaneously (e.g. Rubin and James, 1973; Willis and Rubin, 1987). The one-step method is generally more complicated to formulate than the two-step procedure and model variations can be inserted only under difficulties. The two-step method decouples the biochemical reaction equations from the transport equation. Both parts are solved sequentially, with or without iterations in between (e.g. Grove and Wood, 1979; Reardon, 1981; Narasimhan et al., 1986; Liu and Narasimhan, 1989; Kinzelbach et al., 1991). In the present multicomponent transport-reaction model, the two-step procedure is applied to solve the transport equations and the biochemical reaction equations of both submodels. This procedure eases the implementation of new model developments. Additionally, the two-step method generally reduces time and memory storage requirements (Liu and Narasimhan, 1989) and makes the model applicable for realistic large-scale field simulations (Vogt, 1991).

3. Application

The simulations presented must be regarded as a first attempt to model the complex coupled transport and microbially mediated chemical processes within the subsurface flow path. Therefore, the main interest was to simulate the pattern of concentration changes during percolation. In future, the model will be expanded to simulate the transport in more detail. Hence the flow field was reduced to one dimension. The subsurface flow path (Fig. 1) is about 100 m long, starts at storage reservoir Hengsen and intersects observation wells I/B at 35 m and I/C at 90 m. A steady-state flow field was assumed according to a measured mean flow regime.

A transient transport computation was performed. The concentrations of the chemical equilibrium situation of the storage reservoir are chosen as Dirichlet-type boundary conditions (Table 5). The same concentrations were assumed on the whole flow path as initial conditions. Additionally, the four bacterial groups started with a uniform distribution at low concentration. The hydroxides MnO_2 and $Fe(OH)_3$ are considered only in the aerobic and postoxidic zone up to 65 m. After a simulation time of about 100 days, the function bacterial groups reached a steady state. The following figures show the numerical results for the steady-state situation at 250 days simulation time (in which dashed lines represent numerical results and asterisks represent measurements).

The simulated concentrations of the electron acceptors agree well with the measured concentrations, especially for oxygen, nitrate, and sulfate (Fig. 3). Iron and manganese show only the expected distribution pattern. Their exact concentrations

Table 5
Mean values of measurements and boundary conditions

	Units	Mean values of measurements	Boundary condition
O_2	($mg\,l^{-1}$)	10.3	10.0
NO_3^-	($mg\,l^{-1}$)	16.0	16.0
SO_4^{2-}	($mg\,l^{-1}$)	44.9	44.9
DOC	($mg\,l^{-1}$)	3.55	3.55
Ca^{2+}	($mg\,l^{-1}$)	47.1	46.8
Mg^{2+}	($mg\,l^{-1}$)	5.7	5.7
Na^+	($mg\,l^{-1}$)	19.0	18.2
K^+	($mg\,l^{-1}$)	3.1	3.1
HCO_3^-	($mg\,l^{-1}$)	102.6[a]	101.2
pH		7.67	7.62
Mn^{2+}	($ng\,l^{-1}$)	52.1[a]	52.0
Fe^{2+}	($ng\,l^{-1}$)	162.4[a]	162.4
Cl^-	($mg\,l^{-1}$)	29.0	34.4
SiO_2	($mg\,l^{-1}$)	5.1	5.0
Al^{3+}_{Tot}	($\mu g\,l^{-1}$)	n.m.	10.0
H_2S	($ng\,l^{-1}$)	n.m.	0.01

[a] Computed.
n.m., not measured.

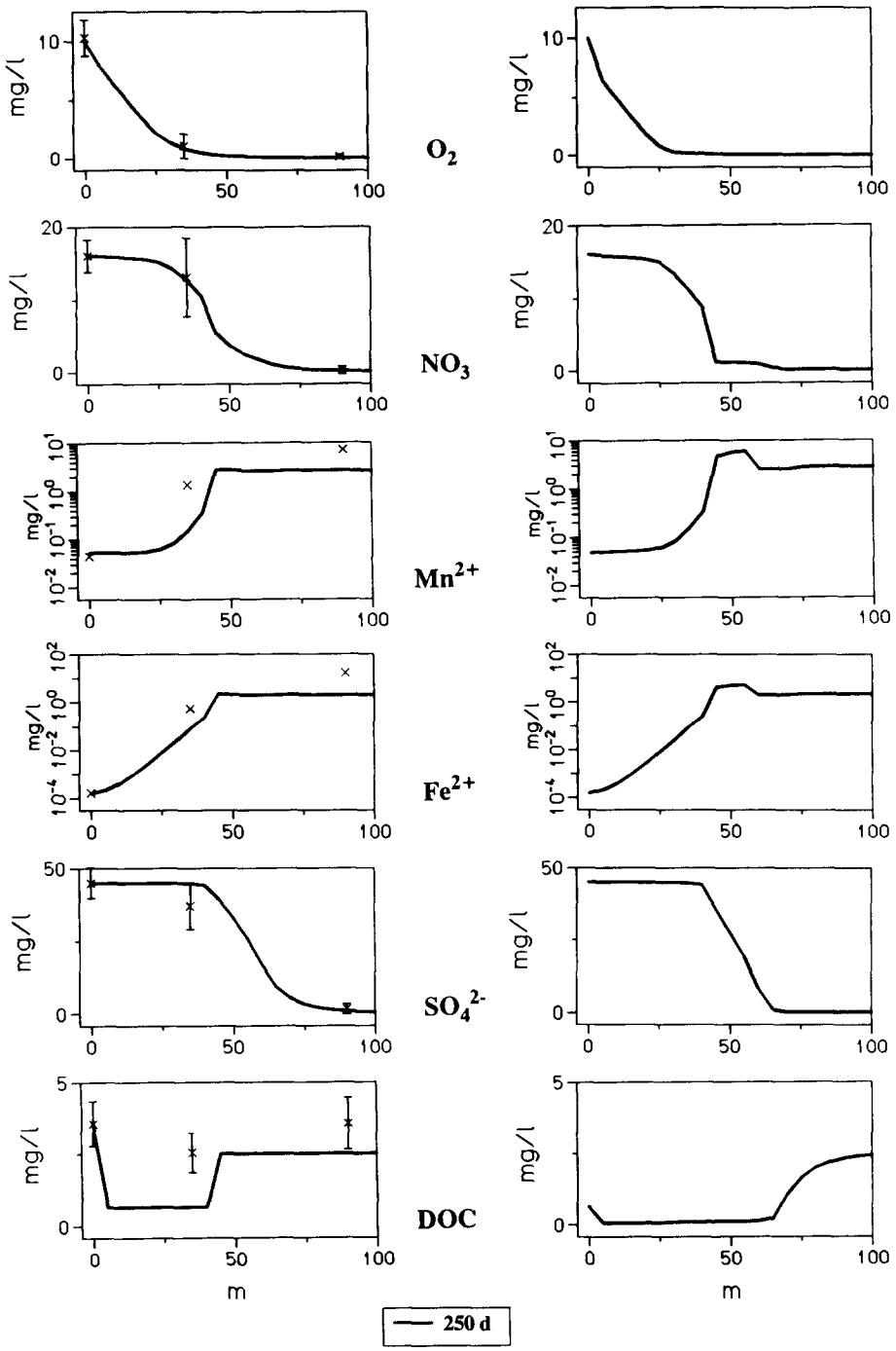

Fig. 3. Concentrations of O_2, NO_3^-, Mn^{2+}, Fe^{2+}, and DOC (left, mobile pore water; right, immobile biophase).

could not be simulated with this simplified model approach. The groundwater can be oversaturated with respect to several minerals for a long time. Additionally, suspended solids having dimensions of less than 0.45 μm could be interpreted as dissolved species.

A comparison of the simulated concentrations in the mobile pore water and the immobile biophase (Fig. 3) shows that the DOC supply is the limiting factor for the growth of the microorganisms in the model. The low DOC concentrations in the biophase result from microbial consumption and diffusion-limited supply from outside. In natural, uncontaminated aquifers, the rate of biodegradation is usually limited by the availability of organic carbon (Kindred and Celia 1989). Kinzelbach et al. (1991) found that in the natural aquifer case they modeled the release of organic carbon from the matrix controls the activities of the bacteria. In the subsurface flow path presented the diffusive exchange between mobile pore water and biophase limit the bacterial growth in the model. The high and homogeneous DOC concentrations in the mobile pore water suggest that desorption or DOC release from the aquifer material is fast in this case. Further studies of redox sequences in aquifers should include differential analysis of fate, degradation rate and composition of the several organic carbon fractions. The excessive consumption of dissolved organic carbon released from the matrix can deplete the high reduction capacity of the subsurface flow path with time.

Fig. 4 shows the resulting steady-state distribution of the four bacterial groups defined. The first part of the subsurface flow path is dominated by bacterial group X1 (facultative denitrificans), followed by bacterial groups X4 and X5 (Mn(IV)- and Fe(III)-reducers). At the end of Transect I bacterial group X3 (consortia with sulfate-reducing bacteria) is the dominant microbial group. In accordance with field measurements and theoretical studies, the more energy-yielding mediated reactions take precedence over processes that have lower energy yields (Stumm and Morgan, 1981).

Figs. 5 and 6 demonstrate the impact of the heterotrophic activities on the chemical milieu of the aquifer. The activities of the microorganisms lead to

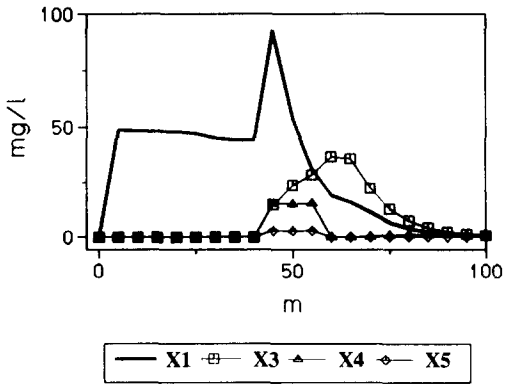

Fig. 4. Distribution of the bacterial groups in the steady state.

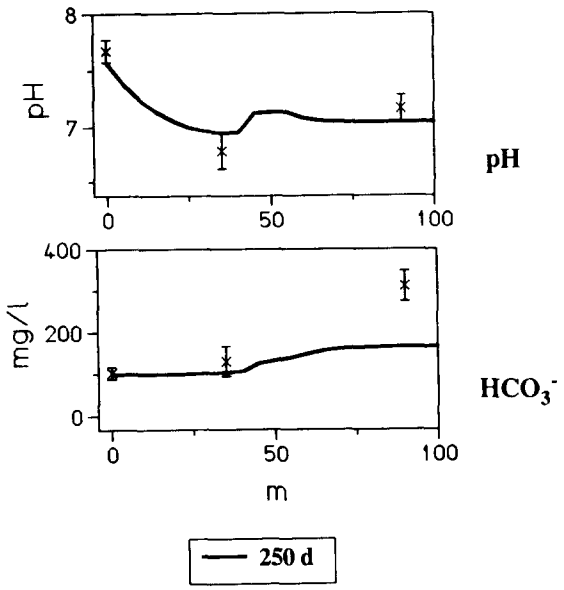

Fig. 5. pH and HCO_3^- concentration in the steady state.

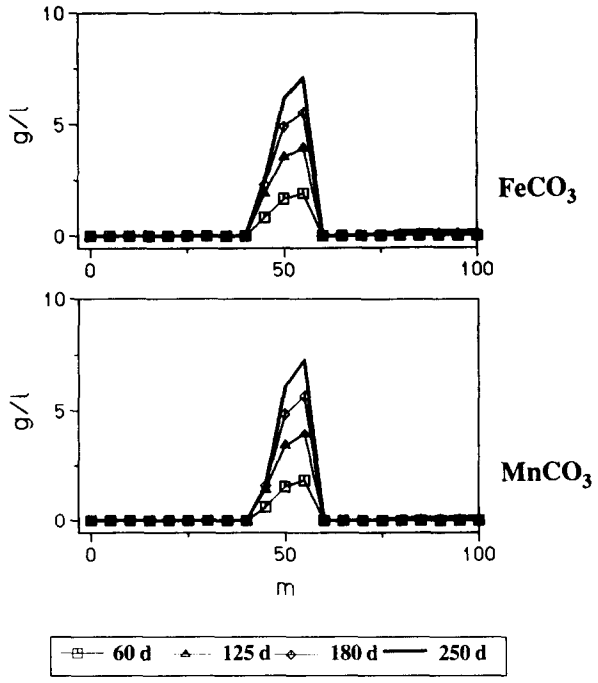

Fig. 6. Precipitation of siderite and rhodocrosite.

increasing HCO_3^- concentrations along the subsurface flow path. The pH value reflects the overall combination of all implemented reactions (Fig. 5) and shows the influence of the four defined bacterial groups. The pH value drops directly after the storage reservoir, because the heterotrophic oxygen reduction of bacterial group X1 is combined with CO_2 production. The Mn(IV)- and Fe(III)-reduction by bacterial groups X4 and X5 leads to an increasing pH. The pH decreases slightly with the activities of the consortia of microorganisms X4. This is due to the assumption that the bacteria reduce CH_2O and not fatty acids, which, if implemented, would lead to an increase in pH (Scott and Morgan, 1989). The calculated precipitation of the carbonates siderite and rhodocrosite in the middle of the subsurface flow path (Fig. 6) results in limited iron and manganese concentrations in the mobile water phase. Precipitation of these minerals was observed during the field measurements in this area.

4. Summary and outlook

The slow redox reactions of Transect I are modeled with a kinetic, microbially based concept. The two components of this approach are the Monod-type kinetics of microbial growth and the diffusion-limited transfer of substrate and electron acceptors between the different phases in the system. Thus, the kinetic submodel introduced is conceptually similar to conventional biophase models. Further, for the modeling of the complete redox sequence, the microorganisms are divided into four dominating functional bacterial groups. This model concept agrees with the requirements of Kindred and Celia (1989) for the modeling of complex redox sequences in groundwater. For the hydrochemical calculations, a conventional chemical equilibrium submodel is used.

The multicomponent transport reaction model introduced was applied to a natural subsurface flow path, a highly reactive surface water–groundwater system. The initial conditions for the numerical simulations were homogeneous aerobic conditions and a uniform low-level distribution of the four defined functional bacterial groups. Starting from this situation, the transient simulation leads to the observed pattern of the steady-state redox sequence.

The kinetic submodel and the chemical equilibrium submodel are coupled by the equations of the microbially catalyzed redox reactions. Contrary to conventional thermodynamic equilibrium models, this numerical technique permits the direct mechanistic modeling of the influence of the several microbial activities on the chemical milieu of the aquifer.

A promising field of further applications of the simulation model is in situ bioremediation, where redox sequences can become important. The complete computation of the microbially influenced parameters can lead to a better understanding of the processes activated and permit an evaluation of the simultaneous changes in the chemical milieu of the aquifer. Further, the simulation model allows the use of more, and easily measurable, quantities to control the realization of in situ remediation.

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7. Appendix: nomenclature

aer	aerobic
$c, [\,]$	concentration (M l^{-3})
dec	decay
den	denitrifying
$\mathbf{D}_{i,j}$	tensor of hydrodynamic dispersion ($l^2\ T^{-1}$)

im	immobile phase
k	adsorption coefficient ($\mathrm{l}^3\,\mathrm{M}^{-1}$)
K	half-velocity concentration ($\mathrm{M\,l}^{-3}$)
mat,s	matrix
mob	mobile phase
n	effective porosity
S	source–sink term ($\mathrm{M\,l}^{-3}\,T$)
t	time T
v_{dec}	decay rate ($\mathrm{l}\,T^{-1}$)
v_{i}	vector of average phase velocity ($\mathrm{l}\,T^{-1}$)
$v_{\max}$	maximum growth rate of bacteria ($\mathrm{l}\,T^{-1}$)
x, y	coordinates
X_i	concentration of bacteria ($\mathrm{M\,l}^{-3}$)
Y	yield coefficient

7.1. Greek letters

α, β, γ	exchange coefficients ($\mathrm{l}\,T^{-1}$)

7.2. Subscripts

i, j	indices: $i = 1, 2$; $j = 1, 2$