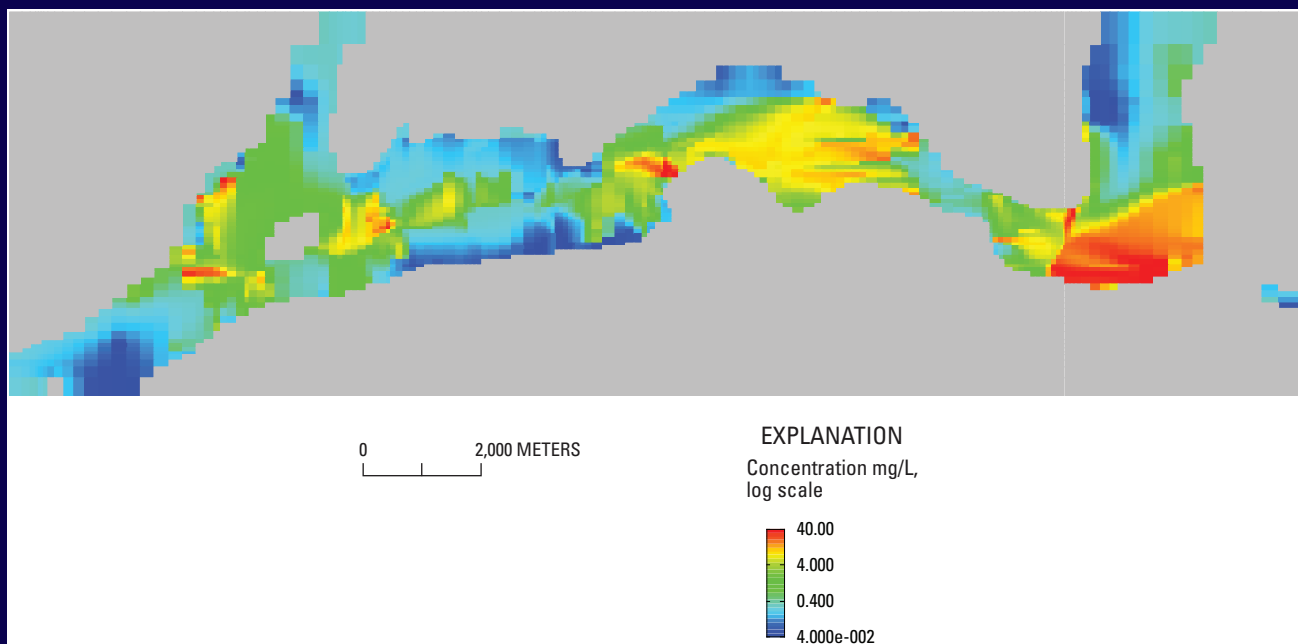


National Water-Quality Assessment Program

Hypothetical Modeling of Redox Conditions Within a Complex Ground-Water Flow Field in a Glacial Setting



Scientific Investigations Report 2008–5066

Hypothetical Modeling of Redox Conditions Within a Complex Ground-Water Flow Field in a Glacial Setting

By Daniel T. Feinstein and Mary Ann Thomas

Scientific Investigations Report 2008–5066

**U.S. Department of the Interior
U.S. Geological Survey**

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U.S. Geological Survey

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Cover. Map showing simulated concentration of dissolved Fe^{2+} for random organic carbon scenario, lower aquifer (layer 3).

Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). The NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991-2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>).

In the second decade of the Program (2001–2012), a major focus is on regional assessments of water-quality conditions and trends. These regional assessments are based on major river basins and principal aquifers, which encompass larger regions of the country than the Study Units. Regional assessments extend the findings in the Study Units by filling critical gaps in characterizing the quality of surface water and ground water, and by determining status and trends at sites that have been consistently monitored for more than a decade. In addition, the regional assessments continue to build an understanding of how natural features and human activities affect water quality. Many of the regional assessments employ modeling and other scientific tools, developed on the basis of data collected at individual sites, to help extend knowledge of water quality to unmonitored, yet comparable areas within the regions. The models thereby enhance the value of our existing data and our understanding of the hydrologic system. In addition, the models are useful in evaluating various resource-management scenarios and in predicting how our actions, such as reducing or managing nonpoint and point sources of contamination, land conversion, and altering flow and (or) pumping regimes, are likely to affect water conditions within a region.

Other activities planned during the second decade include continuing national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology; and continuing national topical studies on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on stream ecosystems, and transport of contaminants to public-supply wells.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Matthew C. Larsen
Associate Director for Water

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Conversion Factors and Abbreviations

Multiply	By	To obtain
Length		
meter (m)	3.281	foot (ft)
Flow rate		
cubic meter per second (m ³ /s)	22.82	million gallons per day (Mgal/d)
Hydraulic conductivity and dispersivity		
meter per day (m/d)	3.281	feet per day (ft/d)

Concentrations of chemical constituents are given in milligrams per liter (mg/L). Production and depletion rates of redox reactants are given in milligrams per liter per day (mg/L/d).

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Elevation, as used in this report, refers to distance above the vertical datum.

Hypothetical Modeling of Redox Conditions Within a Complex Ground-Water Flow Field in a Glacial Setting

By Daniel T. Feinstein and Mary Ann Thomas

Abstract

This report describes a modeling approach for studying how redox conditions evolve under the influence of a complex ground-water flow field. The distribution of redox conditions within a flow system is of interest because of the intrinsic susceptibility of an aquifer to redox-sensitive, naturally occurring contaminants—such as arsenic—as well as anthropogenic contaminants—such as chlorinated solvents. The MODFLOW-MT3D-RT3D suite of code was applied to a glacial valley-fill aquifer to demonstrate a method for testing the interaction of flow patterns, sources of reactive organic carbon, and availability of electron acceptors in controlling redox conditions. Modeling results show how three hypothetical distributions of organic carbon influence the development of redox conditions in a water-supply aquifer. The distribution of strongly reduced water depends on the balance between the rate of redox reactions and the capability of different parts of the flow system to transmit oxygenated water. The method can take account of changes in the flow system induced by pumping that result in a new distribution of reduced water.

Introduction

Redox conditions of ground water influence the mobilization and transport of chemical constituents such as arsenic (Welch and others, 2000), chlorinated solvents (Moran and others, 2007), and pesticides (Barbash, 2004). An increased understanding of the distribution of redox conditions within an aquifer would allow for a better assessment of its susceptibility to contamination by a wide range of natural and anthropogenic constituents.

The current study is an outgrowth of a USGS National Water-Quality Assessment (NAWQA) regional study of arsenic in the glacial aquifer system of the northern United States (Thomas, 2007). One of the major findings was that the highest arsenic concentrations were associated with reducing ground water. The crucial importance of the relation between the mobility of contaminants such as arsenic and the degree to which ground water is reduced invites a research effort aimed at combining principles of subsurface chemistry with

fine-scale simulations of ground-water flow fields in order to deepen what is known about the controls on redox conditions in aquifer systems.

The distribution of redox zones in the subsurface is a product of microbe-mediated reactions, and it is influenced by the interaction between the spatially varying ground-water flow field and the availability of electron donors and electron acceptors in the subsurface. Reducing conditions can be maintained only if the advection and diffusion of dissolved oxygen from the surface are less rapid than the consumption of oxygen by redox reactions (Smedley and Kinniburgh, 2002).

In this report, the evolution of redox is evaluated in a glacial valley-fill aquifer characterized by complex flow paths, pronounced heterogeneity, and streams that are both gaining and losing. The primary objective of this study is to show the importance of the ground-water flow field in determining the spread and distribution of reduced waters in a glacial valley-fill aquifer. Although the flow system used to test the methodology is real, the geochemical conditions and geochemical simulations are hypothetical. A methodology for modeling redox has been applied to three hypothetical distributions of organic carbon and the robustness of the methodology has been tested through a sensitivity analysis of one scenario. Availability of a pumping history within the flow system also enabled investigation of the possible effect of stresses on the redistribution of reduced water emanating from the hypothetical source areas.

Methods and Assumptions

The approach to the problem of simulating redox reactions in a field setting was to combine a heterogeneous, three-dimensional ground-water flow model—which incorporates a sophisticated geologic model of glacial deposition in bedrock valleys—with a relatively simple geochemical model for redox reactions. The MODFLOW-MT3D-RT3D suite of code (McDonald and Harbaugh, 1988; Zheng and Wang, 1998; Clement, 2001) was used for this purpose. Although the flow model was calibrated to real conditions, the geochemical inputs to the transport model were not derived from local data but instead are representative of water-quality data from the

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glacial aquifer system of the northern United States, collected as part of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey. The geometries of the organic-rich material horizons that function as electron donors for the modeled redox reactions are hypothetical.

Flow Model

The ground-water flow model adopted for this study is based on a three-facies interpretation of glacial deposition in the eastern United States (Randall, 2001). The conceptual model is applicable to bedrock valley deposits (also called valley-train deposits) that commonly contain sufficient coarse material from ice-contact and outwash deposits to support high-capacity public-supply wells. In Randall’s conceptual model, based on extensive field mapping across the northeastern United States, the ice-contact deposits form the bottom of the system and are separated from more recent outwash (and alluvial) deposits at the top of the system by generally fine-grained layers of lacustrine origin. However, the geometry of the three facies can be complex.

Randall incorporated the three-facies geologic model into a ground-water flow model of an important aquifer system in southern New York State associated with the Susquehanna River Valley (Randall, 1986); this original model was later upgraded by Wolcott and Coon (2001). A typical geologic section from the ground-water flow model shows the complicated geometry of the facies within the bedrock valley (fig. 1).

The aquifer system consists of an upper aquifer containing outwash and alluvial deposits (mostly sand and gravel) and a lower aquifer dominated by ice-contact deposits (also generally coarse grained), separated by confining lenses of silt and clay of lacustrine origin. The thickness of the confining layer is varied and is locally absent, putting the two aquifers locally in direct hydraulic connection. The system is characterized by a pronounced heterogeneity due to wide ranges in horizontal and vertical hydraulic conductivity. In the model, the median horizontal hydraulic conductivity of the upper aquifer in layer 1 is 40 m/d, with 95 percent of cells assigned values between 2 and 70 m/d. The median value for the lacustrine material in layer 2 is 0.002 m/d, with 95 percent of cells between 0.0002 and 0.5 m/d. The median value for the lower aquifer in layer

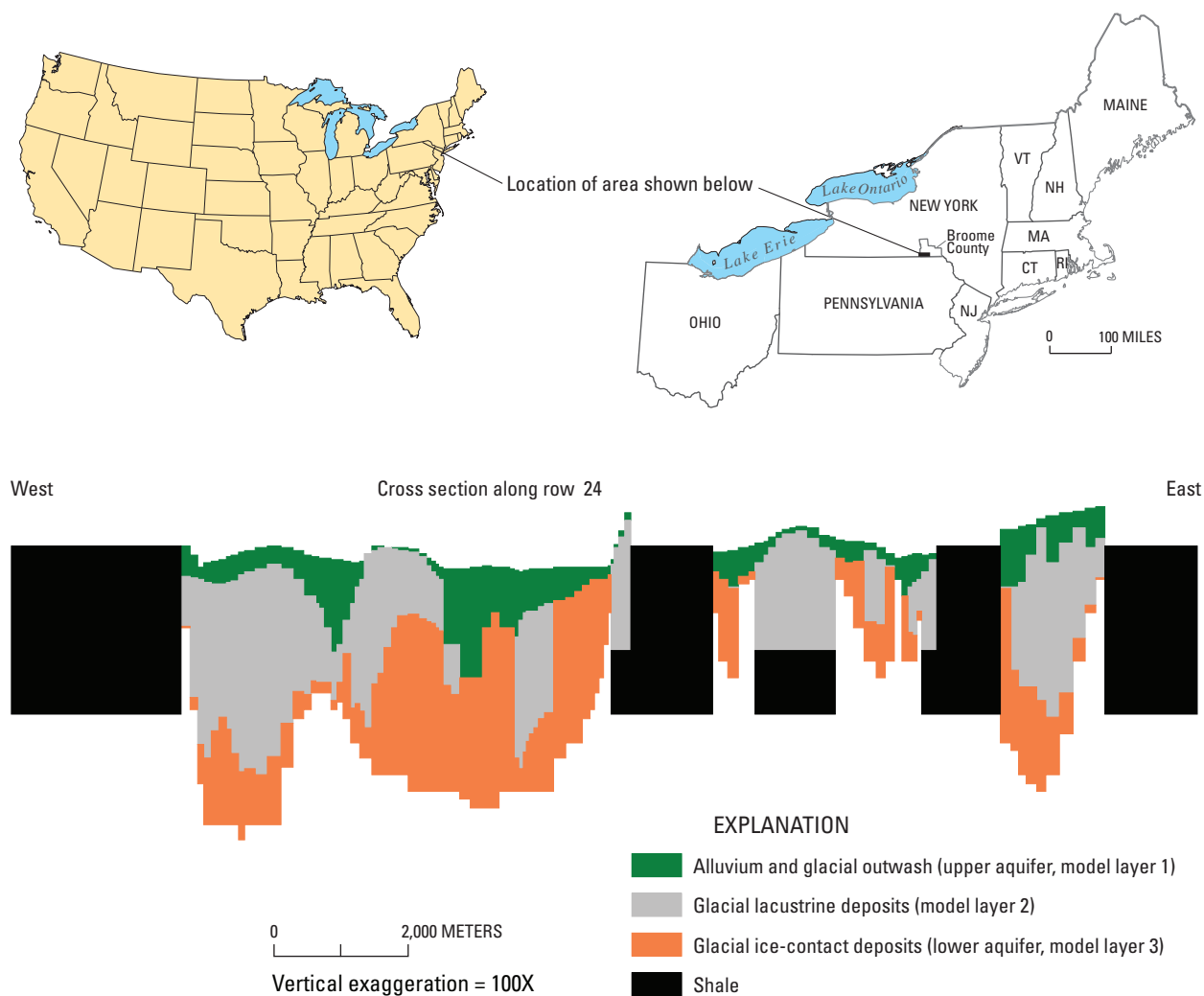


Figure 1. Diagrammatic geologic section of the Susquehanna River Valley, Broome County, N.Y. [Modified from Randall (1986) and Wolcott and Coon (2001)].

3 is 66 m/d, with 95 percent of cells between 4 and 400 m/d. The hydraulic conductivity pattern for the upper aquifer is particularly heterogeneous. Hydraulic conductivities for the aquifer layers were based on about 260 geologic logs, specific-capacity tests from about 80 large-capacity or test wells, and pumping-test results from 20 wells (Randall, 1986). Hydraulic conductivities for the lacustrine material were estimated from observed texture and literature values (Randall, 1986).

Ground water originates from three sources: recharge to the water table, lateral infiltration due to unchanneled runoff from the surrounding shale-covered uplands, and natural or induced infiltration along losing stretches of streams, including parts of the Susquehanna River.

Figure 2 shows the model grid and surface-water network in plan view. The model grid contains 61 rows and 157 columns for each layer, with nonuniform cell spacing. Average cell size is 100 m on a side. Recharge due to precipitation is added at the water table, whereas lateral infiltration is simulated by constant-flux boundaries. Rivers and streams are head-dependent boundaries. In some places, the surface water loses to the ground water. The contact between the unconsolidated glacial material and the underlying shale is a no-flow boundary.

The ground-water flow solution is solved by applying the flow-model code MODFLOW (McDonald and Harbaugh, 1988). The water table generally slopes from the valley walls toward the surface-water network (fig. 3).

Geochemical Model

The geochemical model adopted for this study posits that reducing conditions occur in ground water because microbes gain energy from redox reactions involving electron donors and electron acceptors. Naturally occurring electron donors include reactive organic carbon derived from plant decay and sulfide minerals such as pyrite. For the hypothetical simulations, the electron donor is assumed to be organic carbon. The electron acceptors are dissolved oxygen, dissolved nitrate, solid-phase ferric iron, dissolved sulphate, and dissolved carbon dioxide. Typically, the microbes utilize the electron acceptors sequentially (Chapelle and others, 1995; Guoping and others, 1999; Schreiber and others, 2004).

The geochemical model also requires the assumption that these reactions approximately follow a first-order law with respect to the electron donor and zero order with respect to the electron acceptors, implying that the rate of reaction between the electron donor and any electron acceptor is directly proportional to the concentration of the electron donor. Although more sophisticated Monod-type kinetic models could have been used (Bekins and others, 1998; Rolle and others, 2006), the difficulty in quantifying the parameters necessary for a Monod formulation led to adoption of the simpler model. This simple geochemical model does not directly simulate the reaction of the electron donor with solid-phase ferric iron, Fe^{3+} . Instead, the assumption is that once a given amount of

dissolved ferrous iron, Fe^{2+} , is produced, then either the Fe^{3+} on sediments is no longer available to be reduced or (as is more likely) iron reduction continues but any additional Fe^{2+} derived from the solid phase precipitates out of solution or is sorbed to solid-phase minerals. At this point, it is assumed that sulfate reduction replaces iron reduction even though it is likely that iron reduction continues to occur (but at too slow a rate to offset ferrous iron precipitation and thereby increase the concentration of dissolved Fe^{2+}).

The sequential first-order geochemical model incorporates four key assumptions. First, the electron donor is represented by the simplest organic carbon molecule, CH_2O , and the stoichiometry of the reactions corresponds to the degradation of this molecule. An alternative electron donor, such as pyrite, can replace CH_2O in the redox reactions with little change in the reaction stoichiometry. Second, the availability of electron donors in local source areas (associated with individual model cells) is assumed to be unlimited, and the donors are assumed to move freely from the solid to liquid phase in those areas. Third, electron donors are assumed to be mobile; that is, dissolved species in ground water are able to move downgradient from the source areas and continue to react with dissolved electron acceptors according to the posited first-order rate law. (This assumption was relaxed for some sensitivity simulations.) Finally, sources and sinks for electron acceptors other than recharge and river water are neglected, even though transfers within the subsurface can at times be important. The transient effect of water-table fluctuations that sometimes influences the availability of electron acceptors is also neglected. Within the limits imposed by these simplifying assumptions, the methodological approach is designed to simulate the crucial interaction between the rate of influx of young oxygenated water and the rates of redox reaction in the presence of a variable velocity field.

The transport code MT3D (Chunmiao and Wang, 1998), which is linked to MODFLOW, incorporates advection, dispersion, and sink/sources for the electron donor and acceptors. The reaction code RT3D (Clement, 2001), which simulates reactive multispecies transport, is, in turn, linked to MT3D. We used RT3D to simulate strictly sequential first-order decay reactions between a single electron donor (naturally occurring organic carbon) and five electron acceptors via five pathways: aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis. Reaction pathways switch from favored to less favored when the concentration of the favored electron acceptor falls to near zero. For example, when the dissolved oxygen concentration in a model cell falls below 0.01 mg/L, the redox reaction switches from aerobic respiration to denitrification. Similarly, when the nitrate concentration falls below 0.01 mg/L, the redox reaction switches from denitrification to iron reduction. However, the electron acceptor Fe^{3+} is not explicitly simulated in the routine because it is a solid-phase constituent. Therefore, the switching from iron reduction to sulfate reduction in the RT3D code is triggered by the buildup of the reaction product, Fe^{2+} , to a maximum concentration that reflects iron reduction and the

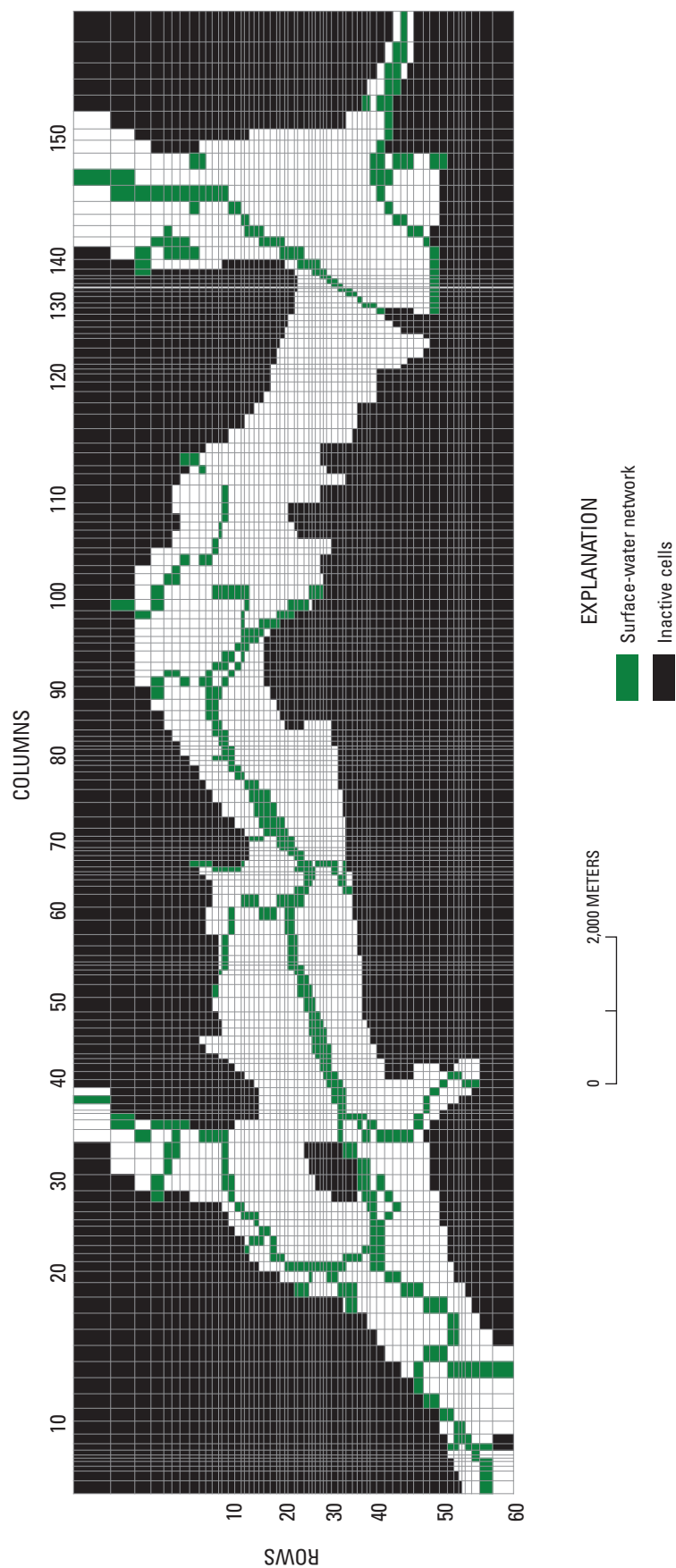


Figure 2. Plan view of model grid and surface-water network (green cells). Black cells are inactive.

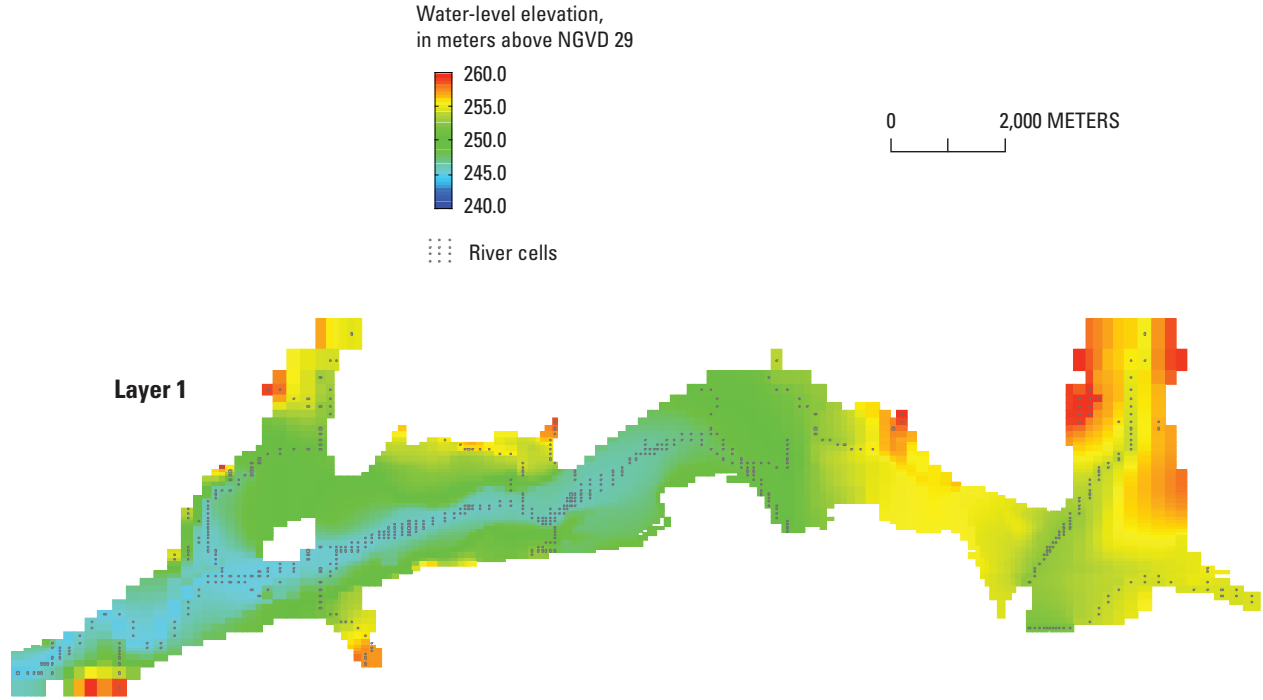


Figure 3. Simulated water-table elevation.

effect of sorption and precipitation reactions that remove Fe^{2+} from the dissolved phase. Finally, sulfate reduction conditions yield to methanogenesis when the sulfate concentration falls below 0.01 mg/L.

The transient transport simulations begin with background conditions for electron acceptors that correspond to the concentrations in recharge and river water. The simulations are run until equilibrium conditions are attained with respect to all reactants in all model cells.

Redox conditions become stable when the rate at which electron acceptors are supplied by incoming water balances the rate at which they are consumed by redox reactions.

Equations of the Geochemical Model

Module 3 of the RT3D code (Clement, 2001) was adapted to model the distribution of reduced ground water. The module simulates kinetic-limited degradation by way of multiple electron acceptors. It was intended originally to model BTEX degradation (Clement and others, 1997), but it was used in this study to model degradation of any electron donor, such as CH_2O , via the five degradation pathways mentioned previously.

RT3D Module 3 contains one equation for each of the five reaction pathways. In this study, the equations were applied in a simplified form and effectively eliminated inhibition and Monod half-saturation variables. The resulting expressions are strictly sequential—with no overlapping reactions at a given location at a given time—and they are

first-order with respect to the electron donor and zero-order with respect to the electron acceptors. The reformulated equations are as follows:

$$r_{\text{DONOR},\text{O}_2} = -k_{\text{O}_2} \times [\text{DONOR}] \text{ for } [\text{O}_2] \geq 0.01 \text{ mg/L}$$

$$r_{\text{DONOR},\text{NO}_3} = -k_{\text{NO}_3} \times [\text{DONOR}] \text{ for } [\text{O}_2] < 0.01 \text{ mg/L and } [\text{NO}_3] \geq 0.01 \text{ mg/L}$$

$$r_{\text{DONOR},\text{Fe}^{2+}} = -k_{\text{Fe}^{3+}} \times [\text{DONOR}] \text{ for } [\text{O}_2] < 0.01 \text{ mg/L, } [\text{NO}_3] < 0.01 \text{ mg/L and } [\text{Fe}^{3+}] \geq 0.01 \text{ mg/L}$$

$$r_{\text{DONOR},\text{SO}_4} = -k_{\text{SO}_4} \times [\text{DONOR}] \text{ for } [\text{O}_2] < 0.01 \text{ mg/L, } [\text{NO}_3] < 0.01 \text{ mg/L, } [\text{Fe}^{3+}] < 0.01 \text{ mg/L and } [\text{SO}_4] \geq 0.01 \text{ mg/L}$$

$$r_{\text{DONOR},\text{CH}_4} = -k_{\text{CO}_2} \times [\text{DONOR}] \text{ for } [\text{O}_2] < 0.01 \text{ mg/L, } [\text{NO}_3] < 0.01 \text{ mg/L, } [\text{Fe}^{3+}] < 0.01 \text{ mg/L, } [\text{SO}_4] < 0.01 \text{ mg/L, and } [\text{CO}_2] \geq 0.01 \text{ mg/L}$$

where

[] indicates concentration, in milligrams per liter,

r_{DONOR} is the destruction rate of the electron donor (for example, organic carbon), and

$k_{\text{O}_2} = k_{\text{NO}_3} = k_{\text{Fe}^{3+}} = k_{\text{SO}_4} = k_{\text{CO}_2}$ is a single first-order reaction constant.

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Because the concentration of Fe^{3+} and CO_2 are not dissolved species and cannot be measured under normal field conditions (Wiedermeier and others, 1995), these concentrations are replaced in module 3 of RT3D with “assimilative capacity terms” defined as

$$[\text{Fe}^{3+}] = [\text{Fe}^{2+}\text{max}] - [\text{Fe}^{2+}]$$

$$[\text{CO}_2] = [\text{CH}_4\text{max}] - [\text{CH}_4],$$

where

the concentration term for Fe^{3+} and CO_2 should be considered as a hypothetical term that represents the iron reduction and methanogenic capacity of the system and where $[\text{Fe}^{2+}\text{max}]$ and $[\text{CH}_4\text{max}]$ are the maximum concentrations of Fe^{2+} and CH_4 allowed to occur in the model.

The RT3D code simulates the consumption of electron acceptor as well as electron donor for any given redox reaction. It applies the following equations:

$$r_{\text{O}_2} = Y_{\text{O}_2/\text{DONOR}} \times r_{\text{DONOR},\text{O}_2}$$

$$r_{\text{NO}_3} = Y_{\text{NO}_3/\text{DONOR}} \times r_{\text{DONOR},\text{NO}_3}$$

$$r_{\text{Fe}^{2+}} = -Y_{\text{Fe}^{2+}/\text{DONOR}} \times r_{\text{DONOR},\text{Fe}^{2+}}$$

$$r_{\text{SO}_4} = Y_{\text{SO}_4/\text{DONOR}} \times r_{\text{DONOR},\text{SO}_4}$$

$$r_{\text{CH}_4} = -Y_{\text{CH}_4/\text{DONOR}} \times r_{\text{DONOR},\text{CH}_4}$$

where

Y is the appropriate yield coefficient in each chemical reaction; that is, the mass ratio of electron acceptor consumed to electron donor (for example, CH_2O) consumed.

Because the reactions are strictly sequential, only one electron acceptor is consumed at any location (model cell). The active reaction at a location can change over time, but only one reaction is permanently active once equilibrium conditions are achieved. All reactions are assumed to occur in the aqueous phase.

Initial Geochemical Conditions

The model requires concentrations of electron donors and electron acceptors for recharge, river water, and initial ground water. The electron donor was assumed to be organic carbon. Input values for organic carbon and electron acceptors are hypothetical but are generally consistent with literature values (table 1) and with water-quality data collected from the northern U.S. glacial aquifer system as part of NAWQA studies during 1991–2002 (table 2).

The literature values reflect a range of dissolved organic carbon concentrations in surficial settings and in carbon-rich

Table 1. Concentrations of dissolved organic carbon in varied hydrogeologic settings.

[All data in milligrams per liter; <, less than; --, not available; **bold** values indicate median value]

Site description	Range	Mean or median	Source
Water in equilibrium with atmosphere	--	10	Drever, 2002
Soil solutions:			
O/A horizon	21–32	--	Drever, 2002
B horizon	5–7	--	Drever, 2002
Ground water	Most <2	0.7	Drever, 2002
Rivers	2–15	4–6	Drever, 2002
Waters draining wetlands	5–60	25	Drever, 2002
Lakes:			
Low productivity	1–3	--	Drever, 2002
Eutrophic	2–5	--	Drever, 2002
Shallow ground water in glacial outwash, Wisconsin	Up to 25	4	Keating and Bahr, 1998
Clay-rich confining unit, southern Alberta	--	16 (typical)	Hendry and Wassenaar, 2005
Boom clay, Belgium	100–500	--	Hendry and Wassenaar, 2005
Mexico City clay plain confining unit	300–580	--	Hendry and Wassenaar, 2005

Table 2. Concentrations of electron acceptors and electron donors in ground-water samples from the glacial aquifer system in the northern United States, 1991–2002.

[mg/L, milligrams per liter; <, less than]

Acceptor or donor	All samples ¹	Samples from the northeastern United States
Electron-acceptor concentrations		
Dissolved oxygen		
Median (mg/L)	1.5	3.0
Range (mg/L)	<0.1–14	<0.1–13
Number of samples	799	170
Nitrate		
Median (mg/L)	0.5	0.8
Range (mg/L)	<0.06–77	<0.06–26
Number of samples	800	173
Iron		
Median (mg/L)	0.015	<0.010
Range (mg/L)	<0.010–38	<.010–38
Number of samples	810	172
Sulfate		
Median (mg/L)	30	13
Range (mg/L)	<0.3–2,600	<0.3–340
Number of samples	811	172
Electron-donor concentrations		
Dissolved organic carbon		
Median (mg/L)	1.0	0.6
Range (mg/L)	0.2–260	0.2–14
Number of samples	769	172

¹ Samples collected by the National Water-Quality Assessment (NAWQA) Program during 1991–2003 and used for analysis in Thomas (2007).

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subsurface areas (for example, waters draining wetlands and some confining units) but show concentrations consistently close to 1.0 mg/L in most shallow ground water (table 1). The NAWQA glacial-aquifer database indicates some variability in the central tendency of electron-acceptor and dissolved organic carbon concentrations, especially for dissolved nitrate and sulfate (table 2). The values selected for the hypothetical simulations (table 3) are generally in line with the median values from the NAWQA glacial-aquifer dataset for the northeastern United States and are considered representative of shallow, recently recharged ground water.

Reactive organic carbon is inserted into the model in two ways: as diffuse background loadings, and as elevated concentrations in source areas, such as buried wetlands. The diffuse loading occurs mostly through recharge but also from losing river reaches. The organic carbon concentration in recharge, river water, and initial background ground water was set constant at 1 mg/L, which is intended to represent typical conditions for shallow ground water. As the transport simulation proceeds, the organic carbon concentrations outside the source areas are free to change with the arrival of upgradient water. Redox reactions occur until an equilibrium is reached at any non-source location between the decay of the organic carbon and the amount replenished by incoming ground-water flow in the same period of time. The elevated organic carbon concentrations assigned to the source areas are discussed in a later section of the report.

Other inputs to the reaction model in MT3D/RT3D include the decay-rate constants for each sequential reaction, the reaction mass ratios, the maximum allowed Fe^{2+} and CH_4 concentration, and the solver scheme.

For the primary simulations, a first-order rate constant of 0.001 day^{-1} was applied to all redox reactions. The resulting

Table 3. Assumed initial reactant concentrations and reaction yield coefficients.

[mg/L, milligrams per liter]

Reactant	Concentration (mg/L)	Yield coefficient
Organic carbon, as CH_2O	1	1
O_2	6	1.07
NO_3	0.3	1.65
Fe^{2+}	0.005	7.44
SO_4	10	1.60
CH_4	0	0.267

depletion rate of CH_2O as a function of CH_2O concentration is shown in fig. 4.

The selected first-order decay rate falls between a reported high of 0.1 day^{-1} for deep-sea sediments and a reported low of $0.000001 \text{ day}^{-1}$, for regional aquifer systems in the United States with long flow paths (derived from Chapelle, 1993, fig. 7.6, assuming that the electron-donor compound is CH_2O). It seems reasonable that the decay rate in a shallow glacial system would fall between these end-members. The use of a single decay rate for all electron acceptors is, in part, a simplification in the absence of hard data on individual rates. However, this adapted convention is also consistent with findings by Bohlke and others (2002) that first-order rate constants in glacial sand aquifers were similar for oxygen reduction, nitrate reduction, and sulfate reduction.

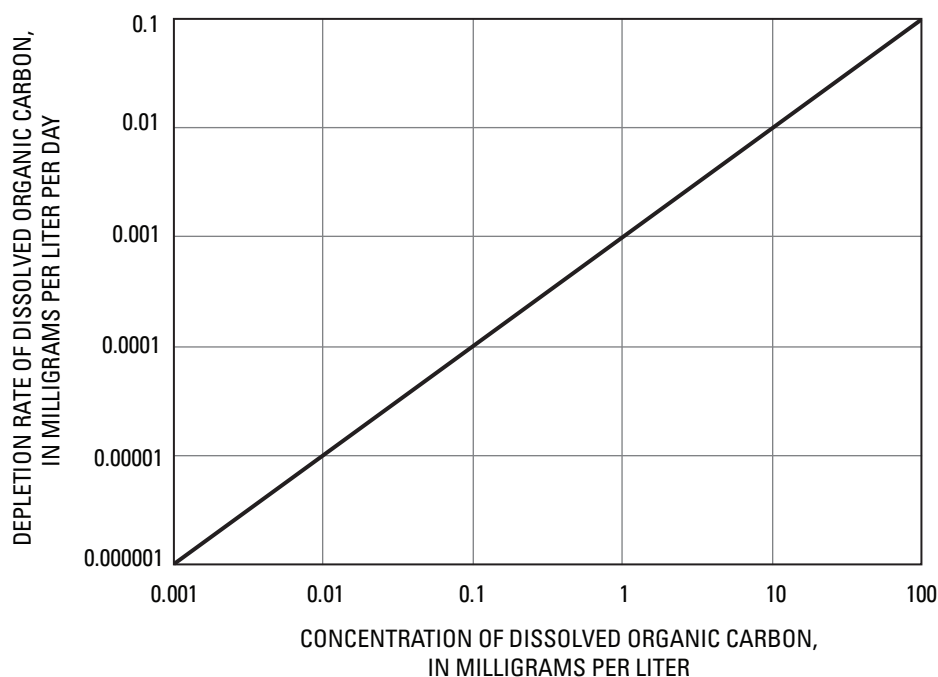


Figure 4. Relation between concentration and depletion rate of dissolved organic carbon for decay constant equal to 0.001 day^{-1} .

The yield coefficients for redox reactions between CH_2O and electron acceptors are listed in table 3. They account for the consumption of electron acceptors during redox reactions. For example, if 10 mg/L of dissolved organic carbon is present in a model cell and the concentration of oxygen is greater than 0.01 mg/L, then the depletion rate of the organic carbon is 0.001×10 or 0.01 mg/L/d and the depletion rate of dissolved oxygen, using its yield coefficient, is 1.07×0.01 or 0.0107 mg/L/d. If dissolved oxygen and nitrate concentrations are less than 0.01 mg/L and the concentration of Fe^{2+} is less than 40 mg/L, then the depletion rate of the organic carbon is still 0.01 mg/L/d but the production rate of Fe^{2+} is 7.44×0.01 or 0.0744 mg/L/d.

The maximum allowable Fe^{2+} was set at 40 mg/L. This is the concentration at which modeled redox reactions switch from iron reducing to sulfate reducing. One way to think about this 40 mg/L threshold is that it represents the reduced aqueous concentration achieved when all available Fe^{3+} on the sediments has been completely transferred to the aqueous phase. However, this assumption is wrong because there is no direct relation between the Fe^{3+} available in the glacial material and the resulting Fe^{2+} that could be produced by redox reactions. In other words, it is incorrect to assume that the dissolved Fe^{2+} measured in the aquifer pore water has a valid quantitative relation to the assimilative iron-reducing capacity of the sediments. For example, at the Bemidji, Minnesota site, if all the bioavailable sediment Fe^{3+} were converted to Fe^{2+} , then the resulting Fe^{2+} concentration would reach about 5,700 mg/L. However, the observed concentration at Bemidji is only 50 mg/L (Essaid and others, 1995; Bekins and others, 2005). The discrepancy is probably due to removal of aqueous Fe^{2+} reduced from Fe^{3+} through precipitation as sulfides, carbonates, or mixed-iron-phase oxides (Bekins and others, 2001). The simple geochemical model adopted in this study cannot reproduce the transfer of iron from Fe^{3+} to Fe^{2+} and the subsequent removal of some of the Fe^{2+} by other chemical reactions. Instead, it simply assigns a maximum Fe^{2+} concentration of 40 mg/L that is assumed to be the maximum concentration that would arise *in the absence of any sorption and precipitation of the Fe^{2+} derived from solid-phase Fe^{3+}* . Work at contaminated sites (Bekins and others, 2001; Chapelle and others, 2002) suggests that the 40 mg/L value could underestimate

the concentration of dissolved Fe^{2+} concentration that would arise from the reservoir of bioavailable iron on sediments and would then be subject to sorption and precipitation. The implications of underestimating the bioavailable iron from the standpoint of the modeling are to shorten the iron-reducing phase in the redox reaction chain and to minimize the importance of iron in oxidizing organic carbon relative to the other strongly reduced phases. For the purposes of this study, it is effectively assumed that naturally occurring bioavailable iron is quite low in the glacial sediments from the start, thereby allowing the redox reactions to continue beyond iron reduction to sulfate-reducing and methanogenic phases without exhausting available organic carbon.

The maximum allowable CH_4 concentration was set to 10 mg/L. This value is a likely maximum because it is roughly equal to the aqueous solubility of methane in shallow ground water. This concentration of CH_4 would be simulated only under extremely reducing conditions.

The transport model was solved by means of implicit finite-difference methods. Routine application of an alternative solver scheme that would minimize numerical dispersion was impractical because of the duration of the simulations, but alternative schemes were applied in the sensitivity phase.

Definition of Redox Zones

In the context of the model simulations, redox conditions can be presented in two ways: in terms of the active redox reaction in each model cell or in terms of the concentrations of redox reactants or products in each cell. The two approaches differ somewhat because the concentration of redox reactants or products in each cell depends not only on the active redox reaction but also on the chemistry of the water that is transported into the cell by advective and dispersive flow. As a result, concentrations of redox reactants or products can overlap in ways that depart from the strict sequencing of reactions, a condition commonly detected in field ground-water sampling (for example, as described by Schreiber and others, 2004). For this reason, we present the model results in terms of the concentration of redox reactants or products, using a method based on Paschke (2007). Six redox water-chemistry zones are listed in table 4. The first and second zones are dominated by

Table 4. Definition of redox water-chemistry zones in terms of dissolved species.

[mg/L, milligrams per liter; \geq , greater than or equal to; $<$, less than; strongly reducing zones are shaded]

Water-chemistry zone	Speciation
Oxic	$\text{O}_2 \geq 0.5 \text{ mg/L}$; $\text{Fe}^{2+} < 0.1 \text{ mg/L}$
Nitrate reducing	$\text{O}_2 < 0.5 \text{ mg/L}$; $\text{NO}_3 \geq 0.1 \text{ mg/L}$; $\text{Fe}^{2+} < 0.1 \text{ mg/L}$
Mixed: Oxic with Fe^{2+}	$\text{O}_2 \geq 0.5 \text{ mg/L}$; $\text{NO}_3 < 0.1 \text{ mg/L}$; $\text{Fe}^{2+} \geq 0.1 \text{ mg/L}$
Mixed: Nitrate reducing with Fe^{2+}	$\text{O}_2 < 0.5 \text{ mg/L}$; $\text{NO}_3 \geq 0.1 \text{ mg/L}$; $\text{Fe}^{2+} \geq 0.1 \text{ mg/L}$
Iron reducing with high sulfate	$\text{O}_2 < 0.5 \text{ mg/L}$; $\text{NO}_3 < 0.1 \text{ mg/L}$; $\text{Fe}^{2+} \geq 0.1 \text{ mg/L}$; $\text{SO}_4 \geq 4 \text{ mg/L}$
Iron reducing with low sulfate	$\text{O}_2 < 0.5 \text{ mg/L}$; $\text{NO}_3 < 0.1 \text{ mg/L}$; $\text{Fe}^{2+} \geq 0.1 \text{ mg/L}$; $\text{SO}_4 < 4 \text{ mg/L}$

the dissolved electron acceptors oxygen and nitrate, respectively. The third and fourth represent the overlap of some dissolved Fe^{2+} with oxygen or nitrate. The last two zones (negligible dissolved oxygen and nitrate, dissolved Fe^{2+} greater than 0.1 mg/L) are collectively referred to as “strongly reducing.”

Hypothetical Scenarios—A Single Ground-Water Flow Field with Varied Distributions of Organic Carbon

The MODFLOW-MT3D-RT3D suite of codes combines a flow field with controls on transport that allow the simulation of sequential redox reactions for particular configurations of electron donors and electron acceptors. Numerical experiments were conducted for a single flow system using three different hypothetical distributions of elevated organic carbon concentrations (source areas). The flow system and source areas are described below.

Ground-Water Flow System

In general, ground-water flow fields are complex in the sense that waters of different ages and origins mix under the influence of different scales of subsurface heterogeneity. This mixing typically yields waters of varying chemistry within a single aquifer or confining unit.

In the Susquehanna River model, pronounced heterogeneity in hydraulic conductivities that is associated with small-scale grain-size differences in glacial deposits gives rise to a complicated velocity and age-distribution pattern. The velocity is also influenced by the effective porosity of the sediments, assumed to be 0.2 in aquifer sediments and 0.02 in lacustrine sediments. Velocities in the aquifers range over several orders of magnitude (fig. 5A, 5B), and the rate of vertical flow also is highly variable in magnitude and direction (fig. 5C). Flow between the aquifers is mostly downward except along the course of the Susquehanna River.

The transport model considers not only movement due to the advective velocity in each cell but also the movement due to assumed heterogeneity at a scale smaller than the grid size, the so-called macrodispersion term. Because the cell-by-cell heterogeneity is so large in this model, the assumed dispersion terms are relatively small, equal to 0.3 m/d in the longitudinal

direction, 0.03 m/d in the transverse horizontal direction, and 0.003 m/d in the transverse vertical direction.

The ages of the waters in the model were calculated by use of the MT3D transport model to take account of movement both by advection and dispersion (following the method of Goode, 1996). The average age of ground water in the upper aquifer is 3.2 years, with ground water in 95 percent of the cells between 0.2 and 10 years. The average age of ground water in the lacustrine confining unit is 33.4 years, with ground water in 95 percent of the cells between 2 and 132 years. The average age of ground water in the lower aquifer is 10.4 years, with ground water in 95 percent of the cells between 1 and 31 years. The spatial distribution of ground-water age for the lower aquifer is shown in figure 6.

If ground water less than 10 years old is assumed to be young, then these results indicate that the water in the upper aquifer is young, the water in the lower aquifer is young or not very old, and the water in the confining unit is mostly old.

Organic Carbon Source Areas

In this part of the Susquehanna Valley, the most likely sources of elevated organic carbon are landfills (Allan D. Randall, U.S. Geological Survey (retired), written commun., 2006). However, for this study, the distribution of elevated organic carbon concentrations (source areas) was hypothetical. For each hypothetical source area, an unlimited reservoir of organic carbon was assumed to exist on the solid phase in contact with the ground water. The dissolved organic carbon concentration in contact with this solid phase over a model cell was assumed to be a constant value between 10 and 100 mg/L, which is at the high end of dissolved organic carbon concentrations detected in the glacial aquifer system (table 2). The source areas were configured to represent naturally occurring deposits of elevated organic carbon that might be present in a glacial aquifer system.

The three scenarios are not mutually exclusive and do not represent competing hypotheses to explain the redox distribution observed at an actual study site. Rather, they are presented to test a method for simulating redox under a range of conditions. By considering multiple scenarios, it is possible to demonstrate how different organic carbon distributions interact with the ground-water flow field to produce different patterns of reduced water. The three hypothetical source areas are described below.

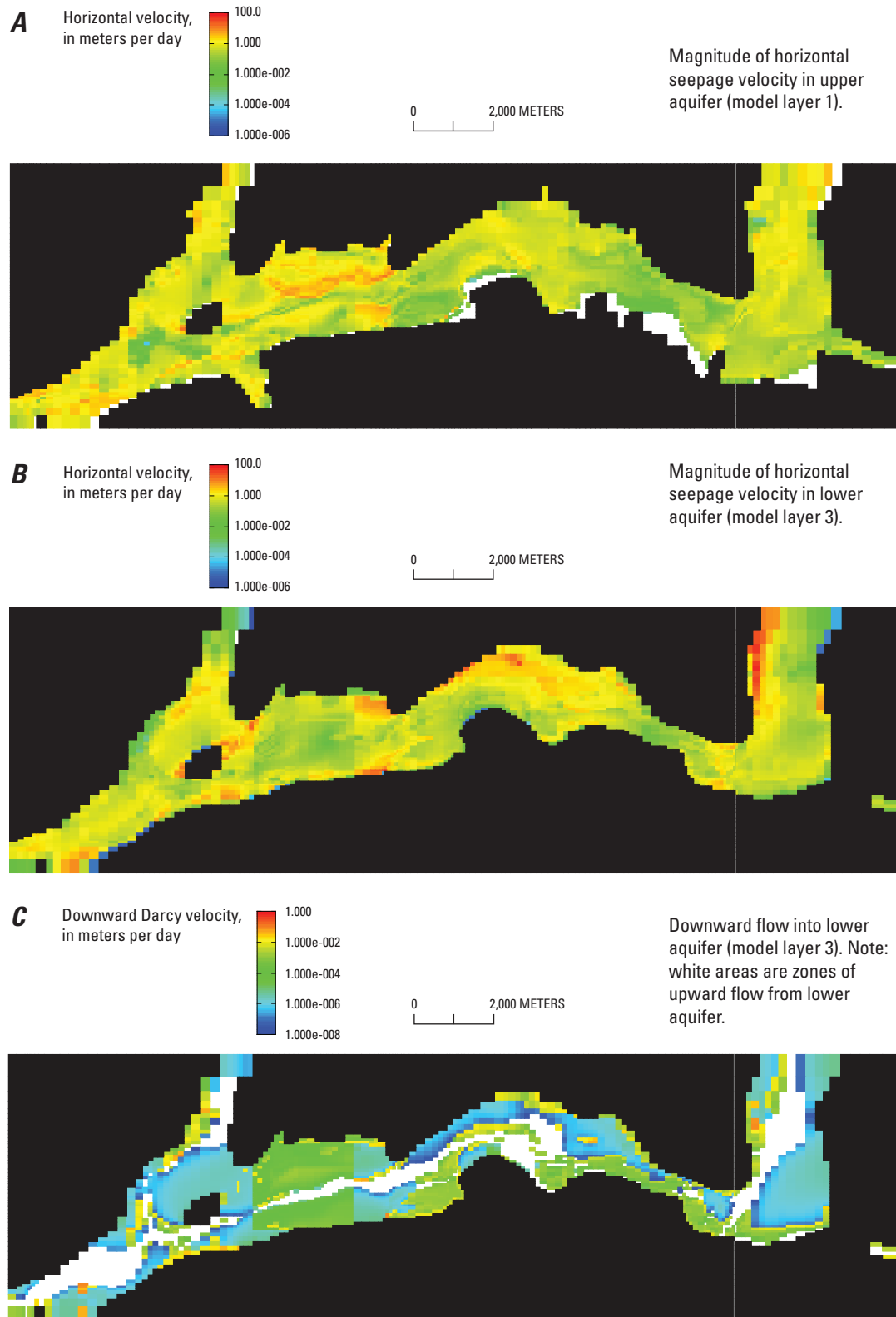


Figure 5. Model-computed flow velocities in upper and lower aquifers. **A**, Magnitude of horizontal seepage velocity in upper aquifer (model layer 1). **B**, Magnitude of horizontal seepage velocity in lower aquifer (model layer 3). **C**, Downward flow into lower aquifer (model layer 3). Note: white areas are zones of upward flow from lower aquifer.

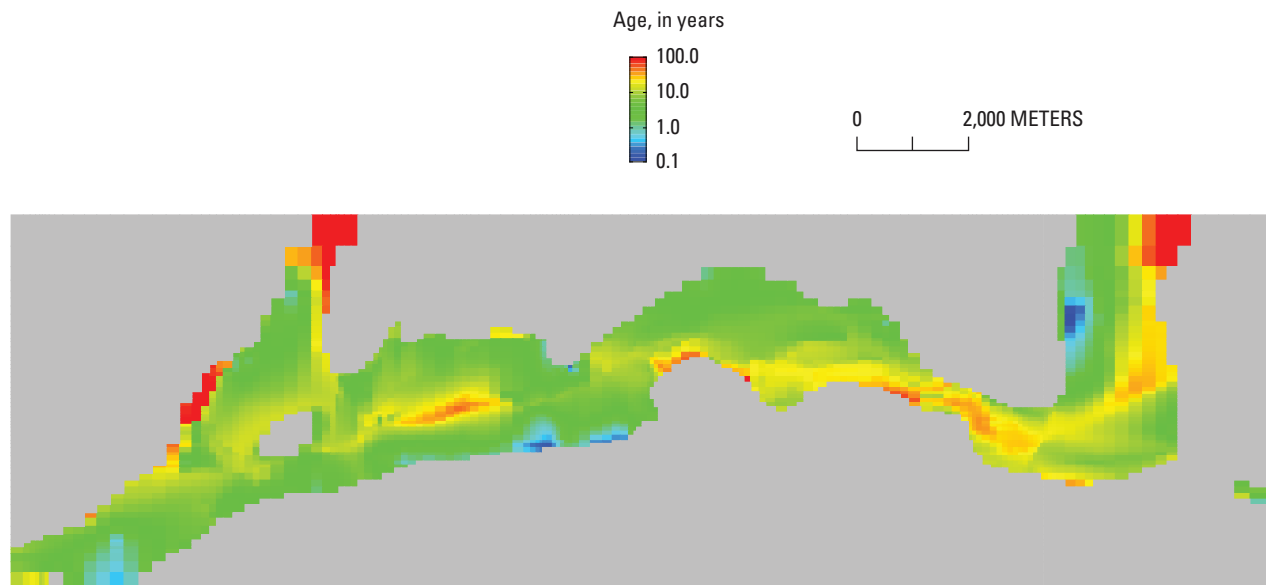


Figure 6. Spatial distribution of ground-water age in the lower aquifer.

Random Source Area

For this scenario, dissolved organic carbon concentrations of 20 mg/L were added at random locations in the upper aquifer (model layer 1), occupying 3.8 percent of the total saturated volume of the upper aquifer (fig. 7A). This source area is intended to represent randomly distributed pockets of organic carbon associated with buried wetlands or kettle-hole infilling.

Lacustrine Source Area

For this scenario, fine-grained material in the confining unit (model layer 2) was assumed to have a dissolved organic carbon concentration of 10 mg/L. The fine-grained material amounted to 78 percent of the volume of the layer (fig. 7B). It is likely that the glacial lacustrine facies identified by Randall (1986) was deposited under permafrost conditions and is not a host of organic material (Jeffrey Starn, U.S. Geological Survey, written commun., 2006). This scenario is included nonetheless to investigate how a clay-rich confining unit with elevated concentrations of organic carbon would affect redox conditions in the adjacent aquifer.

Wetland Source Area

For this scenario, dissolved organic carbon concentrations of 100 mg/L were added to the upper aquifer (model layer 1) at four locations, amounting to 4.6 percent of the saturated volume (fig. 7C). This scenario was intended to represent active wetlands or marshland with very high concentrations of organic carbon at land surface. Of the four wetland source areas, two are along the rivers in areas of upward

ground-water flow, and two are in pitted depressions in areas of downward ground-water flow.

The flow system transports dissolved organic carbon from the source areas; redox reactions occur at any model-cell location as long as the concentrations of the organic carbon and at least one electron acceptor are greater than 0.01 mg/L. The redox simulations were allowed to proceed in time until stable conditions were achieved everywhere in the three-layer system for both the electron donor and the five electron acceptors. In all cases, stable conditions were achieved in less than 500 years. This result suggests that the flow system and the geochemical reactions interact at a timescale that is short relative to the age of the glacial deposits.

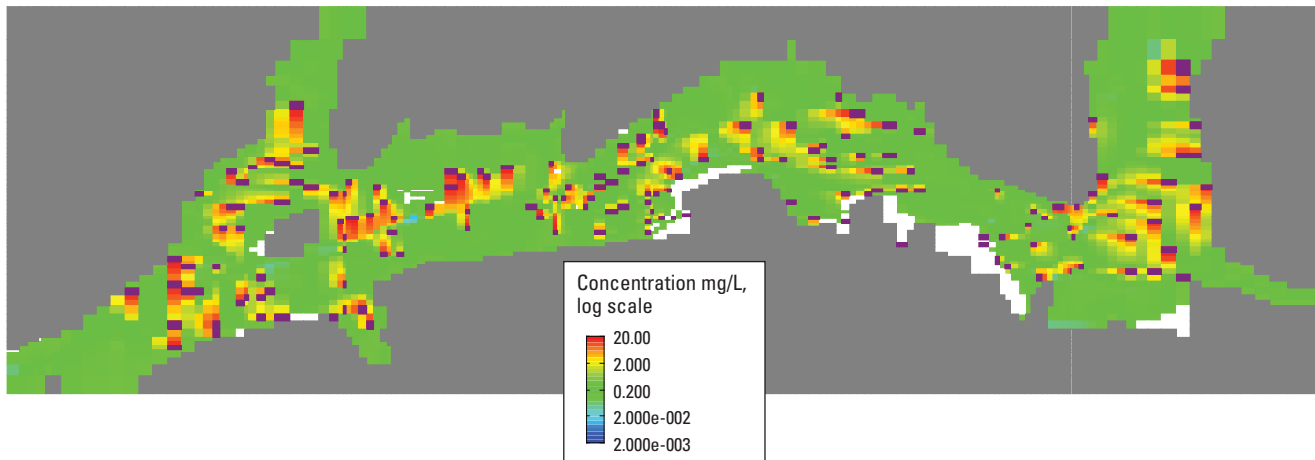
Results of Hypothetical Scenarios

Equilibrium Organic Carbon Concentrations

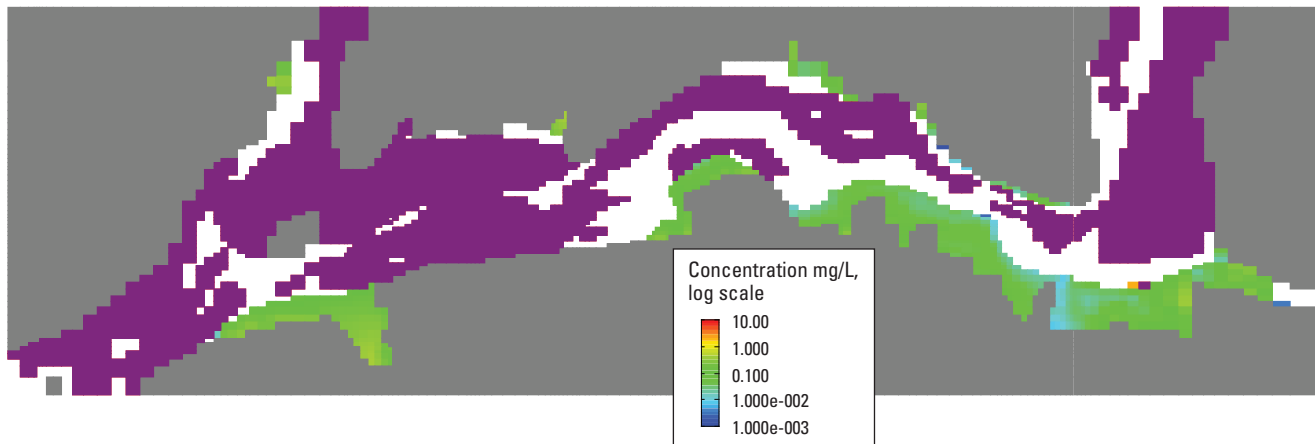
The interaction of the ground-water flow field, the presence of localized sources of organic carbon, and the sequence of redox reactions yield an equilibrium distribution of dissolved organic carbon in the ground water that is very different from the initial uniform concentration of 1 mg/L. The equilibrium concentration of dissolved organic carbon at any model cell is between 0 and the concentration at source areas, which is fixed to 20 mg/L in the random scenario, 10 mg/L in the lacustrine scenario, and 100 mg/L in the wetland scenario. Figure 8 shows the spatial distribution of the dissolved organic carbon that results at equilibrium in the lower aquifer for the three simulated scenarios.

ARandom organic carbon scenario ($C_{\text{source}} = 20 \text{ mg/L}$)

Purple areas show electron donor source in upper aquifer. Upper aquifer absent where white.

**B**Lacustrine organic carbon scenario ($C_{\text{source}} = 10 \text{ mg/L}$)

Purple areas show electron donor source in aquitard. Aquitard absent where white.

**C**Wetland organic carbon scenario ($C_{\text{source}} = 100 \text{ mg/L}$)

Purple areas show electron donor source in upper aquifer. Upper aquifer absent where white.

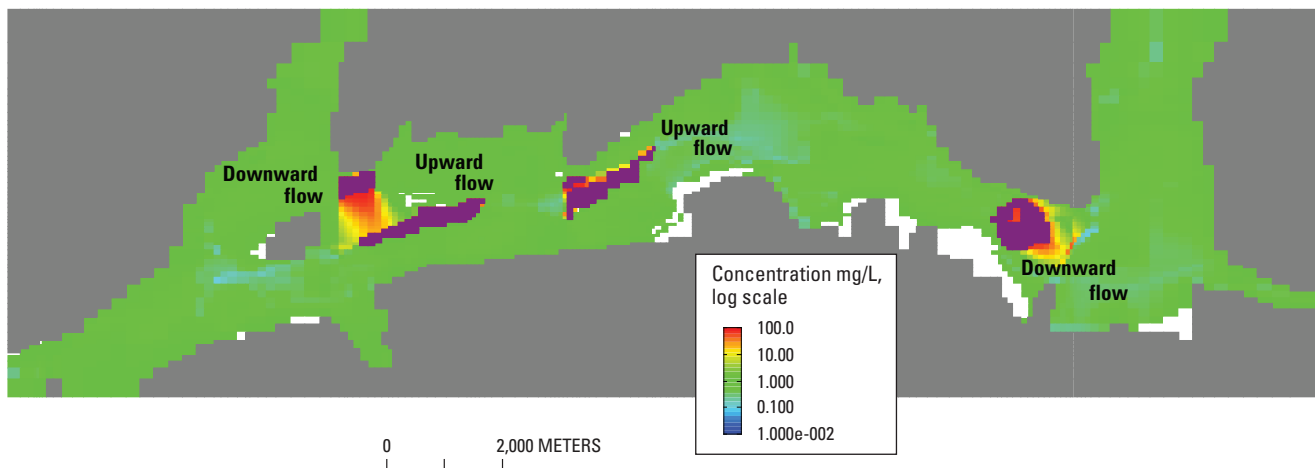


Figure 7. Electron-donor source areas and simulated electron donor concentrations in source layer for three organic carbon source scenarios. **A**, Random organic carbon scenario ($C_{\text{source}} = 20 \text{ mg/L}$). Electron donor source in upper aquifer. **B**, Lacustrine organic carbon scenario ($C_{\text{source}} = 10 \text{ mg/L}$). Electron donor source in aquitard. **C**, Wetland organic carbon scenario ($C_{\text{source}} = 100 \text{ mg/L}$). Electron donor source in upper aquifer. [C_{source} = source concentration; mg/L, milligrams per liter]

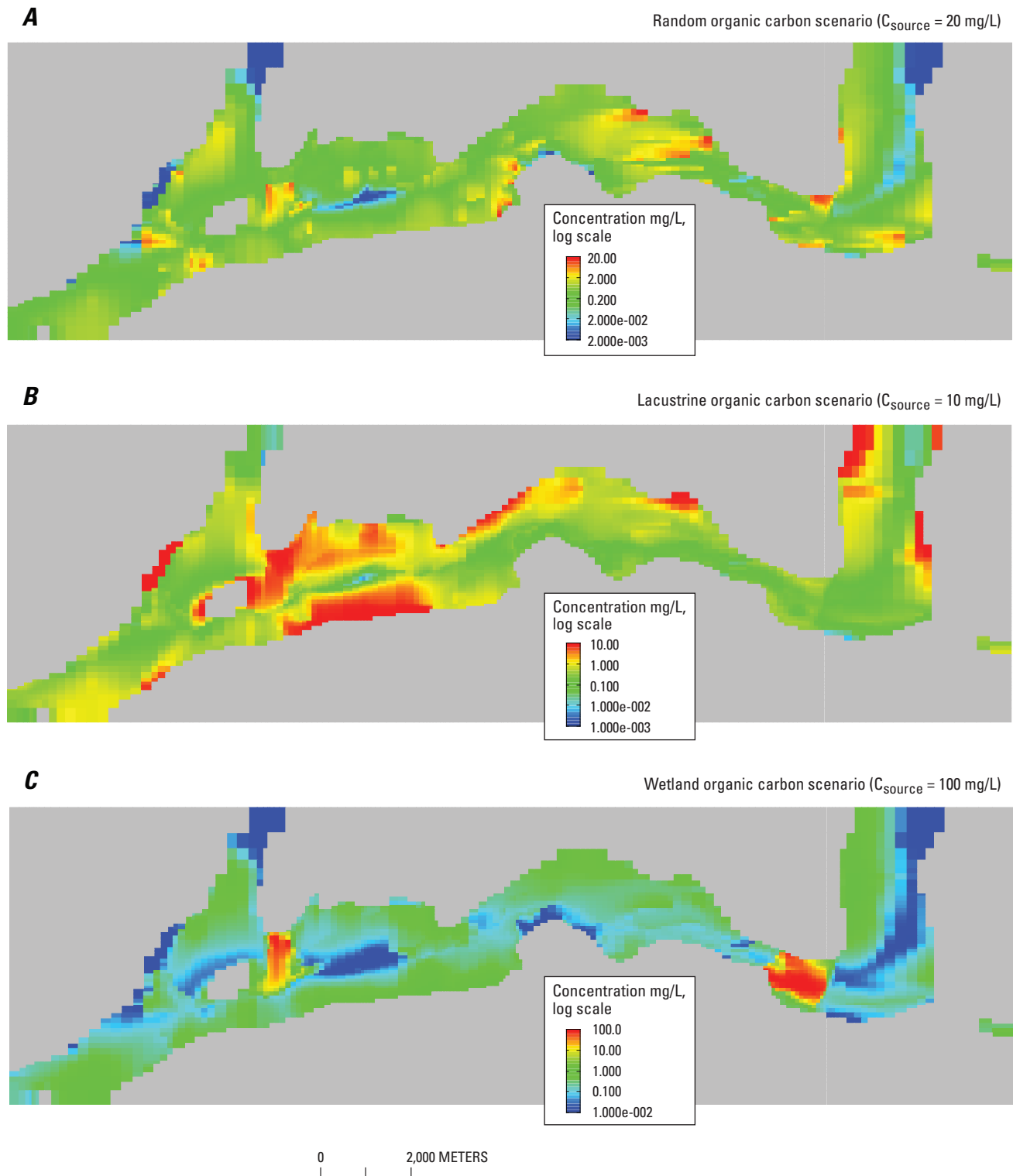


Figure 8. Simulated dissolved organic carbon concentrations in the lower aquifer for three source scenarios. **A**, Random organic carbon scenario ($C_{\text{source}} = 20 \text{ mg/L}$). **B**, Lacustrine organic carbon scenario ($C_{\text{source}} = 10 \text{ mg/L}$). **C**, Wetland organic carbon scenario ($C_{\text{source}} = 100 \text{ mg/L}$). [C_{source} , source concentration; mg/L, milligrams per liter]

Equilibrium Redox Water-Chemistry Conditions

The output of the three hypothetical scenarios is presented in terms of redox water-chemistry zones in the lower aquifer (fig. 9; table 5).

For the random scenario, elevated organic carbon (20 mg/L) is randomly distributed within the upper aquifer to simulate buried former wetlands. At equilibrium, the redox water chemistry in the lower aquifer is predominantly oxic (55 percent) and mixed (39 percent), with isolated areas that are strongly reduced (6 percent) (fig. 9A; table 5). The ratio of strongly reduced water in the upper aquifer to that in the lower aquifer is close to 1, indicating similar volumes of reduced water in the upper and lower aquifer—although with very different spatial patterns.

For the lacustrine scenario, elevated organic carbon (10 mg/L) is associated with fine-grained material within the confining unit to simulate an old, buried source of dispersed organic carbon that is less reactive than an active or buried wetland. At equilibrium, the redox water chemistry in the lower aquifer is predominantly mixed (69 percent), with lesser amounts of oxic water (20 percent) and strongly reduced water (11 percent) (fig. 9B; table 5). For this scenario, about 7 times more strongly reduced water is in the confining unit than in the lower aquifer.

For the wetland scenario, four source areas were located at the water table to simulate active wetlands with very high concentrations of organic carbon (100 mg/L). Two of the wetland source areas are in areas of upward ground-water flow (river wetlands), and the other two are in areas of downward flow (pitted wetlands). At equilibrium, the redox water chemistry in the lower aquifer is predominantly oxic (93 percent), with a small, strongly reducing zone beneath the pitted wetlands (fig. 9C; table 5). For this scenario, about twice as much strongly reduced water is in the upper aquifer than in the lower aquifer.

The loading rates of oxygen and sulfate are constant across the three scenarios, but the loading rates of the organic carbon differ markedly, as do the rates at which Fe^{2+} and methane are produced (table 6).

Comparison of mass-flux data for the three scenarios shows that rates of organic carbon loading do not correspond to rates of Fe^{2+} and methane production (table 6). In particular, although the random scenario sustains the highest overall rate of organic carbon loading to the ground water, the wetland scenario yields by far the largest mass of reduced products. The random and wetland source areas cover about the same fraction of the upper aquifer, but half of the wetland source areas are in ground-water discharge areas and therefore do not contribute to organic carbon loading of the lower aquifer. In contrast, for the random-source scenario, the great majority of elevated organic carbon is in recharge areas and therefore increases organic carbon loading to the lower aquifer. Despite the generally more favorable location of the random sources relative to the wetland sources with respect to the spread of

reduced water, the wetland scenario yields a larger overall mass of reduced products as a result of higher source intensity. The large contribution of reduced products in the wetland scenario is associated with the very strong reducing conditions that are generated around and under the wetlands, which in turn is associated with the elevated concentrations (100 mg/L) of dissolved organic carbon hypothesized to occur. These elevated concentrations promote sequential redox reactions that go beyond the aerobic and nitrate-reducing stage to iron-reducing and even methanogenic conditions, as indicated by the iron-reducing, low-sulfate water-chemistry zone in fig. 9C.

It is also noteworthy that the lacustrine scenario yields the smallest overall mass of reduced products (table 6), even though it has a very large volumetric extent and yields a large volume of strongly reduced ground water (77 percent of the confining unit; table 5). This discrepancy is related to the location of the lacustrine confining unit with respect to the ground-water flow field. Although the lacustrine material separates the upper from the lower aquifer over more than three-quarters of the area, about 95 percent of the exchange between the two aquifers occurs where they are in direct connection. Consequently, the amount of water passing through the source areas is small, and the rate of transfer of organic carbon from the solid to dissolved phase is limited. Moreover, the reduced water leaking out of the lacustrine source areas to the lower aquifer is strongly diluted by oxic water moving directly downward from the upper aquifer. However, this dilution effect is not sufficient to prevent reducing waters in one large area of the lower aquifer (fig. 9B).

A comparison of a map of simulated redox reaction zones (defined by the RT3D equations) to the simulated water chemistry (based on the classification in table 4) demonstrates one difficulty in relating observed reactant concentrations to the reducing conditions that produce them. For the purposes of the comparison, a special simulation based on the random source scenario was done with the cutoff for switching from aerobic reactions to more reducing reactions set to 0.5 mg/L instead of 0.01 mg/L. In this way, the cutoff for switching reactions is the same as the cutoff for distinguishing oxic redox water chemistry from other redox water chemistry. The model-generated redox reaction zones, which cannot be observed directly in the field, show that almost all the lower aquifer has sufficient oxygen to support aerobic reactions (fig. 10A). The accompanying map of model-generated water-chemistry zones, which can, in principle, be observed in the field, show that most of the lower aquifer falls into a mixed zone where dissolved oxygen is greater than 0.5 mg/L and Fe^{2+} is greater than 0.1 mg/L (fig. 10B). The overlap of dissolved iron with dissolved oxygen can be attributed to the spreading by advection and (or) dispersion of iron-enriched water (from reduced zones influenced by organic carbon source areas in the upper aquifer) with oxic water (which did not pass through those source areas and which contains a background Fe^{2+} concentration of 0.005 mg/L).

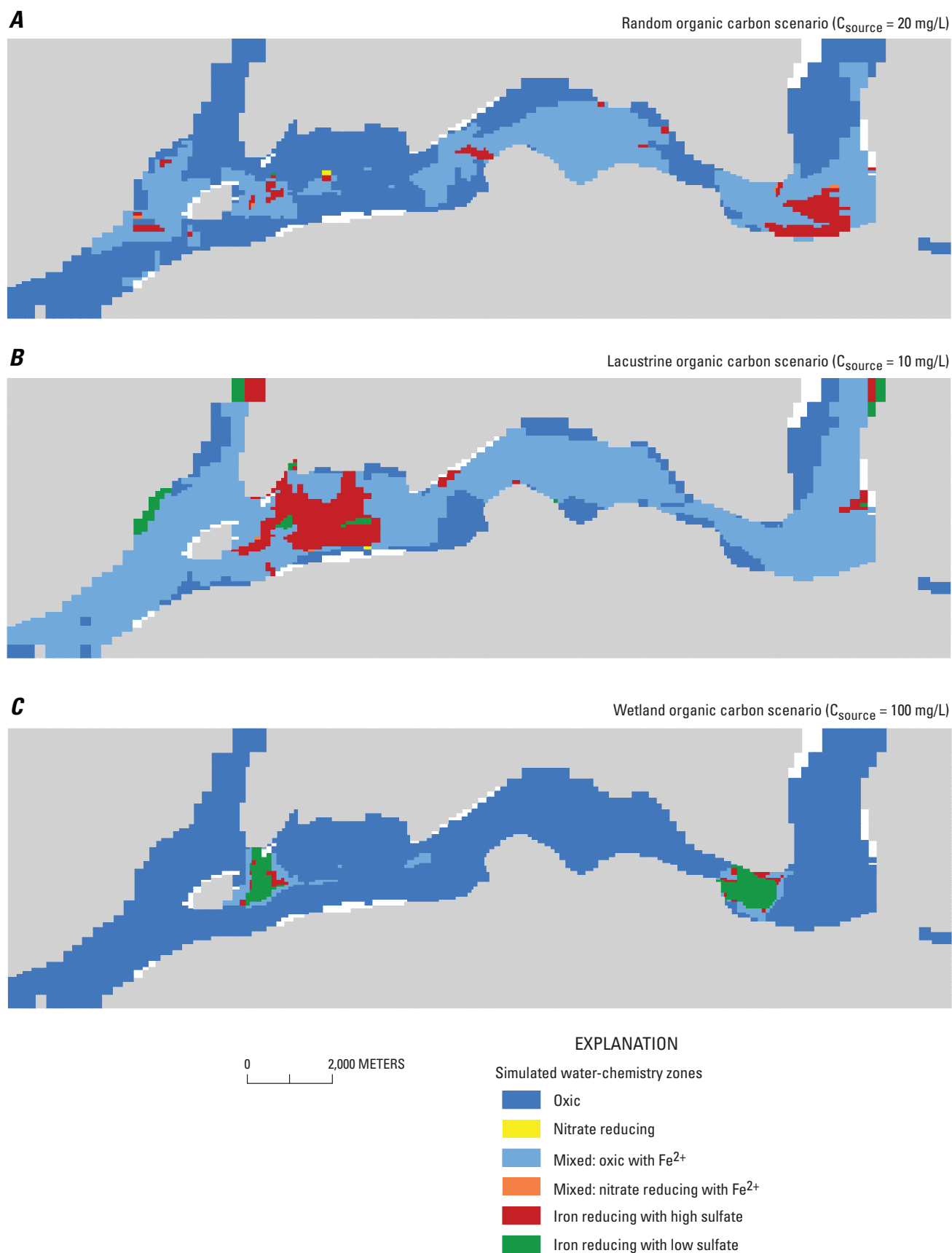


Figure 9. Simulated redox water chemistry in the lower aquifer (layer 3) for three organic carbon source scenarios. Cells shown in white represent areas where the lower aquifer is pinched out. **A**, Random organic carbon scenario ($C_{\text{source}} = 20 \text{ mg/L}$). **B**, Lacustrine organic carbon scenario ($C_{\text{source}} = 10 \text{ mg/L}$). **C**, Wetland organic carbon scenario ($C_{\text{source}} = 100 \text{ mg/L}$). [C_{source} , source concentration; mg/L, milligrams per liter]

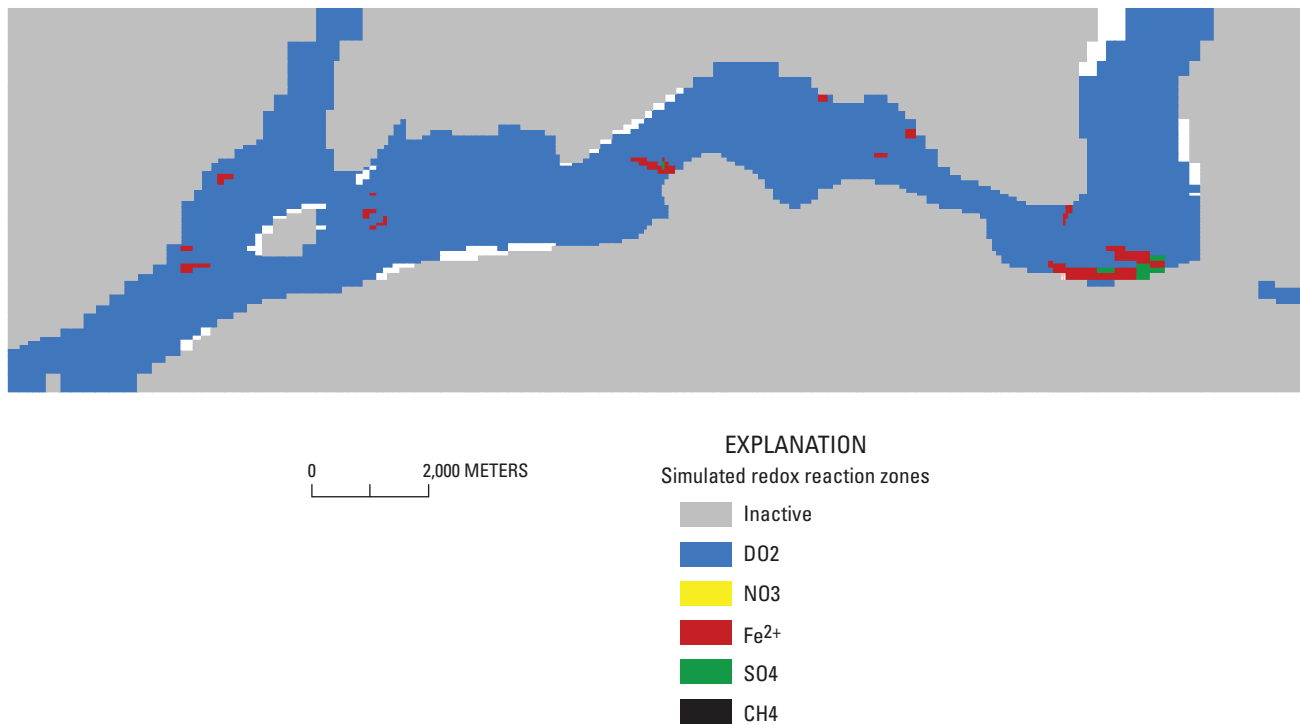
Table 5. Simulated redox water-chemistry zones in the upper aquifer, confining unit, and lower aquifer by percent volume.[C_{source}, source concentration; mg/L, milligrams per liter; strongly reducing categories are shaded]

Water-chemistry zones	Percent volume		
	Upper aquifer	Confining unit	Lower aquifer
Random organic carbon scenario (C _{source} = 20 mg/L)			
Source formation is upper aquifer.			
Ratio of volume of strongly reduced water, upper aquifer to lower aquifer = 1.14			
Oxic	61.7	59.2	54.9
Nitrate reducing	0.0	0.0	0.2
Mixed: Oxic with Fe ²⁺	31.9	25.3	39.2
Mixed: Nitrate reducing with Fe ²⁺	0.0	0.1	0.1
Iron reducing with high sulfate	6.0	12.9	5.6
Iron reducing with low sulfate	0.4	2.6	0.0
TOTAL	100.0	100.1	100.0
Lacustrine organic carbon scenario (C _{source} = 10 mg/L)			
Source formation is confining unit.			
Ratio of volume of strongly reduced water, upper aquifer to lower aquifer = 7.25			
Oxic	38.9	20.9	20.4
Nitrate reducing	0.0	0.0	0.0
Mixed: Oxic with Fe ²⁺	61.0	2.2	69.0
Mixed: Nitrate reducing with Fe ²⁺	0.0	0.0	0.0
Iron reducing with high sulfate	0.1	6.6	9.7
Iron reducing with low sulfate	0.0	70.3	0.9
TOTAL	100.0	100.0	100.0
Wetland organic carbon scenario (C _{source} = 100 mg/L)			
Source formation is upper aquifer.			
Ratio of volume of strongly reduced water, upper aquifer to lower aquifer = 1.95			
Oxic	88.7	94.0	92.7
Nitrate reducing	0.0	0.0	0.0
Mixed: Oxic with Fe ²⁺	3.2	1.5	3.2
Mixed: Nitrate reducing with Fe ²⁺	0.0	0.0	0.0
Iron reducing with high sulfate	1.3	0.8	0.8
Iron reducing with low sulfate	6.7	3.7	3.3
TOTAL	99.9	100.0	100.0

Table 6. Mass flux of redox constituents for organic carbon source scenarios for entire model.[All data are in kilograms per day; O₂, SO₄, and organic carbon loaded to system are either consumed by redox reactions or discharged to surface water.]

Redox constituent	Recharge and river, all scenarios	Organic carbon source scenario		
		Random	Lacustrine	Wetland
O ₂ loading	729	0	0	0
SO ₄ loading	1,193	0	0	0
Organic carbon loading	117	267	48	193
Fe ²⁺ produced by reduction of Fe ³⁺	0	157	133	422
CH ₄ produced by reduction of CO ₂	0	0.2	8	40

A



B

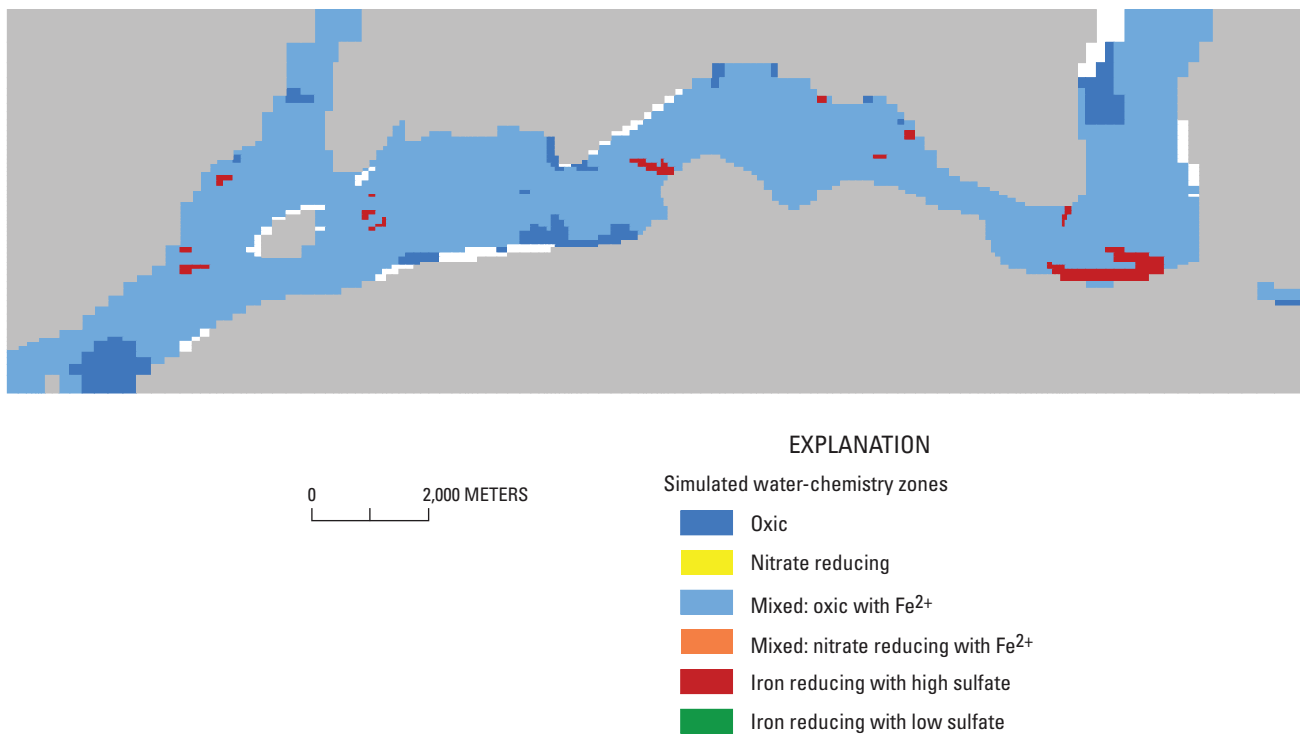


Figure 10. Comparison of **A**, simulated redox reaction zones to **B**, simulated redox water-chemistry zones for random organic carbon scenario, lower aquifer (layer 3). Cells shown in white represent areas where the lower aquifer is pinched out. The lower aquifer is represented by layer 3 in the model.

The variability of the dissolved Fe^{2+} concentration in the lower aquifer for this simulation (fig. 11) shows the extent of the mixing that occurs as a result of the interaction of the flow system with the electron-donor source areas. Although almost all of the lower aquifer in this hypothetical simulation is oxic, there are broad areas of elevated dissolved Fe^{2+} .

Sensitivity Analysis

The methodology described here for simulating redox at the field scale depends on inputs that control the solver strategy, rates of reaction, the availability of terminal electron acceptors, and the reactivity of electron donors. An analysis was performed to evaluate the sensitivity of the results to each category of input using a version of the random-source

scenario in which the source concentration cells are set to constant values of 100 mg/L instead of 20 mg/L. The high concentration of electron donors results in large areas across the lower aquifer with strongly reduced water for the base run (fig. 12). Each sensitivity run is a variation of the base run with one input changed. The change in outcome relative to the base run was quantified in terms of the redox water-chemistry zones (table 4)—specifically, the percentage of the lower-aquifer volume classified as strongly reducing and the ratio of the strongly reduced volume in the upper aquifer to that in the lower aquifer.

In the base sensitivity simulation, the volume of reduced water in the lower aquifer is 29.6 percent, and the ratio of the reduced volume in the upper to lower aquifer is 0.88, implying slightly more reduced water in the lower aquifer than in the upper aquifer.

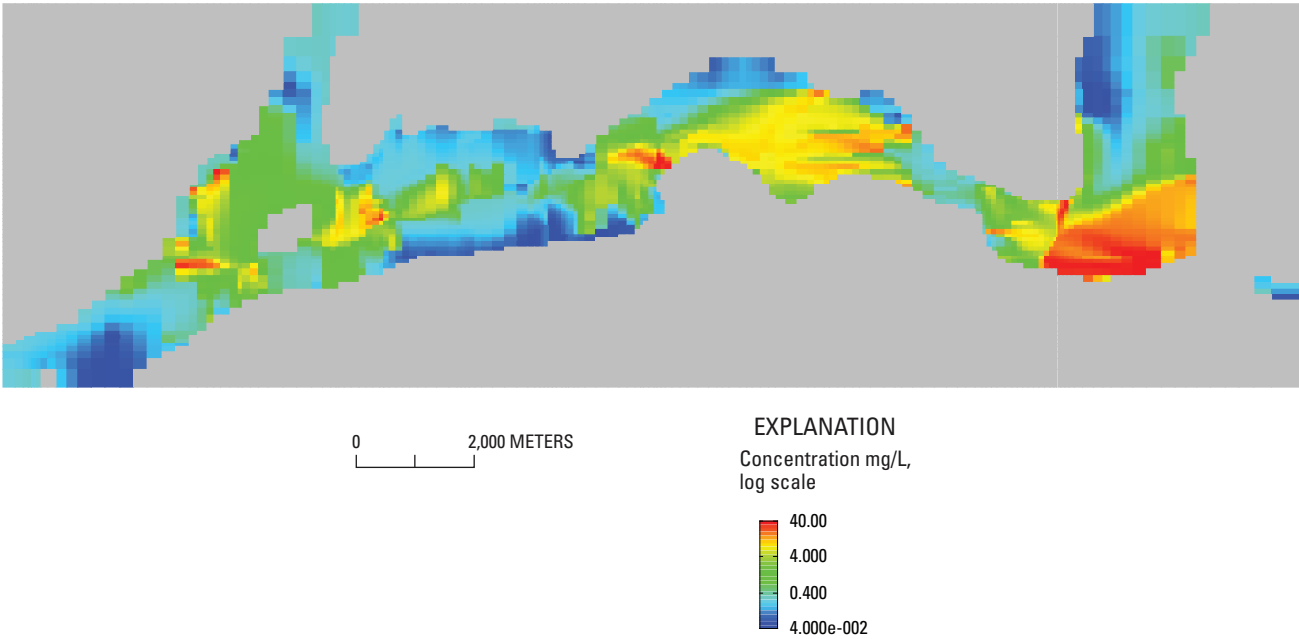


Figure 11. Simulated concentration of dissolved Fe^{2+} for random organic carbon scenario, lower aquifer (layer 3). Cells shown in white represent areas where the concentration is below 4.000e-002.

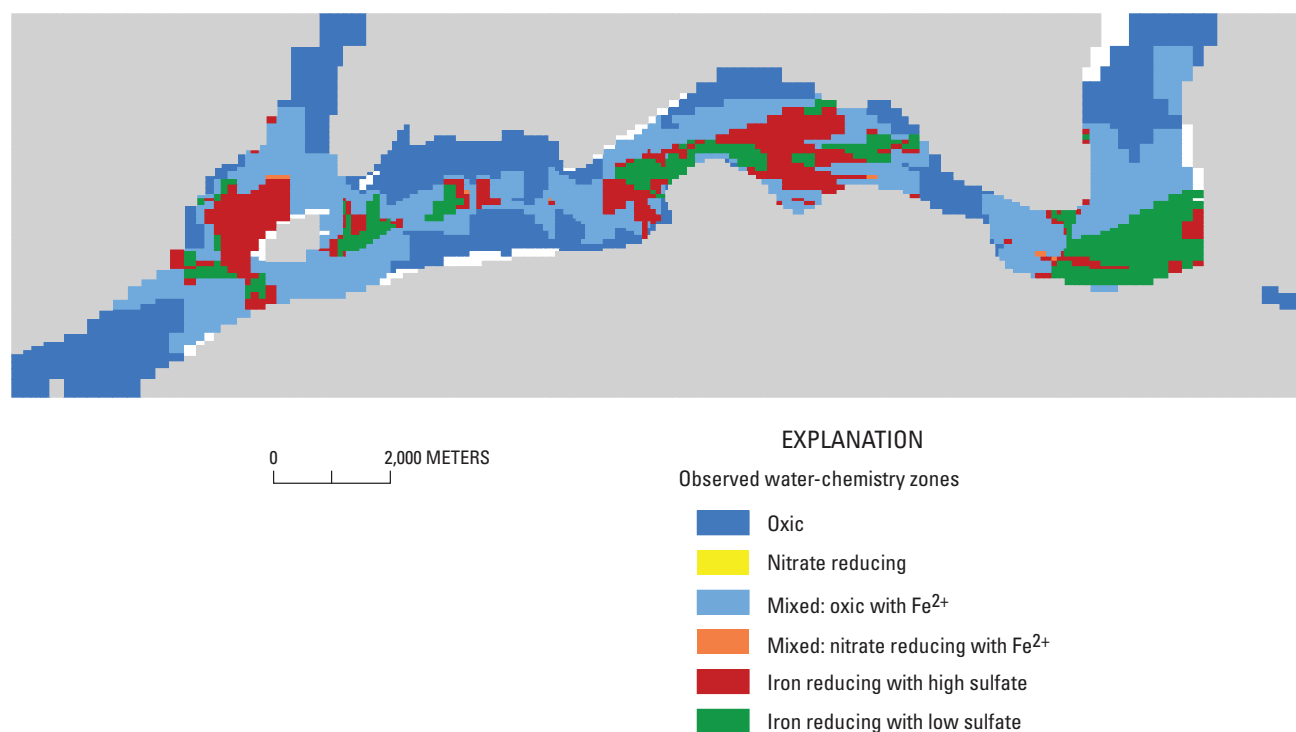


Figure 12. Random organic carbon scenario for sensitivity analysis ($C_{\text{source}} = 100 \text{ mg/L}$); simulated redox water-chemistry conditions in lower aquifer (layer 3). Cells shown in white represent areas where the lower aquifer is pinched out.

Sensitivity to Solver Strategy

The following was performed to test the robustness of the numerical solution: (1) the vertical discretization was increased within the confining unit, (2) the finite-difference solution, which is subject to numerical dispersion, was replaced with the TVD (total-variation-diminishing) solver, which requires longer runtimes but is less subject to numerical dispersion (Chunmiao and Wang, 1998), and (3) the transport time step was decreased from 5 days to 0.5 day. These input changes yield very small changes with respect to the reduced volume in the lower aquifer or the ratio of reduced volume in the upper to the lower aquifer (table 7). They imply that numerical dispersion does not strongly influence the solution.

Sensitivity to Attenuation Parameters

Attenuation parameters quantify processes that cause the concentration of a redox reactant to decrease. They include the assumed decay rate for the first-order reactions, the consideration of retardation, and the degree of assumed dispersion mostly to account for heterogeneities at a scale smaller than the grid size (table 7). The sensitivity runs show that the solution is insensitive to the first-order decay constant assumed in the organic carbon source areas, but it is moderately sensitive to an overall increase of the decay rate from 0.001 to

0.01 day^{-1} and strongly sensitive to a decrease from 0.001 to 0.0001 day^{-1} . In the latter case, the slow rate of reaction means that although the equilibrium volume of reduced water in the lower aquifer is small (8.5 percent), it is 4 times the volume in the upper aquifer.

Retardation of the electron donor has negligible effect on the equilibrium solution, whereas the choice of dispersivity parameters has moderate influence within the range tested (that is, an increase of 10 times causes a small increase of reduced water in the lower aquifer).

Sensitivity to Concentrations of Electron Acceptors

The background water quality was altered to test the sensitivity of the model to changes in concentrations of electron acceptors (table 7). For the alternate background water quality, concentrations were decreased for dissolved O_2 (from 6 to 4 mg/L), increased for NO_3 (from 0.2 to 9 mg/L), increased for Fe^{2+} (from 0.005 to 0.01 mg/L), and increased for SO_4 (from 10 to 100 mg/L). The alternate background water quality was judged to be representative of high-nitrate and high-sulfate waters from the glacial aquifer system in parts of Nebraska (Thomas, 2007). Results show that increasing the concentrations of electron acceptors in the recharge and river water yielded a lower volume of strongly reduced water in the lower

Table 7. Results of sensitivity simulations.

[mg/L, milligrams per liter; --, not applicable]

Simulation	Volume of strongly reduced water		Sensitivity
	Lower aquifer (percent)	Ratio of upper aquifer to lower aquifer	
Sensitivity to solver strategy			
Scenario: Random donor source concentration in upper aquifer = 20 mg/L	5.6	1.14	--
Base run: Source concentration changed to 100 mg/L	29.6	0.88	--
1. Lacustrine confining unit represented as 3 layers instead of 1	29.0	0.89	Weak
2. TVD solver instead of finite difference solver	29.2	0.83	Weak
3. Transport time step = 0.5 day instead of 5 days	29.5	0.88	Weak
Sensitivity to attenuation parameters			
Scenario: Random donor source concentration in upper aquifer = 20 mg/L	5.6	1.14	--
Base run: Source concentration changed to 100 mg/L	29.6	0.88	--
1. First-order rate constant in source areas = 0.1 instead of 0.001 day ⁻¹	29.9	0.89	Weak
2. First-order rate constant everywhere = 0.01 instead of 0.001 day ⁻¹	25.9	1.01	Moderate
3. First-order rate constant everywhere = 0.0001 instead of 0.001 day ⁻¹	8.5	0.27	Strong
4. Donor retardation = 10 instead of 1 outside of source areas	29.6	0.88	Negligible
5. Increased dispersivity by 10x: longitudinal = 10 feet instead of 1 foot	32.0	0.84	Moderate
Sensitivity to concentrations of electron acceptors			
Scenario: Random donor source concentration in upper aquifer = 20 mg/L	5.6	1.14	--
Base run: Source concentration changed to 100 mg/L	29.6	0.88	--
1. Alternate background water quality ¹	17.5	0.99	Strong
2. Nitrate loading: concentration in recharge set to 10 mg/L for 20 years	15.7	1.00	Strong
3. Maximum allowable dissolved Fe ²⁺ concentration 10 mg/L instead of 40 mg/L	29.7	0.89	Weak
Sensitivity to electron-donor behavior			
Scenario: Random donor source concentration in upper aquifer = 20 mg/L	5.6	1.14	--
Base run: Source concentration changed to 100 mg/L	29.6	0.88	--
1. No electron-donor source areas, only in recharge and river water	0.0	--	Strong
2. Redox reactions only occur in electron donor source areas (fixed instead of mobile source)	0.1	37	Strong

¹ Recharge and river concentrations changed: O₂ from 6 to 4 mg/L, NO₃ from 0.2 to 9 mg/L, Fe²⁺ from 0.005 to 0.01 mg/L, and SO₄ from 10 to 100 mg/L.

aquifer at equilibrium conditions. Specifically, the relatively high concentration of dissolved nitrate causes more of the available organic carbon to be exhausted when going from aerobic to nitrate conditions and, therefore, redox reactions cease in many areas before attaining strongly reduced conditions.

The influence of nitrate loading (due to fertilizer applications, for example) was evaluated by extending the equilibrium base solution for 20 years with 10 mg/L of nitrate added to recharge. The effect is similar to the case above: the sequential reactions in much of the lower aquifer never pass beyond the nitrate-reducing phase, so there is less strongly reduced water (table 7).

To test the sensitivity of the solution to the assumption that Fe^{2+} produced by the reduction of solid-phase Fe^{3+} cannot exceed an assumed amount, the maximum dissolved Fe^{2+} threshold was reduced from 40 mg/L to 10 mg/L. The effect of this change on the overall amount of strongly reduced water in the lower aquifer is weak (table 7), but the distribution of reduced water shifted from plentiful iron-reduced water in the base case to more sulfate-reduced water in the sensitivity run.

Sensitivity to Electron-Donor Behavior

A sensitivity run was done to test the effect of limiting the availability of electron donors to the 1 mg/L dissolved organic carbon concentration assumed in the recharge water and river water (that is, the source areas of organic carbon were eliminated). Under this assumption, the oxygen supplied by the inflow to the upper aquifer overwhelms the low availability of electron donors to the point that there is no strongly reduced water in the lower aquifer (table 7).

The proposed methodology includes the key assumption that redox reactions between electron donors and electron acceptors continue to occur in the dissolved phase downgradient from the fixed electron donor source areas. In other words, it is assumed that a mobile dissolved source of electron donor carried downgradient by the ground water causes redox reactions to spread, although they tend to occur at a decreasing rate as the concentration of the dissolved electron donor declines. This conceptual framework is not necessarily consistent with typical behavior in the presence of localized anthropogenic electron donor sources, where almost all the reducing activity appears to occur in close proximity to the fixed, solid-phase source areas. It is not clear whether this model associated with contaminated sites is applicable to natural systems. But if, for testing purposes, the assumption is made that the locus of reaction in natural systems is limited to the solid-phase organic carbon, thereby eliminating downgradient reactions in the dissolved phase, then the volume of strongly reduced water in the lower aquifer drops to almost zero (table 7).

By calculating the difference in the rates of reaction between the base run with both fixed and mobile sources of reaction and the sensitivity run with only fixed sources, it is possible to determine what fraction of the reducing activity occurs in model cells defined as electron-donor source areas and what fraction occurs in downgradient waters. The rates of consumption of dissolved oxygen and sulfate (table 8) and the rates of production of Fe^{2+} and methane (table 8) are each about 4 times those in the base case than in the case of no downgradient reactions. Consequently, for the hypothetical geochemical conditions of the random-source case, about three-quarters of the activity occurs downgradient from the

Table 8a. Simulated degradation rates of redox reactants for mobile versus fixed electron donor source.

[All data are in kilograms per year; C_{source} , source concentration; mg/L, milligram per liter]

Simulated degradation rates of redox reactants (base sensitivity run: random organic carbon source, $C_{\text{source}} = 100$ mg/L)

Location of redox reaction	Organic carbon degradation	Dissolved oxygen degradation	Sulfate degradation
Redox reactions occur everywhere (fixed and mobile donor source)	715	385	252
Redox reactions occur in source areas only (fixed donor source)	0.0	86	68

Table 8b. Simulated production rates of redox products for mobile versus fixed electron donor source.

[All data are in kilograms per year; C_{source} , source concentration; mg/L, milligram per liter]

Simulated production rates of redox products (base sensitivity run: random donor source, $C_{\text{source}} = 100$ mg/L)

Location of redox reaction	Ferrous iron production	Methane production
Redox reactions occur everywhere (fixed and mobile donor source)	1,411	64
Redox reactions occur in source areas only (fixed donor source)	414	16

source areas. Further research would be needed to determine whether this is a realistic ratio or whether a greater proportion of the redox activity occurs in the fixed source areas.

Influence of Pumping on Distribution of Reduced Waters

The lower aquifer (model layer 3) in the bedrock valley along the Susquehanna River is important for water supply. Records show that in the 1980s, 21 municipal water-supply wells collectively discharged about 21 Mgal/d from the lower aquifer (Walcott and Coon, 2001). Model simulations of pumping produce a steady-state flow field with cones of depression around the wells (fig. 13).

According to the flow model, pumping discharges about 55 percent of inflow to the flow system from recharge and river loss. Pumping causes increased downward leakage from the upper to lower aquifer and an increased proportion of leakage (from 95 percent to 98 percent) in areas where the two aquifers are in contact.

The transport code was used to simulate the hypothetical geochemical response of the lower aquifer to the new flow field after 20 years of pumping for each of the three source scenarios. A major effect is to induce more oxygenated water from rivers into the subsurface and lower aquifer, thereby moderately increasing the extent of the oxic zones and moderately shrinking the size of the strongly reducing zones in the lower aquifer.

The effect of pumping on concentrations of redox reactants for the three hypothetical scenarios (table 9) indicates that, in general, the increased circulation of water due to pumping has a more pronounced effect on the chemistry of water entering wells than it does on the average concentration

of reactants across the entire lower aquifer. For example, the decrease in average Fe^{2+} concentrations is appreciable in well discharge for all three scenarios. This reflects the close connection of the deep aquifer to the shallow water bodies in the Susquehanna River Valley intervening low-permeability lacustrine deposits. The aquifers under study constitute an open system from the standpoint of redox, and pumping wells capture mostly young water.

The differences among scenarios are also noteworthy. For the random scenarios, the average dissolved oxygen concentration in the lower aquifer is minimally affected by pumping, but the dissolved oxygen in well water increases by 50 percent. In contrast, for the lacustrine and wetland scenarios, the dissolved oxygen concentrations in the aquifer and well water do not change greatly. These differences are at least partly attributable to the exact location of wells in relation to the organic carbon source areas and to areas of good hydraulic connection between the two aquifers. In the case of the random scenario, the wells are able to draw mostly young water from well-oxygenated shallow areas that are not in close contact with electron-donor source areas. In the case of the lacustrine scenario, mixing of older water emanating from the large volume of organic-rich fine-grained material likely limits the increase of dissolved oxygen at the wells. In the case of the wetland scenarios, which locally produce the most reduced water, some wells show increased dissolved oxygen; however, the average value in all well water decreases slightly because some wells underlying wetlands capture very reduced water. The wetland scenario also shows, on average, less reduction in dissolved Fe^{2+} in well water than do the other two scenarios. These subtle differences indicate the difficulty in predicting the effect of pumping on redox conditions in well water without a good knowledge of both the flow field and the distribution of electron donors. This difficulty carries over to predicting the effect of pumping on redox-sensitive constituents.

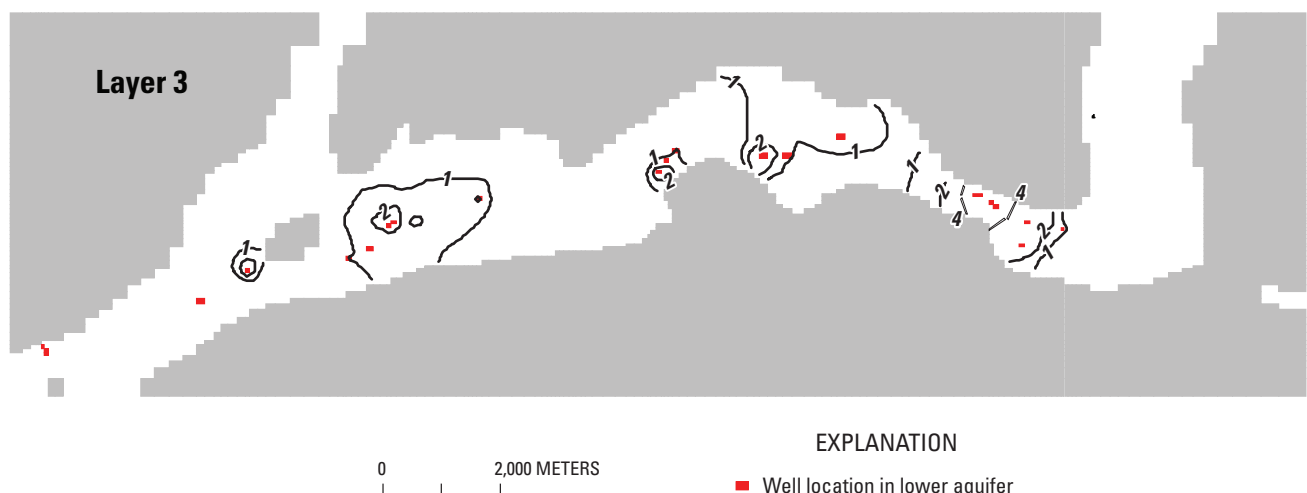


Figure 13. Simulated drawdown contours (meters) around pumping wells.

Table 9. Effect of pumping on concentrations of redox reactants for the three hypothetical scenarios.

[Concentrations are in milligrams per liter]

Scenario	Reactant	Average concentration in well boreholes in lower aquifer		Average concentration in entire lower aquifer	
		No pumping	20 years of pumping	No pumping	20 years of pumping
Random donor source	O ₂	2.8	4.2	4.2	4.1
	Fe ²⁺	4.5	0.7	1.7	1.6
	CH ₄	0.0	0.0	0.0	0.0
Lacustrine donor source	O ₂	4.5	5.0	4.6	4.4
	Fe ²⁺	4.9	1.5	4.5	3.1
	CH ₄	0.2	0.1	0.1	0.1
Wetland donor source	O ₂	3.9	3.7	5.1	4.8
	Fe ²⁺	10.2	7.3	1.7	2.1
	CH ₄	1.2	0.6	0.3	0.2

Limitations of the Study

The primary objective of this study was to show the importance of the ground-water flow field in determining the spread and distribution of reduced waters in a glacial valley-fill aquifer. Very different patterns of redox conditions are produced by the interaction of distinct organic carbon source areas with aspects of the ground-water flow field, such as (1) the degree of vertical connectedness between aquifers, and (2) local velocity variations induced by contrasts in hydraulic conductivity values of the unconsolidated glacial sediments. Pumping alters the ground-water flow field and, therefore, changes the distribution of strongly reduced water, most notably in the vicinity of a pumping well.

A chief limitation of this study is that the assumed distribution and concentration of organic carbon is hypothetical, although the flow model is calibrated to field observations and the transport inputs reflect real-world conditions. Consequently, the model results are useful primarily for advancing the general understanding of subsurface redox processes. Extension of this hypothetical methodology to other glacial settings (for example till and outwash plains) would add to the general understanding of the processes, but calibration to field studies would be necessary to test the predictive capability of the method.

A further limitation arises from the simplicity of the geochemical model adopted. The geochemical framework could be made more sophisticated in a variety of ways—for example, by substituting Monod for first-order kinetics (Wad-dill and Widdowson, 2000), by allowing for overlapping redox reactions (Schreiber and others, 2004), by allowing for sources and sinks of constituents such as sulfate within the subsurface (Chapelle and others, 1995) or—perhaps most importantly—by explicitly accounting for the transfer of iron from the solid to dissolved phase (Rolle and others, 2006). However, if the

methodology was to be applied to a field site where understanding of redox is important, such as an area of natural arsenic contamination, it would be advantageous to combine a sophisticated flow model with a simple geochemical framework requiring few parameters for calibration. Complexity in the geochemical model could be limited by calibrating to distinct first-order decay constants for each electron acceptor. A field application of the modeling methodology would work best in an area where the rate of flow is fast enough that the time to equilibrium of the reactants is relatively short (on the order of hundreds of years), resulting in relatively short computer runtimes.

An inherent assumption in the adopted geochemical model is that redox reactions occur away from the source areas of naturally occurring electron donors, although at a reduced rate according to a first-order law proportional to electron donor concentration. It is possible that reducing reactions are limited chiefly to the proximity of source areas so that the ground-water flow system serves only to spread reduced water rather than to spread both reduced water and reducing reactions. Application of the modeling methodology to an actual ground-water system might contribute to a better understanding of the amount of redox activity that actually occurs down-gradient from natural electron-donor sources.

An important assumption particular to this modeling effort is that the iron reduction state can be exhausted in the ground-water system because the reservoir of bioavailable iron in the glacial sediments is quite limited. It is assumed that its reduction *in the absence of any sorption or precipitation* would yield a maximum of only 40 mg/L of dissolved Fe²⁺. The distribution of bioavailable iron in distinct sediment types is still poorly understood, although some studied sites show levels of bioavailable iron that would support aqueous Fe²⁺ concentrations, net of sorption and precipitation, that are much higher than 40 mg/L (Bekins, 2001; Chapelle, 2002).

In natural settings, it would be particularly useful to obtain a suite of bioavailable iron measurements on sediments to better judge the likelihood that, in environments with plentiful electron-donor source areas, reducing conditions would stop at the iron-reducing phase (indicative of relatively high levels of bioavailable iron) or, alternatively, would move beyond it to sulfate-reducing and methanogenic conditions (indicative of low or possibly very low levels of bioavailable iron). It would also be useful to correlate concentrations of bioavailable iron in sediments with the age of the associated ground water and with naturally occurring contaminants that tend to accumulate in particular redox phases—arsenic, for example, which tends to dissolve in iron-reducing and methanogenic phases and to precipitate in sulfate-reducing phases (Smedley and Kinniburgh, 2002).

Conclusions

Recent studies have emphasized the connection between the dynamics of a ground-water flow field and the mobilization of redox-sensitive contaminants in terms of the relation between flow rates and the kinetics of redox reactions (Smedley and Kinniburgh, 2002; Harvey and others, 2006). To explore this link, the MODFLOW-MT3D-RT3D suite of code was applied to combine a ground-water flow model of a complex depositional system with a relatively simple geochemical model. The geochemical model posits that (1) reducing conditions are present in ground water when, due to microbial respiration, redox reactions involving electron donors and electron acceptors occur and (2) reactions are approximately first-order with respect to the electron donor and sequential with respect to electron acceptors. Hypothetical distributions of electron-donor sources such as organic carbon were simulated in conjunction with a real flow field typical of a heterogeneous glacial valley-fill aquifer to demonstrate how strongly reducing conditions can arise in areas not immediately adjacent to electron-donor source areas, such as an underlying aquifer, because of flow and mixing of water along three-dimensional flow paths. The modeling simulates the parts of the aquifer where strongly reduced water is present because the rate at which oxygenated water is introduced from the water table is insufficient to offset the rate of redox reactions fueled by available electron acceptors. By comparing the simulated spatial distribution of active redox reactions with the simulated spatial distribution of water chemistry, it is possible to identify the role of advection and dispersion in mixing waters and in transporting, for example, dissolved iron into oxic zones. Discharge from wells increases flow and mixing which, where the pumped aquifer is in close connection with shallow oxygenated waters, can reverse reduced conditions in ground water.

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