CONF-9710105--

1 Modeling Subsurface Contaminant Reactions and Transport at the Watershed Scale

2
3
4
5 Jin-Ping Gwo¹⁺, Glenn V. Wilson², Philip M. Jardine³, and Eduardo F. D'Azevedo⁴

6
7
8 ¹Center for Computational Sciences, ³Environmental Sciences Division, ⁴Computer
9 Sciences and Mathematics Division, Oak Ridge National Laboratory*, P.O. Box 2008,
10 Oak Ridge, TN 37831-6203

11
12 ²Water Resources Center, Desert Research Institute, P.O. Box 19040, Las Vegas, NV
13 89132

14
15 ⁺Corresponding author

16
17 Submitted to Chapman Conference on November 26, 1997

18
19
20 DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
21 *ph*

MASTER

22
23 *Managed by Lockheed Martin Energy Research Corp., under contract DE-AC05-

24 96OR22464 with the U.S. Department of Energy

DTIC QUALITY INSPECTED 3

19980402 055

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Abstract

The objectives of this research are (1) to numerically examine the multiscale effects of physical and chemical mass transfer processes on watershed scale, variably saturated subsurface contaminant transport and (2) to conduct numerical simulations on watershed scale reactive solute transport and evaluate their implications to uncertainty characterization and cost-benefit analysis. Concurrent physical and chemical nonequilibrium, caused by interaggregate gradients of pressure head and solute concentration and intraaggregate geochemical and microbiological processes, respectively, may arise at various scales and flowpaths. To this date, experimental investigations of these complex processes at watershed scale remain a challenge and numerical studies are often needed for guidance of water resources management and decision making. This research integrates the knowledge bases developed during previous experimental and numerical investigations at a proposed waste disposal site at the Oak Ridge National Laboratory to study the concurrent effects of physical and chemical nonequilibrium. Comparison of numerical results with field data indicates that (1) multiregion, preferential flow and solute transport exist under partially saturated condition and can be confirmed theoretically and that (2) mass transfer between pore regions is an important process influencing contaminant movement in the subsurface. Simulations of watershed scale, multispecies reactive solute transport suggest that dominance of geochemistry and hydrodynamics may occur simultaneously at different locales and influence the movement of one species relative to another. Execution times on the simulations of the reactive solute transport model also indicate that the model is

- 1 ready to assist the selection of important parameters for site characterization. Multiple
- 2 simulations based on these parameters may be conducted later to optimize the cost-
- 3 benefit ratio of remediation strategies before they are implemented.

Introduction

Spreading of contaminants in the subsurface environment is often dramatically complicated by the presence of preferential flowpaths and by the effect of local-scale mass transfer. For example, on the U.S. Department of Energy's Oak Ridge Reservation (ORR), low-level waste generated by energy-related research programs were often buried in unlined subsurface trenches that may subject to the direct influence of surface infiltration. These trenches were designed to confine the waste at one single locale for the ease of management and, if necessary, waste water collection and treatment. However, as suggested by one recent report (Solomon et al., 1992), "transport processes in the subsurface -- diffusion from fractures to the rock matrix, sorption, and exchange -- have resulted in an accumulation of contaminants downgradient of the sources." The rapid flow regime in the interconnected fracture networks causes quick and widespread movement of the contaminants; on the other hand, the slower, diffusive mass transfer processes between the fractures and rock matrix enhance the dispersion and storage of the contaminants in a scale much larger than the trenches. Over a period of 50 years or so, the nature of contamination has been transformed from point source primarily in the trench to secondary, distributed source in the soil matrix.

This transformation has been largely attributed to the coupled processes of preferential flow and diffusive mass transfer that are well documented in the literature (e.g., Shaffer et al., 1979; Seyfried and Rao, 1987; Jardine et al., 1990; McKay et al., 1993; Wilson et al., 1993; Reedy et al., 1996; Selim and Ma, 1997). The processes are caused primarily by the bimodal structure of soils and geological formations: (1)

1 fractures, cracks, interaggregate features, root channels, and animal burrows and (2) rock
2 matrix, clay lenses, and soil aggregates. In the case of the vadose zones on the ORR, the
3 B horizon is mostly silt and clay abundant in plant roots, animal burrows, and other
4 macroporous features. In the C horizon, a large number of fractures between the matrix
5 blocks of the saprolite are also visible (Dreier et al., 1987; Dorsch and Katsube, 1996).
6 The parent materials of these soil horizons are mostly interbedded shale and limestone
7 sequences. A recent survey suggested that nearly half of the United States' land surface
8 is derived from shale (Gonzales and Johnson, 1985). Adding to the consequences of this
9 widespread geological feature is the growing popularity of conservative tillage technique
10 that is designed to increase surface infiltration and soil water storage (Tanaka and
11 Anderson, 1997). Preferential flow resulting from the farming technique not only
12 deepens the migration of water and agrichemicals but also increases the risk of
13 groundwater contamination (Kladivko et al., 1991). It is therefore of great concerns and
14 interests that more scientific investigations be directed towards the multiscale effects and
15 implications of the coupled processes.

16
17 The objectives of this research is to numerically examine the multiscale effects of
18 physical and chemical mass transfer processes on watershed scale, variably saturated
19 subsurface contaminant transport. Multiplicity in physicochemical processes, as contrast
20 to heterogeneity in soil types and geological formations, is of particular interest to the
21 characterization efforts in which this research is involved. A tracer release at the Melton
22 Branch Watershed on the ORR (Wilson et al., 1993) has provided a solid basis for the
23 calibration and validation of multiregion subsurface flow and solute transport models in a
24 previous study (Gwo et al., 1994). In this study, the predicted tracer breakthrough is
25 further compared qualitatively with experimental data from a pedon-scale bromide tracer
26 release at the Walker Branch Watershed on the ORR (Jardine et al., 1990). Additionally,
27 as site characterization efforts gradually move towards mixed waste problems influenced

1 by coupled hydrogeological, geochemical and microbiological processes (e.g.,
2 <http://www.lbl.gov/NABIR/> and <http://www.esd.ornl.gov/programs/ETPI/>), there are
3 increasing needs for hydrogeochemistry modeling that may help identify important
4 reactive solute transport parameters and thus reduce characterization costs. Therefore,
5 hydrogeochemistry simulations of the Melton Branch Watershed were also conducted.
6 The interrelation of chemical speciation and watershed scale solute transport is examined
7 and the implication of these simulations to the feasibility of uncertainty and cost-benefit
8 analysis is evaluated.

11 **Field Site Hydrogeology and Mathematical Methodology**

13 Field scale numerical models of subsurface reactive solute transport are usually built on
14 conceptual understandings of a particular field site. Conceptual models derived from
15 these understandings assist in establishing hydrogeologic frameworks for the field site,
16 including hydrology, geochemistry, and characteristics of soils and geological
17 formations. Sound mathematical representations of the field site can then be formulated
18 and numerical models can be devised. The conceptual understanding of site specific
19 hydrogeology is therefore critical to the outcome of a field scale modeling exercise.

21 *Hydrogeology, Field Facilities, and Numerical Model of the Melton Branch Watershed*

23 Most of the waste disposal operations at the Oak Ridge National Laboratory (ORNL)
24 have historically taken place within the Conasauga group of the eastern Tennessee ridge
25 and valley areas. Because of this, tracer release and monitoring facilities for subsurface
26 solute transport were constructed in a 0.67 ha subcatchment of the watershed, or the
27 Melton Branch Experimental Station (MBES), in a deciduous forest located on the

1 Conasauga formation (Luxmoore and Abner, 1987). The strata of the Conasauga group
2 weather to a shallow (< 1m) B horizon soil overlying saprolite that retains the bedding
3 and structure of the parent limey shale rocks. The saprolite is highly fractured with
4 densities up to 200 fractures/m (Drier et al., 1987). Containing in the rock-like matrix
5 blocks between the fractures are μm -size fractures (microfractures) that are coated with
6 Fe and Mn oxides and contain translocated clay (Wilson et al., 1993). Preferential solute
7 transport was found to occur under partially saturated conditions through the
8 microfractures (Jardine et al., 1993). Average annual rainfall on the ORR is about 1250
9 mm (Moore and Toran, 1992). Waste storage problems at ORNL are typical of much of
10 the humid regions of the eastern United States where highly fractured materials are often
11 overlain by shallow soil horizons.

12
13 The MBES has been intensively characterized for spatial variability in chemical and
14 physical properties (Watson and Luxmoore, 1986; Wilson and Luxmoore, 1988; Wilson
15 et al., 1992). The geometric mean of hydraulic conductivity of the surface and
16 subsurface soil horizons were found to be 9.56×10^{-5} m/s and 0.76×10^{-5} m/s,
17 respectively, with lag distances less than 30 m on the basis of exponential correlation
18 models (Wilson et al., 1989). Additionally, natural-recharge, event-driven tracer releases
19 were conducted in February 1991 to study field-scale solute transport under variably
20 saturated conditions, during which subsurface stormflow discharge and solute
21 breakthrough were closely monitored in a subsurface trench located at the convergent
22 area of the subcatchment (Fig. 1b). The subsurface trench measures 2 m deep by 16 m
23 wide. Six stainless steel pans were pressed into the face of the trench to intercept
24 subsurface outflow. Two H-flumes equipped with Manning ultrasonic level recorders
25 were positioned in the trench to measure integrated flow rates of the six pans, a surface
26 runoff collector, and water from below the pans (1.8-2.0m) (Wilson et al., 1993). A
27 buried line source of length 6 m at the depth of 0.5 m is located at the top of the eastern

hillslope, and 15 banks of tensiometers and transducers were installed downslope of the line source (Fig. 1a). Fifteen additional piezometers were also installed at two nearly orthogonal transects to monitor subsurface stormflow dynamics.

For numerical studies to be described later, the soils are conceptualized to be composed of three pore regions: macropore, mesopore, and micropore (equivalent pore size > 0.1 cm, between 0.1 cm and 0.001 cm, and < 0.001 cm, respectively, see Luxmoore, 1981 and Wilson et al., 1992). A pore region is a flow domain that possesses discernable mass transport characteristics and is identified by transport parameters unique to the pore region only. Mass transfer between pore regions is driven by advection and diffusion caused by interregion hydraulic and concentration gradients, respectively (Fig. 2). A Cauchy boundary with variable rainfall rates is used for the soil surface of the finite-element numerical model, and the trench face is chosen to be a seepage boundary. No-flux boundaries are used for the other sides of the numerical model. For each change of rainfall intensity, the initial time step size is 0.1 hour and is increased by 10% for the subsequent time steps. A typical vertical cross-section of the three-dimensional model has a B horizon of depth 0.3 m near the top of the ridge and 1.5 m near the trench. The C horizon extends from the bottom of the B horizon to the bedrock at depths 3 m to 5 m. The hydraulic and solute transport parameters of the numerical model are listed in Table 1. Corresponding water retention and hydraulic conductivity relationships can be found in Table 2.

Mass Conservation Laws of Reactive Solute Transport

Translation of mechanistic, multiscale understandings of hydrogeochemistry into mathematical representation usually involves complicated volume averaging (e.g.,

1 Hassanizadeh, 1986) or homogenization (e.g., Arbogast et al., 1989) operations that
 2 integrates numerous microscopic thermomechanic and hydrodynamic processes. On the
 3 other hand, numerical schemes such as finite element and finite difference methods often
 4 use building blocks of macroscopic sizes (meters to tens of meters) for watershed models.
 5 A building block of macroscopic sizes may be very heterogeneous locally (e.g., see
 6 <http://www.ccs.ornl.gov/staff/gwo/champman.html>) and local-scale preferential solute
 7 transport may result. This gap between mechanistic understanding and numerical
 8 representation has prompted numerous studies to resolve the physical and chemical
 9 nonequilibrium caused by local scale heterogeneity (e.g., van Genuchten and Wierenga,
 10 1976; Rao et al., 1980; Skopp et al., 1981; Beven and Germann, 1982; Seyfried and Rao,
 11 1987; Brusseau et al., 1989; Jardine et al., 1990; Wilson et al., 1992; Gerke and van
 12 Genuchten, 1993; Tsuboyama et al., 1994; Gwo et al., 1996a; Mohanty et al., 1997). On
 13 the basis of the mechanistic understandings derived from previous laboratory and field
 14 studies at the Melton and Walker Branch Watersheds (Wilson and Luxmoore, 1988;
 15 Jardine et al., 1990; Wilson et al., 1992; Wilson et al., 1993), a three-region pore structure
 16 model, originally proposed by Luxmoore (1981), is used in this study. The three-pore-
 17 region mass conservation of water can be described by the following equations (e.g.,
 18 Duguid and Lee, 1977; Gwo, 1992; Gerke and van Genuchten, 1993; Hutson and
 19 Wagenet, 1995; Gwo et al., 1996):

$$\frac{\partial \theta_i}{\partial t} = \nabla \cdot (\mathbf{K}_i \cdot \nabla (h_i + z)) + Q_i - \sum_{\substack{k=1 \\ k \neq i}}^3 \varepsilon_{ik}^f (h_i - h_k), \quad i = 1, 2, 3, \quad (1)$$

$$\mathbf{v}_i = -\mathbf{K}_i \nabla (h_i + z), \quad i = 1, 2, 3, \quad (2)$$

24
 25 where t , θ_i , h_i , z , $\mathbf{v}_i$, Q_i , and $\mathbf{K}_i$ are time (T), water content, pressure head (L), elevation

(L), fluid velocity vector (L/T), external fluid sources ($L^3/L^3/T$), and the hydraulic conductivity tensor (L/T), respectively. Note in eq. (2) that we assume that Darcy's law is valid in describing the specific discharge of the pore regions. The last term in eq.(1) is the internal source term resulting from mass transfer between pore domains, in which ϵ_{ik}^f (1/LT) is the advective mass transfer coefficient between pore domains i and k and is a function of hydraulic conductivity and soil aggregate geometry (e.g., Duguid and Lee, 1977). Similarly, the solute transport equation of an aqueous component j can be represented by the following equations (Skopp et al., 1981; Gwo, 1992; Gerke and van Genuchten, 1993; Hutson and Wagenet, 1995; Gwo et al., 1996):

$$\begin{aligned} \frac{\partial T_{i,j}}{\partial t} + \frac{\partial \theta_i}{\partial t} (S_{i,j} + P_{i,j}) = & -\mathbf{v}_i \cdot \nabla C_{i,j} + \nabla \cdot (\theta_i \mathbf{D}_i C_{i,j}) - \theta_i \Lambda_{i,j}^a + M_{i,j}^a - Q_i C_{i,j} \\ & + \sum_{\substack{k=1 \\ k \neq i}}^3 \epsilon_{ik}^f (h_i - h_k) C_{i,j}^* - \sum_{\substack{k=1 \\ k \neq i}}^3 \epsilon_{ik}^f (h_i - h_k) C_{i,j} - \sum_{\substack{k=1 \\ k \neq i}}^3 \epsilon_{ik}' (C_{k,j} - C_{i,j}) \end{aligned} \quad (3)$$

where $T_{i,j}$, $S_{i,j}$, $P_{i,j}$, $C_{i,j}$ are the total analytical concentration (M/L^3), the concentration (M/L^3) in the absorbed, the precipitated, and the aqueous phases, respectively; $\Lambda_{i,j}$ and $M_{i,j}$ are decay and source/sink rates ($M/L^3/T$); and $\mathbf{D}_i$ is the hydrodynamic dispersion tensor (L^2/T). The last three terms in eq.(3) represent the contribution of advective mass transfer from an upstream pore region to the pore region of interest i , the advective mass transfer between pore domains i and k , and the diffusive mass transfer. The upstream concentration $C_{i,j}^*$ is a function of the hydraulic gradient and the diffusive mass transfer is characterized by the coefficient ϵ_{ik}' (1/T), which is a function of molecular diffusion coefficient, tortuosity, and soil aggregate geometry (e.g., Rao et al., 1980; van

1 Genuchten, 1985). The mass balance equation of an absorbent component j is (Yeh and
2 Tripathi, 1990; Gwo and Yeh, 1997):

3

$$4 \quad \theta_i \frac{\partial W_{i,j}}{\partial t} + \frac{\partial \theta_i}{\partial t} W_{i,j} = -\theta_i \Lambda_{i,j}^s + M_{i,j}^s, \quad (4)$$

5

6 where $W_{i,j}$ is the total absorbent analytical concentration (M/L^3). The balance equation of
7 ion-exchange site is similarly represented by (Yeh and Tripathi, 1990; Gwo and Yeh,
8 1997):

9

$$10 \quad \theta_i \frac{\partial N_{i,eq}}{\partial t} + \frac{\partial \theta_i}{\partial t} N_{i,eq} = -\theta_i \Lambda_{i,eq} + M_{i,eq}, \quad (5)$$

11

12 where $N_{i,eq}$ is the number of equivalents of the ion-exchange site per volume of solution
13 (M/L^3). In equations throughout this section, the superscript a and s , and the subscript i
14 and eq represent aqueous phase, solid phase, pore region, ion-exchange sites,
15 respectively. The law of mass action for aqueous complex species j is (Yeh and Tripathi,
16 1990; Gwo and Yeh, 1997):

17

$$18 \quad A_{i,j}^x = K_{i,j}^x \prod_{k=1}^{N_a} X_{i,k}^{a_k}, \quad (6)$$

19

20 where $A_{i,j}^x$ and $X_{i,k}^{a_k}$ are the activities (M/L^3) of the complex and aqueous component
21 species, respectively; $K_{i,j}^x$ is the equilibrium constant, N_a is the number of aqueous

1 components, and a_{jk}^x is the stoichiometric coefficient. The law of mass action for
 2 absorbed species j can be represented by (Yeh and Tripathi, 1990; Gwo and Yeh, 1997):

3

$$4 \quad B_{i,j}^y = K_{i,j}^y \left(\prod_{k=1}^{N_i} X_{i,k}^{a_{jk}^y} \right) \left(\prod_{k=1}^{N_s} Y_{i,k}^{b_{jk}^y} \right), \quad (7)$$

5

6

7

8 where $B_{i,j}^y$ and $Y_{i,k}^{b_{jk}^y}$ are the activities (M/L^3) of the absorbed and absorbent component

9

species, respectively, $K_{i,j}^y$ is the equilibrium constant, N_s is the number of absorbent

10 species, and a_{jk}^y and b_{jk}^y are the stoichiometric coefficients. The law of mass action for

11 ion-exchange species j is represented as (Yeh and Tripathi, 1990; Gwo and Yeh, 1997):

12

$$13 \quad K_{i,jk} = \left(\frac{B_{i,j}}{A_{i,j}} \right)^{v_k} \left(\frac{A_{i,k}}{B_{i,k}} \right)^{v_j}, \quad (8)$$

14

15 where $K_{i,jk}$ is the effective equilibrium constant of the ion-exchanged species, $A_{i,j}$ and $B_{i,j}$

16 are the activities (M/L^3) of an aqueous species and an ion-exchanged species, and v is the

17 charge of an ion-exchanged species. The law of mass action for a precipitated species is

18 (Yeh and Tripathi, 1990; Gwo and Yeh, 1997):

19

$$20 \quad 1 = K_{i,j}^p \prod_{k=1}^{N_d} X_{i,k}^{a_{jk}^p}, \quad (9)$$

21

1 where $K_{i,j}^p$ is the equilibrium constant. The superscript x , y , and p in eqs.(6), (7) and (9),
2 suggest complexed, absorbed, and precipitated species, respectively. The subscript jk of
3 a and b suggests the association of aqueous and absorbent component species k with the
4 complexed, precipitated, and absorbed species j , respectively. Redox and acid-base
5 reactions are considered as subclasses of aqueous complexation by invoking the principle
6 of electron conservation and the proton condition, respectively. With appropriate
7 boundary conditions, eqs.(1) - (9) completely define a multiregion hydrogeochemical
8 system.

9 10 *Parallel Supercomputer Model of the Melton Branch Watershed*

11
12 Watershed scale models are often built with imperfect information of the subsurface and
13 uncertainties associated with model parameters and processes arise inevitably. In order
14 to characterize the uncertainties, modern applications of these computer models may
15 therefore involve in multiple executions of complicated computer codes. Consequently,
16 there are compelling needs for computational capacity and efficient numerical
17 algorithms. This study uses a suite of high performance FORTRAN codes: 3DMURF
18 and 3DMURT (D'Azevedo and Gwo, 1997), PFEM (West and Toran, 1994), and
19 PHGC3D (Gwo and Yeh, 1997), that implement highly efficient parallel algorithms. The
20 multiregion flow and solute transport codes, 3DMURF (3-Dimensional MUltiRegion
21 subsurface Flow) and 3DMURT (3-Dimensional MUltiRegion solute Transport),
22 respectively, were used to study a single-species, multiregion solute transport problem
23 that will be discussed later. The variably saturated flow code PFEM (Parallel Finite

1 Element Model for variably saturated subsurface flow) and the multispecies
2 hydrogeochemistry code PHGC3D (Parallel HydroGeoChemistry, 3-Dimensional) were
3 used to study a uranium tailing problem that will be detailed in the next section. The
4 numerical model of the MBES consists of 10,500 elements and 12,090 nodes. For the
5 single-species, multiregion solute transport problem, each of the finite element nodes
6 accommodates three pore regions or three degrees of freedom. The entire model,
7 therefore, consists of 36,270 degrees of freedom. The uranium mill tailing problem
8 includes 7 chemical components that result in 84,630 degrees of freedoms for solute
9 transport calculations and 49 nonlinear algebra equations on each node, or more than half
10 a million equations in the entire MBES model, for chemical equilibrium calculations.
11 The MBES model was decomposed into multiple subdomains consisting of thousands of
12 degrees of freedom (Fig. 3). Each of these subdomains is mapped onto a processor of a
13 parallel computer so that reactive solute transport can be simulated efficiently on an array
14 of processors. The efficiency gain of such implementation will be discussed in the next
15 section.

18 **Solute Transport Modeling of the Melton Branch Watershed**

19

20 Two simulation scenarios were examined in this study: (1) single species solute transport
21 in multiple pore regions and (2) multispecies reactive solute transport in one single pore
22 region. The first scenario was designed to simulate a bromide tracer release at the MBSE
23 conducted in February 1991 (Wilson et al., 1993). As a result, we are able to compare
24 field observation and model prediction and to conclude on the likelihood of preferential

1 solute transport under partially saturated conditions. Details about the comparison are
2 discussed later in this section. The second scenario was designed to examine the coupled
3 geochemical and hydrogeological processes at the watershed scale and to test the
4 feasibility of multiple, field scale reactive solute transport simulations. Currently
5 available information regarding field scale hydrogeochemistry at the MBES does not
6 warrant detailed numerical studies of reactive solute transport, which may incur a high
7 degree of uncertainty. However, numerical studies of hypothetical scenarios have
8 become feasible, given the recent advances in parallel algorithms and the exponential
9 growth in computational power. Results from these studies are presented later in this
10 section and the implication to sensitivity analysis that may be translated into uncertainty
11 and risk assessment is discussed.

12

13 *Field Scale Bromide Tracer Release*

14

15 A series of subsurface tracer release was conducted in February 1991 at the MBES to
16 study field scale solute transport under variably saturated conditions (Wilson et al.,
17 1993). The tracer release lasted for 16.5 hours, at a rate of $0.194 \text{ m}^3/\text{h}$ with a solution
18 concentration 8000 mg Br/L (as MgBr_2). Tracer migration was driven by a series of
19 storm events from February 17 to 23 and the natural gradient thus incurred in the
20 subsurface. Water content and groundwater table fluctuation were intensively monitored
21 at the tensiometer banks and transducer transects during and after the storms.
22 Measurements of subsurface flow rates and soil horizon Br concentrations were also
23 taken regularly from discharge water in the subsurface trench during and after the tracer
24 release (Wilson et al., 1993). The bromide concentrations and subsurface flow rates of

1 the C horizon are reproduced in Fig. 4, in which predicted, flux-averaged Br
2 concentrations from the three-pore-region model were also given. A series of storms
3 prior to the tracer injection were used to calibrate the model to obtain optimal advective
4 mass transfer coefficients. Measured hydraulic properties, dispersion coefficients
5 upscaled from laboratory tracer studies (Gwo et al., 1995), and diffusive mass transfer
6 coefficients calculated using available information in the literature were used to predict
7 subsurface flow rates and bromide concentrations during the storm events of February
8 17-23 (Gwo et al., 1994).

9
10 The simulation results are reasonably satisfactory, with minimal amount of calibration
11 and validation efforts. The predicted bromide concentrations, as shown in Fig. 4, are two
12 times of the measured and have more variations that may be caused by the simulation
13 time-steps that are much finer than the measurement intervals. These variations, in
14 addition, indicate the contribution from the macropores and mesopores in which flow
15 rates and concentration variations are more likely to be affected by surface recharge than
16 the micropores. Evidences of such connection were previously observed in the Walker
17 Branch Watershed where a two-pore-region solute transport experiment was conducted
18 on a soil pedon (Jardine et al., 1990). The movement of bromide in the soil pedon was
19 driven by natural rainfall events and measurements of bromide concentration were taken
20 at two suction heads representative of the micropores and mesopores. The experimental
21 data obtained at the depth of 120 cm is reproduced in Fig. 5, together with the predicted
22 three-pore-region bromide concentration history in the C horizon of the MBES. The
23 striking resemblance of the concentration variations in the two large pore regions (Fig.

1 5a) with those measured in the large pores (Fig. 5b), and similarly, those in the
2 micropores (Fig. 5a) with those in the small pores (Fig. 5b), suggest qualitatively the
3 following:

- 4
- 5 1. Natural rainfall events may trigger preferential flow and solute transport under
- 6 partially saturated conditions that are frequently observed in forested watersheds.
- 7 2. Preferential flow and solute transport may occur through large pore domains
- 8 while mass transfer results in exchange of water and solutes between pore
- 9 domain.
- 10 3. Multiregion flow and solute transport processes can be experimentally observed
- 11 and theoretically confirmed.

12

13 Preferential flow and solute transport under partially saturated conditions have been

14 experimentally observed previously (e.g., Watson and Luxmoore, 1986; Wilson and

15 Luxmoore, 1988; Jardine et al., 1990; Vepraskas et al., 1991; Jardine et al., 1993). This

16 study theoretically confirms the phenomenon by qualitatively comparing field

17 experimental data with numerical results. Previous investigations also suggest that mass

18 transfer processes between pore regions are responsible for phenomena such as matrix

19 diffusion (e.g., Sudicky and Frind, 1981; Maloszewski and Zuber, 1991; Jardine et al.,

20 1993; Ma and Selim, 1995; Reedy et al., 1996). The steady increase of solute

21 concentrations in the small pores in both experimental and numerical results also

22 indicates the significance of these processes in subsurface solute transport, as has been

23 suggested in previous investigations (e.g., Maloszewski and Zuber, 1985; Jardine et al.,

1 1990; Solomon et al., 1992; Reedy et al., 1996). Finally, in addition to the results
2 presented here and previous studies (e.g., Wilson et al., 1993; Gwo et al., 1994; Gwo et
3 al., 1995), recent experimental and modeling studies (Tsuboyama et al., 1994; Mohanty
4 et al., 1997) also confirm the significance of multiregion mass transport phenomenon.

5

6 *A Hypothetical Scenario of Field Scale Reactive Solute Transport*

7

8 A hypothetical scenario of waste treatment tank leakage of uranium mill tailings is
9 simulated to examine the coupled geochemical and hydrogeological processes and to
10 study the feasibility of multiple, field scale reactive solute transport modeling. Uranium
11 mill tailing is part of the legacy of the Manhattan project and the Atomic Energy
12 Commission from 1940s to 1960s. The waste discharge from the processing of uranium
13 ores is often very acidic and has resulted in various health hazard to communities
14 downstream and downwind of the mills (The Task Commission on Low-Level
15 Radioactive Waste Management of the Technical Committee on Nuclear Effects, 1986).
16 The hypothetical scenario simulates a leakage event of constant source term, with the
17 total analytical concentration of uranium at 5.0×10^{-4} M and H^+ at 2.0×10^{-2} M, into an
18 aquifer of initial, total uranium concentration at 1.0×10^{-7} M and H^+ at 1.0×10^{-3} M.
19 The acidic leachate, consisting of UO_2^{2+} , H^+ , Ca^{2+} , CO_3^{2-} , PO_4^{3-} , SO_4^{2-} , and Fe^{2+} as its 7
20 component species, enters the MBES from the southeastern corner (Fig. 6). At the
21 beginning of the simulation, the computed pH in the tailing waste is 1.3 and that of the
22 aquifers is 7.6. The tailing is supersaturated with gypsum and the aquifer with calcite.
23 The components are assumed to undergo equilibrium complexation, precipitation-
24 dissolution, and acid-base reactions to produce 49 product species (Table 3) while they

1 move from the source area to the subsurface trench where groundwater is collected. The
2 soil surface of the MBES model is taken as an infiltration-seepage boundary and the other
3 surfaces of the model, except the subsurface trench area, are set up as no-flux boundaries.
4 Subsurface water is allowed to freely discharge through the collection facilities in the
5 trench.

6
7 Two generic characteristics were observed in the hydrogeochemistry model of the
8 MBES. First, the movement of reactive solutes in the subsurface is often different from
9 that predicted by a single-species model, in which only one single total analytical
10 concentration of a concerned species is calculated. For example, the acid-base reactions
11 involving in H^+ , CO_3^{2-} , and PO_4^{3-} may result in precipitation of UO_2^{2+} in areas of high
12 PO_4^{3-} concentration and pH (~ 7) at the tailing plume front, which even models with non-
13 uniform adsorption parameters cannot adequately describe. Secondly, the interplay
14 between hydrodynamics and geochemistry may result in the dominance of geochemistry
15 in one area but hydrodynamics in another. Figure 6 depicts the isosurfaces of total
16 uranium and H^+ concentrations, at a simulation time of 26.5 days, in which geochemistry
17 near the source area dominates the movement of UO_2^{2+} and H^+ and results in effects
18 similar to retardation. On the other hand, the lack of a constant supply of H^+ causes the
19 pH near the subsurface trench area to slightly increase, which results in a concave surface
20 of H^+ concentration.

21
22 Reactive solute transport modeling tasks involving tens to hundreds of species in a
23 subcatchment usually need a large amount of computational power for a single code

1 execution that represents one likely scenario among hundreds or thousands. To
2 determine uncertainties from a hydrogeochemistry model such as the MBES would have
3 required 3 months to 2 years of CPU time on one single computational processor of
4 moderate speed. For practical applications, this is at best infeasible. However, the
5 coming of age of parallel supercomputers has dramatically improved the possibility of
6 such modeling efforts. Shown in Fig. 7 is the relative time of executing 8 time steps of
7 the MBES model on the Intel Paragon (xps35, see <http://www.ccs.ornl.gov>) managed by
8 the Center for Computational Sciences at ORNL. For the one processor case, 8 time
9 steps took about 20 hours to execute, while using 65 processors the execution time was
10 reduced to less than an hour. The speed-up of the MBES model, which is moderate
11 compared with the most optimized parallel computer codes of today, suggests that
12 techniques such as Monte Carlo and Latin-hypercube simulations may now be used, in a
13 timely fashion, to select important hydrogeochemistry parameters for site
14 characterization (e.g., Gwo et al., 1996) and to conduct preliminary cost-benefit analysis
15 for remediation strategy design (e.g., James, et al., 1996). Characterization funds thus
16 saved may be redirected to more elaborate laboratory and field experiments and scientific
17 discovery may be accelerated.

20 Summary and Conclusions

21
22 Aided by recent advances in computer technologies and scientific understanding of
23 subsurface biogeochemical processes, sophisticated models of the coupled

1 hydrogeological, geochemical, and microbiological processes have gradually become an
2 important tool for environmental decision-making. This study presents two simulation
3 scenarios that may be encountered in practical applications of these models. We have
4 investigated (1) a single species solute transport in multiple pore regions and (2) a
5 multispecies reactive solute transport in one single pore region using a numerical model
6 of the Melton Branch Watershed at the Oak Ridge National Laboratory. The result from
7 the first scenario was compared with experimental data at the Melton Branch Watershed
8 and the Walker Branch Watershed on the Oak Ridge Reservation. This comparison
9 suggests both quantitatively and qualitatively that (1) multiregion, preferential flow and
10 solute transport exist under partially saturated conditions and can be confirmed
11 theoretically and that (2) mass transfer between pore regions is an important process
12 influencing contaminant movement in the subsurface. Findings from the second scenario
13 suggest that dominance of geochemistry and hydrodynamics may occur simultaneously at
14 different locales in a watershed scale model and influence the movement of one species
15 relative to another. Execution times on the simulations of the reactive solute transport
16 model also indicate that the model is ready to assist the selection of important parameters
17 for site characterization. Multiple simulations based on these parameters may be
18 conducted later to optimize the cost-benefit ratio of remediation strategies before they are
19 implemented.

20

21 Study of multiscale effects of subsurface coupled processes on reactive solute transport is
22 a growing scientific discipline that requires multidisciplinary efforts. Future focus of this
23 research will emphasize integrated approaches that closely coordinate laboratory and

1 field scale experiments with multiscale modeling efforts through a graphical front end
2 (see <http://www.esd.ornl.gov/programs/ETPI/>). The modeling efforts will also utilize
3 existing geostatistical libraries (e.g., GSLIB, Deutsch and Journel, 1992) and adopt a
4 similar media scaling and conditional simulation approach (e.g., Miller and Miller, 1956;
5 Peck et al., 1977; Rockhold et al., 1996) to account for field scale heterogeneity with
6 minimal amount of characterization efforts. Eventually the goal is to be able to
7 characterize uncertainties efficiently and economically for engineering decision-making
8 and designs.

10 **Acknowledgment**

11
12 This research was previously supported by the Subsurface Sciences Program of the U.S.
13 Department of Energy under the direction of Dr. Frank Wobber. It is being supported by
14 the Environmental Technology Partnership Program of the U.S. Department of Energy
15 under the direction of Dr. Paul Bayer. The authors are also in debt to Dr. Gour-Tsyh Yeh
16 at the Pennsylvania State University for his programmatic support in hydrogeochemistry
17 model development.

19 **References**

- 20
21 Arbogast, T, J. Douglas, Jr., and U. Hornung. 1989. Derivation of the double porosity
22 model of single phase flow via homogenization theory. SIAM J. Math. Anal.
23 21(4): 823-836.

1

2 Beven, K. and P. Germann. 1982. Macropores and water flow in soils. Water Resour.
3 Res. 18: 1311-1325.

4

5

6 Brusseau, M. L., R. E. Jessup, and R. S. C. Rao. 1989. Modeling the transport of solutes
7 influenced by multiprocess nonequilibrium. Water Resour. Res. 25: 1971-1988.

8

9 D'Azevedo, E. F., and J. P. Gwo. 1997. Parallelization of a multiregion flow and
10 transport code using software emulated global shared memory and high
11 performance FORTRAN. In Tentner, A. (ed.), High Performance Computing
12 1997: Grand Challenges in Computer Simulation, p21-26.

13

14 Deutsch, C. V., and A. G. Journel. 1992. GSLIB, Geostatistical Software Library and
15 User's Guide. Oxford University Press, New York, 340pp.

16

17 Dorsch, J., and T. J. Katsube. 1996. Effective Porosity and Pore-Throat Sizes of
18 Mudrock Saprolite from the Nolichucky Shale Within Bear Creek Valley on the
19 Oak Ridge Reservation: Implication for Contaminant Transport and Retardation
20 Through Matrix Diffusion. ORNL/GWPO-025, Oak Ridge National Laboratory.

21

22 Dreier, R. B., D. K. Solomon, and C. M. Beaudoin. 1987. Fracture characterization in the
23 unsaturated zone of a shallow land burial facility. In: Flow and transport through

1 unsaturated rock, D. D. Evans and T. J. Nicholson (eds.), Geophysical Monograph
2 42: 51-59.

3
4 Duguid, J. O. and P. C. Y. Lee. 1977. Flow in fractured porous media. Water Resour.
5 Res. 13: 558-566.

6
7 Gerke, H. H. and M. T. van Genuchten. 1993. A dual-porosity model for simulating the
8 preferential movement of water and solutes in structured porous media. Water
9 Resour. Res. 29(2): 305-319.

10
11 Gonzales, S., and K. S. Johnson. 1985. Shales and Other Argillaceous Strata in the
12 United States. ORNL/Sub-84-64794-1, Oak Ridge National Laboratory.

13
14 Gwo, J.P. 1992. Multi-region Flow and Transport Modeling in Subsurface Media, Ph.D.
15 dissertation, The Department of Civil and Environmental Engineering, The
16 Pennsylvania State University.

17
18 Gwo, J. P., P. M. Jardine, G. V. Wilson, and G. T. Yeh. 1994. Modeling small-scale
19 physical non-equilibrium and large-scale preferential fluid and solute transport in
20 a structured soil. p465-472. In A. Peters, G. Wittum, B. Herrling, U. Meissner,
21 C. A. Brebbia, W. G. Gray, and G. F. Pinder (eds.), Computational Methods in
22 Water Resources X, Vol. 1. Kluwer Academic, Dordrecht.

23

- 1 Gwo, J. P., P. M. Jardine, G. V. Wilson, and G. T. Yeh. 1995. A multiple-pore-region
2 concept to modeling mass transfer in subsurface media. *J. Hydrol.* 164: 217-237.
3
- 4 Gwo, J. P., P. M. Jardine, G. V. Wilson, and G. T. Yeh. 1996a. Using a multiregion
5 model to study the effects of advective and diffusive mass transfer on local
6 physical nonequilibrium and solute mobility in a structured soil. *Water Resour.*
7 *Res.* 32: 561-570.
8
- 9 Gwo, J. P., L. E. Toran, M. D. Morris, and G. V. Wilson. 1996b. Subsurface stormflow
10 modeling with sensitivity analysis using a Latin-hypercube sampling technique.
11 *Ground Water* 34: 811-818.
12
- 13 Gwo, J. P., and G. T. Yeh. 1997. Application of a parallel 3-dimensional
14 hydrogeochemistry HPF code to a proposed waste disposal site at the Oak Ridge
15 National Laboratory. In Tentner, A. (ed.), *High Performance Computing 1997:*
16 *Grand Challenges in Computer Simulation*, p128-133.
17
- 18 Hassanizadeh, M., 1986. Derivation of basic equations of mass transport in porous
19 media, Part 1. Macroscopic balance laws. *Adv. in Water Resour.* 9: 196-206.
20
- 21 Hutson, J. L., and, R. J. Wagenet. 1995. A multiregion model describing water flow and
22 solute transport in heterogeneous soils. *Soil Sci. Soc. Am. J.* 59: 743-751.
23

- 1 James, B. R., J. P. Gwo, and L. E. Toran. 1996. Risk-cost decision framework for
2 aquifer remediation design. *J. Water Resour. Plan. and Manag.* 122: 414-420.
3
- 4 Jardine, P. M., G.V. Wilson, and R. J. Luxmoore. 1990. Unsaturated solute transport
5 through a forest soil during rain storm events. *Geoderma*. 46: 103-118.,
6
- 7 Jardine, P. M., G. K. Jacobs, and G. V. Wilson. 1993. Unsaturated transport processes in
8 undisturbed heterogeneous porous media: I. Inorganic contaminants. *Soil Sci.*
9 *Soc. Am. J.* 57: 945-953.
10
- 11 Kladivko, E. J., G. E. Van Scoyoc, E. J. Monke, K. M. Oates, and W. Pask. 1991.
12 Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in
13 Indiana. *J. Environ. Qual.* 20: 264-270.
14
- 15 Luxmoore, R. J. 1981. Micro-, meso-, and macroporosity of soil. *Soil Sci. Soc. Am. J.*
16 45: 671-672.
17
- 18 Luxmoore, R. J. and C. H. Abner. 1987. Field facilities for subsurface transport research,
19 DOE/ER 0329, US Department of Energy, Washington, D. C.
20
- 21 Ma, L., and H. M. Selim. 1995. Transport of a nonreactive solute in soils: A two-flow
22 domain approach. *Soil Sci.* 159(4): 224-234.
23

- 1 Maloszewski, P., and A. Zuber. 1985. On the theory of tracer experiments in fissured
2 rocks with a porous matrix. *J. Hydrol.* 79: 333-358.
3
- 4 Maloszewski, P., and A. Zuber. 1991. Influence of matrix diffusion and exchange
5 reactions on radiocarbon ages in fissured carbonate aquifers. *Water Resour. Res.*
6 27(8): 1937-1945.
7
- 8 McKay, L. D., R. W. Gillham, and J. A. Cherry. 1993. Field experiments in a fractured
9 clay till. 2. Solute and colloid transport. *Water Resour. Res.* 29: 3879-3890.
10
- 11 Miller, E. E., and R. D. Miller. 1956. Physical theory for capillary flow phenomena. *J.*
12 *Appl. Phys.* 27: 324-332.
13
- 14 Mohanty, B. P., R. S. Bowman, J. M. H. Hendrickx, and M. T. van Genuchten. 1997.
15 New piecewise-continuous hydraulic functions for modeling preferential flow in
16 an intermittent-flood-irrigated field. *Water Resour. Res.* 33: 2049-2063.
17
- 18 Moore, G. K. and L. E. Toran. 1992. Supplement to a Hydrologic Framework for the Oak
19 Ridge National Reservation, Oak Ridge, Tennessee, ORNL/TM-12191, Oak
20 Ridge National Laboratory.
21
- 22 Peck, A. J., R. J. Luxmoore, J. L. Stolzy. 1977. Effects of spatial variability of soil
23 hydraulic properties in water budget modeling. *Water Resour. Res.* 13: 348-354.

- 1
- 2 Rao, P. S. C., R. E. Jessup, D. E. Rolston, J. M. Davidson, and D.P. Kilcrease. 1980.
- 3 Experimental and mathematical description of nonadsorbed solute transfer by
- 4 diffusion in spherical aggregates. Soil Sci. Soc. Am. J. 44: 684-688.
- 5
- 6 Reedy, O. C., P. M. Jardine, G. V. Wilson, and H. M. Selim. 1996. Quantifying the
- 7 diffusive mass transfer of nonreactive solutes in columns of fractured saprolite
- 8 using flow interruption. Soil Sci. Soc. Am. J. 60: 1376-1384.
- 9
- 10 Rockhold, M. L., R. E. Rossi, and R. G. Hills. 1996. Application of similar media scaling
- 11 and conditional simulation for modeling water flow and tritium transport at the
- 12 Las Cruces trench site. Water Resour. Res. 32: 595-609.
- 13
- 14 Selim, H. M., and L. Ma. 1997. Physical Nonequilibrium in Soils: Modeling and
- 15 Application, Ann Arbor Press Inc., Chelsea, Michigan. (in press)
- 16
- 17 Seyfried, M. S., and P. S. C. Rao. 1987. Solute transport in undisturbed columns of an
- 18 aggregated tropical soil: preferential flow effects. Soil Sci. Soc. Am. J. 51:
- 19 1434-1444.
- 20
- 21 Shaffer, K. A., D. D. Fritton, and D. E. Baker. 1979. Drainage water sampling in a wet,
- 22 dual-pore soil system. J. Environ. Qual. 6: 255-259.
- 23

1 Skopp, J., W. R. Gardner, and E. J. Taylor. 1981. Solute movement in structured soils :
2 two-region model with small interaction. Soil Sci. Soc. Am. J. 45: 837-842.

3
4 Solomon, D. K., G. K. Moore, L. E. Toran, R. B. Dreier, and W. M. McMaster. 1992.
5 Status Report A Hydrologic Framework for the Oak Ridge Reservation,
6 ORNL/TM-12026, Oak Ridge National Laboratory.

7
8 Tanaka, D. L., and R. L. Anderson. 1997. Soil water storage and precipitation storage
9 efficiency of conservation tillage systems. J. Soil and Water Cons. 52(5): 363-
10 367.

11
12 Tsuboyama, Y., R. C. Sidle, S. Noguchi, and I. Hosoda. 1994. Flow and solute transport
13 through the soil matrix and macropores of a hillslope segment. Water Resour.
14 Res. 30(4): 879-890.

15
16 The Task Commission on Low-Level Radioactive Waste Management of the Technical
17 Committee on Nuclear Effects. 1986. Management of inactive uranium mill
18 tailing. J. of Environ. Engr., 112(3): 490-537.

19
20 van Genuchten, M. Th., and P. J. Wierenga. 1976. Mass transfer studies in sorbing
21 porous media I. analytical solutions. Soil Sci. Soc. Am. J. 40: 473-80.

22

- 1 van Genuchten, M. Th. 1985. A general approach for modeling solute transport in
2 structured soils. Proc. 17th Int. congress, IAH, Hydrogeology of Rocks of Low
3 permeability, Jan. 7-12, 1973, Tucson, AZ. Mem. Int. Assoc. Hydrogeol. 17(2):
4 513-526.
- 5
- 6 Vepraskas, M.J., A.G. Jongmans, M.T. Hoover, and J. Bouma. 1991. Hydraulic
7 conductivity of saprolite as determined by channels and porous groundmass. Soil.
8 Sci. Soc. Am. J. 55:932-938.
- 9
- 10 Watson, K. W. and R. J. Luxmoore. 1986. Estimating macroporosity in a forest watershed
11 by use of a tension infiltrometer. Soil Sci. Soc. Am. J. 50: 578-582.
- 12
- 13 West, O. M. and L. E. Toran. 1994, Development of a Three-Dimensional Groundwater
14 Flow Model for Western Melton Valley: Application of P-FEM to a DOE Waste
15 Site, ORNL/TM-12474, Oak Ridge National Laboratory.
- 16
- 17 Wilson, G. V., and R. J. Luxmoore. 1988. Infiltration, macroporosity, and mesoporosity
18 distribution on two forested watersheds. Soil Sci. Soc. Am. J., 52, 329-335.
- 19
- 20 Wilson, G. V., J. M. Alfonsi, and P. M. Jardine. 1989. Spatial variability of saturated
21 hydraulic conductivity of the subsoil of two forested watersheds. Soil Sci. Soc.
22 Am. J., 53, 679-685.
- 23

- 1 Wilson, G.V., P.M. Jardine, J.P. Gwo. 1992. Modeling the hydraulic properties of a
2 multi-region soil. Soil Sci. Soc. Am. J. 56: 1731-1737.
- 3
- 4 Wilson, G. V., P. M. Jardine, J. D. O'Dell and M. Collineau. 1993. Field-scale transport
5 from a buried line source in variably saturated soil. J. Hydrol. 145: 83-109.
- 6
- 7 Yeh, G.-T. and V. S. Tripathi. 1990. HYDROGEOCHEM, A Coupled Model of
8 HYDROlogic Transport and GEOCHEMical Equilibria in Reactive
9 Multicomponent Systems. ORNL-6371. Oak Ridge National Laboratory.

Tables

1

2

3 Table 1. Pore region hydraulic and solute transport parameters.

4

5 Table 2. Functional relations of pore-region water retention and hydraulic conductivity.

6

7 Table 3. Components and product species of the reactive solute transport model.

Figures

Figure 1. The Melton Branch Experimental Station and site facilities. Two transects of piezometers, a line source and 15 banks of tensiometers, solution samplers, and piezometers were instrumented (a) and a subsurface trench within which six stainless steel pans were used to collect subsurface water and two H-flumes were used to measure integrated flow rates were constructed at the convergent area (b).

Fig. 2. A three-pore-region multiregion mass transfer mechanism. The interregion mass flux is composed of advective and diffusive mass transfer. The pressure heads in the pore regions are represented by h_u , h_e , and h_i , for macropores, mesopores, and micropores, respectively.

Figure 3. Mapping of computational subdomains to processors on a massively parallel computer.

Figure 4. Observed flux rates and bromide concentration and predicted, flux-averaged three-pore-region bromide concentration of the C horizon.

Figure 5. Solute concentrations in pore regions, (a) predicted three-region bromide concentrations at MBES, and (b) observed two-region bromide concentrations at the Walker Branch Watershed. Notice the similar, quick response in the large pore regions and the steady increase in the small pore regions in both (a) and (b).

- 1 Figure 6. Isosurfaces of UO_2^{2+} at concentration 1.1×10^{-7} M/L and H^+ at 9.90×10^{-4} M/L.
- 2
- 3 Figure 7. CPU times of executing 8 time steps of the MBES model, relative to one single
- 4 processor on the Intel Paragon (100%). The optimal number of processors occurred at
- 5 65, where an 80% reduction of execution time was observed.

1 Table 1. Pore region hydraulic and solute transport parameters.

Properties	Macropores	Mesopores	Micropores
saturated water content, $\theta_{s\alpha}$	0.39	0.35	0.31
residual water content, $\theta_{r\alpha}$	0.35	0.31	0.0
γ_a (cm ⁻¹)	0.47	-	-
$h_{\theta\alpha}$ (cm)	-5	-	-
β_α (cm ⁻¹)	-	0.2212	0.0028
n_α	-	1.1456	1.379
saturated hydraulic conductivity, $K_{s\alpha}$ (cm-hr ⁻¹)	8.28	0.72	0.000234
ξ_α (cm ⁻¹)	8.5	7.32	1000
κ_α (cm ⁻¹)	0.65	0.03	0.00075
$h_{\kappa\alpha}$ (cm)	-15	-250	-15000
longitudinal dispersivity, $a_{L\alpha}$ (cm)	8.0046	12.007	26.682
^a anisotropy ratios of hydraulic conductivity and dispersivity, K_{sy}/K_{sx} , K_{sz}/K_{sx} , and $a_{T\alpha}/a_{L\alpha}$	0.1	0.1	1.0

- 2 ^a K_{sx} , K_{sy} , and K_{sz} are the saturated hydraulic conductivities in the principle x, y, and z
3 directions; and $a_{T\alpha}$ is the transverse dispersivity.

1 Table 2. Functional relations of pore-region water retention and hydraulic conductivity.

pore regions	water retention relation ^a	hydraulic conductivity relation ^b
macropores	$\theta_{\alpha} = \frac{\theta_{s\alpha} - \theta_{r\alpha}}{1 + \exp[-\gamma_{\alpha}(h - h_{\theta\alpha})]}$	$\text{Log}_{10}(K_{a\alpha} / K_{s\alpha}) = \frac{\xi_{\alpha}}{1 + \exp[-\kappa_{\alpha}(h - h_{\kappa\alpha})]} - \xi_{\alpha}$
mesopores	$\theta_{\alpha} = \frac{\theta_{s\alpha} - \theta_{r\alpha}}{[1 + (-\beta_{\alpha}h)^{n_{\alpha}}]^{m_{\alpha}}}$	$\text{Log}_{10}(K_{a\alpha} / K_{s\alpha}) = \frac{\xi_{\alpha}}{1 + \exp[-\kappa_{\alpha}(h - h_{\kappa\alpha})]} - \xi_{\alpha}$
micropores	$\theta_{\alpha} = \frac{\theta_{s\alpha} - \theta_{r\alpha}}{[1 + (-\beta_{\alpha}h)^{n_{\alpha}}]^{m_{\alpha}}}$	$\text{Log}_{10}(K_{a\alpha} / K_{s\alpha}) = \frac{\xi_{\alpha}}{1 + \exp[-\kappa_{\alpha}(h - h_{\kappa\alpha})]} - \xi_{\alpha}$

2 ^aThe definitions of parameters are: θ_{α} is the pore-region water content; $\theta_{s\alpha}$ and $\theta_{r\alpha}$ are the
3 saturated and residual pore-region water contents; γ_{α} , $h_{\theta\alpha}$, β_{α} , n_{α} , and $m_{\alpha}=1-1/n_{\alpha}$ are the
4 function parameters; and h is pore-region pressure heads.

5 ^bThe definitions of parameters are: h is pore-region pressure heads; $K_{a\alpha}$ and $K_{s\alpha}$ are
6 absolute and saturated pore-region hydraulic conductivities, and ξ_{α} , κ_{α} , and $h_{\kappa\alpha}$ are
7 equation parameters.

1 Table 3. Components and product species of the reactive solute transport model.

component	reaction	product species
Ca^{2+}	aqueous complexation	CaCO_3 , CaSO_4 , CaPO_4^-
	acid-base reaction	HCaCO_3^+ , $\text{CaH}_2\text{PO}_4^+$, CaHPO_4 , CaOH^+ , $\text{CaH}_4\text{UO}_2(\text{PO}_4)_2^{2+}$, $\text{CaH}_5\text{UO}_2(\text{PO}_4)_2^{3+}$
	precipitation-dissolution	CaSO_4 , CaCO_3 , $\text{Ca}_5\text{OH}(\text{PO}_4)_3$, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$, $\text{Ca}_4\text{H}(\text{PO}_4)_3$, CaHPO_4 , $\text{Ca}(\text{OH})_2$
CO_3^{2-}	aqueous complexation	CaCO_3 , UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$
	acid-base reaction	CaHCO_3^+ , $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, HCO_3^- , H_2CO_3
	precipitation-dissolution	CaCO_3 , FeCO_3 , UO_2CO_3
UO_2^{2+}	aqueous complexation	UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$
	acid-base reaction	UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_4(\text{OH})_7^+$, $(\text{UO}_2)_3(\text{OH})_7^-$, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, $\text{H}_2\text{UO}_2\text{PO}_4^+$, $\text{H}_3\text{UO}_2\text{PO}_4^{2+}$, $\text{CaH}_4\text{UO}_2(\text{PO}_4)_2^{2+}$, $\text{CaH}_5\text{UO}_2(\text{PO}_4)_2^{3+}$
	precipitation-dissolution	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$, $\text{UO}_2(\text{OH})_2$, UO_2CO_3 , $\text{Fe}(\text{UO}_2)_2(\text{PO}_4)_2$, $\text{HUO}_2(\text{PO}_4)_2$
PO_4^{3-}	aqueous complexation	CaPO_4^-
	acid-base reaction	$\text{CaH}_2\text{PO}_4^+$, CaHPO_4 , $\text{H}_2\text{UO}_2\text{PO}_4^+$, $\text{H}_3\text{UO}_2\text{PO}_4^{2+}$, $\text{CaH}_4\text{UO}_2(\text{PO}_4)_2^{2+}$, $\text{CaH}_5\text{UO}_2(\text{PO}_4)_2^{3+}$, HPO_4^{2-} , H_2PO_4^- , H_3PO_4
	precipitation-dissolution	$\text{Ca}_5\text{OH}(\text{PO}_4)_3$, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$, $\text{Ca}_4\text{H}(\text{PO}_4)_3$, CaHPO_4 , $\text{Fe}_3(\text{PO}_4)_2$, $\text{Fe}(\text{UO}_2)_2(\text{PO}_4)_2$, $\text{HUO}_2(\text{PO}_4)_2$
SO_4^{2-}	aqueous complexation	CaSO_4 , FeSO_4 , UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$
	acid-base reaction	HSO_4^-
	precipitation-dissolution	CaSO_4
Fe^{2+}	aqueous complexation	FeSO_4
	acid-base reaction	FeOH^+ , $\text{Fe}(\text{HO})_2$, $\text{Fe}(\text{HO})_3^-$, $\text{Fe}(\text{OH})_4^{2-}$
	precipitation-dissolution	FeCO_3 , $\text{Fe}_3(\text{PO}_4)_2$, $\text{Fe}(\text{HO})_2$, $\text{Fe}(\text{UO}_2)_2(\text{PO}_4)_2$
H^+	acid-base reaction	OH^- , HCaCO_3^+ , $\text{CaH}_2\text{PO}_4^+$, CaHPO_4 , CaOH^+ , FeOH^+ , $\text{Fe}(\text{HO})_2$, $\text{Fe}(\text{HO})_3^-$, $\text{Fe}(\text{OH})_4^{2-}$, UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_4(\text{OH})_7^+$, $(\text{UO}_2)_3(\text{OH})_7^-$, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, $\text{H}_2\text{UO}_2\text{PO}_4^+$, $\text{H}_3\text{UO}_2\text{PO}_4^{2+}$, $\text{CaH}_4\text{UO}_2(\text{PO}_4)_2^{2+}$, $\text{CaH}_5\text{UO}_2(\text{PO}_4)_2^{3+}$, HCO_3^- , H_2CO_3 , HSO_4^- , HPO_4^{2-} , H_2PO_4^- , H_3PO_4
	precipitation-dissolution	$\text{Ca}_5\text{OH}(\text{PO}_4)_3$, $\text{Ca}_4\text{H}(\text{PO}_4)_3$, CaHPO_4 , $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{HO})_2$, $\text{UO}_2(\text{OH})_2$, $\text{HUO}_2(\text{PO}_4)_2$

(a)

Figure 1. The Melton Branch Experimental Station and site facilities. Two transects of piezometers, a line source and 15 banks of tensiometers, solution samplers, and piezometers were instrumented (a) and a subsurface trench within which six stainless steel pans were used to collect subsurface water and two H-flumes were used to measure integrated flow rates were constructed at the convergent area (b).

(b)

SURFACE- AND SUBSURFACE-FLOW WEIR
AND MONITORING CELLAR

Figure 1. The Melton Branch Experimental Station and site facilities. Two transects of piezometers, a line source and 15 banks of tensiometers, solution samplers, and piezometers were instrumented (a) and a subsurface trench within which six stainless steel pans were used to collect subsurface water and two H-flumes were used to measure integrated flow rates were constructed at the convergent area (b).

$$h_a > h_e > h_i$$

macropores mesopores micropores

advective exchange
diffusive exchange

Fig. 2. A three-pore-region multiregion mass transfer mechanism. The interregion mass flux is composed of advective and diffusive mass transfer. The pressure heads in the pore regions are represented by h_a , h_e , and h_i , for macropores, mesopores, and micropores, respectively.

Figure 3. Mapping of computational subdomains to processors on a massively parallel computer.

Measured and Predicted Flux-Averaged Br Breakthrough, C horizon

Figure 4. Observed flux rates and bromide concentration and predicted, flux-averaged three-pore-region bromide concentration of the C horizon.

(a)

Figure 5. Solute concentrations in pore regions, (a) predicted three-region bromide concentrations at MBES, and (b) observed two-region bromide concentrations at the Walker Branch Watershed. Notice the similar, quick response in the large pore regions and the steady increase in the small pore regions in both (a) and (b).

(b)

Figure 5. Solute concentrations in pore regions, (a) predicted three-region bromide concentrations at MBES, and (b) observed two-region bromide concentrations at the Walker Branch Watershed. Notice the similar, quick response in the large pore regions and the steady increase in the small pore regions in both (a) and (b).

Figure 6. Isosurfaces of UO_2^{2+} at concentration 1.1×10^{-7} M/L and H^+ at 9.90×10^{-4} M/L.

PHGC3D Performance (Dec. 1996)

Figure 7. CPU times of executing 8 time steps of the MBES model, relative to one single processor on the Intel Paragon (100%). The optimal number of processors occurred at 65, where an 95% reduction of execution time was observed.

M98003140

Report Number (14) ORNL/CP--95547
CONF-9710165

Publ. Date (11) 199712

Sponsor Code (18) DOE, XF

JC Category (19) UC-900, DOE/ER

DOE