A Parallel Multiphase Numerical Model for Subsurface Contaminant Transport with Biodegradation Kinetics

Todd Arbogast
Clint N. Dawson
Mary F. Wheeler

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Center for Research on Parallel Computation
Rice University
P.O. Box 1892
Houston, TX 77251-1892

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A PARALLEL MULTIPHASE NUMERICAL MODEL FOR SUBSURFACE CONTAMINANT TRANSPORT WITH BIODEGRADATION KINETICS*

TODD ARBOGAST, CLINT N. DAWSON, and MARY F. WHEELER

Department of Computational and Applied Mathematics
Rice University
Houston, Texas 77251–1892
U.S.A.

ABSTRACT

We discuss the formulation of a simulator in three spatial dimensions for two phase groundwater flow and transport with biodegradation kinetics that has been developed at Rice University for massively parallel, distributed memory, message passing machines. The numerical procedures employed are a fully implicit mixed finite element method for flow and a characteristics-mixed method for transport and reactions of dissolved chemical species in groundwater. Domain decomposition solvers have been employed for solving the systems of equations resulting from the discretization of the model. Results from applying this simulator to a bioremediation field problem using a recirculation well in an air-water system are discussed.

1. INTRODUCTION

Microbial biodegradation is an innovative, emerging technology for handling subsurface water contamination [4,6,7,8,9,11,13,14,15,17]. It is a natural process that can be accelerated by the injection of certain nutrients such as dissolved oxygen, nitrates, and acetate. U.S. Environmental Protection Agency studies [15] have shown that this strategy can result in complete removal of contaminants, whereas other proposed restoration strategies have not proven as effective. Biodegradation technologies are being employed at several U.S. Department of Energy Laboratories in an effort to remove or contain volatile organic compounds.

Biological decontamination is physically and chemically complex. It involves flow and transport in both unsaturated soils and the aquifer, and the interaction of hydrocarbons, microbes, oxygen, nitrogen, and various other chemical compounds. Numerical simulation of these processes is a critical step in understanding and designing biorestoration applications [4,6,9,17]. Indeed, without computational science, wide scale in situ biodegradation of contaminants is impractical.

New parallel supercomputers, allowing simultaneous use of hundreds to thou-

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sands of processors, have greatly expanded the potential for building detailed models of these processes. Parallel computing provides the capability of solving larger, more realistic and practical problems faster and more economically. This includes the ability to use an adequately refined discretization mesh, to incorporate complex chemical and physical effects associated with the transport of both hydrocarbons and organic contaminants in porous media, and to employ stochastic or conditional simulation. The latter is essential for simulating a realistic geologic aquifer, since much of the data needed to characterize it cannot be quantified accurately, and since often the chemical and physical processes are not well understood.

Herein we emphasize the modeling of flow and transport for a two phase system, water and air. The development of our multiphase, three spatial dimension code, RPGW/MP, has involved combining and modifying two codes: RPGW, Rice Parallel Groundwater Code for transport and reactions [1,4,2], and PIERS, Parallel Implicit Experimental Reservoir Simulator for flow [16]. RPGW/MP is under development and future generalizations are discussed at the end of the paper.

The outline of the paper is as follows. In §2 we describe the governing flow and transport equations with biodegradation in an unsaturated/saturated porous medium. For simplicity, we assume linear sorption and aerobic conditions. More general kinetics such as Michaelis-Menton can be treated with the numerical techniques described in this paper. In §3, we describe the parallel implementation of the model, and in §4 we present three dimensional, parallel, bioremediation simulation results for a recirculation well problem. Conclusions and current directions on parallel implementation are given in §5.

2. TWO PHASE FLOW AND CONTAMINANT TRANSPORT WITH BIODEGRADATION

We first present the two phase flow model. It is very similar to the well known black oil model from petroleum engineering and the formulation presented by Parker [12]. The coupled equations are:

Water Phase
$$\frac{\partial(\phi\rho_w s_w)}{\partial t} + \nabla\cdot(\rho_w u_w) = Q_w + \gamma_w; \tag{1}$$

Air Phase
$$\frac{\partial(\phi\rho_a s_a)}{\partial t} + \nabla\cdot(\rho_a u_a) = Q_a + \gamma_a; \tag{2}$$

Equations of State
$$\rho_w = \rho_w^0 e^{c_w p_w}, \quad \rho_a = \rho_a^0 e^{c_a p_a}; \tag{3}$$

Darcy's Law
$$u_w = -\frac{K k_{rw}(s_w)}{\mu_w}(\nabla p_w - \rho_w g \nabla z), \tag{4}$$
$$u_a = -\frac{K k_{ra}(s_a)}{\mu_a}(\nabla p_a - \rho_a g \nabla z); \tag{5}$$

Capillary Pressure
$$p_c(s_w) = p_a - p_w; \tag{6}$$

Volume Balance
$$s_w + s_a = 1. \tag{7}$$

Here ϕ is porosity, p phase pressure, ρ phase density, K absolute permeability, k phase relative permeability, μ phase viscosity, s phase saturation, c phase compressibility, g gravitational constant, z depth, Q an external phase source or sink, and γ are source or sink terms due to mass transfer between phases (subscripts have been omitted for simplicity).

Multicomponent transport and biodegradation are governed by a system of advection-diffusion-reaction equations consisting of m_s electron donors (substrates) and m_n electron acceptors or nutrients, and a system of m_x ordinary differential equations involving microbial mass (transport of microbes can be treated also if one assumes instead a system of advection-diffusion-reaction equations for the microbes). They can be written in terms of the concentration dissolved in water, $C_i = C_i^w$, as:

Electron Donor (Substrate)
$$\frac{\partial(\phi_i C_i)}{\partial t} - \nabla \cdot (D_i \nabla C_i - u_i C_i) = \phi \chi_i + g_i, \quad i = 1, \ldots, m_s; \tag{8}$$

Electron Acceptor (Nutrient)
$$\frac{\partial(\phi_i C_i)}{\partial t} - \nabla \cdot (D_i \nabla C_i - u_i C_i) = \phi \chi_i + g_i, \quad i = m_s + 1, \ldots, m_s + m_n; \tag{9}$$

Microbial Mass
$$\frac{\partial(\phi C_i)}{\partial t} = \phi \chi_i, \quad i = m_s + m_n + 1, \ldots, m_s + m_n + m_x. \tag{10}$$

Since we assume that mass transfer between phases is based on equilibrium partitioning among the phases, we have

Equilibrium Phase Partitioning
$$C_i^a = \Gamma_{ia} C_i^w, \quad C_i^s = \Gamma_{is} C_i^w \quad i = 1, \ldots, m_s + m_n, \tag{11}$$

where Γ_{ia} and Γ_{is} are the equilibrium phase partitioning constants between an air/water system and a soil/water system, respectively, for component i. Here we define

$$\begin{gathered} \phi_i = \phi(s_w + s_a \Gamma_{ia}) + \Gamma_{is}, \quad u_i = u_w + u_a \Gamma_{ia}, \\ D_i = \phi(s_w D_{iw} + s_a \Gamma_{ia} D_{ia}), \end{gathered} \tag{12}$$

where $D_{iw}(u_w)$ is the hydrodynamic diffusion/dispersion tensor, and $D_{ia}(u_a)$ is defined similarly for the air phase. The χ_i are possibly nonlinear kinetic terms which account for biodegradation of contaminants, utilization of nutrients, and growth and decay of microorganisms. The number and complexity of specific metabolic pathways or chemical reactions varies with the application. The source/sink terms g_i represent production and injection wells.

3. PARALLEL IMPLEMENTATION

Our two-phase flow and transport code, as stated above, involves the coupling of

two subroutines, RPGW and a modified version of PIERS.

RPGW is a subroutine developed to simulate the transport and reactions of dissolved chemical species in the groundwater. This fully parallel code uses the characteristics-mixed method; that is, it combines characteristics and the mixed finite element method with operator splitting. The code handles an arbitrary number of component chemical species, as well as microbial mass and radionuclide decay. The code treats an arbitrary number of phases including the solid phase (adsorption). Each component is dissolved in one or more of these phases. The distribution of mass in the phases is assumed to follow the linear Raoult's or Henry's Law. This code achieves almost linear parallel scaling [4,2]; thus, it is highly effective when run on a parallel machine. Details regarding the formulation and analysis of this procedure can be found in [3] and application to contaminant transport in single phase groundwater flow in [1] and [4].

PIERS, a fully implicit two phase flow code with fully coupled wells, was originally developed at Exxon Production Research by J. Wheeler and Smith for the INTEL iPSC/2 [16]. Capillary pressure and relative permeability are functions of water saturation and formation type. Functional forms can be defined by tables or by definition as piecewise C^2 splines. Nonlinearities are treated implicitly by Newtonian iteration. Rice University, in cooperation with J. Flower of Parascope, ported this code to a collection of parallel machines. Scaling studies have been carried out in [16,10].

We now describe briefly how the combined code solves the model (1)–(12). PIERS first approximates (1)–(7) using a fully implicit method that is finite difference in time. In space it is a cell-centered finite difference method, or equivalently a mixed finite element method with the approximating space RT_0 and a special quadrature rule. The system (1)–(7) can be rewritten so that for $t = t^n$ one need only solve for the primary unknowns $P^n_{w,h}$ and $S^n_{w,h}$. The resulting nonlinear system is solved by a parallel domain decomposition Newtonian iteration that involves a nonsymmetric linearization, a three level multigrid solver for approximating the aerial domain, and SOR in the vertical direction. The linear solver is very sensitive to the selection of the SOR acceleration parameter and to the choice of convergence parameters. Even so this code has been employed to solve over one million nonlinear equations each time step. Implicit upstream weighting on the phase transmissibilities, $\lambda = k_r\rho/\mu$, is an option in the code and is generally employed.

Given the saturations and phase velocities, the subroutine RPGW is called. Here the advection-diffusion-reaction system (8)–(12) involving donor, acceptor, and biological mass equations are approximated using a time splitting scheme. One global time step of RPGW or the transport code involves the following three sequential steps:

(A) Pure transport. For each electron donor or acceptor, characteristics are traced backwards in time to locate their origin at the previous time level. This may be done by taking small micro time steps. This solves (8)–(9) without the reaction

terms χ_i and the dispersion terms D_i.

(B) Reactions. The coupled system of reaction equations (i.e. (8)–(10) without the two divergence terms and without the g_i source terms) are approximated using a fourth order Runge-Kutta procedure. Initial conditions are the cell averages from (A) for acceptors and donors, and the previous time step concentrations for the microbes. Many small time steps may be taken to improve the accuracy.

(C) Diffusion and dispersion. The diffusion/dispersion step involves approximating a parabolic system for each donor or acceptor using initial data from (B) and applying the mixed finite element method, again implemented as a cell-centered finite difference method. A tensor product trapezoidal rule is used in treating the diffusion/dispersion term. A finite stencil is obtained for each component, nine points in two dimensions and nineteen in three. The discrete system is solved using a Jacobi preconditioned conjugate gradient algorithm. Details may be found in [1,4,5].

After having completed the transport and reactive step, mass transfer source and sink terms γ_p are computed. The time step is then incremented and the flow subroutine is called to obtain new saturations and phase velocities.

4. SOME BIOREMEDIATION RESULTS

The Hanford Site in Washington State occupies approximately 560 square miles of semiarid terrain and was selected in 1943 for producing materials (primarily plutonium) in support of the United States' World War II efforts. Chemical processes employed to recover and purify plutonium produced waste containing actinide compounds and typical aqueous and organic liquid industrial wastes. The primary organic contaminant carbon tetrachloride (CCl_4) totaled 637 to 1200 tons discharged. Today, plutonium production has ceased, and the primary mission has shifted to environmental restoration of the Hanford Site [7,8,11,13,14].

Rice University and Pacific Northwest Laboratory (PNL) began a collaborative research effort in 1992 that involves laboratory, field, and simulation work directed toward validating remediation strategies. We discuss below some preliminary computational results based on some recent microbial CCl_4 destructive kinetics developed by Skeen and Chan of PNL [14].

The model has six components: electron acceptors nitrate NO_3^-, nitrite NO_2^-, and acetate CH_3COO^-, CCl_4, microbial mass $C_5H_9O_3N$, and a nonreactive tracer. We also assume that the retardation factor for acetate is 1.8. The chemical reactions for this system are:

$$
\begin{aligned}
8NO_3^- + 2CH_3COO^- + 2H^+ &\rightarrow 4CO_2 + 8NO_2^- + 4H_2O,\\
8NO_2^- + 3CH_3COO^- + 11H^+ &\rightarrow 6CO_2 + 4N_2 + 10H_2O,\\
7CH_3COO^- + 2NO_3^- + 9H^+ &\rightarrow 4CO_2 + 6H_2O + 2C_5H_9O_3N,\\
13CH_3COO^- + 4NO_2^- + 17H^+ &\rightarrow 6CO_2 + 10H_2O + 4C_5H_9O_3N,
\end{aligned}
$$

and bioremediation is described, for the two parameters μ and k_i, by

$$\frac{d(CCl_4)}{dt} = \frac{-\mu(CCl_4)(C_5H_9O_3N)}{1 + k_i((NO_3^-) + (NO_2^-))}.$$

The two figures below show simulation results at 3 days. We assumed that CCL_4 uniformly contaminates the medium, both in the vadose zone and in the aquifer, and that microbes uniformly populate the medium. Nitrate and acetate are injected into the system. Recirculation is approximately 50 gals/min; fluid is collected at the production part of the well (depth 205–213 feet) and reinjected at the injected part of the well (depth 171–187 feet).

Fig. 1 shows concentration fronts at 3 days. Observe that the microbial population grows in regions where nutrients are available, that acetate movement is retarded, and that nitrite takes some time to form by kinetic reaction. Observe also the drawing of the CCL_4 from the aquifer up to the vadose zone where a large microbial population has grown. At 3 days the CCL_4 has decreased by four orders of magnitude. Fig. 2 shows the water table and the concentration front of the tracer over the full computational domain at 3 days.

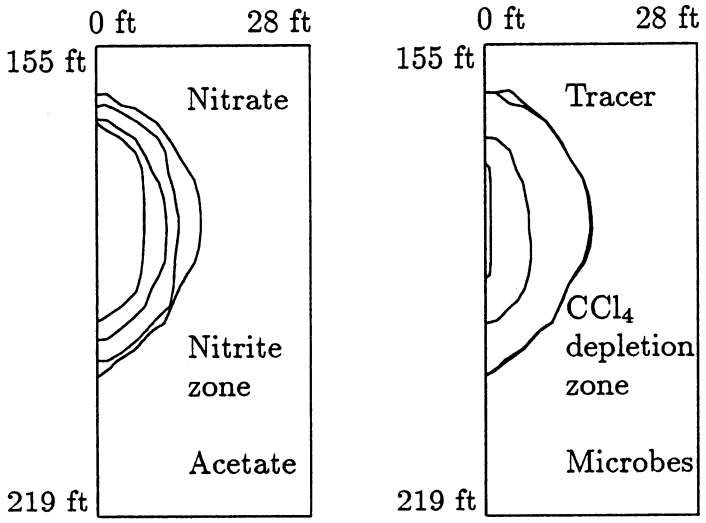

Fig. 1. Radial cross-sections of the concentration fronts of the six components

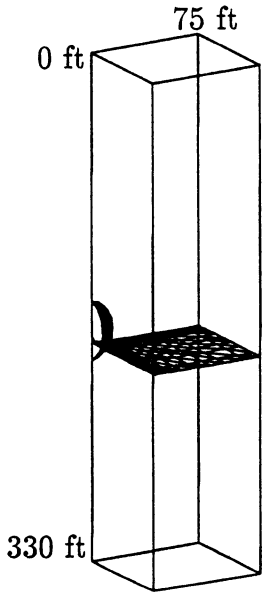

Fig. 2. Water table and front of the tracer concentration

5. CONCLUSIONS AND FUTURE DIRECTIONS

The Rice 3D Parallel Groundwater Reactive Multiphase Flow and Transport Simulator (RPGW/MP) is a parallel code under development at Rice University. Its purpose is to simulate the flow and transport of reacting chemical species in the

groundwater. This code is based on combining locally conservative schemes: a mixed finite element method for flow with a characteristics-mixed finite element method for transport. Computational experiments indicate that this approach is useful in solving grand challenge problems such as bioremediation and that the code achieves good parallel scaling.

We are presently adding general boundary conditions to the code as well as modifying the code to treat three phases (air, non-aqueous phase liquid, and water). Future plans include the incorporation of meshes defined by fairly general geometry [5] and the development of robust, fully implicit multilevel solvers for modeling three phase flow. In addition we plan to add more chemistry and microbiology as well as the capability of simulating fractured media.

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