FINAL REPORT

Title: Grand Challenge Problems in Environmental Modeling and Remediation: Groundwater Contaminant Transport (Partnerships in Computational Science)

Principal Investigator: Michael A. Celia

Period of Performance: July 1995 - January 1998

Recipient Organization: Department of Civil Engineering and Operations Research
Princeton University
Princeton, NJ 08544

DOE Award Number: DE-FG02-95ER25267

RECEIVED
MAR 29 1999
OSTI

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, make 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.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

The over-reaching goal of the Groundwater Grand Challenge component of the Partnership in Computational Science (PICS) was to develop and establish the massively parallel approach for the description of groundwater flow and transport and to address the problem of uncertainties in the data and its interpretation. This necessitated the development of innovative algorithms and the implementation of massively parallel computational tools to provide a suite of simulators for groundwater flow and transport in heterogeneous media. This report summarizes the activities and deliverables of the Princeton University component of the Groundwater Grand Challenge project funded through the High Performance Computing grand challenge program of the Department of Energy from 1995 through 1998.

Seven institutions were primarily involved in this project: Brookhaven National Laboratory, Oak Ridge National Laboratory, Princeton University, SUNY at Stony Brook, Texas A&M University, The University of South Carolina, and the University of Texas at Austin, with contributing efforts from the Westinghouse Savannah River Technology Center. Each institution had primary responsibility for specific research components, but strong collaboration among all institutions was essential for the success of the project and in producing the final deliverables.

PICS deliverables include source code for the suite of research simulators and auxiliary HPC tools, associated documentation, and test problems. These materials will be available as indicated from each institution's web page or from the Center for Computational Sciences Oak Ridge National Laboratory in January 1998.

1 INTRODUCTION

The groundwater grand challenge component of the Partnership in Computational Science (PICS) High Performance Computing initiative was formed to apply the members' collective efforts towards the mathematical and scientific challenges presented by complex groundwater, soil, contaminants, and air interactions. The numerical modeling of the fate of groundwater contaminants is a critical step in the formulation of remediation policies to be used to address contaminated groundwater and soils. Such strategies as pump-and-treat and in-situ vitrification require accurate knowledge of the location and extent of the contaminant plume; furthermore, some remediation strategies themselves use complex physical and chemical processes, requiring, for example, the placement of chemical "traps" or the injection of surfactants, bacteria, or nutrients.

Remediation methods remain extremely (and potentially prohibitively) expensive and unpredictable in their success. This is due to a number of factors, including significant geologic heterogeneity, incomplete characterization of the subsurface, and the complexity of underground contaminant reactions and remediation processes.

Groundwater contamination problems typically involve organic liquids, ionic solutes, and/or radionuclides. The transfer of chemical species between the contaminant-bearing phase, the soil or aquifer, and the groundwater may involve interphase mass transfer as well as a host of intraphase chemical reactions such as dissolution, aqueous phase complexation, ion exchange, adsorption, precipitation, oxidation/reduction, and even biological degradation kinetics. The extent of mass transfer and chemical reaction is ultimately limited by thermodynamic equilibrium, but compositions far from equilibrium often arise locally because of kinetic and surface area constraints.

In addition to the basic research on coupled multi-phase flow and multi-component transport in porous media, the development of parallel algorithms for the solution of these coupled equations, and the development of computational science tools for better analysis and understanding, specific deliverables provided an overriding guide for the collaborative work among consortium members.

This report summarizes the activities and deliverables of the Groundwater Grand Challenge project funded through the High Performance Computing grand challenge program of the Department of Energy from 1995 through 1997. The goal of the project are to develop and establish the massively parallel approach for the description of groundwater flow and transport and to address the problem of uncertainties in the data and its interpretation. This required the development of innovative algorithms and the implementation of massively parallel computational tools to provide a suite of simulators for groundwater flow and transport in heterogeneous media.

Seven primary institutions were involved in this project: Brookhaven National Laboratory, Oak Ridge National Laboratory, Princeton University, SUNY at Stony Brook, Texas A&M University, The University of South Carolina, and the University of Texas at Austin. Each

institution had primary responsibility for specific research components as outlined in each institutions' section of this report, but strong collaboration among institutions was essential for the success of the project and in producing the final deliverables.

PICS deliverables include source code for the suite of research simulators and auxiliary HPC tools, associated documentation, and test problems. These materials will be available from each institution's web page or from the Center for Computational Sciences Oak Ridge National Laboratory in January 1998.

Software Deliverables:

- GCT1.2:
Saturated/Unsaturated Flow and Multicomponent transport
Flow based on Galerkin FEM and transport based on mixed method of characteristics and Godunov schemes.
- GCT1.3:
Two-phase Flow and Multicomponent transport.
- G3D:
Graphical pre- and post-processing software.
- Steer:
Steering and Tracking Library.
- Parsimm:
Single-phase flow, radionuclide decay, and biogeochemistry.
- EDONIO/DOLIB:
Scalable I/O library and Parallel distributed object library.
- PERM:
Parameter estimation.
- US3D-MP:
Saturated/Unsaturated Flow and Single component transport based on Galerkin FEM
- Front tracking code from SUNY-SB.

2 Princeton University Component

Princeton University contributed primarily in four distinct but related areas to the PICS project: (1) development and implementation of a procedure to quantify risks associated with ground-water contamination from complex, multi-component mixtures; (2) development and implementation of a general three-dimensional contaminant transport simulator based on the Eulerian-Lagrangian Localized Adjoint Method (ELLAM); (3) a computational investigation of the fractional flow approach for infiltration problems; and (4) applications to field problems associated with the aquifer being studied in detail by the U.S. Geological Survey at Cape Cod, Massachusetts. We have also worked closely with the University of South Carolina, providing technical guidance for their field applications, providing both computer codes and technical guidance for their ELLAM developments, and providing guidance on their development of

graphical interfaces. One result of that collaboration is the publication by Johnson et al. (1997). The following is an overview of accomplishments for each of the four primary topics identified above.

2.1 Risk Assessment and Quantification for Complex Mixtures

It has become obvious that ground-water contamination sites must be prioritized in terms of importance of the resource and severity of the contamination. Severity of the problem can be quantified through use of risk assessment procedures that combine advanced numerical simulations procedures with risk-assessment measures provided by the Environmental Protection Agency. The result is a measure of total risk, and of relative risks for each compound, as a function of both space and time. Such an algorithm allows sites to be prioritized through use of a common metric, and also allows the effectiveness of potential remediation schemes to be quantified and compared.

The model we have developed is based on a set of standard advection-diffusion-reaction transport equations, with the additional features that (1) both an aqueous phase and a non-aqueous-phase liquid (NAPL) exist within the subsurface; (2) the NAPL is composed of many components; (3) the NAPL and aqueous phases interact through kinetic mass-transfer processes that are dependent on the composition of the NAPL phase; and (4) the state of the NAPL components depends on the NAPL composition, so that some of the NAPL components can solidify and precipitate out of the mixture as the NAPL composition changes. All of these processes are included because they are necessary to describe properly the behavior of known environmental contaminants such as coal tars and various petroleum products. The model, described in detail in Blackburn (1998) and Peters et al. (1998), combines numerical approximations with certain analytical solutions to solve the coupled set of nonlinear equations. Numerical methods are applied to solve the contaminant transport equations (one equation for each component), while the individual mass-transfer equations are linearized and solved analytically. These solutions are coupled in a nonlinear iterative solution procedure. While the solution procedure is complicated, in part because the nonlinearities become more difficult when specific components begin to precipitate, the overall result is a numerical solution for aqueous-phase concentrations for each component, mass fractions within the NAPL for each component, identification of any solidified components, and calculation of phase saturations for the NAPL and water phases. These solutions are then augmented by calculations of risk associated with each component.

Risk calculations are usually performed to measure the effects of exposures over a 30-year window of time. While most estimates of risk use a given (constant) concentration applied over 30 years, we use an integrated measure of concentration over 30 years of simulation to capture the temporal evolutions of the concentrations as computed in the model. The risk associated with each component is then calculated using this integrated concentration, and exposure factors compatible with U.S. Environmental Protection Agency guidance, as outlined in Peters et al. (1996). These EPA measures include carcinogenic slope factors for each component, which are either known from prior estimates in the literature, or are estimated using compound-specific

toxic equivalency factors.

We have run simulations using realistic aquifer properties (taken from the Cape Cod field site) and somewhat realistic NAPL mixtures. We have looked at up to 17 components, with the compositions based on measurements of coal tars. The results, as reported in Blackburn (1998) and discussed briefly in Peters et al. (1998), show the space-time evolution of the risk factors, with the lighter components dominating the NAPL composition at early times but their relatively high mass-transfer rates lead to dominance of heavier, and more toxic, components at later times, with some of those components solidifying and precipitating out of solution. This leads to complex risk maps, showing the importance of spatial location, of the time-averaging window used, and of solidification effects. Details may be found in the references.

2.2 Development of Three-dimensional ELLAM Algorithms

After experiencing the expected difficulties with finite element transport simulators, we developed a fully three-dimensional Eulerian-Lagrangian Localized Adjoint Method (ELLAM) solution algorithm that can solve general transport problems. The algorithm takes advantage of our previous experience (Celia et al., 1990; Zisman and Celia, 1990; Celia, 1994; Binning, 1994; Binning and Celia, 1996a; Ewing et al., 1995) as well as the experiences of many others (Healy and Russell, 1993, 1998; Wang et al., 1997). All of those previous studies provided important input and guidance, but were restricted to either one spatial dimension or two spatial dimensions. As is evident in Binning and Celia (1996a), boundary condition implementation, and evaluation of integrals at the known time level, are the two major difficulties in the ELLAM approach. These difficulties increase as the dimensionality of the problem increases. We decided on the following approach, which is now implemented.

The ELLAM scheme uses the forward tracking approach first proposed by Healy and Russell (1993). In that approach, the integrals that arise at the known time level, and along inflow boundaries, are approximated using numerical integration. Because the solution is known at all points within the domain at the known time level, it turns out that the only unknown is the value of the test function. Because the test function is easily defined at the unknown (new) time level, each integration point is forward-tracked to the new time level, and the value of the test function is determined. A similar approach is used along inflow boundaries. Analytic tracking is used to track each integration point. The code allows for a choice of both numerical integration schemes and of test functions. Numerical integration schemes include one-, two-, and three-point Gaussian integration; trapezoidal-rule integration; and Simpson's-rule integration, all applied cell-by-cell. Test function choices are piecewise linear, which we recommend, and piecewise constant. The code only tracks integration points in cells that have non-zero concentrations; in this way, we do not waste computations where there is no contribution to the right-hand-side vector. We have run a number of test problems to verify the code, and are now running simulations related to some of the Cape Cod field experiments. The code and some of these calculations are described in Celia and Binning (1998).

2.3 A Computational Investigation of the Fractional Flow Formulation for Infiltration Problems

Fractional flow formulations for two-phase flow problems exhibit several attractive attributes for numerical simulations, including the direct application of characteristic-based methods for the saturation equation, and the elliptic form of the pressure equation. These have been exploited effectively in the petroleum industry. Because these approaches are a strong candidate for two-phase ground-water problems, we investigated the methods and compared them to a finite element solver, based on a two-pressure formulation that we had previously developed. The focus of the study was, in large part, on the implementation of boundary conditions, because the fractional flow approach does not naturally accommodate the mix of pressure and flux conditions that occur at the land surface in most infiltration problems.

We used as a test problem an experiment that had been reported previously in the literature, and which we had solved previously with the finite element code. The fractional flow solver was written so that boundary conditions were implemented in an iterative fashion; details of the implementation are in Binning and Celia (1996b) and Binning and Celia (1998). A modified-method-of-characteristics approach was used to solve the saturation, with local grid refinement also used to capture the sharp infiltration front. We observed that the fractional flow solver allowed time steps that were 10 to 30 times larger than those required in the finite element solver. However, the additional iterations required for the boundary conditions, the nonlinear characteristic tracking, and overhead associated with grid refinement largely offset the computational advantage, especially at early times when the frontal shape changes rapidly and the number of iterations in the fractional flow solver was large. Details of the numerical approaches, and of the results, can be found in Binning and Celia (1996b) and Binning and Celia (1998).

2.4 Field Applications

For field application, we have focused on the Cape Cod field site, which is a field research site operated and maintained by the U.S. Geological Survey. We have looked at simulation problems involving the nonreactive tracer bromide, both with and without density dependence. The study focused on the effects of density, and the effects of dimensionality of the model (two dimensions versus three dimensions). As expected, sinking of the plume is enhanced as the dimensionality increases. Finite element methods required very fine grids to capture the proper dynamics. This provided some of our motivation to develop the ELLAM approach.

In addition to the simulations involving saturated-zone, miscible displacement, we also used the Cape Cod field site for hypothetical simulations of the complex-mixture NAPL dissolution and transport simulations, for which we calculated risks. This was done by placing a fixed volume of NAPL, at residual saturation, into the flow field to simulate a leak. The subsequent dissolution and transport were modeled, and space-time measures of risk were calculated. See Peters et al. (1998) and Blackburn (1998) for details.

3 References

(* indicates publication resulting from DOE Grant DE-FG05-95ER25267)

Binning, P.J., Modeling Unsaturated Zone Flow and Contaminant Transport in the Air and Water Phases," PhD Thesis, Department of Civil Engineering and Operations Research, Princeton University, 1994.

Binning, P. and M.A. Celia, "A Finite Volume Eulerian-Lagrangian Localized Adjoint Method for Solution of the Multiphase Contaminant Transport Equations in Two Dimensions," *Water Resources Research*, 32(1), 103-114, 1996a.

*Binning, P. and M.A. Celia, "Practical Application of the Fractional Flow Approach to Multi-Phase Flow Simulation", *Proc. Eleventh Int. Conf. on Computational Methods in Water Resources*, Cancun, Mexico, 1996b.

*Binning, P. and M.A. Celia, "Practical Implementation of the Fractional Flow Approach to Multiphase Flow Simulation", in press, *Advances in Water Resources*, 1998.

*Blackburn, E.D., "Simulation of Dissolution and Transport of Complex-Mixture NAPL's", Masters Thesis, Department of Civil Engineering and Operations Research, Princeton University, 1998.

Celia, M.A., "Eulerian-Lagrangian Localized Adjoint Methods for Contaminant Transport Simulations," Featured Paper, *Proc. X Int. Conf. Computational Methods in Water Resources*, Peters et al. (Eds.), Kluwer Publ., 207-216, 1994.

Celia, M.A., T.F. Russell, I. Herrera, and R.E. Ewing, "An Eulerian-Lagrangian Localized Adjoint Method for the Advection-Diffusion Transport Equation," *Advances in Water Resources*, 13, 187-206, 1990.

Celia, M.A. and S. Zisman, "An Eulerian-Lagrangian Localized Adjoint Method for Reactive Transport in Groundwaters," *Invited Paper, Proc. Eight Int. Conf. Comp. Meth. Water Resources*, Gambolati et al. (eds.), Springer, 383-392, 1990.

*Celia, M.A. and P. Binning, "Development and Application of a Three-dimensional ELLAM Simulator for Ground-water Contaminant Transport", to be submitted to *Computational Geosciences*, 1998.

Ewing, R.E., H. Wang, and M.A. Celia, "An Eulerian-Lagrangian Localized Adjoint Method for Reactive Transport with Biodegradation," *Numerical Methods for Partial Differential Equations*, 11, 229-254, 1995.

- Healy, R.W. and T.F. Russell, "A Finite-Volume Eulerian-Lagrangian Localized Adjoint Method for Solution of the Advection-Diffusion Equation", *Water Resources Research*, 29, 399-413, 1993.
- Healy, R.W. and T.F. Russell, "Solution of the Advection-Diffusion Equation in Two Dimensions by a Finite-Volume Eulerian-Lagrangian Localized Adjoint Method", *Advances in Water Resources*, 21(1), 11-26, 1998.
- *Johnson, L.S., A. Kaulgud, R.C. Sharpley, M.A. Celia, R.E. Ewing, Z. Leyk, J. Pasciak, and J.R. Brannan, "Integration of Contaminant Transport Simulators on Parallel Machines with a Graphical User Interface for Remote Interactive Modeling", in *High Performance Computing 1997: Grand Challenges in Computer Simulation*, A. Tentner (ed.), 319-324, 1997.
- Peters, C.A., P.A. Labieniec, and C.D. Knightes, "Multicomponent NAPL Composition Dynamics and Risk", *Proc. ASCE Annual Convention: Non-Aqueous Phase Liquids (NAPLs) in the Subsurface Environment: Assessment and Remediation*, L.N. Reddi (ed.), 681-692, 1996.
- *Peters, C.A., E.D. Blackburn, and M.A. Celia, "Spatial and Temporal Variation of Composition in Multicomponent NAPLs", to appear, *Proc. 11th Int. Conf. Comp. Meth. in Water Res.*, 1998.
- Wang, H., H.K. Dahle, R.E. Ewing, M.S. Espedal, R.C. Sharpley, S. Man, "An Eulerian-Lagrangian Localized Adjoint Method for Advection-Dispersion Equations in Two Dimensions and its Comparison to Other Schemes", to appear, *SIAM J. Sci. Comp.*, 1997.