

Use of reactive-transport models in field studies: Experience with the PHAST simulator

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1 INTRODUCTION

PHAST is a computer program for simulation of reactive-transport in three dimensions, which has been developed by the U.S. Geological Survey. The simulator is used to model constant-density ground-water flow, in confined or unconfined conditions, coupled with multi-component solute transport and a wide range of chemical reactions, including mineral, gas, ion-exchange, surface-complexation, and solid-solution equilibrium reactions and user-defined kinetic reactions. PHAST has been applied to field-scale studies of arsenic in the Central Oklahoma aquifer, aquifer storage and recovery (ASR) in Charleston, South Carolina, and phosphorus transport in a sewage plume at the Massachusetts Military Reservation (MMR), Cape Cod, Massachusetts. Development of the reactive-transport models for these studies has relied on extensive field and laboratory investigations. The PHAST simulations have aided in evaluating the pertinent transport and geochemical processes in the study areas and have provided predictive results that are being used in making water-resource-management decisions.

2 CAPABILITIES OF THE PHAST SIMULATOR

PHAST was developed by coupling the geochemical model PHREEQC (Parkhurst and Appelo, 1999) with a solute transport model derived from HST3D (Kipp, 1987; 1997). The simulator uses operator splitting to solve sequentially the coupled set of flow, transport, and chemical reaction equations, without iteration. This solution method is denoted as the sequential, non-iterative approach (SNIA) (Yeh and Tripathi, 1989). The advantages of SNIA are the simplicity of implementation and the ease of incorporation of complex chemical reactions. The numerical method has truncation errors arising from finite-difference discretization and operator splitting; but it appears possible to control these errors with sufficiently small spatial and temporal discretization.

PHAST uses an ion-association model to describe the thermodynamics of aqueous solutions. The reactions that can be modeled include homogeneous equilibrium within the aqueous phase and heterogeneous equilibria among the aqueous phase and minerals, gases, ion exchangers, surface complexation, and solid solutions. PHAST has a general method for kinetic reactions, where virtually any rate expression can be defined with Basic-language statements. The kinetic reactions are integrated either by a Runge-Kutta method or an implicit method. Both methods have automatic time-step adjustments to control errors.

The chemical calculations are the most computationally intensive part of reactive-transport simulations with PHAST. However, operator splitting between the chemical reaction step and the flow and transport steps leads to a natural parallelization of the calculations. The chemical reactions in each model cell are independent of all other cells and it is possible to distribute the workload to multiple processors with each processor calculating the chemistry for a subset of cells. The parallel version of PHAST distributes the workload of the chemical calculations by using the Message Passing Interface (MPI) (Parkhurst and Kipp, 2002). Randomization and reassignment of cells are used to balance the load among the processors. Using 30 processors, calculation time can be decreased by as much as a factor of 25.

The parallel version of PHAST makes it possible to run problems that have 100,000 nodes and 100s of time steps in a matter of hours on a cluster of Pentium IV computers. The parallel version was used to run field-scale simulations of Central Oklahoma aquifer, the Charleston ASR experiment, and the Cape Cod sewage plume.

3 NATURALLY OCCURRING ARSENIC IN THE CENTRAL OKLAHOMA AQUIFER

A 3-dimensional reactive transport model was developed to simulate the evolution of water chemistry in the Central Oklahoma aquifer over geologic time (10s of thousands of years) with special emphasis on large naturally occurring arsenic concentrations in the confined part of the aquifer, which limit the suitability of the aquifer for water supply. Model development relied on field investigations, including measurement of water levels and chemical analyses of ground water samples; and laboratory studies, including mineral identification by scanning electron microscope and X-ray diffraction, measurement of exchangeable cations in clays, and sequential extractions to identify the sorbed fraction of arsenic in the sediments (Parkhurst and others, 1996; Mosier and others, 1991).

The reactions for the reactive transport model include carbonate mineral equilibrium, cation exchange, and complexation of arsenic on sediment surfaces. The flow system was modeled as an unconfined aquifer in the east and a confined aquifer in the west. After 100,000 years of simulation, model results were consistent with field observations, showing calcium magnesium bicarbonate water in the unconfined aquifer and sodium bicarbonate water with large concentrations of arsenic in the confined aquifer. The simulations indicate that large concentrations of arsenic are likely to be a regional problem, which limits the utility of the aquifer as a water supply.

In detail, the simulations were not definitive. The largest concentrations of arsenic in the simulation did not extend as far south as is observed in the aquifer. This discrepancy between the model results and the observations can be attributed primarily to uncertainties in the representation of the flow system in the confined part of the aquifer.

4 AQUIFER STORAGE AND RECOVERY AT CHARLESTON, SOUTH CAROLINA

As part of an investigation of the possibility of storing potable water in a brackish aquifer for use during emergencies, a 3-dimensional reactive transport model was developed to consider the effects of chemical reactions in the aquifer on water chemistry and to estimate the amount of potable water that could be recovered from storage. The field investigation included two aquifer tests to determine hydraulic conductivity and aquifer storage, and four ASR experiments, where water chemistry at observation and recovery wells was measured at intervals during each experiment. X-ray diffraction was used to identify minerals and to estimate cation-exchange capacity of the aquifer sediments.

PHAST simulations indicated calcite equilibrium and cation-exchange reactions were sufficient to explain water-chemistry changes during the course of the ASR experiments. The most sensitive parameters for accurate simulation of the recoverable water were aquifer dispersivity coefficients, which described the dispersive transport in the system. After calibrating the dispersivities to match in the simulated and observed freshwater breakthrough at the observation wells, it was found that approximately one quarter of injected water could be recovered as potable water, regardless of the amount of water injected. This efficiency of recovery can now be used in the design of a full-scale ASR system.

5 PHOSPHORUS TRANSPORT IN A SEWAGE PLUME AT THE MMR, CAPE COD, MASSACHUSETTS

Past disposal of sewage effluent through infiltration beds at a now-dismantled sewage treatment plant at the Massachusetts Military Reservation has generated a phosphorus plume that

may potentially impact Ashumet Pond. The site has been extensively studied as part of the USGS Toxics Program and detailed information is known about porous media properties, ground-water velocities, and dispersivity in the aquifer (see for example, Garabedian and others, 1991; and LeBlanc and others, 1991). For the investigation of phosphorus transport, the key information for model development was delineation of the plume by analysis of water from many multilevel samplers, evaluation of sorption processes by laboratory column experiments with aquifer sediments, and investigation of oxygen consumption by degradation of organic matter accumulated in the sediments by laboratory batch and column experiments (Parkhurst and others, 2003).

Simulation of the flow system relied almost entirely on previous work at the site (including Garabedian and others, 1991; and LeBlanc and others, 1991). The chemical evolution of the plume was modeled with equilibrium reactions—surface complexation and reaction of iron and manganese oxide minerals—and kinetic reactions—organic decomposition and formation of iron phosphate minerals. Surface-complexation constants were derived by parameter estimation using a reactive-transport model of column experiments. The reactive-transport simulations indicated that loading of phosphorus to Ashumet Pond is near its peak currently and will decrease over the next few decades. The load estimates can be used in the process of developing a management strategy for the beneficial uses of Ashumet Pond. In this study, identification and parameterization of the chemical reactions was the greatest source of uncertainty.

6 CONCLUSIONS

The PHAST reactive-transport simulator has been developed by using SNIA for solution of the coupled flow, transport, and chemical reactions. A parallel version of the simulator has allowed simulation of field-scale problems in Oklahoma, South Carolina, and Massachusetts. The development of reactive transport models for these sites has relied on extensive field and laboratory investigations. Each study highlights data requirements for one of the three processes simulated in reactive transport modeling: the flow system in Oklahoma, dispersive transport in South Carolina, and chemical reactions in Massachusetts. The studies demonstrate that reactive-transport modeling is useful in understanding natural processes, in designing engineering projects, and in making management decisions for contamination issues.

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