



Project Summary

Denitrification in Nonhomogeneous Laboratory Scale Aquifers: 1. Preliminary Model for Transport and Fate of a Single Compound

F.T. Lindstrom and L. Boersma

A two-dimensional mathematical model for simulating the transport and fate of organic chemicals in a laboratory scale, single layer aquifer is presented. The aquifer can be nonhomogeneous and anisotropic with respect to its fluid flow properties. The physical model has open inlet and outlet ends and is bounded by impermeable walls on all sides. Fully penetrating injection and/or extraction wells can be placed anywhere in the flow field. The inlet and outlet boundaries have user prescribed hydraulic pressure fields. The steady state hydraulic pressure field is obtained first by using the two-dimensional Darcy flow law and the continuity equation, with the time partial derivatives being set to zero. The transverse and longitudinal components of the Darcy velocity are estimated by using Darcy's law. The chemical transport and fate equation is then solved in terms of user stipulated initial and boundary conditions. The model accounts for the major physical processes of storage, dispersion, and advection, and also can account for linear equilibrium sorption, three first-order loss processes, including microbial degradation, irreversible sorption and/or dissolution into the organic phase, metabolism in the sorbed state, and first-order loss in the sorbed state. The chemical may be released internally via distributed leaks, sources that do not perturb the flow field, or from fully penetrating injection wells.

Chemical compound may also enter at the inlet boundary. Chemical mass balance type inlet and outlet boundary conditions are used. The solution to the field equation for hydraulic pressure is approximated by a nodal point centered finite difference method using the strongly implicit procedure with a user specified heuristic for choosing the iteration parameter. A solution to the transport and fate equations is approximated with a forward in time Euler-Lagrange time integrator applied to the chemical transport and fate semi-discretization.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Laboratory scale, physical, test aquifers are increasingly being used for the study of transport and fate processes. It is generally less expensive to evaluate hypotheses for pollutant fate and transport using laboratory scale aquifers than to work under field conditions. Furthermore, numerical models of the fate and transport of chemicals in aquifers are now rapidly coming within the reach of environmental scientists. These models are even cheaper and faster to operate than are laboratory systems. The current investigation will



analyze the ability of laboratory aquifers to validate mathematical models. This interim report presents a mathematical analysis of two-dimensional horizontal transport and fate processes in aquifers. This analysis led to development of a computerized model. Further development (later report) will add microbiological processes to the physical and chemical processes already addressed in this report. In addition, results obtained from the mathematical model will be compared to the results obtained in a laboratory test aquifer used to study in situ denitrification as the first test case.

Aquifer pollution is an emerging and rapidly growing problem in the United States. Groundwater contamination is insidious because measurements of the problem have only recently been made on a consistent basis. The magnitude of the pollution problem is becoming increasingly clear as the data base increases.

Pollution can result from catastrophic events such as spills of toxic or otherwise hazardous compounds. Other important point sources include leaking storage facilities and waste product disposal. A growing concern in many areas is the effect of agricultural practices on groundwater quality. This form of contamination, generally described as nonpoint source pollution, has a cumulative effect both across a land area and in time. Nitrate contamination of groundwater is an example of agricultural pollution. The problem is increasing and, partly because the source of pollutant is poorly defined now, it is likely to continue to grow in significance as more information becomes available.

Methods to decrease nitrate levels in aquifers include decreasing or eliminating the pollutant source. This approach is reasonable since loss of nitrate from agricultural systems constitutes an economic loss to producers. This quantitative factor and the more qualitative factor of decreasing environmental pollution have direct benefits to society. A second, more expensive method to improve groundwater quality is to remove the pollutant from the ground water.

A variety of methods have been used to restore the quality of groundwater. The two major categories are physical containment and chemical and/or biological treatment. Physical methods, including placement of barriers or hydrodynamic control by pumping, have been used with some success but are most effective when used to isolate point sources of pollution. Removal of the pollutant from the groundwater is a more

reasonable strategy for pollutants contributed by nonpoint sources or by widely distributed sources. Chemical and biological methods are commonly used in situations where water is pumped out, treated, and used. This class of methods is used extensively for drinking water supplies where the end product is important enough to justify the expense.

A significant advantage of chemical and biological methods is the possibility of in situ aquifer restoration. A number of chemical techniques have been used in situ, and there is considerable interest in the rapidly growing field of bioremediation. The challenge of in situ methods is maintaining appropriate conditions in the aquifer itself. For bioremediation, the important factors affecting rate and efficiency of contaminant degradation are 1) presence of microbes suitable for degrading the pollutants; 2) energy sources and electron acceptors to sustain adequate microbial growth; 3) distribution of pollutant, substrate, and organisms in the aquifer; and 4) flow properties of the aquifer, including well locations and flow rates.

A number of studies have demonstrated that there is microbial activity in aquifers. Such organisms are generally considered to be substrate limited, particularly in anaerobic environments. In fact, pollutants have probably stimulated microbial activity by increasing substrate concentrations. Biological denitrification has been observed in aquifers and in saturated sediments. Findings from low temperature environments indicate that denitrifiers can function under normal aquifer conditions. There are also limited data that suggest that carbon substrate additions may increase nitrate utilization. Several studies provide evidence that bioremediation processes occur in aquifers. The evidence is clear for degradation of hydrocarbons in aerobic aquifer environments where microbial counts, oxygen consumption and hydrocarbon loss all increase. Denitrification has been observed in aquifers, artificial aquifers, and in microcosms constructed of aquifer materials. In addition, biological denitrification is commonly observed in reactors designed to treat groundwater after it has been pumped to a surface treatment site.

The experiments listed above indicate the potential for aquifer restoration by biological denitrification. The utility of bioremediation methods depends on establishing the proper conditions for microbial population growth. In addition, field scale restoration depends on the distribution of microbes, substrate, and

nitrate. The limiting factor among these is usually substrate concentration. Therefore, effective bioremediation methods require injection of a carbon source. Aquifer injection and plume movement have been studied extensively, particularly using solute transport models. Models have been useful for developing an understanding of basic processes affecting solute distribution in aquifers but are generally not precise enough to predict field situations reliably.

The common failing of models for field situations is the treatment of dispersion. If inadequate data are available to characterize aquifer hydraulic conductivity, the dispersion coefficient must be increased to include the apparent dispersion caused by variation in aquifer material properties. This results in a scale dependent dispersion coefficient based on the specific properties of the flow system under investigation rather than the properties of the porous medium.

Predictions of substrate spreading are only as good as the theoretical understanding and the field data that are available. This includes understanding dispersion and availability of hydraulic conductivity coefficients applicable to field situations. Understanding of the flow field at an aquifer restoration site is critical because methods for spreading added constituents throughout the aquifer depend on reliable prediction of the effects of injection rate and concentration, injection pulsing, and pumping from adjacent wells.

If biological denitrification is to be used as an effective technique for restoration, a fundamental understanding of the transport and fate processes is required. In addition, knowledge about the important limiting factors, or limiting system properties must be acquired. Therefore, the immediate objective was to develop a preliminary mathematical model and associated computer code to describe substrate injection into an aquifer and to use the model in a sensitivity fashion to assess the magnitude of the physical and biological factors controlling aquifer denitrification processes and identify those which can be manipulated to enhance the process.

The preliminary mathematical model addresses primarily aquifer fluid transport phenomena including perturbations due to presence of injection and withdrawal wells. Solute movement includes advection, dispersion, molecular diffusion, and simple first-order chemical and/or biological reactions in the aquifer. The mathematical modeling effort presented here is part of an ongoing study of aquifer

restoration being conducted by the Environmental Protection Agency at the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma.

One of the long-term goals of this study is development of a mathematical model of aquifer denitrification processes enhanced by stimulation of microbial population. The experience gained from developing the preliminary model is currently being used to develop a two-dimensional model for the simultaneous transport and fate of oxygen, substrate (methanol), nutrients, and nitrate in the single layer aquifer. Two independently operating microbial populations are included in the model, both using modified Monod kinetics.

Physical Aquifers at RSKERL

Two large (4 ft wide, 4 ft high, 16 ft long) physical aquifers were constructed at the USEPA Robert S. Kerr Environmental Research Laboratory in Ada, Oklahoma. Each aquifer contains three horizontal layers of material, with each layer assumed to be homogeneous and isotropic with respect to water flow. These systems can be used for validation of mathematical models that simulate the hydrodynamic pressure distribution, for the study of transport and fate of chemicals, and for evaluation of the growth characteristics of indigenous microbial populations. The physical aquifers will also be used for the study of proposed physical and biological remediation schemes.

Long-term Goals of the Mathematical Modeling Effort

The goals of the present mathematical modeling effort are to describe the fate and transport of the physical models. Mathematical modeling will include three space dimensions for steady state hydraulics and simultaneous transport and fate. Dissolved oxygen, nutrients (phosphorus), a carbon based substrate (methanol), and dissolved nitrate, as well as two spatially and temporally changing microbial populations are all factors that are to be included. The model will be used to study scenarios for bioremediation of aquifers contaminated with nitrates.

The procedures followed to achieve these goals are to first develop a preliminary model of the transport and fate of chemical compounds. Constant first-order loss processes and linear equilibrium sorption are to be assumed. This model is for two space dimensions and simulates the "aquifer" slab only.

The preliminary two-dimensional model, called LT2VSI, will be used to make

preliminary numerical studies of several scenarios for injection and/or extraction well placement. LT2VSI will be expanded to include four chemical compounds and two microbial populations. This will be LT3VSI. Next, LT3VSI will be expanded to the full three-dimensional space. The last model, LT4VSI will simulate the physical aquifers and will allow for a nonhomogeneous flow field and nonhomogeneous chemical and biological conditions.

Detailed Assumptions in the Preliminary Model

The preliminary mathematical model is the first step in the model development. With the long-term goal being the description of the transport and fate of chemicals in the full three-dimensional, laboratory scale, physical aquifers at the Robert S. Kerr Environmental Research Laboratory (RSKERL). An intermediate objective was to develop a preliminary, two-dimensional model for horizontal water and chemical transport and fate. LT2VSI was developed for a situation which consists of a single layer representing the aquifer part of the three soil layers making up the RSKERL aquifers.

The RSKERL physical models have been constructed in such a way that homogeneous and isotropic soil slabs were obtained. They have impermeable (no flow) side walls, an open top, partially open ends, and an impermeable lower or bottom boundary. The same assumptions regarding the walls and the bottom are made in the preliminary mathematical model. However, the top boundary is assumed to be a "no flow" boundary. The hydraulic head distributions at the open inlet and exit boundaries are prescribed. Fully penetrating injection and extraction wells may be present.

The model, hereafter referred to as LT2VSI, makes it possible to evaluate and validate a large number of the relevant individual transport and fate process laws. The important features of LT2VSI are: 1) two-dimensional, horizontal, steady state, fluid flow field defined by a hydraulic head field which depends on appropriate Dirichlet and Neumann boundary conditions and the characterizing spatial dependency of the longitudinal and transverse components of the hydraulic conductivity tensor at saturation and 2) two-dimensional transport and fate of chemicals in the nonhomogeneous aquifer.

The distribution of chemicals is affected by 1) advection and dispersion in both the longitudinal and transverse

directions, 2) linear equilibrium adsorption/desorption processes on each of the porous medium fractions, 3) three different first-order loss processes either metabolism by soil microbes or chemical reaction with other soil components in the free phase, 4) other irreversible processes in the free phase, either metabolism or chemical reaction in the sorbed phase, 5) the presence of zero order sources of chemical, 6) appropriate Dirichlet and Neumann boundary conditions with a provision for nonzero initial distribution of the chemical, and 7) presence of fully penetrating injection and/or extraction wells.

It is assumed that most, if not all, of the chemical and biological process coefficients are at least once continuously differentiable functions of the transverse coordinate and the longitudinal coordinate.

Fluid Flow Field

The porous medium may be nonhomogeneous and anisotropic with respect to fluid flow and has impervious walls on all sides. These conditions allow evaluation of two-dimensional transport and fate. The assumptions concerning the fluid flow field are: 1) the fluid flow field operates at steady state conditions at all times and 2) any fluid flow perturbations introduced at the flow boundaries propagate extremely rapidly throughout the flow field, so that a new steady state is achieved rapidly. Under these conditions the fluid storativity term in the fluid flow model may be neglected for aquifers of the size we are considering; 3) the aquifer material can be nonhomogeneous as well as anisotropic, with the principal components of the saturated hydraulic conductivity tensor assumed to be once continuously differentiable over the interior of the flow domain; 4) Dirichlet boundary conditions hold at both the inlet and outlet ends. The hydraulic head at the inlet end and at the outlet end are specified. No flow Neumann or flux type boundary conditions are specified along the walls.

Chemical Transport and Fate Model

This model provides for unsteady transport and fate of chemicals either present initially at low concentrations or injected at low concentrations into the aquifer. Mass transport is via advection (convection) and dispersion. The dispersion components are assumed to be linearly dependent upon the moduli of the velocity components of the flow field. The longitudinal and transverse dispersivities

as well as the tortuosity are assumed to be once continuously differentiable functions. The porous medium is partitioned into three distinct fractions: sorbing particles (clay minerals and small silt particles), mildly sorbing particles (large silt and sand particles), and strongly sorbing organic matter. Chemical can be introduced into the aquifer with the "feed stream" at the inlet end or from constantly emitting sources in the aquifer. Fluids added by these methods must have a low volumetric concentration and the flow rates must be low so that the previously established fluid flow field is not disturbed. It is assumed that density gradients, density stratification, or local changes in the transport and/or fate properties of the porous medium do not occur in time. Water containing chemicals can be introduced via fully penetrating injection wells or extracted from similar wells by pumping. Loss of chemical can occur via

first-order loss processes including microbial and/or irreversible processes such as chemical transformations and precipitation in both the free and sorbed phases. All the above chemical first-order loss process coefficients are assumed to be continuous functions.

Analytical solutions could not be found for the initial and boundary conditions of the problem stated here. This made it necessary to approximately solve the transport equations. The method used for this in this report is a type of finite difference Euler-Lagrange procedure which is a modification of the method of characteristics.

Conclusions

Methods were developed for solving equations that describe transport and fate of chemicals in laboratory scale models of aquifers. The mathematical model is for aquifers consisting of a single layer of

material, which can be either heterogeneous or homogeneous and either anisotropic or isotropic with respect to the water flow field and can be either heterogeneous or homogeneous but isotropic with respect to the chemical transport field properties.

The two-dimensional, horizontal depth-averaged, transport and fate model can be used for study of the important physical aspects of remediation of contaminated aquifers. A broad range of remediation scenarios may be considered, including placement of injection/extraction wells to induce plume spreading or plume shaping and the effects of regions of varying hydraulic conductivity on the shape of the plumes. A comprehensive treatment of the inlet and exit port induced boundary conditions, included with the analysis, represents a significant step forward in modeling the transport and fate of chemicals in laboratory scale physical aquifers.

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The complete report, entitled "Denitrification in Nonhomogeneous Laboratory Scale Aquifers: 1. Preliminary Model for Transport and Fate of a Single Compound," (Order No. PB90-186 305/AS; Cost: \$17.00, subject to change) will be available only from:

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