SUMMARY OF THE MOST IMPORTANT RESULTS

Our investigation focused on a few selected fundamental processes. The underlying groundwater flow and transport properties at a given contamination site are common to a wide range of chemical and chemical mixtures. Thus, issues related to up-scaling arise in modeling transport and transformation of any contaminant. Rather than focus on many contaminants, our study has focused.

(continued on next page)
on fundamental processes that can be investigated with a high degree of precision and control in our intermediate-scale experiments. The understanding of up-scaling issues gained from our study can be abstracted for application to a wider range of contaminants. Our study provides a valuable database for validation of up-scaling theories and understanding the complexities of entrapment of non-aqueous phase liquids (NAPLs) in heterogeneous media. The specific issues addressed in our investigation are:

1. **Entrapment of NAPLs in heterogeneous formations, sensitivity of solute transport to entrapped NAPLs and prospects for detecting NAPL spills using tracer tests.**

2. **Solute transport in heterogeneousporous media, including the behavior under radial flow conditions.**

3. **Adsorption of dissolved chemicals in chemically heterogeneous aquifers**

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Final Technical Report

T. Illangasekare
H. Rajaram
1. FORWARD

This combined experimental, modeling and theoretical study was funded by the Army Research Office through the Terrestrial Science Branch of the Mechanical and Environmental Sciences Division. The Senior Program Manager for the project was Dr. Russell S. Harmon. The investigators collaborated with Dr. Stacy Howington and Dr. John Peters at the U.S. Army Waterways Experiment Station in designing the experiments and conducting some of the analysis. Dr. Jeffery Holland was the Army laboratory representative. Dr. Mary Hill at US Geological Survey also contributed to the project.

A large amount of laboratory experimental data was generated as a part of this research project. Most of these data appears in the thesis and dissertations of the graduate students who were supported through the grant. Investigators who would like to obtain this data in electronic form should contact the principal investigators.
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**Appendices**

1. Multiple Experimental Realizations of Dense Nonaqueous Phase Liquid Spreading in Water-Saturated Heterogeneous Porous Media.


3. Intermediate-scale experiments and numerical simulations of transport under radial flow in a two-dimensional heterogeneous porous media.

4. Experimental Investigation of One-dimensional reactive solute transport.
3. LIST OF APPENDIXES, ILLUSTRATIONS AND TABLES

Appendices:

1. Multiple Experimental Realizations of Dense Nonaqueous Phase Liquid Spreading in Water-Saturated Heterogeneous Porous Media.


3. Intermediate-scale experiments and numerical simulations of transport under radial flow in a two-dimensional heterogeneous porous media.

4. Experimental Investigation of One-dimensional reactive solute transport.

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4. STATEMENT OF THE PROBLEM STUDIED

Remediation of aquifers contaminated with waste chemicals is a topic of public concern and of considerable interest to the Army. Carefully designed and properly validated numerical models can be used as tools to design and evaluate remediation strategies for these aquifers. Numerical models that simulate groundwater flow and physical, chemical and biological behavior of chemicals in the subsurface, require values for relevant aquifer properties/parameters and the state of contamination. A broad range of physical and chemical parameters are needed in order to model groundwater flow, transport of dissolved substances, multiple fluid flow and entrapment, dissolution of entrapped chemicals and chemical and biological processes. Techniques for the determination of these parameters in the laboratory under controlled conditions are fairly well developed. Measurements at the laboratory scale are typically carried out on small cores, within which the soil properties are fairly homogeneous. At the field scale, however, these parameters exhibit significant spatial variations. Realistic modeling of groundwater contamination at the field scale should incorporate the influence of these spatial variations.

Due to limitations in the available technologies and high instrumentation costs, it is not always possible to obtain all the necessary data at large number of sampling points in the aquifer. Hence, methodologies are needed to use sparse data to fully characterize aquifer systems both at spill site scale and regional scale to provide inputs to numerical models. Sparse data may include either Apoint-values based on small-scale samples or integrated measurements obtained from forced-gradient tracer tests. The development of methodologies for aquifer characterization using sparse data requires an understanding of relationships between Apoint-values and the parameters that control the flow and transport behavior at the field-scale. In the case of integrated measurements, the influence of aquifer heterogeneity is reflected in the integrated behavior and inverse methods need to be developed to quantify aquifer heterogeneity. The methods that are used to determine the field-
scale (or effective) parameters from small-scale measurements is referred to as \( A_{\text{up-scaling}} \). The investigation of basic processes, development of experimental methods, validation of numerical models for up-scaling is the basic focus of the research study reported here.

Various theories have been developed for up-scaling and effective parameter estimation based on numerical, geostatistical and stochastic methods for characterizing field systems based on sparse data. However, these theories have not been systematically validated. The data available for the validation of these methods have come from a few field experiments. Field experiments are generally expensive and all the controls needed to obtain accurate data cannot be implemented adequately. Furthermore, field tests in highly heterogeneous media are difficult to execute and with the exception of the tracer test at the MADE (macrodispersion experiment) site in Columbus Mississippi, most of the available field data are from fairly homogeneous sand and gravel aquifers. In this research, we generated accurate laboratory data in intermediate-scale soil tanks for the validation of up-scaling theories and modeling approaches pertinent to heterogeneous media, such as the GMS (Groundwater Modeling System) of the U.S. Army Waterways Experimental Station. The experimental systems were designed with heterogeneities resembling those observed in field sites. Some of the experimental systems were constructed with a fairly large degree of heterogeneity, to provide high quality data sets on transport processes in highly heterogeneous media, which are lacking in the current literature. Our investigation also examined the value of sparse data, as in convergent flow tracer tests, for aquifer characterization.

5. SUMMARY OF THE MOST IMPORTANT RESULTS

Our investigation focused on a few selected fundamental processes. The underlying groundwater flow and transport properties at a given contamination site are common to a wide range of chemical and chemical mixtures. Thus, issues related to up-scaling arise in modeling transport and transformation of any contaminant. Rather than focus on many contaminants, our study has focused
on fundamental processes that can be investigated with a high degree of precision and control in our intermediate-scale experiments. The understanding of up-scaling issues gained from our study can be abstracted for application to a wider range of contaminants. Our study provides a valuable database for validation of up-scaling theories and understanding the complexities of entrapment of non-aqueous phase liquids (NAPLs) in heterogeneous media. The specific issues addressed in our investigation are:

1. **Entrapment of NAPLs in heterogeneous formations, sensitivity of solute transport to entrapped NAPLs and prospects for detecting NAPL spills using tracer tests.**

2. **Solute transport in heterogeneous porous media, including the behavior under radial flow conditions.**

3. **Adsorption of dissolved chemicals in chemically heterogeneous aquifers**

One Ph.D. student (H-C Chao) and one MS student (R. Compos) was fully supported through this research grant. The experimental components of research of a second Ph.D. student (G. Barth) and MS student (S. Mehl) were supported through this grant. The important findings of their research are summarized here. The details of research results and data can be found in Chao (1999), Compos (1998), Barth (1998) and Mehl (1998). The findings will also appear in a number of journal articles that have been submitted for publication and/or in preparation (Barth et al., 1999a, 1999b, 1999c, Chao et al. 1999, Compos et al, 1999).

1. **Entrapment of nonaqueous phase liquids (NAPLs) and sensitivity**

   Recent research has focused on a class of contaminants known as dense nonaqueous phase liquids (DNAPLs) which have drawn much interest due to their toxicity and widespread presence at waste sites. DNAPLs, particularly chlorinated organic solvents, pose far more significant
problems in the context of remediation methodology due to the propensity of the liquids to penetrate the water table and sink deep within the aquifer. Some common DNAPLs include 1,1,1-trichloroethane (TCA), polychlorinated biphenyls (PCBs), trichloroethene (TCE) and tetrachloroethene (PCE).

A significant fraction of dense nonaqueous phase liquid (DNAPL) spills remain entrapped in the spread-zone of heterogeneous aquifers at residual to almost full saturation. Estimation of the highly variable saturation distribution of the DNAPL is of value in the context of remediation design and risk assessment. However, this is extremely difficult to quantify in the field. Past research has indicted that soil heterogeneity has a significant effect on flow and entrapment behavior (Illangasekare et al, 1995). Heterogeneity induce lateral spreading and unstable flow (Held and Illangasekare, 1995a, 1995b) and may increase the extent of the entrapment zone. The results presented here involve the unique combination of a complex heterogeneous porous media structure and accurate quantification of NAPL spill characteristics. Multiple realizations of random fields with the same stochastic parameters were generated and formed the basis for the laboratory porous media configurations. Two-dimensional DNAPL spill simulations were conducted in water-saturated randomly heterogeneous porous media and a gamma-attenuation system was used to quantify the entrapment distribution. Our experiments also reveal that the important role of pore-scale instabilities influencing DNAPL spreading, a feature which is not typically incorporated in continuum multiphase flow formulations. The wetting phase spatial structure distribution and hydraulic conductivities are significantly altered as a result of NAPL entrapment. Statistical analyses of the modified wetting phase hydraulic conductivity field indicated an apparent similarity, which may be as useful description of the extent of the entrapment zone. We believe that this controlled dataset will be useful in validating numerical models and physical conceptualization of NAPL spreading in heterogeneous media.

**Results:**
(a) Process of DNAPL migration and entrapment:

The process of NAPL migration through the heterogeneous two-dimensional aquifers is dependent upon heterogeneity and the influence of fingering. Figure 1 shows the packing configuration created using five test sands. Figure 2 shows an example of an entrapment distribution resulting from a spill. The five sands were packed to represent a spatially correlated random field. The migration process follows a pattern of vertical migration, pooling and horizontal spreading at the interface with a lower permeability lens.

Figure 1. Experiment 1, sand configuration.

Figure 2. Experiment 1, NAPL saturation after 7 days.
The NAPL distribution is strongly influenced by the heterogeneity of the soil. Some high permeability regions exhibited the presence of nonwetting fluid although they were not visibly connected to the continuous non-wetting phase plume. NAPL migration into these regions may be explained by fingering mechanisms. The size and location of the high permeability regions are the primary influences upon the entrapment distribution of the NAPL. The distribution of the non-wetting phase in each of the five sand types is plotted in Figure 2. The greatest percentage of NAPL was found in the coarser #50 sand regions. The NAPL did not infiltrate the fine #110 lenses. However a relatively high percentage of NAPL was found to reside in the coarse #16 mesh sand lenses. To account for the low frequency of the #16 mesh sand, the distribution of NAPL was normalized with the frequency of the sand type (Figure 3). The high-normalized NAPL percentage within the higher permeability sands further reinforces the influence of the permeability structure.

![Normalized phase density](image)

**Figure 3:** Normalized distribution of NAPL.

(b) Entrapment structure:
The extent of lateral spreading may be quantified by calculation of the non-wetting phase second moment. The experiments in which the non-wetting fluid spread furthest horizontally had the largest second moments (Figure 4 and 5). In Experiments 1, 2 and 3 the NAPL plume reached the lateral impermeable boundaries of the tank. Experiments 4 and 5 did not exhibit as much horizontal spreading and the non-wetting fluid did not spread to the lateral boundaries. The sand configurations of Experiments 4 and 5 had a greater density of higher permeability regions centered within the experimental, and consequently the second moments in Experiments 4 and 5 were considerably less than in the Experiments 1, 2 and 3.
The extent of vertical infiltration tended toward some ensemble average but the extent of lateral spreading was more variable. The horizontal and vertical centroids of the NAPL plume are shown in Figure 6 and 7. The horizontal centroids are calculated about a vertical axis through the center of the NAPL source. The origin for the vertical centroids was the upper boundary. The spills with the largest horizontal second moments exhibited horizontal centroids farther from the vertical
axis as the NAPL migrated off center. The vertical centroids did not vary much and had a mean value of 16 cm below the source. A large DNAPL spill under the water table will decrease the water permeability of the aquifer.
Modified values of $ln(K)$ are calculated at each grid point and are used to construct the modified horizontal and vertical variograms of $ln(K)$ for each NAPL entrapment distribution (Figures
8 and 9). The stochastic parameters before and after the introduction of NAPL are shown in Table 1. The mean $\ln(K)$ decreased for all the spills due to the permeability depression caused by NAPL entrapment and the variance increased due to the wider range of permeabilities in the sand packing.

The modified variogram curves were larger after the spill due to the wider range of $\ln(K)$ and the presence of isolated NAPL saturated lenses. The NAPL plume increases the permeability correlation scale in each experiment. At small separation the horizontal and vertical modified variograms were similar for all experiments suggesting a correlation in the NAPL saturation at small scales regardless of the random porous media heterogeneity.

(c) Flow and transport in the NAPL entrapment zone:

The modification of the hydraulic conductivity field resulting from relative-permeability effects caused by the spill appears to be statistically invariant between different realizations of the underlying random field. Our experimental results established that the modified statistical structure of the hydraulic conductivity distribution contains information about the spill volume and extent. We conducted a detailed set of tracer tests across the spill regions in a large intermediate scale soil flume to obtain the characteristics of the modified flow and transport field due to the NAPL entrapment. The results of this investigation are summarized.
Figure 8  Modified horizontal variograms.

Figure 9  Modified vertical variograms.
Table 1. Stochastic Parameters Before and After Spill

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(i) Tracer density guidelines for heterogeneous porous media:

Tracer experiments provide information about aquifer material properties vital for accurate site characterization. Unfortunately, density effects can distort tracer movement, leading an inaccurate assessment of material properties. Guidelines for judging density effects are available and have been used for homogeneous media, but their extension to heterogeneous media is unclear. A series of experiments were conducted to develop guidelines for tracer tests in heterogeneous aquifers. Homogeneous and heterogeneous zones were created in a 10 X 1.5 X 0.05 meter tank using six sands. Experimental results illustrate the sensitivity of tracer tests to the initial density of injected solute. Rewriting the traditional measure of density effects yields a new dimensionless parameter: a ratio of density gradient to hydraulic gradient that is more appropriate for heterogeneous systems. Incorporation of hydraulic gradient variability into the dimensionless parameter allows evaluation of the potential for density effects in heterogeneous systems that are less well characterized than our intermediate-scale experiments. Applying this dimensionless parameter to our experiments and two
classic field tracer tests demonstrates the need to account for local gradient variation when evaluating tracer experiments in heterogeneous systems.

(ii) Predictive modeling of flow and transport experiments in heterogeneous media:

   Predictive simulation of flow and conservative transport through porous media requires measured physical parameter values capable of representing system characteristics at the numerical grid scale. Practical considerations require that predictive simulation of field-scale systems focus on the issue of parameter upscaling. With field data it is not possible to isolate the cause of discrepancies, as the explicit spatial distribution of materials in the subsurface is unknown. Heterogeneous intermediate-scale experiments were used to provide a complex system in which the distribution of materials and boundary conditions are characterized. Explicit representation of heterogeneity allows analysis of the fundamental issue of whether simulations using values measured at the scale of heterogeneity produce predictions that match measured pressures, tank effluent, and conservative transport. Predictive numerical simulations, using the mean measured values of hydraulic conductivity, under-predicted the observed tank effluent by 15% and poorly reproduced the observed conservative transport suggesting that even detailed field-site simulations will under-predict ground water budgets by about 15 percent. Nonlinear regression methods using the observed tank effluent and pressure measurements throughout the intermediate scale experiment successfully determined hydraulic conductivity values that resulted in close matches between simulated and observed flows, pressures and transport. The estimated hydraulic conductivity values are similar to only the highest measured values suggesting that the packing or design of the tank was conducive to permeabilities greater than the laboratory experiments indicated despite exhaustive efforts to avoid such a bias. The results imply that attempts to validate a scaling theory by comparison of observations and predictions simulated must account for the significant contribution of measured parameter predictability.

(iii) Solute flux sensitivity to entrapped nonaqueous phase liquids:
Detailed characterization of their distribution in the subsurface is required for efficient remediation. Characterization efforts at NAPL contaminated sites rely heavily on core scale evaluation of material properties and NAPL saturation distribution. As an alternative, tracer tests provide parameter values based on the continuous system. Many published field tracer tests relied on extensive sampling networks to evaluate the tracer concentration spatial distribution. Practical limitations force most field investigations to rely on temporal data from a limited number of samplers. In series of experiments we investigated the sensitivity of a conservative tracer-sampling network to the entrapment of NAPLs. A series of intermediate-scale tracer experiments were performed in a heterogeneous porous media. Tracer tests performed prior to the introduction of any NAPL provide the baseline response of the heterogeneous porous media. Following each of two NAPL spills, tracer tests were performed to obtain the impacted solute flux characteristics. The effect of the NAPL entrapment was compared to variability between realizations using flow and transport models calibrated with the experimental data. Analysis of the results reveals a distinct impact on solute transport characteristics in the two-dimensional heterogeneous experiments.

2. Solute transport under radial flow conditions in heterogeneous porous media

The focus of this investigation was on examining the scale-dependence of dispersivities obtained from radial flow tracer tests and the variability of these estimates. The dispersivity is an aquifer parameter that controls the rate of spreading or dilution of contaminants in aquifers. It is well established that the dispersivity in a heterogeneous medium is scale-dependent. However, the scale-dependence under radial flow conditions was not investigated previously. Several theories of scale-dependence in dispersivities have however used observations from radial flow tracer tests, which are easier to execute than natural gradient tracer tests.

Field data on dispersivity estimates from uniform and radial flow tracer tests are often interpreted without distinction. Can the same macrodispersivity values apply regardless of the type
of mean flow? This question is addressed based on intermediate-scale experiments and numerical simulations in two-dimensional heterogeneous porous media. The scale-dependence of dispersivities estimated from radial flow tracer tests in two-dimensional heterogeneous porous media, and the variability of these estimates are quantified. The results presented demonstrate that even in the same random hydraulic conductivity realization, the scale-dependence inferred from uniform flow and radial flow tracer experiments can be very different. In particular, dispersivities estimated using type-curve matching from radial flow tracer experiments continue to exhibit a scale-dependence, even at scales where an asymptotic constant dispersivity value applies for transport in a uniform mean flow. Furthermore, the dispersivity estimated from radial flow tracer tests is significantly smaller than that observed in uniform flow [Figure 10]. The discrepancy between the behavior of transport in uniform and radial flows is apparently due to the converging nature of the radial flow, and the small source size involved in forced-gradient tracer tests.

In both intermediate-scale experiments [Figure 11] and numerical simulations, there is substantial variability in dispersivity values estimated from different injection points at the same radial distance from the pumping well. Numerical simulations suggest that the coefficient of variation of the dispersivity values estimated at the same radial distance, approaches a value of about 1.0, for radial distances much larger than the correlation scale [Figure 12].

This investigation suggests that the widely used convergent radial flow tracer test, which is a very useful type of sparse data for aquifer characterization, must be used cautiously. The high degree of variability in dispersivity estimates obtained from radial flow tracer tests, suggests that the sparse data may be somewhat misleading. The results obtained here suggest that a few tracer tests, with different injection points and the same pumping well, may be a more effective approach for aquifer characterization. Our results will also be useful for validating future theories, which will aim to estimate the statistical structure of aquifer heterogeneity based on the data from a few radial flow tracer tests.
Figure 10 A comparison of dispersionsities estimated from radial flow and uniform flow tracer test simulations. This figure presents results from point source injection simulations. The dispersionsities estimated from radial flow are much smaller than those estimated from uniform flow.
Figure 11 Scale-dependence and variability of dispersivities estimated from radial flow tracer tests in the laboratory tank. Dispersivity estimates corresponding to all injection ports are shown.
Figure 12 Coefficient of variation ($\sigma_\alpha$/mean $\alpha$) of dispersivity estimates as a function of dimensionless radius (distance between injection and pumping well divided by correlation scale).
3. Adsorption of contaminants in chemically heterogeneous aquifers

Recent field experiments at Borden and Cape Cod also included sorptive tracers such as halogenated hydrocarbons (PCE, CTET, DCB, HCA, BROM), and inorganicspecies such as Lithium and Molybdate. These experiments revealed two important new features related to sorptive transport: (i) enhanced dispersion (i.e. dispersivities observed for sorbing solutes are much larger than dispersivities for non-reactive solutes), and (ii) time-dependence of the retardation factor. These observations have spawned diverse theories explaining the mechanisms contributing to these phenomena. [Garabedian et al., 1988; Dagan, 1989; Roberts et al., 1986; Goltz and Roberts, 1986; Ball and Roberts, 1991; Brusseau et al, 1989a; Kabala and Sposito, 1989; Miralles-Wilhelm and Gelhar, 1996; Rajaram, 1997; Burr et al., 1994; Mishra, 1997; Brusseau and Srivastava, 1997]. It is apparent that the research community is yet to accept a single definitive explanation for the enhanced dispersion and time dependent velocity observed during the Borden and Cape Cod field experiments.

In summary, the main mechanisms that have been proposed to explain the time dependence of the retardation factor and enhanced macrodispersivity are intraparticle diffusion, nonequilibrium sorption, and aquifer heterogeneity. The relative importance of these mechanisms depends on the sorption rates, the groundwater flow velocity and the spatial variability of aquifer properties (i.e. hydraulic conductivity and sorption parameters).
Large-scale field experiments like those at Borden and Cape Cod are very expensive and difficult to carry out on a routine basis. Furthermore, the complexity of field systems may cause difficulties in interpreting results wherein the influential factors are hard to isolate. Theoretical developments and numerical simulations have their advantages in cost-effective and flexibility. However, without validation through physical experiments, the usefulness of both approaches may be questionable. Our research is motivated by a recognition of the need for experiments under controlled conditions in well characterized media, incorporating physical and chemical heterogeneity.

Intermediate-scale flow cells incorporating porous media with random heterogeneities have been used in previous investigations of physical processes (e.g., Silliman and Simpson, 1987; Schincariol and Schwartz, 1990; Illangasekare et al., 1995; Barth et al., 1999; Chao et al. 1999). Furthermore, the correlation structure of the permeability field has been explicitly controlled and quantified (Welty and Elsner, 1997; Chao et al. 1999). However, correlated random fields with chemical heterogeneity have not been constructed previously. In this research, we showed that a correlated random sorption field composed of silica sands having a known set of statistical properties can be constructed in the laboratory. By carefully selecting a reactive tracer and characterizing its sorptive interactions with test sands via batch and column experiments, we presented an approach for constructing a chemical heterogeneous porous medium.

A negative correlation between $\ln K$ and $\ln K_d$ was observed in both batch and column experiments. Thus, we can construct a cross-correlated random field with physical and chemical heterogeneity. In column experiments, asymmetrical breakthrough curves, extended tailing and apparent retardation factors increasing with decreasing pore-velocity were observed. The transport and sorption parameters were estimated by fitting column breakthrough curves to a two-site model with the well-known computer code, CXTFIT (Toride et al. 1995). The sorption parameters of individual sands were used to construct a layered heterogeneous column. The transport behavior of the heterogeneous column was examined and compared to individual homogeneous column tests,
suggesting the effective retardation factor is within the range of retardation factors estimated for the different sands. The methodology presented here can be extended to higher dimensions, which will lead to more realistic systems representative of field scale systems. Such experimental systems will be useful for validating stochastic theories and numerical models for a variety of reactive transport problems. This will be pursued in a current ARO funded project that is in progress.
6. LIST OF PUBLICATIONS AND TECHNICAL REPORTS


7. LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

1. R. Compos, MS Student, Completed in December 1998.
2. H-C Chao, PhD Student, Completed in December 1998.
3. G. R. Barth, PhD Student, Completed in December 1998.
4. S. Mehel, MS Student, Completed in December 1998.

8. REPORT OF INVENTIONS

None

9. BIBLIOGRAPHY


Barth, G. R., M. C. Hill, T. H. Illangasekare and H. Rajaram, 1999c. Predictive and regression modeling of intermediate-scale flow and transport experiments in heterogeneous porous media,
in review.


