

FINAL REPORT
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**Partitioning Tracers for In-Situ Measurement of
Nonaqueous Phase Liquids in the Subsurface**

Principal Investigator: M.L. Brusseau
Dept. of Soil, Water, and Environmental Science
Dept. of Hydrology and Water Resources
University of Arizona, Tucson, Arizona 85721

Collaborators: N.T. Nelson¹, M. Oostrom², M. White², T.W. Wietsma³

¹Now at Daniel B. Stephens & Associates, Inc.
Albuquerque, New Mexico

²Environmental Technology Division, and

³Environmental Molecular Science Laboratory
Pacific Northwest National Laboratory

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EXECUTIVE SUMMARY

Non-aqueous phase (immiscible organic) liquids (NAPLs) occur in the subsurface at numerous contaminated sites and can act as long-term sources of both vapor-phase and groundwater contamination. Accurate evaluations of contaminant transport, effective risk assessments, and successful remediation for NAPL-contaminated sites requires knowledge of the occurrence and distribution of NAPL, and its dissolution behavior. The availability of such information is limited by current site characterization techniques, which include analysis of soil gas, core sampling, cone penetrometer testing, and monitoring well sampling. A major limitation of these methods is that they provide data at discrete points, such that the probability of sampling a zone of localized NAPL is quite small. In addition, the use of point-sampling methods for characterizing large domains is constrained by sample-size limitations. Specifically, because of the heterogeneity inherent to the subsurface, it is very difficult to accurately characterize a large system without a cost- and time-prohibitive number of sampling points. Thus, methods that provide measurements at larger scales are being developed to complement the point-sampling methods. One such group of methods is based on the use of tracer tests.

The overall goal of the proposed project is to explore the use of an innovative in-situ method, partitioning tracer tests, for the detection and quantification of NAPLs in subsurface systems. In addition, the influence of factors such as physical heterogeneity, non-uniform NAPL distribution, and dilution effects on NAPL-water mass transfer is examined. This latter issue is important with respect to both the efficacy of the partitioning tracer method and the dissolution behavior of NAPLs. Lastly, the use of gas-phase partitioning tracer tests to measure soil-water content and fluid-fluid interfacial areas is evaluated.

As part of this project, experiments were conducted in intermediate-scale flow cells to examine the impact of physical heterogeneity, non-uniform NAPL distribution, and dilution effects on partitioning tracer test performance and on NAPL dissolution behavior. The results of these experiments demonstrate that partitioning tracer tests can provide accurate measurements of NAPL saturation distributed in domains through which water flow is not constrained. However, the results suggest that partitioning tracer tests may not be able to completely measure NAPL that is entrapped in lower-permeability zones. Although the quantitative performance of the partitioning tracer test may in some cases be constrained by factors such as those investigated herein, the method is a viable tool for characterizing sites that may be contaminated by NAPL.

The aqueous concentrations of TCE and DCA measured in the flow-cell effluent were significantly less than solubility, due primarily to dilution associated with the non-uniform immiscible-liquid distribution and by-pass flow effects associated with physical heterogeneity. A quantitative analysis of flow and transport was conducted using a three-dimensional mathematical model wherein immiscible-liquid distribution, permeability variability, and sampling effects were explicitly considered. Independent values for the global initial dissolution rate coefficients were obtained from dissolution experiments conducted using homogeneously packed columns.

The independent predictions obtained from the model provided good representation of NAPL dissolution and aqueous-phase transport behavior, signifying model robustness. This indicates that for the complex 3-D model, explicit consideration of the larger-scale factors that influenced immiscible-liquid dissolution in the flow cells allowed the use of a dissolution rate coefficient that represents only local-scale mass transfer processes. Conversely, the use of simpler models that did not explicitly consider the non-

uniform immiscible-liquid distribution required the use of dissolution rate coefficients that are approximately three orders-of-magnitude smaller than the values obtained from the column experiments. The rate coefficients associated with the simpler models represent composite or lumped coefficients that incorporate the effects of the larger-scale dissolution processes associated with the non-uniform immiscible-liquid distribution, which are not explicitly represented in the simpler models, as well as local-scale mass transfer. These results demonstrate that local-scale dissolution rate coefficients, such as those obtained from column experiments and which represent local-scale dissolution processes, can be used in models to successfully predict dissolution and transport of immiscible-liquid constituents at larger scales when larger-scale factors influencing dissolution behavior are explicitly accounted for in the model.

Given the potential significance of interfacial and bulk-water retention for contaminant transport and remediation, it is important to consider methods for characterizing these processes at the field scale. Gas-phase tracer experiments using a suite of phase-selective partitioning tracers in combination with nonreactive tracers, as presented herein, may be one viable approach. For example, partitioning tracer tests were used successfully to measure the soil-water content for experiments conducted in columns and in a large lysimeter. In addition, the use of partitioning tracer tests to measure effective gas-water interfacial areas was demonstrated.

RESEARCH OBJECTIVES AND BACKGROUND

Goals and Objectives

Non-aqueous phase (immiscible organic) liquids (NAPLs) occur in the subsurface at numerous contaminated sites and can act as long-term sources of both vapor-phase and groundwater contamination. Both effective risk assessment and remediation of NAPL-contaminated sites is limited by current site characterization techniques, which include analysis of soil gas, core sampling, cone penetrometer testing, and monitoring well sampling. A major limitation of these methods is that they provide data at discrete points, such that the probability of sampling a zone of localized NAPL is quite small. Finding and removing dense NAPLs (DNAPL) sources is further complicated because they are denser than water, can migrate below the water table, and move along pathways that may differ from those of water flow.

The overall goal of the proposed project is to explore the use of an innovative in-situ method, partitioning tracer tests, for the detection and quantification of DNAPLs in subsurface systems. In addition, the influence of factors such as physical heterogeneity, non-uniform NAPL distribution, and dilution effects on NAPL-water mass transfer is examined. This latter issue is important with respect to both the efficacy of the partitioning tracer method and the dissolution behavior of NAPLs. Lastly, the use of gas-phase partitioning tracer tests to measure soil-water content and fluid-fluid interfacial areas is evaluated.

The specific objectives that will be addressed to accomplish these goals are as follows:

1. Investigate the use of partitioning tracer tests to detect and measure NAPL saturation in porous media.

2. Investigate the effect of rate-limited mass transfer on the transport behavior of partitioning tracers.
3. Investigate the effect of porous-media heterogeneity, non-uniform NAPL distribution, and dilution effects on the transport behavior of partitioning tracers and on the dissolution behavior of NAPLs.
4. Evaluate the use of gas-phase partitioning tracer tests to measure soil-water content.
5. Investigate the use of partitioning tracer tests to measure fluid-fluid interfacial areas in porous media.
6. Develop and evaluate mathematical models capable of simulating the dissolution of NAPLs and the transport of partitioning tracers in complex systems.

Background

NAPL Characterization and Partitioning Tracer Tests

Soil and groundwater pollution has become one of our most pervasive environmental problems, and remediating contaminated sites has proven to be a formidable challenge. Risk assessments, as well as remediation efforts, are often limited by the complexity of the subsurface environment and by our limited knowledge of that environment. As noted in a National Research Council report, advances in characterizing subsurface properties and processes are essential for improving subsurface assessments and cleanup technologies (1). Most current characterization methods, such as the use of monitoring wells for collecting groundwater or soil-gas samples and coring for solid-phase sampling provide what are essentially point values. Many newer technologies, such as those based on "geoprobes", are also point-sampling methods. These methods have the potential to provide accurate and precise data for a small domain, which is an

advantage for certain applications. However, the use of point-sampling methods for characterizing large domains is constrained by sample-size limitations. Specifically, because of the heterogeneity inherent to the subsurface, it is very difficult to accurately characterize a large system without a cost- and time-prohibitive number of sampling points. Thus, methods that provide measurements at larger scales are being developed to complement the point-sampling methods. One such group of methods is based on the use of tracer tests.

The presence of immiscible liquids in the subsurface is often the single most important factor limiting remediation of sites contaminated by organic compounds (1). Unfortunately, because the subsurface distribution of immiscible-liquid saturation is complex, the use of point-sampling methods is often problematic. This has fomented interest in the use of partitioning tracer tests for characterizing the occurrence, quantity, and distribution of immiscible-liquid saturation in subsurface systems. The conceptual and theoretical basis of the method has been presented in several recent works (2, 6-8, 13, 16, 17, 22) and need not be repeated herein.

The use of partitioning tracer tests to measure immiscible organic-liquid saturation in the subsurface was developed by the petroleum industry in the 1970's as a means to determine residual oil saturation in oil fields (3,4). Since then, numerous partitioning tracer tests have been conducted, as reviewed by Tang (5). The use of the partitioning tracer method for measuring immiscible-liquid saturation in environmental systems was demonstrated in the laboratory by Jin et al. (6) and Wilson and Mackay (7). Both groups of investigators showed that partitioning tracer tests provided accurate estimates of the amount of chlorinated-solvent saturation emplaced in sand-packed columns.

The field-scale application of the partitioning tracer method for characterizing immiscible-liquid contamination has been illustrated recently in several published works. Nelson and Brusseau (8) conducted partitioning tracer tests to detect and measure immiscible-liquid saturation in a chlorinated-solvent contaminated aquifer associated with a Superfund site in Tucson, AZ. Retardation of the partitioning tracer (SF_6) relative to the nonreactive tracer (bromide) was observed at certain monitoring locations, indicating the probable presence of immiscible-liquid saturation within portions of the swept zone. These results were in accordance with other lines of evidence, such as the removal of large volumes of solvent during the operation of a soil venting system in the vadose zone directly above the location of the tracer tests, and the long-term tailing behavior exhibited for trichloroethene elution during operation of the pump-and-treat system (9,10).

Numerous pilot-scale partitioning tracer tests have been conducted at Hill Air Force Base in Utah as part of a multiple-institution program to evaluate innovative subsurface remediation and characterization technologies (11). In these studies, several alcohol tracers were used for measuring the amount of petroleum-based immiscible-liquid saturation associated with the water-saturated zones confined within approximately 3 m by 5 m fully enclosed cells. For each cell, partitioning tracer tests were conducted before and after a pilot test of an innovative remediation technology. The results obtained from the partitioning tracer tests were used to help evaluate the mass of contamination removed by the remediation technology.

A comparison of the results of partitioning tracer tests conducted before and after a cosolvent flood indicated a reduction in immiscible-liquid saturation of approximately 80% (12,13). This value can be compared to mass-removal values calculated using data obtained from analysis of core samples collected before and after the cosolvent flood. These values ranged from 77% to

90% for the five contaminants measured (12). Jawitz et al. (14), who examined the performance of a cosolvent/surfactant flood, reported a reduction in immiscible-liquid saturation of 72% based on the results of their partitioning tracer tests. This value compares relatively well to the mass-removal values calculated from core data, which ranged from 65% to 96% for the seven compounds reported. Brusseau and colleagues (15-17), who examined the performance of a complexing-sugar flood, reported a reduction in immiscible-liquid saturation of 43% based on the results of their partitioning tracer tests. This value compares very well to the weighted-mean mass removal value of 41% determined from core data collected for 12 constituents. In addition, the saturation values (ranging between 10 and 15%) obtained from the tracer data collected at the three extraction wells for the initial partitioning tracer test were similar to saturations (12 to 18%) estimated from the results of total organic-carbon analysis of core samples collected prior to the test. Falta et al. (18,19), who examined the performance of a cosolvent flood, reported a reduction in immiscible-liquid saturation of 78% based on the results of their partitioning tracer tests. This value is identical to the mean mass-removal value of 78% determined from the core data.

The results reported above indicate that the partitioning tracer method produced mass-removal values similar to those obtained with traditional coring. Dissimilar results were reported for two other Hill AFB-associated investigations. The results of the partitioning tracer tests reported by Gierke et al. (20), who examined the performance of air sparging, did not reflect a measurable change in saturation, although the mass-removal values based on the core data ranged from 33% to 59%. Blanford et al. (21), who examined the performance of vertical recirculation with in-well aeration, reported an apparent increase in immiscible-liquid saturation of 32% based on the results of the partitioning tracer tests. This apparent increase, which was attributed to

mobilization of immiscible liquid caused by the vertical-oriented flow field, was matched by the results obtained for the core data (increase of 27%).

Two sets of partitioning tracer tests, reported by Pope and colleagues (22,23), have been conducted in conjunction with pilot-scale surfactant floods of chlorinated-solvent contaminated aquifers. One set was conducted at the Portsmouth Gaseous Diffusion Plant in Ohio (22) and the other was conducted at Hill AFB (23). For both cases, comparison of the tracer test results obtained before and after the surfactant flood indicated removal of a substantial amount of solvent mass.

Hayden and Linnemeyer (24) reported the results of a partitioning tracer test conducted to measure coal-tar saturations in an aquifer underlying a former coal gasification plant in Vermont. An average saturation value of 2.4% was estimated from the field tests. This value compares relatively well to values, which ranged from 0.8% to 2.2%, obtained from the results of analysis of three sets of core samples collected from the site.

A different approach was used by Hunkeler et al. (25) in their application of a partitioning tracer test to measure diesel-fuel saturation at a site in Switzerland. In their approach, the distribution of a naturally occurring radioactive isotope (^{222}Rn) was monitored across the contaminated site. A reduction in ^{222}Rn activities was observed for groundwater samples collected within the fuel-contaminated zone, compared to values measured for samples collected upgradient of the contaminated zone. The reduction in ^{222}Rn activity, due to partitioning of the ^{222}Rn into the diesel fuel, was used to estimate an average diesel-fuel saturation of 1.5%. This value compares well to the value of 1.9% obtained from analysis of a single core sample. The use of radon to characterize immiscible-liquid contamination was also recently examined by Semprini et al. (26).

The results discussed above indicate that the partitioning tracer test has been used successfully to detect the presence and measure the amount of immiscible-liquid saturation in water-saturated subsurface systems. Furthermore, partitioning tracer tests have been shown to be a viable method for evaluating the mass-removal performance of remediation systems. However, it must be pointed out that for the field-scale applications reported above, those associated with the Hill AFB project are the only ones wherein the results obtained from partitioning tracer tests have been compared to a substantial set of independently obtained saturation data (i.e., core data). These applications, as noted above, were implemented by conducting the tracer tests in 3 X 5-m fully enclosed test cells. In addition, the immiscible liquid was widely distributed throughout the cells and occurred at relatively high saturations, ranging from 5% to 12%. These conditions are relatively ideal for successful performance of the partitioning tracer method. Additional tests should be conducted under a variety of conditions, where the results of the partitioning tracer tests are compared to robust independent measures of saturation. Given the difficulty and expense of conducting fully controlled field experiments, intermediate-scale experiments have been used to examine larger-scale phenomena under controlled conditions. This approach is used for the current project.

Gas-Phase Partitioning Tracer Tests and Measuring Soil-Water Content

The work presented above focused on measuring bulk immiscible-liquid saturation in water-saturated zones using partitioning tracer tests based on water flow. A similar approach could also be used to measure immiscible-liquid saturation in the vadose zone. However, given the relative rates of water and gas flow, a more practical approach would be to conduct gas-phase partitioning

tracer tests. The major difference between gas- and water-phase tracer tests is the selection of the tracers to reflect the gas phase as the mobile fluid. The use of gas-phase partitioning tracer tests to determine residual oil saturation in gas-saturated petroleum reservoirs was introduced by Tang and Harker (27). More recently, the use of gas-phase partitioning tracer tests to measure immiscible-liquid contamination in vadose-zone systems has been examined in laboratory (28,29) and field (30-33) experiments.

For applications involving gas-phase partitioning tracers, it is important to evaluate the potential retention of the partitioning tracers by water. Such retention, if not accounted for, could result in erroneous estimates of NAPL saturation. Thus, the water-partitioning behavior of the compounds must be known, as well as the soil-water content of the target domain. There are several methods with which to measure soil-water content, such as neutron thermalization, time-domain reflectometry, and gravimetric analysis of core samples. These methods have a history of successful use. However, the majority of methods in current use provide "point values" of soil-water content (i.e., small sample volumes). While this is an advantage for obtaining accurate information at small scales, it is a disadvantage for determining soil-water contents for larger (field) scales. The partitioning-tracer concept can be applied in this situation to develop a larger-scale method for measuring soil-water content, as discussed by Brusseau et al. (34). Such a method would be of interest not only for evaluating the total retention of NAPL-phase partitioning tracers during NAPL characterization activities, but for many other activities, given the critical importance of soil-water content to agriculture, forestry, hydrology, and engineering.

The application of gas-phase partitioning tracer tests for measuring soil-water content has been recently demonstrated at the laboratory scale (34, 35). In related work, Deeds et al. (36) used

column experiments to measure the Henry's coefficient for a water partitioning tracer (difluoromethane), with the assumption that the tracer measured all of the water. Water-partitioning tracer tests have also been conducted at the field scale, in association with gas-phase partitioning tracer tests designed to characterize immiscible-liquid contamination in vadose-zone systems (30-32). However, the soil-water contents obtained in these tests were not compared to independently measured values. Thus, the efficacy of the method for field-scale applications needs to be further evaluated. As a first step, a series of intermediate-scale experiments were conducted as part of this project.

Fluid-Fluid Interfacial Areas

The interfaces between immiscible organic liquid and water, between organic liquid and air, and between water and air are of great significance for contaminant transport in the subsurface. The interfacial areas are, in part, reflections of the pore-scale distribution of the fluids in the porous medium. As such, knowledge of the interfacial areas could provide insight into the movement and redistribution behavior of the fluids in the system. In addition, mass transfer across an interface is a function of the interfacial area. Thus, knowledge of the interfacial areas would provide greater understanding of mass-transfer phenomena, such as dissolution and evaporation of immiscible organic liquids. Fluid-fluid interfaces may also directly influence the retention behavior of volatile organic contaminants. For example, accumulation of organic contaminants at the air-water interface has been shown to influence their retention (37-39) and transport (34, 40, 41) behavior in unsaturated systems.

The magnitude and disposition of fluid-fluid interfaces in porous media is clearly of great significance. Unfortunately, measuring interfacial areas has to date been problematic. A recent surge in interest in this topic, however, has led to several potentially viable approaches. Static column methods based on the use of water-insoluble surfactants have recently been proposed as a means to measure interfacial areas (42-45). In addition, experimental methods based on visualization techniques have been proposed (e.g., 46). These methods have shown promise for estimating or measuring interfacial areas for simplified, well-controlled laboratory systems, which will enhance our ability to examine flow and transport processes. However, given the limitations inherent to these methods, it is unlikely that they can be used routinely for complex systems or for in-situ applications. The interfacial partitioning tracer test is an alternative method that may be better suited for these latter applications.

The application of the aqueous-phase interfacial partitioning tracer method has recently been illustrated with several laboratory investigations conducted using sand-packed columns. Saripalli et al. (47) used a surfactant (sodium dodecylbenzenesulfonate) as a tracer to measure interfacial areas for decane-water and air-water systems. Kim et al. (48) used the same surfactant to measure air-water interfacial areas for several soil-water contents. Saripalli et al. (49) and Kim et al. (50) used two surfactants to measure interfacial areas between several organic immiscible liquids and water. Kim et al. (41) used two alcohols to measure air-water interfacial areas. In all cases, the results of the experiments, which were conducted with water as the mobile phase, produced interfacial-area values that were similar to those estimated using geometric and thermodynamic models.

Brusseau et al. (34) used a gas-phase partitioning tracer method to measure air-water interfacial areas in unsaturated packed columns. They used the interfacial area determined from the

partitioning tracer (heptane) test to successfully predict the retardation and transport of trichloroethene in the same system. This information was used to help evaluate the relative contributions of (solid-phase) sorption, retention in bulk water, and interfacial accumulation to retardation of volatile organic contaminants during gas-phase transport in unsaturated porous media.

Kim et al. (35) used decane as a gas-phase interfacial partitioning tracer and observed increasing interfacial areas as soil-water content decreased. In addition, the interfacial areas obtained with the gas-phase method were larger than those obtained using the aqueous-phase tracer method.

Clearly, the use of partitioning tracer tests as a method for measuring fluid-fluid interfacial areas is in its infancy, and much more research is needed to fully define its potential as well as its limitations. In addition, research is needed to examine the results obtained from the various methods (static, aqueous-phase dynamic, gas-phase dynamic), and to characterize any observed differences. Furthermore, mathematical models incorporating fluid-fluid interfacial areas need to be developed and evaluated. Such developmental work was a component of this project.

METHODS AND RESULTS

This project was implemented using an integrated approach for accomplishing the associated goals and objectives. The approach combined one-dimensional laboratory experiments, three-dimensional intermediate-scale experiments, independent methods for NAPL and water measurement, and advanced modeling techniques. The methods and results for the major components of the project are presented below.

1. The Impact of Physical Heterogeneity, Non-uniform NAPL Distribution, and Dilution Effects on Partitioning Tracer Test Performance

Relevant Publications:

(1) Nelson, N.T., Oostrom, M., Wietsma, T.W., and Brusseau, M.L. Partitioning Tracer Method for the In Situ Measurement of DNAPL Saturation: Influence of Heterogeneity and Sampling Method. *Environmental Science and Technology*, 33(22), 4046-4053, 1999.

(2) Two additional manuscripts are currently in preparation.

The experiments were conducted in two flow cells, the approximate average dimensions of which are 1.9 x 0.75 x 0.05 m. The flow cells were equipped with several “depth-specific” sampling ports, which were integrated across the width of the flow cell, and “vertically integrated” sampling ports, which were integrated across the width, and spanned 0.3 m in height. An injection well and an extraction well, each screened over the entire thickness of the sand pack, were installed at opposite ends of the flow cells.

Bromide (as CaBr_2) served as the non-reactive tracer, and trichloroethene (TCE) and 1,2-dichloroethane (DCA) were used as the model immiscible liquids. The immiscible liquids were dyed with a hydrophobic red dye, Sudan IV (100 mg/L), to allow visualization of the change in saturation during the

experiments. Fluorescein dye [sodium salt form] was used to conduct a visualization tracer test to help characterize the flow field. The porous media used in this study were a medium-grained 20/30-mesh sand and a fine-grained 70-mesh sand (Unimin Corporation, Le Sueur, MN).

Two distinct zones containing residual TCE saturation were established in the first flow cell, which was packed with the 20/30 mesh sand. Zone 1 consisted of TCE saturation formed within 70-mesh sand to examine the effect of physical-heterogeneity induced preferential flow on immiscible-liquid dissolution. This zone represents a system wherein site conditions promoted penetration of immiscible liquid into lower permeability layers (in this case a fine sand). This might occur for example, when immiscible liquid enters a variably saturated (e.g. vadose zone) profile, which afterwards becomes water saturated due to a rise in the water table. Zone 2 consisted of TCE saturation formed within the same sand as comprised the matrix, and was used to examine the effect of potential bypass flow associated with the reduced relative permeability caused by a localized zone of immiscible-liquid saturation. For the second flow cell, a TCE zone formed within the same sand as used for the matrix (20/30 mesh) was placed in the position equivalent to zone 2 of the first flow cell, while a DCA zone formed within the 20/30-mesh sand was placed in the position equivalent to zone 1 of the first flow cell. It must be stressed that the configuration used in these experiments was designed expressly to examine the impact of potential constraining factors on immiscible-liquid dissolution in a general sense. The system was not designed to mimic an immiscible-liquid spill into a water-saturated profile with this exact configuration.

A fully automated dual-energy (280 mCi Americium and 100 mCi Cesium) gamma radiation system was used to measure the immiscible-liquid saturations in the flow cells. To obtain saturation measurements, the flow cells were scanned prior to the start of each dissolution experiment and at the completion of each

dissolution experiment. An additional scan was conducted midway through the second experiment. Because the immiscible liquid was added to the flow cells concurrent with packing, it was necessary to remove all immiscible liquid from the zones prior to obtaining “background” measurements. This was done by flushing the flow cells with a 4% anionic-surfactant solution. The counting times for all scans were 60 seconds per location. Measurement uncertainty ranged from approximately 1% for immiscible-liquid saturations of 10%, to 4% for saturations of 0.1%, which is effectively considered to be the quantifiable detection limit.

The saturations estimated using the tracer data collected at sampling ports located downgradient of Zone 2 (medium-grained sand) were approximately 90% to 100% of the gamma-measured value, indicating accurate performance of the partitioning tracer method. However, the saturations estimated using the tracer data obtained from downgradient of Zone 1 (fine-grained sand surrounded by medium-grained sand) were less than 10% of the gamma-measured value. Finally, the saturation estimated using the extraction-well data was about 50% of the cell-wide averaged value obtained from the gamma measurements. These results indicate that the presence of porous-media heterogeneity and a variable distribution of NAPL saturation can influence the accuracy of the partitioning tracer test. The results obtained from the flow-cell experiments are consistent with the results obtained from applying a mathematical model to the system.

The results of these experiments demonstrate that partitioning tracer tests can provide accurate measurements of NAPL saturation distributed in domains through which water flow is not constrained. However, the results suggest that partitioning tracer tests may not be able to completely measure NAPL that is entrapped in lower-permeability zones. Although the quantitative performance of the partitioning tracer test may in some cases be constrained by factors such as those investigated herein, the method is a viable

tool for characterizing sites that may be contaminated by NAPL. At sites where the presence of NAPL is suspected, but not confirmed, partitioning tracers may be useful as "detectors" of NAPL saturation. Partitioning tracers may also be useful as "performance indicators" of a chosen remedial action. Tracer tests can be conducted before, during, and after site clean up to evaluate the relative performance of the remediation system. Additional research in this area is certainly justified due to a continued need to characterize the large number of sites contaminated by complex and persistent NAPL phases.

2. The Impact of Physical Heterogeneity, Non-uniform NAPL Distribution, and Dilution Effects on NAPL Dissolution

Relevant Publication:

Brusseau, M.L., Nelson, N.T., Oostrom, M., Zhang, Z., Johnson, G.R., and Wietsma, T.W. Influence of Heterogeneity and Sampling Method on Aqueous Concentrations Associated with NAPL Dissolution. *Environmental Science and Technology*, 34(17), 3657-3664, 2000.

The purpose of this work was to examine the effects of nonuniform distributions of nonaqueous phase liquid (NAPL) saturation, porous-media heterogeneity, and sampling method on the magnitude of aqueous concentrations measured under dynamic conditions of flow and transport. Dissolution experiments were conducted in an intermediate-scale flow cell packed with sand in which two zones of residual trichloroethene (TCE) saturation were placed, as described above. One was created in the same medium-grained sand as used for the flow-cell matrix (zone 2), and the other was created in finer sand (zone 1). Aqueous samples were collected using depth-specific sampling ports, vertically integrated sampling ports,

and at the fully screened extraction well. A dual-energy gamma radiation system was used to measure TCE saturation before and after the experiment.

The results indicate that mass removal occurred relatively uniformly across the upgradient edge of zone 2, and continued progressively along the longitudinal axis of the zone throughout the course of flushing. Conversely, mass removal was confined primarily to the perimeter of zone 1. The magnitude of the aqueous-phase TCE concentrations varied as a function of location and sampling method. The concentrations measured at the point-sampling ports downgradient of zone 2 were close to the value of aqueous solubility. Conversely, the concentrations measured at the point-sampling ports downgradient of zone 1 were about one-fourth of solubility. The TCE concentrations measured at the vertically integrated ports and at the extraction well were significantly less than the concentrations measured at the point-sampling ports. Given that substantial TCE saturation remained at the end of the experiment, the less-than-solubility concentrations observed for zone 1 and for the extraction well appear to reflect in part a steady state dynamic equilibrium with the physical-heterogeneity induced nonuniform flow field. The less-than-solubility concentrations, especially for the integrated ports and the extraction well, were also influenced significantly by sampling-associated dilution related to the nonuniform NAPL distribution. These observations are supported by the results of a nonreactive tracer test, a dye-tracer test, and by a quantitative analysis of flow and transport obtained using a three-dimensional mathematical model.

Relevant Publication:

Brusseau, M.L., Zhang, Z., Nelson, N.T., Cain, R.B., Tick, G., and Oostrom, M. Dissolution of Non-Uniformly Distributed Immiscible Liquid: Simulating Intermediate-Scale Experiments Using Local-Scale Mass-Transfer Coefficients. 2001 (in review).

The purpose of this work was to examine the effect of non-uniform distributions of non-aqueous phase immiscible liquid (NAPL) on dissolution behavior, with a specific focus on the condition-dependency of dissolution (i.e., mass transfer) rate coefficients associated with applying mathematical models of differing complexity to measured data. Dissolution experiments were conducted using intermediate-scale flow cells packed with sand in which well-characterized zones of residual trichloroethene (TCE) and 1,2-dichloroethane (DCA) saturation were emplaced, as described above. Aqueous samples were collected at several sampling ports and at the fully screened extraction wells. A dual-energy gamma radiation system was used for in-situ measurement of NAPL saturation.

The aqueous concentrations of TCE and DCA measured in the flow-cell effluent were significantly less than solubility, due primarily to dilution associated with the non-uniform immiscible-liquid distribution and by-pass flow effects associated with physical heterogeneity. A quantitative analysis of flow and transport was conducted using a three-dimensional mathematical model wherein immiscible-liquid distribution, permeability variability, and sampling effects were explicitly considered. Independent values for the global initial dissolution rate coefficients were obtained from dissolution experiments conducted using homogeneously packed columns.

The independent predictions obtained from the model provided good representation of NAPL dissolution and aqueous-phase transport behavior, signifying model robustness. This indicates that for the complex 3-D model, explicit consideration of the larger-scale factors that influenced immiscible-liquid

dissolution in the flow cells allowed the use of a dissolution rate coefficient that represents only local-scale mass transfer processes. Conversely, the use of simpler models that did not explicitly consider the non-uniform immiscible-liquid distribution required the use of dissolution rate coefficients that are approximately three orders-of-magnitude smaller than the values obtained from the column experiments. The rate coefficients associated with the simpler models represent composite or lumped coefficients that incorporate the effects of the larger-scale dissolution processes associated with the non-uniform immiscible-liquid distribution, which are not explicitly represented in the simpler models, as well as local-scale mass transfer. These results demonstrate that local-scale dissolution rate coefficients, such as those obtained from column experiments and which represent local-scale dissolution processes, can be used in models to successfully predict dissolution and transport of immiscible-liquid constituents at larger scales when larger-scale factors influencing dissolution behavior are explicitly accounted for in the model.

3. Measuring Soil-Water Content

Relevant Publication:

Nelson, N.T., Brusseau, M.L., Carlson, T.D., Costanza, M.S., Young, M.H., Johnson, G.R., and Wierenga, P.J. A Gas-Phase Partitioning Tracer Method for In Situ Measurement of Soil-Water Content. *Water Resources Research*, 35(12), 3699-3707, 1999.

The water-partitioning tracer method was tested at the intermediate scale with a series of experiments conducted in a large (4.0 m deep, 2.5 m in diameter) weighing lysimeter. The lysimeter contains a homogeneous packing of fine sand, and is instrumented with multiple methods by which to measure soil-water content. The lysimeter is equipped with 6 tensiometers, 21 TDR probes, a neutron-probe access tube, 3 thermocouples, and 48 porous stainless steel cups for gas

injection and sampling. The weighing scales have a capacity of 45 Mg and can detect a 200-g mass change, equivalent to ~ 0.04 mm of water on the surface. The instrumentation allows the values of soil-water content estimated from the partitioning tracer experiment to be compared to values obtained with established methods. Pressure transducers (model 136PC15G2, Microswitch, Freeport, IL) installed in the injection line, extraction line, and at 50 cm increments along the lysimeter allow pressure to be monitored throughout the entire system. All instrumentation (excluding TDR) is connected to a data logger (Model CR7, Campbell Scientific, Inc. Logan, UT) for data collection and storage. Software (PC208W, Campbell Scientific) for a personal computer connected to the data logger allows real time monitoring of all data during the experiment.

Several tracer experiments were conducted in the lysimeter. For the first experiment, a non-partitioning tracer (SF_6) was used to test the flow system and gas-sampling techniques, and to obtain estimates of travel times. For the second, third and fourth experiments, SF_6 was used as the non-partitioning tracer and bromochlorodifluoromethane, dibromodifluoromethane, or trichlorofluoromethane was used as the water-partitioning tracer. These experiments were conducted at a relatively low soil-water content. A fifth experiment was conducted at a higher soil-water content.

For the lower soil-water content, values of 0.04, 0.06, and 0.06 were calculated for the soil-water content using the tracer data collected at the effluent sampling location for bromochlorodifluoromethane, dibromodifluoromethane, and trichlorofluoromethane, respectively. These values, especially the latter two, compare favorably to independently measured values obtained using gravimetric analysis of core samples (0.06) and time-domain-reflectometry (0.06). For the higher soil-water content, a value of 0.12 was calculated for the soil-water content using the

tracer data collected at the effluent sampling location for trichlorofluoromethane. This value is relatively close to independently measured values obtained using time-domain-reflectometry (0.15), neutron thermalization (0.15), and conversion of soil-tension data (0.15). These results suggest that the gas-phase partitioning tracer method holds promise as a means to measure soil-water content.

4. Measuring Fluid-Fluid Interfacial Areas

Relevant Publication:

Brusseau, M.L., Popović, J., and Silva, J. Characterizing Gas-Water-Interfacial and Bulk-Water Partitioning for Gas-Phase Transport of Organic Contaminants in Unsaturated Porous Media. *Environmental Science and Technology*, 31(6), 1645-1649, 1997.

This study was performed to investigate the impact of interfacial and bulk-water partitioning on the retention and retardation of gas-phase contaminants during transport in unsaturated porous media. Gas-flow experiments were conducted using columns packed with three types of sandy porous media. Moisture contents were 11.9%, 16.0%, and 9.4% for the columns packed with glass beads, silica sand, and aquifer material, respectively.

Contaminant retardation was the sum of retention by the gas, aqueous, and solid phases, and accumulation at the gas-water interface. The results indicated that 29 to 73% of total trichloroethene retardation was due to accumulation at the gas-water interface, depending on porous-media type. Partitioning into the bulk water accounted for 12 to 30% of total trichloroethene retardation for the various systems. Sorption by the solid phase was relatively small.

Given the potential significance of interfacial and bulk-water retention for contaminant transport and remediation, it is important to consider methods for characterizing these processes at the field scale. Gas-

phase tracer experiments using a suite of phase-selective partitioning tracers in combination with nonreactive tracers, as presented herein, may be one viable approach. For example, CO₂ was used successfully to measure the bulk water content of the system, and heptane was used to determine the effective gas-water interfacial area. Measurements obtained from use of these tracers were employed successfully to predict the retardation observed for trichloroethene.

Relevant Publication:

Costanza-Robinson, M.S. and Brusseau, M.L. Air-Water Interfacial Areas in Unsaturated Soils: Evaluation of Interfacial Domains. 2001 (in review).

A gas-phase miscible-displacement method, using decane as the interfacial tracer, was used to measure air-water interfacial areas at water contents ranging from ~2-20%. Experiments were conducted using a natural porous medium, Vinton fine sand. Decane was observed to demonstrate relatively ideal interfacial tracer properties, including that its dominant retention mechanism was adsorption at the air-water interface. The interfacial areas measured using decane displayed the expected trend of decreasing interfacial area with increasing water content. The maximum estimated interfacial area of 19,500 cm⁻¹ appears reasonable in that it is smaller than the measured total specific surface area of the medium (60,888 cm⁻¹), and is in the same range as the measured external surface area.

Comparison of the experimental data presented herein with literature data provided further insight into the nature of the air-water interface in porous media. Specifically, comparison of gas- and aqueous-phase data indicates that the gas-phase method generally yields larger interfacial areas than do the aqueous-phase methods, even when differences in water content and physical properties

of the porous media are accounted for. The observations are consistent with proposed differences in interfacial domains accessed by the aqueous- and gas-phase interfacial tracers. Evaluation of the data in light of functional interfacial domains leads to the hypothesis that aqueous interfacial tracers measure primarily air-water interfaces formed by “capillary water”, while gas-phase tracers measure air-water interfaces formed by both capillarity and adsorbed water. The data further indicate that adsorbed-water domains may comprise a larger fraction of the total air-water interfacial area for systems examined here. A deeper understanding of the functional interfacial domains and their link to existing interfacial area methods will serve to improve the methods and the interpretation of their results.

The surfactant- and gaseous tracer methods appear complimentary, in that the two are most readily applied to different water-content ranges. The gaseous tracer method is expected to perform better at low to intermediate water contents, where disconnected air-porosity is less significant. For analogous reasons, the aqueous tracer method is restricted to higher water-content systems. In addition, the gas- and aqueous-phase methods may each provide interfacial area information that is more relevant to specific problems of interest. For example, gas-phase interfacial area measurements may be most relevant to contaminant transport in unsaturated systems, where retention at the air-water interface may be significant. Conversely, the aqueous-phase methods may yield information with direct bearing on multiphase flow processes that are dominated by capillary-phase behavior.

5. Development of Mathematical Models

Relevant Publication:

Oostrom, M., White, M.D., and Brusseau, M.L. Theoretical Estimation of Free and Entrapped Non-wetting Fluid Interfacial Areas in Porous Media. *Advances in Water Resources*, 24, 887-898, 2001.

Fluid-fluid interfacial areas play important roles in numerous subsurface processes such as dissolution, volatilization, and adsorption. Integral expressions have been derived herein to estimate both entrapped (discontinuous) and free (continuous) nonwetting fluid-wetting fluid specific interfacial areas in porous media. The expressions, compatible with widely used capillary head-saturation and entrapment models, require information on capillary head-saturation relation parameters, porosity, and fluid-pair interfacial tension. In addition, information on the maximum entrapped nonwetting fluid saturation as well as the main drainage branch reversal point for water and total liquid saturations is necessary to estimate entrapped fluid interfacial areas.

Implementation of the interfacial area equations in continuum-based multi-fluid flow simulators is straightforward since no additional parameters are needed than those required by the simulators to complete the multifluid flow computations. A limited sensitivity analysis, based on experimentally obtained parameter values, showed that imposed variations resulted in logical and consistent changes in predicted specific interfacial areas for both entrapped and free nonwetting fluid-wetting fluid systems. A direct comparison with published experimental work to test the derived expressions was limited to free air-water systems and yielded reasonable results. Such comparisons are often not possible because of the lack of information given on retention parameters, and variables used to determine nonwetting fluid entrapment.

Relevant Publication:

Oostrom, M. and White, M.D. STOMP---Subsurface Transport Over Multiple Phases: Water-Oil with Kinetic Solute Partitioning Operational Mode. Addendum Report, Environmental Technology Division, Pacific Northwest National Laboratory, 2001.

A specified component of this research project was the development of a mathematical model capable of simulating the transport of partitioning tracers in complex systems. The objectives for this component of research were achieved in part through modifications to the Water-Oil Operational Mode (Mode 4) of the STOMP simulator for solute transport under equilibrium conditions, and the development of the Water-Oil with Kinetic Solute Partitioning Operational Mode (OM24) for nonequilibrium partitioning of the solute tracer between the aqueous phase and NAPL. This addendum documents the theory, use and application of OM24.

Intended users of this software include scientists and engineers applying partitioning tracer techniques to the characterization of field sites contaminated with free or trapped NAPL. The software can additionally be applied to laboratory-scale experimental research involving aqueous-nonaqueous partitioning tracers, specifically as an aid in designing new experiments and analyzing experimental results. Principal design goals for this operational mode are similar to those of all operational modes of the STOMP simulator and include broad applicability, verified solution schemes, quality assurance controls, and validation against laboratory and field data, where available. The fundamental purpose of this operational mode is to produce numerical predictions of partitioning tracer transport through heterogeneous fields of aqueous and NAPL saturation, under nonequilibrium or unknown partitioning conditions.

This operational mode numerically solves the governing equations for aqueous and NAPL flow through variably saturated geologic media, assuming equilibrium dissolution of NAPL into the aqueous

phase and no dissolution of water into NAPL. NAPL can concurrently exist in trapped (immobile) and free (mobile) forms, by considering entrapment hysteresis, where the aqueous-phase is considered the wetting fluid. Solution of the flow equations are followed by a coupled solution of the transport equations for aqueous- and NAPL-dissolved solutes; where equilibrium partitioning is assumed between aqueous-dissolved and sorbed solute. The model allows the user to choose between linear, Freundlich and Langmuir isotherms for equilibrium partitioning between aqueous-dissolved and sorbed solute. Likewise for nonequilibrium partitioning of solute between aqueous-phase and NAPL the user can specify linear, Freundlich and Langmuir equilibrium models. Advective, diffusive and dispersive transport of solutes is solved using either the first-order Patankar power-law scheme, the second-order Roe's superbee flux limiting scheme, or Leonard third-order flux limiting scheme. Kinetic dissolution of solutes between the aqueous-phase and NAPL can be declared either through an effective mass transfer coefficient or through an interfacial area dependent mass transfer coefficient. For the later case, the aqueous-NAPL interfacial area is computed based on pore-scale distributions of trapped and free NAPL using integrations of the soil moisture retention characteristics.

Relevant Publication:

Brusseau, M.L., Zhang, Z., Nelson, N.T., Cain, R.B., Tick, G., and Oostrom, M. Dissolution of Non-Uniformly Distributed Immiscible Liquid: Simulating Intermediate-Scale Experiments Using Local-Scale Mass-Transfer Coefficients. 2001 (in review).

Additional model development work for this project was undertaken to construct a model to describe NAPL dissolution and partitioning tracer transport in heterogeneous systems. As previously described, this model was used to examine the effect of non-uniform distributions of non-aqueous phase immiscible liquid (NAPL) on dissolution behavior, with a specific focus on the condition-dependency of dissolution (i.e., mass transfer) rate coefficients. The results of this work were described above in subsection 2.

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PUBLICATIONS

Peer-Reviewed Publications

Brusseau, M.L., Popovicová, J., and Silva, J. Characterizing Gas-Water-Interfacial and Bulk-Water Partitioning for Gas-Phase Transport of Organic Contaminants in Unsaturated Porous Media. *Environmental Science and Technology*, 31(6), 1645-1649, 1997.

Nelson, N. T., Oostrom, M., Wietsma, T. W., and Brusseau, M. L. Partitioning Tracer Method for the In Situ Measurement of DNAPL Saturation: Influence of Heterogeneity and Sampling Method. *Environmental Science and Technology*, 33(22), 4046-4053, 1999.

Nelson, N. T., Brusseau, M. L., Carlson, T. D., Costanza, M. S., Young, M. H., Johnson, G. R., and Wierenga, P. J. A Gas-Phase Partitioning Tracer Method for In Situ Measurement of Soil- Water Content. *Water Resources Research*, 35(12), 3699-3707, 1999.

Costanza, M. and Brusseau, M. L. Influence of Adsorption at the Air-Water Interface on the Transport of Volatile Contaminants in Unsaturated Porous Media. *Environmental Science and Technology*, 34(1), 1-11, 2000.

Brusseau, M. L., Nelson, N. T., Oostrom, M., Zhang, Z., Johnson, G. W., and Wietsma, T. W. Influence of Heterogeneity and Sampling Method on Aqueous Concentrations Associated with NAPL Dissolution. *Environmental Science and Technology*, 34(17), 3657-3664, 2000.

Oostrom, M., White, M. D., and Brusseau, M. L. Theoretical Estimation of Free and Entrapped Non-wetting Fluid Interfacial Areas in Porous Media. *Advances in Water Resources*, 24, 887-898, 2001.

Brusseau, M. L., Zhang, Z., Nelson, N. T., Cain, R. B., Tick, G., and Oostrom, M. Dissolution of Non-Uniformly Distributed Immiscible Liquid: Simulating Intermediate-Scale Experiments Using Local-Scale Mass-Transfer Coefficients. 2001 (in review).

Costanza-Robinson, M. S. and Brusseau, M. L. Air-Water Interfacial Areas in Unsaturated Soils: Evaluation of Interfacial Domains. 2001 (in review).

Two additional manuscripts are currently in preparation (final titles are not yet available).

Other Publications

Oostrom, M. and White, M.D. STOMP---Subsurface Transport Over Multiple Phases: Water-Oil with Kinetic Solute Partitioning Operational Mode. Addendum Report, Environmental Technology Division, Pacific Northwest National Laboratory, 2001.

Abstracts associated with conference presentations listed below.

INTERACTIONS (Conference Presentations)

Nelson, N. T., Brusseau, M. L., and Silva, J. Field Test of Water-Partitioning Tracers to Measure Bulk Water Content. Presented at the American Geophysical Union National Meeting, Baltimore, MD, May 27-30, 1997.

Brusseau, M.L., White, M., Nelson, N., and Oostrom, M. Partitioning Tracers for In-situ Detection and Quantification of Dense Nonaqueous Phase Liquids in Groundwater Systems. Presented at the Environmental Management Science Program Workshop, sponsored by U.S. Department of Energy, Chicago, IL, July 27-30, 1998.

Nelson, N.T., Brusseau, M.L., Oostrom, M., and Wiestma, T.T. Influence of Porous Media Heterogeneity and DNAPL Distribution on the Dissolution and Removal of Trichloroethene.

Presented at the American Geophysical Union National Meeting, San Francisco, CA, Dec. 6-10, 1998.

Nelson, N.T., Oostrom, M., Wietsma, T.W., and Brusseau, M.L. The Partitioning Tracer Method for the In Situ Measurement of DNAPL Saturation: Influence of Heterogeneity and Sampling Method. Presented at the Geological Society of America National Meeting, Denver, CO, October 25-29, 1999.

Brusseau, M.L. and Cain, R.B. Partitioning Tracers for In-situ Detection and Quantification of DNAPLs in Groundwater Systems. Presented at the Environmental Management Science Program Workshop, sponsored by the U.S. Dept. Energy, April 24-28, 2000.

Brusseau, M.L., Nelson, N.T., Zhang, Z., Cain, R.B., Tick, G., Oostrom, M. Dissolution of Non-uniformly Distributed Immiscible Liquid. Presented at the Geological Society of America National Meeting, Reno, NV, November 13-17, 2000.

LITERATURE CITED

1. National Research Council. Alternatives for Ground Water Cleanup. National Academy Press, Washington, D.C. 1994.
2. Brusseau, M.L. Water Resour. Res., 1993, 28, 33.
3. Cooke, C.E. U.S. Patent Number 3,590,923, 1971.
4. Deans, H.A. U.S. Patent Number 3,623,842, 1971.
5. Tang, J.S. SPE Formation Evaluation, 1995, 33.
6. Jin, M.; Delshad, M.; Dwarakanath V.; McKinney D.C.; Pope G.A.; Sepehrnoori K.; Tilburg C.E. Water Resour. Res., 1995, 31, 1201.
7. Wilson, R.D.; Mackay D.M. Environ. Sci. Technol., 1995, 29, 1255.
8. Nelson, N.T.; Brusseau, M.L. Environ. Sci. Technol., 1996, 30, 2859.
9. Brusseau, M.L.; Rohrer, J.W.; Decker, T.M.; Nelson, N.T.; Linderfelt, W.R.
Chapter 19 in: **Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies**, Brusseau, M.L.; Sabatini, D.; Gierke, J., Annable, M, eds. American Chemical Society, Wash. D.C., 1999.
10. Zhang, Z.; Brusseau, M.L. Water Resour. Res., 1999, 35, 2921.
11. Bedient, P.B.; Holder, A.W.; Enfield, C.G.; Wood, A.L. Chapter 4 in: **Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies**, Brusseau, M.L.; Sabatini, D.; Gierke, J., Annable, M, eds. American Chemical Society, Wash. D.C., 1999.
12. Rao, P.S.C.; Annable, M.D.; Sillan, R.K.; Dai, D.; Hatfield, K.; Graham, W.D.; Wood, A.L.; Enfield, C.G. Water Resour. Res., 1997, 33, 2673.
13. Annable, M.; Rao, P.S.C.; Hatfield, K.; Graham, W.; Wood, L. J. Environ. Engin., 1998, 124, 498.
14. Jawitz, J.W.; Annable, M.D. Rao, P.S.C.; Rhue, R.D. Environ. Sci. Technol., 1998, 32, 523.
15. McCray, J.E.; Brusseau, M.L. Environ. Sci. Technol., 1998, 32, 1285.
16. Brusseau, M.L.; Nelson, N.T.; Cain, R.B. Chapter 15 in: **Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies**, Brusseau, M.L.; Sabatini, D.; Gierke, J., Annable, M, eds. American Chemical Society, Wash. D.C., 1999.
17. Cain, R.B.; Johnson, G.R.; McCray, J.E.; Blanford, W.J.; Brusseau, M.L. Ground Water, 38(5), 752-761, 2000.

18. Falta, R.W.; Lee, C.M.; Brame, S.E.; Roeder, E.; Wood, L.; Enfield, C. Chapter 8 in: **Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies**, Brusseau, M.L.; Sabatini, D.; Gierke, J., Annable, M, eds. American Chemical Society, Wash. D.C., 1999.
19. Falta, R.W.; Lee, C.M.; Brame, S.E.; Roeder, E.; Coates, J.T.; Wright, C.; Wood, A.L.; Enfield, C.G. *Water Resour. Res.*, 1999, 35, 2095.
20. Gierke, J.S.; Wojick, C.L.; Hutzler, N.J. Chapter 11 in: **Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies**, Brusseau, M.L.; Sabatini, D.; Gierke, J., Annable, M, eds. American Chemical Society, Wash. D.C., 1999.
21. Blanford, W.J.; Klingel, E.J.; Johnson, G.R.; Enfield, C.; Brusseau, M.L. Chapter 12 in: **Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies**, Brusseau, M.L.; Sabatini, D.; Gierke, J., Annable, M, eds. American Chemical Society, Wash. D.C., 1999.
22. Young, C.M.; Jackson, R.E.; Jin, M.; Londergan, J.T.; Mariner, P.E.; Pope, G.A.; Anderson, F.J.; Houk, T. *Ground Water Monit. Rem.*, 1999, 19, 84.
23. Brown, C.L.; Jackson, R.E.; Delshad M.; Pope, G.A. Chapter 6 in: **Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies**, Brusseau, M.L.; Sabatini, D.; Gierke, J., Annable, M, eds. American Chemical Society, Wash. D.C., 1999.
24. Hayden, N.J.; Linnemeyer, H.C. Chapter 16 in: **Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies**, Brusseau, M.L.; Sabatini, D.; Gierke, J., Annable, M, eds. American Chemical Society, Wash. D.C., 1999.
25. Hunkeler, D.; Hoehn, E.; Hohener, P.; Zeyer, J. *Environ. Sci. Technol.*, 1997, 31, 3180.
26. Semprini, L.; Hopkins, O.S.; Tasker, B.R. *Transport Porous Media*, 2000, 38, 223.
27. Tang, J.S.; Harker B. J. *Can. Pet. Technol.*, 1991, 30, 76.
28. Whitley, G.A.; Pope, G.A.; McKinney, D.C.; Rouse, B.A.; Mariner, P.E. Pg. 211-221 In: *Monitoring and Verification of Bioremediation*, Battelle Press, 1995.
29. Whitley, G.A.; McKinney, D.C.; Pope, G.A.; Rouse, B.A.; Deeds, N.E. *J. Environ. Engin.*, 1999, 125, 574.
30. Simon, M.; Brusseau, M.L.; Golding, R.; Cagnetta, P.J. In: *Proc. Inter. Conf. Remediation of Chlorinated and Recalcitrant Compounds*, May 18-21, Monterey, CA, Battelle, 1998.
31. Mariner, P.E.; Jin, M.; Studer, J.E.; Pope, G.A. *Environ. Sci. Technol.*, 1999, 33, 2825.

32. Deeds, N.E.; Pope, G.A.; McKinney. *Environ. Sci. Technol.*, 1999, 33, 2745.
33. Bronson, K.; Nelson, N.T.; Brusseau, M.L. 2000. (in review).
34. Brusseau, M.L.; Popovicova, J.; Silva, J. *Environ. Sci. Technol.*, 1997, 31, 1645.
35. Kim, H.; Rao, P.S.C.; Annable, M.D. *Soil Sci. Soc. Amer. J.*, 1999, 63, 1554.
36. Deeds, N.E.; McKinney, D.C.; Pope, G.A.; Whitley, G.A. *J. Environ. Engin.*, 1999, 125, 630.
37. Pennell, K.D.; Rhue, R.D.; Rao, P.S.C.; Johnston, C.T. *Environ. Sci. Technol.*, 1992, 26, 756.
38. Hoff, J.T.; Gillham, R.W.; Mackay, D.; Shiu, W.Y. *Environ. Sci. Technol.*, 1993, 27, 2789.
39. Hoff, J.T.; Gillham, R.W.; Mackay, D.; Shiu, W.Y. *Environ. Sci. Technol.*, 1993, 27, 2174.
40. Conklin, M.H.; Corley, T.L.; Roberts, P.A.; Davis, J.; vandeWater, J.G. *Water Resour. Res.*, 1995, 31, 1355.
41. Kim, H.; Annable, M.D.; Rao, P.S.C. *Environ. Sci. Technol.*, 1998, 32, 1253.
42. Karkare, M.V.; Fort, T. *Langmuir*, 1993, 9, 2398.
43. Karkare, M.V.; Fort, T. 1996. *Langmuir*, 12, 2041.
44. Anwar, A.; Bettahar, M.; Matsubayashi, U. *J. Contamin. Hydrol.*, 2000, 43, 129.
45. Schaefer, C.E.; DiCarlo, D.A.; Blunt, M.J. *Water Resour. Res.*, 2000, 36, 885.
46. Montemagno, C.D.; Gray, W.G. *Geophysical Res. Lett.*, 1995, 22, 425.
47. Saripalli, K.P.; Kim, H.; Rao, P.S.C.; Annable, M.D. *Environ. Sci. Technol.*, 1997, 31, 932.
48. Kim, H.; Rao, P.S.C. *Water Resour. Res.*, 1997, 33, 2705.
49. Saripalli, K.P.; Rao, P.S.C.; Annable, M.D. *J. Contamin. Hydrol.*, 1998, 30, 375.
50. Kim, H.; Rao, P.S.C.; Annable, M.D. *J. Contamin. Hydrol.*, 1999, 40, 79.