LOWLAND TECHNOLOGY INTERNATIONAL Vol. 15, No. 2, 31-40, December 2013
International Association of Lowland Technology (IALT), ISSN 1344-9656

COUPLING INFLUENCES OF AQUIFER SPATIAL VARIABILITY AND WASTE COMPOSITIONS ON DISTRIBUTION AND RECOVERY OF DNAPL IN STATISTICALLY HOMOGENEOUS NONUNIFORM POROUS MEDIA

A. Putthividhya[1] and S. Rodphai[1]

ABSTRACT: PCE and TCE saturation distributions are generated with stochastic models to incorporate spatially varying aquifer properties. The influence of aquifer property correlation on fluid migration and entrapment is explored in cross-sectional 2D numerical two-phase saturated flow models extracted from 3D geostatistical realizations generated from well-published aquifer data in a nonuniform sandy aquifer. An effort to model a mixture of DNAPL is exercised by employing five compounds DNAPL; a 6:1:1:1:1 by volume ratio of PCE, toluene, 2-chlorotoluene, 1-bromohexane, and 1-bromoheptane. Comparisons of PCE, TCE, and DNAPL mixture suggest that the choices involving chemical waste compositions greatly influenced the saturation and distribution of DNAPL (i.e., pathways and organic spreading). The organic wastes released into the system can escape to the other 2D cross sections as the waste mixtures are more mobile compared to pure phase. Coupled application of stochastic model of aquifer spatial variability as well as chemical waste compositions can significantly influence predicted DNAPL infiltration depth, entrapment, and recovery. The resultant distribution profiles of DNAPL mass within the source zone also have implications for DNAPL recovery and subsequent downstream mass fluxes in remediation operations.

Keywords: Groundwater contamination, DNAPL, Spatially variable, Geostatistics, Recovery, Mixed Waste, Homogeneous uniform.

INTRODUCTION

Many illegal releases of hazardous wastes worldwide are depositories of industrial liquid wastes, many of them are in nonaqueous phase liquids (NAPL) form with the exact composition of the chemical wastes disposed of is often unknown. Because DNAPL are denser than water, they are able to migrate through the vadose or saturated zones under gravitational and capillary forces and become entrapped as residual source zone in the subsurface environment (Wilson et al. 1990). Nonuniformity and heterogeneity in soil properties (Dekker and Abriola 2000a) and DNAPL composition contribute to further spreading and irregular distributions of entrapped NAPL. DNAPL source zone architecture (Sale and McWhorter 2001) as well as the variance and spatial correlation of the aquifer permeability field (Dekker and Abriola 2000b) can strongly influence remedial performance and downstream mass flux.

Several researchers have revealed substantial influences of the spatial distribution of parameters such as permeability and capillary retention on the prediction of immiscible flow pathways and organic spreading (Rathfelder and Abriola 1998; Dekker and Abriola 2000a) in both single phase (Fogg 1986; Anderson 1990, 1991; McKenna and Poeter 1994) and multiphase (Abriola and Bradford 1998; Dekker and Abriola 2000a) systems. Characterization of spatial variability poses significant geological and geostatistical challenges at many groundwater contamination sites, particularly where extensive field sampling is either physically or fiscally prohibited. Two issues of particular concern where significant volumes of DNAPL were disposed are the physical spatial heterogeneity of the subsurface formation and chemical heterogeneity of the chemical wastes released at the sites.

The motivation for this research stems from a need to better understand the consequences of aquifer and chemical waste heterogeneities in the context of the common hazardous waste spill situation where limited site characterization data are available. The stochastic methods have been applied to incorporate macroscopic heterogeneity in physical aquifer parameters contributing to contaminant dispersion (i.e., porosity and permeability). Porosity and permeability distributions within a single glacial depositional unit are stochastically

[1] Department of Water Resources Engineering, Faculty of Engineering, Chulalongkorn University, 254 Phayathai Road, Pathumwan, 10330, THAILAND
Note: Discussion on this paper is open until June 2014

modeled based on a 3D array of sediment particle size distributions and repacked porosity measurements (data reported by Lemke 2002). Subsequent transfer of multiple stochastic realizations to flow and transport simulators permits DNAPL distribution statistics for equally possible 3D ensembles of realizations generated using the chosen geostatistical simulation algorithm. The resulting differences in predicted source zone configuration metrics, including vertical penetration and lateral spreading, are quantified under single and mixed DNAPL spill scenarios so that differences among the sets can be examined herein. The evolution of generated DNAPL source zone architecture is also analyzed in response to the application of natural dissolutions in terms of organic recovery and downstream aqueous phase contaminant mass flux.

MATERIALS AND METHODS

Aquifer and Aquifer Materials

The aquifer chosen as a study area is located in Oscoda, Michigan, USA, at the site of a former dry cleaning business. The aquifer is composed of relatively homogeneous glacial outwash sands underlain by a thick clay layer approximately 8 m below the ground surface. Lemke et al. 2002 obtained grain size distributions (GSDs) of the aquifer materials based on 167 samples collected from 12 vertical and directional cores. Also, the arithmetic mean porosity value of 0.36 measured in a subset of 162 repacked samples was reported (Lemke et al. 2002). Isotropic K (hydraulic conductivity) values for all samples were estimated from normalized grain size distributions using the Kozeny-Carman (K-C) equation:

$$K = \frac{\rho_w g}{\mu_w} k = \frac{\rho_w g}{\mu_w}\left[\frac{d_m^2}{180}\frac{\phi^3}{\left(1-\phi\right)^2}\right] \qquad (1)$$

K = Hydraulic conductivity (L/T)
ρ_w = Water density (M/L^3)
g = Gravitational acceleration (L/T^2)
μ_w = Viscosity of water (M/L-T)
k = Intrinsic permeability (L^2/T)
d_m = Representative grain size (L)
ϕ = Porosity (-)

Lemke et al. (2002) reported the estimated nonuniform K values ranging from 1 to 48 m/d and assumed normalized d_{10} values as the representative grain size. Five individual soil classification based on KMEANS clustering of the 167 measured grain size distributions following the approach of Schad (1993) was performed and the results are presented in Fig. 1.

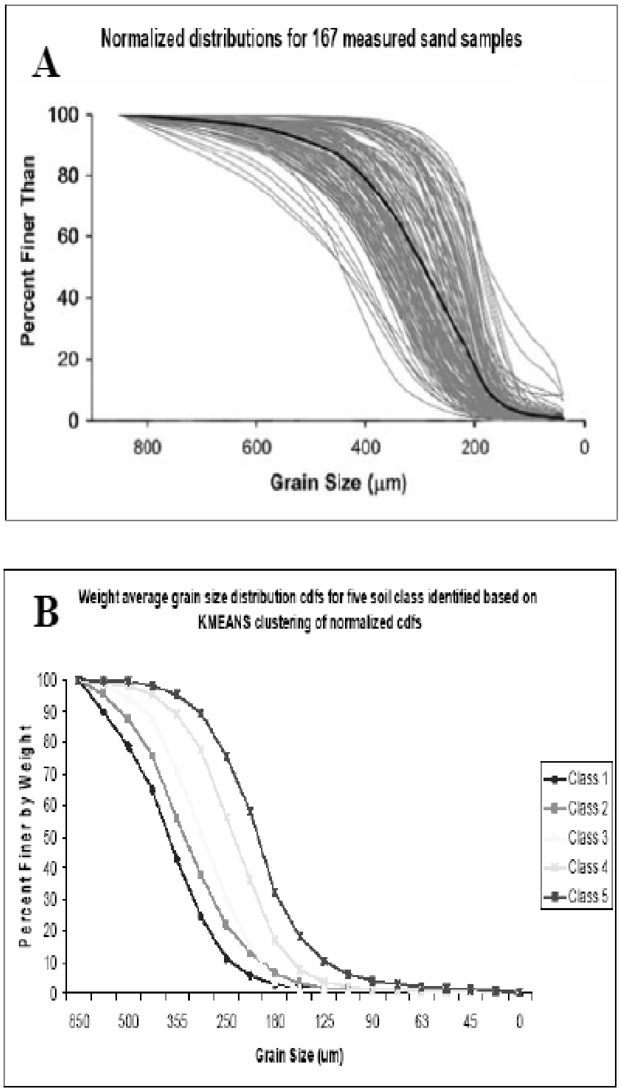

Fig. 1 Grain size cumulative distribution function (cdf) plots: (A) normalized distribution for 167 measured sand samples (reanalyzed from Lemke et al. 2004); (B) newly developed weighted average grain size distribution for 5 classes

Geostatistical Simulation Approaches

Two most common geostatistical simulation algorithms, sequential Gaussian simulation (SGS) and sequential indicator simulation (SIS) (Deutsch and Journel 1998), were particularly of our interest and therefore employed to generate 3D nonuniform ϕ and K fields.

SGS relies on an analytical model for the random function distribution. It assumes that the random function multivariate distribution is Gaussian so that the univariate distribution can be completely characterized by two parameters, the mean and variance, and the bivariate (i.e., two-point) distribution requires only the covariance or semivariogram as additional information.

Conversely, in SIS no assumption is made about the shape of the random function distribution, which consequently can be used to characterize the spatial variability of categorical (i.e., discrete valued random functions) as well as continuous variables. SIS, in fact, has been known as the most widely used non-Gaussian simulation technique, allows one to account for class-specific patterns of spatial continuity through different indicator semivariogram models.

Our previous work (Rodphai and Putthividhya 2009) employed SGS and SIS algorithms to create four ensemble sets (i.e., Reference Set, Set 1, Set 2, and Set 3) to investigate the influence of alternative geostatistical approach accounting for physical aquifer heterogeneity on representative DNAPL infiltration and redistribution. The results suggested that by assuming uniform porosity of 0.36 and generating K by SGS from 3D distributions of d_{10} values using K-C relationship resulted in a direct correlation between d_{10} and K values and therefore yielded the most conservative results based on the maximum DNAPL vertical infiltration profiles and lateral spreading in physically heterogeneous porous media. Although SIS algorithm allows one to account for class-specific patterns of spatial continuity through different indicator semivariogram models, a high degree of stratification was visible as depicted in Fig. 4. Therefore, simulations of source zone architecture accounting for physical aquifer and chemical waste composition heterogeneities will be conducted herein according to the reference set conditions proposed by Rohphai and Putthividhya (2009) (Fig. 4).

Model Formulation

UTCHEM (Center of Petroleum and Geosystems Engineering, University of Texas at Austin) is a highly sophisticated, 3D, multi-phase flow and multi-constituent, reactive transport model capable of performing a wide variety of groundwater simulations. UTCHEM was originally developed to model surfactant enhanced oil recovery but modified for applications such as source zone contamination, dissolution, water flush, surfactant flush, and pre- and post-flush PITT.

The assumptions imposed when developing the flow equations are local thermodynamic equilibrium except for tracers and dissolution of organic component, immobile solid phases, slightly compressible soil and fluids, Fickian dispersion, ideal mixing, and Darcy's law. The boundary conditions are no flow and no dispersive flux across the impermeable boundaries. The model conceptually deals with solving the continuity of mass, energy balance, and pressure equations. More information may be expected from Delshad et al. (1996).

Simulated DNAPL Release

Releases of pure PCE and TCE (i.e., DNAPL representatives in this study) were simulated using UTCHEM in 2D profiles extracted from 3D geostatistical realizations. In each realization, 96 L of PCE or TCE was released over 0.3 m^2 area from a point source at the top layer of the domain, at a constant flux of 2,400 mL/day for 400 days. An additional 330 days was simultaneously simulated to allow for organic liquid infiltration and redistribution without further release of waste into the system. Assume all constant pressure and saturated boundary along the domain sides and no-flow condition at the bottom boundary. This infiltration rate was assured to not result in any significant pooling of waste across the lateral as well as the vertical profile boundaries. Table 1 shows a list of UTCHEM simulation input parameters.

Table 1 UTCHEM simulation input parameters

Variable	Water	PCE
Density (kg/m^3)	999.032	1623.0
Viscosity (kg/m-s)	0.001139	0.00089
Compressibility (1/Pa)	4.4×10^{-10}	0

DNAPL chemical heterogeneity

In an effort to model the complex mixtures often found within DNAPL, five compounds were used to make up DNAPL in this study, a 6:1:1:1:1 by volume ratio of PCE, toluene, 2-chlorotoluene, 1-bromohexane, and 1-bromoheptane. The physical and chemical properties of these compounds were reported with density of 1.386 g/mL and the kinematic viscosity of 0.5801 ± 0.0003 mm^2/s (Imhoff et al. 2003). Schematic diagram summarizing the research methodology is presented in Fig. 2.

RESULTS

Aquifer Parameter Distributions

Previous work (Rodphai and Putthividhya 2009) demonstrated that stratification in the ϕ profile using SIS algorithm was observed while a strong random component of ϕ was evidenced from SGS algorithm. With a high degree of stratification observed in the indicator class simulations based on five indicator classes employed in the previous study, simulated profiles of d_{10} were totally diverged from those generated based on 6 indicator classes which were visually similar to those generated directly using SGS. The discrepancy was perhaps contributable to the porous media classification into individual 6 classes as it resulted in the extent of decomposition of the essentially monomodal nonuniform d_{10} pdf into subsidiary distributions with smaller overlapping probability distributions ranges associated with individual classes (Lemke et al. 2004), leading to a more spatial randomization of d_{10} values of each subsidiary set compared to the case of 5 individual indicator classes used in this work.

The high degree of stratification observed could additionally result in significant pooling of organic contaminants, which might be detrimental when comparisons of infiltration and distribution behaviors among pure and mixed DNAPL wastes are required. Therefore, simulations of source zone architecture accounting for physical aquifer and chemical waste composition heterogeneities were conducted herein using SGS instead of SIS algorithm. By assuming constant porosity of 0.36 and generating K by SGS algorithm from 3D distributions of d_{10} values based on collected aquifer media properties using K-C relationship resulted in aquifer property distribution for 3D and extracted 2D representative profiles depicted in Fig. 3. The conservative uniform ϕ assumption employed in geostatistical simulations in this work resulted in a direct correlation between d_{10} and K values in Fig. 3.

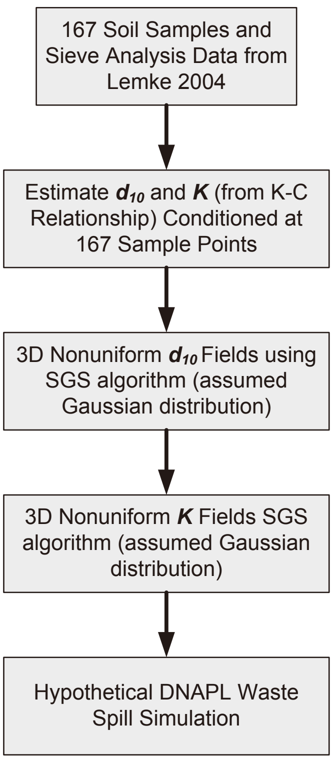

Fig. 2 Schematic diagram summarizing the research methodology

Simulated PCE Infiltration and Distribution

The study examined the influence of physical and chemical heterogeneities on organic waste infiltration and spreading in the source zone of a statistically homogeneous (i.e., physically heterogeneous) but nonuniform sand aquifer. An important motivation for the modeling of DNAPL infiltration and entrapment is the need to derive realistic models of organic liquid distribution within DNAPL source zones for the use in pre- and post-remediation contaminant mass flux estimation. Ensemble statistics for PCE saturation, vertical infiltration, and lateral spreading are presented in Table 2. Figure 5 illustrates simulated PCE saturation for 9 representative realizations from the total of 50 simulated realizations. PCE saturation was scaled from 0.0008 to 0.2295 to enhance the depiction of low saturation variability. Maximum PCE saturations ranged from 0.0007 to 0.23 as illustrated in Table 2. By assuming uniform ϕ and simulating d_{10} using SGS algorithm, simulations exhibited a relatively small variance in maximum PCE saturation, an overall increase in vertical penetration (z), and a decrease in the degree of lateral spreading (x).

Table 2 Ensemble statistics for PCE distribution metrics

Property	Min	Mean	Max	Standard Deviation
Concentration (VF)	0.0026	0.0833	0.2295	0.0552
Z_m	0.35	2.51	4.55	0.97
X_m	2.33	-	7.67	0.79

Comparison of simulated entrapped PCE distributions for the entire ensemble revealed that aquifer parameter spatial variability in a statistically homogeneous media involving the representation of permeability or porosity have major influences on PCE infiltration and distribution. In general, with additionally independent incorporation of aquifer parameters such as ϕ and/or d_{10} values leads to a significantly greater variability in the distribution of PCE saturation (in terms of PCE spreading and pooling behavior) as well as the maximum vertical infiltration depth and lateral spreading in the aquifer domain.

Profiles from all the simulation sets display irregular downward migration paths or channeling of PCE due to incorporation of macroscopic parameter variations as discussed by Kueper and Frind (1991). Qualitatively, this behavior is consistent with conceptual DNAPL source zone models consisting of fingers of DNAPL entrapped at residual saturation and pools (Mercer and Cohen 1990; Anderson et al. 1992; Sale and McWhorter

2001). Increased spill rates and/or volume led to higher organic liquid saturations and decreased spreading, resulting in a significant pooling of PCE observed at the bottom of the domain (data not shown). This observation is consistent with previous reported results by Kueper and Gerhard (1995) and Dekker and Abriola (2000a).

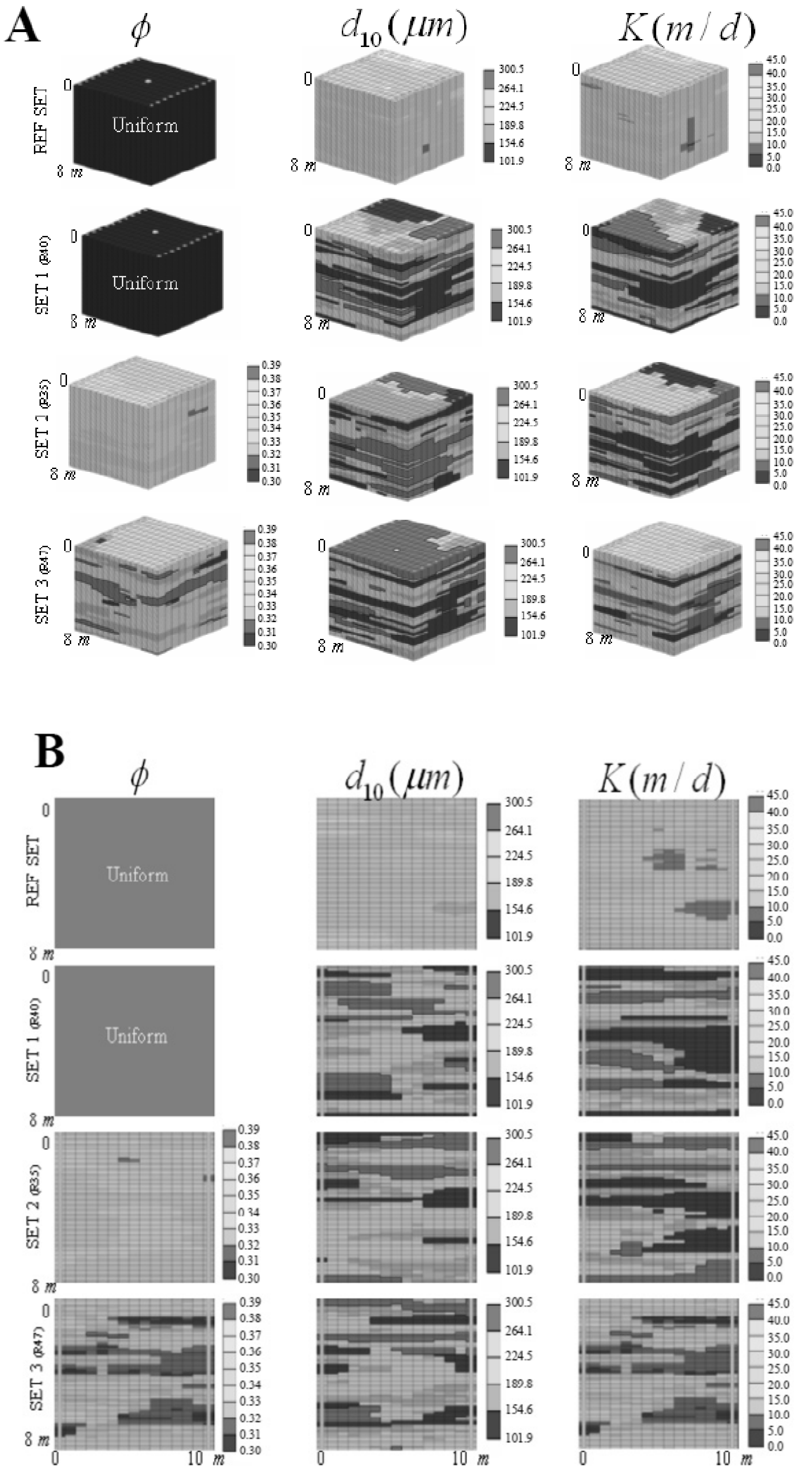

Fig. 3 Aquifer geostatistical simulations in: (A) 3D Realizations; and (B) representative 2D profiles extracted from 3D realizations (uniform ϕ and SGS d_{10})

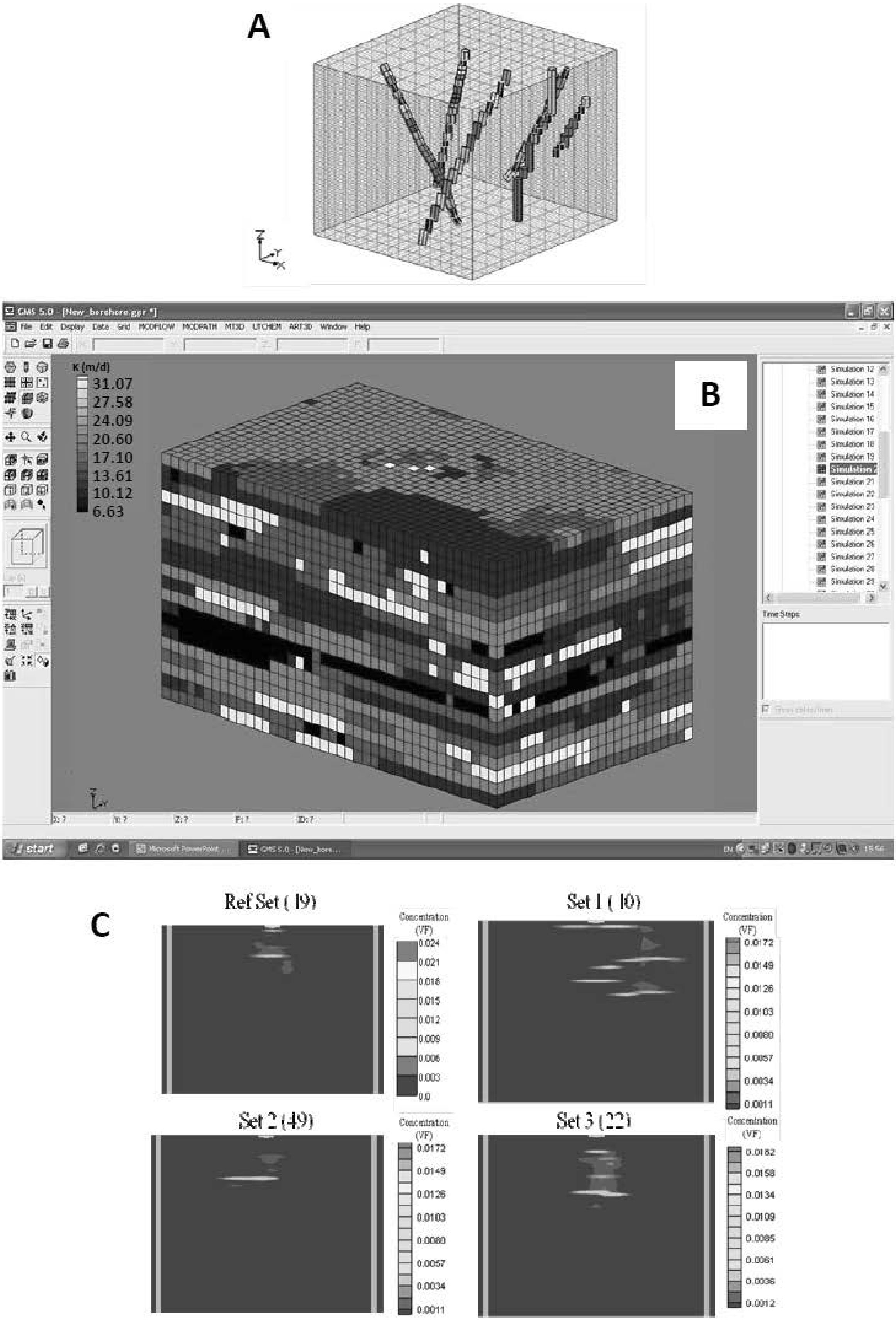

Fig. 4 (A) Bore log information used to generate 3D subsurface structure; (B) 3D stochastic realizations generated from real bore log information in the study area with assigned hydraulic conductivity (*K*); (C) PCE plume simulated in 2D ensembles

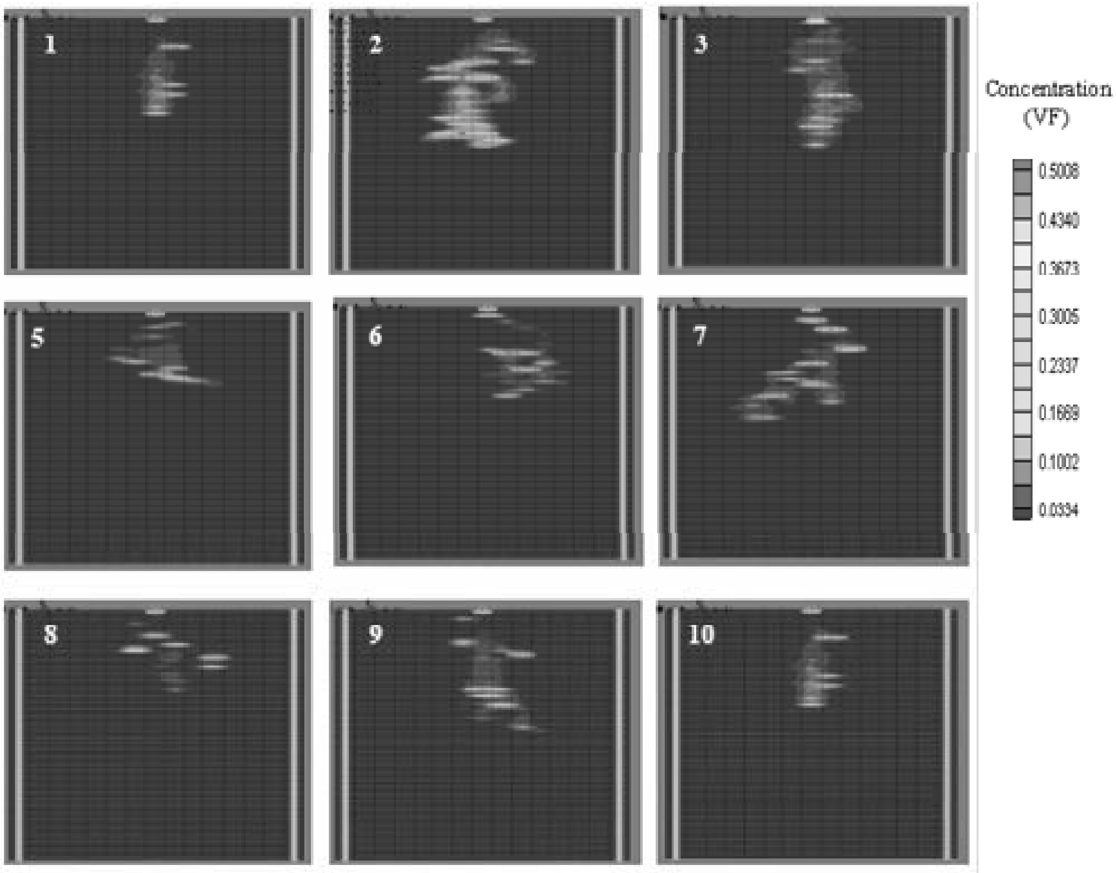

Fig. 5 Representative PCE saturation distributions (9 from the total of 50 realizations in the ensemble)

Although all of the simulations are qualitatively consistent with DNAPL source zone conceptual models, the procedure used in this study may not represent the realistic source zone for two reasons. Firstly, the assumption of uniform capillary-saturation parameters within the simulated domain may be limiting as they may also vary spatially. It was reported that the correlation between residual water saturation (S_{wr}) vs. k and residual organic liquid saturation (S_{or}) vs. k had statistically insignificant effects on simulated PCE spill behavior in a saturated sand aquifer (Dekker and Abriola 2000a) and therefore may be treated as spatially uniform. The relationship between variability in parameters λ (i.e., pore size parameter), and entry pressure (P_b) with variability in aquifer properties ϕ, and k may play an important role in DNAPL source zone architecture, which is not yet the primary focus of this investigation. Second, use of proper SIS method may capture more information from the original aquifer data set compared to SGS (Lemke et al. 2004) as the spatial variability in contrasting grain size distribution curve shapes is represented in the distribution of geostatistical indicator classes. Assignment of Pc-Saturation parameters on the basin of indicator class distribution preserves the simulated spatial continuity of the indicator classes, taking advantage of the GSD information embedded within those classes.

Simulated Mixed DNAPL Infiltration and Distribution

Figure 6 illustates simulated mixed DNAPL saturations for three representative realizations from the total of 50 realizations. Here, realizations generating the minimum, maximum, and value closest to the mean were chosen to represent each set. Comparison of maximum vertical infiltration profiles from point source DNAPL infiltration simulations illustrated in Fig. 7 reveal the deepest vertical spreading in pure PCE system (i.e., 5 m) while the mixture of DNAPL used in this study resulted in the shallowest vertical spreading of 3.32 m (33.6% less). The deepest vertical spreading of single DNAPL and mixed DNAPL in Fig. 7 suggest the greater variability in the distribution of DNAPL saturation due to additional random d_{10} values incorporated into the reference set conditions. On the other hand, less stratified aquifer field parameters as a result of SGS simulation algorithm lead to less DNAPL pooling which was mainly attributable to the limited entry pressure.

Although less contaminant vertical penetration was observed in the mixed DNAPL system, the lateral spreading and organic saturation were surprisingly similar to the case of pure PCE spill based on the maximum spreading observed from the simulations, indicating the loss of DNAPL from the 2D cross section of interest. The observed behavior seems to be plausible as the mixed waste of focus employed in this investigation was lighter and more mobile compared to pure PCE as it contained some light nonaqueous phase liquid (LNAPL) contaminants.

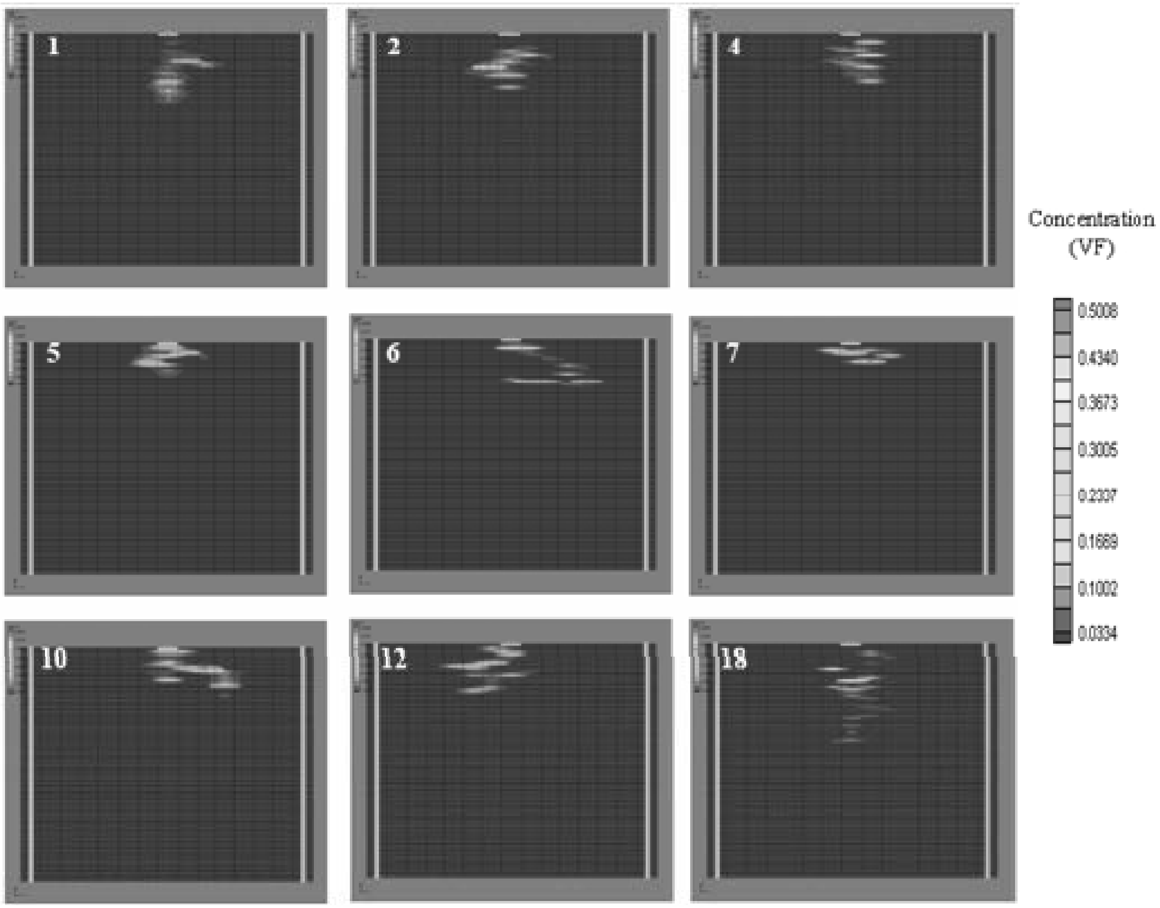

Fig. 6 Representative mixed DNAPL saturation distributions

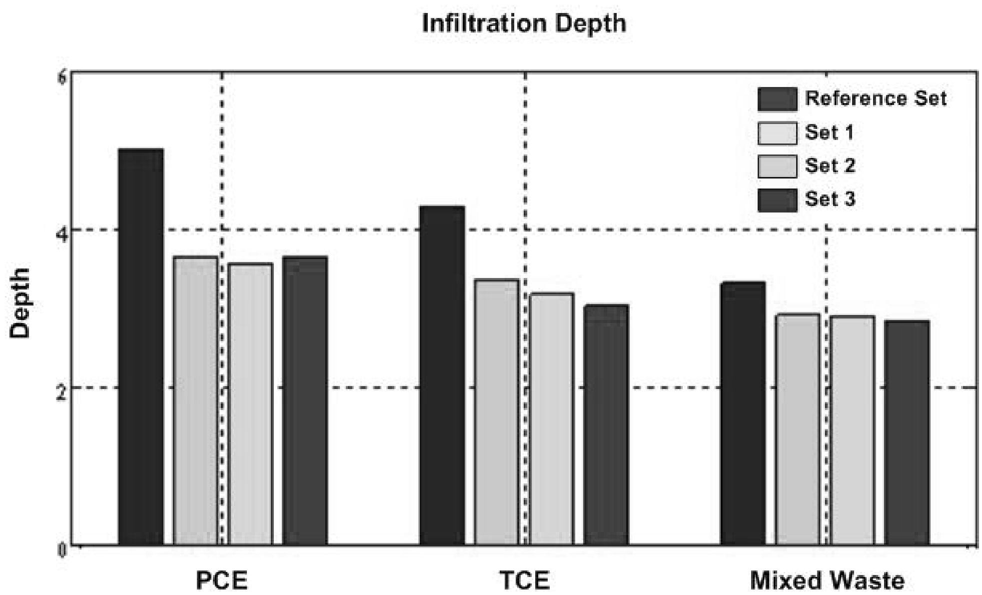

Fig. 7 Vertical infiltration profiles of PCE and mixed DNAPL

CONCLUSIONS

This study examined the influence of physical and chemical heterogeneities on organic waste infiltration and spreading in the source zone of a statistically homogeneous but nonuniform sand aquifer. An important motivation for the modeling of DNAPL infiltration and entrapment is the need to derive realistic models of organic liquid distribution within DNAPL source zones for use in pre- and post-remediation contaminant mass flux estimation. Mathematical modeling effort suggests that DNAPL source zone architecture will govern mass transfer and organic source persistence in aquifers with uniform flow fields (Sale and McWhorter 2001). Because of the contrast in the spatial distribution of predicted maximum organic saturations as well as maximum vertical infiltration and lateral spreading distance in the simulations incorporating physical aquifer heterogeneity and chemical heterogeneity due to DNAPL waste compositions, it is anticipated that predicted dissolved contaminant effluent concentrations and response to simulated DNAPL remediation technologies will differ using results generated with spatial variability compared to those without. It is thus important to assess the influence of physical and chemical heterogeneities on source zone representations.

The results of these sets of numerical simulations demonstrate that independent variation in aquifer parameter can increase the variance of model performance metrics (e.g., observed infiltration depths and lateral spreading). For statistically homogeneous, nonuniform sand aquifers considered in this investigation, the uniform porosity and spatially variable d_{10} values have a relatively minor effect on predicted DNAPL distributions compared to the influence due to chemical waste compositions employed. The contrast in predicted DNAPL distributions is highly expected to result in differing behavior with respect to contaminant mass flux and remediation efficiency in terms of subsequent contaminant recovery.

REFERENCES

Abriola, L. M. and Bradford, S. A. (1998). Experimental investigations of the entrapment and persistence of organic liquid contaminants in the subsurface environment. Environmental Health Perspectives. 106: 1083-1095.

Anderson, M. P. (1990) Aquifer Heterogeneity – A Geological Perspective. In: Hitchon, B. (Editor), National Water Well Association, Bariff, Alberta, Canada.

Anderson, M. R., Johnson, R. L. and Pankow, J. F. (1992). Dissolution of Dense Chlorinated Solvents into Groundwater. 3. Modeling Contaminant Plumes from Fingers and Pools of Solvent. Environ. Science Technol, 26: 901-908.

Dekker, T. J. and Abriola, L. M. (2000a). The influence of field scale heterogeneity on the infiltration and entrapment of dense nonaqueous phase liquids in saturated formations. J. Cont. Hydrol., 42: 187-218.

Dekker, T. J. and Abriola, L. M. (2000b). The influence of field scale heterogeneity on the surfactant-enhanced remediation of entrapped nonaqueous phase liquids. J. Cont. Hydrol., 42: 219-251.

Deutsch, C. V. and Journel, A. G. (1998). GSLIB: Geostatistical Software Library and User’s Guide, 2nd ed.; Oxford University Press, New York.

Fogg, G. E. (1986). Groundwater flow and sand body interconnectedness in a thick, multiple-aquifer system. Water Resources Res., 22: 679-694.

Goovaerts, P. (1999). Impact of the simulation algorithm, magnitude of ergodic fluctuations and number of realizations on the spaces of uncertainty of flow properties. Stochastic Environmental Research Risk Assessment, 13: 161-182.

Imhoff, P. T., Mann, A. S., Mercer, M. and Fitzpatrick, M. (2003). Scaling DNAPL migration from the laboratory to the field. J. Cont. Hydrol., 64: 73-92.

Kueper, B. H. and Frind, E. O. (1991). Two-phase flow in heterogeneous porous media 1. model development. Water Resources Res., 27: 1049-1057.

Kueper, B. H. and Gerhard, J. I. (1995). Variability of point source infiltration rates for two-phase flow in heterogeneous porous media. Water Resources Res., 31: 2971-2980.

Lemke, L. D., Abriola, L. M. and Goovaerts, P. (2004). Dense nonaqueous phase liquid (DNAPL) source zone characterization: influence of hydraulic property correlation on predictions of DNAPL infiltration and entrapment. Water Resources Res., 40: W01511.

McKenna, S. A. and Poeter, E. P. (1994). Simulating Geological Uncertainty with Imprecise Data for Groundwater Flow and Advective Transport Modeling. In: Yarus, J.M. and Chambers, R.L. (Editors), Stochastic Modeling and Geostatistics: Principles, Methods, and Case Studies. American Association of Petroleum Geologists, Tulsa, Oklahoma, USA: 241-248.

Mercer, J. W. and Cohen, R. M. (1990). A review of immiscible fluids in the subsurface: properties, models, characterizations, and remediation. J. Cont. Hydrol., 6: 107-163.

Rathfelder, K. M. and Abriola, M. (1998). Influence of capillarity in numerical modeling of organic liquid redistribution in two-phase systems. Advances in Water Resources, 21: 159-170.

Rodphai, S. and Putthividhya, A. (2009). Use of geostatistical models in DNAPL source zone architecture and dissolution profiles assessment in spatially variable aquifer. Proceedings of International Groundwater Symposium (IGS-TH), Bangkok, Thailand.

Sale, T. C. and McWhorter, D. B. (2001). Steady state mass transfer from single-component dense nonaqueous phase liquids in uniform flow fields. Water Resources Res., 37: 393-404.

Schad, H. (1993). Geostatistical analysis of hydraulic conductivity related data based on core samples from a heterogeneous fluvial aquifer. In: Vincenzon, C., Giovanni, G., and Donato, P. (Editors) Statistics of Spatial Process: Theory and Applications; It. Stat, Soc., Bari, Italy: 205-212.

UTCHEM, UTCHEM-9.0 (2000). A Three-Dimensional Chemical Flood Simulator, report, Center for Petroleum and Geosystems Engineering, The University of Texas at Austin, Austin, TX.

Wilson, J. L., Conrad, S. H., Mason, W. R., Peplinski, W. and Hagan, E. (1990). Laboratory investigations of residual liquid organics from spills, leaks, and disposal of hazardous wastes in groundwater. Rep. EPA/600/6-90-004, U.S. Environmental Protection Agency, Ada, Oklahoma.