The Impact of Well-Field Configuration and Permeability Heterogeneity on Contaminant Mass Removal and Plume Persistence

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Abstract

The purpose of this study is to investigate the effects of well-field hydraulics and permeability heterogeneity on mass-removal efficiency for systems comprising large groundwater contaminant plumes. A three-dimensional (3D) numerical model was used to simulate the impact of different well-field configurations on pump-and-treat mass removal for heterogeneous domains. The relationship between reduction in contaminant mass discharge (CMDR) and mass removal (MR) was used as the metric to examine remediation efficiency. The impacts of well-field configuration on mass removal behavior are attributed to mass-transfer constraints related to regions of low flow associated with the well field, which can be muted by the influence of permeability heterogeneity. These impacts are reflected in the associated CMDR-MR profiles. Systems whose CMDR-MR profiles are below the 1:1 relationship line are associated with more efficient well-field configurations. The impact of domain heterogeneity on mass-removal effectiveness was investigated in terms of both variance and correlation scale of the random permeability distributions and indexed by the CMDR-MR relationship. Data collected from pump-and-treat operations conducted in a section of the Tucson International Airport Area (TIAA) federal Superfund site were used as a case study. The comparison between simulated and measured site data supports the general validity of the numerical model, and results from the case study are consistent with the conclusions of the theoretical study. These results illustrate that the CMDR-MR relationship can be an effective way to quantify the impacts of different factors on mass-removal efficiency.

Key words: Plume; back diffusion; mass flux

1. Introduction

Contamination of groundwater resources by a variety of organic and inorganic contaminants continues to be a significant issue of import for human health and water-resources sustainability in many regions of the US and elsewhere. The remediation of groundwater-contamination sites is a costly, time-consuming endeavor that is constrained by the persistence of groundwater contaminant plumes [1]. Understanding and quantifying the factors that contribute to plume persistence is critical to effective site cleanup.

The results of prior investigations have clearly indicated that the presence of source zones containing organic liquids (NAPL sources) is typically a primary factor limiting the cleanup of groundwater contaminant plumes at many sites. However, research conducted at sites for which the source zone has been remediated or contained indicates that the contaminant plumes have continued to persist [e.g., 1-8], indicating that additional factors contribute to persistence. The factors beyond uncontrolled source zones that contribute to plume persistence include dispersed reservoirs of dissolved and sorbed contaminant present in lower-permeability zones [e.g., 9-16] and hydraulic-related factors such as non-optimal remedial well-field performance [e.g., 9, 17-20].

The results of several modeling- and field-based studies conducted over the past decade clearly illustrate the contribution of dispersed mass to plume persistence [e.g., 2-7, 21-23]. The impact of this dispersed mass on plume persistence and its significance for constraining mass removal via for example pump and treat operations will depend on several factors, including the properties of the contaminant and associated transport and fate behavior, the magnitude of contaminant mass present, and physical properties of the domain (e.g., heterogeneity). Several studies have examined the impact of permeability heterogeneity on contaminant-mass removal

[e.g., 13, 18, 24-26]. However, these studies employed domains with relatively small degrees of heterogeneity. For example, the variance of permeability ($\sigma_{\ln K}^2$) is often used as an index of the magnitude of permeability variability. In the prior studies cited, the $\sigma_{\ln K}^2$ values were small and spanned a relatively narrow range (0.5-3). However, recent field studies have shown that typical subsurface systems have significantly larger $\sigma_{\ln K}^2$ values, in the range of 5-15, and in some cases as high as 30 [e.g., 27, 28]. Thus, studies need to be conducted with larger $\sigma_{\ln K}^2$ (>5) to more fully investigate mass-removal processes in heterogeneous systems.

As noted above, well-field hydraulics is another factor that can influence plume persistence. The impact of well-field hydraulics, such as well location and distribution, has been investigated by numerical modeling [e.g., 17, 18] and in a field study [e.g., 20]. While the significance of well-field hydraulics for remediation effectiveness has long been recognized, there has to date been minimal investigation of the quantitative impacts on mass-removal efficiency or comparative analysis to other factors.

The objective of this research is to quantify the influence and significance of permeability heterogeneity and well-field hydraulics on mass-removal efficiency for domains with large degrees of heterogeneity. Numerical modeling is conducted for a wide range of permeability variabilities and several well-field configurations. The results are evaluated using a recently-developed metric that examines the relationship between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR). This metric has been demonstrated to be an effective method to examine remediation efficiency [e.g., 4, 6, 29-35]. The previous research efforts that have applied the CMDR-MR metric were conducted for source-zone systems or for systems with combined sources and plumes. The work reported herein

represents an initial application focused solely on mass removal for plume-scale systems in the absence of NAPL sources.

2. Methods

The flow model used in this work was the finite-difference numerical model MODFLOW developed by the U.S. Geological Survey [36, 37]. The solute transport model MT3DMS [38] was used to simulate solute transport. Groundwater Vista (GV) [39] and Groundwater Modeling System (GMS) [40] were used as graphical user interfaces. The model study area was 400,000 square meters. The domain was divided into a regular orthogonal grid consisting of 40 rows and 100 columns with grid space 10-m x 10-m. Specified head boundaries were used along the four borders of the domain, with a natural gradient (0.001) inducing groundwater flow under confined conditions from the west to east. Details of the model domain and associated input parameters are provided in the supplementary materials. Details

Sets of simulations were conducted to examine the impact of permeability heterogeneity on mass removal. A fully heterogeneous domain was developed using the standard stochastic approach. The application and potential limitations of this approach are discussed in section 1 of Supplementary Materials. A random field generator [41] was used to derive realizations of K for the aquifer unit of the domain (5 m thickness), which was divided into 20 layers with thickness of 0.25 m for each layer. The permeability was treated as a stationary, lognormally distributed stochastic property, with a mean $\langle \ln K \rangle$ and variance σ_Y^2 . The random fields were generated with an arithmetic mean value of K equal to 20 m/d and correlation scales of 50-m (longitudinal) x 20-m (transverse) x 0.25-m (vertical). R_λ was used to represent the ratio of domain length to correlation length,

$$R_\lambda = L / \lambda ,$$

where L [L] is the domain length, and λ [L] is the correlation length. Scenarios with or without adjoining clay units present above and below the aquifer unit were simulated (Table SM-2). The total thickness of the domain with adjoining clay units is 15 m (60 layers). Simulations were also conducted to investigate the impact of well-field hydraulics. This was done by testing four different well-field configurations (Fig. SM-1). Details of the model configurations and simulations are provided in Supplementary Materials (SM-1.1 and SM-1.2). Additional simulations were conducted for a contaminated site that is part of the Tucson International Airport Area (TIAA) federal Superfund site in southern Arizona. Details are presented in SM-1.4. Simulation results were analyzed by evaluating CMDR-MR profiles (see details in supplementary materials).

3. Results and discussion

3.1. Impact of well-field configuration

The impact of well-field configuration on mass removal is presented in Fig. 1. The simulated elution curves for four different well-field configurations are presented in Fig. 1A. The elution curve for the natural-gradient scenario shows the most ideal behavior in which the concentration decreased rapidly to lower values. In contrast, for scenarios with pumping wells, the elution curves express earlier concentration decreases and asymptotic approach to low concentrations (tailing). Notably, the simulation for the Downgradient well-field configuration shows multi-step behavior, with an initial sharp decrease followed by a steady state period, and then a rapid decline to low concentration. The varying degrees of non-ideal behavior for simulations produced for all three well-field systems compared to the natural-gradient control is

due to mass-transfer constraints associated with stagnation zones that are caused by well-field hydraulics.

The contaminant mass distributions at selected time periods for each simulation are presented in Fig. SM-7. Fig. SM-7A shows the mass distribution at 160 days of the natural gradient simulation when CMD started to decrease with approximately 25% of mass removed. Apparent preferential flow is observed and lower concentration zones start to appear in downgradient regions much earlier compared to the expected time frame for a homogeneous domain, which is due to preferential flow associated with the higher K regions. 90% of the initial mass was removed by day 920 (1.6 PV). Fig. SM-7B and D present the mass distributions after 180 days of pumping for the simulations with Longitudinal and Distributed well-field configurations, respectively. With more wells, the Distributed well-field configuration was less influenced by preferential flow compared to the Longitudinal well-field configuration. This is reflected in the elution curve wherein relatively rapid concentration decrease is observed for the Distributed well-field configuration at the early period. Fig. SM-7C and E present the mass distributions at 1600 day for the simulations with the Longitudinal and Distributed well-field configurations, respectively. It is apparent that more mass remained for the Distributed well-field configuration as a result of more inter-well stagnation zones, which results in the longer tailing shown in the elution curve. It takes 3320 days to remove 90% of the mass for the simulation with the Distributed well-field configuration compared to 2710 days for the simulation with the Longitudinal well-field configuration.

For the Downgradient well-field simulation, the concentration decreased rapidly after pumping started. The rate of decrease slowed after 470 days (0.8 PV) for a short period until 730 days (1.3 PV), after which the rate of decrease increased again. Fig. SM-7F presents the mass

distribution after 60 days of pumping for the Downgradient well-field simulation. The concentration decreased quickly because of the rapid mass removal and strong dilution occurring in the vicinity of the wells. Fig. SM-7G displays the mass distribution after 470 days. The mass removal was mediated by slow advective transport of the upgradient mass via natural-gradient flow. However, because of preferential flow, the impact of the upgradient mass was not as significant and the migration-limited period didn't last long as was observed for parallel simulations conducted for a homogeneous domain [42]. Fig. SM-7H shows the mass distribution at 1600 day. By this time, most of the remaining contaminant mass residing in accessible zones had migrated into the zone of influence of the extraction wells, allowing for more rapid removal and attendant reduction in concentration. The mass removal was constrained by the slow mass-transfer process associated with the poorly accessible zones. It takes 2020 days to remove 90% of mass for the simulation with the Downgradient well-field configuration, significantly less than for the Distributed and Longitudinal systems.

The CMDR-MR profiles are presented in Fig. 1B. The CMDR-MR relationship for the natural gradient simulation exhibits a curvilinear convex-downward profile residing below the one-to-one reference line. The CMD did not start to decrease until 20% of the initial mass was removed, reflecting more efficient mass removal compared to the other three simulations. Because no pumping wells (and associated stagnation zones) were applied for the natural gradient scenario, no associated mass-transfer limitation was present.

The CMDR-MR curves for the Longitudinal and Distributed well-field scenarios exhibit convex-upward profiles residing above the reference line. As discussed above, at early stage, the well distribution for the Distributed well-field configuration decreased the influence of preferential flow. The curve for the Distributed well-field configuration resides to the right of the

curve for the Longitudinal well-field configuration, reflecting that a CMD reduction similar to that observed for the Longitudinal configuration required more mass removed. After approximately 50% of mass was removed, the curve for the Distributed well-field configuration shifts leftward because of the relatively significant mass-transfer constraints associated with more inter-well stagnation zones. The Downgradient simulation shows a multi-step CMDR-MR profile wherein CMD started to decrease after minimal mass removal, and attained ~60% reduction by 20% mass removal. After this point there was minimal further reduction in CMD until approximately 60% mass removal, after which the rate of CMD reduction increased until all mass was removed.

The differences among the CMDR-MR profiles illustrate the impact of well-field configuration for the heterogeneous domain. However, the disparities between the curves are not as significant as the observed differences for a homogenous domain (Fig. 1C). These results indicate that the influence of permeability heterogeneity mutes the impact of well-field configuration.

3.2. Impact of permeability heterogeneity

For simulations conducted for the heterogeneous domain without adjoining clay units present, the CMDR-MR relationship for the natural gradient scenario exhibits a convex-downward profile residing below the 1:1 reference line. Conversely, the CMDR-MR curves shift leftward for simulations with pumping wells (Fig. 1). The non-ideal behavior is attributed to mass-transfer constraints caused by both low flow zones and permeability heterogeneity. For simulations conducted in the heterogeneous domain with adjoining clay units present, the CMDR-MR curves shifts further leftward and are asymptotic at larger mass reductions (Fig. SM-

8). This is a result of impacts of low flow zones, permeability heterogeneity, and back diffusion associated with the adjoining clay units.

The influence of the degree of permeability heterogeneity on contaminant elution curves and associated CMDR-MR profiles for the heterogeneous domain was examined by varying the magnitude of the variance of $\ln K$. Significantly larger values of σ_Y^2 were used in the present study compared to the range of values (0.5~3) used in prior research [e.g., 13, 18, 26]. Results for simulations conducted with σ_Y^2 of 2, 5, 10, 15, and 30 for the natural gradient configuration are presented in Fig. 2. The early truncation of the curve for $\sigma_Y^2 = 30$ is because of the extremely long simulation time and is not due to model instability. Increasing the variance results in longer tailing reflected in the elution curves and progressive leftward shifts of the CMDR-MR curves. This is due to the increased proportion of lower-K regions and the attendant greater proportion of contaminant mass they contain, and thus greater proportion of mass influenced by mass-transfer constraints. The CMDR-MR curves reside primarily below the 1:1 line and exhibit singular curvilinear profiles oriented convex-downward for smaller variances. As the variance increases, the CMDR-MR profiles shift leftward and transition to a more sigmoidal shape.

The inflection points wherein the CMD starts to decrease also shift leftward for larger variance. The mass distribution maps for each simulation at the time when CMD starts to decrease are presented in Fig. SM-10. The light red, which represents concentration lower than initial concentration, appears in the downgradient region from day 28 (coincident with the start of the concentration decrease for the elution curve) for the simulation with σ_Y^2 of 30. Conversely, this occurs after 200 days for the simulation with small variance, σ_Y^2 of 2. These

results illustrate the impact of greater preferential flow through higher-K zones for simulations with larger σ_Y^2 , and resultant earlier reductions in concentration and CMD.

The correlation length for the random permeability field was also investigated as another representation of permeability heterogeneity. The impact of this entity was examined by conducting simulations with different correlation lengths for natural-gradient flow in the heterogeneous system without adjoining clay units. The results were evaluated in terms of R_λ .

The resultant elution curves and CMDR-MR profiles are presented in Fig. 3. It is evident that relatively ideal behavior is observed for the simulations conducted with R_λ equal to or greater than 100. This reflects the pseudo-homogeneous nature of the domains extant for such large R_λ values. For the simulation with $R_\lambda = 20$, the elution curve exhibits earlier concentration decrease and longer tailing, and the CMDR-MR curve shifts leftward. For the $R = 1$ simulation, the CMDR-MR exhibits a sigmoidal profile. The impact of R_λ for higher variance ($\sigma_Y^2=15$) with natural gradient is shown in Fig. 2. The elution curve for simulation with $R_\lambda=1$ presents longer tailing compared to the curve for simulation with $R_\lambda=20$, and the CMDR-MR curve shifts leftward.

As expected, both R_λ and σ_Y^2 influence the overall mass-removal behavior. In Fig. 3, for two curves that have the same $R_\lambda (=1)$, the elution curve for larger variance ($\sigma_Y^2=15$) presents longer tailing than the curve for the simulation with smaller variance ($\sigma_Y^2=5$). The CMDR-MR relationship for the simulation with $\sigma_Y^2=15$ exhibits convex-upward profile and shifts leftward compared to the profile for simulation with $\sigma_Y^2=5$. The curve “ratio=1_variance=15 mean” is the

mean of 10 realizations simulated with $\sigma_Y^2=15$ and $R_\lambda=1$. The curve “ratio=1_variance=15_R1” is the result of a single realization that was simulated with the same random seed as the other curves shown in Fig. 3. Apparent disparities between the two curves are observed, but the overall behavior is similar.

The influence of the degree of permeability heterogeneity was also examined for the Longitudinal well-field configuration, and the results are presented in SM-2. Results reveal that the influences of R_λ and σ_Y^2 on the overall mass-removal behavior are consistent to the results for the natural-gradient configuration. The impact of back diffusion was also investigated for the Longitudinal well-field configuration. Mass removal from the adjoining clay units via back diffusion is highly dependent on the permeability distribution for the aquifer region adjacent to the adjoining clay units. Fig. SM-12 shows the K-distribution for the aquifer unit in the vicinity of the bottom adjoining clay unit. Fig. SM-13A presents the corresponding concentration contours for this aquifer unit after 5000 days of pumping. Overall, the contaminant distribution reveals a good agreement with the K-distribution in Fig. SM-12. Higher concentrations correspond to lower permeable zones, and the contaminant residing in higher K regions was preferentially removed. The concentration change with time in the bottom adjoining clay unit is similar to that observed in the aquifer unit. After 5000 days, the higher-concentration zones in the adjoining clay unit occurred in regions right above the high concentration zones in the aquifer unit (Fig. SM-13B). With the initial condition of uniform concentration in both aquifer unit and adjoining clay units, the higher permeable regions in aquifer unit wherein the mass was removed more rapidly because of faster flushing resulted in a larger concentration gradient between the aquifer unit and the adjoining clay unit, leading to faster mass transfer from clay to aquifer unit and thereby lower concentrations in the adjoining clay unit within these regions. As

expected, such concentration changes are delayed for regions farther from the clay-aquifer interface (Fig. SM-13C).

3.3 Literature data

Relevant data sets were collected from the literature to further investigate the impact of permeability heterogeneity on the CMDR-MR relationship. Raw concentration and flow-rate data were tabulated from several studies that examined contaminant mass removal via natural-gradient flow [26-28, 43]. Table SM-3 presents basic information for these previous studies. In studies [26], [43], and [27], the permeability fields were generated randomly, and results with different variances of $\ln K$ were reported. In [28], the K field was generated randomly with four hydrofacies properties, debris flow, floodplain, levee and channel, with fixed proportions. Part of the floodplain was considered as an immobile domain. The raw concentration-time data reported were used to determine CMD and mass removal values, which were then used to create the CMDR-MR profiles presented in Fig. 4. For [28], the concentration data for scenarios wherein the ratio of the mass in the immobile phase to the mass in the mobile phase at equilibrium was 0.01, 0.03 and 0.1 were used herein.

Because the model domains are not identical, the curves are not directly comparable. However, inspection of the data sets shows that for each study, a larger variance resulted in CMDR-MR profiles shifting leftward, similar to the results reported for the present study. For the Zhang et al. [28] data, their immobile domain acted similarly to the low permeability layers used for the simulations conducted for domains with adjoining clay units present in the present study. The associated CMDR-MR profiles shift leftward residing above the 1:1 reference line compared to the profiles for simulations conducted in the other studies, which indicates the

impact of constrained mass removal from low permeability layers in later periods. Notably, the curve for variance of 3.5 in [26] study shifts slightly to the left of the curve with the variance of 5 in the present study. This can be attributed to the different correlation lengths. The R_λ was 10 for the former study, whereas it was 20 for this study. It is possible that differences in correlation lengths are also responsible for the observation that the results of variance of $\ln K$ as 4 and 8 in the study [43] show greater ideal behavior than the data in [26]. The CMDR-MR profiles for scenarios with larger variance, as 24.9 and 37.1 in the study [27], are sigmoidal, consistent with the sigmoidal profiles for the simulations with variance of 15 and 30 in this work.

3. Case Study

The measured and simulated time continuous profiles of mass discharge are presented in Fig. 5. Measured and simulated concentrations are compared for each plume extraction well in Fig. SM-14. The simulated results match well with the measured concentrations for the individual wells and the composite curve except for EW2 in the later period. The perturbation observed in the simulated curves at month 30 was the result of changing pumping rates at the site. The numerical simulation provides a reasonable representation of the measured CMD data. This is particularly noteworthy given the simplifications used for developing the K field and the fact that no parameter fitting was conducted.

Inspection of Fig. 5 and Fig. SM-14 reveals that the CMD and the associated contaminant concentrations decrease asymptotically after approximately 40 months of operation. This tailing behavior suggests the impact of mass-transfer constraints, which could be caused by incomplete source isolation, back diffusion of mass trapped in low permeability zones, nonideal (rate-limited, nonlinear) desorption, hydraulic-related factors such as discussed above, or some

combination thereof. Additional simulations were conducted to further explore the impact of these potential factors.

Results for the simulation conducted assuming complete removal of the source are shown in Fig. 5. The simulated curve matches the measured data during the early period, which is dominated by removal of the contaminant in accessible zones of the plume. However, in the later period, the simulated CMD reduces to lower values compared to the measured data. Simulations were conducted with continuous 60-month and 150-year long-term source contribution. Detailed results are presented in SM-3. Based on the simulation results, it is possible that the source is not fully isolated, and that it provides a contribution to plume persistence.

The results of two simulations with the modified well configurations compared to the original well-field configuration are shown in Fig. SM-16. The time continuous CMD curve for the simulation with the wells in high K zones presents longer tailing due to the greater influence of preferential flow phenomena, which is elucidated by the results of the particle tracking presented in SM-3. The CMDR-MR relationships for all three scenarios are presented in Fig. SM-16B. It is apparent that the system with wells located in the low K zones exhibits the most ideal behavior among three scenarios and can remove more mass within a given time period. For these simulations, the disparities reflected in the CMD curves and CMDR-MR profiles are not significant. As discussed in theoretical study, the heterogeneity of the site adds its own non-ideal behavior, which can mute the impact of the well-field configuration to a certain degree.

Results for simulations with the modified K fields are presented in Fig. SM-18. As expected, the greater the disparity of hydraulic conductivity between layers, the earlier the breakthrough and the longer tailing are observed for the elution curves. Comparing the simulation with the original heterogeneity condition to the simulation conducted for a vertically

homogeneous domain evident differences are observed. For the modified simulation, the concentration reduction rate decreased slightly in the later period of the simulation compared to long tailing for the original simulation, and the CMDR-MR relationship is more ideal residing below the one to one reference line.

4. Summary

Different well-field configurations were simulated for a heterogeneous domain to examine the impact of well-field hydraulics and permeability heterogeneity on mass removal efficiency. The CMDR-MR relationship was used as a key indicator to quantitatively evaluate the impacts of the parameters. Results indicate that well-field configuration has a measurable impact on mass-removal efficiency, which is reduced for the heterogeneous systems because of the influence of permeability heterogeneity. CMDR-MR relationship profiles for simulations with different well-field configurations shifted further left compared to the profiles for natural gradient simulations as a result of low flow regions. CMDR-MR relationships for simulations with Longitudinal and Distributed well-field configurations present curvilinear profiles, whereas a multi-step profile shifted further leftward is observed for the Downgradient well-field configuration.

For simulations with adjoining clay units present, the CMDR-MR relationships present convex-upward profiles and mass was removed asymptotically. Complete removal of mass is constrained by diffusive mass transfer of solute from the low K zones. In terms of permeability heterogeneity, both R_λ and σ_Y^2 influence the overall mass-removal behavior. For domains with larger R_λ or smaller σ_Y^2 , the CMDR-MR relationships exhibit convex-downward profiles that are similar to the curves for simulations conducted for the homogeneous domain. Conversely,

sigmoidal profiles are observed for domains with small R_λ or large σ_Y^2 . The results from the case study agree with the conclusions made in the prior theoretical study.

Time continuous mass-removal data were collected from the literature, and analyzed using CMDR-MR relationships. For each study, the CMDR-MR profiles shifted leftward for larger variances, similar to the results reported for our study. In addition, sigmoidal profiles are observed for the results of Zhang et al. [27] for simulations with large variance, similar to our results. The similarities observed between the literature data and the present study indicate that the CMDR-MR results reported herein are representative of a broad range of conditions relevant to pump and treat operations or plume migration scenarios.

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References

- [1] NRC (National Research Council), Alternatives for managing the nation's complex contaminated groundwater sites. Washington, D.C. 2013.
- [2] S.W. Chapman, B.L. Parker, Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation, *Water Resour. Res.*, 41 (2005) W12411.
- [3] B.L. Parker, S.W. Chapman, M.A. Guilbeault. Plume persistence caused by back diffusion from thin clay layers in a sand aquifer following TCE source-zone hydraulic isolation, *J. Contam. Hydrol.* 102 (2008), 86-104.
- [4] M.L. Brusseau, N.T. Nelson, Z. Zhang, J.E. Blue, J. Rohrer, T. Allen, Source-Zone Characterization of a Chlorinated-Solvent Contaminated Superfund Site in Tucson, AZ. *J. Contam. Hydrol.* 90 (2007) 21-40.
- [5] M.L. Brusseau, J. Hatton, W. DiGuseppi, Assessing the impact of source-zone remediation efforts at the contaminant-plume scale through analysis of contaminant mass discharge, *J. Contam. Hydrol.* 126 (2011) 130-139.

- [6] M.L. Brusseau, Z. Guo, Assessing contaminant-removal conditions and plume persistence through analysis of data from long-term pump-and-treat operations, *J. Contam. Hydrol.* 164 (2014) 16-24.
- [7] D.E. Matthieu III, M.L. Brusseau, Z. Guo, M. Plaschke, K.C. Carroll, F. Brinker, Persistence of a groundwater contaminant plume after hydraulic source containment at a chlorinated-solvent contaminated site, *Groundwater Monitoring and Remediation*, 34 (2014)23-32.
- [8] E. Rasa, S.W. Chapman, B.A. Bekins; G.E. Fog, K.M. Scow, D.M. Mackay, Role of back diffusion and biodegradation reactions in sustaining an MTBE/TBA Plume in alluvial media, *J. Contam. Hydrol.* 126 (2011) 235-247.
- [9] J.F. Keely, Performance evaluations of Pump-and-Treat remediations, EPA/540/4-89/005, 1989.
- [10] R. L. Johnson, J. F. Pankow, Dissolution of dense chlorinated solvents into groundwater .2. Source functions for pools of solvent, *Environ. Sci. Technol.* 26 (1992) 896-901.
- [11] R.D. Mutch, J.I. Scott, D.J. Wilson, Cleanup of fractured rock aquifers - implications of matrix diffusion, *Environ. Monit. Assess.* 24 (1993) 45-70.
- [12] D.J. Wilson, R.D. Mutch, J.I. Scott, Matrix Diffusion Effects in the Cleanup of Heterogeneous Aquifers, *Environ. Monit. Assess.* 26 (1993) 49-64.
- [13] A.J. Rabideau, C.T. Miller, 2-Dimensional modeling of aquifer remediation influenced by sorption nonequilibrium and hydraulic conductivity heterogeneity, *Water Resour. Res.* 30 (1994) 1457-1470.
- [14] M.N. Goltz, M.E. Oxley, Analytical modeling of aquifer decontamination by pumping when transport is affected by rate-limited sorption, *Water Resour. Res.* 27 (1991) 547-556.

- [15] M.L. Brusseau, The effect of porous-media heterogeneity and rate-limited desorption on Pump-and-Treat remediation, Abstr. Pap. Am. Chem. S. 205 (1993) 108-ENVr.
- [16] S. Berglund, V. Cvetkovic, Pump-and-Treat remediation of heterogeneous aquifers - Effects of rate-limited mass-transfer, Ground Water. 33 (1995) 675-685.
- [17] R.L. Satkin, P.B. Bedient, Effectiveness of various aquifer restoration schemes under variable hydrogeologic conditions, Ground Water, 26 (1988) 488-498.
- [18] W. Schafer, W. Kinzelbach, Stochastic modeling of in situ bioremediation in heterogeneous aquifers, J. Contam. Hydrol. 10 (1992) 47-73.
- [19] R.M. Cohen, J.W. Mercer, R.M. Greenwald, M.S. Beljin, Design guideline for conventional pump-and-treat systems, EPA/540/S-97/504, 1997.
- [20] M.O. Rivett, S.W. Chapman, R.M. Allen-King, S. Feenstra, J.A. Cherry, Pump-and-treat remediation of chlorinated solvent contamination at a controlled field-experiment site, Environ. Sci. Technol. 40 (2006) 6770-6781.
- [21] C.X. Liu, W.P. Ball, Back diffusion of chlorinated solvent contaminants from a natural aquitard to a remediated aquifer under well-controlled field conditions: Predictions and measurements, Ground Water, 40 (2002) 220-220.
- [22] M.A. Seyedabbasi, C.J. Newell, D.T. Adamson, T.C. Sale, Relative contribution of DNAPL dissolution and matrix diffusion to the long-term persistence of chlorinated solvent source zones, J. Contam. Hydrol. 134 (2012) 69-81.
- [23] R.A. Dearden, D.J. Noy, M.R. Lelliott, R. Wilson, G.P. Wealthall, Release of contaminants from a heterogeneously fractured low permeability unit underlying a DNAPL source zone, J. Contam. Hydrol. 153 (2013) 141-155.

- [24] E.A. Sudicky, A natural gradient experiment on solute transport in a sand aquifer: Spatial variability of hydraulic conductivity and its role in the dispersion process, *Water Resour. Res.* 22 (1986) 2069-2082.
- [25] R. Ababou, D. McLaughlin, L.W. Gelhar, A.F.B. Tompson, Numerical simulation of three-dimensional saturated flow in randomly heterogeneous porous media, *Transp. Porous Media.* 4 (1989) 549-565.
- [26] R. Srivastava, M.L. Brusseau, Effect of physical and chemical heterogeneities on aquifer remediation by pump and treat. In: *Proceedings of the American Chemical Society National Meetings, Environmental Chemistry Division, San Diego, CA, March 13-18, 1994, Vol.34(1).* American Chemical Society, Washington, DC, pp.262-265.
- [27] Y. Zhang, C.T. Green, G.E. Fogg, The impact of medium architecture of alluvial settings on non-Fickian transport, *Adv. Water Resour.* 54 (2013) 78-99.
- [28] Y. Zhang, C.T. Green, B. Baeumer, Linking aquifer spatial properties and non-Fickian transport in mobile-immobile like alluvial settings, *J. Hydrol.* 512 (2014) 315-331.
- [29] C.G. Enfield, A.L. Wood, M.C. Brooks, M.D. Annable, Interpreting tracer data to forecast remedial performance. In: Thornton S., Oswald S. (Eds.), *Groundwater Quality 2001: Natural and Enhanced Restoration of Groundwater Pollution, Proceedings of the Groundwater Quality 2001 Conference.* IAHS Publ. No. 275, 2002, pp. 11– 16.
- [30] M.C. Brooks, M.D. Annable, P.S.C. Rao, K. Hatfield, J.W. Jawitz, W.R. Wise, A.L. Wood, C.G. Enfield, Controlled release, blind test of DNAPL remediation by ethanol flushing, *J. Contam. Hydrol.* 69 (2004) 281–297.

- [31] J.W. Jawitz, A.D. Fure, G.G. Demmy, S. Berglund, and P.S.C. Rao, Groundwater contaminant flux reduction resulting from nonaqueous phase liquid mass reduction, *Water Resour. Res.* 41 (2005) W10408.
- [32] M.L. Brusseau, E.L. DiFilippo, J.C. Marble, M. Oostrom, Mass-removal and mass-flux-reduction behavior for idealized source zones with hydraulically poorly-accessible immiscible liquid, *Chemosphere*, 71 (2008) 1511-1521.
- [33] A.J. Kaye, J. Cho, N.B. Basu, X. Chen, M.D. Annable, J.W. Jawitz, Laboratory investigation of flux reduction from dense non-aqueous phase liquid (DNAPL) partial source zone remediation by enhanced dissolution, *J. Contam. Hydrol.* 102 (2008) 17–28.
- [34] E.L. DiFilippo, K.C. Carroll, M.L. Brusseau, Impact of organic-liquid distribution and flow-field Heterogeneity on reductions in mass flux, *J. Contam. Hydrol.* 115 (2010) 14-25.
- [35] M.L. Brusseau, D.E. Matthieu III, K.C. Carroll, J. Mainhagu, C. Morrison, A. McMillan, A. Russo, M. Plaschke, Characterizing long-term contaminant mass discharge and the relationship between reductions in discharge and reductions in mass for DNAPL source areas, *J. Contam. Hydrol.* 149 (2013) 1-12.
- [36] M.G. McDonald, A.W. Harbaugh, A modular three-dimensional finite-difference ground-water flow model. U.S. Geological Survey Techniques of Water-Resources Investigations. Chapter A1, 586 p, 1988.
- [37] A.W. Harbaugh, E.R. Banta, M.C. Hill, M.G. McDonald, MODFLOW-2000, The U.S. Geological Survey modular ground-water model-user guide to modularization concepts and the ground-water flow process, U.S. Geological Survey Open-File Report 00-92, 2000.

- [38] C. Zheng, MT3D: a modular three-dimensional transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems. Report 74280. U.S. EPA Robert S. Kerr Environmental Research Laboratory, Ada, OK, USA, 1990.
- [39] J.O. Rumbaugh, D.B. Rumbaugh, Groundwater Vistas. Environmental Solutions Inc., Reinholds, PA, www.groundwatermodels.com, 2007.
- [40] Environmental Modeling Research Laboratory (EMRL), Groundwater Modeling System (GMS) version 6.5. Brigham Young University, Provo, UT, 2005.
- [41] A. Gutjahr, Fast Fourier transforms for random field generation, New Mexico Tech report, contract 4-RS of Los Alamos National Laboratory, N. M. Inst. of Min. and Technol., Socorro, N. M., 1989.
- [42] Z. Guo, Understanding the factors influencing contaminant attenuation and plume persistence (Doctoral Dissertation), University of Arizona, Tucson, AZ, 2015.
- [43] A. Fiori, I. Jankovic, G. Dagan, The impact of local diffusion upon mass arrival of a passive solute in transport through three-dimensional highly heterogeneous aquifer, *Adv. Water Resour.* 34 (2011) 1563-1573.
- [44] P.S.C. Rao, J.W. Jawitz, C.G. Enfield, R.W. Falta, M.D. Annable, A.L. Wood, Technology integration for contaminated site remediation: clean-up goals and performance criteria. In: *Groundwater Quality – Natural and Enhanced Restoration of Groundwater Pollution*, IAHS Publ. 275. pp. 571–578, 2002.
- [45] J.C. Parker, E. Park, Modeling field-scale dense nonaqueous phase liquid dissolution kinetics in heterogeneous aquifers, *Water Resour. Res.* 40 (2004) W05109.
- [46] J. Zhu, J.F. Sykes, Simple screening models of NAPL dissolution in the subsurface. *J. Contam. Hydrol.* 72 (2004) 245–258.

- [47] T.J. Phelan, L.D. Lemke, S.A. Bradford, D.M. O'Carroll, L.M. Abriola, Influence of textural and wettability variations on predictions of DNAPL persistence and plume development in saturated porous media, *Adv. Water Resour.* 27 (2004) 411 – 427.
- [48] E.L. DiFilippo, M.L. Brusseau, Relationship between mass flux reduction and source-zone mass removal: analysis of field data, *J. Contam. Hydrol.* 98 (2008) 22–35.
- [49] J.A. Christ, L.D. Lemke, L.M. Abriola, The influence of dimensionality on simulations of mass recovery from nonuniform dense non-aqueous phase liquid (DNAPL) source zones, *Adv. Water Resour.* 32(2009) 401–412.

Figure Captions

Figure 1. Impact of well-field configuration on mass removal behavior in 3D domain $< R_\lambda = 20$ and $\sigma_Y^2 = 5 >$: A. Elution curves; B. CMDR-MR relationships. The curves are the mean of 10 realizations simulated in the domain. The results for all individual realizations are presented in Fig. SM-6. C. CMDR-MR relationships for simulations conducted with a homogeneous domain.

Figure 2. Impact of degree of permeability heterogeneity on mass removal behavior in heterogeneous domain with natural gradient $< R_\lambda = 20 >$: A. Elution curves; B. CMDR-MR relationships. The curves “5”, “15” and “15_R_1” are the mean of 10 realizations with $\sigma_Y^2 = 5$ and $R_\lambda = 20$, $\sigma_Y^2 = 15$ and $R_\lambda = 20$, and $\sigma_Y^2 = 15$ and $R_\lambda = 1$. The results for all individual realizations are presented in Fig. SM-9.

Figure 3. Impact of correlation length on mass removal behavior for natural gradient and Longitudinal well-field in heterogeneous domains without clay present $< \sigma_Y^2 = 5 >$: A. Elution curves; B. CMDR-MR relationships. Results of simulations with natural gradient and Longitudinal well field in heterogeneous domain with $R_\lambda = 1$ and $\sigma_Y^2 = 15$ are also presented. The curve “L_ratio=1_variance=15” is the results of simulation conducted with Longitudinal well field in domain with $R_\lambda = 1$ and $\sigma_Y^2 = 15$. The curves “ratio=1”, “ratio=20”, and “ratio=1_variance=15mean” are the mean of 10 realizations simulated in domain with variance=5 and $R_\lambda = 1$, variance=5 and $R_\lambda = 20$, variance=15 and $R_\lambda = 1$. Results for single realization are present in Fig. SM-9. The curve “ratio=1_variance=15_R1” is results of the single

realization that the domain was generated using same random seeds as the domain generated for other simulations in this figure.

Figure 4. CMDR-MR relationship for data collected from the literature. Natural gradient or induced gradient were applied in these studies and concentration was monitored downgradient of the domains.

Figure 5. Relative contaminant mass discharge as a function of elapsed time obtained from monitored field data and modeling results.

Figure 1A

Figure 1B

Figure 1C

Figure 2A

Figure 2B

Figure 3A

Figure 3B

Figure 4

Figure 5