UNDERSTANDING THE FACTORS INFLUENCING CONTAMINANT ATTENUATION AND PLUME PERSISTENCE

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ABSTRACT

The phenomenon of plume persistence was observed for five federal Superfund sites by analysis of historical groundwater-withdrawal and contaminant-concentration data collected from long-term pump-and-treat operations. The potential factors contributing to plume persistence are generally recognized to include incomplete isolation of the source zone, permeability heterogeneity, well-field hydraulics, and non-ideal (rate-limited, nonlinear) desorption. However, the significance of each factor, especially the site-specific contribution is undetermined, which is very important for site development and management. One objective of this study is to quantify the impacts of different factors on mass-removal efficiency. Three-dimensional (3D) numerical models were used to simulate the impact of different well-field configurations on pump-and-treat mass removal. The relationship between reduction in contaminant mass discharge (CMDR) and mass removal (MR) was used as the metric to examine remediation efficiency. Results indicate that (1) even with effort to control the source, residual impact of source can still be a factor causing plume persistence, (2) the well-field configuration has a measurable impact on mass-removal efficiency, which can be muted by the influence of permeability heterogeneity, (3) in terms of permeability heterogeneity, both variance and correlation scale influence the overall mass-removal behavior, (4) the CMDR-MR relationship can be used to quantify the impacts of different factors on mass-removal efficiency at the plume scale.

It has been recognized that the use of pump and treat for groundwater remediation will require many decades to attain site closure at most complex sites. Thus, monitored
natural attenuation (MNA) and enhanced attenuation (EA) have been widely accepted as alternatives because of their lower cost and sustainable management for large, complex plumes. However, the planning and evaluation of MNA/EA applications require greater levels of characterization data than typically collected. Advanced, innovative methods are required to characterize specific attenuation processes and associated rates to evaluate the feasibility of MNA/EA. Contaminant elution and tracer (CET) tests have been proposed as one such advanced method. Another objective of this study is to investigate the use of modified well-field configurations to enhance the performance of CET tests to collect critical site-specific data that can be used to better delineate attenuation processes and quantify the associated rate coefficients. Three-dimensional numerical models were used to simulate the CET test with specific well-field configurations under different conditions. The results show that the CET test with a nested (two-couplet) well-field configuration can be used to characterize transport and attenuation processes by eliminating the impact of the surrounding plume. The results also show that applying select analytical mass-removal functions can be an efficient method for parameter estimation, as it does not require the use of mathematical transport modeling and does not require the attendant input data that are costly and time-consuming to obtain.
CHAPETER I

INTRODUCTION

I.1. Background

Compounds such as chlorinated solvents (e.g., trichloroethene, tetrachloroethene, carbon tetrachloride), 1,4-dioxane, methyl tertiary-butyl ether (MTBE), and perchlorate used in industrial, commercial, and other applications continue to pose significant threats to human health through contamination of groundwater resources. These compounds generally have high aqueous solubilities compared to regulatory limits (maximum contaminant level for groundwater), generally low retardation, and typically relatively low potential to be biodegraded or otherwise attenuated. These features result in formation of large contaminant plumes at many sites. These large plumes, which are typically hundreds of meters to several kilometers long, present complex and costly challenges to remediation and closure of the sites. In fact, a recent National Research Council report concludes that it is unlikely that remediation of these complex sites will be achieved in a time frame of 50-100 years under current methods and standards (NRC, 2013).

The results of prior investigations have clearly indicated that the presence of source zones containing organic liquids is typically a primary factor limiting the cleanup of many sites. These sources can provide long-term and consistent contaminant supply to the downgradient plume, thereby leading to plume persistence. 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. Chapman and Parker, 2005; Rivett et al., 2006; Parker et al., 2008; Rasa et al., 2011; Brusseau et al., 2007,2011; Brusseau and Guo, 2014; Matthieu et al., 2014). Improved understanding of the factors and processes that contribute to plume persistence, and development of methods to characterize and manage such plumes, is a current critical focus of research. The factors beyond uncontrolled source zones that contribute to plume persistence include dispersed reservoirs of dissolved contaminant present in lower-permeability zones (e.g., Keely, 1989; Johnson and Pankow, 1992; Mutch et al., 1993; Wilson et al., 1993; Rabideau and Miller, 1994), sorbed contaminant (e.g., Keely, 1989; Goltz and Oxley, 1991; Brusseau, 1993; Rabideau and Miller, 1994; Berglund and Cvetkovic, 1995), and hydraulic-related factors such as non-optimal remedial well-field performance (e.g., Satkin and Bedient, 1988; Keely, 1989; Schafer and Kinzelbach, 1992; Cohen et al., 1997; Rivett et al., 2006).

I.1.1 Impacts of permeability heterogeneity on plume persistence

Keely (1989) discussed contaminant behaviors in groundwater and plume dynamics for sites wherein the pump and treat was operated. He summarized the geologic, hydrologic, chemical and biological variations, such as site heterogeneities, hydrodynamic isolation, and sorption influences, that limited the pump and treat remediation.

Chapman and Parker (2005) conducted a study at an industrial site in Connecticut where the source zone at the aquifer bottom was isolated. They sampled from three aquifer monitoring wells located approximately 330 m downgradient of the source zone
and found TCE concentration declined to between 200 and 2,000 ug/L from the original range between 5,000 and 30,000 ug/L over the following 2-3 years. However, after the strong decline, TCE plume was observed to persist for years beyond the time frame that the plume should have been flushed out of the monitor area. Analysis of vertical cores and numerical simulation results indicated that the long plume tailing could be attributed to back diffusion from the aquitard. Mass was stored in the aquitard before source isolation, and diffused back to the aquifer slowly after the concentration in aquifer decreased below the concentration in the aquitard. Existence of sorbed mass in the aquitard was another contribution to back diffusion that resulted in the plume persistence.

Parker et al. (2008) conducted a field study at a TCE contaminated site in Florida. The DNAPL source zone was hydraulically isolated by a groundwater extraction and reinjection system. However, the persistent TCE plume was present long after the calculated time period to remove the plume in a homogeneous sand aquifer. Tests of continuous coring indicated the existence of thin clay units in the aquifer wherein a large quantity of dissolved and sorbed mass was stored, which resulted in back diffusion effects. The further numerical model simulations were conducted for scenarios that represented the field site hydrogeologic conditions and hypothetical situation with more thin clayey units in the sand aquifer and an underlying aquitard present. The results indicated that thin clayey beds that have a large storage capacity can cause long-term back diffusion effects, thereby leading to plume persistence for decades after source zone impact was eliminated.
Rasa et al. (2011) conducted two-dimensional reactive transport simulations on a methy tert-butyl ether (MTBE)/tert-butyl alcohol (TBA) plume at Vandenberg Air Force Base. The plume continued to persist after the source zone was removed because of the effects of back diffusion of both MTBE and TBA. The reproduction of the process of TBA became the dominant solute after 2014 demonstrated that the plume concentration was sustained much longer because of back diffusion of mass stored in silt layers compared to the simulation results that back diffusion process was absent.

Brusseau et al. (2007) and Brusseau et al. (2011) presented measured plume data of a site-characterization project conducted at Tucson International Airport Area (TIAA) Superfund site. The source management was conducted on site. The impact of remediation efforts on plume was investigated by analyzing the concentration change and contaminant mass discharge (CMD). A plume scale numerical model was develop to simulate the plume behavior for two scenarios that the source zone were either controlled or not. The simulation results for the scenario with no controlled source presented a much higher level for both concentration and CMD in plume tailing compared to the results of the scenario with a controlled source zone and measured data of the site. The results of this project indicated the significant impact of the source zone. However, even for the controlled source scenario, the elution curve and CMD profiles still presented long tailing. The results showed CMD reached asymptotic condition after initial dropping, which indicated the plume persistence. Further mathematical modeling simulation illustrated that back diffusion and nonideal sorption/desorption processes contributed to long-term plume persistence.
Brusseau and Guo (2014, in this dissertation) analyzed groundwater-withdrawal and contaminant-concentration data collected from long-term pump-and-treat operations for multiple relatively aged sites to examine contaminant removal behaviors. Data collected from each site demonstrated that CMD declined at different rates, which was consistent with contaminant distributions and subsurface properties of the sites. The mass removal constraints were observed for the plume in all three sites, which as discussed, was attributed to influence from back diffusion, a not-fully-isolated source zone, and well-field hydraulics.

Matthieu et al. (2014) presented 60 months of measured data in the plume area of the three hanger site, which is part of the TIAA site, after pump-and-treat was initiated. The concentration, mass discharge, and plume size were observed with measurable decrease. However, the total CMD associated plume dropped rapidly in the first year, then presented asymptotic behavior. The areal extent of the plume decreased less than the anticipated extent based on ideal mass removal behavior. Further study of the site suggested that the plume persistence was caused by contribution from permeability heterogeneity, back diffusion, well-field hydraulics, and imperfect isolation of the source zone, which were confirmed by the numerical simulation conducted for the sites. According to the results of the numerical model, because of impacts of the above factors on the plume, it will take decades for TCE concentration to decrease below maximum contaminant levels with the long-term operation of pump-and-treat.
These studies and additional modeling and field based studies (e.g., Liu and Ball, 2002; Seyedabbasi et al., 2012; Dearden et al., 2013) conducted over the past decade have clearly illustrated the contribution of dispersed mass to plume persistence.

**I.1.2 Impacts of well-field configuration on plume persistence**

Another important factor that can contribute to plume persistence is well-field hydraulics. Satkin and Bedient (1988) evaluated seven well-field patterns under different hydrogeologic conditions using numerical modeling. The results showed significant differences in cleanup time, with the location of wells, pumping rate and other hydrogeologic conditions exerting significant influences on cleanup time. The three-spot well pattern that has an extraction well in the center of the plume and two injection wells located both upgradient and downgradient of the plume is most effective in low and high hydraulic gradient conditions. Still, the best well pattern is highly dependent on the site conditions and the remediation goals such as whether to contain the plume or remove the contaminants.

Schafer and Kinzelbach (1992) conducted a numerical simulation for a heterogeneous domain. The remediation time was much longer compared to that obtained for a homogeneous domain. An improved pump-and treat operation method was proposed and simulated. Twice the number of wells compared to the common scheme was used and locations of active injection and extraction wells were changed by an angle of 90° after a certain time of operation to change the flow direction and decrease the impact of stagnation zones. Time required to remove 90% of mass (RMT$_{90}$) was used as an indicator to evaluate the efficiency of the well-field configuration. The method
improved efficiency of the contaminant removal from the heterogeneous system significantly. For less heterogeneous cases, RMT\textsubscript{90} was in a range of 22 days to 85 days for simulations without location change of wells, whereas RMT\textsubscript{90} was in a range of 22 days to 28 days for simulations with change of wells location. For most the heterogeneous case, the probability of a doubling of remediation time compared to the homogeneous case is 50%, which was reduced to 20% for simulations with well-location adjustment.

Cohen et al. (1997) summarized pump-and-treat remediation strategies and scheme design guidance. The potential limitations of pump-and-treat operation and the factors that cause the problems were discussed. Some numerical simulation results conducted with different well fields were presented. They showed that appropriate setup of the system can decrease the cleanup time significantly.

Rivett et al. (2006) conducted a small field experiment at the Bordern (ON) research site to examine the plume removal behavior with an isolated source zone. In this study, a permeable reactive barrier and an extraction well were used to contain the source zone and two downgradient plume- centerline wells were used to removal contaminants in the plume. They recognized that the back diffusion and nonideal sorption processes had minimal impacts on plume persistence since the experiment was conducted in a mildly heterogeneous sandy aquifer and the plume was freshly formed. They concluded that the concentration tailing of the plume was attributed to the inter-well stagnation zones. The remediation process was slow but still decreased the concentration to close to drinking water standards in 550 days, which indicated the relatively efficient mass
removal compared to decades of removal time periods for the scenarios with long-term source supply.

The significance of well-field hydraulics, such as well location, distribution, and pumping rate, for remediation effectiveness has long been recognized. However, there has to date been minimal investigation of the quantitative impacts on mass-removal efficiency or comparative analysis to other factors. More research is needed to further investigate the impact of well-field hydraulics, especially site-specific significance, on mass-removal efficiency.

I.1.3 Relationship between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR)

The relationship between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR) has been demonstrated to be an effective method to examine remediation efficiency (e.g., Jawitz et al., 2005; Brusseau et al., 2008; Kaye et al., 2008; DiFilippo and Brusseau, 2008; DiFilippo et al., 2010; Brusseau et al., 2013; Brusseau and Guo, 2014).

Lemke et al. (2004) and Lemke and Abriola (2006) conducted a simulation on a PCE spill in a homogeneous, nonuniform sand aquifer located in Oscoda, Michigan to investigate the impact of source architecture on mass recovery and contaminant flux. Surfactant-enhanced aquifer remediation was used for PCE recovery. The ganglia-to-pool metric was developed to define the source architecture. The contaminant flux reduced more significantly for low ganglia-to-pool ratio than scenarios with high ganglia-to-pool
ratio. The contaminant flux was not reduced significantly until the DNAPL distributions changed after certain mass was removed and the distribution went from ganglia-dominated to pool-dominated. This demonstrated the understanding that a large percentage of the source should be removed before the mass flux can show evident reduction. The simulation results suggested the strong impacts of source-zone architecture on contaminant flux behaviors.

Parker and Park (2004) used a three dimensional numerical model to simulate DNAPL releases and dissolved phase transport, coupled with a percolation model to simulate the distribution of DNAPL in the source zone. The initial DNAPL geometries included the fingers as vertical pathways for DNAPL movement and a DNAPL pool in the bottom of the aquifer. For DNAPL geometry with more laterally extensive lenses, the contaminant flux showed a slow reduction rate associated with mass depletion, while for DNAPL geometry with more randomly distributed units, the contaminant flux decrease steadily as the mass was depleted.

Jawitz et al. (2005) presented the stream tube model and used the approach to investigate the relationship between mass flux and mass removal associated with hydrodynamic heterogeneities and NAPL spatial distribution heterogeneity. Nonreactive travel time distribution and reactive travel time distributions were used to describe the hydrodynamic heterogeneity and NAPL spatial distribution heterogeneity respectively. The results indicated that travel time variability had significant impact on the relationship between contaminant flux and mass removal. For sites with small travel time variability, such as homogeneous aquifer, the contaminant flux will not decrease until a large portion
of mass has been removed, while for sites with large travel time variability, such as heterogeneous aquifer, the contaminant flux will decline with minimum mass being removed. Rate-limitation dissolution can result in the decline of mass removal efficiency and early contaminant flux reduction.

Kaye et al. (2008) conducted laboratory experiments with different cosolvent mixture and surfactant mixture in heterogeneous aquifer to examine the impacts of fluid property on mass reduction ($R_m$) and reduction in mass flux ($R_j$) relationship ($R_j(R_m)$). PCE was naturally distributed with water after it was injected in the domain. The source architecture for each experiment was constructed similarly. Both single injection and pulsed injected were tested for each experiment. For single injection experiment, the $R_j$ decreased with minimum $R_m$, and the $R_j(R_m)$ relationship was identical for experiments with different flushing fluids. While for pulsed experiment, the $R_j$ decreased after certain mass reduction occurred, and the $R_j(R_m)$ for experiments with different flushing fluids was observed with difference. The differences were attributed to the varied source architecture in the experiments Modeling simulations were conducted using UTCHEM in systems with same source zone for each experiment. The difference between results of pulsed injection scenarios with four flushing fluids was not as significant as the experiment results, which demonstrate that the $R_j(R_m)$ relationship difference can be caused by source architecture rather than the fluid properties.

Brusseau et al. (2008) presented laboratory data collected from a series of flow-cell experiments. The mass-removal, mass-flux processes, and the relationship between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass
(MR) were analyzed for systems with hydraulically poorly accessible immiscible liquid source zones. For the control experiment that designed for ideal mass-transfer process, CMD presented minimum reduction until a large proportion of mass (>80%) was removed. For other systems, CMD started to reduce with moderate mass was removed. The study also indicated that in general, the relationship between CMDR and MR followed one to one relationship.

Difilippo and Brusseau (2008) evaluated the relationship between CMDR and MR for source zone mass removal by studying published data collected for several fields that had various source-zone architectures and immiscible-liquid compositions, and applied different remediation technologies. The results analyzed based on end-point analysis showed that more than 60% mass was removed for all but three of the studies. These three were ones for which water flushing was used for mass removal. Time-continuous analysis performed for two sites showed significant difference in CMDR for similar mass removals. This illustrated the impacts of source-zone architecture and associated mass-transfer processes on CMDR-MR relationship. A multi-step behavior was observed in the CMDR-MR relationship for one studied site, which demonstrated the failure of the simple mass-removal estimation functions to predict the complex mass-removal process.

Difilippo et al. (2010) also presented the results of flow-cell experiments. The experiments were designed with different systems such that having mixing source at both residual and pool saturations, or having different permeability heterogeneities in the domain. The purpose of the study was to show the heterogeneity and contaminants distribution impacts on CMDR-MR relationship in source zone. Results indicated that for
systems with unimodal distribution of contaminants in accessible flow domain, the CMD will decrease until a large proportion of mass was removed; while for systems have both residual and pool present in the domain and permeability heterogeneity in source zone, the multi-step behaviors were observed. In these situations, the simple function was no longer accurate to characterize the source zone.

Brusseau et al. (2013) reported time continuous CMD data for a very heterogeneous and highly contaminated source zone in the three hanger site. The CMD presented significant decrease. Two methods were used to estimate the total initial mass in source zone. The CMD data was then integrated to produce CMDR-MR relationship with estimated initial mass. The CMDR-MR relationship for the site is consistent with the relationship of system wherein large quantities of mass were hydraulically poorly accessible in low permeability units. The results demonstrated that CMDR-MR relationship can provide information of system properties and dynamics of mass removal and help characterize the site qualitatively. By comparing to results from other field study, it indicated the strong influence from source architecture, which is highly associated with source age, on behavior of CMDR-MR relationship.

In Brusseau and Guo (2014), time continuous CMD curves and the CMDR-MR relationship were used to determine the remediation performance. CMD curves were plotted with source and plume contribution respectively, and compared to the total CMD for the AFP44, MOT, and PGN sites. CMDR-MR profiles with plume contribution and contribution from both source and plume were also studied for these three sites. The CMD started to reduce just after minimum mass was removed, and the profiles of
CMDR-MR for all sites presented convex-upward behaviors residing above 1 to 1 relationship, which can be considered constrain mass removal processes in sites.

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. No reported work has been found representing the application of the CMDR-MR metric solely on mass removal for plume-scale systems.

I.1.4 Contaminant elution and tracer (CET) test for mass-transfer process evaluation

The realization that the complex contaminant sites will require many decades or longer to reach the cleanup goal under current methods and standards has resulted in the examination of alternatives for cost-effective long-term management of plumes at these sites (NRC, 2013). Monitored natural attenuation (MNA) and enhanced attenuation (EA) have been widely accepted as alternatives because of their lower cost and sustainable management for large, complex plumes. Advanced methods are required to characterize specific attenuation processes and associated rates to evaluate the feasibility of MNA/EA. Matrix diffusion, sorption, and transformation processes are critical attenuation processes that can impact remediation effectiveness. Understanding more about these processes can provide guidance for long-term management (NRC, 2013; SERDP, 2013). Moreover, improved predictive modeling that can account for the various attenuation and transport processes is needed for cost-effective site management (e.g., EPA, 2009). This in turn requires better determination of the relevant input parameters.
Several methods have been used for evaluating attenuation processes and feasibility of MNA/EA. One standard method is based on obtaining spatial concentration profiles along the longitudinal axis of the plume (e.g., Newell et al. 2002). An alternative approach measures the contaminant mass flux at several control planes placed perpendicularly to the mean direction of groundwater flow in different locations along the plume (e.g., Borden et al., 1997; King et al., 1999; Basu et al., 2006; Bockelmann et al., 2001). These methods provide measures of aggregate attenuation at the plume scale, and the rate coefficients obtained are composite parameters. Thus, it is not possible to delineate the contributions of specific individual attenuation processes. In addition, preferential flow phenomena and the presence of the plume introduce uncertainties to characterizing attenuation processes at the local scale. These factors limit their usefulness to evaluate the specific process impacts and spatial variability of attenuation (Brusseau, 1998; Chapelle et al., 2007). Another standard method is based on analyzing vertically resolved concentration data collected from high-resolution samples of sediment cores or of groundwater (e.g., Johnson et al., 1989; Ball et al., 1997; Chapman and Parker, 2005). These methods provide concentration profiles that reflect the aggregate, composite impact of all mass-transfer and attenuation processes acting at that specific location. As above, this precludes the ability to evaluate specific attenuation processes individually.

Single-well push-pull tests have also been used to provide local-scale characterization of attenuation processes (e.g., Drever and McKee, 1980; Istok et al., 1997). These tests have been demonstrated to provide robust characterization of transformation processes under certain conditions. A major potential limitation of the
push-pull method is increased uncertainty due to poor tracer recovery in some cases. One case occurs for systems wherein the rates of attenuation are relatively slow compared to the hydraulic residence times (i.e., sites relatively large groundwater velocities), as illustrated by Burbery et al. (2004). This is of particular concern for sites with operating pump-and-treat systems. Another limitation is the influence of the contaminant plume, wherein it may be difficult to separate the impact of attenuation processes from the advective flux associated with the dissolved mass migrating in the higher-permeability domains during mixing induced by extraction.

Tracer tests conducted at the scale of interest can produce more robust characterization of processes and associated parameters. The application of the coupled injection-extraction concept for evaluating the impact of mass-transfer and attenuation processes on transport has been illustrated in a small number of prior experiments (Thorbjarnarson and Mackay, 1997; Blue et al., 1998; Brusseau et al., 1999a; Nelson et al., 2003; Sandrin et al., 2004; Brusseau et al., 2007).

Thorbjarnarson and Mackay (1997) conducted an elution tracer test in a plume region with heterogeneous sand aquifer at the Rocky Mountain Arsenal, Denver, Colorado. Iodide tracer and contaminants, such as TCE and TCA were used in the experiment to estimate the hydraulic conductivity, dispersivities and retardation factors. Samples were collected from one fully penetrating monitoring well and four drive points, and moment analysis and modeling simulation were conducted for tracer breakthrough curves and contaminants elution curves. The elution curves were absent for TCE and TCA sampled from lowest permeability stratum, and presented short elution time for
samples from highest permeability stratum. The elution curve for samples collected from the fully penetrating monitor wells presented major response from high permeable strata but the observed tailing was attributed to the constraint mass removal from low permeable strata.

Blue et al. (1998) conducted an elution tracer test in TIAA superfund site to investigate the possible factors that contribute to the plume tailing after 10 years of operation of pump-and-treat system. Bromide and TCE was used to examine the processes, such as desorption, dissolution, diffusion. Data were collected from extraction well and multi-level centerline monitor well. Modflow was used to determine the vertically averaged hydraulic conductivity. Bromide breakthrough curve and TCE elution curve were analyzed. The study indicated that multi-level samples can provide an insight into the aquifer according to the elution curve responses. The modeling results demonstrated that the multi-level sampling results were more robust to characterize the size as the simulation results with six layer model provided a better match with the field collected data compared to the single layer simulation results.

Brusseau et al. (1999) presented a case study conducted at a jet-fuel contaminated site in Hill Air Force Base, Utah to investigate the biodegradation potential of the site. The fjeld-scale biotracer test method was used. Benzoate, salicylate and ethanol were chose as biotracers to biodegrade different component of contaminants and pentafluorobenzoate was used as nonreactive tracer. A line of fully screened injection wells and a line of fully screened extraction wells located normal to the low direction were installed to generate the test zone. The breakthrough curves for each tracer were
plotted, and the mass recovered were calculated. For pentafluorobenzoate, 100% mass was recovered, while for other three biotreacers, the recovered mass was less than 100%, which is attributed to the degradation processes. The nonlinear biodegradation occurred in the system as observed from the breakthrough curves of biotracers. The results indicated that biotracer method can be selected to characterize the degradation potential in contamination sites. The selection of tracers is site-dependent. The breakthrough curve can be analyzed to decide whether the biodegradation is linear or nonlinear.

Brusseau et al. (2007) conducted an induced-gradient contaminant elution tests in source zone of TIAA Superfund site at Tucson, AZ. The purpose of the work was to characterize the source zone, investigate the potential presence of immiscible liquid in saturated zone and the impacts from source remediation. Two tests were conducted using different injection-extraction well couplets, one of which had the depart distance as 7.5m and another has the distance between injection and extraction wells as 57 m. A fully-screened monitoring wells was located in the centerline of injection-extraction well couplets in each test. Groundwater samples were collected from the monitoring well, the extraction well and other fully-screened monitoring wells located within the swept zone. The extensive tailing were observed and rebound occurred after pumping stopped, which indicate the continuous source supply. However, whether the supply was coming from the contaminant mass was within or adjacent to the aquifer, or the aqueous-phase contaminants from outside of the control region that swept by the injection wells is undetermined because contaminants outside of swept zone were pulled into the extraction well. But the data collected from monitoring well, which is fully isolated from
contaminants outside of the swept zone, was considered unaffected by the contaminant outside. The results indicated the contribution from desorption from solid phase, diffusion from low permeability zone, and dissolution from free phase. And further numerical study demonstrated the presence of the immiscible liquid. The study illustrated the filed-scale induced contaminant elution tests be an effective way to characterize the site properties, and mass transfer processes occurring at site that influence the remediation.

For all prior CET test applications, the test was implemented using a standard injection-extraction dipole configuration. The extraction well remains influenced by the surrounding plume for this configuration, which can be a significant limitation in attempting to delineate specific attenuation processes. This is particularly true for mass-transfer or transformation processes with slower characteristic rates. Hence, there is interest in investigating alternative well-field configurations that may enhance the implementation and analysis of CET tests.

A number of studies have been conducted to evaluate effective well-field configurations for various applications. For example, their impact on contaminant mass removal has been investigated for pump-and-treat systems (e.g., Satkin and Bedient, 1988; Keely, 1989; Schafer and Kinzelbach, 1992; Cohen et al., 1997; Rivett et al., 2006; Guo, 2015). In addition, two-well recirculation systems have been investigated for in-situ bioremediation of groundwater (Gandhi et al., 2002; Luo et al., 2006b).

Luo et al., 2006b studied two well-field configurations on recirculation ratio and residence time to enhance the performance of in situ bioremediation. A traditional single
pair of injection-extraction well configuration was compared to a nested-cell approach using a four-well system that created nested inner cell. A Field experiment was conducted with the four-well nested-cell approach at the Field Research Center in Oak Ridge, Tennessee wherein the metal concentration was high. Results indicated that the inner cell was protected by the outer cell and formed a favorable condition for U (VI) reduction.

Luo et al., 2007a conducted another field experiment at the same site with the four-well system to investigate the hydraulic performance for an in situ bioremediation of uranium. The transfer function and temporal moments of the breakthrough curves that were plotted using data collected from both extraction wells and monitor wells were analyzed. The results demonstrated the strategy using the four-well system to create the recirculation zone as the treatment zone for in situ bioremediation. The analysis of results also indicated that flow field may be influence by biodegradation process and the initial site characterization would be unreliable for long-term site management. Hydraulic performance, such as the recirculating flow fraction and flow field change, was analyzed using the methods of transfer function and temporal moments. Mass recovery fraction and mean travel time were also obtained from the satisfactory fitting of the transfer function to measured data. Results demonstrate the effectiveness of the four-well system for evaluating the performance of in situ bioremediation. Minimal research has been conducted to investigate optimal well-field configurations for CET tests, especially for applications focused on characterizing natural attenuation processes.

For a system that extraction well was fully isolated from surrounding plume, the concentrations and fluxes measured from the extraction well can represent the influence
from processes, such as diffusion, retardation, and transformation, within the isolated area. Applying a suite of tracers for CET test can characterize specific individual attenuation processes, rather than a lumped parameter that determined by standard method for attenuation characterization. Parameters associated with different processes can be estimated by analysis of breakthrough curves in conjunction with mathematical models. Selected functions, such as first-order decay function (e.g., Newell et al., 2002) and power-law functions (e.g., Haggerty et al., 2000; Luo et al., 2007b), can be used to fit the contaminant/tracer elution curves to obtain rate coefficients. Temporal-moment analysis of the breakthrough curves can be conducted to determine rate coefficients (e.g., Leij and Dane, 1992; Das and Kluitenberg, 1996; Srivastava et al., 2004; Luo et al., 2006a). The estimation of parameters for individual process can provide more accuracy of the prediction model and benefit the long-term site management.

I.1.5 Models to estimate the parameters

Breakthrough curves (comprising both arrival and elution waves) plotted using collected concentration data from elution tracer tests can be used for qualitative and quantitative analysis of attenuation. Parameters can be estimated by analysis of breakthrough curves in conjunction with mathematical models. One method used to obtain rate coefficients is based on fitting selected functions to the contaminant/tracer elution curves. These functions range from a simple first-order decay function (e.g., Newell et al., 2002) to power-law functions, for which the power-law magnitude has been correlated to specific mass-transfer behavior (e.g., Haggerty et al., 2000; Luo et al., 2007b). For the breakthrough curves obtained for the tracers, temporal-moment analysis
can be conducted to determine rate coefficients (e.g., Leij and Dane, 1992; Das and Kluitenberg, 1996; Srivastava et al., 2004; Luo et al., 2006). Specific methods have been developed to estimate rate coefficients from the results of push-pull tests (e.g., Haggerty et al., 1998).

In AFCEE (2007) and McDade et al. (2013), a method based on the matrix diffusion model was developed. The model configuration in this study is two clay layers on top and bottom, and a sand layer in the middle. And two processes happened. First, the loading process, the contaminants were first introduced in sand layer uniformly and the clay layers were clean, which induced the contaminant diffusing into the clay layers. After a certain time of loading process, the mass was removed from sand, concentration gradient was reversed, mass loaded into clay layers in previous process started diffuse back to sand. The mass loaded into and mass remain in clay layers were solved with analytical solutions, which are the function of diffusion coefficient (D) or retardation factor (R). McDade et al. (2013) compared the results of matrix modeling to the results of ADR model that only considered advection, dispersion and retardation. The matrix model presented better fits for TCE elution curves plotted using data collected from all 15 plume wells at the Middlefield-Ellis-Whisman (MEW) Superfund Study Area in Mountain View, California. This indicated the significant matrix diffusion impacts on plume persistence at the site.

Cunningham et al. (1997) proposed the analytical solutions for mass transport in groundwater under different source function and boundary conditions. Haggerty et al. (2000) derived more sophisticated analytical solutions to investigate the tailing behavior
for mobile-immobile (dual porosity) tracer test behavior based on the previous studies. A simple expression for the later-time concentration, which is defined for different model, such as first order model, diffusion infinite layer model, and so on. Two single-well injection-extraction tracer tests were conducted at the Waste Isolation Pilot Plant (WIPP) site in southeastern New Mexico. The breakthrough curves, which can help to evaluate the rate-limited mass transfer process, were plotted. The late-time behavior of the breakthrough curves were analyzed, and the analytical solution with a lognormal density function of diffusion coefficients did a good job to represent it.

I.2 Purpose of Study

The purpose of this study is to:

1. Investigate the factors, such as incomplete source isolation, permeability heterogeneity, well-field hydraulics, that impact plume remediation in contamination sites.

2. Study the CMDR-MR relationships for different conditions and the applicability of CMDR-MR relationship as a metric to evaluate performance of remediation in plume scale.

3. Explore the specific well-field configuration for improving the contaminant elution and tracer test to collect critical site-specific data, which can be used to delineate attenuation processes.

4. Propose a concept of enhanced contaminant elution and tracer test to characterize specific attenuation process and determine associated rate coefficients.
I.3 Dissertation Organization

This dissertation comprises two chapters and six appendices. Chapter I is the introduction explaining the background for this research, the research objectives and the dissertation organization. Chapter II is a summary of the results of the present study, which has been divided into six appendices with Appendices A, B and D as three manuscripts. A brief overview of each study is discussed below.

Appendices A and D are manuscripts and will be submitted to peer-reviewed journals. My advisor Dr. Brusseau provided advice and guidance in all of the work presented in the Appendices.

Appendix A investigated the plume persistence by analysis of the data collected from different site that long-term pump-and-treat systems are in operation. The author collected and analyzed the data from remediation reports of each site and studied the site properties, and Dr. Brusseau compiled and wrote the manuscript.

Appendix B studied the impacts of well-field hydraulics and permeability heterogeneity on plume remediation using a numerical model. The author conducted the simulations and analyzed the results, and Dr. Brusseau provided guidance and supervised as advisor.

Appendix C presented a case study for Tucson International Airport Area Superfund site. The potential factors impacting the observed plume persistence were investigated. The author conducted the simulations and analyzed the results, and Dr. Brusseau provided guidance and supervised as advisor.
Appendix D tested specific well-field configurations for improving the contaminant elution and tracer test. Simulations were conducted with different hydraulic conditions using numerical modeling. The diffusion coefficient was estimated by fitting the analytical results of the selected functions to the breakthrough curves plotted using simulated results. The author conducted the simulations and analysis of the results, and Dr. Brusseau provided guidance and supervised as advisor.

Appendix E presented an illustrative application of enhanced contaminant elution and tracer test based on simulations produced with a 3-D mathematical model. The author conducted the simulations and analysis of the results, and Dr. Brusseau provided guidance and supervised as advisor.

Appendix F presented the additional work that has been done but did not show in above manuscripts.
CHAPTER II

PRESENT STUDY

II.2 Research Summary

The methods, materials, results and conclusions of this study are presented in the appendices appended to this dissertation. The following is a summary of the most notable findings in the research presented herein.

II.2.1 Assessing contaminant-removal conditions and plume persistence through analysis of data from long-term pump-and-treat operations. (Appendix A)

Historical groundwater-withdrawal and contaminant-concentration data collected from long-term pump-and-treat operations were analyzed for five federal Superfund sites, Air Force Plant 44 (AFP44), which is part of the Tucson International Airport Area (TIAA) site in Tucson AZ; Tucson airport remediation project (TARP), also part of the TIAA site; Motorola/52nd St OU1 (MOT) in Phoenix AZ; Phoenix/Goodyear North (PGN) in Phoenix AZ; and Chem-dyne (CD) in Hamilton OH. All five sites have different contaminant distributions and subsurface properties. Continuous mass removal occurred, but the removal rate reached asymptotic conditions in all sites. The contaminant mass discharge (CMD) and mass-removal behavior were used as metrics to examine the remediation performance. Data collected from each site demonstrated that CMD declined at different rates, which was consistent with contaminant distributions and subsurface properties of the sites. The MOT site comprises a combination of alluvium
and fractured bedrock, a large quantity of poorly accessible contaminant mass were present. This resulted in the lowest CMD reduction rate.

The initial mass before remediation was initiated was determined to plot the CMDR-MR profiles. For AFP44, the initial mass was determined using the results of partitioning tracer tests conducted at the primary source zone, supplemented with mathematical modeling analysis (Nelson and Brusseau, 1996; Zhang and Brusseau, 1999). For MOT site, inventory of solvent disposal reported was used as the initial mass. For the PGN and CD sites, the initial pre-remediation mass was estimated based on fitting a mass-depletion function to the temporal contaminant mass discharge data. For all sites, the CMD started to reduce just after minimum mass was removed, and the CMDR-MR profiles for all sites presented convex-upward behaviors residing above the 1 to 1 relationship, which can be considered as constrained mass removal processes in sites.

The relative contributions of the source zones versus the plumes to total CMD were determined for AFP44, MOT, and PGN site. It shows a decreasing contribution from plume but relatively constant contribution from source zone. Constrained contaminant mass removal was observed to influence the plumes for all three sites, and was attributed to a combination of uncontrolled (or imperfectly controlled) sources, back diffusion, and well-field hydraulics. The results presented herein illustrate that detailed analysis of operational pump-and-treat data can be a cost-effective method for providing value-added characterization of contaminated sites.
II.2.2 The Impact of Well-Field Configuration and Permeability Heterogeneity on Plume Persistence (Appendix B)

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 homogeneous, layered, and heterogeneous aquifers. The relationship between reduction in contaminant mass discharge (CMDR) and mass removal (MR) was used as the metric to examine remediation efficiency.

Results indicate that well-field configuration has a measurable impact on mass-removal efficiency. The results of simulations conducted for homogeneous and layered domains reveal the maximum potential of well-field impacts, while the impact of well-field configuration is reduced for the 3D 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 low permeable layers 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 $\sigma^2_Y$ and correlation scale influence the overall mass-removal behavior. The impact of correlation scale was evaluated in terms of the ratio of domain length to correlation length ($R_\lambda$). 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 for the natural gradient scenario reside primarily below the 1:1 line, whereas the curves for the Longitudinal well field configuration reside primarily above. For the natural gradient system, the curves for smaller variances exhibit singular curvilinear profiles oriented convex-downward. As the variance increases, the CMDR-MR profiles shift leftward and transition to a more sigmoidal shape. For the Longitudinal system, the curves exhibit primarily singular curvilinear profiles oriented convex-upward.

It is evident that relatively ideal behavior is observed for the simulations conducted with $R_\lambda$ equal to or greater than 100. This reflects the pseudo-homogeneous nature of the domains extant for such large $R_\lambda$ 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.

Time continuous concentration 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. (2013) 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.

The CMDR-MR relationship is a useful tool to quantitatively assess mass-removal efficiency. Under certain conditions, the CMDR-MR profiles can help to evaluate the effectiveness of the well-field configuration and show the impacts of field heterogeneity on remediation. More research is needed to further study the applicability of the CMDR-MR relationship for evaluating mass-removal processes in field sites with large degree of heterogeneity.

II.2.3 Case Study: Factors impacting plume persistence at the Tucson International Airport Area (TIAA) Superfund site (Appendix C)

Operation of the pump-and-treat system was simulated using numerical modeling to help evaluate observed behavior. MODFLOW (McDonald and Harbaugh, 1988; Harbaugh et al., 2000) and MT3D (Zheng, 1990) were applied with Groundwater Vista (Rumbaugh and Rumbaugh, 2007) and Groundwater Modeling System (GMS) (EMRL, 2005) as the graphical user interfaces. Parameters such as hydraulic conductivity, porosity, diffusion coefficients, used for input were determined from information collected at the site, generated from geologic borehole-logs, pumping tests, and other prior characterization activities.
The results indicate 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.

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

The impact of long-term source contribution was studied in this work. Results indicate that it is possible that the source is not fully isolated, and that it provides a contribution to plume persistence. Moreover, well-field configuration and permeability heterogeneity are also factors cause the observed CMD tailing. The non-ideal desorption had minimal impact on the observed asymptotic CMD behavior.

II.2.4 Modified Well-Field Configurations for Improved Performance of Contaminant Elution and Tracer Tests (Appendix D)

Contaminant elution and tracer (CET) tests are one method for characterizing the impact of mass transfer, transformation, and other attenuation processes on contaminant transport and mass removal for subsurface systems. The purpose of this research is to explore specific well-field configurations for improving CET tests by reducing the influence of preferential-flow and surrounding plume effects. Three injection-extraction well configurations were tested for different domain conditions using a three dimensional
numerical model. The three configurations were the traditional configuration with a single pair of injection-extraction wells, modified configuration I with one extraction well located between two injection wells, and modified configuration II with two pairs of injection-extraction couplets (one nested within the other). Elution curves for resident contamination and breakthrough curves from simulated tracer tests were produced and examined for specific landmarks such as the presence and extent of steady-state (relatively high concentrations) and asymptotic (asymptotic decrease to low concentrations) phases, as well as distinct changes in slope. Temporal-moment analysis of the breakthrough curves was conducted to determine dilution and mass recovery. Rate coefficients were obtained by fitting selected functions to the elution curves.

Based on simulation results for the homogeneous domain, the concentration measured from the inner extraction well of the modified configuration II stayed at zero during the test period, which indicates full isolation of the extraction well from the surrounding plume. Conversely, the concentrations for the extraction well reached asymptotic conditions for the other two configurations because of the impact of the surrounding plume. Therefore, configuration II was used for additional simulations conducted with layered and heterogeneous domains.

Tracer-test simulations for homogeneous and layered domains indicate 100% mass recovery for the inner extraction well, whereas the recovery was lower (69%) for the heterogeneous-domain simulations because of the preferential flow phenomena. However, changing the distance between the inner injection-extraction well couplet and the pumping-rate distribution between the two extraction wells increased the mass
recovery to 99%. Two functions were selected to perform parameter determination. Both methods provided lower estimations for effective diffusion coefficient, but the calculated error of estimated value with input value for method 1 is approximately 20%.

Results demonstrate that CET test can be an effective way to collect critical site-specific data, which can be used to delineate attenuation processes. Applying the selected functions can be an efficient method for parameter estimation, as it does not require the use of mathematical transport modeling and does not require the attendant input data that are costly and time-consuming to obtain. This characterization concept can be a useful and economical tool to understand the transport and attenuation processes, and also can provide guidance for long-term site management.

II.2.5 The Enhanced Contaminant Elution and Tracer Test for Improved Characterization of Natural Attenuation and Plume Persistence (Appendix E)

Natural and enhanced attenuation are primary alternatives for long-term management of groundwater contaminant plumes. The Enhanced Contaminant Elution and Tracer (ECET) test is developed as an improved method for characterizing critical natural-attenuation processes that impact the transport, fate, and remediation of contaminants in complex, heterogeneous subsurface environments. Specific well-field configuration can remove the resident aqueous contaminant mass present in the higher-permeability zones and isolates the test zone from the surrounding plume. A suite of standard and novel tracers is used to delineate specific attenuation processes, such as back diffusion, desorption and transformation, that are active at a given site, and to
quantify the associated mass-transfer and transformation rates. An illustrative application based on simulations produced with a 3-D mathematical model is presented.

Four tracer tests and one contaminant elution test were simulated. Two injection wells were used with flow rate of 10 m$^3$/d for each well and one extraction well located between injection wells was used with extraction rate of 20 m$^3$/d. The injection and extraction wells were screened through the entire thickness of the domain. For tracer tests, the initial contaminant concentration was zero for the entire domain, the tracers were injected via the upgradient injection well and clean water was injected via the downgradient injection well. Four different tracers were used: two non-reactive tracers (NRT) with different diffusion coefficients, sorptive tracer, and transformation tracer. For the contaminant elution test, the entire domain was contaminated with initial concentration as 1 g/m$^3$, clean water was injected via injection wells. Temporal continuous data were collected from the extraction well for all simulations.

According to the produced elution curve for the resident contaminant and breakthrough curves for the tracers, the different transport behaviors with different amounts of spreading and different extents of tailing are observed for two tracers with different diffusion coefficients. The breakthrough of the curve for the sorptive tracer occurs much later compared to the curves for non-reactive tracers because of the impact of retardation. The concentrations for the transformation tracer test were much lower as a result of degradation. The long tailing is observed in the elution curve for the resident contaminant, which is attributed to the influences of surrounding plume and back diffusion. These different behaviors reflected in the breakthrough curves are the results of
the contributions of individual processes to natural attenuation, including back diffusion, desorption, biotransformation, and abiotic transformation.

II.2.6 Impact of vertical dispersivity and diffusion (Appendix F)

The dispersion is an important factor that impacts transport processes. The vertical dispersion, composed by the diffusion and mechanical dispersion, is the dominant factor that control the dissolution process, which induces the contaminant transport from low K layer to higher K layer:

\[ D_v = D_{diff} + \alpha_v \bar{v} \]  

where \( D_v \) is the vertical dispersion coefficient (m²/d), \( D_{diff} \) is the diffusion coefficient (m²/d), \( \alpha_v \) is vertical dispersivity, and \( \bar{v} \) is the average groundwater velocity (m/d).

The impacts cannot be ignored when the vertical variance of heterogeneity is significant. In this study, five different vertical dispersivity coefficient \( \alpha_v \), 0, 0.0005, 0.001, 0.005, 0.05 m were tested in layered domain with natural gradient water flush. The elution curves were plotted using flux-averaged concentration data collected downgradient boundary. The curves were compared to the results of two-domain model of two-domain model developed by Dr. Brusseau (For details, see Brusseau, 1991). The vertical dispersivity \( \alpha_v \) used in study is 0.001, which obtained the best match with results of the two-domain model.

The diffusion impact on mass removal behavior was tested. In homogenous domain, elution curves and CMDR-MR profiles are identical for simulations with or without diffusion. This is because that the whole domain was accessible by groundwater,
and advection is the primary process to remove contaminants. Whereas, in layered domain, the simulations that mass transfers without diffusion impact have relatively longer tailing than their counterparts with diffusion. The tailing for simulation without diffusion impact is a result of vertical dispersivity as discussed above. This eventually leads to that within the same time, the simulations with diffusive mass-transfer removed more mass than the simulations wherein mass was only removed under advection and dispersion influence.

This suggests that advection is the dominant factor in contaminant removal process from the sand, so mass residing in the sand could be removed rapidly by advection. Meanwhile, the diffusion contribution can be ignored compared to the mass removed by advection. Back then, all remaining mass was in clay, with less groundwater flowing through, advection had less impact. Instead, the diffusion impact on the mass removal for low K layers was indispensable in this situation, and the mass removal could be attributed to the back diffusion from clay to sand. Complete removal of mass is constrained by diffusive mass transfer from the low K zone.

II.2.7 Conclusion

The primary goals of this research are to investigate the impact of well-field configuration and permeability heterogeneity on mass-removal efficiency in different domain conditions, and to explore specific well-field configurations for improving CET tests to characterize attenuation processes.

Historical groundwater-withdrawal and contaminant-concentration data collected from long-term pump-and-treat operations were analyzed for five federal Superfund sites.
Mass-removal processes were studied. The asymptotic decrease of CMD for plume are observed even after isolation of source zone, which is caused by 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.

Further study was conducted with numerical model to understand the impacts of factors on mass-removal efficiency. Typically, even with effort to control the source, residual impact of source can still be a factor cause plume persistence. The well-field configuration has a measurable impact on mass-removal efficiency. In terms of permeability heterogeneity, both variance and correlation scale influence the overall mass-removal behavior. These impacts can be reflected in CMDR-MR profiles. The CMDR-MR relationship is a useful tool to quantitatively assess mass-removal efficiency. Under certain conditions, the CMDR-MR profiles can help to evaluate the effectiveness of the well-field configuration and show the impacts of field heterogeneity on remediation at the plume scale.

With the observed asymptotic behaviors of plume CMD, long-term operations of pump and treat system are expected in most complex contaminant sites associated with high cost. Monitored natural attenuation (MNA) and enhanced attenuation (EA) have been widely accepted as alternatives because of their lower cost and sustainable management for large, complex plumes. Advanced methods are required to characterize specific attenuation processes and associated rates to evaluate the feasibility of MNA/EA. Contaminant elution and tracer test with specific well-field configuration can eliminate the impact of surrounding plume, therefore, critical site-specific data can be collected.
Using a suite of standard and novel tracers can delineate specific attenuation processes that are active at a given site, and to quantify the associated mass-transfer and transformation rates. Applying the selected functions can be an efficient method for parameter estimation, as it does not require the use of mathematical transport modeling and does not require the attendant input data that are costly and time-consuming to obtain. This characterization concept can be a useful and economical tool to understand the transport and attenuation processes, and also can provide guidance for long-term site management.

The results of this research can provide guidance for management of large complex sites that apply pump and treat by using the CMDR-MR relationship as a metric to evaluate effectiveness of well-field configuration and impact of other factors on the remediation process. The characterization concept proposed in this research by applying CET test with specific well-field configuration can be used to delineate attenuation processes and quantify the associated rate coefficients, thereby determining the feasibility to conduct MNA/EA as an alternative in these sites.

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Appendix A

Assessing Contaminant-Removal Conditions and Plume Persistence through Analysis of Data from Long-term Pump-and-Treat Operations

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Abstract

Historical groundwater-withdrawal and contaminant-concentration data collected from long-term pump-and-treat operations were analyzed and used to examine contaminant mass discharge (CMD) and mass-removal behavior for multiple sites. Differences in behavior were observed, and these differences were consistent with the nature of contaminant distributions and subsurface properties of the sites. For example, while CMD exhibited a relatively rapid decline during the initial stage of operation for all three sites, the rate of decline varied. The greatest rate was observed for the PGN site, whereas the lowest rate was observed for the MOT site. In addition, the MOT site exhibited the lowest relative reduction in CMD. These results are consistent with the actuality that the MOT site likely contains the greatest proportion of poorly accessible contaminant mass, given that it comprises a combined alluvium and fractured-bedrock system in which solvent and dissolved mass are present directly in the bedrock. The relative contributions of the source zones versus the plumes to total CMD were determined. Constrained contaminant mass removal was observed to influence the plumes for all three sites, and was attributed to a combination of uncontrolled (or imperfectly controlled) sources, back diffusion, and well-field hydraulics. The results presented herein illustrate that detailed analysis of operational pump-and-treat data can be a cost-effective method for providing value-added characterization of contaminated sites.

Keywords: DNAPL; mass flux; source depletion
Introduction

Contamination of groundwater by chemicals used in industrial, commercial, and other applications continues to pose significant threats to human health and the environment. Examples of compounds of concern include chlorinated solvents (e.g., trichloroethene, tetrachloroethene, carbon tetrachloride), 1,4-dioxane, methyl tertiary-butyl ether (MTBE), and perchlorate. Extensive dissolved-phase groundwater contaminant plumes typically form at sites contaminated by these compounds because of their relatively high aqueous solubilities (in comparison to regulatory standards), limited retardation, and generally low (or very site dependent) transformation potential. In many cases, the plumes are hundreds of meters to several kilometers long. These large plumes are very expensive to contain and remediate, and present difficult challenges to long-term management of contaminated sites.

It is now recognized that most complex sites with large groundwater plumes comprising these contaminants will require many decades before cleanup will be achieved under current methods and standards (e.g., NRC, 2013). The primary factors contributing to constrained contaminant removal and plume persistence have been noted long ago (e.g., Keely, 1989; Mackay and Cherry, 1989), and include source-zone mass discharge (primarily organic-liquid dissolution), diffusive mass transfer (back diffusion) of dissolved contaminant associated with lower-permeability zones, nonideal (rate-limited, nonlinear) desorption of contaminant from the sediment phase, and well-field hydraulics (inter-well stagnation zones, dilution effects). The central importance of source-zone discharge on the creation and maintenance of plumes is well recognized.
Prior research conducted at sites for which the source zone has been remediated or contained indicates that the contaminant plumes have continued to persist beyond the timeframe expected based upon ideal contaminant-removal conditions (e.g., Zhang and Brusseau, 1999; Chapman and Parker, 2005; Rivett et al., 2006; Brusseau et al., 2007; Parker et al., 2008; Brusseau et al., 2011; Rasa et al., 2011), indicating the potential importance of diffusive mass transfer, desorption, and well-field hydraulics. Understanding the specific contributions of these factors to plume persistence, and their potential temporal variability, is critical to effective design, and implementation, and management of remediation efforts.

One of the primary constraints to delineating the specific factors influencing plume persistence for a given site is uncertainty in site properties (e.g., geologic, hydrologic) and conditions (e.g., nature and distribution of contamination). Recent reviews have identified the need to develop improved methods and approaches for site characterization that will enhance understanding of the factors and processes that influence contaminant removal and persistence (e.g., DOD, 2011; NRC, 2013). Pump and treat is currently a primary method used to contain and treat contaminated groundwater at sites with large groundwater contaminant plumes. Groundwater-withdrawal and contaminant-concentration data are routinely collected under regulatory requirement for the pump-and-treat operations. However, these data are rarely used for purposes other than to monitor the mass of contaminant removed. These data sets constitute a source that can be mined to provide additional information to enhance site characterization activities and remediation-performance assessments (Brusseau et al., 2007, 2011a,b, 2013). The
information obtained from mining of the data can be used to update the site conceptual model, to revise the design and operation of the remediation systems, and to support decision-making concerning remedy modification and closure.

The objective of this paper is to investigate plume persistence and the associated contributory factors for sites contaminated by chlorinated solvents, including the presence of organic liquids in source zones. Historical operations data were collected from long-term pump-and-treat systems for multiple sites. The data were analyzed to evaluate mass-removal constraints and to delineate the relative impact of source discharge versus other factors on plume persistence.

Materials and Methods

Data collected from four federal Superfund sites (i.e., listed on the Environmental Protection Agency, EPA, National Priorities List) are used herein. The sites are Air Force Plant 44 (AFP44), which is part of the Tucson International Airport Area (TIAA) site in Tucson AZ; Tucson airport remediation project (TARP), also part of the TIAA site; Motorola/52nd St OU1 (MOT) in Phoenix AZ; Phoenix/Goodyear North (PGN) in Phoenix AZ; and Chem-dyne (CD) in Hamilton OH. Maps for all of the sites are provided in the supplementary material. All of the sites are contaminated by chlorinated-solvent compounds and have large groundwater contaminant plumes (see Table 1). Pump-and-treat systems have been in operation at the sites for approximately 20 years or longer. The data, generally reported in official site-related documents, were graciously
provided by EPA project managers and/or subcontractors working with the EPA or responsible parties.

All of the sites can be considered to be aged sites with respect to contaminant removal. Specifically, a fraction of the initial mass of contamination that entered the subsurface in the source areas has since been removed by natural groundwater flushing, as evidenced by the extensive groundwater contaminant plumes present. It should be noted that the data for each of the sites, with the exception of the TARP and PGN sites, represents the contributions of extraction wells located within identified source zones (areas with organic liquid present in the subsurface) as well as within the plume. The pump-and-treat systems represent the sole source of mass removal for the saturated zone for these sites, as no source remediation efforts have been implemented. The exception is AFP44, at which in-situ chemical oxidation was used for source remediation starting in year 16 (Brusseau et al., 2011b). Note that soil vapor extraction systems have been operated at all of the sites at some point to remediate vadose-zone contamination in the source areas.

There are some relevant differences in properties and conditions for the five sites. The aquifer at the AFP44 site comprises sand and gravel alluvium, and is bounded at the top and bottom by silty clay units that represent more than half of the total treatment-zone thickness. Prior site-characterization activities have shown that dissolved/sorbed contaminant is present in these units, serving as a source of back diffusion to the aquifer (Brusseau et al., 2007). Solvent disposal occurred via surface pits. Multiple lines of evidence indicate that solvent fluid is present in the source zones at the site (Nelson and
Brusseau, 1996; Brusseau et al., 2007). The contaminated groundwater, comprising primarily trichloroethene (and 1,1-dichloroethene at much lower concentration), extends to ~60 m below ground surface. The AFP44 site comprises the south section of the primary contaminant plume at the TIAA site. The well field for the pump-and-treat system (started in 1987) is designed such that several extraction wells are located within each of the three primary source zones, which are located at different regions within the plume. Several other extraction wells are distributed within the plume, for a combined (source and plume) total of ~20 wells. Treated groundwater is reinjected into 16 wells located primarily along the perimeter of the plume.

The TARP site comprises the north section of the primary contaminant plume at the TIAA site. The geologic and hydrologic conditions for the TARP site are similar to those for AFP44. In contrast to the AFP44 site, however, no source areas are located within or adjacent to the plume. Groundwater contamination comprising the TARP plume is thought to have originated by migration from the AFP44 and other source areas upgradient (south) of TARP. The well field for the pump-and-treat system (started in 1994) is designed such that five wells are located in a line, normal to the mean gradient, in the center of the plume, and four other wells are located at the downgradient perimeter of the plume. Treated groundwater is not reinjected.

The contaminated zone at the MOT site encompasses a sand and gravel alluvium unit residing above a fractured bedrock unit. Solvent disposal occurred primarily via fluid injection into a dry well, the total volume of which was approximately 350,000 liters. Notably, solvent fluid has been directly observed to exist in the fractured bedrock of the
source zone, and ~60 liters have been recovered from a well screened solely in the bedrock. The contaminated groundwater, comprising primarily trichloroethene (and several other chlorinated aliphatics at much lower concentrations), extends to ~60 m below ground surface. The well field for the pump-and-treat system (started in 1992) is designed such that five extraction wells are located within the source zone, and nine other extraction wells are distributed along a single line (normal to direction of natural hydraulic gradient) located midway within the plume approximately 800 m downgradient of the source. Treated groundwater is not reinjected at this site.

The aquifer at the PGN site comprises sand and gravel alluvium, with a ~20-m thick silty clay unit (unit B) bisecting the coarse zone in to upper (unit A) and lower (unit C) sections. The lower permeability unit represents roughly less than one-quarter of the total treatment-zone thickness. Solvent disposal occurred via gravity injection into shallow (~4 m deep) dry wells. The contaminated groundwater, comprising essentially solely trichloroethene, extends to ~85 m below ground surface. The well field for the pump-and-treat system (started in 1994) is designed such that there are no extraction wells located directly within the source area. Two extraction wells, one screened in unit A and one in unit B, are located approximately 100 m downgradient from the source zone, with all other extraction wells distributed further within the plume. These wells are grouped in two sets. One set of six wells is located approximately 330 m downgradient of the plume and serves as a hydraulic interception barrier. The other set of six wells is arranged along the perimeter of the plume. Treated groundwater extracted from the nearer-source wells is reinjected into wells located approximately 600 m upgradient of
the source zone. Treated water extracted from the wells located on the east and northeast perimeter is reinjected into wells located approximately 800 m further east. Treated water extracted from the wells located on the west and northwest perimeter is discharged to a distant canal. The wells located on the eastern and northern perimeter have come online only recently, and thus have been in operation for two to five years.

The aquifer at the CD site consists of glaciofluvial deposits comprising primarily sand and gravel, overlain by a shallow unit of silts, clayey silts, and silty and fine sands. Contamination is associated with the prior storage of more than 100,000 liquid waste drums. The contaminated groundwater, comprising a mix of volatile organic compounds including several chlorinated aliphatics, extends to ~15 m below ground surface. The pump-and-treat system (started in 1987) consists of several extraction wells distributed within and at the perimeter of the plume. A portion of the treated water is reinjected on site.

Contaminant concentrations measured for samples collected from the extraction-well systems and groundwater withdrawal totals were used to determine the contaminant mass removed per year, which we will refer to as contaminant mass discharge (CMD). This value represents an integrated measure of contaminant mass being removed from the treatment zones via operation of the pump-and-treat systems. The contributions of the source areas and of the plumes to total CMD were delineated when feasible by separate tabulation of data obtained from extraction wells located within source areas and those within the plume proper, respectively. Note that total measured volatile organic compound mass is used for all sites for which multiple contaminants are present in
groundwater. The total annual pumpage rates for the pump-and-treat systems have varied somewhat at all of the sites. The well-field configurations have not been changed significantly, except for the PGN site (as noted above). To enhance data comparison, the data were re-plotted in terms of relative CMD (measured CMD normalized by the peak CMD) and pore volumes (relative time) for the sites for which this was feasible. The resident pore volume for the site was estimated using the reported dimensions of the treatment domain and the porosity. Pore volumes pumped were then calculated as the quotient of groundwater withdrawal and the resident pore volume.

The initial masses of contaminant present at the start of pump-and-treat operations, which will be designated “initial pre-remediation mass”, were estimated for each site. This was determined for the AFP44 site using the results of partitioning tracer tests conducted at the primary source zone, supplemented with mathematical modeling analysis (Nelson and Brusseau, 1996; Zhang and Brusseau, 1999). The initial pre-remediation mass was estimated using the reported inventory of solvent disposal for the MOT site. For the PGN and CD sites, the initial pre-remediation mass was estimated based on fitting a mass-depletion function to the temporal contaminant mass discharge data (Butcher and Gauthier, 1994; Basu et al., 2009; Brusseau et al., 2013). The power function is one such, widely used, function (e.g., Zhu and Sykes, 2004; Falta et al., 2005):

$$\frac{dM}{dt} = -(Q_0C_0/M_0^\Gamma)M^\Gamma$$

where $C_0$ is initial contaminant concentration, $M_0$ is initial contaminant mass, $M$ is contaminant mass at time $t$, $Q_0$ is initial discharge, $Q$ is discharge at time $t$, and $\Gamma$ is the power index term, representing the impact of a host of conditions and processes on mass-
removal behavior. Given that the terms in parentheses are constants, one can define \( k = Q_0 C_0 / M_0 \Gamma \) as a source depletion rate coefficient, as noted in prior applications (e.g., Zhu and Sykes, 2004; Falta et al., 2005). For the special case wherein \( \Gamma = 1 \), the equation reduces to a first-order, exponential function, with a solution for contaminant mass discharge given as \( QC_t = QC_0 \exp(-kt) \). The function was fit to the measured CMD data, optimizing for \( k \). \( M_0 \) was then calculated with the optimized \( k \) and the known value for initial CMD (the initial measurement after the start of pump and treat, \( Q_0 C_0 \)). This method was also used to estimate the initial pre-remediation contaminant mass associated with the plume for the plume-based analyses for the MOT site. The initial pre-remediation plume-associated mass for the AFP44 site was reported by Zhang and Brusseau (1999).

**Results and Discussion**

**Mass Removal and Contaminant Mass Discharge**

The mass of contaminant removed with time, the data typically reported for pump-and-treat systems, is presented in Figure 1. The plots exhibit reduced rates of mass removal as the operations continue. This behavior is consistent with what is typically observed for pump-and-treat systems. The total mass removed for the TARP site is much less than the totals for the other sites, reflecting the fact that this site has no on-site source areas and thus involves primarily plume-only mass removal.

The historical CMD for the sites, determined from analysis of the pump-and-treat data, is presented in Figure 2. The initial CMD is observed to range between
approximately 0.6 and 10 kg/d. These values are quite large in comparison to the range of values reported in a recent summary (ITRC, 2010). This is reflective of the significant impact of the highly contaminated source zones owing to the large quantities of solvent disposed of therein in combination with the induced-gradient conditions associated with the pump-and-treat systems.

Some degree of asymptotic behavior is observed for the later stage of operation for all of the sites. As noted above, all of the sites are considered to be aged sites with respect to contaminant removal and distribution. First, it is anticipated that the mass that was removed from the source areas prior to the start of the remediation efforts (i.e., during plume formation) comprised primarily the mass that was more readily accessible to flowing groundwater. Concomitantly, it is expected that the mass remaining in the sources at the start of pump and treat comprised a significant fraction that is more poorly accessible to groundwater flushing. Second, the contaminant plumes have been present at the site for several decades, and it is expected that significant quantities of dissolved and sorbed mass are present within the extensive lower-permeability units that are present at the sites. The observed asymptotic behavior is attributed to the impact of this poorly accessible contaminant mass on mass transfer and mass removal. Other factors, such as the impact of well-field hydraulics, may also influence the observed behavior.

The significant increase in CMD that began within the last five years for the PGN site is related primarily to the introduction of additional extraction wells located along the eastern and northern perimeter of the plume. The asymptotic phase for the AFP44 site was truncated by the advent of the source remediation efforts that were started in year 16
(Brusseau et al., 2011b). Essentially steady state behavior was observed for the TARP site from year 4 through year 16, with an apparent decline since then (note pumpage rates have remained essentially constant). This site has no on-site source areas, and the plume is considered to have been generated by contaminant migration from source areas located upgradient, as noted above. Thus, this site represents primarily plume-only mass removal. However, the continued contribution of upgradient sources is indicated by the observation that the mass of contaminant removed to date is roughly four times larger than the mass estimated to have been present in the plume prior to the start of pump and treat. The contributions from AFP44, a primary potential source, should have been minimized with the advent of the AFP44 pump-and-treat system that started in 1987 (which predates that start of TARP operations). The contributions from another potential source, the Three Hangers facility, should have been minimized with the startup of pump-and-treat at that site in late 2007. Interestingly, the decline in CMD observed for the TARP site coincides with the startup at Three Hangers.

Comparative analysis of the CMD data is complicated by the fact that the design and operation of the well fields varies among the sites. To enhance data comparison, the data were re-plotted in terms of relative CMD (measured CMD normalized by the peak CMD) and pore volumes (relative time). The normalized CMD data are presented in Figure 3 for the three sites for which the calculations could be conducted. It is noted for all three sites that the equivalent of only approximately two pore volumes of groundwater have been pumped during the ~20 years of operation. This illustrates the very low rates of flushing inherent to pump-and-treat systems associated with large groundwater plumes.
As a result, long cleanup times should be expected even under the most ideal conditions (e.g., minimal mass-removal constraints).

Inspection of the figure shows that differences are revealed in the temporal CMD profiles among the three sites. For example, while CMD exhibits a relatively rapid decline during the initial stage of operation for all three sites, the rate of decline varies. The greatest rate is observed for the PGN site, whereas the lowest rate is observed for the MOT site. In addition, the MOT site exhibits the lowest relative reduction in CMD. These results are consistent with the conditions of the sites, wherein the MOT site likely contains the greatest proportion of poorly accessible contaminant mass given that it comprises a combined alluvium and fractured-bedrock system in which solvent and dissolved mass are present directly in the bedrock. The greater rate of decline observed for the PGN site compared to the AFP44 site is also consistent with site conditions. First, the relative portion of poorly accessible contaminant mass associated with lower-permeability domains is likely to be greater for the AFP44 site based on the differences in the relative fractions of lower-permeability units comprising the two sites, which is larger for the AFP44 site. Second, the CMD data for the AFP44 site includes the contribution of extraction wells that are located directly within the source zones (which are distributed within the plume). Conversely, there are no extraction wells located directly within the source zone for the PGN site, and thus contaminant discharge from the source is closer to natural-gradient conditions, thereby muting the source contributions.

The CMD and initial-mass data can be used to determine the relationship between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass.
The CMDR-MR relationship is a defining characteristic of system behavior, and is mediated by system properties and conditions such as permeability distribution, contaminant distribution, and mass-transfer processes. The CMDR-MR profiles provide a more robust assessment of contaminant-removal conditions compared to analysis of temporal CMD data alone, and also facilitate comparison among different sites.

The CMDR-MR profiles determined for the five sites are presented in Figure 4. It is observed that the profiles reside primarily above the one-to-one line. The nature of the profiles are indicative that substantial amounts of contaminant mass exist at the sites that is poorly accessible to groundwater flushing associated with the pump-and-treat system. The MOT site in particular shows a very sharp decrease in CMD associated with a very small fraction of mass reduction. This is most likely a function primarily of the presence of liquid solvent as well as dissolved mass in the fractured bedrock. The profiles exhibit multi-step behavior, particularly those for AFP44, TARP, and CD. These profiles are considerably more complex than the smooth singular curves predicted by the simplified source-depletion functions often used, as has been discussed previously (Brusseau et al., 2008; DiFilippo and Brusseau, 2008; Christ et al., 2010; DiFilippo et al., 2010).

Potential uncertainties associated with the CMDR-MR profiles, primarily related to uncertainty in the initial-mass estimates (pre-remediation mass in this case), should be considered in the analysis. For example, estimates of initial mass may often be lower than actual values. In such cases, using the larger initial-mass value will result in a leftward shift of the CMDR-MR profile. A very large estimated initial mass was used for the MOT site, based on waste-disposal inventories. The use of a smaller value would result in a
rightward shift of the curve. While the positions of the profiles along the *abscissa* may have a larger degree of uncertainty, the general shapes of the profiles are expected to have significantly less given the typically more robust nature of the CMD measurements.

**Plume Persistence**

The data presented in the previous section included the contributions of the source zones to total contaminant mass discharge and recovery. The persistence of the contaminant plumes in the absence of source-zone effects can be investigated by examining data specifically associated with only those extraction wells located within the plumes. For the AFP44 and MOT sites, the pump-and-treat systems are designed and operated such that extraction wells located in the source zones in effect serve to minimize mass discharge from the sources to the plumes. Collection of well-specific data allows determination of aggregate contaminant mass discharge and recovery for plume-associated versus source-associated extraction wells for these two sites. For the PGN site, the contributions of EA-01, the extraction well located closest to the source area, the hydraulic interceptor wells (MTS), and the wells located at the plume perimeter (non-MTS) are delineated.

A comparison of the separate contributions of the source zones and the plumes to total CMD is shown in Figure 5 for the AFP44, MOT, and PGN sites. It is observed that the plume provided a greater contribution than the source zones during the initial system startup for the AFP44 and MOT sites. The near-source extraction well (EA-01) provided a greater contribution than the plume during the early operation for PGN. During the
course of operation, the CMD values declined for the plumes, whereas they remained relatively stable (MOT) or declined at a lower rate (AFP44) for the source zones. Hence, the relative contribution of the plumes to total CMD decreased during the course of operation for both sites. While extraction rates have varied for the sites, a decrease in contaminant concentrations is the primary cause of the decrease in CMD observed for the plumes. These results illustrate the continued importance of the source zones to overall site remediation.

Essentially steady state CMD behavior was observed during years 9-14 for the near-source extraction well EA-01 at the PGN site, likely reflecting the impact of the uncontrolled source area. A significant decrease in CMD has been observed for the past four years. This is hypothesized to result from site-wide changes in the direction of the hydraulic gradient, induced in part by the startup of the new eastern plume-extraction wells, such that the near-source well may not be capturing the source discharge to the same degree. This example illustrates the potential significance of well-field hydraulics on mass removal behavior.

The relative CMD profiles for the plume systems in absence of source-zone contributions are presented in Figure 6. The data reinforce that asymptotic mass-removal conditions are present for the plumes. The impact of mass-transfer constraints is also illustrated by the CMDR-MR profiles for the plume-only data, wherein they reside above the one-to-one line (Figure 7). Dissolved contaminant associated with lower-permeability zones is prominent for all of the sites and, hence, back diffusion is anticipated to be a significant common factor contributing to the observed plume persistence. This is
supported by the results of prior investigations conducted at the AFP44 site to examine source-zone remediation efforts and associated plume behavior (Nelson and Brusseau, 1996; Blue et al., 1998; Brusseau et al., 1999; Zhang and Brusseau, 1999; Nelson and Brusseau, 2003; Brusseau et al., 2007, 2011a,b). Multiple methods, including forced-gradient contaminant elution tests, multiple-solute tracer tests, sediment coring, analysis of historic pump-and-treat operations data, laboratory experiments, and mathematical modeling, were used to characterize the relative impacts of plume-scale back diffusion, plume-scale sorption/desorption, and dissolution of organic liquid trapped in the source zones on contaminant removal and plume persistence. The results indicated that organic-liquid dissolution was the primary factor influencing contaminant removal and plume persistence. Back diffusion was delineated as a moderate factor, whereas the impact of nonideal sorption was minor in comparison to the other two (consistent with the very low magnitude of sorption measured for the contaminant). Assessment of the historic integrated plume-scale contaminant mass discharge, along with the results of mathematical modeling, indicated that the plume would persist for many decades even with the isolation or removal of the source zones, primarily due to back diffusion of contaminant associated with the lower-permeability units and hydraulic effects.

Based on the prior analyses conducted for AFP44 and the extant conditions for the other two sites, it is hypothesized that back diffusion and well-field hydraulics, in addition to the impact of uncontrolled (or imperfectly controlled) sources, are the primary factors contributing to plume persistence for the sites. Delineating the relative significance of the factors for the sites would require additional analyses that are beyond
the scope of this presentation. While the potential effects of uncontrolled sources and back-diffusion processes have been well documented, the impacts of well-field hydraulics on contaminant-removal behavior have been less so. The results for the PGN site discussed above, specifically the significant recent decline in CMD observed for the near-source extraction well that is suspected to be related to changes in hydraulic conditions, is one such illustration. Another are the results presented by Rivett et al. (2006) for a study conducted at the Borden site in Canada.

**Summary**

Groundwater-withdrawal and contaminant-concentration data collected from long-term pump-and-treat operations were analyzed and used to examine contaminant-removal behavior for five sites, all of which are considered to be relatively aged with respect to contaminant removal and distribution. Differences in behavior were observed, and these differences were consistent with the nature of contaminant distributions and subsurface properties of the sites. For example, while CMD exhibited a relatively rapid decline during the initial stage of operation for all sites, the rate of decline varied. The greatest rate was observed for the PGN site, whereas the lowest rate was observed for the MOT site. In addition, the MOT site exhibited the lowest relative reduction in CMD. These results are consistent with the actuality that the MOT site likely contains the greatest proportion of poorly accessible contaminant mass, given that it comprises a combined alluvium and fractured-bedrock system in which solvent and dissolved mass are present directly in the bedrock.
The relative contributions of the source zones versus the plumes to total CMD were determined for the AFP44, MOT, and PGN sites. The plume contributions were observed to decrease with time, whereas that of the source zones remained relatively constant for the first two sites. Conversely, CMD was observed to decrease significantly in the last few years for the PGN site, which was attributed to the impact of changes in well-field hydraulics. The data were also used to investigate the relationship between reductions in contaminant mass discharge and reductions in contaminant mass. Constrained contaminant mass removal was observed to influence the plumes for all the sites, and was attributed to a combination of back diffusion, uncontrolled (or imperfectly controlled) sources, and well-field hydraulics. The data sets exemplified the recalcitrance typically associated with chlorinated-solvent contaminated sites, and the impact on plume persistence and associated implications for site cleanup.

Acknowledgements

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Table 1. Selected Properties of Sites Evaluated

<table>
<thead>
<tr>
<th>Site</th>
<th>Plume Area(^b) (km(^2))</th>
<th>Annual Pumpage(^c) (M m(^3))</th>
<th>Mass Recovered to Date(^d) (kg)</th>
<th>Estimated Initial Mass(^e) (kg)</th>
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<tr>
<td>AFP44</td>
<td>4</td>
<td>5.0</td>
<td>13,000</td>
<td>24,000</td>
</tr>
<tr>
<td>MOT</td>
<td>2</td>
<td>0.6</td>
<td>10,000</td>
<td>570,000</td>
</tr>
<tr>
<td>PGN</td>
<td>4</td>
<td>2.4</td>
<td>20,000</td>
<td>29,000</td>
</tr>
<tr>
<td>TARP</td>
<td>4</td>
<td>8.7</td>
<td>2,100</td>
<td>7,000</td>
</tr>
<tr>
<td>CD</td>
<td>0.2</td>
<td>1.5</td>
<td>16,000</td>
<td>20,000</td>
</tr>
</tbody>
</table>

\(^a\)Site names are presented in the Materials and Methods section

\(^b\)Approximate

\(^c\)Mean value

\(^d\)For pump-and-treat systems only, as of last data available

\(^e\)Total mass (in sources and plume) estimated to be present at the start of pump and treat operations. Methods used to obtain estimates are detailed in the text.
**Figure Captions**

Figure 1. Cumulative mass of contaminant removed with pump and treat of groundwater for five Superfund sites contaminated by chlorinated-solvent compounds.

Figure 2. Contaminant mass discharge profiles obtained from analysis of pump-and-treat data for the five sites. Note that data beyond year 16 are not presented for AFP44 due to the impact of source remediation efforts. Time zero corresponds to the start of pump-and-treat operations.

Figure 3. Relative contaminant mass discharge (CMD) as a function of pore volumes of groundwater pumped for three sites; includes contributions from source zones and plumes.

Figure 4. Relationships between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR) for three sites; includes contributions from source zones and plumes.

Figure 5. Contaminant mass discharge (CMD) profiles obtained from analysis of pump-and-treat data for three sites, comparing the contributions of source zones and plumes to total contaminant mass discharge: (A) AFP44 site (Figure reproduced from Brusseau et al. (2011)); (B) MOT site; (C) PGN site. Note for the PGN site, EA-01 is the extraction
well located nearest to the source area, MTS comprises EA-01 and the other wells serving as the downgradient hydraulic interception barrier, non-MTS represent all other extraction wells (which are all located on the downgradient perimeter of the plume), and “plume” represents the contributions of all wells except EA-01.

Figure 6. Relative contaminant mass discharge (CMD) as a function of pore volumes of groundwater pumped for three sites; includes contributions from only the groundwater contaminant plumes (see discussion in text for PGN site caveat). Note that source remediation via in-situ chemical oxidation started at approximately two pore volumes for the AFP44 site.

Figure 7. Relationships between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR) for three sites; includes contributions from only the groundwater contaminant plumes.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5A

Figure 5B
Figure 5C
Figure 6
Figure 7
APPENDIX B

The Impact of Well-Field Configuration 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 homogeneous, layered, and heterogeneous aquifers. The relationship between reduction in contaminant mass discharge (CMDR) and mass removal (MR) was used as the metric to examine remediation efficiency. Results of the simulations for homogeneous and layered domains reveal the maximum potential impacts of well-field configuration on mass removal behavior, which is attributed to mass-transfer constraints associated with regions of low flow. These impacts are reflected in the associated CMDR-MR profiles. Systems whose CMDR-MR profiles are below the 1:1 relationship curve are associated with more efficient well-field configurations. However, for the 3D heterogeneous domain, the impacts of the well–field configuration are muted by the influence of permeability heterogeneity. The impacts of aquifer heterogeneity, pumping rate, and aquifer thickness on mass-removal effectiveness were also investigated and indexed by the CMDR-MR relationship. These results illustrate that the CMDR-MR relationship can be a straightforward way to quantify the impacts of different factors on mass-removal efficiency.

Key words: Plume; back diffusion; mass flux
1. Introduction

Compounds such as chlorinated solvents (e.g., trichloroethene, tetrachloroethene, carbon tetrachloride), 1,4-dioxane, methyl tertiary-butyl ether (MTBE), and perchlorate used in industrial, commercial, and other applications continue to pose significant threats to human health through contamination of groundwater resources. These compounds generally have high aqueous solubilities compared to regulatory limits (maximum contaminant level for groundwater), generally low retardation, and typically relatively low potential to be biodegraded or otherwise attenuated. These features result in formation of large contaminant plumes at many sites. These large plumes, which are typically hundreds of meters to several kilometers long, present complex and costly challenges to remediation and closure of the sites. In fact, a recent National Research Council report concludes that it is unlikely that remediation of these complex sites will be achieved in a time frame of 50-100 years under current methods and standards (NRC, 2013).

The results of prior investigations have clearly indicated that the presence of source zones containing organic liquids is typically a primary factor limiting the cleanup of many sites. These sources can provide long-term and consistent contaminant supply to the downgradient plume, thereby leading to plume persistence. 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., Chapman and Parker, 2005; Parker et al., 2008; Brusseau et al., 2007, 2011; Rasa et al., 2011; Brusseau and Guo, 2014; Matthieu et al., 2014). The factors beyond uncontrolled source zones that
contribute to plume persistence include dispersed reservoirs of dissolved contaminant present in lower-permeability zones (e.g., Keely, 1989; Johnson and Pankow, 1992; Mutch et al., 1993; Wilson et al., 1993; Rabideau and Miller, 1994), sorbed contaminant (e.g., Keely, 1989; Goltz and Oxley, 1991; Brusseau, 1993; Rabideau and Miller, 1994; Berglund and Cvetkovic, 1995), and hydraulic-related factors such as non-optimal remedial well-field performance (e.g., Satkin and Bedient, 1988; Keely, 1989; Schafer and Kinzelbach, 1992; Cohen et al., 1997; Rivett et al., 2006).

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., Liu and Ball, 2002; Chapman and Parker, 2005; Brusseau et al., 2007,2011; Parker et al., 2008; Seyedabbasi et al., 2012; Dearden et al., 2013; Brusseau and Guo, 2014; Matthieu et al., 2014). The significance of well-field hydraulics, such as well location, distribution, and pumping rate, for remediation effectiveness has long been recognized. However, 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 well-field hydraulics on mass-removal efficiency for a range of site conditions. The results were 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., Jawitz et al., 2005; Brusseau et al., 2008; Kaye et al., 2008; DiFilippo et al., 2010; Brusseau et al., 2013; Brusseau and Guo, 2014). 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.

2. Materials and Methods

2.1. Numerical Model

The flow model used in this work was the 3D finite-difference numerical model MODFLOW developed by the U.S. Geological Survey (McDonald and Harbaugh, 1988; Harbaugh et al., 2000). The 3D solute transport model MT3D (Zheng, 1990) was used to simulate solute transport. Groundwater Vista (GV) (Rumbaugh and Rumbaugh, 2007) and Groundwater Modeling System (GMS) (EMRL, 2005) 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 20 rows and 50 columns with grid space 20-m x 20-m. Specified head boundaries were used along the four borders of the domain, with 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 given in Table SM-1. Parameters used in the model were determined according to information generated from geologic borehole-logs, pumping tests, and historic data collected for the Tucson International Airport Area Superfund site (Zhang and Brusseau, 1999). Initial solute concentration was set as 1 g/m³ in the whole domain, representing a mature site.
that has been formed over decades. No additional contaminants were introduced into the system.

Three types of permeability distribution were used for the simulations, homogeneous (control), layered, and a fully heterogeneous domain developed using the standard stochastic approach. For the homogeneous and layered systems, the domain was split into three layers of equal, uniform thickness (5 m). For the homogenous system, characteristics such as hydraulic conductivity (K) and porosity were identical for each layer. For the layered system, the upper and lower layers were set as low hydraulic conductivity representing clay layers, while the center layer was set as high permeability representing a sand layer.

For the fully 3D heterogeneous system, a random field generator (Gutjahr, 1989) was used to derive realizations of K for the sand unit of the domain. It was assumed that the permeability of the sand was lognormally distributed with mean \( \langle \ln K \rangle \) and variance \( \sigma^2 \). The random fields were generated with an arithmetic mean value of K equal to the value used for the sand layer in layered scenarios and correlation scale 50-m x 20-m x 0.25-m. Scenarios with clay layers present and absent were simulated (Table SM-2). Single realizations were conducted, with Monte Carlo analysis (10 realizations) done for selected simulations (result presented as the mean of the 10 realizations).

In all cases, the pumping wells were screened through the entire sand layer(s) for comparison. The boundary conditions were changed to constant head boundaries in west and east borders to prevent mass loss from north and south boundaries.
2.2. Simulations

Four major variables, well-field configuration, pumping rate, permeability heterogeneity, and aquifer thickness were investigated in this study. The simulations were organized into 4 groups (Table 1). Aquifer thickness and pumping rates were varied within reasonable ranges.

Group 1 was designed to investigate the impact of well-field configuration. Four different well-field configurations were tested (Fig. 1). The Distributed configuration comprises 9 wells distributed uniformly within the plume. The Downgradient configuration comprises 3 wells located at the downgradient edge of the plume, oriented normal to the mean flow direction. The Longitudinal configuration comprises 3 wells placed along the centerline of the plume, oriented parallel to the mean flow direction. In addition, a “natural-gradient” configuration (with no extraction wells) was used as a control. Solute mass removal was monitored at the downgradient edge of the domain for this simulation, and the magnitude of the natural hydraulic gradient was increased to match the total extraction-well discharge for the other scenarios. The simulations were conducted for three permeability-distribution conditions: homogeneous, layered, and random 3D heterogeneity.

One additional simulation was performed for the Longitudinal well-field scenario to investigate the impact of well-field modification during operations. Specifically, the total time was split into 3 periods. In period 1, the original well locations were used; in period 2, the well locations were moved to regions wherein concentrations remained
relatively high because of stagnation zones caused by pumping in period 1; in period 3, the wells were relocated to their original locations.

Group 2 was set up to test the impact of pumping rate on mass-removal efficiency. The majority of the simulations were conducted using the Distributed well-field configuration that was used in the Group 1 simulations. These simulations were conducted for the homogeneous and layered domains (Table 1). Three different pumping rates (Q), 300, 100, 50 m$^3$/d, were tested, with pumping continuous and constant throughout the simulation period. An additional simulation was conducted to test the impact of changes in Q during operation. For this simulation, the total simulation time was divided into three periods. For the 1$^{st}$ and 3$^{nd}$ periods, pumping was constant at 100 m$^3$/d. For the 2$^{nd}$ period, the pumping rates of individual wells were adjusted (Table SM-3). A final set of simulations was conducted for the heterogeneous system, using the Longitudinal well-field configuration. One simulation was conducted using a pumping rate of 300 m$^3$/d for each well, and another simulation with Q = 3000 m$^3$/d. The Damkohler number (ω), which represents the ratio of the characteristic time of mass transfer to the residence time, was used to identify conditions wherein mass transfer was constrained and thus limiting to mass removal. Definition of ω is provided in the Supplemental Materials.

The purpose of Group 3 is to examine the impact of permeability heterogeneity and back diffusion, using the same conditions as used for Group 1 simulations. For the 3D domain without clay present, additional simulations were conducted with natural gradient and Longitudinal well-field configurations to investigate the impact of
permeability heterogeneity, reflected by variance of ln K and the correlation length, on mass removal. For simulations with Longitudinal well-field configuration, a larger pumping rate (total Q = 3000 m$^3$/d) was used to ensure the complete capture of mass in the domain. Group 4 was developed to examine the impact of aquifer thickness on mass removal. The simulations were conducted for homogeneous and layered domains with different thicknesses. The total thickness was 1.5 m for the first set of simulations and 15 m for the second simulation set.

2.3. Data analysis

Elution curves were plotted and compared for different scenarios. Simulations with more significant mass-transfer constraints are anticipated to produce more non-ideal behavior, including earlier reductions in concentrations and more extensive tailing. The simulated time-continuous profile of CMD was determined as the product of the pumping rate and the simulated concentration. The cumulative mass removed was calculated from the CMD-time function. The CMDR-MR profile was constructed using the CMD and mass removal data. Alternatively, for simulations wherein a portion of mass was not recovered with the extraction wells due to flow leaving the domain, the CMDR-MR curve was generated using the mass remaining in the model domain at each time step.

Generally, the relationship between reductions in contaminant mass discharge and mass removal exhibits one of three types of behavior (Fig. SM-2). One is the 1 to 1 relationship, which represents for example the special case of first-order mass removal. The second is a curvilinear convex-upward profile residing above the 1 to 1 reference
line, which shows significant initial reduction in CMD with minimal mass removed, followed in later stages by smaller rates of CMD reduction. This behavior is often associated with the impacts of mass-transfer constraints related to contaminant mass present in hydraulically poorly accessible zones. The third relationship is the convex-downward profile residing below the reference line, which shows relatively ideal mass removal behavior wherein there is minimal reduction in CMD until a large proportion of mass has been removed. In this study, for scenarios wherein mass was lost due to boundary outflow, the CMDR-MR relationship curves were corrected using the final total removed mass to force the mass removal fraction to reach 1. Analysis of both temporal concentration data and the CMDR-MR profiles make the assessment of contaminant removal dynamics more robust.

3. Results and discussion

3.1. Impact of well-field configuration

3.1.1. Homogeneous domain

The simulated elution curves with four different well-field configurations for the homogeneous domain are presented in Fig. 2A. The elution curve for the natural-gradient scenario shows the most ideal behavior in which the concentration decreased rapidly after approximately 1 pore volume (PV) of water was displaced. In contrast, for scenarios with pumping wells, the elution curves express earlier concentration decreases and asymptotic approach to low concentrations (tailing). The simulation for the Distributed well-field configuration shows first-order mass removal behavior. 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 results presented above show that varying degrees of nonideal behavior were observed for the simulations produced for all three well field systems compared to the natural-gradient control. Given that the simulations were conducted for a homogenous domain with uniform initial concentration, the non-ideal mass removal behavior must be caused by mass-transfer constraints associated with well-field hydraulics. The formation of stagnation zones wherein contaminant removal is delayed due to low groundwater velocities is an obvious source of such constraints.

The contaminant mass distributions at selected time periods for each simulation are presented in Fig. SM-3. Fig. SM-3A shows the mass distribution at 1000 days of the natural gradient simulation, which produced a near-ideal elution curve. The mass was completely removed by day 4040 (2.4 PV). This is consistent with the absence of stagnation zones. Fig. SM-3B and E present the mass distributions after 1000 days of pumping for the simulations with Longitudinal and Distributed well-field configurations, respectively. It is apparent that more mass remained for the Distributed well field, which is a result of more inter-well stagnation zones formed for the Distributed well field.

For the Downgradient well-field simulation, the concentration started to decrease 15 days after pumping started, and stabilized after 860 days (0.5 PV). The steady state period lasted until 6520 days (3.9 PV), after which concentration began to decrease again until the remaining mass was removed. Fig. SM-3F presents the mass distribution after 500 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-3G displays the mass distribution after 4000 days. This is during the steady state period for contaminant removal, which is mediated by slow advective transport of the upgradient mass via natural-gradient flow. Fig. SM-3H shows the concentration distribution at 8000 days. By this time, all of the remaining contaminant mass had migrated into the zone of influence of the extraction wells, allowing for more rapid removal and attendant reduction in concentration.

The differences in the proportion of mass remaining in the domain for the different simulations indicate that the Longitudinal well field developed the least amount of stagnation area among the three systems with pumping wells. The scenario with the Downgradient well-field configuration, which presented multi-step mass removal behavior, had the greatest proportion of regions with low flow that included the downgradient stagnation zones and the upgradient low flow area where no wells were present.

Low flow regions were introduced as a result of well-field operation. Under these circumstances, initiating pumping in these stagnation zones can remove the trapped mass more effectively. The impact of changing well location was investigated for the Longitudinal well-field configuration, with the first adjustment implemented after 1500 days. Inspection of the elution curve in Fig. 2A shows that the concentration increases after the change of locations of the pumping wells, as would be expected. The contaminant distribution after 1700 days of operation for both scenarios are presented in Fig. SM-3C and Fig. SM-3D, respectively. It is apparent that the mass remaining after
operation of 1700 days is much less for the modified scenario. After adjustment, it took 2040 days to remove 90% of the mass instead of 2120 days.

The CMDR-MR profiles are presented in Figure 2B. 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 60% of the initial mass was removed, indicating ideal mass-removal conditions. This result is expected given that the simulation employed a homogeneous domain with no pumping wells (and associated stagnation zones), and therefore no non-accessible mass, nor associated mass-transfer limitation, was present.

The CMDR-MR curve for the Longitudinal well-field scenario also exhibits a convex-downward profile residing below the reference line. However, it is shifted leftward such that CMD started to decrease after approximately 15% mass removal, reflecting the presence of mass-transfer constraints associated with stagnations zones. For the simulation with adjusted locations of wells, the CMDR-MR profile shifts rightward after the adjustment reflecting the reduced mass-transfer constraint. The similar shapes of the two profiles indicate that repositioning the well locations did not have a significant impact on the general shape of the CMDR-MR profile.

The Distributed well-field simulation expresses an approximately one-to-one profile, consistent with the pseudo first-order concentration reduction exhibited by the elution curve. The Downgradient simulation shows a multi-step CMDR-MR profile wherein CMD started to decrease after minimal mass removal, and attained ~80% reduction by 30% mass removal. After this point there was minimal further reduction in
CMD until approximately 80% mass removal, after which the profile exhibited approximate one-to-one behavior.

Rivett et al. (2006) conducted a small field experiment at the Borden (ON) research site to examine plume removal behavior after isolation of the source zone. The experiment was conducted in a sandy aquifer with mild heterogeneity. A permeable reactive barrier and an extraction well were used to contain the source zone. Two extraction wells located along the centerline of the plume were used for mass removal. This configuration is similar to the Longitudinal well-field configuration used herein. The rate of contaminant removal was observed to be slower than expected for ideal conditions, and the elution curves exhibited concentration tailing. The authors concluded that permeability heterogeneity and sorption processes had minimal impact on plume persistence because the experiment was conducted in a mildly heterogeneous sandy aquifer and the plume was freshly formed. Hence, the mass-removal limitation was attributed to inter-well stagnation zones associated with the well field. The raw concentration-time data reported in Rivett et al. were used herein to determine CMD and mass removal values, which were then used to create the CMDR-MR profile presented in Fig. 2B. The measured profile for the Borden study is similar to the simulated profile obtained for the Longitudinal well-field configuration, which supports the validity of the simulation results.

3.1.2. Layered domain
The elution curves obtained for the 2D-layered domain, with a sand layer sandwiched between two clay layers, are presented in Fig. SM-4A. For the natural gradient simulation, the concentration decreased asymptotically after an initial sharp decrease. The initial decrease represents removal of mass from the sand layer, while the tailing represents the impact of back diffusion from the clay layers. Similar results were observed for the Longitudinal and Distributed well-field configuration scenarios. Conversely, the simulation results for the Downgradient well-field configuration shows multi-step behavior, as discussed for the homogeneous domain, followed by low-concentration tailing. For all of the layered-domain simulations, essentially all contaminant mass was removed from the sand layer before the start of the asymptotic stage. The mass distributions in the sand layer were very similar to those obtained for their corresponding homogeneous-domain simulations (data not shown).

The CMDR-MR profiles for the 2D-layered domain simulations are presented in Fig. SM-4B. The profile for the natural gradient simulation is strongly sigmoidal, with an initial steady-state period, during which the mass discharge reduction was minimal. After approximately 15% of the mass was removed, the mass discharge decreased significantly (>90%) with a small reduction in mass (<10%). Finally, the remaining mass discharge reduction occurred asymptotically. For the Longitudinal and Distributed well-field configurations, the mass discharge started to decrease significantly (~95%) after a very small fraction of mass was removed, and then revealed asymptotic behavior. The simulation results of the Downgradient well-field configuration display a multi-step profile as observed for the homogeneous domain.
The CMDR-MR profiles for mass removal from the middle (sand) layer are presented in Fig. SM-4C. The profiles are observed to be very similar to the corresponding profiles obtained for the homogeneous-domain simulations. The different mass removal behaviors during this period are the result of different well-field configurations as discussed above. The CMD reduction reached asymptotic condition immediately after the contaminant mass in the middle layer was removed for all the layered-domain simulations (Fig. SM-4B), which indicates that the persistence of CMD in the latter period was due to mass-transfer constraints associated with back diffusion of the contaminants present in the upper and lower clay layers.

The results of two simulations for the layered domain with K of the clay layers equal to 0.1 m/d and 0.00001 m/d are presented in Fig. 4. As expected, minimal differences are observed for the elution curves and CMDR-MR profiles. Simulations were also conducted to examine the impact of clay-layer thickness. Also as expected, greater nonideal behavior was observed for the simulation with thicker clay layers (Fig. SM-14).

### 3.1.3. Heterogeneous domain

The results of the simulations for the 3D heterogeneous domain are consistent with the homogeneous and layered simulation results. This is illustrated by the comparison of results obtained for the different well-field configuration in the domain with variance of ln K of 5 presented in Fig. SM-5. The elution curves for the simulations with pumping wells show earlier concentration decrease and longer tailing compared to
the curve for the natural gradient simulation. Inspecting the CMDR-MR profiles, the relationship for the natural gradient scenario exhibits a convex-downward profile, reflecting more efficient mass removal compared to the three simulations with wells that present a convex-upward profile. A multi-step profile is observed for the Downgradient simulation, similar to that observed for the homogeneous and layers domains.

The differences among the CMDR-MR profiles illustrate the impact of well-field configuration for the 3D heterogeneous domain. However, the disparities between the curves are not as significant as the observed differences for the homogenous and layered simulations. These results indicate that the influence of permeability heterogeneity mutes the impact of well-field configuration.

3.2. Impact of permeability heterogeneity

Elution curves and CMDR-MR profiles for the homogeneous and layered simulations presented in Fig. 2 and Fig. SM-4 were discussed in section 3.1. For the homogenous-domain simulations, the CMDR-MR relationship exhibit convex-downward profiles residing below the 1:1 reference line for natural gradient flow. With the advent of low-flow zones formed for different well-field configurations, the CMDR-MR curves shift leftward, from convex-downward profiles for natural gradient and Longitudinal to first-order behavior for Distributed, and further leftward to a sigmoidal profile for the Downgradient well-field configuration (Fig. 2B). The observed non-ideal behavior for these simulations is attributed solely to mass-transfer constraint caused by formation of low flow regions (i.e., well hydraulics). In contrast, for the layered simulations, the
CMDR-MR relationships for the different well-field configurations exhibit convex-upward profiles (Fig. SM-4B). For the layered-domain simulations with pumping wells present, the observed results are influenced by the impact of two mass-transfer constraints, low flow zones and back diffusion.

For simulations conducted in 3D heterogeneous domain without clay present, the CMDR-MR relationship for natural gradient exhibits a convex-downward profile residing below the 1:1 reference line. Conversely, the CMDR-MR curves shift leftward for simulations with pumping wells. The non-ideal behavior is attributed to mass-transfer constraints caused by both low flow zones and permeability heterogeneity. For simulations for the 3D heterogeneous domain with clay present, the CMDR-MR curves shifts further leftward and are asymptotic at larger mass reductions. This is a result of impacts of low flow zones, permeability heterogeneity, and back diffusion.

The influence of the degree of permeability heterogeneity on contaminant elution curves and associated CMDR-MR profiles for the 3D heterogeneous domain was examined by varying the magnitude of the variance of ln K. Results for simulations conducted with $\sigma^2_Y$ of 2, 5, 10, 15 and 30 for the natural gradient configuration are presented in Fig. 3. 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-15. 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 $\sigma_y^2$ of 30. Conversely, this occurs after 200 days for the simulation with small variance, $\sigma_y^2$ of 2. These results illustrate the impact of greater preferential flow through higher-K zones for simulations with larger $\sigma_y^2$, and resultant earlier reductions in concentration and CMD.

The influence of the degree of permeability heterogeneity on mass-removal efficiency was also examined in domains with $\sigma_y^2$ of 2, 5, 10, 15 for the Longitudinal well-field configuration. The longer tailing in elution curves and progressive leftward shifts of the CMDR-MR curves are also observed as $\sigma_y^2$ increases. The CMDR-MR curves exhibit primarily singular curvilinear profiles oriented convex-upward and reside above 1:1 reference line. The latter two properties are in contrast to the profiles observed for the natural-gradient configuration.

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 3D heterogeneous system without clay ($\sigma^2_Y=5$). The results were evaluated in terms of the ratio of domain length to correlation length ($R_\lambda$). The resultant elution curves and CMDR-MR profiles are presented in Fig. 5. It is evident that relatively ideal behavior is observed for the simulations conducted with $R_\lambda$ equal to or greater than 100. This reflects the pseudo-homogeneous nature of the domains extant for such large $R_\lambda$ 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 $R_\lambda$ for higher variance ($\sigma^2_Y=15$) with natural gradient is shown in Fig. 3. 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. The impact of $R_\lambda$ was also examined with simulations for the Longitudinal well–field configuration. The results of simulation conducted in domain with $\sigma^2_Y=15$ and $R_\lambda =1$ are presented in Fig. 4. The longer tailing was observed in elution curve and the CMDR-MR profile shifts leftward compared to the CMDR-MR profile for simulation with $\sigma^2_Y=15$ and $R_\lambda =20$.

In Fig. 5, the results for simulations with natural gradient for the layered and 3D heterogeneous domains with $R_\lambda$ equal 1 and variance of ln K as 15 are presented. As expected, both $R_\lambda$ and $\sigma^2_Y$ influence the overall mass-removal behavior. 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 $\sigma_y^2=5$. Moreover, for the layered simulation, which can be considered to represent in effect a heterogeneous system with an $R_\lambda$ equivalent to 1 and ln-K variance of 47, the sigmoidal profile is observed and the mass removal reached asymptotic condition after approximately 40% mass was removed.

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. 5. Apparent disparities between the two curves are observed, but the overall behavior is similar.

The result for the simulation with Longitudinal well-field configuration conducted in same domain with simulation “ratio=1_variance=15_R1” is also presented in Fig. 5. In this larger heterogeneity domain, the mass was not completely captured by the extraction wells. Therefore, the difference between this curve and the curve “ratio=1_variance=15_R1” for natural gradient is not due solely to the impacts of well-field configuration, but also the influence of natural gradient flow out of the domain.

The elution curves and CMDR-MR profiles for simulations conducted for the Longitudinal well field configuration in the 3D heterogeneous domain with and without clay layers are presented in Fig. SM-6. The concentration for the simulation with clay
absent decreases smoothly, whereas the concentration decreases asymptotically with much longer tailing after an initial significant decrease for the simulation with clay present. Inspection of the CMDR-MR profiles shows that the relationship for the 3D simulation without clay present exhibits a convex-upward profile residing above the 1:1 reference line. For the simulation with clay present, the profile shifts further to the left and reaches asymptotic condition after approximately 25% mass was removed as a result of constrained mass-transfer of contaminant associated with the clay layers.

Mass removal from the clay layers via back diffusion is highly dependent on the permeability distribution for the sand region adjacent to the clay. Fig. SM-7 shows the K-distribution for the sand in the vicinity of the bottom clay layer. Fig. SM-8A presents the corresponding concentration contours for this sand layer after 5000 days of pumping. Overall, the contaminant distribution reveals a good agreement with the K-distribution in Fig. SM-7. 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 clay layer is similar to that observed in the sand. After 5000 days, the higher-concentration zones in the clay layer occurred in regions right above the high concentration zones in the sand (Fig. SM-8B). With the initial condition of uniform concentration in both sand and clay, the higher permeable regions in sand wherein the mass was removed more rapidly because of faster flushing resulted in a larger concentration gradient between the sand and adjoining clay, leading to faster mass transfer from clay to sand and thereby lower concentrations in clay within these regions.
As expected, such concentration changes are delayed for regions farther from the clay-sand interface (Fig. SM-8C).

### 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 (Srivastava and Brusseau, 1994; Fiori, et al., 2011; Zhang et al., 2013, 2014). Table SM-4 presents basic information for these previous studies. In Srivastava and Brusseau, Fiori et al., and Zhang et al., 2013, the permeability fields were generated randomly, and results with different variances of ln K were reported. In Zhang et al., 2014, the K field was generated randomly with four hydrofacies properties, debris flow, floodplain, leeve and channel, with fixed proportions. Part of the floodplain was considered as an immobile phase. 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. 6. For Zhang et al., 2014, 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 our study. For the Zhang et al. (2014) data, their immobile phase acted similarly to the
low permeability layers used for the simulations conducted for domains with clay 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 Srivastava and Brusseau’s 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 $R_z$ 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 Flori et al.’s study show greater ideal behavior than the Srivastava and Brusseau’s data. The CMDR-MR profiles for scenarios with larger variance, as 24.9 and 37.1 in Zhang et al.’s (2013) study, are sigmoidal, just as the CMDR-MR profile for the simulation with variance of 15 and 30 in this work.

3.4 Impacts of other factors

Additional simulations were conducted to investigate the impacts of pumping rate, aquifer thickness and other factors, such as diffusion and vertical dispersivity. The results for all cases are consistent with expected behavior. Regarding pumping rate impacts, under circumstances wherein mass transfer is very slow compared to the residence time (i.e., small \( \phi \) values), and the pumping rates are sufficient to capture the whole plume, increasing the pumping rate will exert little influence on mass removal efficiency in system that pumping rates for wells are constant during the operation.
Decreasing the pumping rate at some point resulted in an incomplete capture of the plume. Adjustment of the pumping rate during the operation period can increase mass removal efficiency. Changing the magnitude of the diffusion coefficient or vertical dispersivity has the anticipated impacts on mass removal behavior (Guo, 2015).

4. Summary

Different well-field configurations were simulated for homogenous, 2D-layered, and 3D-heterogeneous domains 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. The results of simulations conducted for homogeneous and layered domains reveal the maximum potential of well-field impacts, while the impact of well-field configuration is reduced for the 3D 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 low permeable layers 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 $R_\lambda$ and $\sigma^2_\gamma$ influence the overall mass-removal behavior. For domains with larger $R_\lambda$ or smaller $\sigma^2_\gamma$, the CMDR-MR relationships exhibit convex-downward profiles that are similar to the curves for simulations conducted for the homogeneous domain. Whereas sigmoidal profiles are observed for domains with small $R_\lambda$ or large $\sigma^2_\gamma$.

Time continuous concentration 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. (2013) 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.

With interest in contaminant mass discharge and CMDR-MR relationships, approaches based on simple “mass-removal” functions and “source-depletion” models have been proposed to simulate or predict the CMDR-MR relationships for sites with NAPL source present (e.g., Enfield et al., 2002; Rao et al., 2002; Parker and Park, 2004; Zhu and Sykes, 2004; Jawitz et al., 2005). Prior research has shown that these simple functions cannot reproduce the sigmoidal or multi-step profiles observed for some NAPL-source systems (e.g., Phelan et al., 2004; Brusseau et al., 2008; DiFilippo and
Brusseau, 2008; Christ et al., 2009). The sigmoidal or multi-step profiles are also observed for plume systems with larger degrees of heterogeneity in this study, which cannot be reproduced by these simple functions.

The CMDR-MR relationship is a useful tool to quantitatively assess mass-removal efficiency. Under certain conditions, the CMDR-MR profiles can help to evaluate the effectiveness of the well-field configuration and show the impacts of field heterogeneity on remediation. More research is needed to further study the applicability of the CMDR-MR relationship for evaluating mass-removal processes in field sites with large degree of heterogeneity.

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<td>Test 2: (R_{\alpha}=1,20,100,200,1000)</td>
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\(^a\)3D represents simulations with stochastic random K field
Figure Captions

Figure 1. Schematic presenting the three tested well-field configurations. The fourth configuration tested was a natural-gradient system with no wells.

Figure 2. Impact of well-field configuration on mass removal behavior in homogeneous domain: A. Elution curves; B. CMDR-MR relationships, results from Rivett et al. (2006) also included in the figure.

Figure 3. Impact of degree of permeability heterogeneity on mass removal behavior in 3D 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 simulated in domain with $\sigma_\gamma^2 = 5$ and $R_\lambda = 20$, $\sigma_\gamma^2 = 15$ and $R_\lambda = 20$, $\sigma_\gamma^2 = 15$ and $R_\lambda = 1$. The results for all individual realizations are presented in Fig. SM-16.

Figure 4. Impact of degree of permeability heterogeneity on mass removal behavior for Longitudinal well-field configuration in 3D domains without clay present and layered systems with different K values for clay layers $R_\lambda = 20$: A. Elution curves; B. CMDR-MR relationships.

Figure 5. Impact of correlation length on mass removal behavior for natural gradient and Longitudinal well field in 3D domains without clay present $\sigma_\gamma^2 = 5$: A. Elution curves;
B. CMDR-MR relationships. Results of simulations with natural gradient and Longitudinal well field in 3D domain with $R_x=1$ and $\sigma^2_Y=15$ are also presented. The curve “L_ratio=1_variance=15” is the results of simulation conducted with Longitudinal well field in domain with $R_x=1$ and $\sigma^2_Y=15$. The curves “ratio=1”, “ratio=20”, and “ratio=1_variance=15mean” are the mean of 10 realizations simulated in domain with variance=5 and $R_x = 1$, variance=5 and $R_x = 20$, variance=15 and $R_x = 1$. The results for single realization are present in Fig. SM-16. 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 6 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.
### Contaminant Treatment Zone

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</tbody>
</table>

- **Distributed**
- **Downgradient**
- **Longitudinal**

Figure 1
Figure 2A

Figure 2B
Figure 3A

Figure 3B
Figure 4A

Figure 4B
Figure 5A

Figure 5B
Figure 6
Supplementary Materials

The Impact of Well-Field Configuration and Back Diffusion on Plume Persistence

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This supplementary material includes definition of the Damkohler number, impacts of boundary condition, pumping rates and domain thickness on mass removal, and tables and figures referenced in the manuscript.

1. Damkohler number

The Damkohler number is a dimensionless parameter describing the magnitude of nonideal transport associated with a mass-transfer process, such as diffusive mass transfer between domains with lower and higher hydraulic conductivity (K). It can be calculated by the equations:

\[ \omega = \frac{\gamma L}{q} \]  

(1)

\[ \gamma = \frac{aD_{\text{app}}\theta}{\tau l^2} \]  

(2)

where \( \gamma \) is the mass transfer rate coefficient (d\(^{-1}\)), \( L \) is the length of the system (m), \( q \) is the discharge rate (m/d), \( a \) (equal to 3 here) is a shape factor dependent upon the type of structure, \( \theta \) is porosity, \( \tau \) is tortuosity, \( l \) is the diffusive path length (m), which is the length of low K layer in this study. From Fig. SM-1, when \( \omega \) is less than 0.01 and larger than 100, the concentration change is insensitive with the changing of the discharge rate, whereas when \( \omega \) is larger than 0.01 but smaller than 100, it is the sensitive zone wherein a change of residence time, which is dependent on discharge rate, could exert a significant impact on the concentration change.

2. Boundary condition impact on mass removal behavior
Boundary condition was revised for simulations with natural gradient in 3D heterogeneous domain from constant head boundaries in four bounds to right and left constant head boundaries to prevent mass lost from north and south boundaries. For consistency, simulations with Longitudinal configuration in 3D heterogeneous domain were conducted with revised boundary condition. Fig. SM-6D and Fig. SM-6E reveal distinct mass removal behaviors under two different boundary conditions for simulations with Longitudinal well field in different domains. In systems with revised boundary conditions that constant heads, when pumping started, pulling water from east and west sides resulted in a decrease of concentration first. At the same time, very little of the mass in the north and south of the wells was removed. After the western and eastern regions were clean, with the high concentration surrounding the middle well and low flow rate in the north and south, the dilution effect on middle well was small. Concentration decreased asymptotically before the clean water was captured by the middle well and more dilution of concentration occurred. Then the concentration started to decrease rapidly again until all mass in the sand layers was removed (Fig. SM-9). In contrast, with the original boundary condition, water can be pulled from all directions uniformly and less uneven mass distribution occurred outside the pumping well region (Fig. SM-3). As a result, the mass was removed gradually during the pumping period. For the systems with 3D heterogeneity features, the impact of boundary condition change was not as significant as homogenous and layered systems because the preferential flow paths decreased impacts of low-flow regions.
3. Impact of pumping rate

The impact of pumping rate on mass removal efficiency in the homogeneous and 2D-layered domains with the Distributed well-field configuration and in the 3D heterogeneous domain with the Longitudinal well-field configuration was examined. The results are presented in Fig. SM-10 and Fig. SM-11. For the simulations conducted for the homogeneous domain with pumping rates of each well 50 m$^3$/d, 100 m$^3$/d, 300 m$^3$/d, the $\omega$ values are 0.028, 0.014, and 0.005, respectively. Given these low values (close to or less than 0.01), according to Fig.SM-1, concentration changes are not sensitive to the variance of pumping rates, which is also reflected in the similar mass removal behaviors (Fig. SM-10). High pumping rates were applied in this study to capture the large plume. However, with the pumping rate as 50 m$^3$, the contaminant in the domain cannot be captured completely and a portion of mass was not recovered with the extraction wells. The CMDR-MR curve was generated using the mass remaining in the model domain at each time step, resulting in the profile shifting leftward with a larger mass removal fraction. For simulations conducted with the layered domain, similar mass-removal behaviors were observed before mass was completely removed from the sand (Fig. SM-11B), and the asymptotic condition were reached for all simulations with different pumping rates because of mass-transfer constraint associated with the clay units (Fig. SM-11A). For simulations conducted with heterogeneous domain with variance of $\ln K$ as 10 and 15, incomplete mass capture resulted in the evident disparities between CMDR-MR profiles with different pumping rates (Fig. SM-11C).
The CMDR-MR profile for the simulation for which pumping rates were adjusted 1000 days after the operation started is also presented in Fig. SM-10 and Fig. SM-11. The adjusted pumping rates for each well are listed in Table SM-3. The CMDR-MR curve for the simulation with adjusted pumping rates shifts to the right of the curve obtained for the system with constant pumping rates. After the pumping rates were adjusted, the contaminant that was trapped in the inter-well stagnation zones was pumped out along the changed flow paths, removing more mass with higher CMD. It took 2750 days for the system with changed pumping rates to remove 90% of mass instead of 3760 days for the system with constant pumping rates. For the simulations conducted for the layered domain, this effect was reflected in the process when removing mass from the sand (Fig. SM-11B). After all contaminant was removed from the sand, mass removal was dominated by back diffusion from the clay units, therefore, the impact of pumping rate was not significant anymore. The system with constant pumping rates took 2430 days to remove all mass from the sand layer, whereas the system with adjustment of pumping rates only took 2020 days, shortening the period by approximately one year. Fig. SM-12 presents mass distribution maps for the simulations conducted for the layered domain after 1500 days of pumping for both the constant-Q (Fig. SM-12A) and non-constant-Q (Fig. SM-12B) systems. The mass remaining in the domain was much less for the simulation with pumping rates changed.

In summary, under circumstances wherein mass transfer is very slow compared to the residence time (i.e., small \( \omega \) values), and the pumping rates are sufficient to capture the entire plume, increasing the pumping rate will exert little influence on mass removal
efficiency. Decreasing the pumping rate at some point resulted in an incomplete capture of the plume. Instead, adjustment of the pumping rates during the operation period can change the flow patterns, reduce and even remove the stagnation zones formed by previous well-field hydraulics, and therefore, increase mass-removal efficiency.

4. Impact of aquifer thickness

The comparison between simulations conducted for the homogeneous and layered domains with a thickness of 15 m and 1.5 m are illustrated in Fig. SM-13 and Fig. SM-14. For simulations conducted with the homogeneous domain, as expected, both the elution curves and CMDR-MR profiles for simulations with natural gradient in domains with thickness of 1.5 m and 15 m are identical, so are curves for simulations with Longitudinal well-field configuration. The CMDR-MR relationships for natural gradient simulation exhibit convex-downward profiles representing ideal mass-removal processes, whereas the relationships for the Longitudinal well-field configuration shift leftward because of the impact of well-field configuration. The thickness does not exert influence on the mass-removal behaviors because the dominant advection occurred in the entire systems, and the impact of mass-transfer constraints is only caused by well-field hydraulics (Fig. SM-13).

Distinct disparities are observed for the simulations conducted with the layered domain. For simulations conducted with natural gradient in domain with the thickness of 1.5 m, minimum tailing is observed for the elution curve and the CMDR-MR relationship exhibits a convex-downward profile residing below the one to one reference line. In
contrast, early concentration decrease and long tailing are observed for the elution curve for the simulation conducted for the domain with a thickness of 15 m, and the associated CMDR-MR relationship exhibits a convex-upward profile. The significant non-ideal mass-removal behavior for simulations conducted with 15 m domain is influenced only by the mass-transfer constraint associated with the clay layer. For simulations conducted with the Longitudinal well-field configuration, the greater concentration decrease at early period and longer tailing for the elution curve are observed for the domain with 15 m thickness compared to the curve for the domain with 1.5 m thickness. For the CMDR-MR relationships, the curve for the domain with 1.5m thickness shows approximately one to one profile, whereas the curve for the domain with 15 m presents a convex-upward profile. The non-ideal mass-removal behavior in the layered-domain cases are influenced by both well-field configuration and back diffusion. As discussed above, the contaminant residing in clay is removed by diffusive mass transfer, and it takes more time for the mass in the clay unit that far from the sand to be transferred out. As expected, the curves for the domain with 15m thickness show less ideal behaviors due to more evident mass-transfer constraints. Thus, for those sites wherein contaminants are trapped in the thick clay, the long-term site management is inevitable.
### Table SM-1 Aquifer hydrology, geometry and transport parameter

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### Table SM-2 Summary of 3D heterogeneous scenarios

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Table SM-3 Adjusted pumping rate in period 2 for Distributed well-field configuring

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Figures

Figure SM-1. Impact of residence time (pumping rate and system length) on mass removal behavior, as represented by the Damkohler number. Elution curves are presented in pairs (with flow rate varying by a factor of 3) for 4 sets of $\omega$ values spanning several orders of magnitude.
Figure SM-2 Three relationships between mass flux reduction and mass removal

(Bursseau et al. 2008)
Figure SM-3. Contaminant distribution maps in homogeneous domain at different time periods: A. Natural Gradient, 1000 d; B. Longitudinal, 1000 d; C. Longitudinal, 1700 d; D. Longitudinal, adjusting location period 2, 1700 d; E. Distributed, 1000 d; F. Downgradient, 500 d; G. Downgradient, 4000 d; H. Downgradient, 8000 d. Red represents the highest concentration and blue represents the lowest concentration.
Figure SM-4. Impact of well-field configuration on mass removal behavior in layered domain: A. Elution curves; B. CMDR-MR relationships. C. CMDR-MR for mass removal process in sand layer.
Figure SM-5. 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-17.
Figure SM-6. Impact of heterogeneity and back diffusion on mass removal behavior in longitudinal well-field systems. For 3D domain, $R_d = 20$ and $\sigma_Y^2 = 5$. A. Elution curves; B. CMDR-MR relationships; C. CMDR-MR profiles for layered and 3D scenarios. The fraction of mass removal is determined by the amount of removed mass and the initial mass in sand layers only; D. Elution curves for scenarios with original constant head boundary condition in four boundaries and revised condition in east and west boundaries; E. CMDR-MR profiles for scenarios with original constant head boundary condition in four boundaries and revised condition in east and west boundaries.
Figure SM-7. K-distribution of top sand layer in 3D heterogeneity system that sand layers were generated with mean K value as 20 m/d, $\sigma_j^2=5$, and $R_j=20$. Red represents the regions with low K, blue represents high-permeability zones.
Figure SM-8. Selected concentration distribution maps in 3D heterogeneity system that sand layers were generated with mean K value as 20m/d, $\sigma_f^2 = 5$, and $R_f = 20$. A. Layer 21: top layer of sand; B. Layer 20: bottom layer of clay; C. Layer 10: clay layer far from sand.
Figure SM-9. Mass distribution maps at different time periods for scenario with the Longitudinal well-field configuration in homogeneous domain with constant head boundaries in east and west. A. 100 days after pumping initiated; B. 330 days after
pumping initiated when the concentration decreased asymptotically; C. 850 days after
pumping initiated when the concentration started to decrease rapidly.
Figure SM-10. Impact of total pumping rate on mass removal for Distributed well-field configuration in homogeneous domain. Damköhler numbers are <0.01.
A

B
Figure SM-11. Impact of total pumping rate on mass removal. A. Distributed well-field configuration in Layered domain; B. Distributed well-field configuration in Layered domain only for mass removal process in sand layer; C. Longitudinal well-field configuration in heterogeneous domain.
Figure SM-12. Contaminants distribution maps of sand layer in layered domain: A. Distributed, 1500d; B. Distributed, adjusting pumping rate, 1500d.
Figure SM-13. Impact of aquifer thickness on mass removal behavior for the Longitudinal well-field and natural gradient simulations in homogeneous domain: A. Elution curves; B. CMDR-MR relationships.
Figure SM-14. Impact of aquifer thickness on mass removal behavior for the Longitudinal well-field and natural gradient simulations in Heterogeneous domain: A. Elution curves; B. CMDR-MR relationships.
Figure SM-15 Contaminant mass distribution maps for simulations with natural gradient:

A. $\sigma_y^2 = 2$, 200 day; B. $\sigma_y^2 = 5$, 140 day; C. $\sigma_y^2 = 10$, 84 day; D. $\sigma_y^2 = 15$, 60 day; E. $\sigma_y^2 = 30$, 27 day.
A

B

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Figure SM-16 Results of Monte Carlo analysis for single realization and the mean of the 10 realizations conducted in different domain with natural gradient: A. Elution curves for
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Figure SM-17 Results of Monte Carlo analysis for single realization and the mean of the 10 realizations conducted with different well-field configuration in domain with $\sigma_Y^2=5$, $R_{\lambda}=20$: A. Elution curves for Longitudinal well-field configuration; B. Elution curves for Distributed well-field configuration; C. Elution curves for Downgradient well-field configuration; D. CMDR-MR profiles for Longitudinal well-field configuration; E. CMDR-MR profiles for Distributed well-field configuration; F. CMDR-MR profiles for Downgradient well-field configuration.

References


APPENDIX C

Factors Impacting Plume Persistence at the Tucson International Airport Area

Superfund Site

This appendix includes initial numerical simulation results used in Matthieu et al., 2014 and the results of additional simulations.

1. Site information

The selected site is part of the Tucson International Airport Area (TIAA) federal Superfund site in southern Arizona. The site corresponds to a facility that was used in the past to clean aircraft parts and the external surfaces of military aircraft. TCE vapor degreasers, decarbonizers, and parts-cleaning tanks were located in several small buildings at the site. During the 1940’s to mid-1970’s, unlined pits and other features were used for the disposal of organic solvents, and contaminants entered the subsurface by seepage. At early 80’s, TCE was detected from several potable water supply wells. In responsible to this, the TIAA site was placed on the National Priorities List in 1983. A large, multiple-source plume of TCE exists in the upper portion of the regional aquifer. Administratively, the TIAA site is separated into three major zones, the North, Central, and South sections. The current study site is located within the central section of the complex.
The study site has a small source area of approximately 8400 m², with a groundwater contaminant plume extending approximately 600 m to the west (Fig. 1) that resides in a localized shallow saturated zone (Brusseau et al., 2013). Aqueous concentrations of TCE as high as 100 mg/L have been reported for groundwater sampled from monitoring wells located within the source zone. Given the previous on-site activities, the high observed aqueous concentrations, and the quantity of contaminant mass removed via soil vapor extraction and pump and treat, it is highly probable that liquid TCE is present in the subsurface. Based on the degree of contamination and extensive lower-permeability materials present at the site, attaining remediation to standard regulatory objectives was deemed to likely be technically impracticable, and therefore, a technical impracticability waiver was granted by U.S. EPA for the source zone (EPA, 2012).

The potentiometric surface of the shallow groundwater zone is 28~29 m below land surface (bls). The saturated interval consists of clay and silty clay units, sand and/or gravel units, and an underlying, laterally extensive, clay unit starting at ~37 m bls separating the shallow groundwater zone from the regional aquifer (Brusseau et al., 2013). Based on pumping tests, hydraulic conductivities ranging from $4 \times 10^{-5}$ to $3 \times 10^{-4}$ m/s were measured for the gravel sub-unit, and values from $1 \times 10^{-6}$ to $5 \times 10^{-6}$ m/s were measured for the primary clay unit above the gravel sub-unit. Natural hydraulic gradients for the gravel sub-unit have ranged historically between $5 \times 10^{-3}$ and $1 \times 10^{-2}$.

A pump-and-treat remediation project was initiated in the fall of 2007, with two extraction wells for source control and five extraction wells for plume containment. The total extraction rate for the two source-control wells is approximately 75 m³/d, whereas
the total for the four plume wells is approximately 300 m3/d. Contaminant mass discharge was calculated as the product of flow rate and TCE concentration monitored since system startup, which provides a measure of integrated contaminant mass discharge from 2007 to spring 2012. Approximately 700 kg of volatile organic compounds have to date been removed from groundwater by the extraction system. A soil vapor extraction system was also initiated at the same time, which has to date removed approximately 3000 kg of contaminant.

2. Numerical Simulation

The flow model used in this work was the 3D finite-difference numerical model MODFLOW developed by the U.S. Geological Survey (McDonald and Harbaugh, 1988; Harbaugh et al., 2000). The 3D solute transport model MT3D (Zheng, 1990) was used to simulate solute transport. Groundwater Vista (GV) (Rumbaugh and Rumbaugh, 2007) and Groundwater Modeling System (GMS) (EMRL, 2005) were used as graphical user interfaces.

The numerical model was developed according to site geologic and hydraulic features. The simulated domain was 1000 (L) by 600 (W) by 19 (H) m, encompassing an area from the source area to the western margin of the plume, and some distance north and south of the plume. Grid spacing and time step were selected based on the standard grid-Peclet number and Courant number criteria, respectively, to ensure robust simulations. Specified head boundaries were used along the east and west borders of the
domain, and specified flow boundaries were used along the north and south boundaries. A natural gradient of 0.004 was imposed, with groundwater flow from the east to west.

To simplify the model, the domain was divided into 3 layers with upper and lower lower-permeability units (each 7-m thick) and a gravel unit (5-m thick) in the middle. The middle layer was simulated with areal (x-y) spatial variability of K based on measured data collected from sediment coring results and aquifer tests. Conversely, K in the upper and lower low-K units was uniform in the x-y plane. The spatial variability of K within the middle layer was represented through the use of discrete zones, wherein K was treated homogeneously within each zone. The geometric mean of K for the middle unit (6.6 m/d) was approximately 25 times the K for the upper and lower units (0.26 m/d). Longitudinal, transverse, and vertical dispersivities were set to 5, 0.5, and 0.075 m, respectively. Porosities of 0.25 and 0.37 were used for the gravel and lower-permeability units, respectively. The aqueous diffusion coefficient was $7.6 \times 10^{-5}$ m2/d. First order kinetics was used for sorption of TCE, with a distribution coefficient of 0.04 cm3/g and mass transfer coefficient of 15 d-1, based on measured data for sediments collected from the site (Zhang and Brusseau, 1999). The initial concentrations in the plume were set according to data collected from the monitoring well network. The initial concentration in the source was set at 20 g/m3, providing continuous contaminant supply to the plume. The two source control wells and five plume extraction wells were screened in the middle layer. Samples of extracted water were collected and analyzed approximately once per month. The pumping rates, recorded continuously and tabulated monthly throughout the course of operation, for each well were used as input.
An additional two simulations were conducted to test the impact of the source zone. Simulation 1 was conducted with the contaminant concentration in the source as zero, which represents complete isolation of the source zone. The initial mass was determined by the mass present only in the plume area. Simulation 2 was conducted with initial concentration in the source as 20 g/m³ for 150 years. The initial mass was determined by the total mass present in the plume and the total mass supply from the source until the end of the simulation.

Two simulations were conducted to investigate the impact of the well-field configuration. In the first simulation, all five extraction wells were located in lower K zones in the middle layer, and in another simulation, the wells were located in higher K zones in the middle layer. The pumping rates were the same. Additional simulations were conducted to investigate the impact of preferential flow for the two modified configurations and also for the original well-field configuration. Dozens of particles were placed in different hydraulic conductivity zones and Modpath (Pollock, 1994) was used to conduct the particle tracking.

Another two simulations were conducted by modifying the K field of the original domain to investigate the impact of heterogeneity. For the first simulation, the upper and lower low-permeability layers were modified to have the same spatial (x-y) variability of K as the middle layer, thereby producing a vertically homogeneous domain. For the second, the K values of the upper and lower layers were decreased to 1000 times smaller than the geometric mean K of the middle layer (compared to 25 times for the original). In
addition, a simulation with no sorption was conducted to test the impact of sorption on mass removal.

3. Results and discussion

The measured and simulated time continuous profiles of mass discharge are presented in Fig. 2. Measured and simulated concentrations are compared for each plume extraction well in Fig. 4. The composite concentrations are also presented, which are calculated according to the total CMD and total discharge from the plume. The simulated results match well with the measured concentrations for the individual wells and the composite curve except for EW2 in the later period. Considering the low pumping rate (approximately 15~20 times lower than EW1 and EW4), EW2 does not exert significant impact on the composite concentration or associated CMD. 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. 2 and Fig. 4 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. 2. 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. The profile of the CMDR-MR relationship is presented in Fig. 5B. With the complete removal of the source zone, the initial mass was calculated based on the initial concentration in the plume only, which results in much higher mass removal faction (79%) compared to the results (53%) of simulations with continuous source contribution after 60 months of remediation. The CMDR-MR relationship presented in Fig. 5C reveals the impact of long-term (150 years) source contribution. The curve shifts leftward compared to the curves for the other two simulations (Fig. 5A and B) because more mass was supplied by the source zone, which has been counted as initial mass, and asymptotical behavior is observed in the later period. For this simulation, the results show that only approximately 35% of the initial mass was removed during the initial 60 months of operation, and that an additional approximately 85 years will be needed to remove 99.9%. 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. 3. 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. The results of the particle tracking are presented in Fig. 6. Preferential flow can be clearly observed, by-passed contaminants
were then transported slowly out of the low K zones, leading to longer tailing. The degree of by-pass flow for the original configuration (Fig. 6A) is much less than for the case with the wells located in high K zones. Relatively efficient mass removal performance is observed for the simulation with the wells located in low K zones (Fig. 6C). The CMDR-MR relationships for all three scenarios are presented in Fig. 3B. 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. 7. 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.

The simulation results with or without sorption are presented in Fig. 8. No significant differences are observed. This result is consistent with the conclusion of Zhang and Brusseau (1999), who investigated the factors impacting the non-ideal
transport behavior of TCE during pump and treat remediation at Tucson International Airport Area Superfund site. They concluded that non-ideal desorption had minimal impact on the observed asymptotic CMD behavior.

4. Summary

The TIAA site was used as a case study to examine the impacts of well-field hydraulics and heterogeneity. The time continuous profiles of contaminant mass discharge and CMDR-MR curves obtained from the model simulations show good agreement to the measured field data, which indicates that the model provides a reasonable representation of mass-removal behavior at the site. The impact of long-term source contribution was studied in this work. The results from the case study agree with the conclusions made in the prior theoretical study.

Reference


Figure Captions

Figure 1. TIAA site plume map.

Figure 2. Relative contaminant mass discharge as a function of elapsed time obtained from monitored field data and modeling results.

Figure 3. Mass removal behavior for 3 different well-field configurations: A. Relative contaminant mass discharge (CMD) as a function of elapsed time; B. Relationships between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR).

Figure 4. Comparisons of Elution curves produced by monitored field data and modeling results for each extraction well and composite results.

Figure 5. Impact of source zone on plume mass removal: A. CMDR-MR relationships with 5 years source contribution (Real field case); B. CMDR-MR relationships with complete source removal at the beginning of operation; C. CMDR-MR relationships with long-term source, 20 years source contribution.

Figure 6. Particle trace maps for different well-field configurations: A. Field configuration; B. Wells located in high K zones; C. Wells located in low K zones. Red lines representing particle traces, black lines representing head contours. Different cell-
colors represent different hydraulic conductivity zones. Red means lowest permeability, and blue means highest permeability. Red lines are the particle traces.

Figure 7. Impact of site heterogeneity on mass removal: A. Relative contaminant mass discharge (CMD) as a function of elapsed time; B. Relationships between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR).

Figure 8. Impact of sorption on mass removal behavior.
Figure 1
Figure 2
Figure 3A

Figure 3B

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Figure 4
Figure 5A

Figure 5B
Figure 5C
Figure 6A

Figure 6B
Figure 6C
Figure 7A

Figure 7B
Figure 8
Appendix D

Modified Well-Field Configurations for Improved Performance of Contaminant Elution and Tracer Tests

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Abstract

Contaminant elution and tracer (CET) tests are one method for characterizing the impact of mass transfer, transformation, and other attenuation processes on contaminant transport and mass removal for subsurface systems. The purpose of this research is to explore specific well-field configurations for improving CET tests by reducing the influence of preferential-flow and surrounding plume effects. Three injection-extraction well configurations were tested for different domain conditions using a three dimensional numerical model. The three configurations were the traditional configuration with a single pair of injection-extraction wells, modified configuration I with one extraction well located between two injection wells, and modified configuration II with two pairs of injection-extraction couplets (one nested within the other). Elution curves for resident contamination and breakthrough curves from simulated tracer tests were produced and examined for specific landmarks such as the presence and extent of steady-state (relatively high concentrations) and asymptotic (asymptotic decrease to low concentrations) phases, as well as distinct changes in slope. Temporal-moment analysis of the breakthrough curves was conducted to evaluate mass recovery. Rate coefficients were obtained by fitting selected functions to the elution curves. Based on simulation results for a homogeneous domain, the concentration measured from the inner extraction well of the modified configuration II stayed at zero during the test period, which indicates full isolation of the extraction well from the surrounding plume. Conversely, the concentrations for the extraction well reached asymptotic conditions for the other two configurations because of the impact of the surrounding plume. Therefore, configuration
II was used for additional simulations conducted with layered and heterogeneous domains. Tracer-test simulations for homogeneous and layered domains indicate 100% mass recovery for the inner extraction well, whereas the recovery was lower (69%) for the heterogeneous-domain simulations because of preferential flow phenomena. However, changing the distance between the inner injection-extraction well couplet and the pumping-rate distribution between the two extraction wells increased the mass recovery to 99%.

**Key words:** plume; site characterization; attenuation
1. Introduction

Compounds such as chlorinated solvents (e.g., trichloroethene, tetrachloroethene, carbon tetrachloride), 1,4-dioxane, methyl tertiary-butyl ether (MTBE), and perchlorate used in industrial, commercial, and other applications continue to pose significant threats to human health through contamination of groundwater resources. A recent National Research Council report stated that most sites with large groundwater contaminant plumes will require many decades or longer before cleanup will be achieved under current methods and standards (NRC, 2013). This realization has resulted in the examination of alternatives for cost-effective long-term management of plumes at these sites.

Monitored natural attenuation (MNA) and enhanced attenuation (EA) have been widely accepted as alternatives because of their lower cost and sustainable management for large, complex plumes. Advanced methods are required to characterize sites for the occurrence of specific attenuation processes and to determine their associated rates to evaluate the feasibility of MNA/EA. Matrix diffusion, sorption, and transformation are critical attenuation processes that can impact remediation effectiveness. Understanding more about these processes can provide guidance for long-term management (NRC, 2013; SERDP, 2013). Moreover, improved predictive modeling that can account for the various attenuation and transport processes is needed for cost-effective site management (e.g., EPA, 2009). This in turn requires better determination of the relevant input parameters.
Several methods, such as plume-scale spatial concentration transects, mass-flux fences, and single-well push-pull tests, have been used for evaluating attenuation processes and the feasibility of MNA/EA (e.g., Newell et al. 2002; Borden et al., 1997; King et al., 1999; Basu et al., 2006; Bockelmann et al., 2001; Johnson et al., 1989; Ball et al., 1997; Chapman and Parker, 2005; Drever and McKee, 1980; Istok et al., 1997). These methods provide measures of aggregate attenuation and can have significant uncertainties because of preferential flow phenomena, which can limit their usefulness to evaluate and quantify specific attenuation processes (e.g., Brusseau, 1998; Chapelle et al., 2007).

Induced-gradient contaminant elution and tracer tests are another option for characterization of mass-transfer and attenuation processes and associated parameters (Brogan and Gailey, 1995; Thorbjarnarson and Mackay, 1997; Blue et al., 1998; Brusseau et al., 1999a; Nelson et al., 2003; Sandrin et al., 2004; Brusseau et al., 2007). For all of these prior CET test applications, the test was implemented using a standard injection-extraction dipole configuration. The extraction well remains influenced by the surrounding plume for this configuration, which can be a significant limitation in attempting to delineate specific attenuation processes. This is particularly true for mass-transfer or transformation processes with slower characteristic rates. Hence, there is interest in investigating alternative well-field configurations that may enhance the implementation and analysis of CET tests.

A number of studies have been conducted to evaluate effective well-field configurations for various applications. For example, their impact on contaminant mass
removal has been investigated for pump-and-treat systems (e.g., Satkin and Bedient, 1988; Keely, 1989; Schafer and Kinzelbach, 1992; Cohen et al., 1997; Rivett et al., 2006; Guo, 2015). In addition, two-well recirculation systems have been investigated for in-situ bioremediation of groundwater (Gandhi et al., 2002; Luo et al., 2006). Gandhi et al. (2002) examined the performance of the recirculation system with a single injection-extraction well pair. Luo et al. (2006) tested the performance of two well-field configurations for enhancing the efficiency of in situ bioremediation. A traditional configuration of a single pair of injection-extraction wells was compared to a configuration that employed a four-well system to create a nested inner cell. Field tracer tests (Luo et al., 2007) were conducted to evaluate capture and recovery effectiveness and residence times. Minimal research has been conducted to investigate optimal well-field configurations for CET tests, especially for applications focused on characterizing natural attenuation processes.

The purpose of this research was to investigate the ability of two modified well-field configurations to isolate the extraction well in comparison to the standard injection-extraction well couplet. Numerical modeling was used to generate synthetic CET test data, namely elution curves for resident contaminants and breakthrough curves (comprising both arrival and elution waves) for tracers. The data were used to determine mass recoveries and dilution factors to evaluate performance. Effective diffusion coefficients were estimated by fitting the analytical solutions of selected functions to the breakthrough curves plotted using the simulated measured data.
2. Materials and Methods

2.1. Numerical Model

The flow model used in this work was MODFLOW, the three-dimensional (3D) finite-difference numerical model developed by the U.S. Geological Survey (McDonald and Harbaugh, 1988; Harbaugh et al., 2000). The 3D solute transport model MT3D (Zheng, 1990) was used to simulate solute transport. Groundwater Vista (GV) (Rumbaugh and Rumbaugh, 2007) and Groundwater Modeling System (GMS) (EMRL, 2005) were used as graphical user interfaces.

The model domain was 247,500 square meters. The domain was divided into a regular orthogonal grid consisting of 45 rows and 50 columns with grid space ranging from 0.625 m to 73 m. The test zone where the injection-extraction well systems were set up was 10x5 m with 0.625x0.625 m for each grid cell.

Specified head boundaries were used along the four borders of the domain, with natural gradient 0.001 under confined conditions inducing groundwater flow from the left to right side. Parameters used in the model were determined according to information generated from geologic borehole-logs, pumping tests, and historic data from the Tucson International Airport Area Superfund site (Zhang and Brusseau, 1999). K of 10 m/d and porosity of 0.2 were used for sand units, whereas K of $10^{-4}$ m/d and porosity of 0.3 were used for clay units. Longitudinal dispersivity was set to 0.05 m, and transverse, and vertical dispersivities were set to 0.005, and 0.0005 m, respectively. The aqueous diffusion coefficient was $7.6 \times 10^{-3} \text{ m}^2/\text{d}$. 
2.2. Approach

The simulation experiments were designed to represent implementation of a single set of CET tests conducted at a site with existing contamination. The zone influenced by the CET tests will be referred to as the test zone. The test zone is assumed to be surrounded by a groundwater contaminant plume, wherein regional flow occurs under the original natural hydraulic gradient.

Three specific well-field configurations were evaluated. The first one is the traditional configuration with a single pair of injection-extraction wells (Fig. 1A), which was used as a control. The second one is modified configuration I, with one extraction well located between two injection wells (Fig. 1B). The third one is modified configuration II, with two pairs of injection-extraction couplets wherein one is nested within the other (Fig. 1C).

Four types of domains were simulated, homogeneous (control), layered, 2D heterogeneous, and fully 3D heterogeneous. For the homogeneous simulation, the domain was set as sand with a thickness of 3 m. For the layered simulation, the domain was split into three units, with the upper and lower units as clay of 1 m thickness for each and the middle unit as sand with 3 m thickness. For the fully 3D heterogeneous system, a random field generator (Gutjahr, 1989) was used to derive realizations of K for the sand unit of the domain. It was assumed that the permeability of the sand was lognormally distributed with mean \( \langle \ln K \rangle \) and variance \( \sigma_y^2 \). The random fields were generated with an arithmetic mean value of K equal to 10 m/d, \( \sigma_y^2 \) as 10, and correlation scales of 0.5 m (longitudinal).
x 0.25-m (transverse) x 0.1-m (vertical). For the 2D heterogeneous system, the domain was generated randomly similarly to the fully heterogeneous domain, but with uniform K in vertical direction.

Four scenarios were simulated for the homogeneous domain. The purpose of scenario 1 is to investigate the isolation of the extraction well from the surrounding plume. In scenario 1, the test zone was clean, and the surrounding plume was present. For the standard (control) configuration, clean water was injected with an injection rate of 3 m$^3$/d, and extracted at the same rate. For modified configuration I, water was injected into both injection wells with the injection rate of 1.5 m$^3$/d for each and was extracted from the middle well with rate of 3 m$^3$/d. For configuration II, the injection rates for In1 and In2 were 1 and 2 m$^3$/d, respectively, and the extraction rate was 1.5 m$^3$/d for each extraction well.

Scenarios 2, 3, and 4 were simulated only for configuration II. Table 1 lists a summary of simulations conducted with configuration II for various conditions. For scenario 2, the time needed to remove resident contaminant from the test zone was examined. In scenario 2, the entire domain was contaminated, and clean water was injected via both injection wells with rates of 2 m$^3$/d for In2 and 1 m$^3$/d for In1. Scenario 3 was simulated to test the magnitude of mass recovery for the inner extraction well Ex1. In scenario 3, the initial contaminant concentration was zero for the entire domain, clean water was injected via In2 with an injection rate of 2 m$^3$/d, and tracers were injected via In1 continuously during the simulation period with an injection rate of 1 m$^3$/d. The
extraction rates were 1.5 m$^3$/d for each extraction well for all three scenarios, and the simulated time periods were 500 days.

For scenario 4, pulse injection of tracer was applied, and the concentration was monitored from Ex1 for much longer period than the injection time. Breakthrough curves plotted using collected concentration data were analyzed and used to determine attenuation parameters. In scenario 4, clean water was injected via In2 with an injection rate of 2 m$^3$/d, and tracer was injected via In1 with a rate of 1 m$^3$/d continuously for 10 days followed by clean water injection for 100 days. No background plume was present. In scenario 4, the distance between inner injection-extraction well couplet for configuration II was 3.125 m, whereas for the other three scenarios, the distance was 4.375 m. Breakthrough curves of data collected from the extraction wells were plotted to analyze the performance of each configuration.

The same scenario setup used above was used for the layered simulations, with modifications to address the presence of the clay units. In scenario 1a, the clay units within the test zone were contaminated whereas the sand unit within the test zone was clean, and the plume was present. In scenario 1b, the entire test zone was clean and the plume was present. In scenario 1c, the upper and lower units were contaminated and K values for the upper and lower units were changed such that all three units were set as sand (homogeneous). For Scenarios 2, 3, and 4, the plume is present in the sand and clay units. Simulations for all scenarios were repeated for the 2D heterogeneous domain. Additional CET tests with different extraction rate distributions and distance between the inner injection-extraction well couplet were simulated for the 2D heterogeneous system.
Simulations for scenarios 1, 2 and 4 were conducted for the 3D heterogeneous domain. In all scenarios, the injection and extraction wells were screened only in the vertically central 3 m of the domain.

2.3. Estimation of effective diffusion coefficients

Breakthrough curves and mass discharge data collected from Ex1 in CET tests with configuration II were analyzed. Two selected mathematical functions were used to determine the effective diffusion coefficient. Method 1 is based on the matrix diffusion model that was developed by Parker et al. 1994 with configuration of two clay units on top and bottom, and a sand unit in the middle. In a tracer test, the only contamination source was the injection via the well screened in the sand unit. When the injection started, the contaminant concentration in the sand unit was higher than the clay unit, which induced diffusion into the clay units. The mass discharge rate and the total mass loaded into clay during this period can be described as (Parker et al. 1994; AFCEE, 2007; Mcdade et.al, 2013):

\[ J_a (t \leq t') = \phi_{\text{clay}} C_r A \left[ \sqrt{\frac{R_{\text{clay}} D_e}{\pi t}} \right] (1), \]

\[ M (t \leq t') = 2\phi_{\text{clay}} C_r A \sqrt{\frac{R_{\text{clay}} D_e t}{\pi}} (2), \]

where \( J_a [M/T] \) is the mass discharge rate from the sand to clay unit, \( M [M] \) is the total mass loaded into the clay unit, \( t' \) is the time when injection stopped. \( \phi_{\text{clay}} \) is the porosity.
of the clay unit, $C_p [M/L^3]$ is the average concentration in the study area (with the continuous injection, we assume it equals to the concentration injected), $A [L^2]$ is the area that is influenced by extraction well, $R_{clay}$ (equal to 1 in this study) is the retardation factor for clay units, and $D_e$ is the effective coefficient.

The model was developed with the major assumption that the mass in the sand unit is immediately removed after the loading period stops at time $t'$. Then mass starts to diffuse back to the sand unit. Here we considered as the residence time, $t_R [T]$ that is calculated by moment analysis with $M_0, M_1$ are zeroth and first moment, respectively:

$$t_R = \frac{M_1}{M_0} - \frac{t'}{2} \quad (3)$$

The mass discharge rate and the estimated mass that remains in the clay unit during the back diffusion period are (AFCEE, 2007; Mcadde et.al, 2013):

$$J_e(t \geq t') = \phi_{clay} C_p A \left\{ \sqrt{\frac{R_{clay} D_e}{\pi(t-t')}} - \sqrt{\frac{R_{clay} D_e}{\pi t}} \right\} \quad (4),$$

$$M(t \geq t') = 2\phi_{clay} C_p A \sqrt{\frac{R_{clay} D_e}{\pi}} (\sqrt{t} - \sqrt{t-t'}) \quad (5)$$

Based on total mass that was loaded in the clay and the remaining mass, corrected by residence time, the mass diffused out from the clay can be calculated by:

$$M_{out}(t > t') = 2\phi_{clay} C_p A \sqrt{\frac{R_{clay} D_e}{\pi}} \left( \sqrt{t-t'} - \frac{t_R}{2} - \sqrt{t} + \sqrt{t + \frac{t_R}{2}} \right) \quad (6)$$
Results calculated by analytical solution (6) will be fitted to simulated cumulative mass collected from Ex1 during time period from $t' + \frac{t_e}{2} \text{ to } t$ by optimizing the $D_e$ value. Here we assume that all mass that diffused back to the sand unit was recovered by Ex1, which is true according to the simulated results.

Method 2 is based on fitting a selected function to breakthrough curves (Cunningham et al., 1997; Haggerty et al., 2000). Based on the modeling setup, the total simulation time ($t$) and the mean residence time in the immobile domain (clay units) are much longer than the mean residence time ($t_{ad}$) in the advective domain. Therefore, the mass balance equation can be written as:

$$-\frac{v}{R_a} \frac{\partial C}{\partial x} = \Gamma(x, t), \quad (7)$$

where $\psi$ [L/T] is pore fluid velocity, $R_a$ is the retardation factor in mobile zone, $C$ [M/L$^3$] is the solute concentration, and $\Gamma(x, t)$ [M/L$^3$/T] is the source-sink term based on mass exchange with immobile domain and sorption. We can solve the equation (7) by integration:

$$C(x = L, t) = -\int_0^t \frac{R_a(x)}{\psi(x)} \Gamma(x, t) dx \quad (8)$$

It can be further simplified as:

$$C(x = L, t) = -t_{ad} \Gamma(t) \quad (9)$$

For linear mass transfer problem with uniform initial conditions, it can be expressed as:

$$\Gamma(t) \cong M_0 \frac{\partial g}{\partial t} - C_0 g, \quad (10)$$
where \( M_0 \) is the zeroth moment of injection, \( g(\tau) \) is a “memory function” to be defined \([T^{-1}]\) and in this problem using finite layer model, the corresponding function is:

\[
g(t) = \sum_{j=1}^{\infty} 2 \beta_{\text{tot}} D_u a^2 \exp \left[ -\frac{(2j-1)^2 \pi^2 D_u a^2}{4} t \right], \quad (11)
\]

where \( \beta_{\text{tot}} \) is the capacity coefficient that represents the ratio of mass in immobile to mass in mobile domain (sand units), which can be expressed as:

\[
\beta_{\text{tot}} = \frac{R_{im} \theta_{im}}{R_m \theta_m} \quad (12)
\]

\( D_a[L^2/T] \) is apparent diffusion coefficient, equal to:

\[
D_u = \frac{D_a}{R_{im}} \quad (13)
\]

\( D_u \) is effective pore diffusion coefficient, \( a[L] \) is the distance from the center to the edge of immobile zone, and \( j \) is index of \( N \) distinct immobile phase. \( C_0[M/L^3] \) is the initial concentration. Employing (9) and (10), we obtain the solution for concentration:

\[
C = t_{\text{ad}} (C_0 g - M_0 \frac{\partial g}{\partial t}) \quad (14)
\]

The diffusion coefficient was determined by fitting the late-time tailing of breakthrough curves plotted using the analytical solution (14) to the simulated curves obtained from the numerical modeling.

### 3. Results and Discussion

#### 3.1. Isolation of the extraction well
Three well-field configurations were tested to determine the isolation of the extraction well from the surrounding plume. Breakthrough curves for scenario 1 in the homogeneous domain are shown in Fig. 2A. For the simulation with modified configuration II, data were collected from Ex1. After a small concentration increase at the beginning of the test, the concentration decreases to zero and stays at zero during the test period for configuration II. After the test started, contaminant from the surrounding plume was pulled into the extraction well, resulting in the concentration increase at the beginning. However, after water injected via In2 was captured by Ex2, Ex1 was isolated from the regional plume. Conversely, concentrations for both the traditional configuration and configuration I reach asymptotic conditions in later periods because the regional flow was captured by the extraction well. The results indicate that configuration II provided full isolation of Ex1 from the plume. Therefore, this configuration was the focus of additional investigation.

Breakthrough curves for scenario 1b with configuration II in the layered domain are presented in Fig. 2B. Concentrations stabilize at certain values in the later period as a result of back diffusion. For the simulation in which the entire clay was contaminated, the concentration stabilizes at a higher value than does the simulation in which the entire test zone was clean. These results are in contrast to those obtained for the simulations for the homogeneous domain, wherein the concentrations decrease to 0.

Breakthrough curves for scenario 1 for the 2D heterogeneous domain with clay present and absent are presented in Fig. 2C. An asymptotic elution curve is observed for the simulation where clay was absent. Conversely, as noted above, no tailing was
observed for the homogeneous simulations. These results suggest that Ex1 is still influenced by the surrounding plume for the 2D heterogeneous simulation, which can be attributed to the preferential flow caused by the permeability heterogeneity. The breakthrough curve for the simulation with clay present shows greater tailing than the curve for the corresponding simulation with no clay, exhibiting the additional impact of back diffusion.

A simulation was conducted with an adjusted distance between the inner well couplet, In1 and Ex1, from 4.375 m to 3.125 m. It shows that the concentration stabilizes at a very low C/C₀ value. Therefore, full isolation of Ex1 was established with the adjustment.

The isolation status of Ex1 was examined for the 3D heterogeneous domain and the results are presented in Fig. 2C. It shows breakthrough at a higher concentration value and longer tailing than the results for the 2D heterogeneous domain. Clearly, Ex1 was influenced by the outside plume. However, in fields that have less heterogeneity, the isolated region is relatively easy to be formed with appropriate distribution of wells as discussed above.

A contaminant plume is typically present at sites of interest, which may influence results obtained for CET tests. Therefore, the time required to remove resident dissolved contaminant from the advective portion of the test zone was simulated. Forty three days (2.2PV) were required to sweep the test zone for the homogeneous simulation, whereas 90 days (4.5PV) were required for the layered simulation (Fig. SM-2). The late-time tailing of the breakthrough curve for this scenario and the curves for scenario 1 in which
the sand unit within the test zone was clean are essentially identical, which indicates that after the test zone was swept, Ex1 was fully isolated from the plume and the tailing is caused by back diffusion. For the 2D simulation, approximately 150 days (7.7 PV) was required to sweep the test zone. For the 3D simulation, because of preferential flow, Ex1 remained impacted by the surrounding plume.

3.2. Magnitude of mass recovery

The magnitude of mass recovery for concentration data collected from Ex1 for the homogeneous and layered simulations was investigated in scenario 3 for which the entire domain was clean and the tracer was injected via In1. Data were collected from both extraction wells. Cumulative mass extracted from each well was calculated. The magnitude of mass recovery for Ex1 was defined as the ratio of mass extracted from Ex1 to the total mass extracted from both wells. Results are presented in Fig. SM-1 and Table 2. Mass balance was checked by comparing the mass injected in the domain to the total mass extracted from wells and mass remaining in the domain. Mass balance was conserved for all simulations with errors within ±5%. All mass was recovered by Ex1 for the homogeneous and layered simulation (Table 2). As seen in Fig. SM-1, the concentration for Ex1 for both homogeneous and layered simulations reached steady state and the concentration for Ex2 stabilized at 0 during the entire simulation period. According to the results of scenario 1, with the same well-field configuration, Ex1 was completely isolated from the surrounding plume, therefore, the dilution for Ex1 was only
caused by water injected via ln2. All mass removed from the domain was attributed to extraction from Ex1.

The mass recovery proportions for Ex1 were also calculated for scenario 4 that the tracer was injected for 10 days followed by clean water injection in different conditions: homogeneous, layered, and 2D and 3D heterogeneous domains and listed in Table 2. Low mass recovery for Ex1 was observed for both 2D and 3D heterogeneous simulations due to preferential flow phenomena. As discussed above for results of scenario 1, with the same well-field configuration, Ex1 was still impacted by the surrounding plume, therefore, significant dilution caused by the regional flow also occurred in this scenario. Additional simulations wherein the distance between injection and extraction wells and flow rates were changed were simulated in the 2D heterogeneous domain to investigate the impact of these two factors on mass recovery and dilution. These simulations and the corresponding mass recovery proportions are listed in Table SM-1. With the closer distance between inner well couplets changed from 4.375 m to 3.125 m, and larger pumping rate in Ex1, the mass recovery increased to 99%. Moreover, according to the results for scenario 1, full isolation for Ex1 from the surrounding plume was established with adjustment of distance between inner well couplets. These results indicate that appropriate distance between coupled injection-extraction wells and flow rates distribution can increase the mass-recovery proportion and decrease the dilution impact from regional flow for Ex1 significantly.

3.3. Parameter estimation for tracer tests with pulse injection
Breakthrough curves produced for scenario 4 are presented in Fig. 3. The breakthrough curve for the homogeneous simulation shows the most ideal behavior wherein after breakthrough, the concentration drops continuously to 0. Conversely, the breakthrough curves exhibit different degrees of tailing for the layered and heterogeneous simulations. The asymptotic condition is attained at a much lower concentration value for the 2D heterogeneous simulation than the layered simulation. This occurred because the mass was trapped in the region north of Ex1 in the sand (Fig. SM-3) wherein the permeability was the relatively low. As a result, after tracer injection stopped, the concentration in the regions of the clay layer right above the sand wherein Ex1 was screened was lower than the concentration in the regions surrounding Ex1 within the sand unit (Fig. SM-4), leading to a lower persistent concentration.

Effective diffusion coefficients were estimated for layered and heterogeneous simulations using two selected functions. Results are shown in Table 3. The values estimated by both methods are lower than the input value used for the numerical model. The calculated errors of the estimation compared to the input value are approximately 20% for method 1 and 60%~80% for method 2. According to the results in Table 3, method 1 provided close estimations in three different conditions, which indicates that the heterogeneity of the field did not have a significant impact on parameter estimation.

Method 1 was based on a matrix diffusion model. The configuration that was used to develop the model was based on uniformly distributed concentration in the high-permeability unit during the loading period and a key assumption was made that the plume was removed immediately at time t’ when the loading process stopped (McLade
et.al, 2013). Conversely, for this study, the contaminants were injected via the injection well, transported along with groundwater flow, and captured by the extraction well screened in the high permeable units within the test zone. Therefore, the concentration was not uniformly distributed and a certain amount of time was needed until the contaminant was removed from the transmissive unit. The differences in configurations contributed to the lower estimation of the effective diffusion coefficient.

The breakthrough curves for model simulations and associated analytical solutions for method 2 are presented in Fig. SM-6. The analytical solutions match the late-time tailing behavior of the simulated breakthrough curves for the three different conditions, but the calculated errors of the estimation compared to the input value are as high as 79%. This is because the analytical solution was developed to characterize the coefficient from a single-well injection-withdrawal tracer test. For the coupled injection-extraction system in this study, the flow field around Ex1 is impacted by the pumping of Ex2, which is another reason for the resulting smaller estimated results.

Both methods, with appropriate modification, can be used to estimate other parameters such as retardation factor by using a suite of tracers. Therefore, conjunction of the collected field data from a CET test with appropriate functions can be used to investigate specific attenuation process and provide a decent estimation of field parameters, which is efficient and economical for site characterization.

4. Summary
Two modified well-field configurations were studied in homogenous, layered, and heterogeneous domains using 3D numerical modeling. Different scenarios were simulated to investigate the isolation status of and mass recovery for the extraction well, and the time frame to remove resident contaminant from the test zone. Results demonstrate that the inner extraction well (Ex1) can be fully isolated from the plume with configuration II. The impact of dilution from regional flow on concentration for Ex1 can be eliminated with appropriate well and flow rate distributions. The time period to remove resident contaminant from the test zone depends on the domain size and pumping rate.

CET tests were simulated with configuration II under different conditions. Two functions were selected to perform parameter determination. Both methods provided lower estimations for effective diffusion coefficient, but the calculated error of estimated value with input value for method 1 is approximately 20%. The results of the simulated scenarios demonstrate that CET test can be an effective way to collect critical site-specific data, which can be used to delineate attenuation processes. Applying the selected functions can be an efficient method for parameter estimation, as it does not require the use of mathematical transport modeling and does not require the attendant input data that are costly and time-consuming to obtain. This characterization concept can be a useful and economical tool to understand the transport and attenuation processes, and also can provide guidance for long term site management.
Acknowledgements

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Reference


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Technology & Regulatory Council, Enhanced Attenuation Chlorinated Organics (EACO)
Team.

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Table 1 Summary of simulations conducted with configuration II in various conditions

<table>
<thead>
<tr>
<th>Cases</th>
<th>Simulation ID</th>
<th>Well-field</th>
<th>Aquifer</th>
<th>Initial condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigate Isolation of extraction well</td>
<td>1</td>
<td>Traditional ECET</td>
<td>Homo</td>
<td>Test zone was clean, background was contaminated. Clean water was injected via injection well.</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>*MWC I</td>
<td>Homo</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>MWC II</td>
<td>Homo</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>MWC II</td>
<td>Layered</td>
<td></td>
</tr>
<tr>
<td>S1a</td>
<td>5</td>
<td>MWC II</td>
<td>2D Heter</td>
<td>The clay layers were all contaminated.</td>
</tr>
<tr>
<td>S1b</td>
<td>6</td>
<td>MWC II</td>
<td>2D Heter</td>
<td>The regions in clay above and below the test zone were clean.</td>
</tr>
<tr>
<td>S1c</td>
<td>7</td>
<td>MWC II</td>
<td>3D Heter</td>
<td>The upper and lower layers were contaminated, and all three layers were set as sand.</td>
</tr>
<tr>
<td>Note: Distance of inner well couplets was 4.375 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time period to clean test zone</td>
<td>1</td>
<td>MWC II</td>
<td>Homo</td>
<td>The whole domain was contaminated. Clean water was injected via both injection wells.</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>MWC II</td>
<td>Layered</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>MWC II</td>
<td>2D Heter</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>MWC II</td>
<td>3D Heter</td>
<td></td>
</tr>
<tr>
<td>Magnitude of dilution of extraction well</td>
<td>1</td>
<td>MWC II</td>
<td>Homo</td>
<td>The whole domain was clean. In2 injected clean water, In1 injected contaminants with constant concentration 1g/m³. Dilution of Ex1 was determined.</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>MWC II</td>
<td>Layered</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>MWC II</td>
<td>2D Heter</td>
<td></td>
</tr>
<tr>
<td>CET test</td>
<td>1</td>
<td>MWC II</td>
<td>Homo</td>
<td>The whole domain was clean. In2 injected clean water, In1 injected tracer for 10 days followed by clean water injection.</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>MWC II</td>
<td>Layered</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>MWC II</td>
<td>2D Heter</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>MWC II</td>
<td>3D Heter</td>
<td></td>
</tr>
</tbody>
</table>

* Modified well configuration
### Table 2 Magnitude of mass recovery for Ex1

<table>
<thead>
<tr>
<th></th>
<th>Mass in (g)</th>
<th>Mass out (g)</th>
<th>Remaining mass (g)</th>
<th>Error</th>
<th>Magnitude of mass recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>injected</td>
<td>extracted by Ex1</td>
<td>extracted by Ex2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homo¹</td>
<td>500.00</td>
<td>498.9</td>
<td>0.003</td>
<td>8.67</td>
<td>-1.5%</td>
</tr>
<tr>
<td>Layered¹</td>
<td>500.00</td>
<td>473.9</td>
<td>0.002</td>
<td>8.57</td>
<td>3.5%</td>
</tr>
<tr>
<td>Homo²</td>
<td>10.00</td>
<td>10.09</td>
<td>0.073</td>
<td>0.00</td>
<td>-1.7%</td>
</tr>
<tr>
<td>Layered²</td>
<td>10.00</td>
<td>9.63</td>
<td>0.07</td>
<td>0.29</td>
<td>0.1%</td>
</tr>
<tr>
<td>2D Heter²</td>
<td>10.00</td>
<td>7.73</td>
<td>1.94</td>
<td>0.29</td>
<td>0.3%</td>
</tr>
<tr>
<td>3D Heter²</td>
<td>10.00</td>
<td>4.74</td>
<td>3.89</td>
<td>1.24</td>
<td>1.3%</td>
</tr>
</tbody>
</table>

¹ For scenario 3, mass was injected constantly via In1 through the entire simulation period.
² For scenario 4, mass was injected via In1 for 10 days followed by clean water injection for 100 days.
Table 3 Estimated diffusion coefficient (cm$^2$/d) using two selected functions in different conditions

<table>
<thead>
<tr>
<th>Domains</th>
<th>Method 1 estimation (Error)</th>
<th>Method 2 estimation (Error)</th>
<th>Model input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered</td>
<td>60 (-21%)</td>
<td>31 (-59%)</td>
<td>76</td>
</tr>
<tr>
<td>2D heterogeneous</td>
<td>56 (-26%)</td>
<td>16 (-79%)</td>
<td></td>
</tr>
<tr>
<td>3D heterogeneous</td>
<td>60 (-21%)</td>
<td>25 (-67%)</td>
<td></td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. CET tests well-field configuration. A. Traditional single injection-extraction dipole configuration. B. Modified coupled injection-extraction configuration I. C. Modified coupled injection-extraction configuration II.

Figure 2. Breakthrough curves for scenario 1 with three different well configurations. A. Homogeneous domain. B. Layered domain. C. 2D and 3D heterogeneous domain. In figure 2B, different IC represents the results for scenario 1a that the clay within the test zone has different initial concentration with the sand within the test zone, and same IC represents the results for scenario 1b that initial concentration in test zone is uniformed. In figure 2C, the results for simulations conducted in 2D and 3D heterogeneous domain with clay present are shown. Additional results for simulations conducted in 2D heterogeneous domain with clay absent are also present.

Figure 3. CET tests for scenario 4 with modified configuration II under different conditions. A. Arithmetic scale. B. Logarithmic scale.
Figure 1
Figure 2A
Figure 2B
Figure 2C
Supplementary Materials

Modified Well-Field Configurations for Improved Performance of Contaminant Elution and Tracer Tests

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To be determined

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This supplementary material includes tables and figures referenced in the manuscript.

Table SM-1 Simulations conducted in horizontal heterogeneous domain with different distance between well couplet and flow rates.

<table>
<thead>
<tr>
<th>Simulation ID</th>
<th>Distance In1-Ex1 (m)</th>
<th>Injection rate (m$^3$/d)</th>
<th>Extraction rate (m$^3$/d)</th>
<th>mass recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In1</td>
<td>In2</td>
<td>Ex1</td>
</tr>
<tr>
<td>1</td>
<td>4.375</td>
<td>1</td>
<td>2</td>
<td>-1.5</td>
</tr>
<tr>
<td>2</td>
<td>4.375</td>
<td>2</td>
<td>4</td>
<td>-3</td>
</tr>
<tr>
<td>3</td>
<td>3.125</td>
<td>2</td>
<td>4</td>
<td>-3</td>
</tr>
<tr>
<td>4</td>
<td>3.125</td>
<td>1</td>
<td>2</td>
<td>-2</td>
</tr>
<tr>
<td>5</td>
<td>3.125</td>
<td>2</td>
<td>4</td>
<td>-4</td>
</tr>
</tbody>
</table>
Figure SM-1. Breakthrough curves for scenario 3 with Modified configuration II to investigate the dilution impact on Ex1. A. Homogeneous domain. B. Layered domain.
Figure SM-2. Breakthrough curves for scenario 2 with Modified configuration II to investigate the time frame to clean a test zone. A. Homogenous domain. B. Layered domain. C. 2D and 3D heterogeneous domain.
Figure SM-3. Hydraulic conductivity distribution map of top layer in sand that adjoining with clay.
Figure SM-4. Concentration contour map of clay layer adjoining with sand in 2D heterogeneous domain. A. 1 day after stop tracer injection. B. 40 days after stop tracer injection.
Figure SM-5. Concentration contour map of clay layer adjoining with sand in layered domain. A. 1 day after stop tracer injection. B. 40 days after stop tracer injection.
C

Figure SM-6. Fitting curves produced by selected function 2 with breakthrough curves plotted by modeling results. A. Layered domain. B. 2D heterogeneous domain. C. 3D heterogeneous domain.
Appendix E

The Enhanced Contaminant Elution and Tracer Test for Improved Characterization of Natural Attenuation and Plume Persistence

This appendix includes results that will be used to support development of a future manuscript.

Natural and enhanced attenuation are primary alternatives for long-term management of groundwater contaminant plumes. The ECET test is developed as an improved method for characterizing critical natural-attenuation processes that impact the transport, fate, and remediation of contaminants in complex, heterogeneous subsurface environments. The test is based on the use of extended groundwater extraction to stress the system and induce hydraulic and concentration gradients. Injection wells are coupled to the extraction well to allow injection of clean water, which removes the resident aqueous contaminant mass present in the higher-permeability zones and isolates the test zone from the surrounding plume. Hence, this method ensures that the concentrations and fluxes measured within the isolated area are directly and predominantly influenced by the mass-transfer (back diffusion, desorption) and transformation processes controlling attenuation. A suite of standard and novel tracers is used to delineate specific attenuation processes that are active at a given site, and to quantify the associated mass-transfer and transformation rates. An illustrative application based on simulations produced with a 3-D mathematical model is presented.
Numerical Model

The flow model used in this work was MODFLOW, the three-dimensional (3D) finite-difference numerical model developed by the U.S. Geological Survey (McDonald and Harbaugh, 1988; Harbaugh et al., 2000). The 3D solute transport model MT3D (Zheng, 1990) was used to simulate solute transport. Groundwater Vista (GV) (Rumbaugh and Rumbaugh, 2007) and Groundwater Modeling System (GMS) (EMRL, 2005) were used as graphical user interfaces.

The model domain was 625 square meters. The domain was divided into a regular orthogonal grid consisting of 100 rows and 100 columns with grid space 0.25-m x 0.25-m. The test area where the injection-extraction well systems were set up was 5-m x 3-m. The thickness of the domain was 10 m, which was split into 10 layers with 1 m thickness for each layer. A random field generator (Gutjahr, 1989) was used to derive realizations of $K$ for the domain. It was assumed that the permeability of the sand was lognormally distributed with mean $\langle \ln K \rangle$ and variance $\sigma^2$. The simulations were conducted in a domain with permeability heterogeneity of mean $K$ as 10 m/d and $\sigma^2$ as 5. Specified head boundaries were used along right and left borders of the model, with natural gradient 0.01 under confined conditions inducing groundwater flow from the left to right side. Parameters used in the model were determined according to information generated from geologic borehole-logs, pumping tests and historic data of Tucson International Airport Area Superfund site (Zhang and Brusseau, 1999). Porosity of 0.3 was used. Longitudinal dispersivity was set to 0.05 m based on standard grid-Peclet number criteria,
and transverse, and vertical dispersivities were set to 0.005, and 0.0005 m, respectively. The aqueous diffusion coefficient of $7.6 \times 10^{-3}$ m$^2$/d and porosity of 0.2 were used (Table 1).

Four tracer tests and one contaminant elution test were simulated. Two injection wells were used with flow rate of 10 m$^3$/d for each well and one extraction well located between injection wells was used with extraction rate of 20 m$^3$/d. The injection and extraction wells were screened through the entire thickness of the domain. For tracer tests, the initial contaminant concentration was zero for the entire domain, the tracers were injected via the upgradient injection well and clean water was injected via the downgradient injection well. Four different tracer were used: in first simulation, non-reactive tracer (NRT) with diffusion coefficient of 0.0076 m$^2$/d was injected; in second simulation, NRT with diffusion coefficient of 0.00076 m$^2$/d was used; in third simulations, sorptive tracer with diffusion coefficient 0.0076 m$^2$/d and retardation as 3 was used. First order kinetics was applied with mass transfer coefficient as 15 d$^{-1}$; in fourth simulation, first order irreversible kinetics was used to simulate the transformation process, with dissolved rate constant as 0.04 d$^{-1}$. For the contaminant elution test, the entire domain was contaminated with initial concentration as 1 g/m$^3$, clean water was injected via injection wells. Temporal continuous data were collected from the extraction well for all simulations.

**Results**
The elution curve for the resident contaminant and breakthrough curves for the tracers produced using the time continuous concentrations are presented in Figure. 1. The different transport behaviors with different amounts of spreading and different extents of tailing are observed for two tracers with different diffusion coefficients. The breakthrough of the curve for the sorptive tracer occurs much later compared to the curves for non-reactive tracers because of the impact of retardation. The concentrations for the transformation tracer test were much lower as a result of degradation. The long tailing is observed in the elution curve for the resident contaminant, which is attributed to the influences of surrounding plume and back diffusion. These different behaviors reflected in the breakthrough curves are the results of the contributions of individual processes to natural attenuation, including back diffusion, desorption, biotransformation, and abiotic transformation. The applied well-field configuration minimized the impact of surrounding plume to a certain degree, however, the extraction well was still not completely isolated. Further studies on specific well-field configurations to better apply the ECET test should by conducted.

Reference


Figure 1
Appendix F

Impact of vertical dispersivity and diffusion

This appendix includes the results of additional simulations conducted to investigate impact of the vertical dispersivity and diffusion on the mass-removal process.

Impacts of vertical dispersivity

The dispersion is an important parameter that impact the contaminant transport process. Mechanical dispersion (D) describe the mixing process that caused by variation of velocity around the mean flow velocity. It comprises of three components along three perpendicular coordinates (x, y, z):

\[
D = D_L + D_T + D_V = \alpha_L u_x + \alpha_T u_y + \alpha_V u_z
\]

where \(\alpha_L, \alpha_T, \alpha_V\) are dispersivities in three directions, longitudinal, transverse, vertical dispersivity; \(u_x, u_y, u_z\) are velocities in three directions. The longitudinal dispersivity is generally determined by field pumping tests, the transverse dispersivity is in a range of 5%~30% of longitudinal dispersivity, and the vertical dispersivity if in a range of 0.5%~5% of longitudinal dispersivity (e.g., Morrison, 2000; Lovanh et al., 2000). In this study, the longitudinal dispersivity was determined as 5 m according to the pumping tests conducted at TIAA site. The vertical dispersivity represents the vertical extent of distance that the dissolved contaminant phase can spread in aquifer. It cannot be neglected when the vertical variance of permeability is significant, such as the low permeable lenses or aquitard present in the aquifer. In these situations, the vertical dispersivity is one of the
important components that control the mass transports among the regions with different permeability.

Five different vertical dispersivity coefficient $\alpha_v$, 0, 0.0005, 0.001, 0.005, 0.05 m were tested in layered domain with natural gradient. The vertical dispersion, composed by the diffusion and mechanical dispersion, is the dominant factor that control the dissolution process, which induces the contaminant transport from low K layer to higher K layer. It is generally expressed as (Johnson and Pankow, 1992):

$$D_v = D_{\text{diff}} + \alpha_v \bar{v}$$

(2)

where $D_v$ is the vertical dispersion coefficient (m$^2$/d), $D_{\text{diff}}$ is the diffusion coefficient (m$^2$/d), and $\bar{v}$ is the average groundwater velocity (m/d). The results of sensitivity of mass removal process on $\alpha_v$ are presented in Fig.1. Clearly, mechanical dispersion influences prominently in the vertical dispersion process. For the scenario $\alpha_v$=0, the evident tailing suggests the weak diffusion contribution to the mass removal. The $\alpha_v$ in this study was set as 0.001 by comparing the elution curves to results of two-domain model developed by Dr. Brusseau (For details, see Brusseau, 1991). Based on previous researches, it is reasonable having the transverse dispersivity coefficient ($\alpha_T$) value as 0.5 m and vertical dispersivity coefficient ($\alpha_v$) value as 0.001 m.

**Impact of diffusion**

The diffusion impact on mass removal behavior for homogenous simulations with Longitudinal well field is presented in Fig. 2. Elution curves and CMDR-MR profiles are
identical for simulations with or without diffusion. This is because that the whole domain was accessible by groundwater, and advection is the primary process to remove contaminants.

The comparison results for the Longitudinal and Downgradient well-field configurations with diffusion and without diffusion in layered domain are presented in Fig. 3. It is obvious that according to the elution curves, the simulations that mass transfers without diffusion impact have relatively longer tailing than their counterparts with diffusion. The tailing for simulation without diffusion impact is a result of vertical dispersivity as discussed above. This eventually leads to that within the same time, the simulations with diffusive mass-transfer removed more mass than the simulations wherein mass was only removed under advection and dispersion influence. Take the Longitudinal well field simulations as examples, by the end of the simulation, the total mass removed for the simulation that had undergone diffusion is 63% of initial mass, whereas the one that didn’t conduct diffusion was 53%, approximately 10% less. However, before the mass in the high K zone was completed removed, there was no obvious difference between mass removal behaviors with diffusion or without diffusion effect, because during this period, the advection influence was significant and diffusion impact was negligible (Fig. 3C).

Fig. 4 presents the remaining mass distribution in the scenarios with the Longitudinal well field in the layered domain. After 0.8 PV of water was pumped out, almost all of the mass in the sand unit had been removed and the remaining mass was in the clay units; since then, the concentration decrease reached steady state for both
scenarios with or without diffusion impact (Fig. 3A). As expected, the concentration started to decrease asymptotically after this point.

Reference


Figure 1. Impact of mechanical dispersion on mass removal behavior, as represented by vertical dispersivity coefficient: (A) Elution curves; (B) Relationships between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR).
Figure 2. Impact of diffusion on mass removal behavior for the Longitudinal well-field configuration under homogeneous situation: A. Elution curves; B. CMDR-MR relationships.
C

Figure 3. Impact of diffusion on mass removal behavior for the Longitudinal and Downgradient well-field configurations in layered domain: A. Elution curves; B. CMDR-MR relationships; C. CMDR-MR relationships during the mass removal process in sand layer.
Figure 4. Mass distribution of longitudinal well-field simulation at different time periods.