

**Engineered Injection and Extraction to Enhance
Reaction for Improved In-Situ Remediation**

by

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Engineered Injection and Extraction to Enhance Reaction for Improved In-Situ Remediation

Thesis directed by Professor Roseanna M. Neupauer

Energy-efficient methods of remediating contaminated groundwater, such as in-situ remediation, have become increasingly relevant given the current state of rising water and energy usage across the globe. During in-situ remediation, a treatment solution is injected into a contaminated aquifer to degrade the groundwater contaminant in place. Since contaminant degradation reactions only occur at locations where the treatment solution and groundwater contaminant overlap each other, advective spreading of the treatment solution into the contaminated region is necessary. However, spreading in aquifers is generally poor as groundwater flow is laminar, and lacks turbulent eddies responsible for spreading in open flow systems. Researchers have demonstrated that stretching and folding can lead to spreading in laminar flow environments. These findings motivated the development of a technique known as engineered injection and extraction (EIE), which incorporates the principles of stretching and folding to improve spreading during in-situ remediation. During EIE, clean water is injected and extracted at wells surrounding a contaminant plume to create transient flow fields that stretch and fold the interface between the treatment solution and contaminant. Other researchers have conducted simulations to show that this technique leads to enhanced spreading; however, no evidence has been presented that enhanced spreading correlates to enhanced reaction. This study demonstrates that EIE enhances degradation of groundwater contamination in homogeneous and heterogeneous aquifers. Furthermore, this study shows that the reaction provided by the spreading due to EIE is greater than the reaction due to spreading from heterogeneity alone.

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Chapter 1

Introduction

1.1 Motivation

The “looming water crisis” is a prominent issue worldwide, as one fifth of the world’s population does not have access to clean water [UNESCO, 2000]. Since access to clean water is directly correlated to human health [Prüss-Üstün, 2008] and ninety-eight percent of the earth’s freshwater is groundwater (excluding freshwater locked away in icecaps), the protection of pure aquifers and the treatment / restoration of tainted aquifers is vital [UNESCO, 2000].

Conventional groundwater treatment methods, such as pump-and-treat, extract groundwater from the contaminated aquifer and treat it externally, using techniques like carbon adsorption or air-stripping [Berger, 1987]. Significant energy is required to extract and treat the contaminated groundwater. Byproducts of the external treatment systems can be hazardous, so their proper disposal is costly. The chosen destination of the treated groundwater dictates the degree to which the contaminant must be reduced. For instance, if the treated groundwater will be reintroduced to the aquifer, it must first be treated to land disposal restriction standards [EPA,

2000], which can be difficult to achieve (and therefore costly) depending on the particular contamination scenario.

In-situ remediation is an alternative method of groundwater treatment that avoids many of the problems associated with conventional methods. During in-situ remediation, a chemical treatment solution is injected into a contaminated aquifer to degrade the groundwater contaminant to a benign species [*Domenico and Schwartz, 1998*]. Common pairings of treatment solution and groundwater contaminant include chemical oxidants like potassium permanganate to treat chlorinated solvents like trichloroethene [*Zhang and Schwartz, 2000*]. Bioremediation is another form of in-situ remediation where nutrients and/or electron acceptors such as oxygen are injected into contaminated aquifers to enhance the natural propensity of soil microbes to reduce organic contaminants [*Nyer, 1985*] via terminal electron transfer [*Chapelle, 1992*].

Since in-situ remediation takes place at the location of the contamination (underground), this technology offers significant energy savings over conventional groundwater treatment methods, which extract the contaminated water from the subsurface to treat it externally [*Nyer, 1985*]. Furthermore, hazardous waste disposal is not an issue with in-situ remediation as the contaminated groundwater is never removed from the aquifer [*Nyer, 1985*]. For these reasons, in-situ remediation was recognized by the *EPA* [2008] as a form of “green remediation” in their guide for “Incorporating Sustainable Environmental Practices into Remediation of Contaminated Sites.”

As our world becomes increasingly dependent on groundwater resources, effective solutions to treat contaminated aquifers are ever more relevant. “Green” solutions are especially appropriate given the multitude of environmental issues faced presently. In-situ remediation provides an effective solution to groundwater treatment that uses less energy than conventional

treatment methods with minimal associated wastes. For these reasons, I regard the research / development of techniques to improve in-situ remediation to be a valuable and timely endeavor.

Although the beneficial aspects of in-situ remediation were already mentioned, some aspects of this technology could be improved. During in-situ remediation, the contact area between the treatment solution and contaminated groundwater limits the rate of contaminant degradation [*National Research Council, 2009*]. Typically, the contact area is small because only the perimeter of the treatment solution, which is relatively compact upon injection to the aquifer, touches the surrounding contaminant plume. Better spreading of the reactants to increase their contact area could dramatically increase reaction rate. To that end, the ultimate goal of this research is to enhance reaction during in-situ remediation by improving the spreading of reactants.

Spreading can occur in numerous natural and engineered systems. Of all systems, aquifers present a unique challenge for spreading since porous media prevents any traditional forms of mechanical stirring, and by definition, laminar flows (like groundwater flow) do not have turbulent eddies to create spreading in open channels and engineered reactors. *Spreading, stirring, and stretching* are all used to describe transport due to advection and macrodispersion, whereas *mixing* actually refers only to molecular diffusion and pore-scale dispersion. In this study, spreading is enhanced during transport to increase contact between treatment solution and groundwater contaminant during in-situ remediation. As many researchers have investigated spreading under various flow regimens, the next section will outline previous studies that provide relevant background for this one.

1.2 Background

Spreading depends on the structure of the flow [Dentz and Carrera, 2005]. In groundwater aquifers, the structure of the flow is primarily dictated by the heterogeneity of the porous media [Kitanidis, 1994]. However, recent studies modify this premise by asserting that *heterogeneous velocity* (rather than just heterogeneity) determines the structure of the flow, and consequently the spreading that ensues [Le Borgne et al., 2010], where heterogeneous velocity is not only attributed to heterogeneity, but also to other mechanisms such as temporal variations in fluid velocity [Dentz and Carrera, 2005].

Chaotic advection is one example where heterogeneous velocity can be generated without heterogeneity. Aref [1984] pioneered the field of chaotic advection, which many researchers have since applied. Particles in a fluid flow with chaotic advection exhibit sensitive dependence on their initial conditions, such that small changes in the initial conditions can result in progressively larger changes at later system states. Although chaotic advection can occur under a variety of flow conditions [Stremmer et al., 2004], it requires at least two-dimensional (2D) unsteady or three-dimensional (3D) steady flow [Ottino, 1989].

Several theoretical models demonstrate chaotic advection in laminar flows, including the blinking vortex [Aref, 1984], eccentric cylinders [Swanson and Ottino, 1990], and the pulsed dipole model [Jones and Aref, 1988], and the rotating pulsed dipole [Trefry et al., 2012]. The pulsed dipole, the sequential operation of one injection well and one extraction well, is most realistic model for groundwater remediation because it does not rely on rotational flow. When Jones and Aref [1988] simulated pulsed dipole flow to create chaotic advection, they found that spreading was enhanced in certain regions between the wells. Trefry et al. [2012] produced similar results with the rotating pulsed dipole, simulated by applying certain transient pressure

switching schedules at different wells. In a related study of chaotic advection created by pulsed dipoles, however, *Stremmer et al.* [2004] demonstrated that conditions of maximum chaos do not necessarily correlate to maximum spreading. The conclusions of *Stremmer et al.* [2004] were consistent with prior work of *Ganesan et al.* [1997] on an analogous investigation of heat transfer enhancement using chaotic advection. *Ganesan et al.* [1997] cautioned against assuming that greater degrees of chaos imply better global transport rates.

Weeks and Sposito [1998] demonstrated that spreading is more effective if chaotic advection leads to both stretching and folding. In fact, stretching and folding is a consistent theme in the spreading literature. *Reynolds* [1984] made early references to stretching and folding using the process of rolling out and folding dough repeatedly as an example. *Ottino* [1989] includes stretching and folding in his definition of fluid mixing as the "...efficient stretching and folding of material lines and surfaces." The baker's transformation, which is a progression of stretching, cutting, and fusing, has been called the best possible mixing device [*Chakravarthy and Ottino*, 1995; *Ottino*, 1989, *Ottino et al.*, 1994]. The role of folding is emphasized repeatedly in the spreading literature [*Reynolds*, 1984] as it allows stretching to continue even within a bounded domain [*Aref*, 2002]. This is especially pertinent in the context of in-situ remediation of groundwater since it is necessary to contain the contaminant within the impacted region.

While pulsed dipole flow and the baker's transformation can achieve stretching and folding to enhance spreading, neither technique is suitable for in-situ groundwater remediation. Generating pulsed dipole flow to stimulate spreading for practical scenarios like groundwater remediation is not plausible because it requires assumptions of timing and orientation of particles at reinjection that are physically unrealistic. Since the baker's transformation requires cutting and fusing, it is not directly applicable to spreading in aquifers.

Some recent studies have explored the practical use of chaotic advection for groundwater remediation in heterogeneous aquifers. The simulations of *Bagtzoglou and Oates* [2007] showed that three randomly oscillating wells, connected through a recirculation system, can produce substantial spreading in heterogeneous aquifers. *Zhang et al.* [2009] conducted lab-scale experiments to study the spreading of solutes in porous media due to oscillatory flow generated by multiple wells. They found that spreading was enhanced by oscillatory flow, which may enhance the processes of biological and chemical remediation.

Mays and Neupauer [2012] proposed a strategy to enhance spreading in aquifers, called engineered injection and extraction (EIE), in which a sequence of injections and extractions of clean water at multiple wells in an aquifer is performed to stretch and fold the interface between the treatment solution and contaminated groundwater. *Mays and Neupauer* [2012] simulated the movement of the interface between the treatment solution and the contaminated groundwater during an engineered injection and extraction sequence in a hypothetical contaminated aquifer. They found that EIE can stretch and fold the interface, leading to enhanced spreading in aquifers. When the sequence was repeated multiple times, evidence of chaotic advection was observed [*Mays and Neupauer*, 2012].

While *Mays and Neupauer* [2012] demonstrated that EIE can lead to stretching and folding of the interface between the treatment solution and contaminated groundwater, no evidence was presented that this stretching and folding actually leads to enhanced reaction in in-situ remediation. In this thesis, I investigate the amount of reaction that occurs during engineered injection and extraction, and I demonstrate that reaction is enhanced relative to standard in-situ remediation methods. Since spreading can be achieved by both aquifer heterogeneity and by transient flow fields (such as with engineered injection and extraction), we also compare the

amount of spreading caused by varying degrees of heterogeneity and the amount of spreading resulting from engineered injection and extraction.

1.3 Parallel Studies on Engineered Injection and Extraction

As mentioned, *Mays and Neupauer* [2012] developed a technique known as engineered injection and extraction (EIE) that enhances spreading in aquifers by stretching and folding the interface between the treatment solution and groundwater contaminant plumes. *Mays and Neupauer* [2012] proceeded to quantify the degree of spreading from stretching and folding using chaotic advection principles. Since the particular sequence of EIE used by *Mays and Neupauer* [2012] is just one example of a sequence that can generate stretching and folding, *Kulha* [2012] expanded upon their work to determine whether a new sequence of EIE with rotation would result in more spreading as quantified by chaotic features. The new sequence was identical to the sequence used by *Mays and Neupauer* [2012] except the order of well operation was reversed in the second and fourth cycles of their four-cycle sequence. For the same sequence length as *Mays and Neupauer* [2012], *Kulha* [2012] found that the new sequence resulted in an increased number of hyperbolic periodic points, which represent regions of good spreading.

The original sequence of EIE used by *Mays and Neupauer* [2012] was devised heuristically by changing the active well location and rate of injection or extraction, and examining the length and geometry of the ensuing interface between the treatment solution and contaminated groundwater. Since the original sequence was developed in an ad-hoc manner, optimization of the sequence was a logical subsequent query. *Fuller* [2011] developed a genetic algorithm for this purpose based on the cumulative interface length during each step of the sequence and the cumulative incremental interface length, where the incremental length is the

change in interface length between each step of the sequence. Interface length is a simple indicator of whether the sequence generates good spreading, since we can expect more degradation reactions with increasing contact of treatment solution and contaminant. Incremental interface length is worth consideration such that the optimization does not converge at early steps of the sequence. The optimization was constrained by the following conditions: 1) the total volume of clean water injected and extract was limited, 2) the amount of clean water injected had to equal the amount extracted, and 3) the plume had to be contained within a set boundary. *Fuller* [2011] demonstrated the performance of the genetic algorithm for a simplified two-well scenario.

While *Mays and Neupauer* [2012], *Kulha* [2012], and *Fuller* [2011] have shown that EIE can enhance spreading, it is ultimately more relevant to show that EIE can enhance reaction, since the purpose of in-situ remediation is to degrade groundwater contaminant. *Abeyasinghe* [2011] modeled the reaction between treatment solution and contaminant during EIE using MODFLOW [*Harbaugh*, 2000] to simulate the flow fields and RT3DV1 [*Clement*, 1997] to simulate the reaction. When *Abeyasinghe* [2011] compared the reaction during EIE to the reaction during ambient flow only for the same initial configuration of treatment solution and groundwater contaminant, they found that both cases produced nearly the same amount of reaction. This result was contrary to our hypothesis that EIE would improve reaction. Investigation of a plausible explanation revealed that the numerical dispersion in RT3DV1 was sizeable enough that the differences in flow fields for each scenario did not influence the simulated reaction. This finding was instrumental in shaping the methods used to simulate reaction in this study, as detailed in Chapter 2.

1.4 Thesis Overview

Chapter 2 is a stand-alone paper presenting the methods and results of this research. It will be submitted to *Water Resources Research*. Chapter 3 discusses conclusions and gives recommendations for future work.

Chapter 2

Engineered Injection and Extraction for Improved In-Situ Remediation

2.1 Introduction

Groundwater is becoming an increasingly essential resource in a world with dwindling freshwater supplies, as indicated by its accelerated rate of usage in the United States at present [*Groundwater Foundation*, 2011]. However, groundwater can be contaminated during various industrial, agricultural, and municipal practices; for instance, over twenty thousand abandoned hazardous waste sites are currently known to exist in the U.S. alone [*Groundwater Foundation*, 2011]. While prevention of groundwater contamination is preferable, groundwater treatment techniques are necessary for the remediation of current contaminated sites and for sites that will inevitably become contaminated in the future despite preventative efforts.

In-situ remediation is one method of actively treating contaminated groundwater, where a treatment solution (containing oxidants, electron donors, or nutrients) is injected into the aquifer to degrade the contaminant. In current practice of in-situ remediation, tactics to distribute treatment solution in the contaminated area of aquifer are limited. Either the treatment solution is

left to travel with the ambient groundwater flow or it is drawn through the aquifer using a downgradient pumping well [Nyer, 1985]. We hypothesize that the time required for in-situ remediation could be significantly reduced if the contact area between the treatment solution and contaminated groundwater were increased. One would naturally expect that spreading of the two reactants would increase their contact area; however, spreading in aquifers is a challenging and complex problem. The term *spreading* is used intentionally to indicate transport due to advection and macrodispersion, as opposed to the mixing attributed to molecular diffusion and pore-scale dispersion. Because flow in porous media is laminar, it lacks the turbulent eddies that enable spreading in open systems.

Spreading depends on the structure of the flow [Dentz and Carrera, 2005]. In groundwater aquifers, the structure of the flow is primarily dictated by the heterogeneity of the porous media [Kitanidis, 1994]. However, recent studies modify this premise by asserting that *heterogeneous velocity* (rather than just heterogeneity) determines the structure of the flow, and consequently the spreading that ensues [Le Borgne et al., 2010], where heterogeneous velocity is not only attributed to heterogeneity, but also to other mechanisms such as temporal variations in fluid velocity [Dentz and Carrera, 2005].

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Weeks and Sposito [1998] demonstrated that spreading is more effective if chaotic advection leads to both stretching and folding. Stretching and folding is a consistent theme in the spreading literature. Reynolds [1984] made early references to stretching and folding using the process of rolling out and folding dough repeatedly as an example. Ottino [1989] includes stretching and folding in his definition of fluid mixing as the "...efficient stretching and folding of material lines and surfaces." The baker's transformation, which is a progression of stretching, cutting, and fusing, has been called the best possible mixing device [Chakravarthy and Ottino, 1995; Ottino, 1989, Ottino et al., 1994]. The role of folding is emphasized repeatedly in the spreading literature [Reynolds, 1984] as it allows stretching to continue even within a bounded

domain [Aref, 2002]. This is especially pertinent in the context of in-situ remediation of groundwater since it is necessary to contain the contaminant within the impacted region.

While pulsed dipole flow and the baker's transformation can achieve stretching and folding to enhance spreading, neither technique is suitable for in-situ groundwater remediation. Since the baker's transformation requires cutting and fusing, it is not directly applicable to spreading in aquifers. Generating pulsed dipole flow to stimulate spreading for practical scenarios like groundwater remediation is not plausible because it requires assumptions of timing and orientation of particles at reinjection that are physically unrealistic.

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Mays and Neupauer [2012] proposed a strategy to enhance spreading in aquifers, called engineered injection and extraction, in which a sequence of injections and extractions of clean water at multiple wells in an aquifer is performed to stretch and fold the interface between the treatment solution and contaminated groundwater. *Mays and Neupauer* [2012] simulated the movement of the interface between the treatment solution and the contaminated groundwater during an engineered injection and extraction sequence in a hypothetical contaminated aquifer. They found that engineered injection and extraction can stretch and fold the interface, leading to

enhanced spreading in aquifers. When the sequence was repeated multiple times, evidence of chaotic advection was observed [*Mays and Neupauer, 2012*].

While *Mays and Neupauer* [2012] demonstrated that engineered injection and extraction can lead to stretching and folding of the interface between the treatment solution and contaminated groundwater, no evidence was presented that this stretching and folding actually leads to enhanced reaction in in-situ remediation. In this thesis, I investigate the amount of reaction that occurs during engineered injection and extraction, and I demonstrate that reaction is enhanced relative to standard in-situ remediation methods. Since spreading can be achieved by both aquifer heterogeneity and by transient flow fields (such as with engineered injection and extraction), I also compare the amount of spreading caused by varying degrees of heterogeneity and the amount of spreading resulting from engineered injection and extraction.

In the next section, I describe the engineered injection and extraction system, and the approach for modeling transport and reaction. For brevity, I consider only instantaneous reactions between the treatment solution and contaminant. Finally, I present simulation results of reactive transport during engineered injection and extraction and during standard in-situ remediation to show that engineered injection and extraction leads to more reaction, even in heterogeneous aquifer.

2.2 Engineered Injection and Extraction System

The physical system analyzed in this study represents a confined, 2D, isotropic aquifer. A plume of contaminated groundwater centered at the origin is surrounded by four wells, with treatment solution emplaced in the center of the contaminant plume, as shown in Figure 2.1. The wells are identified by cardinal direction and they are located 1m from the origin on the coordinate axes. Ambient groundwater flow travels from east to west at a rate of 0.01m/d.

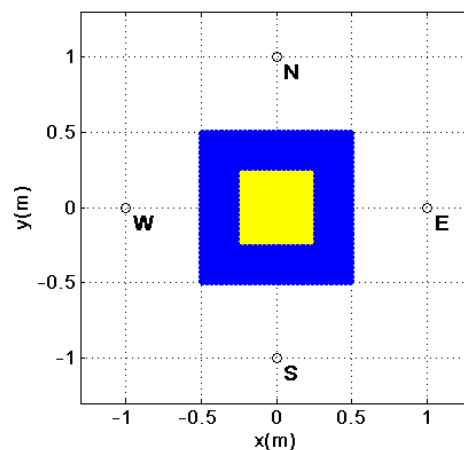


Figure 2.1: Plan view of model aquifer showing the initial positions of the treatment solution (yellow) and contaminant (blue) particles (on a regular grid with 0.01 m spacing) in the center of four wells identified by cardinal direction.

During engineered injection and extraction, wells are operated in a planned sequence at preset rates of injection or extraction of clean water. For this study, a 12-step sequence is considered in which one well is operated during each step. Table 2.1 shows the injection rate and active well for each step of the sequence. Each step of the sequence lasts for one day. The total volume of clean water injected is intentionally made to equal the volume of water extracted, such that no net injection or extraction occurs. The sequence was designed such that no treatment solution is extracted, which allows all reaction to take place in the aquifer rather than in the wells where it could lead to clogging. The particular sequence of engineered injection and extraction is just one example of a sequence that could be used to achieve stretching and folding. This sequence is identical to the sequence used by *Mays and Neupauer* [2012].

Table 2.1: Engineered injection and extraction sequence used in this study. Negative injection rates represent extraction.

Step	1	2	3	4	5	6	7	8	9	10	11	12
Active Well	W	E	W	E	W	E	S	N	S	N	S	N
Injection Rate (m ³ /d)	0.875	0.875	-0.25	-0.75	-0.40	-0.35	0.875	0.875	-0.25	-0.75	-0.40	-0.35

The flow field during each step of engineered injection and extraction is obtained from the groundwater flow equation in a 2D, confined aquifer, given by

$$S_s \frac{\partial h}{\partial t} = \nabla \cdot \mathbf{K} \nabla h + Q_i \delta(x - x_{w_i}) \delta(y - y_{w_i}), \quad (1)$$

where S_s is the specific storage, h is the hydraulic head, t is time, \mathbf{K} is the hydraulic conductivity tensor, Q_i is the rate of injection during the i^{th} step of the injection and extraction sequence, (x_{w_i}, y_{w_i}) are the coordinates of the active well during the i^{th} step, and $\delta(\cdot)$ is the Dirac delta function. The solution of (1) is used to solve for velocity, \mathbf{v} , from Darcy's law given by

$$\mathbf{v} = -\frac{1}{n} \mathbf{K} \nabla h \quad (2)$$

where n is the porosity. Transport of the treatment solution and contaminant in the model aquifer is described by the advection-dispersion-reaction equation, given by

$$\frac{\partial C_j}{\partial t} = -\nabla \cdot (\mathbf{v} C_j) + \nabla \cdot \mathbf{D} \nabla C_j - R \quad (3)$$

where C_j is the concentration of the j^{th} species ($j = 1$ for the treatment solution, $j = 2$ for contaminant, and $j = 3$ for the reaction product), R is the reaction rate, and \mathbf{D} is the dispersion tensor, given by

$$\mathbf{D} = \begin{bmatrix} D_{xx} & D_{xy} \\ D_{yx} & D_{yy} \end{bmatrix}$$

where

$$\begin{aligned} D_{xx} &= \alpha_L \frac{v_x^2}{|\mathbf{v}|} + \alpha_{TH} \frac{v_y^2}{|\mathbf{v}|}, \\ D_{xy} &= D_{yx} = (\alpha_L - \alpha_{TH}) \frac{v_x v_y}{|\mathbf{v}|}, \\ D_{yy} &= \alpha_L \frac{v_y^2}{|\mathbf{v}|} + \alpha_{TH} \frac{v_x^2}{|\mathbf{v}|}, \end{aligned} \quad (4)$$

where α_L and α_T are longitudinal and transverse dispersivities and v_x and v_y are the x - and y -components of the groundwater velocity vector, respectively.

Reaction is modeled as an instantaneous reaction given by



where reactants C_1 and C_2 are the concentrations of the treatment solution and groundwater contaminant, respectively, and C_3 is the concentration of the reaction product, which is assumed to be inert. An instantaneous reaction allows us to evaluate how reaction is enhanced by stretching and folding, not by chemical kinetics. For convenience, the 1:1 stoichiometric ratio in (5) is assumed to imply a 1:1 mass ratio as well.

The contaminated groundwater and treatment solution are simulated as a collection of particles placed on a regular grid spaced 0.01m apart (Figure 2.1). The particles are subject to advection, dispersion, and reaction as shown in (3) using random walk with reaction. The advection component is modeled with MODPATH [Pollock, 2000], based on the flow fields obtained by solving (1) using MODFLOW [Harbaugh, 2000]. Parameter values used in the model are summarized in Table 2.2. In this study, we evaluate both homogeneous and heterogeneous aquifers. To model heterogeneity, a random field of $\ln K$ with statistical properties shown in Table 2.2 was generated using sequential Gaussian simulation in GSLIB [Deutsch and Journel, 1997]. The random $\ln K$ field is shown in Figure 2.2.

Table 2.2: Parameter values used in modeling flow fields, dispersion, and reaction.

Parameter	Value
Specific storage, S_s	0.001
Mean hydraulic conductivity, K (m/d)	0.5
Aquifer thickness, b (m)	1
Aquifer domain length (m)	12.01
Number of treatment solution particles	2601
Number of contaminant particles	7600
Constant head value at east boundary (m)	10.12
Constant head value at west boundary (m)	10
Variance of $\ln K$	0.50
Variogram type	Spherical
Correlation length of $\ln K$ (m)	0.25
Longitudinal dispersivity, α_L (m)	0.0005
Transverse dispersivity, α_T (m)	0.00005
Duration of injection or extraction step, Δt (d)	1
Porosity	0.25
Initial mass per treatment solution particle (g)	4
Initial mass per contaminant particle (g)	1

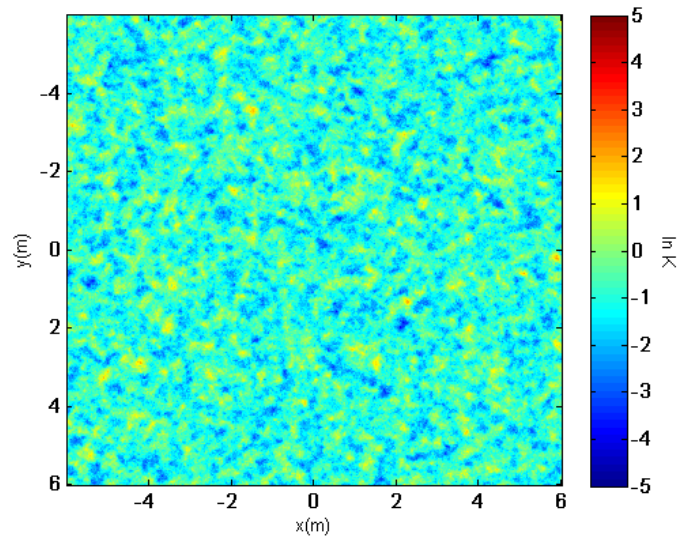


Figure 2.2: Random $\ln K$ field.

The dispersion component of (3) is modeled by adding random displacements to the particle positions prior to the advection step. Random displacements in the direction of the local velocity vector and in the direction perpendicular to the local velocity vector are selected from normal distributions with zero mean and variances of $2\alpha_L|v|\Delta t$ and $2\alpha_T|v|\Delta t$, respectively, where Δt is the duration of the injection or extraction step. Parameter values used to model dispersion are summarized in Table 2.2.

After each advection step, reaction is modeled by binning the treatment solution and contaminant particles into 0.025 m by 0.025 m bins. To simulate instantaneous reaction with a 1:1 stoichiometric ratio between the treatment solution and contaminant, within each bin, the entire mass of the limiting reactant is converted to reaction product, and the mass of the excess reactant is reduced by the mass reacted. The remaining mass is divided evenly among the particles of the excess reactant in the bin.

2.3 Results

Using the approach and techniques described above, reaction during engineered injection and extraction was modeled in a homogeneous aquifer. Figure 2.3 illustrates the positions of treatment solution, groundwater contaminant, and reaction product particles after each step of the engineered injection and extraction sequence shown in Table 2.1. In the first six steps, the west and east wells are operated alternately, first as injection wells (Steps 1 and 2) and then as extraction wells (Steps 3 – 6). In the final six steps, the pattern is repeated with the south and north wells. The position and geometry of the plume reflects the rate and location of injection or extraction performed at that step, given in Table 2.1. For instance, the plume is stretched during the injection steps (Figure 2.3a, b) when flow diverges away from the active well, and the plume is folded during the extraction steps (Figure 2.3c-f) when flow converges to the active well. After the first six steps of the sequence, the plume is folded once, and after the final six steps, the plume is folded a second time.

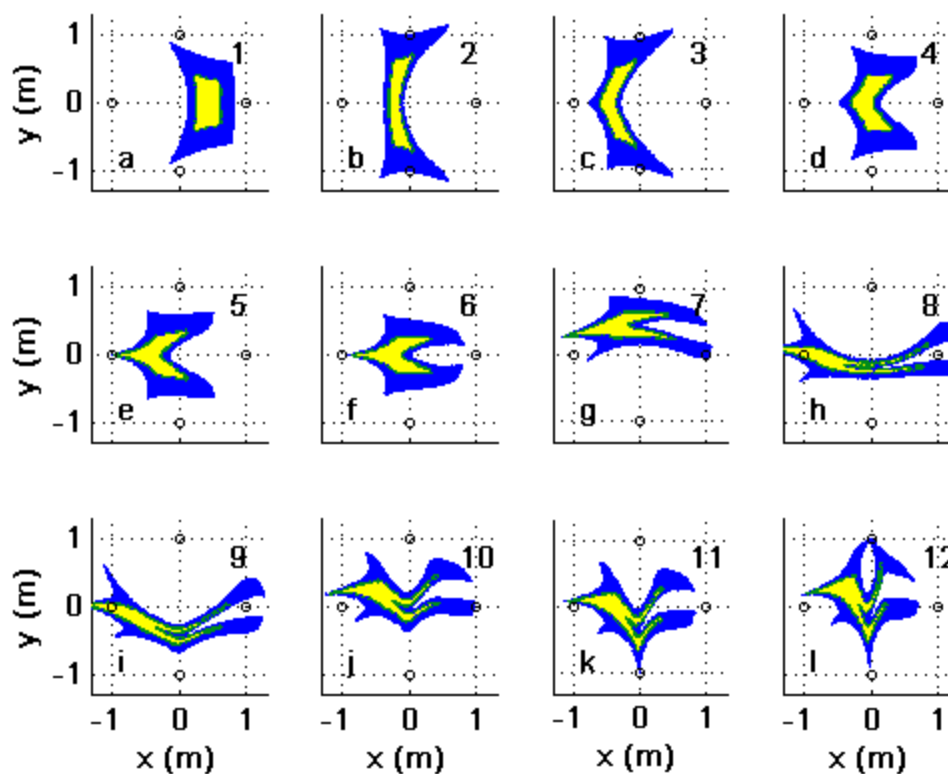


Figure 2.3: Location of treatment solution (yellow), contaminant (blue), and reaction product (green) during EIE in a homogeneous aquifer, where the numbers indicate the step of EIE.

After each step of the engineered injection and extraction (EIE) sequence, reaction of the contaminant and treatment solution was simulated, as discussed above. The locations of the particles of the reaction products are shown in green in Figure 2.3. Figure 2.4 (diamonds) presents cumulative reaction during each step of the EIE sequence. Particles must be in close proximity to react; for instance, since treatment solution and contaminant particles are initially located adjacent to each other as shown in Figure 2.1, significant reaction occurs during step 1 of EIE. EIE reconfigures the arrangement of the particle during each step of the sequence, leading to a measurable amount of reaction in each step. Steps that substantially rearrange the particle positions result in more reaction, assuming that the rearrangements are advantageous for reaction. For example, the plume undergoes significant reconfiguration in Step 8, where the plume center is

compressed while its extremities are stretched transverse to the injection at the active well (Figure 2.3h). This leads to a significant amount of reaction occurring between $t = 7$ days and $t = 8$ days (Figure 2.4).

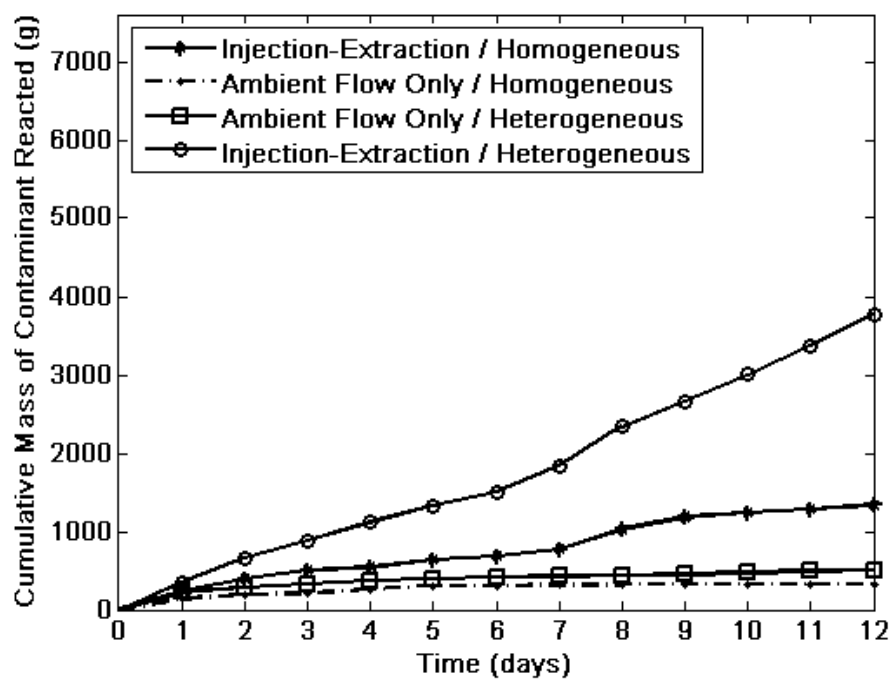


Figure 2.4: Cumulative contaminant mass reacted during in-situ remediation.

To compare the effectiveness of EIE relative to standard in-situ remediation, we simulated the movement of the plume in Figure 2.1 in an aquifer with ambient flow but without EIE. The final positions of treatment solution, contaminant, and reaction product particles after twelve days are shown in Figure 2.5a. The treatment solution and contaminant particles intermix somewhat as a result of dispersion; however, the degree of spreading is much lower than with EIE (c.f. Figures 2.5a and 2.31) for the following reasons. First, when the plume travels with ambient flow only, the plume travels at a lower velocity than with EIE; therefore, it experiences less spreading due to dispersion, since dispersion depends on local velocity, given by (4). Additionally, because we have steady flow, particles do not experience dramatic reconfiguration as with EIE. Figure 2.4 (dot-dash line) shows the cumulative contaminant mass that is reacted each day in this ambient flow system. Initially reaction occurs because contaminant particles and treatment solution particles are adjacent to each other, and because dispersion brings them together. After about 5 days, however, very little additional reaction occurs because the configuration of treatment solution, reaction product, and contaminant remains relatively unchanged. Over the 12-day treatment period, the total reaction with ambient flow is approximately four times lower than with EIE, because the low local velocities result in little dispersion, and steady flow does not lead to reconfiguration of the relative positions of the particles.

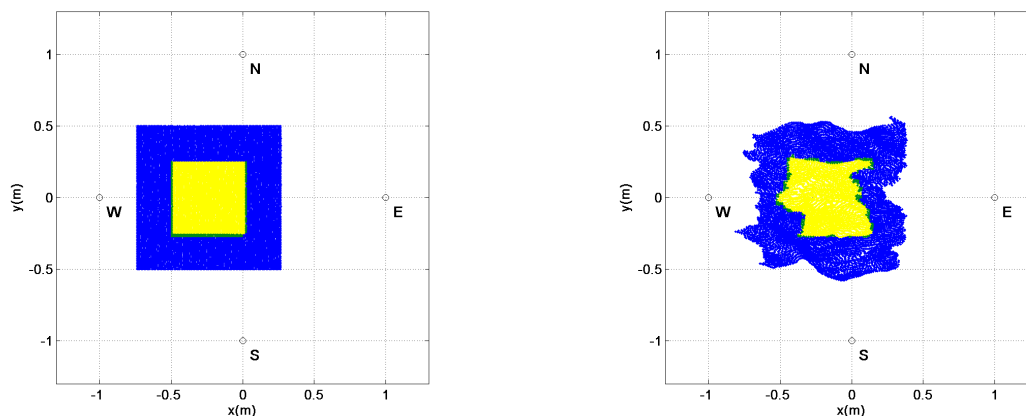


Figure 2.5: Positions of treatment solution (yellow), contaminant (blue), and reaction product (green) particles after twelve days of travel with ambient groundwater flow in (a) a homogeneous aquifer and (b) a heterogeneous aquifer.

As spreading can occur naturally in an aquifer as a result of aquifer heterogeneity, we also simulated the movement of the plume in Figure 2.1 with ambient groundwater flow in a heterogeneous aquifer, represented by the random $\ln K$ field shown in Figure 2.2. The treatment solution, contaminant, and reaction product particles after 12 days are shown in Figure 2.5b. Figure 2.4 (squares) shows the cumulative contaminant mass that is reacted each day in this ambient flow system with heterogeneity. As in the homogeneous aquifer, the amount of reaction plateaus around day 5. After twelve days, the reaction in the heterogeneous aquifer with only ambient flow is slightly greater than homogeneous aquifer with only ambient flow, but close to three times less than in the homogeneous aquifer with engineered injection and extraction. While the plume experiences more reconfiguration in the heterogeneous aquifer than in the homogeneous aquifer, there is still minimal plume reconfiguration as compared to with EIE. And like before, low particle velocities associated with ambient flow result in less dispersion than with EIE.

While EIE in a homogeneous aquifer leads to more reaction than standard in-situ remediation, EIE in a heterogeneous aquifer leads to even greater enhancement of reaction. Figure 2.4 illustrates that EIE enhances reaction by 400% in homogeneous aquifers (diamonds) and 750% in heterogeneous aquifers (circles). To make this comparison, EIE was simulated in a heterogeneous aquifer, where Figure 2.6 illustrates the positions of treatment solution, groundwater contaminant, and reaction product during each step of EIE. The added spreading from heterogeneity results in a more uniform increase in reaction during each step of EIE in the heterogeneous aquifer, as shown in Figure 2.4. For instance, the increase in reaction in Step 8, which was obvious in the homogeneous aquifer, is barely noticeable in the heterogeneous aquifer. When the plume travels by ambient flow only (Figures 2.5a,b), the treatment solution and contaminated groundwater remain relatively isolated, with little opportunity for reaction. On the other hand, with EIE (Figures 2.31 and 2.61), the treatment solution is spread throughout much of the contaminated groundwater, providing ample opportunity for reaction. Furthermore, reaction in a homogenous aquifer with engineered injection and extraction is greater than reaction in a heterogeneous aquifer with ambient flow only (Figure 2.4), indicating that EIE causes more spreading and therefore more reaction than is caused by heterogeneity alone.

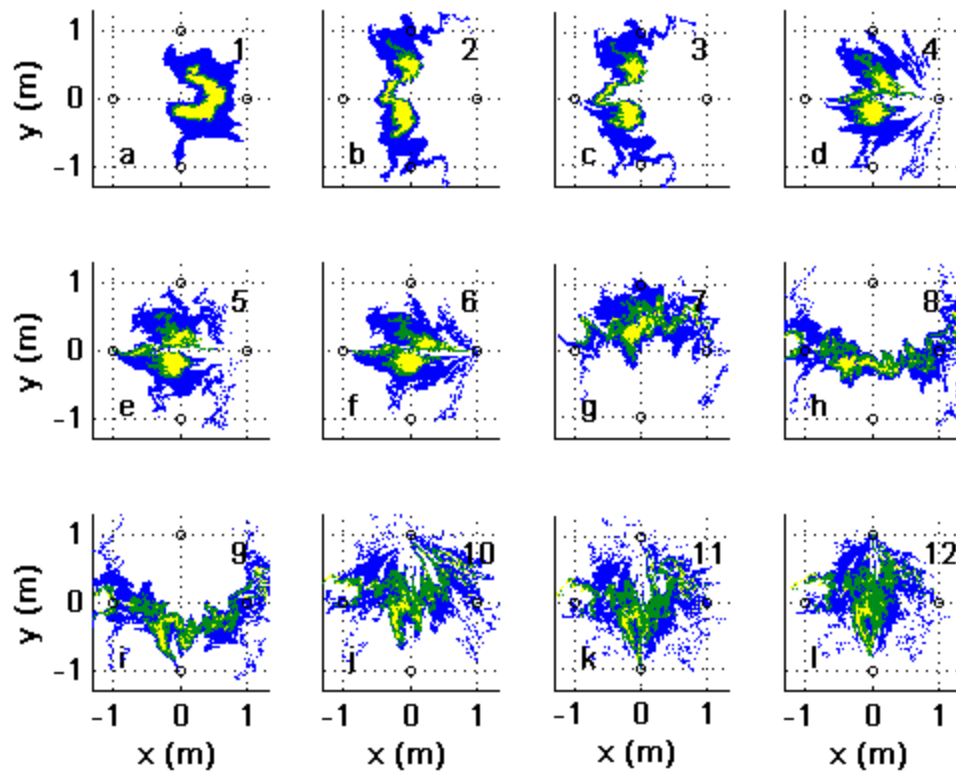


Figure 2.6: Location of treatment solution (yellow), contaminant (blue), and reaction product (green) during each step of injection and extraction in a heterogeneous aquifer.

2.4 Conclusion

Contact of reactants is a key requirement for any chemical reaction, including the degradation reactions of in-situ remediation. While stirring can easily mix reactants in many physical systems, this action is not possible in groundwater aquifers. Spreading is one alternative method to consider, which can be augmented in laminar flow environments through stretching and folding created by transient flow fields. *Mays and Neupauer* [2012] proposed a technique known as engineered injection and extraction, which uses sequential operation of multiple wells to create stretching and folding to enhance spreading in aquifers. Although engineered injection and extraction has been shown to promote stretching and folding [*Mays and Neupauer, 2012*], the enhancement of reaction had not been demonstrated. In this study, I investigated the ability of engineered injection and extraction to improve reaction during in-situ remediation. Results show that engineered injection and extraction increases reaction during in-situ remediation, as compared to traditional in-situ remediation practices. In addition I have shown that while heterogeneity promotes spreading and therefore enhances reaction, the amount of spreading and reaction resulting from engineered injection and extraction exceeds the amount of spreading and reaction caused by heterogeneity.

Chapter 3

Summary and Recommendations for Future Work

3.1 Summary

As our world becomes increasingly dependent on groundwater resources, effective solutions to treat contaminated aquifers are ever more relevant. In-situ remediation is a form of groundwater treatment that offers numerous benefits over conventional treatment methods, such as reduced energy consumption and costs. During in-situ remediation, a treatment solution is injected into a contaminated aquifer to degrade the groundwater contaminant in place. Since contaminant degradation reactions only occur at locations where the treatment solution and groundwater contaminant contact each other, spreading of the treatment solution into the contaminated region is necessary. However, spreading in aquifers is generally poor as groundwater flow is laminar, and lacks turbulent eddies responsible for spreading in many flow systems. The technique known as engineered injection and extraction (EIE) has been shown to improve spreading in aquifers [*Mays and Neupauer 2012*]; however, until the present study no evidence had been presented to show that EIE enhances reaction. This thesis presents a model

that simulates advective transport, dispersion, and reaction during EIE in contaminated homogeneous and heterogeneous aquifers. Results show that EIE enhances degradation of groundwater contamination in homogeneous and heterogeneous aquifers. Furthermore, this thesis demonstrates that the reaction provided by the spreading due to EIE is greater than the reaction due to spreading from heterogeneity alone.

3.2 Recommendations for Future Work

While the sequence of engineered injection and extraction (EIE) used in this study enhanced spreading and reaction by stretching and folding the interface between the treatment solution and groundwater contaminant plumes, the sequence was developed heuristically, and therefore it is not necessarily optimal. Consequently, in upcoming phases of this research, we (myself and my research advisors, Drs. Roseanna Neupauer and David Mays) plan to optimize the sequence of EIE according to the following objectives and constraints. First we must decide how optimal is defined; for in-situ remediation, an optimal sequence should maximize reaction, while minimizing cost and duration. Costs include the well installation, piping between the wells, and energy for pump operation. The optimal sequence must satisfy the following conditions: 1) To avoid potential clogging issues, the treatment solution may not be extracted so that all reaction occurs in the aquifer rather than in the wells, and 2) The cumulative volume of clean water injected must equal the amount extracted such that there are no additional costs for supplying or disposing of injection water. Numerous parameters can be adjusted during the optimization including the location of wells, number of wells, total duration, number of time steps, rate of injection or extraction at each well, and height of the screened interval (for a 3D model). Initial

optimization efforts will fix the majority of the parameters, but eventually we will refine the optimization by relaxing some fixed parameters.

As mentioned, an optimal sequence of EIE should maximize reaction; however, determining the reaction for any given sequence of EIE requires reactive transport simulations, which can be lengthy. Since the rate of contaminant degradation depends on the contact between the reactants, and their contact controlled by spreading, it is plausible that the amount of reaction correlates directly to the amount of spreading. Examination of different metrics that quantify spreading will show whether there is a direct correlation, and if so, spreading could be optimized rather than the reaction to save computational time. We will analyze the following spreading metrics: 1) the length of the interface between the treatment solution and contaminated groundwater [Zhang *et al.*, 2009], 2) the average distance between particles of treatment solution and groundwater contaminant [Bagtzoglou and Oates, 2007], 3) the rate of mixing [De Simoni *et al.*, 2005], the dilution index [Kitanidis, 1994], and 5) the scalar dissipation rate [Flohr and Vassilicos, 1997].

The complexity of the model aquifer will affect the optimization of the EIE sequence. Our optimization will consider aquifer complexities such as ambient flow, storage, and heterogeneity by developing different optimized schemes for each combination of complexities. In addition, we will consider each combination of aquifer complexities in both 2D and 3D domains.

We will conduct the optimization using a genetic algorithm. Genetic algorithms are more computationally efficient than gradient-based search algorithms because costly gradient calculations are not necessary [McKinney and Lin, 1994]. Furthermore, Fuller [2011] has already

demonstrated that genetic algorithm optimization can be used to optimize a sequence of EIE for a simplified two-well scenario.

Thus far, all discussion of EIE has been for a dissolved, non-sorbing contaminant that travels with the same velocity as the groundwater. If we attempt to treat sorbing contaminants with EIE, the nature of the problem is inherently different because the transport of the contaminant is different. Sorbing contaminants do not move passively with groundwater; some of the contaminant may remain attached to the soil, and some may dissolve into the aqueous phase. Since sorbing contaminants also constitute a threat to groundwater quality, later stages of research will optimize sequences of EIE for sorbing contaminants. This optimization work will also be conducted in Matlab using the Genetic Algorithm toolbox.

By considering contaminant type (nonsorbing, sorbing), aquifer complexity (ambient flow, storage, heterogeneity), and domain dimensionality (2D, 3D) we can represent a wide range of possible groundwater contamination scenarios. Dimensionless parameters can be used to characterize the relationship between reaction and transport for each possible scenario in order to identify which parameters are most important in the development of EIE sequences. The dimensionless parameters will include: 1) the Peclet number, 2) the Damköhler number, 3) the ratio of the volumes of injection water to contaminant plume, and 4) the ratio of injection and extraction rates to ambient flow rate. Finally, as there are many unknowns in the characterization of an actual groundwater contamination scenario, such as plume position, aquifer properties, and chemical conditions, it will be necessary to perform some sensitivity analyses to better understand the degree to which errors in characterization can affect the result of the EIE optimization.

We expect that the upcoming research will reveal that EIE is a viable approach for remediation of a variety of possible groundwater contamination scenarios. If so, future work will

include conducting lab-scale experiments to verify the results of our simulations. A possible model aquifer could consist of an acrylic tank containing index-matched porous media [Iskander, 2010]. Colored dyes could be injected through ports installed on the top face of the model aquifer. The changes in contaminant concentration could be measured with digital imagery according to methods used by Zhang [2009]. If the lab-scale experiments demonstrate that EIE can enhance reaction, then a field-scale should follow. Success at this level is anticipated to have a transformative impact on the field of groundwater remediation. EIE could ultimately provide enhanced contaminant degradation in a shortened time frame, while maintaining better control of the contaminant plume, with reduced energy and operational costs.

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Appendix

A.1 Simulation of Reactive Transport during Engineered Injection and Extraction

```

% This code is used to set up the input files for a one-layer, MODFLOW
% simulation for either a homogeneous or spatially-varying heterogeneous
% rectangular domain with no-flow boundaries on two opposite sides and
% constant head boundaries on the other two sides. The column spacing
% is uniform, and the row spacing is uniform.
%
% This code reads in parameters from a parameter file called
% fname.par, where "fname" is a root name that is used in
% all file names.

x_wells=[0,1,0,-1];
y_wells=[1,0,-1,0];

activewell=[4,2,4,2,4,2,3,1,3,1,3,1];
% Well numbers are N = 1, E = 2, S = 3, W = 4
xwell=[-1,1,-1,1,-1,1,0,0,0,0,0,0];
ywell=[0,0,0,0,0,0,-1,1,-1,1,-1,1];

% pumping rates
lambda2=[3.5,3.5,-1,-3,-1.6,-1.4,3.5,3.5,-1,-3,-1.6,-1.4];
twelve=length(lambda2);

flows=reshape([activewell' lambda2'],'',1,twelve*2);  %'

pcolor='rgbm';
plotted=0;

pfile=input('Enter the name of the parameter file. > \n','s');
[~,fname,~]=fileparts(pfile);
fid=fopen(pfile,'r');

```

```

fidnam=fopen(strcat(fname, '.nam'), 'w');
fprintf(fidnam, 'LIST      3 %s.out \n', fname);

X=fscanf(fid, '%f', 3);
fgetl(fid);
Y=fscanf(fid, '%f', 3);
fgetl(fid);
elev=fscanf(fid, '%f', 2);
fgetl(fid);
nper=fscanf(fid, '%f', 1);
fgetl(fid);
nstep=fscanf(fid, '%f', 1);
fgetl(fid);

thick=elev(1)-elev(2);
xmin=X(1);
xmax=X(2);
dx=X(3);
ncol=ceil((xmax-xmin)/dx);

ymin=Y(1);
ymax=Y(2);
dy=Y(3);
nrow=ceil((ymax-ymin)/dy);

xx=xmin:dx:xmax;
yy=ymin:dy:ymax;

fiddis=fopen(strcat(fname, '.dis'), 'w');
fprintf(fiddis, '# MODFLOW Simulation - set up using %s \n', pfile);
fprintf(fiddis, '# %s \n', date);
fprintf(fiddis, '%10d %9d %9d %9d %9d \n', 1, nrow, ncol, 1, 4, 2);
fprintf(fiddis, ' 0 \n');
fprintf(fiddis, 'CONSTANT %f \n', dx);
fprintf(fiddis, 'CONSTANT %f \n', dy);
fprintf(fiddis, 'CONSTANT %f \n', elev(1));
fprintf(fiddis, 'CONSTANT %f \n', elev(2));
fprintf(fiddis, '      1          %d          1.0      TR\n', 1);
fclose(fiddis);
fprintf(fidnam, 'DIS      7 %s.dis \n', fname);

fidbas=fopen(strcat(fname, '.bas'), 'w');
fprintf(fidnam, 'BAS6      8 %s.bas \n', fname);
fprintf(fidbas, '# MODFLOW Simulation - set up using %s \n', pfile);
fprintf(fidbas, '# %s \n', date);
fprintf(fidbas, 'FREE, SHOWPROGRESS, PRINTTIME \n');

ibound=ones(nrow, ncol);
shead=ones(nrow, ncol);

bcxmin=fscanf(fid, '%d', 1);
if bcxmin==1
    minbx=fscanf(fid, '%f', 1);
    shead(:, 1)=minbx;
    ibound(:, 1)=-1;
end
fgetl(fid);

```



```

fprintf(fidoc,'COMPACT BUDGET FILES \n\n');

    fprintf(fidoc,'PERIOD 1 STEP 1 \n');
    fprintf(fidoc,'    PRINT HEAD\n');
    fprintf(fidoc,'    PRINT BUDGET\n');
    fprintf(fidoc,'    SAVE HEAD\n');
    fprintf(fidoc,'    SAVE BUDGET\n\n');

fprintf(fidoc,'    PRINT BUDGET\n\n');
fclose(fidoc);

fidbcf=fopen(strcat(fname,'.bcf'),'w');
fprintf(fidnam,'BCF6    11 %s.bcf \n',fname);
fprintf(fidbcf,'50 -2.000000000000000E+0020 0 5.000000000000000E-0001 1 1 \n');

ltype=fscanf(fid,'%d',1);
fgetl(fid);
SS=fscanf(fid,'%f',1);
fgetl(fid);
k=0.5; % for a homogeneous. Uncomment the 4 lines below for heterogeneous.

% fielddat=fopen('Field_CL25V5.dat','r');
% k=fscanf(fielddat,'%f',[nrow,ncol]);
% fclose(fielddat);
% fprintf(fidnam,'DATA    90 Field_CL25V5.dat \n');
hetero=fscanf(fid,'%d',1);
fgetl(fid);

fprintf(fidbcf,'%2d\n',ltype); % confined?
fprintf(fidbcf,'CONSTANT    1.0\n'); % anisotropy factor
fprintf(fidbcf,'CONSTANT    %f\n',SS); % storage coefficient
fprintf(fidbcf,'CONSTANT    %12.6g \n',k*(1-ltype)*abs(elev(2)-
elev(1))+k*ltype); % transmissivity
% fprintf(fidbcf,'EXTERNAL  90 1 (8F12.4) 0');

fclose(fidbcf);

por=fscanf(fid,'%f',1);
fgetl(fid);

nwells=fscanf(fid,'%d',1);
fgetl(fid);

fidpcg=fopen(strcat(fname,'.pcg'),'w');
fprintf(fidnam,'PCG    23 %s.pcg \n',fname);
fprintf(fidpcg,'        50        30        1\n');
fprintf(fidpcg,'        .001        .001        1        1        1        0
1\n');
fclose(fidpcg);

% bring in treatment solution particle parameters
nsqr=fscanf(fid,'%d',1);
fgetl(fid);
xcs=zeros(nsqr,1);
yqs=zeros(nsqr,1);
hls=zeros(nsqr,1);

```

```

dvs=zeros(nsqr,1);
for i=1:nsqr
    Z=fscanf(fid,'%f',4);
    fgetl(fid);
    xcs(i)=Z(1);
    ycs(i)=Z(2);
    hls(i)=Z(3);
    dvs(i)=Z(4);
end

% bring in contaminant particle parameters
nsqr_c=fscanf(fid,'%d',1);
fgetl(fid);
xcs_c=zeros(nsqr_c,1);
ycs_c=zeros(nsqr_c,1);
hls_c=zeros(nsqr_c,1);
dvs_c=zeros(nsqr_c,1);

for i=1:nsqr
    Z=fscanf(fid,'%f',4);
    fgetl(fid);
    xcs_c(i)=Z(1);
    ycs_c(i)=Z(2);
    hls_c(i)=Z(3);
    dvs_c(i)=Z(4);
end

tpart=fscanf(fid,'%f',1);
fgetl(fid);
outputtype=fscanf(fid,'%d',1);
fgetl(fid);
fclose(fid);

fprintf(fidnam,'DATA(BINARY) 50 %s.bud \n',fname);
fprintf(fidnam,'DATA 51 %s.hed \n',fname);
fprintf(fidnam,'WEL 12 %s.wel \n',fname);
fclose(fidnam);

fid=fopen('modflow.bf','w');
fprintf(fid,'%s.nam \n',fname);
fclose(fid);

if (nsqr + nsqr_c > 0)
    fid=fopen(strcat(fname,'.pnm'),'w');
    fprintf(fid,'LIST 47 %s.mli \n',fname);
    fprintf(fid,'MAIN 10 %s.mpa \n',fname);
    fprintf(fid,'BUDGET 33 %s.bud \n',fname);
    fprintf(fid,'DIS 71 %s.dis \n',fname);
    fprintf(fid,'HEAD 23 %s.hed \n',fname);
    fprintf(fid,'BUDGET 45 %s.bud \n',fname);
    fprintf(fid,'CBF 42 %s.cbf \n',fname);
    fprintf(fid,'LOCATIONS 43 %s.prt \n',fname);
    fprintf(fid,'TIME 44 %s.tim \n',fname);
    fprintf(fid,'ENDPOINT 46 %s.end \n',fname);
    fprintf(fid,'PATHLINE 48 %s.lin \n',fname);
    fclose(fid);
end

```

```

end

% create the *.mpa file
fidmpa=fopen(strcat(fname, '.mpa'), 'w');
fprintf(fidmpa, '%8d%10.0g%10.0g%8d%8d%8d\n \n', 500000, -999.99,
2.000000000000000E+0020, 0, 0, 0);
fprintf(fidmpa, '%2d\n', ltype);
fprintf(fidmpa, 'INTERNAL 1 (FREE) 5 \n');

for i=1:nrow

fprintf(fidmpa, '%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d%3d\n', ibound(i, :));
    if mod(ncol, 20)
        fprintf(fidmpa, '\n');
    end
end

fprintf(fidmpa, 'CONSTANT %f \n', por);
fprintf(fidmpa, '0. \n');
fprintf(fidmpa, '1 1 1 1');
fclose(fidmpa);

% create coordinates of the treatment solution and contaminant particles
for i=1:nsqr
    % filled square (treatment solution)
    dxs=linspace(xcs(i)-hls(i), xcs(i)+hls(i), dvs(i));
    dys=linspace(ycs(i)-hls(i), ycs(i)+hls(i), dvs(i));
    [xxs, yys]=meshgrid(dxs, dys);
    radius=sqrt(2*hls(i)^2);
    rs=sqrt(xxs.^2+yys.^2);
    list=find(rs<=radius);
    xs=xxs(list);
    ys=yys(list);
end

for i=1:nsqr_c
    % filled square (contaminant)
    dxs_c=linspace(xcs_c(i)-hls_c(i), xcs_c(i)+hls_c(i), dvs_c(i));
    dys_c=linspace(ycs_c(i)-hls_c(i), ycs_c(i)+hls_c(i), dvs_c(i));
    [xxs_c, yys_c]=meshgrid(dxs_c, dys_c);
    radius_c=sqrt(2*hls_c(i)^2);
    rs_c=sqrt(xxs_c.^2+yys_c.^2);
    list_c=find(rs_c<=radius_c);
    xs_c=xxs_c(list_c);
    ys_c=yys_c(list_c);

    % remove points in the middle of the contaminant plume (initial condition)
    thislist=find(xs_c>xcs(i)+hls(i) | xs_c<xcs(i)-hls(i) |
ys_c>ycs(i)+hls(i) | ys_c<ycs(i)-hls(i));
    xs_c=xs_c(thislist);
    ys_c=ys_c(thislist);
end

% create the *.tim file
fidtim=fopen(strcat(fname, '.tim'), 'w');

```



```

fprintf(fidtim,' 1 1\n');
fprintf(fidtim,' 0.\n');
fclose(fidtim);

% create the *.rsp file
fidrsp=fopen(strcat(fname,'.rsp'),'w');
if outputtype==1
fprintf(fidrsp,'\n%s.pnm \n1\n1
1\n0\nN\n1\n%d\n1\n1\n1\nN\n1\nN\nN\nY\n',fname,outputtype);
elseif outputtype==2
fprintf(fidrsp,'\n%s.pnm \n1\n1
1\n0\nN\n1\n%d\nN\n1\n1\n1\nN\n1\nN\nN\nY\n',fname,outputtype);
elseif outputtype==3
fprintf(fidrsp,'\n%s.pnm \n1\n1 1\n0\nN\n1\n%d\n1\n1
1\n1000\n1\n1\n1\nN\n1\nN\nN\nY\n',fname,outputtype);
end
fclose(fidrsp);

% before modpath is run, the particle positions are equal to the initial
particle positions
x=xs; y=ys; xc=xs_c; yc=ys_c;

% set distribution of all particles at t=0 (before push)
count=zeros(nrow,ncol);
countc=zeros(nrow,ncol);

for b = 1:nrow;
for c = 1:ncol;
list = find(y>=ymin+(b-1)*dy & y<ymin+b*dy & x>=xmin+(c-1)*dx &
x<xmin+c*dx);
if ~ isempty(list)
count(b,c)=length(list);
end %for if

listc = find(yc>=ymin+(b-1)*dy & yc<ymin+b*dy & xc>=xmin+(c-1)*dx &
xc<xmin+c*dx);
if ~ isempty(listc)
countc(b,c)=length(listc);
end %for if
end %for b
end %for c

% set up initial concentrations for reaction
maxconc=4;
ntreat=length(x);
mass=maxconc*ones(ntreat,1);
ncont=length(xc);
massc=ones(ncont,1);

% initial total mass in each bin
massbin=zeros(ncol,nrow);
masscbin=zeros(ncol,nrow);
initmassc=sum(massc);

% start EIE loop here
for i=1:nper

```

```

% write well file for each iteration of the loop
if ~nwells==0
    fidwel=fopen(strcat(fname, '.wel'), 'w');
    cw=zeros(abs(nwells),1);
    rw=zeros(abs(nwells),1);

    for m=1:nwells
        cw(m)=find(xx<x_wells(m),1,'last');
        rw(m)=nrow-find(yy<y_wells(m),1,'last')+1;
    end

    fprintf(fidwel, '%10d          50 \n',1);
    fprintf(fidwel, '%10d\n',1);
    fprintf(fidwel, '          1 %9d %9d %9g \n',rw(flows(i*2-1)),cw(flows(i*2-1)),flows(2*i)*por);
    fclose(fidwel);
end

% run MODFLOW
eval('! mf2k.exe > screenoutput');

% This routine (below) will read in a MODFLOW binary budget output file and
% will extract right and front face flows. Author: Roseanna Neupauer

fidbud=fopen(strcat(fname, '.bud'), 'rb');

tt=fread(fidbud,2,'int32');
header=setstr(fread(fidbud,16,'uchar'))'; %'
temp=fread(fidbud,4,'int32');
temp1=fread(fidbud,3,'float32');
nc=temp(1);
nr=temp(2);

while ~isempty(temp)

% READ STORAGE

    ilay=abs(temp(3));
    A=fread(fidbud,nc*nr,'float32');
    A=reshape(A,nc,nr)'; %'

% READ CONSTANT HEAD

    tt=fread(fidbud,2,'int32');
    header=setstr(fread(fidbud,16,'uchar'))'; %'
    temp=fread(fidbud,4,'int32');
    temp1=fread(fidbud,3,'float32');
    nlist=fread(fidbud,1,'int32');

    for ilist=1:nlist

        temp=fread(fidbud,1,'int32');
        temp1=fread(fidbud,1,'float32');

    end
end

```

```

% READ FLOW RIGHT FACE (QXX)
tt=fread(fidbud,2,'int32');
header=setstr(fread(fidbud,16,'uchar'))); %'
temp=fread(fidbud,4,'int32');
templ=fread(fidbud,3,'float32');

A=fread(fidbud,nc*nr,'float32');
QXX=flipud(reshape(A,nc,nr))'); %'

% READ FLOW FRONT FACE (QYY)
tt=fread(fidbud,2,'int32');
header=setstr(fread(fidbud,16,'uchar'))); %'
temp=fread(fidbud,4,'int32');
templ=fread(fidbud,3,'float32');

A=fread(fidbud,nc*nr,'float32');
QYY=-flipud(reshape(A,nc,nr))'); %'

% READ WELLS
tt=fread(fidbud,2,'int32');
header=setstr(fread(fidbud,16,'uchar'))); %'
temp=fread(fidbud,4,'int32');
templ=fread(fidbud,3,'float32');

nn=fread(fidbud,1,'int32');
nlist=fread(fidbud,1,'int32');

temp=fread(fidbud,1,'int32');
templ=fread(fidbud,1,'float32');

tt=fread(fidbud,2,'int32');
header=setstr(fread(fidbud,16,'uchar'))); %'
temp=fread(fidbud,4,'int32');
templ=fread(fidbud,3,'float32');

end

fclose(fidbud);

porbdy=por*b*dy;
porbdx=por*b*dx;

icol=ceil((x-xmin)/dx);
irow=ceil((y-ymin)/dy);
vx=[]; vy=[]; v=[];

index=(floor((x-xmin)/dx))*nrow+ceil((y-ymin)/dy);
vx=QXX(index)/porbdy;
vy=QYY(index)/porbdx;
v=sqrt(vx.^2+vy.^2);

icol_c=ceil((xc-xmin)/dx);
irow_c=ceil((yc-ymin)/dy);

```

```

vx_c=[]; vy_c=[]; v_c=[];

index_c=(floor((xc-xmin)/dx))*nrow+ceil((yc-ymin)/dy);
vx_c=QXX(index_c)/porbdy;
vy_c=QYY(index_c)/porbdx;
v_c=sqrt(vx_c.^2+vy_c.^2);

% disperse the particles
[x,y] = disperse_flowface_faster(x,y,vx,vy,v,nstep,0.0005);
[xc,yc] = disperse_flowface_faster(xc,yc,vx_c,vy_c,v_c,nstep,0.0005);

% write the prt file to be reread into MODPATH
fidprt=fopen(strcat(fname, '.prt'), 'w');
for j=1:length(x)
fprintf(fidprt, '%8d%8d%8d%8.4f%8.4f%8.4f%8d%8d%8d\n',1,1,1,x(j)-xmin,y(j)-ymin,0.5,2,2,0,0);
end

for j=1:length(xc)
fprintf(fidprt, '%8d%8d%8d%8.4f%8.4f%8.4f%8d%8d%8d\n',1,1,1,xc(j)-xmin,yc(j)-ymin,0.5,2,2,0,0);
end

fclose(fidprt);

% run MODPATH

cmd=sprintf('! mpathr5_0.exe < %s.rsp',fname);
eval(cmd);

% get the particle positions from the endpoint file
if outputtype==1

fid=fopen(strcat(fname, '.end'), 'r');
fgetl(fid);
temp=fscanf(fid, '%f');
nn=length(temp)/19;
temp=reshape(temp,19,nn)'; %'
fclose(fid);

x=temp(1:length(x),5)+xmin; % variable for x-coords of ts part locations
y=temp(1:length(y),6)+ymin; % variable for y-coords of ts part locations

xc=temp(length(x)+1:length(x)+length(xc),5)+xmin; % variable for x-coords
of contaminant locations
yc=temp(length(y)+1:length(y)+length(yc),6)+ymin; % variable for y-coords
of ts particle locations

end

% new dy and dx to make reaction bins bigger than MODFLOW bins
dyy=0.025; dxx=0.025;
nncol = ceil((xmax-xmin)/dxx);
nnrow = ceil((ymax-ymin)/dyy);

```

```

% set smaller search range than the entire aquifer
sxmin = 1.5*min(x_wells); sxmax = 1.5*max(x_wells);
symin = 1.5*min(y_wells); symax = 1.5*max(y_wells);

% perform reaction here!
for b = 1:nnrow;
    for c = 1:nncol;

        % treatment solution
        listtrmt = find(y>=symin+(b-1)*dyy & y<symin+b*dyy & x>=sxmin+(c-1)*dxx &
            x<sxmin+c*dxx);
        massbin(b,c)=sum(mass(listtrmt));

        % groundwater contaminant
        listcntm = find(yc>=symin+(b-1)*dyy & yc<symin+b*dyy & xc>=sxmin+(c-1)*dxx
            & xc<sxmin+c*dxx);
        masscbin(b,c)=sum(massc(listcntm));

        % perform reaction
        if massbin(b,c)>=masscbin(b,c)
            mass(listtrmt)=(massbin(b,c)-masscbin(b,c))/length(listtrmt);
            massbin(b,c)=massbin(b,c)-masscbin(b,c);
            masscbin(b,c)=0;
            massc(listcntm)=0;
        else
            massc(listcntm)=(masscbin(b,c)-massbin(b,c))/length(listcntm);
            masscbin(b,c)= masscbin(b,c)-massbin(b,c);
            massbin(b,c)=0;
            mass(listtrmt)=0;
        end

    end %for b
end %for c

% find particles at well location
if lambda2(i) < 0;
    listinwell = find(x>xwell(i)-(dx/2) & x<xwell(i)+(dx/2) & y>ywell(i)-
        (dy/2) & y<ywell(i)+(dy/2));
    listcinwell = find(xc>xwell(i)-(dx/2) & xc<xwell(i)+(dx/2) & yc>ywell(i)-
        (dy/2) & yc<ywell(i)+(dy/2));

    cloggedmass(i) = sum(mass(listinwell));
    cloggedmassc(i) = sum(massc(listcinwell));
else
    cloggedmass(i)=0;
    cloggedmassc(i)=0;
end

totrmvd(i)=initmassc-sum(massc)+sum(cloggedmassc)
totrctd(i)=initmassc-sum(massc)

% identify degraded contaminant particles with mass = 0 for plotting
prod=find(mass==0);
prodc=find(massc==0);

```

```

xpc=xc(prodc);
ypc=yc(prodc);

% remove reacted or clogged particles (with mass = 0) to speed up code

%     existmass=find(mass>0);
%     existmassc=find(massc>0);
%
%     x=x(existmass);
%     y=y(existmass);
%     mass=mass(existmass);
%
%     xc=xc(existmassc);
%     yc=yc(existmassc);
%     massc=massc(existmassc);

% show and save single plot
close(figure(1))
figure(1)
plot(x,y,'y.',xc,yc,'b.')
hold on

plot(xpc,ypc,'.','markeredgecolor',[0,0.55,0.1],'markerfacecolor',[0,0.55,0.1])
set(gca,'xgrid','on','ygrid','on')
set(gca,'fontweight','demi','fontsize',13)
hold on
plot(x_wells,y_wells,'ko','markersize',6)
set(gca,'fontweight','demi')
axis equal
axis([-1.3,1.3,-1.3,1.3]);
wname='NESW';
hold on

for j=1:nwells
text(x_wells(j)+0.05,y_wells(j)0.1,wname(j),'fontsize',14,'fontweight','demi')
end

xlabel('x(m)');
ylabel('y(m)');
set(gca,'fontweight','demi')
saveas(gcf,['Step', int2str(i)],'png')

% show multiplot for each stage of dispersed push
% PLOT POSITION VARIABLES
pirow=[3,3,3,3,2,2,2,2,1,1,1,1];
picol=[1,2,3,4,1,2,3,4,1,2,3,4];
pxmin=0.09;
pymin=0.11;
pxwid=0.20;
pywid=0.25;
pdx=0.01;
pdy=0.05;

figure(3)
plabel=['a','b','c','d','e','f','g','h','i','j','k','l'];

```

```

subplot(3,4,i)
text(-0.9,-0.8,plabel(i),'fontsize',12,'fontweight','demi')
hold on subplot('position',[pxmin+(picol(i)-1)*(pdx+pxwid),pymin+(pirow(i)-
1)*(pdy+pywid),pxwid,pywid])
plot(x,y,'y.',xc,yc,'b.','markersize',4.5)
hold on
plot(xpc,ypc,'.','markersize',4.5,'markeredgecolor',[0,0.55,0.1],'markerfaceco
lor',[0,0.55,0.1])
text(0.6,0.75,sprintf('% d',i),'fontsize',12,'fontweight','demi')
set(gca,'xgrid','on','ygrid','on')
plot(x_wells,y_wells,'ko','markersize',4)
hold on
set(gca,'fontweight','demi','fontsize',12)
axis equal
axis([-1.3,1.3,-1.3,1.3]);

% ADDED LINES TO REMOVE TICK LABELS AND LABEL AXES
if pirow (i) ~= 1
    set(gca,'xticklabel',' ');
    else
        xlabel('x (m)')
end

if picol (i) ~= 1
    set(gca,'yticklabel',' ');
    else
        ylabel('y (m)')
end

end

figure(11)
bar(totrctd)
ylabel('Contaminant Particles Reacted')
xlabel('Step of Scheme')

```