1
2
3
4 Optimal design of active spreading systems to remediate sorbing groundwater
5
6 contaminants in situ

7 Amy N. Piscopo^{1*}, Roseanna M. Neupauer¹, Joseph Kasprzyk¹

8
9
10 ¹University of Colorado Boulder, 1111 Engineering Drive, Boulder, CO 80309, USA

11
12 *corresponding author, email: amy.piscopo@colorado.edu, amy.piscopo@gmail.com,
13
14 postal address: UCB 428, Boulder, CO 80309-0428, USA

15
16
17 Keywords: groundwater modeling, groundwater remediation, in situ remediation, multi-
18
19 objective optimization, sorption
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1. Introduction

Sorbing contaminants in groundwater pose many challenges to remediation methods. Because some portion of the sorbing contaminant remains attached to the soil matrix, remediation methods that remove only the aqueous phase contaminant, such as pump-and-treat, have proven unsuccessful at remediating sorbing contaminants (Kavanaugh et al., 2003). With in situ remediation, a treatment chemical is injected into the contaminated aquifer to react with and degrade the aqueous-phase contaminant. As the aqueous-phase contaminant is degraded, the sorbed-phase contaminant partitions into the aqueous phase, allowing the degradation process to continue. The effectiveness of in situ remediation depends on the degree of contact between the injected treatment chemical and the contaminant (Siegrist et al., 2012); therefore, a key challenge in the design of in situ remediation systems is to ensure that the treatment chemical is adequately delivered throughout the contaminant plume.

Some recent advances to address this challenge involve modifying treatment chemical properties or modifying the subsurface flow conditions. Since viscosity is one property that affects the mobility of the treatment chemical in the subsurface, studies have investigated the use of amendments to increase viscosity of the treatment chemical. For instance, McCray et al. (2010) demonstrated in lab experiments with tanks layered with sands of different grain sizes that the proportion of the tank contacted by the treatment chemical could be increased significantly by amending the treatment chemical with xanthan gum to increase its viscosity. To modify subsurface flow, pneumatic and hydraulic fracturing have been applied during in situ remediation to create pathways for treatment chemical transport in the subsurface. In a field study, Scheutz et al. (2010) used hydraulic fracturing to facilitate the transport of the treatment chemical through low-permeability soils, which led to more complete degradation of the chlorinated solvents present at that site.

Active spreading techniques are another option for modifying subsurface flow. These techniques use pre-defined injections and extractions of water at wells surrounding the contaminant plume to generate flow fields that spread the plumes of groundwater contaminant and treatment chemical in a manner that increases their contact. Neupauer and Mays (2014) simulated an injection of treatment chemical into a plume of sorbing

contaminant, followed by extractions of clean water at well locations surrounding the plume to draw the treatment chemical through the contaminated region. Results demonstrated that this active spreading approach achieves nearly complete contaminant degradation for fast rates of contaminant sorption and desorption relative to the treatment period and high reaction rate coefficients, but the approach was less effective for contaminants with slow rates of sorption and low reaction rate coefficients (Neupauer and Mays, 2014).

In this study, a multi-objective evolutionary algorithm (MOEA) is used to optimize active spreading during in situ remediation to remediate a sorbing contaminant in a two-dimensional, isotropic, confined aquifer. We consider both homogeneous and heterogeneous aquifers. To represent a variety of different types of sorbing contaminants, six cases are optimized in this study, each with a different combination of reaction and sorption properties. Three design parameters - the mass of treatment chemical injected, the rate of treatment chemical injection, and the duration of its injection - are optimized to maximize contaminant degradation while minimizing material and energy requirements. Each solution to the optimization problem is comprised of a unique set of design parameter values. Additionally, optimization of the in situ remediation system is conducted for three different ambient velocities and for two different remediation time frames to determine how the solutions to the optimization problem vary under these conditions. All optimal designs (i.e. solutions) are analyzed to understand how the design parameters of the solutions relate to the remediation objectives and to the reaction and sorption properties of the contaminant.

The remainder of this paper is structured as follows. Section 2 introduces the active spreading system considered in this work and provides the governing equations used to model advection, dispersion, sorption, and reaction during in situ remediation. Section 3 introduces multi-objective optimization in the context of groundwater applications and then describes the specific optimization framework used in this study, which includes objective function equations and design parameters definitions. Section 4 presents the results of the multi-objective optimizations, and analyzes how the sorption and reaction rates affect the in situ remediation system design and performance. Section 5

discusses the applicability of the results to the current practice of in situ remediation. Section 6 provides conclusions.

2. Reactive Transport Modeling

This study simulates in situ remediation of a two-dimensional circular plume of sorbing groundwater contaminant, which has an initial mass of m_1^0 and an initial plume radius of r_{init} (Fig. 1a). The contaminated aquifer is assumed to be confined, isotropic, and two-dimensional. At the start of remediation, the contaminant is assumed to have partitioned to equilibrium between the aqueous and sorbed phases. Although some contaminants can require weeks to months to reach equilibrium (Pignatello and Xing 1996), the preparation and implementation of remedial action plans for contaminated groundwater sites are rarely completed in that time frame; thus, the assumption of equilibrium between phases at the start of remediation is valid.

The approach used here to remediate a sorbing contaminant with active spreading is to inject a non-sorbing treatment chemical into a well located at the center of the contaminant plume, forming a circular plume of treatment chemical surrounded by the contaminant plume following the injection phase approach of Neupauer and Mays (2014). During this injection, the treatment chemical and contaminant plumes move radially away from the injection well. Because the contaminant movement is retarded due to sorption, the treatment chemical plume moves more rapidly and overlaps the contaminant plume (Fig. 1b), which provides the opportunity for contaminant degradation. Injection occurs for a time T until the outer edge of the treatment chemical plume has passed beyond the outer edge of the contaminant plume. If no reaction were to occur, the positions of the treatment chemical and contaminant plumes after the injection would be as shown in Fig. 1b, with final radii r_{tc} and r_f for the treatment chemical and contaminant plumes, respectively.

Since the contaminant moves radially away from the injection well during the injection period, treatment chemical injected near the end of the injection period never encounters contaminant. For this reason, it is not necessary to inject the treatment chemical throughout the entire injection period. Instead, the treatment chemical is injected for a duration of $T' < T$, and clean water is injected for the remainder of the

injection period. The treatment chemical and contaminant plumes at time T are shown in Fig. 1c without reaction and Fig. 1d with reaction.

For this system, reactive transport with bimolecular reaction is governed by the advection-dispersion-reaction equation, given by

$$\frac{\partial C_1}{\partial t} + \frac{\rho_b}{n} \frac{\partial S_1}{\partial t} = -\nabla \cdot (\mathbf{v}C_1) + \nabla \cdot (\mathbf{D}\nabla C_2) - kC_1C_2 \quad (1a)$$

$$\frac{\partial C_2}{\partial t} = -\nabla \cdot (\mathbf{v}C_2) + \nabla \cdot (\mathbf{D}\nabla C_2) - kFC_1C_2 + \frac{Q}{B}C_{2I}\delta(\mathbf{x} - \mathbf{x}_w) \quad (1b)$$

$$\frac{\partial S_1}{\partial t} = \alpha_s(K_dC_1 - S_1) \quad (1c)$$

where the numeric subscript indicates the chemical species (1 = contaminant, 2 = treatment chemical), ρ_b is the soil bulk density, n is the soil porosity, $\mathbf{v}$ is the groundwater velocity vector, k is the rate coefficient for reaction between treatment chemical and aqueous-phase contaminant, F is the stoichiometric ratio, i.e. the mass of treatment chemical reacted per mass of contaminant reacted, α_s is the sorption rate constant, K_d is the sorption partition coefficient, Q is the injection rate of treatment chemical, B is the aquifer thickness, C_{2I} is the injected concentration of treatment chemical, $\mathbf{x}_w$ is the location of the injection well, $\delta(\cdot)$ is the Dirac delta function, and $\mathbf{D}$ is the dispersion tensor, with components given by

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

where α_L and α_T are the longitudinal and transverse dispersivities, respectively. The last term in (1b) represents the time-dependent mass loading rate of treatment chemical such that

$$C_{2I} = \begin{cases} \frac{m_2^{inj}}{QT'} & \text{for } t \leq T' \\ 0 & \text{otherwise} \end{cases} \quad (3)$$

We assume that the treatment chemical can only degrade the aqueous-phase contaminant, not the sorbed-phase contaminant. The initial conditions on (1a-c) are

$$C_1(\mathbf{x}, t=0) = \begin{cases} \frac{m_1^o}{\pi r_{init}^2} & \text{for } |\mathbf{x}| \leq r_{init} \\ 0 & \text{otherwise} \end{cases} \quad (4a)$$

$$S_1(\mathbf{x}, t=0) = K_d C_1(\mathbf{x}, t=0) \quad (4b)$$

$$C_2(\mathbf{x}, t=0) = 0 \quad (4c)$$

To solve (1), we use random walk particle tracking, a common method for modeling solute transport in aquifers known for its computational efficiency and absence of numerical dispersion (Salamon et al., 2006). We adapted the particle tracking code RW3D (Fernandez-Garcia et al., 2005; Salamon et al., 2006), where the treatment chemical and contaminant are represented with collections of particles of known mass and phase. All treatment chemical particles are assigned the same initial mass. Similarly, all contaminant particles are assigned the same initial mass, which may be different than the initial mass of the treatment chemical particles. The velocity in (1) is obtained from MODFLOW (Harbaugh et al., 2000). Kinetic sorption in (1) is modeled using the approach described by Salamon et al. (2006). The second-order kinetic reaction of treatment chemical and contaminant particles in (1) was modeled following the approach of Neupauer and Mays (2014).

3. Optimization Approach

The optimization work of this study is conducted using a multi-objective evolutionary algorithm (MOEA). MOEAs have been used to optimize a wide variety of water resources systems, including many groundwater applications such as long term monitoring (Kollat and Reed, 2006; Reed and Minsker, 2004), irrigation supply (Wu et al. 2007), and remediation (Bayer and Finkel, 2004; Dokou and Karatzas, 2013; Piscopo et al., 2015; Schaerlaekens et al., 2005; Yoon and Shoemaker, 1999). A simulation model, such as a groundwater flow and transport model, is embedded in the search process of the MOEA to seamlessly evaluate the performance of candidate designs, or solutions.

Integrating the simulation model into the search process is a desirable feature of MOEAs

since it allows for the best available model to be used to evaluate solutions, providing a high degree of confidence in solution performance.

The output of multi-objective optimization is a non-dominated set of solutions, in which each solution is a unique active spreading design. The performance of each solution is evaluated based on objectives established for the remediation. These solutions are non-dominated because, for each solution in the set, the performance in one objective cannot be improved without diminishing the performance in another objective. This set of solutions reflects the tradeoffs between the different objectives of the design problem.

In this study, for the system shown in Fig. 1, four design parameters can be adjusted – the total duration of the injection, T , the duration of the treatment chemical injection T' ($T' < T$), the injection rate Q , and the injected treatment chemical mass m_2^o . In this work, the total injection duration T is fixed, and the other three design parameters are adjusted during the optimization process, as described below. The injection rate Q is assumed to be constant over the duration of the injection of treatment chemical.

3.1 Dimensionless Design Parameters

Of the design parameters mentioned above, three dimensionless design parameters are optimized in this study. The first dimensionless design parameter is the mass ratio, $m^* = m_2^{inj} / m_1^o F$, where m_1^o is the initial mass of contaminant and m_2^{inj} is the mass of treatment chemical injected to the aquifer. Because the initial contaminant mass, m_1^o , is the same in all scenarios considered in this study, varying m^* is equivalent to varying the mass m_2^{inj} of treatment chemical. To ensure that the injected mass of treatment chemical is adequate to degrade all of the contaminant, the mass ratio must be greater than or equal to the stoichiometric ratio ($m^* \geq F$). During optimization, the value of m^* is allowed to range from 1 to 50.

The second dimensionless design parameter is the injection time ratio, $T^* = T'/T$, where T' is the duration of the treatment chemical injection and T is the duration of the entire injection period, which includes the treatment chemical injection and the subsequent injection of clean water. In this study, T^* is given by $0 < T^* \leq 1$. For $T^* = 1$, treatment chemical is injected for the entire injection period T .

The third dimensionless design parameter is related to the injection rate Q . The injection rate must be sufficiently large that during the injection time T the outer edge of the treatment chemical plume catches up to the outer edge of the contaminant plume. For radial flow in a homogeneous aquifer, the contaminant plume radius r_f at the end of the injection period is given from Neupauer and Mays (2014) as

$$r_f = \sqrt{\frac{QT}{\pi b n R}} + r_{init}^2 \quad (5)$$

where r_{init} is the initial radius of the contaminant plume, r_f is the outer radius of the contaminant plume after injection, b is the aquifer thickness, and $R = 1 + \rho_b K_d / n$ is the retardation coefficient. Also, the outer radius, r_{tc} , of the treatment chemical plume at the end of the injection period is given by Neupauer and Mays (2014) as

$$r_{tc} = \sqrt{\frac{QT}{\pi b n}}. \quad (6)$$

The third dimensionless design parameter is the ratio of these two plume radii, defined as

$$\lambda_o = \frac{r_{tc}}{r_f}. \quad (7)$$

From (5) and (6), the relationship between the injection rate Q and the plume size ratio λ_o is given by

$$Q = \frac{\pi b R \lambda_o^2 r_{init}^2}{T(R - \lambda_o^2)}. \quad (8)$$

In the absence of reaction, the injection rate that is obtained with $\lambda_o = 1$ (or equivalently, $r_f = r_{tc}$) is an appropriate injection rate. With reaction, however, the leading edge of the treatment chemical plume degrades away as it passes through the contaminant plume (shown in Fig. 1d), and therefore its radius at the end of the injection period is less than the value calculated in (6) and depends on the reaction rate. To ensure that the outer edge of the treatment chemical plume reaches the outer edge of the contaminant plume after the injection period, it is necessary that $\lambda_o \geq 1$. In this study, the value of λ_o can range from 0.9 to $\sqrt{R}$.

3.2 Objectives

To measure the performance of each solution, three objectives that reflect remediation goals were established for this study. Since the fundamental purpose of any groundwater remediation process is to eliminate groundwater contamination, the first objective optimizes contaminant degradation by maximizing the total mass of contaminant that is degraded, expressed as a percentage of the initial contaminant mass, given by

$$\text{maximize } f_{\text{degradation}} = 100 \cdot \frac{m_1^o - m_1^f}{m_1^o} . \quad (9)$$

where m_1^f is the contaminant mass remaining in the aquifer at the end of the injection period.

The amount of treatment chemical used for a remediation project represents a material requirement of the project. To minimize material requirements, the second objective minimizes the injected mass of treatment chemical, normalized by F to account for the different reaction stoichiometries of the different contaminants, given as

$$\text{minimize } f_{\text{material}} = m_2^{inj} / F . \quad (10)$$

Another requirement is the amount of energy needed for injection, which is related to the injection rate, Q . The amount of energy needed for injection can vary depending on a number of factors; however, since the relationship between energy and injection rate is the same for all scenarios evaluated in this study, the injection rate serves a reasonable proxy for energy consumption. Therefore, the third objective minimizes the injection rate Q , given as

$$\text{minimize } f_{\text{injection}} = Q . \quad (11)$$

3.3 Optimization Algorithm

The MOEA used in this study is the Borg MOEA (Hadka and Reed, 2013). The Borg MOEA adaptively selects search operators based on their progress in approximating the non-dominated front, a design feature that has allowed it to perform well in comparative studies of MOEA performance (e.g., Reed et al., 2013). For each optimization, the Borg MOEA was run for a search duration of 30,000 function

evaluations (i.e. 30,000 solutions of (1) with different combinations of the design parameters λ_o , m^* , and T^*). The search duration was determined by conducting a series of optimizations with increasing numbers of function evaluations until differences in solution performance between optimizations were negligible.

4. Results

The design of the in situ remediation system was optimized for six cases representing the remediation of three contaminants, trichloroethene (TCE), tetrachloroethene (PCE) and toluene, using the treatment chemical, permanganate (MnO_4). The reaction and sorption properties for these cases are shown in Table 1. The reaction rate coefficient for TCE and MnO_4 (Huang et al., 1999) is one order of magnitude higher than for PCE and MnO_4 (Huang et al., 2002), and several orders of magnitude higher than for toluene and MnO_4 (Rudakov and Lobachev, 2000) in order to represent fast, moderately fast, and slow reaction kinetics, respectively (Table 1). The degradation of these contaminants is modeled under fast and slow sorption kinetics, where the sorption rate constants shown in Table 1 are representative of the sorption kinetics occurring in soils with different amounts of organic carbon, as determined in experimental studies (Maraqua, 2001). We use the aquifer and contaminant properties shown in Table 2, and assume the same soil bulk density ρ_b and the same porosity n for all cases since these parameters do not greatly influence the sorption rate constant as compared to the organic content of the soil. Also, because TCE, PCE, and toluene have similar affinities for water, as inferred from their octanol-carbon partition coefficients, (Garbarini and Lion, 1986; US EPA, 1986), we assume the same distribution partition coefficient K_d for all cases. Lastly, we assume the same dispersivity values in all cases because the reactant overlap that occurs during active spreading is caused almost entirely because of sorption.

The three dimensionless design parameters - mass ratio m^* , injection time ratio T^* , and plume size ratio λ_o - were optimized to maximize contaminant degradation ($f_{\text{degradation}}$), minimize the amount of treatment chemical (f_{material}) and minimize the energy requirements ($f_{\text{injection}}$). Due to tradeoffs between these objectives, the optimization results are a set of many non-dominated solutions, where each solution represents a different

design with a different combination of design parameter values. Optimization was performed for four different remediation scenarios, each with a different combination of injection duration T , ambient groundwater velocity, and aquifer type (homogeneous and heterogeneous), as summarized in Table 3. Both injection durations are shorter than the persistence duration of treatment chemicals like MnO_4 (Huling and Pivetz, 2006), meaning that the treatment chemical is available throughout the duration of the injection period to degrade the groundwater contaminant. To model a heterogeneous aquifer, we used sequential Gaussian simulation in GSLIB (Deutsch and Journel, 1992) to generate spatially-correlated randomly-varying fields of hydraulic conductivity K for the four sets of statistical properties given in Table 4, referred to as heterogeneity models. Twelve realizations of the heterogeneity model were generated for each set of statistical properties. During optimization, the objective function values of each candidate solution were calculated for each realization and the average value from the twelve realizations was evaluated by the MOEA, e.g.

$$\overline{f_{\text{degradation}}} = \sum_{n=1}^{12} (f_{\text{degradation}})_n \cdot \quad (12)$$

This approach leads to solutions that are robust for each heterogeneity model rather than solutions that reflect a particular feature of a specific realization.

4.1 Scenario 1: $T = 56$ days, negligible ambient flow, homogeneous aquifer

The first remediation scenario in this study has negligible ambient flow and a 56-day injection period. Figs. 2 and 3 show the non-dominated sets of solutions for each case. In Fig. 2, each solution is plotted as point in a three-dimensional space in which each dimension represents one of the three objective functions, while in Fig. 3, solutions are plotted in terms of their design parameter values with $f_{\text{degradation}}$ indicated by the color. In Fig. 2, the bottom right front corner of the plot, denoted by the gray star, represents the ideal point for this space, i.e., the point with the highest amount of contaminant degradation ($f_{\text{degradation}}$) and the lowest material requirements (f_{material}) and energy requirements ($f_{\text{injection}}$). The geometric shape of the non-dominated fronts is convex relative to the ideal point, indicating a tradeoff among the objectives. In other words, improving the value of one objective function, such as increasing contaminant

degradation ($f_{\text{degradation}}$), is only possible if another objective function is made worse, such as injecting at higher rate ($f_{\text{injection}}$) or adding more treatment chemical mass to the system (f_{material}).

Fig. 2 shows that the solutions from Case 1 (fast reaction, fast sorption) are closest to the ideal point, meaning that high amounts of contaminant degradation ($f_{\text{degradation}}$) are achieved using less treatment chemical (f_{material}) and less energy ($f_{\text{injection}}$) than the solutions from the other cases. In the $f_{\text{degradation}} - f_{\text{material}}$ plane of Fig. 2, the reaction rate coefficient k most strongly influences the proximity of solutions to the ideal point; Cases 1 and 2 (TCE, i.e. fast reaction) are closest to the ideal point, followed closely by solutions from Cases 3 and 4 (PCE, i.e. moderately fast reaction). Solutions from Cases 5 and 6 (toluene, i.e. slow reaction), which have a reaction rate coefficient three orders of magnitude lower than that of TCE, are substantially farther than the other solutions from the ideal point. This pattern is also evident in Fig. 3, which shows that for a given set of design parameter values, the highest amount of contaminant degradation is achieved in Case 1 and the lowest amount of contaminant degradation is achieved in Case 6. For example, with $\lambda_o = 0.9$, $m^* = 1$, and $T^* = 0.01$ (lower front left corners of the subplots in Fig. 3), Case 1 achieves 96% contaminant degradation, while Cases 2 - 6 achieve 80%, 43%, 37%, 2.5%, and 2.5%, respectively.

From (1), the reaction rate of the aqueous-phase contaminant is kC_1C_2 ; thus the reaction rate depends on the reaction rate coefficient k and the chemical concentrations. With the high reaction rate coefficients (Cases 1 and 2), high amounts of reaction can be achieved even with lower concentrations of treatment chemical, C_2 . Consequently, solutions from cases with high to moderately-high reaction rate coefficients use less treatment chemical mass for a given injection rate and amount of contaminant degradation than solutions from cases with low reaction rate coefficients, as reflected by the low f_{material} values (Fig. 2) and low m^* values (Fig. 3a,d) for Cases 1 and 2 and the moderate f_{material} values (Fig. 2) and moderate m^* values (Fig. 3b,e) of Cases 3 and 4 compared to the high f_{material} values (Fig. 2) and high m^* values of Cases 5 and 6 (Fig. 3c,f). On the other hand, the low reaction rate coefficients of Cases 5 and 6 require a higher treatment chemical concentration, C_2 , to achieve contaminant degradation. These higher concentrations can be attained by injecting more treatment chemical mass, which

is reflected by the high f_{material} values (Fig. 2) and high values of m^* (Fig. 3c,f) of the solutions from Cases 5 and 6 relative to solutions from Cases 1-4.

Fig. 3 shows that the sorption rate strongly influences the optimal design parameters of the remediation system. For example, comparison Fig. 3a (high sorption rate constant) and 3b (low sorption rate constant) shows that a more slowly sorbing contaminant requires higher treatment chemical mass (higher m^*), longer treatment chemical durations (higher T^*), and higher injection rates (higher λ_o) to achieve similar amounts of contaminant degradation as the more rapidly sorbing contaminant. To explain this behavior, Fig. 4 shows the configuration of the treatment chemical and contaminant plumes for two example solutions, denoted in Figs. 2 and 3 as *I* and *II*, from Case 1 (high sorption rate constant, Fig. 4a) and Case 2 (low sorption rate constant, Fig. 4b), respectively. Both solutions are taken from cases with high reaction rate coefficients and achieve similar amounts of contaminant degradation.

With low sorption rate constants, the contaminant spends more time in one phase before partitioning to the other, relative to contaminants with high sorption rate constants. Sorbed-phase contaminant that is initially near the well can remain there for long periods of time, and likewise, aqueous-phase contaminant initially near the perimeter of the contaminant plume can be transported far from the injection well before transitioning to the aquifer phase. Because the treatment chemical is non-sorbing, the leading edge of the treatment chemical plume eventually overtakes the leading edge of the contaminant regardless of the contaminant sorption rate. However, for high sorption rate constants, the treatment chemical will overtake the outer edge of the contaminant plume closer to the well than for low sorption rate constants, because the leading edge of the contaminant plume does not travel as far with high sorption rate constants as compared with low sorption rate constants. This behavior can be seen by comparing the outer edge of the contaminant plumes in Fig. 4, which is closer to the well in the case with a high sorption rate constant (Fig. 4a). Thus, for low sorption rate constants (Fig. 4b), the treatment chemical must be injected at a high rate and over a longer period so it can overlap and degrade the leading edge of the contaminant plume, as reflected by the high $f_{\text{injection}}$ values (Fig. 2) and the high λ_o and high T^* values (Fig. 3d,e) of the solutions from Cases 2 and 4.

The trailing edge of the contaminant plume, however, travels farther with high sorption rate constants than with low sorption rate constants, because fewer contaminant particles remained sorbed near the injection well for long periods as compared to in cases with low sorption rate constants. This behavior can be seen by comparing the inner edge of the contaminant plumes in Fig. 4, which is farther from the well in the fast sorption case (Fig. 4a). Thus, for high sorption rate constants (Fig. 4a), lower injection rates and shorter treatment chemical injection periods can produce sufficient overlap of the treatment chemical with the trailing edge of the contaminant plume to facilitate contaminant degradation, which is reflected by the low $f_{\text{injection}}$ values (Fig. 2) and the low λ_o and low T^* values (Figs. 3a,b) of the solutions from Case 1 (relative to Case 2) and Case 3 (relative to Case 4).

Cases 5 and 6 (low reaction rate coefficients) do not exhibit the same behavior with respect to sorption rate constant as the other cases, although the leading edge of the contaminant plume in Case 6 (low sorption rate constant) travels farther from the injection well than in Case 5 (high sorption rate constant). The reaction rate coefficient of Cases 5 and 6 is substantially lower than in Cases 1-4, which substantially limits the amount of contaminant degradation that can occur during the injection period considered in these simulations ($T = 56$ days). Thus, any additional degradation that could be achieved in Case 6 from using a higher injection rate to catch the leading edge of the contaminant plume is not comparable to the degradation achieved by using a low injection rate to increase the contact time with the contaminant, thereby increasing the reaction rate through kC_1C_2 . Thus for Cases 5 and 6, the tradeoff between the objectives is two-dimensional; the amount of contaminant degradation ($f_{\text{degradation}}$) can be increased by using more treatment chemical mass (f_{material}) but not by increasing the injection rate ($f_{\text{injection}}$).

4.2 Scenario 2: $T = 56$ days, non-negligible ambient flow, homogeneous aquifer

In this subsection, the effects of ambient flow on the in situ remediation system designs are evaluated using two different approaches. First, for each of the non-dominated solutions for Cases 1-4 in Scenario 1, reactive transport during in situ remediation was simulated in an aquifer with ambient flow, and the amount of

contaminant degradation was compared to the amount of degradation in the absence of ambient flow (i.e., to the situation for which the optimization was performed). This analysis evaluates the robustness of the solutions to uncertain ambient flow. In a subsequent analysis, multi-objective optimization is used for Case 2 (low sorption rate constant and high reaction rate coefficients) to obtain the non-dominated solutions that account for ambient flow. This second analysis enables an understanding of how the design parameters can be adjusted to account for ambient flow. For both analyses, low and high ambient flows are simulated, with flow aligned in the x direction and with velocities of $V_x = 0.1\text{m/d}$ and $V_x = 0.5\text{m/d}$, respectively. Upgradient of the well, flow from the injection opposes the ambient groundwater velocity; consequently, a groundwater divide exists which hydraulically separates the aquifer into a zone that is isolated from the injected treatment chemical and a zone that contains the injected treatment chemical. The point on the divide that is directly upgradient of the well is a stagnation point, denoted by (x_o, y_o) (Charbeneau, 1999). For this system with ambient velocity in the $+x$ direction, $y_o = 0$ and $x_o < 0$. For low injection rates Q and therefore low λ_o , the stagnation point is closer to the well, while for high injections rates and high λ_o , the stagnation point is farther from the well.

The results of the first analysis are shown in Fig. 5, which shows a scatterplot of the amount of contaminant degradation ($f_{\text{degradation}}$) that would occur under the low ambient flow and high ambient flow conditions versus the amount of contaminant degradation for the solutions optimized without ambient flow. The solutions along the 1:1 line in Fig. 5 are solutions with high Q (i.e., high λ_o) for which their stagnation points along the groundwater divide are at or upgradient of $(x,y) = (-r_{\text{init}}, 0)$. Consequently, the entirety of the contaminant plume for these solutions is located in the zone that contains the injected treatment chemical and therefore, the amounts of degradation are similar to the case without ambient flow. Solutions above the 1:1 line in Fig. 5 actually have slightly more contaminant degradation with ambient flow than without it, because upgradient of the well, the flow from the injection at the well is opposite to the ambient groundwater flow, pushing the treatment chemical into the groundwater contaminant as both species are advected downgradient. The solutions with low Q (i.e., low λ_o) are located beneath the 1:1 line in Fig. 5 because the stagnation points of these solutions are

located within the contaminant plume. For example, Figs. 6a,b shows the treatment chemical and contaminant plumes traveling in the +x direction under high ambient velocity for an example solution identified in Fig. 5 (Solution III), which has a stagnation point with an x-coordinate equal to -10 m. In this case, a portion of the plume is in the zone that is hydraulically isolated from the injected treatment chemical plume and therefore cannot degrade.

Figs. 7 and 8 show the non-dominated solutions for the second analysis along with the non-dominated solutions for Case 2 in the absence of ambient flow (from Figs. 2 and 3). The solutions are shown in two three-dimensional plots with each dimension representing an objective function value in Fig. 7, and a design parameter value in Fig. 8. The non-dominated front in Fig. 7 for solutions with $V_x = 0.1$ m/d is only slightly farther from the ideal point than the front for solutions without ambient flow. Similarly, in Fig. 8, the solutions with $V_x = 0.1$ m/d have slightly higher m^* values (proportional to f_{material}) and λ_o values (related to $f_{\text{injection}}$) than the solutions without ambient flow. However, solutions with $V_x = 0.5$ m/d inject more treatment chemical mass over longer periods at higher injection rates, as shown by their f_{material} and $f_{\text{injection}}$ values (Fig. 7) and m^* , λ_o and T^* (Fig. 8). With higher injection rates (from higher λ_o), the stagnation point along the groundwater divide is sufficiently far from the well such that at most only a small portion of the contaminant plume is hydraulically isolated from the injected treatment chemical. The increase in Q from increased λ_o decreases the concentration of the treatment chemical, given by $m_2^{\text{inj}}/Q/T'$. Therefore, to ensure that the initial concentration of treatment chemical is adequate to maintain high reaction rates, given by kC_1C_2 (1), the injected mass of treatment chemical must also increase (proportional to m^*). Thus, despite higher ambient flow, the non-dominated solutions still achieve high levels of contaminant degradation, but require more material and energy.

4.3 Scenario 3: $T = 84$ days, negligible ambient flow, homogeneous aquifer

To investigate the effects of different injection durations on the optimal active spreading designs, the optimization for Cases 3-6 were repeated for a longer injection period duration of $T = 84$ days, which allows more time for reaction to occur. Fig. 9 shows the non-dominated solutions for Case 4 for these two values of T . The solutions

with $T = 84$ days use lower injection rates (lower $f_{\text{injection}}$) and achieve slightly more contaminant degradation (higher $f_{\text{degradation}}$) using the same amount of treatment chemical mass (related to f_{material}). When the same mass of treatment chemical is injected at a lower injection rate, the concentration of the injected treatment chemical increases, thereby increasing the rate of reaction through kC_1C_2 in (1), leading to more contaminant degradation. Also, notice from (7) that increasing the injection period T leads to a decrease in the injection rate Q so long as the other parameters remain constant, including the plume size ratio λ_o . Using the same plume size ratio with a longer injection period would result in the same final position of the reactant plumes as seen previously (with $T = 56$ days); however, because the amount of time that the reactants spend in contact increases, more contaminant degradation occurs, especially for cases with low reaction rate coefficients.

The same solutions from Case 4 (Fig. 9) in addition to solutions from Case 3, Case 5, and Case 6 are presented in Fig. 10, but in only two-dimensions to focus on the effect of increasing treatment chemical mass on contaminant degradation for the two injection durations. With a longer injection duration, more contaminant degradation can be achieved for a given amount of treatment chemical mass (related to m^*). In addition, notice that the relative impact on contaminant degradation of increasing the injection duration differs depending on the reaction rate coefficient of the contaminant. For instance, for $m^* = 20$, increasing the injection duration from 56 days to 84 days does not result in any significant increase in contaminant degradation for Case 3 (moderate reaction rate coefficient, fast sorption), but does yield an 11% increase in contaminant degradation for Case 5 (low reaction rate coefficient, fast sorption).

4.4 Scenario 4: $T = 56$ days, negligible ambient flow, heterogeneous aquifer

This last subsection considers a remediation scenario with a heterogeneous aquifer to determine how the optimal active spreading designs can vary depending on aquifer heterogeneity. Figs. 10 and 11 show the non-dominated solutions for Cases 1 -4 for a heterogeneous aquifer using 12 realizations of Heterogeneity Model 1 from Table 4. Solutions are plotted in terms of its objective function values in Fig. 11, along with the non-dominated solutions from Scenario 1 (homogeneous aquifer) for comparison. In

Fig. 12, solutions are plotted in terms of their design parameter values with $f_{\text{degradation}}$ indicated by the color.

The non-dominated solutions in Fig. 11 indicate that the same tradeoffs exist in homogeneous and heterogeneous aquifers; i.e., to increase contaminant degradation ($f_{\text{degradation}}$), greater amounts of injected treatment chemical mass (f_{material}) or higher injection rates ($f_{\text{injection}}$) are required. However, in each case, more treatment chemical mass and higher injection rates are necessary to achieve a given amount of degradation in a heterogeneous aquifer than in a homogeneous aquifer. With heterogeneous aquifers, permeable pathways can cause the reactants to move more quickly in areas with high hydraulic conductivity; therefore, portions of the leading edge of the contaminant plume travel farther from the injection well than in the homogeneous scenarios. Consequently, solutions from the heterogeneous scenario have higher injection rates to catch the leading edge of the contaminant plume (Fig. 11) and, relatedly, higher plume size ratios (Fig. 12). The variability in hydraulic conductivity also causes the transport of the reactants radially away from the injection well to be less uniform than in the homogeneous remediation scenarios, such that the distance between the leading and trailing edges of the contaminant plume is larger. Accordingly, the non-dominated solutions have higher injection time ratios (Fig. 12) to account for the variability in transport.

Fig. 13 shows the non-dominated solutions for a single case (Case 4) for the four heterogeneity models shown in Table 4. Solutions with small variance and short correlation length are closer to the ideal point than solutions with large variance and long correlation length. Greater variability in the hydraulic conductivity fields result in more tortuous paths for the treatment chemical in contaminant during active spreading, which can decrease the contact of the reactants, leading to slightly lower levels of degradation. However, overall the difference in degradation between the different heterogeneity models is relatively small; for example, for 5000 g of treatment chemical mass and an injection rate of 25 m³/d, 80% of the initial contaminant mass is degraded in a homogeneous aquifer (Fig. 2) versus 75% in the spatially-correlated heterogeneous aquifer (Fig. 11).

5. Discussion

The relationships assimilated from the results of this study provide new information for environmental engineers and decision-makers to consider when remediating contaminated aquifers. In current practice, the injection rates of treatment chemical (proportional to the plume size ratio, λ_o) are chosen without consideration of properties such as the sorption rate constant. Our results show that the injection rate should be selected based on the sorption rate constant, in order to catch the leading edge of the contaminant plume, which travels farther from the injection well for scenarios with low sorption rate constant as compared to scenarios with high sorption rate constant. Additionally, in scenarios with high ambient groundwater velocities, the injection rate should be selected to ensure that the groundwater divide encompasses the contaminant plume. Alternatively, the injection well could be installed upgradient of the plume centroid to ensure that none of the contaminant plume is hydraulically isolated from the injected treatment chemical. The optimization of the placement of the well within the contaminant plume was not evaluated in this study.

Our results also demonstrate the importance of selecting the design parameters as a set. For example, although an appropriate plume size ratio ensures that the treatment chemical catches the leading edge of the contaminant plume, this is only effective if the treatment chemical mass is adequate to maintain a fast reaction rate and the treatment chemical injection period is long enough to allow contact with any contaminant that desorbs near the well at late time. For contaminants with low sorption rate constants or in heterogeneous aquifers, results show two general regimes comprised of different sets of design parameters: injecting smaller amounts of treatment chemical mass (proportional to m^*) at higher rates (related to λ_o) over longer durations (proportional to T^*) or injecting high amounts of treatment chemical mass at lower rates over shorter durations. These regimes represent different active spreading options from which decision-makers can choose based on their preference for material or energy use.

To further connect these findings to current in situ remediation practice, here we comment on the performance of solutions from Cases 5 and 6, which represent toluene. Toluene is notably difficult to remediate due to its low reaction rate coefficient (Waldemer and Tratnyek, 2006). In Scenario 1 ($T = 56d$), only 64% and 56% of the

1
2
3
4 initial toluene mass was remediated in Cases 5 and 6 respectively (Fig. 2, Fig. 10b,d)
5 using the maximum allowable treatment chemical mass ($m^* = 50F$). As shown in Fig. 10,
6 increasing the injection duration in Scenario 3 ($T = 84\text{d}$) improves these results:
7 degradation of 77% and 65% of initial toluene mass in Cases 5 and 6, respectively
8 (Fig. 10b,d). Although minimizing the injection duration was not a formal objective of
9 this study, comparing the degradation of toluene in Scenarios 1 and 3 illustrates a
10 relevant tradeoff between the injection duration and the amount of contaminant
11 degradation. While the improvement in degradation for a given mass ratio and injection
12 ratio is not substantial for Cases 3 and 4 (Fig. 10a,c), for toluene, increasing the injection
13 duration provides a plausible solution to improve the remediation effectiveness. The
14 maximum injection duration is limited by the persistence of MnO_4 in the subsurface,
15 which is typically about three months (Huling and Pivetz, 2006). Another option is to
16 increase treatment chemical mass, which would only be constrained by the solubility
17 limit of MnO_4 . (The upper bound on the mass ratio of $m^* = 50$ was chosen arbitrarily in
18 this study). The decision to increase injection duration or to increase the initial treatment
19 chemical mass is subject to the preferences of the project stakeholders, but given that
20 toluene is especially difficult to remediate, these results provide a useful understanding of
21 the viable options.
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38

39 6. Conclusions

40
41 This study optimized active spreading designs to remediate sorbing groundwater
42 contaminant in situ. In this system, injections of treatment chemical and clean water at
43 the center of the contaminant plume move the contaminant, treatment chemical, and clean
44 water radially away from the injection point. Because the sorbing contaminant moves at a
45 slower rate than the treatment chemical, the treatment chemical advances through the
46 contaminant, thereby increasing reactant contact and achieving more degradation. The
47 injections of treatment chemical and clean water are controlled by design parameters,
48 including the mass ratio m^* , the plume size ratio λ_o , and the injection time ratio T^* . These
49 design parameters were optimized according to three objectives established for the
50 remediation – maximizing contaminant degradation, minimizing energy requirements,
51 and minimizing material requirements.
52
53
54
55
56
57
58
59
60
61
62
63
64
65

The optimization solutions for the in situ remediation system were analyzed according to the tradeoffs between remediation objectives, which revealed relationships between the design parameters of the system and the remediation objectives. Analyzing solution sets across cases showed how the reaction and sorption properties of the contaminants influenced the selection of design parameters for the different cases. Solutions for cases with low reaction rate coefficients typically require a high mass ratio (m^*) to increase the treatment chemical mass in the system and thereby increase the concentration of treatment chemical to maintain high reaction rates, given by kC_1C_2 (1). Since slowly-sorbing contaminant travels farther from the well during injection than rapidly-sorbing contaminant, solutions for cases with slow sorption rates require that the treatment chemical is injected at higher rates (related to λ_o) over longer durations (proportional to T^*) to move the treatment chemical through the contaminant plume. Similarly, in heterogeneous aquifers, portions of the contaminant plume passing through areas of high hydraulic conductivity travel farther from the injection well than in the homogeneous scenarios, requiring that the treatment chemical be injected at higher rates to catch the leading edge of the contaminant plume. Since the treatment chemical mass is distributed over a large area, solutions for the slow sorption cases and in the heterogeneous aquifers also require more treatment chemical mass (proportional to m^*) to maintain high treatment chemical concentrations. As such, the material and energy requirements of remediating slowly-sorbing contaminants are higher than for rapidly-sorbing contaminants, and for remediating heterogeneous aquifers are higher than for homogeneous aquifers.

The relationships between remediation objectives, design parameters, and the different properties of the contaminant and soil are relevant to improving in situ remediation of sorbing contaminants. Our results indicate that selecting the injection rate of treatment chemical based on the sorption rate constant can improve the effectiveness of remediating sorbing contaminants in situ, and that the injection rate selection (or equivalently λ_o selection) should be in conjunction with selection of the other design parameters. Furthermore, for scenarios with high ambient groundwater velocities, the injection rate should be selected such that the groundwater divide encompasses the entire contaminant plume. The solutions produced in this study for contaminants with different

1
2
3
4 reaction rate coefficients and sorption rates represent remediation options that maximize
5 contaminant degradation while minimizing material and energy requirements. For the
6 scenarios considered in this study, viable remediation options were demonstrated even for
7 contaminants with low reaction rate coefficients, for which prior approaches (e.g.
8 Neupauer and Mays, 2014) were less effective.
9
10
11
12
13
14

15 **Acknowledgements**

16
17 This work was supported by the Hydrologic Sciences Program of the National Science
18 Foundation (NSF) (EAR-1114060). This work utilized the Janus supercomputer, which is
19 supported by the NSF (CNS-0821794) and the University of Colorado Boulder. We thank
20 the anonymous reviewers for their valuable comments, and our colleagues, Joseph Ryan
21 and Masoud Arshadi, for engaging in helpful discussions during the revision process. We
22 also thank Dani-Fernandez-Garcia and Christopher Henri for their help with RW3D.
23
24
25
26
27
28

29 **References**

- 30
31 Bayer P, Finkel M (2004). Evolutionary algorithms for the optimization of advective
32 control of contaminated aquifer zones. *Water Resour. Res.*, 40(6), W06506.
33 doi:10.1029/2003WR002675.
34
35
36 Charbeneau RJ (1999). *Groundwater Hydraulics and Pollutant Transport*. Prentice Hall,
37 New Jersey.
38
39
40 Christiansen CM, Damgaard I, Broholm MM, Kessler T, Klint KE, Nilsson B, Bjerg PL
41 (2010). Comparison of delivery methods for enhanced *in situ* remediation in clay
42 till. *Ground Water Monit. Remediat.*, 30(4), 107–122.
43
44
45 Crimi M, Silva JAK, Palaia T (2011). Cooperative technology demonstration: polymer-
46 enhanced subsurface delivery and distribution of permanganate. ESTCP Project
47 no. ER-0912 <http://www.serdp.org/>
48
49
50
51 Dokou Z, Karatzas GP (2013). Multi-objective optimization for free-phase recovery
52 using evolutionary computational algorithms. *Hydrolog. Sci. J.*, 58(3), 671-685.
53 DOI: 10.1080/02626667.2012.754103.
54
55
56 Fernandez-Garcia D, Illangasekare TH, Rajaram H (2005). Differences in the scale-
57 dependence of dispersivity estimated from temporal and spatial moments in
58
59
60
61
62
63
64
65

- chemically and physically heterogeneous porous media. *Adv. Water Resour.*, 28, 745-789.
- Garbarini DR, Lion LW (1986). Influence of the nature of soil organics on the sorption of toluene and trichloroethylene. *Environ. Sci. Technol.*, 20, 1263-1269.
- Hadka D, Reed PM (2013). Borg: An auto-adaptive many-objective framework. *Evol. Comput.* 21(2), 213-259.
- Harbaugh AW, Banta ER, Hill MC, McDonald MG (2000). MODFLOW-2000, the U.S. Geological Survey modular ground-water model—User guide to modularization concepts and the ground-water flow process, Open-File Rep. 00-92, U.S. Geol. Surv., Reston, Va.
- Huang KC, Hoag GE, Chheda P, Woody BA, Dobbs GM (1999). Kinetic study of oxidation of trichloroethylene by potassium permanganate. *Environ. Eng. Sci.*, 16(4), 265-274.
- Huang KC, Hoag GE, Chheda P, Woody BA, Dobbs GM (2002). Kinetics and mechanism of oxidation of tetrachloroethylene with permanganate. *Chemosphere*, 46(6), 815-825.
- Huling SG, Pivetz, BE (2006). U.S. EPA Engineering issue: in situ chemical oxidation. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory. EPA/600/R-06/072.
- Kavanaugh MC, Rao PSC, Abriola L, Cherry J, Destouni G, Falta R, Major D, Mercer J, Newell C, Sale T, Shoemaker S, Siegrist RL, Teutsch G, Udell K (2003). The DNAPL cleanup challenge: source removal or long-term management. EPA/600/R-03/143.
- Kasprzyk JR, Reed PM, Kirsch BR, Characklis GW (2009). Managing population and drought risks using many-objective water portfolio planning under uncertainty. *Water Resour. Res.*, W12401. DOI: 10.1029/2009WR008121.
- Kollat JB, Reed PM (2006). A computational scaling analysis of multiobjective evolutionary algorithms in long-term groundwater monitoring applications. *Adv. Water Resour.* 30(3), 408-419.
- Kollat JB, Reed PM, Kasprzyk JR (2008). A new epsilon-dominance hierarchical Bayesian optimization algorithm for large multiobjective monitoring network design problems. *Adv. Water Resour.* 31, 828-845.

- 1
2
3
4 Maraqa MA (2001). Prediction of mass-transfer coefficient for solute transport in porous
5 media. *J. Contam. Hydrol.*, 50, 1-15.
6
7
8 Mays DC, Neupauer RM (2012). Plume Spreading in Groundwater by Stretching and
9 Folding. *Water Resour. Res.*, 48, W07501, doi:10.1029/ 2011WR011567.
10
11
12 McCray JE, Munakata-Marr J, Silva JAK, Davenport S, Smith MM (2010). Multi-scale
13 experiments to evaluate mobility control methods for enhancing the sweep
14 efficiency of injected subsurface remediation amendments. Final report for the
15 SERDP project ER-1486. Arlington.
16
17
18 Neupauer RM, Mays DC (2014). Engineered Injection and Extraction for In Situ
19 Remediation of Sorbing Solutes in Groundwater. *J. Environ. Eng.*, 51, DOI:
20 10.1061/(ASCE)EE.1943-7870.0000923.
21
22
23
24 Nicklow J, Reed P, Savic D, Dessalegne T, Harrell L, Chan-Hilton A, Karamouz M,
25 Minsker B, Ostfeld A, Singh A, Zechman E (2010). State of the art for genetic
26 algorithms and beyond in water resources planning and management. *J. Water*
27 *Resour. Plan. Manage.* 136, 412e432. [http://dx.doi.org/10.1061/\(ASCE\)WR.1943-](http://dx.doi.org/10.1061/(ASCE)WR.1943-5452.0000053)
28 [5452.0000053](http://dx.doi.org/10.1061/(ASCE)WR.1943-5452.0000053).
29
30
31 Pignatello JJ, Xing B (1996). Mechanisms of Slow Sorption of Organic Chemicals to
32 Natural Particles. *Environ. Sci. Technol.*, 30(1).
33
34
35 Piscopo AN, Kasprzyk JR, Neupauer RM (2015). An Iterative Approach to Many
36 Objective Engineering Design: Optimization of Engineered Injection and
37 Extraction for Enhanced Groundwater Remediation. *Env. Modell. Softw.*,
38 [http://dx.doi.org/10.1016/ j.envsoft.2014.08.030](http://dx.doi.org/10.1016/j.envsoft.2014.08.030).
39
40
41 Reed PM, Minsker BS (2004). Striking the balance: long-term groundwater monitoring
42 design for conflicting objectives. *J. Water Resour. Plan. Manage* 130 (2), 140-149.
43 [http://dx.doi.org/10.1061/\(ASCE\)0733-9496\(2004\)130: 2\(140\)](http://dx.doi.org/10.1061/(ASCE)0733-9496(2004)130: 2(140)).
44
45
46
47 Reed PM, Hadka D, Herman JD, Kasprzyk JR, Kollat JB (2013). Evolutionary
48 multiobjective optimization in water resources: The past, present, and future. *Adv.*
49 *Water Resour.* doi:10.1016/j.advwatres.2012.01.005.
50
51
52
53 Rudakov ES, Lobachev VL (2000). The first step of oxidation of alkylbenzenes by
54 permanganates in acidic aqueous solutions. *Russ. Chem. Bull.*, 49, 761-777.
55
56
57 Salamon P, Fernandez-Garcia D, Gomez-Hernandez JJ (2006). Modeling mass transfer
58 processes using random walk particle tracking. *Water Resour. Res.*, 42,
59 doi:10.1029/2006WR004927.
60
61
62
63
64
65

- 1
2
3
4
5
6 Siegrist RL, Crimi M, Broholm MM, McCray JE, Illangasekare TH, Bjerg PL (2012).
7 Advances in groundwater remediation: Achieving effective in situ delivery of
8 chemical oxidants and amendments. Clean soil and safe water, NATO Science for
9 Peace and Security Series C: Environmental Security, DOI 10.1007/978-94-007-
10 2240-8_15. Springer, Dordrecht. p. 197-212.
11
12
13
14 Schaerlaekens J, Carmeliet J, Feyen J. (2005). Multi-objective optimization of the setup
15 of surfactant-enhanced DNAPL remediation. *Envir. Sci. Tech.* 39(7) 2327-2333.
16
17
18 Scheutz C, Broholm MM, Durant ND, Weeth EB, Jørgensen T, Dennis P, Jakobsen CS,
19 Cox E, Chambon J, Bjerg PL (2010). Field evaluation of biological enhanced
20 reductive dechlorination of chloroethenes in clayey till. *Environ Sci. Technol.*
21 44(13): 5134-5141.
22
23
24
25 Smith MM, Silva JAK, Munakata-Marr J, McCray JE (2008). Compatibility of polymers
26 and chemical oxidants for enhanced groundwater remediation. *Environ. Sci.*
27 *Technol.* 42(24): 9296-9301.
28
29
30
31 U.S. Environmental Protection Agency (1986). Superfund Public Health Evaluation
32 Manual; EPA/540/1-86/060; Office of Emergency and Remedial Response, U.S.
33 Government Printing Office: Washington, DC, 1986.
34
35
36 U.S. Environmental Protection Agency (1988). Guidelines for Groundwater
37 Classification under the EPA Groundwater Protection Strategy. U.S. EPA. 1988.
38 EP 813R88001.
39
40
41 U.S. Environmental Protection Agency (2014). National Primary Drinking Water
42 Regulations, <http://water.epa.gov/drink/contaminants/#List>, Cited 24 February
43 2015.
44
45
46 Valocchi AJ, Quniodoz HAM (1989). Application of the random walk method to
47 simulate the transport of kinetically adsorbing solutes. *Proc., Int. Association of*
48 *Hydrological Sciences Third Scientific Assembly: Groundwater Contamination,*
49 *IAHS Press, Wallingford, U.K., 35–38.*
50
51
52 Waldemer RH, Tratnyek PG (2006). Kinetics of Contaminant Degradation by
53 Permanganate. *Envir. Sci. Tech.* 40, 1055-1061.
54
55
56 Wu J, Zheng L, Liu D (1997). Optimizing groundwater development strategies by genetic
57 algorithm; a case study for balancing the needs for agriculture irrigation and
58 environmental protection in northern China. *Hydrogeol. J.* 15, 1265-1278. DOI
59 10.1007/s10040-007-0200-2.
60
61
62
63
64
65

1
2
3
4
5
6 Yeh WW-G (1992). Systems analysis in ground-water planning and management. J.
7 Water Resources Plann. Manage. 118(3), 224-237.
8

9
10 Yoon J, Shoemaker CA (1999). Comparison of optimization methods for ground-water
11 bioremediation. J. Water Resources Plann. Manage. 25(1), 54-63.
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Table 1 Reaction rate coefficients k , mass stoichiometric ratios F , and sorption rate constants α_s for the six cases considered in this study

Case	Contaminant	k (m ³ /g/d)	F	α_s (d ⁻¹)
1	TCE	0.59	1.8	1
2	TCE	0.59	1.8	0.1
3	PCE	0.018	0.96	1
4	PCE	0.018	0.96	0.1
5	Toluene	0.00022	2.6	1
6	Toluene	0.00022	2.6	0.1

Table 2 Aquifer and contaminant properties used in simulations

Parameter	Value
Initial contaminant radius, r_{init} (m)	10 m
Initial contaminant mass, m_1^0 (g)	1960 g
Aquifer thickness, b (m)	10 m
Porosity, n	0.33
Bulk density of the soil, ρ_b (g/cm ³)	1.65 g/cm ³
Mean hydraulic conductivity, K (m/d)	0.5 m/d
Partition coefficient, K_d (cm ³ /g)	0.2 cm ³ /g
Retardation coefficient, R	2
Longitudinal dispersion coefficient, α_L (m)	0.05
Transverse dispersion coefficient, α_T (m)	0.005

Table 3 Remediation scenarios

Scenario	Injection duration, T (d)	Ambient groundwater velocity, V_x (m/d)	Aquifer type
1	56	0.0	Homogeneous
2	56	0.1, 0.5	Homogeneous
3	84	0.0	Homogeneous
4	56	0.0	Heterogeneous

Table 4 Statistical properties for spatially-correlated randomly-varying fields of $\ln K$

Field	Correlation length, Λ (m)	Variance of $\ln K$, S^2
1	6.25	1.0
2	6.25	0.5
3	3.125	1.0
4	3.125	0.5

Fig. 1 Plan view of the contaminant (blue) and treatment chemical (yellow) plumes in a homogeneous aquifer (a) at the initial time (b) after injection of treatment chemical in the well without reaction, (c) after injection of the treatment chemical and clean water in the well without reaction and (d) after injection of treatment chemical and clean water with reaction. The *small black circle* at the center of each subplot represents the well. The radius of the contaminant plume before injection is r_{init} . After injection, if no reaction were to occur, the radii of the contaminant and treatment chemical plumes would be r_f and r_{tc} , respectively.

Fig. 2 Non-dominated solutions for all cases plotted in terms of their objective function values. The colors indicate the case, as shown in the figure legend. *Gray arrows* indicate the direction of optimality and the *gray star* indicates the ideal point. The Roman numerals indicate specific solutions discussed in the paper.

Fig. 3 Non-dominated solutions for Cases 1-6 plotted in terms of their design parameter values. The left column is for a high reaction rate coefficient, the middle column is for a moderate reaction rate, and the right column is for a low reaction rate coefficient. The top row is for a fast sorption rate and the bottom row is for a slow sorption rate. The color of the solution points indicates $f_{\text{degradation}}$, as shown in the figure legend. The Roman numerals indicate specific solutions discussed in the paper.

Fig. 4 Treatment chemical (yellow) and contaminant (blue) plumes after injection for (a) Solution *I* from Case 1 (fast sorption) and (b) Solution *II* from Case 2 (slow sorption), which were identified in Figs. 2 and 3. The *black circle* at the center of each subplot represents the well. The design parameters for each example solution are given in the lower left corner of each subplot.

Fig. 5 Scatterplot of $f_{\text{degradation}}$ with ambient flow vs. $f_{\text{degradation}}$ without ambient flow for (a) each solution from Cases 1 and 3 and (b) each solution from Cases 2 and 4 for high and low ambient velocities, $V_x = 0.1$ m/d (*triangles*) and $V_x = 0.5$ m/d (*asterisks*).

Fig. 6 Treatment chemical (yellow) and contaminant (blue) plumes for Solution III from Case 2, identified in Fig. 5 are plotted at (a) $t = 0.75T$ and (b) $t = T$. The *small black circle* at the center of each subplot represents the well, the *black dashed line* represents the groundwater divide, and the *black arrow* represents the stagnation point. The design parameters for the example solution are shown in the lower left corner of subplot (a).

Fig. 7 Non-dominated solutions for Case 2 ($k = 0.59 \text{ m}^3/\text{g/d}$ and $\alpha_s = 0.1 \text{ d}^{-1}$) for different ambient flows plotted in terms of their objective function values. The *gray star* indicates the ideal point in the domain. Note that the solutions with $V_x = 0.0 \text{ m/d}$ were shown previously in Fig. 2 as the solutions from Case 2.

Fig. 8 Non-dominated solutions for Case 2 ($k = 0.59 \text{ m}^3/\text{g/d}$ and $\alpha_s = 0.1 \text{ d}^{-1}$) for different ambient flows plotted in terms of their design parameter values. Note that the solutions with $V_x = 0.0 \text{ m/d}$ are the same as those shown previously in Fig. 3b.

Fig. 9 Non-dominated solutions for Case 4 ($k = 0.018 \text{ m}^3/\text{g/d}$ and $\alpha_s = 0.1 \text{ d}^{-1}$) for injection period durations of $T = 56 \text{ d}$ and $T = 84 \text{ d}$ plotted in terms of their objective function values. Note that the solutions with $T = 56 \text{ d}$ were shown previously in Fig. 2 as the solutions from Case 4.

Fig. 10 Non-dominated solutions for Cases 3-6 for injection period durations of $T = 56$ d and $T = 84$ d plotted in terms of their $f_{\text{degradation}}$ objective function values and m^*/F design parameter values. Note that the solutions with $T = 56$ d were shown previously in Fig. 2 and Fig. 3c-e.

Fig. 11 Non-dominated solutions for Cases 1-4 plotted in terms of their objective function values for a heterogeneous aquifer, i.e. a field of spatially-varying hydraulic conductivity with a correlation length of 6.25 m and variance of $\ln K$ of 1 (*black points*) and for a homogeneous aquifer (*gray points*). Note that the solutions from the homogeneous aquifer were shown previously in Fig. 2 and Fig. 3a-d.

Fig. 12 Non-dominated solutions for Cases 1-4 plotted in terms of their design parameter values for a heterogeneous aquifer, represented by a field of spatially-varying hydraulic conductivity (as $\ln K$) with a correlation length of 6.25 m and variance of $\ln K$ of 1. The left column is for a high reaction rate coefficient, the right column is for a low reaction rate coefficient, the top row is for a fast sorption rate, and the bottom row is for a slow sorption rate. The color of the solution points indicates $f_{\text{degradation}}$, as shown in the figure legend.

Fig. 13 Nondominated solutions for Case 4 ($k = 0.018 \text{ m}^3/\text{g}/\text{d}$ and $\alpha_s = 0.1 \text{ d}^{-1}$) in a heterogeneous aquifer with four spatially-correlated field of $\ln K$ with the statistical parameters shown in the legend, correlation length (Λ) and variance of $\ln K$ (σ^2). Solutions are plotted in terms of their objective function values and the *gray star* indicates the ideal point. The color of the solution points indicates the different combinations of statistical parameters, as shown in the figure legend.