Engineered Injection and Extraction for In Situ Remediation of Sorbing Solutes in Groundwater

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Abstract: Engineered injection and extraction (EIE) is a method of in situ remediation of contaminated groundwater in which a treatment chemical that reacts with the contaminant is injected into the contaminated aquifer, and a series of injections and extractions of clean water are performed in nearby wells to promote the spreading of the treatment chemical throughout the contaminated aquifer. Numerical simulations are used to investigate the use of EIE for sorbing groundwater contaminants. The aquifer is homogeneous and confined with negligible ambient groundwater flow. A range of sorption parameters are considered for both linear equilibrium sorption and linear kinetic sorption, and both instantaneous and rate-limited bimolecular reactions are discussed. An effective EIE sequence is developed for a sorbing contaminant and is compared with a sequence developed for aqueous, nonsorbing contaminants. The results show that for contaminants that exhibit fast sorption and fast reaction, the EIE sequence developed for sorbing contaminants can achieve nearly complete contaminant degradation. For contaminants with linear equilibrium sorption and rate-limited reaction, the sequence can achieve nearly complete degradation if the duration of the remediation process is scaled with the inverse of the reaction rate constant. For contaminants that exhibit slow sorption, the EIE sequence designed for aqueous, nonsorbing contaminants achieves higher overall contaminant degradation, but requires more energy and higher injection and extraction rates. **DOI: 10.1061/(ASCE)EE.1943-7870.0000923.**

Introduction

Recent reviews have emphasized that sorption influences transport and reaction processes in groundwater remediation, with applications to organic contaminants (Huang et al. 2003), heavy metals (Selim 2013), and radionuclides (Li and Kaplan 2012). In situ remediation is well suited for sorbing contaminants because it sidesteps the difficulty in extracting the sorbed phase, which is particularly challenging when the groundwater velocity is slow relative to the mass transfer rate (Valocchi 1985; Bahr and Rubin 1987). Accordingly, this study adopts a conceptual model for in situ remediation in which a treatment chemical is injected into the contaminated aquifer to neutralize or stabilize the contaminant.

In the context of this conceptual model, Oya and Valocchi (1997, 1998) showed that injection of a treatment chemical produces treatment chemical concentration profiles that proceed as traveling waves that sweep the contaminated area. With one-dimensional or radial flow, these authors observed that the extent of reaction was independent of dispersion. Dispersion is important, however, in the more general case where the plume interface is sometimes perpendicular to the flow and sometimes parallel (Dagan et al. 1996; Schirmer et al. 2000; Cirpka 2005). Moreover, dispersion is amplified by unsteady flow (Dagan et al. 1996; Schirmer et al. 2000) for the following reason. In steady flow, dispersion generates spreading principally through transverse dispersion—that is, dispersion transverse to the preferential flow paths resulting from aquifer heterogeneity (e.g., Cirpka et al. 2011). In unsteady flow, spreading is generated not only by transverse dispersion, which occurs when the plume interface is parallel to the flow, but also by longitudinal dispersion, when the plume interface is perpendicular to the flow (Dagan et al. 1996; Cirpka 2005). Accordingly, Cirpka (2005) found that sorption and unsteady flow enhance dispersion approximately as much as the preferential flow resulting from aquifer heterogeneity.

In situ remediation depends on mixing the treatment chemical and the contaminant. Mixing, in turn, can be accelerated by plume spreading. Mays and Neupauer (2012) used numerical simulation to demonstrate that engineered injection and extraction (EIE) is an effective method for spreading the treatment chemical into an aqueous, nonsorbing contaminant plume. In EIE, wells are placed around the contaminated region of the aquifer and are operated sequentially to create an unsteady flow field that stretches and folds the interface between the treatment chemical and the contaminated groundwater. As the interface stretches, the contact area between the contaminant and the treatment chemical grows, increasing the opportunity for degradation reactions to occur. Piscopo et al. (2013) used numerical simulations to demonstrate that for aqueous contaminants in groundwater, EIE leads to substantially more contaminant degradation than does standard in situ remediation.

Previous studies on EIE, however, were limited to nonsorbing contaminants. In this case, the only way to increase the contact area between the two solutions is to stretch their interface. For sorbing contaminants, the sorbed phase cannot move until it partitions into the aqueous phase; thus contact between the sorbed phase and the treatment chemical can be enhanced by directing the treatment chemical to pass over regions where contamination exists in the sorbed phase. Because of this qualitative difference, EIE sequences developed for in situ remediation of nonsorbing contaminants may not be appropriate for degradation of sorbing contaminants.

To recapitulate, previous research emphasized that heterogeneity, unsteady flow, and sorption all serve to increase the dispersion that is largely responsible for mixing in aquifers. Here these

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findings are extended to suggest that reactive transport can be improved by a deliberate manipulation of the groundwater velocity field designed to leverage the beneficial effect of sorption on mixing. This work considers injection of an aqueous, nonsorbing treatment chemical to remediate a sorbing contaminant in saturated aquifers. Nonsorbing treatment chemicals include, for example, electron acceptors such as oxygen (Oya and Valocchi 1997, 1998; Yan and Schwartz 1999) or nitrate (Oya and Valocchi 1997, 1998). Sorbing contaminants include, for example, the organic solvent toluene (Oya and Valocchi 1998) or the radionuclide uranium(VI) (Tebes-Stevens et al. 2001; Luo et al. 2007). This work considers both linear equilibrium sorption, in which the contaminant partitions instantaneously between the aqueous and sorbed phases, and linear kinetic sorption, in which the contaminant partitions between the aqueous and sorbed phases at a rate defined by a sorption rate constant. Linear sorption was chosen as the simplest model that captures the essential dynamics of reactive transport. A suite of more sophisticated models exists for equilibrium and kinetic sorption, as listed, for example, in a recent review (Selim 2013). This work considers bimolecular reaction between the aqueous treatment chemical and both the aqueous contaminant and the sorbed contaminant, assuming that the sorbed phase remains accessible to the aqueous phase (e.g., Huang et al. 2003). Also considered are both instantaneous and rate-limited reactions. Through a suite of numerical simulations, this work shows that the EIE strategy and the effectiveness of EIE depend on the sorption properties of the contaminant and the porous media, and on the reaction rate between the treatment chemical and the contaminant.

This paper is structured as follows. After a review of the governing equations of transport and reaction, the modeling approach is described, followed by results for remediation of sorbing groundwater contaminants, first with equilibrium sorption and then with kinetic sorption. Both models assume linear sorption with a spectrum of retardation coefficients and reaction rates. Finally, the relationship between the EIE sequences and the model parameters is discussed, with implications for using EIE for in situ remediation.

Methods

The engineered injection and extraction system used in this work is shown in Fig. 1(a). The five wells are operated in a defined sequence such that the net volume of water injected is equal to the net volume of water extracted. Table 1 gives the two EIE sequences considered in this work, where the parameter Λ^2 is defined as

$$\Lambda^2 = \frac{Q\Delta t}{\pi n b L^2} \tag{1}$$

where Q = injection rate ($Q < 0$ implies extraction); Δt = duration of the step; n = porosity; b = aquifer thickness; and L = distance between an outer well and the origin.

Sequence I was used by Mays and Neupauer (2012) and Piscopo et al. (2013) for aqueous contaminants, and was designed to stretch and fold the interface between the contaminant plume and a treatment chemical plume injected into the center well (Mays and Neupauer 2012). Sequence II is designed to exploit the slower apparent velocities of the sorbing contaminant and is explained in more detail in the next section.

The ambient groundwater velocity in the vicinity of the contaminated area is assumed to be negligible relative to the velocity created by the EIE system. Also, the aquifer is assumed to be homogeneous, which allows for simplification of the flow simulation because flow is always radially toward or radially away from the active well. The reactions are assumed to be bimolecular, modeled as

$$R_1 + R_2 \rightarrow P \tag{2}$$

where R_1 = contaminant (which partitions into aqueous and sorbed phases); R_2 = treatment chemical (assumed to be strictly aqueous); and P = reaction product, which does not influence flow, transport, or reaction.

Reactive transport of the contaminant and the treatment chemical is described by the advection-dispersion-reaction equation (ADRE), which, for radial flow in a homogeneous aquifer, is given by

$$\frac{\partial C_1}{\partial t} + \frac{\rho_b}{n}\frac{\partial S_1}{\partial t} = \alpha_L |v_r| \frac{\partial^2 C_1}{\partial r^2} + \frac{\alpha_T |v_r|}{r^2}\frac{\partial^2 C_1}{\partial \theta^2} - v_r \frac{\partial C_1}{\partial r} - k_a C_1 C_2 - \frac{\rho_b}{n} k_s S_1 C_2 \tag{3}$$

$$\frac{\partial S_1}{\partial t} = \alpha_s (K_d C_1 - S_1) - k_s S_1 C_2 \tag{4}$$

Table 1. Engineered Injection and Extraction Sequences

	Sequence I		Sequence II		
Step	Active well	$\pi\Lambda^2$	Active well	Injection rate	Duration
1	W	3.5	O	Q	T'_{inj}
2	E	3.5	O	Q	$T_{\text{inj}} - T'_{\text{inj}}$
3	W	−1.0	W	$-Q/8$	T_{inj}
4	E	−3.0	S	$-Q/8$	T_{inj}
5	W	−1.6	E	$-Q/8$	T_{inj}
6	E	−1.4	N	$-Q/8$	T_{inj}
7	S	3.5	W	$-Q/8$	T_{inj}
8	N	3.5	S	$-Q/8$	T_{inj}
9	S	−1.0	E	$-Q/8$	T_{inj}
10	N	−3.0	N	$-Q/8$	T_{inj}
11	S	−1.6	NA	NA	NA
12	N	−1.4	NA	NA	NA

Note: Positive flow rates represent injection; negative flow rates represent extraction. Non-numerical values are shown in Table 3.

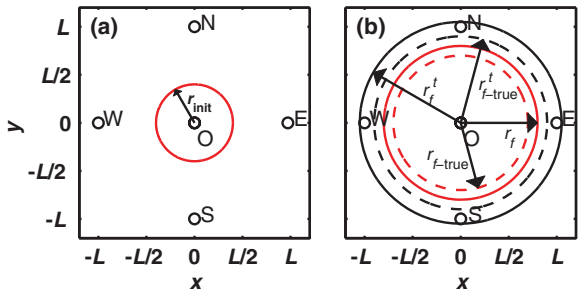

Fig. 1. (Color) Schematic of the EIE system: (a) initial position of contaminant plume with outer radius r_{init}; (b) outer edges of plumes at end of injection period: r_f and r_f^t = final radii of contaminant and treatment chemical plumes if reaction is not considered, and $r_{f\text{-true}}$ and $r_{f\text{-true}}^t$ = final radii of actual contaminant and treatment chemical plumes; small circles = well locations; letters = well identifiers ("W" = west; "S" south; "E" = east; "N" = north; "O" = origin)

$$\frac{\partial C_2}{\partial t} = \alpha_L |v_r| \frac{\partial^2 C_2}{\partial r^2} + \frac{\alpha_T |v_r|}{r^2} \frac{\partial^2 C_2}{\partial \theta^2} - v_r \frac{\partial C_2}{\partial r} - k_a F C_1 C_2 - \frac{\rho_b}{n} k_s F S_1 C_2 \quad (5)$$

where C_1 and C_2 = aqueous concentrations of the contaminant and the treatment chemical, respectively; S_1 = sorbed phase concentration of the contaminant; t = time; r = radial coordinate relative to the active well; ρ_b = bulk density of the solids; K_d and α_s = linear equilibrium partition coefficient and sorption rate constant, respectively, of the contaminant; k_a and k_s = reaction rate constants for the aqueous- and sorbed-phase contaminants, respectively; α_L and α_T = longitudinal and transverse dispersivities, respectively; v_r = groundwater velocity in the radial direction; and F = stoichiometric ratio (i.e., the mass of treatment chemical reacted per mass of contaminant reacted). Since all groundwater flow is generated by injection or extraction of water at the active well, the radial velocity v_r is given by

$$v_r = \frac{Q}{2\pi r b n} \quad (6)$$

For linear equilibrium sorption, the sorption rate constant $\alpha_s \to \infty$; thus from Eq. (4), $S_1 = K_d C_1$ and Eq. (3) can be simplified as

$$R \frac{\partial C_1}{\partial t} = \alpha_L |v_r| \frac{\partial^2 C_1}{\partial r^2} + \frac{\alpha_T |v_r|}{r^2} \frac{\partial^2 C_1}{\partial \theta^2} - v_r \frac{\partial C_1}{\partial r} - R k_a C_1 C_2 \quad (7)$$

where $R = 1 + \rho_b K_d / n$ = retardation coefficient for the contaminant and it is assumed that $k_a = k_s$.

Transport is simulated in a two-dimensional, confined aquifer with homogeneous second-type boundary conditions as $r' \to \infty$, where r' = the radial coordinate relative to the origin. For simplicity, the initial configuration of the contaminant plume is assumed to be circular with radius r_{init} and centered at the origin, with a uniform concentration of C_1'. Under linear equilibrium sorption, the aqueous and sorbed phases of the contaminant are initially in equilibrium; thus the initial conditions are given by

$$C_1(r', \theta, 0) = \begin{cases} C_1' & r' \le r_{\text{init}} \\ 0 & r' > r_{\text{init}} \end{cases} \quad (8)$$

$$S_1(r', \theta, 0) = \begin{cases} K_d C_1' & r' \le r_{\text{init}} \\ 0 & r' > r_{\text{init}} \end{cases} \quad (9)$$

Under linear kinetic sorption, the contaminant is assumed to be initially entirely in the aqueous phase; thus $S_1(r', \theta, 0) = 0$. Accordingly, if sorption is slow, most of the contaminant remains in the aqueous phase after remediation is initiated; if sorption is fast (i.e., approaching equilibrium sorption), the aqueous and sorbed phase concentrations reach equilibrium quickly.

Eqs. (3)–(5), and (7) are solved using random walk, treating the contaminant, the treatment chemical, and the reaction product as a collection of particles of known mass and phase. Each step of the EIE sequence is divided into N_s smaller transport steps of length $\Delta t_i = T_i / N_s$, where T_i is the duration of the ith EIE step. Advection, dispersion, sorption, and reaction are simulated separately in each transport step as described next.

Advection: In the EIE system considered here, one well is operating at a time, so water is flowing either radially away from an injection well or radially toward an extraction well. For homogeneous aquifers, this radial flow leads to advective transport of particles that can be modeled analytically as (Mays and Neupauer 2012)

$$r_{\text{new}} = \sqrt{\frac{Q \Delta t_a}{\pi b n} + r_{\text{old}}^2} \quad (10)$$

where r_{old} and r_{new} = initial and final radial distances of the aqueous particle relative to the active well and Δt_a = amount of time a particle spends in the aqueous phase during the transport step. In Eq. (10), Δt_a is used instead of Δt_i because particles are advected only when they are in the aqueous phase.

Dispersion: The dispersion process is modeled by adding random particle displacements in the longitudinal and transverse directions relative to the local velocity vector. The displacements are normally distributed random variables with zero mean and a standard deviation of $\sqrt{2\alpha_L |v_r| \Delta t_a}$ and $\sqrt{2\alpha_T |v_r| \Delta t_a}$ in the longitudinal and transverse directions, respectively. The time step is Δt_a because dispersion only occurs for particles in the aqueous phase.

Sorption: For linear kinetic sorption, particles can transition from the aqueous phase to the sorbed phase or vice versa; this transition is modeled probabilistically. Let T_{wa} be the random waiting time of a particle in the aqueous phase before it transitions into the sorbed phase. This random waiting time is an exponentially distributed random variable with parameter $\alpha_s(R-1)$ (Valocchi and Quinodoz 1989) and has a cumulative distribution function (CDF) given by

$$F_{T_{wa}}(t_{wa}) = \text{P}(T_{wa} \le t_{wa}) = e^{-\alpha_s (R-1) t_{wa}} \quad (11)$$

Also, let T_{ws} be the random waiting time of a particle in the sorbed phase before it transitions into the aqueous phase, which is an exponentially distributed random variable with parameter α_s (Valocchi and Quinodoz 1989) and with a CDF given by

$$F_{T_{ws}}(t_{ws}) = \text{P}(T_{ws} \le t_{ws}) = e^{-\alpha_s t_{ws}} \quad (12)$$

Because particles are advected and dispersed in the aqueous phase only, the amount of time Δt_a that each particle spends in the aqueous phase during each transport step is calculated by drawing random numbers alternately from Eqs. (11) and (12) until the sum of the waiting times exceeds the duration of the transport step. The sum of the aqueous phase waiting times is Δt_a.

For a solute that exhibits linear equilibrium sorption, particles are not assigned a specific phase. Rather, the particle mass m is partitioned into an aqueous-phase mass m_a and a sorbed-phase mass m_s as

$$m_a = \frac{m}{R} \quad (13)$$

$$m_s = m \frac{R-1}{R} \quad (14)$$

For this case, the time that a particle spends in the aqueous phase is given by $\Delta t_a = \Delta t / R$.

Reaction: To simulate reaction, particles are binned into equal-sized bins based on their positions at the end of each transport step and are allowed to react. In reality, reactions occur continuously, not just at the end of the transport step; however, if the transport step is small, this approach is an accurate approximation of the real system.

For instantaneous reaction, in any bin that contains both reactants, reaction is simulated by reducing the mass of the limiting reactant to zero and reducing the mass of the nonlimiting reactant in accordance with the stoichiometric ratio. For rate-limited reaction, in any bin that contains both reactants, degradation in each bin is approximated using a backward Euler finite-difference

approximation of the temporal derivatives and reaction terms in Eqs. (3)–(5) and (7). The concentrations of each species in a bin are calculated according to

$$C_{jb} = \frac{\sum_{\ell \in b} m_{aj\ell}}{nV_b} \tag{15}$$

$$S_{1b} = \frac{\sum_{\ell \in b} m_{s1\ell}}{\rho_b V_b} \tag{16}$$

where C_{jb} and S_{jb} = aqueous and sorbed phase concentrations of species j in bin; $m_{aj\ell}$ = aqueous mass of the ℓth particle of species; and $m_{s1\ell}$ = sorbed mass of the ℓth particle of the contaminant. The summation is over all particles in bin b, and V_b = volume of the bin.

EIE with Linear Equilibrium Sorption

The role of EIE is to enhance the contact between the treatment chemical and the contaminant to increase the opportunities for degradation reactions to occur. EIE Sequence I (Table 1) was developed for aqueous contaminants, which move at the same velocity as the groundwater and the treatment chemical. Thus the only way to increase the amount of contact between the two chemicals is by stretching the interface between their plumes.

For a contaminant that follows a linear equilibrium sorption model, the apparent velocity of the contaminant is v_r/R, where $R > 1$ = the retardation coefficient, because the contaminant moves only when it is in the aqueous phase. EIE Sequence II (Table 1) is designed to direct the flow of the treatment chemical over the regions where contamination exists in the sorbed phase. Thus EIE Sequence II begins with an injection of the treatment chemical in the center of the contaminant plume (at well O). The contaminant plume will move radially away from well O, creating an annular plume. The treatment chemical will move radially outward into the more slowly moving contaminant plume, resulting in substantial contact between the leading edge of the treatment chemical plume and the trailing edge of the contaminant plume. The injection of fluid will continue for a duration of T_{inj}, until the outer edge of the treatment chemical plume catches up to the outer edge of the contaminant plume. During the later stages of this injection phase, the contaminant will no longer be present near well O because it will have moved radially outward or will have degraded away. Thus it is not necessary to continue injecting the treatment chemical throughout the entire injection phase. For this reason, the total injection phase is divided into two steps in EIE Sequence II. In step 1 the treatment chemical is injected for a duration of T'_{inj}, and in step 2 clean water is injected for a duration of $T_{\text{inj}} - T'_{\text{inj}}$ (Table 1). The injection phase is followed by an extraction phase (steps 3–8 in Table 1), in which water is extracted from sequential operation of the outer wells to ensure that the volume of fluid injected during the injection phase is equal to the volume of fluid extracted during the extraction phase. The extraction provides more opportunities for the treatment chemical and contaminant to interact.

Design of EIE with Linear Equilibrium Sorption

The design of the EIE system has four key components: (1) the distance L between the central well and the outer wells; (2) the total volume $V = QT_{\text{inj}}$ of fluid injected (including the treatment chemical and the clean water), where Q and T_{inj} are shown in Table 1; (3) the volume of treatment chemical injected $V_2 = QT'_{\text{inj}}$; and (4) the total mass of treatment chemical M_2. The values of these four components depend on the chemical properties of the contaminant and on three critical design parameters. Two of these parameters are related to the radii of the contaminant and treatment chemical plumes at the end of the injection phase. The actual plume radii are dependent on reaction kinetics; therefore, to ensure consistency in the comparison of results across the entire range of reaction rates, the values of these design parameters are based on the radii of the contaminant and treatment chemical plumes that would exist in the absence of reaction [i.e, r_f and r_f^t, respectively, in Fig. 1(b)]. The critical design parameters are

- $M^* = M_2/M_1$, where M_2 = the total mass of treatment chemical and M_1 = the initial mass of the contaminant. To allow complete degradation of the contaminant, it is required that $M^* > F$.
- $r_f^* = r_f/L$, where r_f = the outer radius of the contaminant plume at the end of the injection step in the absence of reaction and L = the distance from the origin to the outer wells. To ensure that the contaminant plume is contained within the region delineated by the outer wells, it is required that $r_f^* < 1$.
- $\lambda_o = r_f^t/r_f$, where r_f^t = the final outer radius of the treatment chemical plume at the end of the injection phase, in the absence of reaction. The injection phase is carried out until the true outer radius of the treatment chemical plume $r_{f\text{-true}}^t$ [as shown in Fig. 1(b)] is equal to the true outer radius of the contaminant plume $r_{f\text{-true}}$ [as shown in Fig. 1(b)], or $r_{f\text{-true}}^t/r_{f\text{-true}} = 1$. Because the true final radii depend on the reaction parameters, they cannot be determined explicitly, so λ_o is defined in terms of r_f^t and r_f. Because $r_f^t > r_{f\text{-true}}^t$ and $r_f > r_{f\text{-true}}$, it is required that $\lambda_o > 1$.

In the system analyzed here, the outer wells are placed in a diamond pattern at a distance L from the center of the contaminant plume, which must be beyond the outer edge of the contaminant plume at all times. The position of the outer edge of the contaminant plume at the end of the injection is obtained from Eq. (10) with $r_{\text{new}} = r_f = r_f^* L$ and $r_{\text{old}} = r_{\text{init}}$. In Eq. (10) Δt_a is replaced with $\Delta t_a = T_{\text{inj}}/R$, where T_{inj} = the duration of the injection step, because the contaminant only spends $1/R$ of the time in the aqueous phase. Thus Eq. (10) becomes

$$r_f^* L = \sqrt{\frac{QT_{\text{inj}}}{\pi bnR} + r_{\text{init}}^2} \tag{17}$$

For the outer edge of the treatment chemical plume, the position at the end of the injection is obtained from Eq. (10) with $r_{\text{new}} = \lambda_o r_f = \lambda_o r_f^* / L$ and $r_{\text{old}} = 0$. In Eq. (10) Δt_a is replaced with $\Delta t_a = T_{\text{inj}}$ because the treatment chemical is always in the aqueous phase. Thus Eq. (10) becomes

$$\lambda_o r_f^* L = \sqrt{\frac{QT_{\text{inj}}}{\pi bn}} \tag{18}$$

Rearranging Eqs. (17) and (18) to solve for $QT_{\text{inj}}/(\pi bn)$, equating the two, and solving for L produces

$$L = \frac{r_{\text{init}}}{r_f^*} \sqrt{\frac{R}{R - \lambda_o^2}} \tag{19}$$

The total injection volume is $V = QT_{\text{inj}}$, where Q = injection rate and T_{inj} = duration of the injection step. The injection volume includes both the treatment chemical for duration $T'_{\text{inj}} < T_{\text{inj}}$ and clean water for duration $T_{\text{inj}} - T'_{\text{inj}}$, and must be sufficient to drive the treatment chemical plume and contaminant plume outward until their outer edges meet. Using Eq. (19) in either Eq. (17) or Eq. (18) produces the total injection volume given by

$$V = QT_{\text{inj}} = \frac{r_{\text{init}}^2 \pi bnR\lambda_o^2}{R - \lambda_o^2} \tag{20}$$

The treatment chemical volume is $V_2 = QT'_{\text{inj}}$. As fluid is injected, the contaminant plume forms an annulus. Injecting the treatment chemical for a duration of T'_{inj}, followed by an injection of water for duration $T_{\text{inj}} - T'_{\text{inj}}$, produces an annular treatment chemical plume that can match the annular contaminant plume. The duration T'_{inj} is defined to ensure that the final inner radius of the treatment chemical plume reaches the final inner radius of the contaminant plume. Let r_{in} denote the final inner radii of both plumes. For the contaminant plume, Eq. (10) is used with $r_{\text{old}} = 0$ and $\Delta t_a = T_{\text{inj}}/R$ because the part of the contaminant plume that forms the inner edge of the plume at $t = T_{\text{inj}}$ was at the origin at $t = 0$ and the contaminant spends only $1/R$ of the time in the aqueous phase. For the treatment chemical plume, Eq. (10) is used with $r_{\text{old}} = 0$ and $\Delta t_a = T_{\text{inj}} - T'_{\text{inj}}$ because the last treatment chemical to be injected at well O enters at $t = T'_{\text{inj}}$. Combining these yields

$$r_{\text{in}} = \sqrt{\frac{QT_{\text{inj}}}{\pi bnR}} = \sqrt{\frac{Q(T_{\text{inj}} - T'_{\text{inj}})}{\pi bn}} \tag{21}$$

Rearranging to solve for $V_2 = QT'_{\text{inj}}$ produces

$$V_2 = QT'_{\text{inj}} = QT_{\text{inj}}\frac{R-1}{R} \tag{22}$$

The mass M_2 of the treatment chemical must be sufficiently high to degrade the contaminant. For a circular initial configuration of the contaminant plume [Fig. 1(a)], the contaminant mass is given by

$$M_1 = C'_1 \pi r_{\text{init}}^2 bnR \tag{23}$$

Thus from this equation and the definition of M^*, the total mass of the treatment chemical is

$$M_2 = M^* C'_1 \pi r_{\text{init}}^2 bnR \tag{24}$$

Simulation Procedure with Linear Equilibrium Sorption

The procedure to simulate reactive transport during EIE for a contaminant that exhibits linear equilibrium sorption is as follows. A total of N_{pc} contaminant particles are randomly placed over the initial contaminant plume area shown in Fig. 1(a) to approximate a uniform distribution. Each particle has an initial mass m of

$$m = \frac{C'_1 \pi r_{\text{init}}^2 bn}{N_{pc}} \tag{25}$$

and the mass is distributed between the aqueous and sorbed phases according to Eqs. (13) and (14).

Each step of the EIE sequence is divided into N_s smaller transport steps of duration $\Delta t_i = T_i/N_s$. During the injection phase, a total of N_{pt} particles of the treatment chemical are released at well O. At the end of a transport step of the injection phase, N_{pt}/N_s treatment chemical particles are introduced into the aquifer in a random arrangement that approximates a uniform distribution over the circular region with radius $r = \sqrt{V_t/(N_s \pi bn)}$.

At the start of each transport step, all particles in the aquifer undergo a random dispersive displacement and are then transported by advection to their new positions. Finally, the particles are binned and reacted at these new positions. For this linear equilibrium sorption case, the reaction step reduces the total particle mass, but the relationship between the aqueous- and sorbed-phase masses of each particle always follows Eqs. (13) and (14). The procedure is repeated for each transport step in the first EIE step, and the whole procedure is repeated for subsequent EIE steps.

Table 2. Aquifer Properties and Initial Contaminant Plume Parameters

Parameter	Value
Initial aqueous contaminant concentration C'_1 (equilibrium sorption) (mg/m^3)	500
Initial aqueous contaminant concentration C'_1 (kinetic sorption) (mg/m^3)	2,500
Initial contaminant plume radius r_{init} (m)	10
Aquifer thickness b (m)	1
Porosity n	0.25
Longitudinal dispersivity α_L (m)	0.1
Transverse dispersivity α_T (m)	0.01
Stoichiometric ratio F	1

Examples of EIE with Linear Equilibrium Sorption

Examples using EIE with linear equilibrium sorption for a range of retardation coefficients and reaction rates are presented in this section. The contaminant plume is initially circular with a radius of $r_{\text{init}} = 10$ m and a uniformly distributed concentration of $C'_1 = 500$ mg/m^3. Other aquifer parameters are shown in Table 2. The values of the design parameters are $M^* = 1.25$, $\lambda_o^2 = 1.25\sqrt{R}$, and $r_f^* = 0.65/\lambda_o$; they were selected after testing a range of values. Although they have been shown to provide nearly complete degradation, they are not necessarily optimal.

Instantaneous Reaction

If degradation reactions are instantaneous, all of the degradation occurs at the leading edge of the treatment chemical plume. For this scenario, the contact time between the contaminant and the treatment chemical is irrelevant because the reactions occur instantaneously; thus the choice of T_{inj} is nonunique and any combination of Q and T_{inj} that satisfies Eq. (20) is acceptable. For this work, T_{inj} was set to one day and Q was adjusted according to Eq. (20). Retardation coefficients of $R = 5$ and $R = 10$ were used. For both cases, the parameter values are given in Table 3 and the well sequence is given as Sequence II in Table 1. To account for the randomness of the dispersion and reaction processes, the average amount of contaminant degradation over 30 simulations was found. Using the values stated previously as the design parameters, almost all of the contaminant is degraded during the EIE process (Table 3).

Fig. 2 shows the contaminant and treatment chemical plumes at seven different times during the EIE sequence for $R = 5$. Initially, the contaminant plume is circular and centered at the origin [Fig. 2(a)]. From $t = 0$ to $t = T'_{\text{inj}}$ (step 1 of Sequence II in Table 1), the treatment chemical is injected at well O, causing both the treatment chemical and the contaminant to move radially outward from that well, creating an annular contaminant plume and an approximately circular treatment chemical plume [Figs. 2(b and c)]. Because the contaminant moves more slowly than the treatment chemical, the leading edge of the treatment chemical plume comes into contact with the trailing edge of the contaminant plume and degradation reactions occur. At $t = T'_{\text{inj}}$ [Fig. 2(c)], the width of the annulus of the treatment chemical plume is narrow and a substantial amount of the treatment chemical plume is in the interior of the contaminant plume. By $t = T'_{\text{inj}}$, more than 85% of the contaminant mass has degraded, with most of the unreacted mass lying outside of the treatment chemical plume.

Table 3. Design Parameter Values and Results for Cases with Linear Equilibrium Sorption with Instantaneous and Rate-Limited Reaction

Parameter	Instantaneous reaction		Rate-limited reaction			
	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Retardation coefficient R	5	10	5	5	10	10
Reaction rate constant k_a (m^3/mg/d)	N/A	N/A	0.1	0.001	0.1	0.001
Mass ratio M^*	1.25	1.25	1.25	1.25	1.25	1.25
r_f^*	0.39	0.33	0.39	0.39	0.33	0.33
λ_o	1.67	1.99	1.67	1.67	1.99	1.99
L (m)	38.7	39.3	38.7	38.7	39.3	39.3
Volume of fluid injected V (m^3)	498	513	498	498	513	513
Volume of treatment chemical injected V_2 (m^3)	398	462	398	398	462	462
Duration of injection phase T_{inj} (d)	1	1	1	100	1	100
Duration of treatment chemical injection T'_{inj} (d)	0.8	0.9	0.8	80	0.9	90
Dimensionless reaction rate k^*	N/A	N/A	50	50	50	50
Injection rate Q (m^3/d)	498	513	498	4.98	513	5.13
Initial mass of contaminant M_1 (g)	196	393	196	196	393	393
Mass of treatment chemical M_2 (g)	245	491	245	245	491	491
Concentration of injected treatment chemical C'_2 (mg/m^3)	616	1,060	616	616	1,060	1,060
Contaminant mass degraded (%)	99.2	99.8	99.9	99.9	99.9	99.9

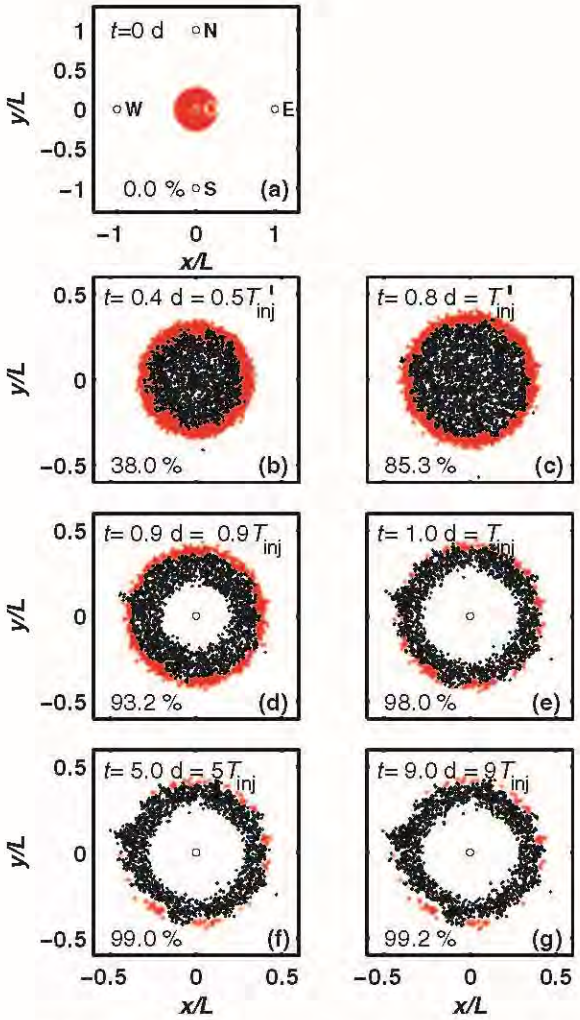

Fig. 2. (Color) For $R = 5$, contaminant (red) and treatment chemical (black) plumes: (a) prior to remediation; (b) halfway through treatment chemical injection; (c) end of treatment chemical injection; (d) halfway through clean water injection; (e) end of clean water injection; (f) halfway through extraction phase; (g) end of extraction phase; time is shown in upper left of each subplot and average percentage contaminant mass degraded on or before indicated time is shown at bottom left

From $t = T'_{inj}$ to $t = T_{inj}$ (step 2 of Sequence II in Table 1), clean water is injected at well O, causing both treatment chemical and contaminant plumes to move radially outward, forming annular plumes that approximately overlap [Figs. 2(d and e)]. The overlap provides substantial opportunities for degradation reactions to occur. By $t = T_{inj}$, 98% of the contaminant mass has been degraded and the unreacted mass lies outside of the treatment chemical plume where randomness due to dispersion has prevented treatment chemical and contaminant particles from coming close enough to react.

In steps 3–10 of Sequence II (Table 1), water is extracted sequentially from each of the outer wells. Both the treatment chemical and contaminant plumes are drawn toward the active extraction well. Through this process, the treatment chemical passes over most of the remaining contaminated groundwater because the contaminant moves more slowly than the treatment chemical [Figs. 2(f and g)], thereby degrading most of the remaining contamination. At the end of the 10-step sequence, almost all of the contaminant mass has degraded. For $R = 10$, similar behavior is observed; however, the system parameters have different values (Table 3).

Rate-Limited Reaction

For rate-limited reaction, reaction at the leading edge of the treatment chemical is incomplete unless the treatment chemical plume moves sufficiently slow to allow complete reaction to occur. A dimensionless reaction rate k^* is defined as

$$k^* = k_a C'_1 T_{inj} \tag{26}$$

Similar plume geometries and amounts of contaminant degradation are obtained in any system with the same value of k^*. The instantaneous reaction results, specified in Sequence II of Table 1 and shown in Fig. 2, can be reproduced using the rate-limited reaction model with $k_a = 0.1$ m^3/mg/d. With $C'_1 = 500$ mg/m^3 and $T_{inj} = 1$ day, the dimensionless reaction rate is $k^* = 50$. For rate-limited reaction, T_{inj} was adjusted to maintain $k^* = 50$ in Eq. (26) and Q was adjusted in Eqs. (20) and (22) to maintain the required V and V_2. The values of the parameters for several different combinations of R and k_a (each with the same k^*) are shown in Table 3. In all cases, nearly complete degradation of the contaminant is achieved.

As the reaction rate constant k_a decreases, the required duration of the remediation activities increases proportionately. In the examples shown in Table 3, the total duration of the radial-flow Sequence II is $9T_{\text{inj}}$. Accordingly, with $R = 5$ and $k_a = 0.1$ m^3/mg/d, remediation requires 9 days whereas with $k_a = 0.001$ m^3/mg/d, remediation requires 900 days. For very low rate constants, this may lead to unreasonably long durations to achieve complete degradation.

EIE with Linear Kinetic Sorption

The goal of EIE, regardless of the sorption properties of the contaminant, is to increase the contact between the contaminant and the treatment chemical plumes. For a nonsorbing contaminant, the EIE strategy is to increase the contact between the two plumes by elongating the interface between them. For a sorbing contaminant that exhibits linear equilibrium sorption, the contact between the two plumes is increased by chasing the slower-moving contaminant plume with a faster-moving treatment chemical plume. For a contaminant that exhibits linear kinetic sorption, the effectiveness of the EIE strategy depends on the sorption rate constant α_s. If $\alpha_s \to 0$ and the contaminant is initially in the aqueous phase, the contaminant will behave like an aqueous, nonsorbing solute; thus an effective EIE strategy is to elongate the interface between the treatment chemical and contaminant plumes. On the other hand, if $\alpha_s \to \infty$, the solute exhibits linear equilibrium sorption, so the EIE strategy introduced in the previous section is more effective.

In this section, the effectiveness of the two EIE sequences in Table 1 for degrading a contaminant that exhibits linear kinetic sorption is investigated. The simulation procedure for linear kinetic sorption is the same as the procedure for linear equilibrium sorption, with one exception. In linear equilibrium sorption, each contaminant particle represents both aqueous-phase and sorbed-phase masses. In linear kinetic sorption, each particle is entirely in the aqueous phase or entirely in the sorbed phase and can transition between the two phases according to Eqs. (11) and (12).

To illustrate the effect of the sorption and reaction rate constants on contaminant degradation, transport and reaction in EIE were simulated using the two sequences in Table 1. The plume and EIE design parameters are shown in Tables 2 and 3, and the retardation coefficient was $R = 5$. The contaminant plume is initially circular with a radius of $r_{\text{init}} = 10$ m, a uniformly distributed aqueous concentration of $C_1' = 2{,}500$ mg/L, and sorbed phase concentration of $S_1' = 0$ mg/g. Although this initial concentration is different from what was used for the linear equilibrium sorption examples, the initial mass of contaminant in the aquifer is equal in both cases. For Sequence I, each step of the sequence lasts for one day. Prior to the start of the 12-step sequence in Table 1, the treatment chemical is injected at the origin for one day at a rate of 74 m^3/d at a concentration of $C_2' = 3330$ mg/m^3 to create a circular treatment chemical plume of radius $r = L/4 = 9.7$ m. During this injection, the transport and reaction of the contaminant plume are also simulated. For the radial-flow Sequence II, we use $T_{\text{inj}} = 1$ d as the length of the injection step. Accordingly, with $T_{\text{inj}}' = 0.8$ d, $Q = 498$ m^3/d, and $M_2 = 245$ g, the treatment chemical concentration of $C_2' = 616$ mg/m^3. Unlike the linear equilibrium sorption simulations with kinetic reaction, T_{inj} is not adjusted to maintain a constant dimensionless reaction rate k^*. Instead, T_{inj} is fixed to isolate the effects of the sorption and reaction rate constants. The range of sorption rate constants used is $\alpha_s = 0.01$, 0.1, 1 and 10 d^{-1}, and the range of reaction rate constants is $k_a = 10^{-5}, 10^{-4.5}, \ldots, 10^{2}$ m^3/mg/d, with $k_s = k_a/2$ in all cases.

For each combination of parameters, the average amount of contaminant degradation over 30 simulations is shown in Fig. 3. Regardless of the EIE sequence, Fig. 3 shows that for very slow reaction (i.e., $k_a < 10^{-4}$ m^3/mg/d, very little degradation occurs regardless of the sorption rate constant because the reactions proceed too slowly for any appreciable degradation to occur in the time specified for the EIE process.

Fig. 3 also shows that for fast reaction (i.e., $k_a > 10^{-2}$ m^3/mg/d), degradation increases with an increasing sorption rate constant—that is, as sorption approaches equilibrium sorption. The physical explanation of this behavior is different for each sequence. To aid the explanation, Figs. 4 and 5 show an example of the

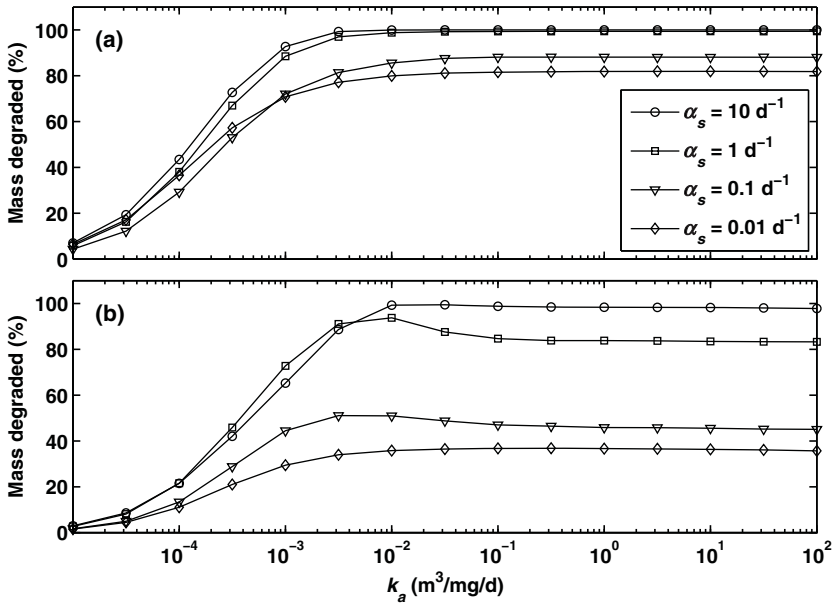

Fig. 3. For $R = 5$, contaminant mass degraded versus reaction rate constant k_a for different values of sorption rate constant α_s: (a) stretching-and-folding Sequence I; (b) radial-flow Sequence II

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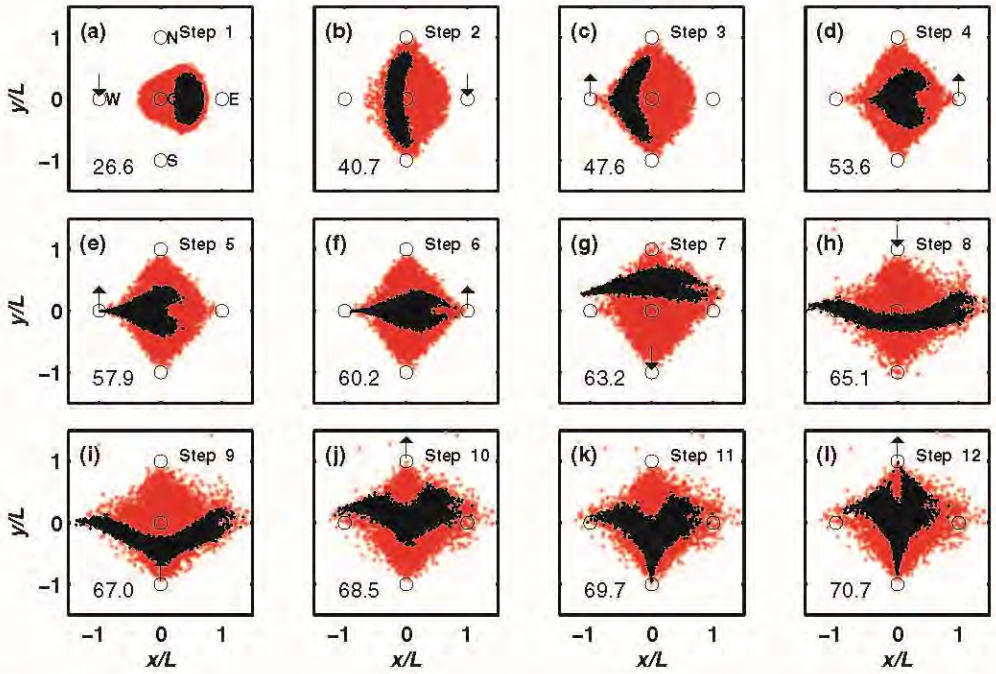

Fig. 4. (Color) For $R = 5$, position of contaminant (red) and treatment chemical (black) plumes after each step of Sequence I with $k_a = 10^{-3}$ m^3/mg/d and $\alpha_s = 0.1$ d^{-1}; circles = well locations; arrows = active wells (downward = injection; upward = extraction)

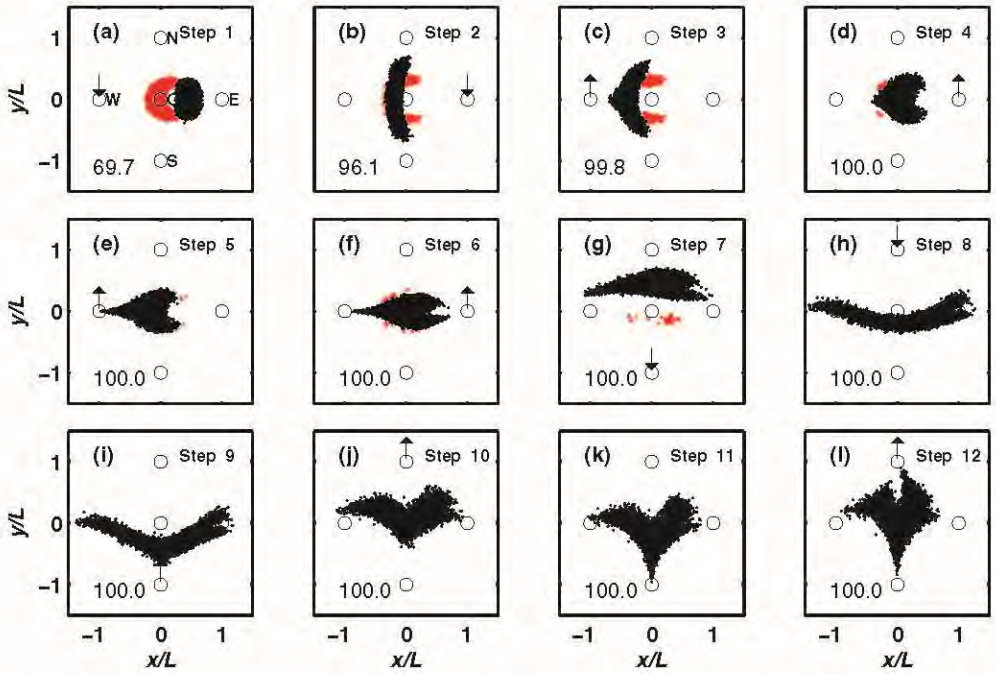

Fig. 5. (Color) For $R = 5$, position of contaminant (red) and treatment chemical (black) plumes after each step of Sequence I with $k_a = 10^{-1}$ m^3/mg/d and $\alpha_s = 10$ d^{-1}; open circles = well locations; arrows = active wells (downward = injection; upward = extraction)

positions of the treatment chemical and contaminant plumes after each step of the stretching-and-folding Sequence I for slow kinetics ($k_a = 10^{-3}$ m^3/mg/d and $\alpha_s = 0.1$ d^{-1}) and fast kinetics ($k_a = 10^{-1}$ m^3/mg/d and $\alpha_s = 10$ d^{-1}), respectively. The treatment chemical plume is placed in the center of the contaminant plume; then, through the 12-step EIE sequence, it moves radially away from an active injection well or radially toward an active extraction well (Figs. 4 and 5) to create for itself a stretched and folded configuration.

A contaminant with slow kinetics (Fig. 4) moves radially away from an active injection well and radially toward an active extraction well, with some particles remaining immobile in the sorbed phase. Degradation reactions occur at the interface between the treatment chemical plume and the aqueous contaminant plume

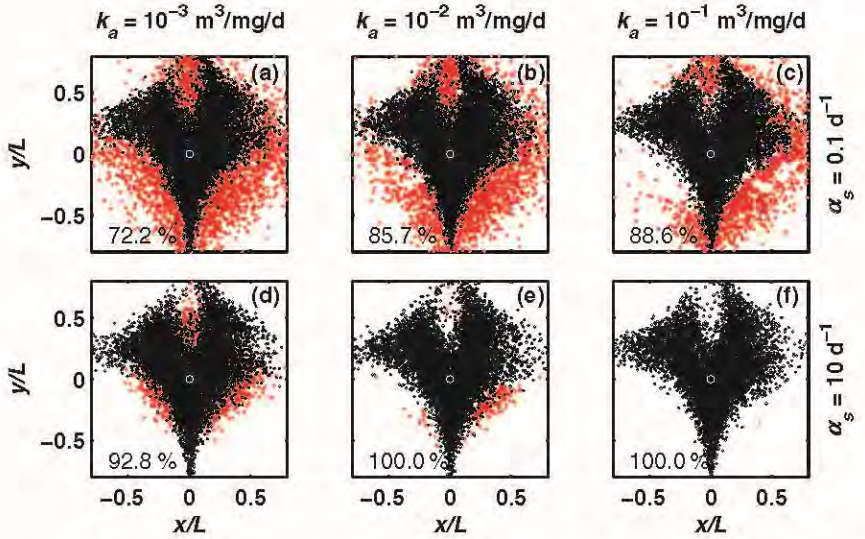

Fig. 6. For $R = 5$, contaminant (red) and treatment chemical (black) particles at end of Sequence I for different values of reaction rate constant k_a and sorption rate constant α_s; the number at the bottom left of each subplot is the amount of contaminant degraded

and where the treatment chemical plume passes over the sorbed, immobile contaminant.

A contaminant with fast kinetics (Fig. 5) moves at a velocity approaching the equilibrium sorption limit of v_r/R, where v_r is the local groundwater velocity; thus the contaminant plume moves more slowly than the treatment chemical plume. As the treatment chemical plume passes over the contaminant plume, the contaminant is degraded. Complete degradation occurs by step 4 of the EIE sequence in the instantaneous reaction example shown in Fig. 5.

Fig. 6 shows the contaminant and treatment chemical plumes at the end of the stretching-and-folding Sequence I for several combinations of sorption and reaction rate constants spanning the extremes shown in Figs. 4 and 5. Some contaminant particles that stay in the aqueous phase remain outside of the treatment chemical plume throughout the EIE sequence [Figs. 6(a–c)] and therefore do not degrade. For rate-limited reaction, some contaminant particles do not have sufficiently long contact with treatment chemical particles to experience complete degradation [Figs. 6(d and e)].

To aid the explanation of radial-flow Sequence II behavior, Figs. 7 and 8 show an example of the contaminant and treatment chemical plumes at the end of the injection step and the extraction step, respectively, for Sequence II for the same combinations of sorption and reaction rate constants shown in Fig. 6. In the case of fast sorption (i.e., $\alpha_s = 10$ d^{-1}) [Figs. 7(d–f)], the contaminant particles travel at a velocity approaching the equilibrium sorption limit of v_r/R, where v_r = the local groundwater velocity. Thus at the end of the injection step, the contaminant plume has a narrow annular shape coinciding with the inner portion of the treatment

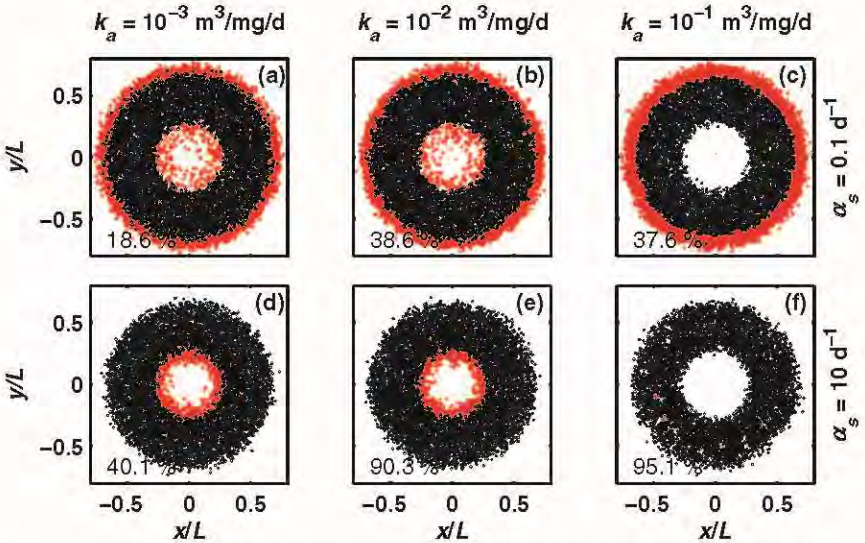

Fig. 7. (Color) For $R = 5$, contaminant (red) and treatment chemical (black) particles at end of Sequence II injection step for different values of reaction rate constant k_a and sorption rate constant α_s; the number at the bottom left corner of each subplot is the amount of contaminant degraded during injection step

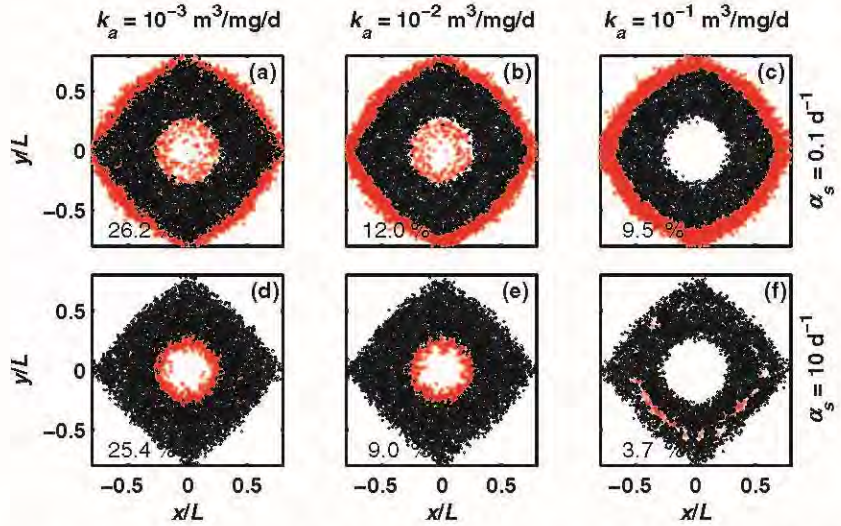

Fig. 8. (Color) For $R = 5$, contaminant (red) and treatment chemical (black) particles at end of Sequence II extraction step for different values of reaction rate constant k_a and sorption rate constant α_s; the number at the bottom left of each subplot is the amount of contaminant degraded during extraction phase of EIE sequence

chemical plume. In the case of slow sorption [i.e., $\alpha_s = 0.1$ d^{-1} in Figs. 7(a–c)], at the end of the injection step the contaminant plume covers a circular region that extends beyond the outer edge of the treatment chemical plume. The contaminant particles beyond the outer edge of the treatment chemical plume have not had the opportunity to degrade; thus the amount of degradation is lower for slow sorption than for fast sorption. During the extraction step, additional opportunities for degradation reactions occur, with an additional 4–26% of the contaminant mass degrading (Fig. 8).

Fig. 3 also shows that in some cases of slow to moderate reaction (i.e., 10^{-4} m^3/mg/d $< k_a < 10^{-2}$ m^3/mg/d) more reaction occurs for lower α_s. For the radial-flow Sequence II, during the injection phase degradation increases as α_s increases (Fig. 7), but during the extraction phase less degradation occurs for higher values of α_s (Fig. 8). This behavior occurs because the contaminant plume at the end of the injection step is confined to a narrow annular region in the case of fast sorption [Fig. 7(d)] and therefore does not have much opportunity to encounter the treatment chemical and degrade during the extraction step. On the other hand, for slow sorption [Fig. 7(a)], the contaminant plume overlaps with the entire treatment chemical plume at the end of the injection step and therefore has ample opportunities for degradation reactions to occur during the extraction step.

Fig. 3 also shows that, for a given sorption rate constant, the amount of degradation increases with an increasing reaction rate constant, with one exception. For lower sorption rate constants (i.e., $\alpha_s < 10$ d^{-1}) with Sequence II, the amount of degradation reaches a maximum around $k_a = 10^{-2}$ m^3/mg/d and then decreases slightly. This behavior can be explained by comparing Figs. 7(a and c). For higher values of k_a, reaction occurs more quickly, so with this EIE sequence the treatment chemical particles at the leading edge of the treatment chemical plume degrade away rapidly and therefore the outer region of the contaminant plume does not come into contact with the treatment chemical and cannot degrade [Fig. 7(c)]. For lower values of k_a, the leading edge of the treatment chemical plume does not degrade away, so a larger extent of the contaminant plume comes into contact with the treatment chemical plume, permitting greater amounts of degradation [Fig. 7(a)].

Discussion

There is a growing body of work supporting the notion that the flow field imposes significant control on reactive transport in aquifers, where the flow field reflects the effects of heterogeneity (Le Borgne et al. 2010; Dentz et al. 2011), precipitation reactions (Morrison et al. 2006; Li et al. 2008), or unsteady flow (Dagan et al. 1996; Schirmer et al. 2000; Cirpka 2005). The work presented here is very much in this spirit. The present work explored alternate extremes taken from a spectrum of engineered flows available to enhance reactions in aquifers. At one end of this spectrum is an essentially radial velocity field, as envisioned by Oya and Valocchi (1998), for sorbing contaminants that partition between aqueous and soil phases quickly (i.e, equilibrium sorption). At the other end of this spectrum is an application of chaotic advection, as envisioned by Mays and Neupauer (2012), for sorbing contaminants that partition slowly (i.e., kinetic sorption).

To demonstrate the importance of the flow field, consider the work of Oya and Valocchi (1998), who analyzed in situ remediation of a sorbing contaminant by a nonsorbing treatment chemical whose injection generates radial flow within the sorbing-contaminant plume. Oya and Valocchi (1998) defined the contaminant degradation rate R_s as

$$R_s = \frac{QC_1'C_2'(R-1)}{FRC_1' + C_2'} \tag{27}$$

where C_2' = the concentration of the treatment chemical in the injection fluid. Notably, R_s does not depend on the dispersion tensor, sorption kinetics, or reaction kinetics. For the linear equilibrium sorption example with the radial-flow Sequence II and $R = 5$ (shown in Fig. 2), the cumulative degradation rate and incremental degradation rate at each of the six times are shown in Fig. 2. The results are shown in Table 4, along with the degradation rate calculated from Eq. (27) using values shown in Table 3. From Eq. (27), $R_s = 197$ g/d, which is essentially identical to the average degradation rate of 192 g/d during the injection phase shown in Figs. 2(b–e) and within a factor of 2 of the first four incremental degradation rates (Table 4). It is striking that these results agree, considering that they are based on different conceptual models

Table 4. Contaminant Degradation Rates for Simulation Shown in Fig. 2

Panel in Fig. 2	Cumulative time (d)	Incremental time (d)	Cumulative mass (%)	Degraded (g)	Cumulative degradation rate (g/d)	Incremental degradation rate (g/d)	R_s from Eq. (27) (g/d)
b	0.4	0.4	38.0	75	187	187	198
c	0.8	0.4	85.3	167	209	232	198
d	0.9	0.1	93.2	183	203	155	198
e	1.0	0.1	98.0	192	192	94	198
f	5.0	4.0	99.0	194	39	0.49	25
g	9.0	4.0	99.2	195	22	0.10	25

of the reaction kinetics. The reaction rate was proportional to the product of the concentrations of the contaminant and the treatment chemical, while Oya and Valocchi (1998) used a multiplicative Monod reaction model that is only equivalent to ours under nutrient limiting conditions that are not assumed here. The similarity of these results suggests that flow field, rather than reaction kinetics, does indeed play a key role for remediation of sorbing contaminants with nonsorbing treatment chemicals, at least when imposing radial flow. In contrast, the incremental reaction rates during the extraction phase of Sequence II are much lower than the rates predicted from Eq. (27) because they reflect a change in the characteristics of flow. Specifically, during the extraction phase of Sequence II, the radial flow is no longer centered at the centroid of the contaminant plume.

The results reported here support the notion that early-time behavior is important when considering the relationship between imposed velocity fields and enhanced reaction transport. Previous research indicated that chromatographic overlap resulting from equilibrium sorption strongly influences solute mixing at early times, whereas plume smearing resulting from kinetic sorption has a larger influence on solute mixing at later times (Cirpka 2005). The results reported here (Fig. 3) indicate that contaminant degradation increases as the sorption kinetics approach equilibrium. This result matches the expectation for early-time behavior reported by Cirpka (2005). The importance of early-time behavior has also been emphasized in a more theoretical analysis of solute mixing (Funakoshi 2008).

Comparison of Figs. 3(a and b) shows that for every combination of sorption rate constant and reaction rate constant, the stretching-and-folding Sequence I leads to more contaminant degradation than does the radial-flow Sequence II and is therefore superior if the only objective is to maximize contaminant degradation. Groundwater remediation is by no means a single-objective activity, however. On the contrary, it must be accomplished in the context of a schedule and a budget. In this context, Sequence I is not necessarily a better option for several reasons. First, Sequence I requires injection and extraction of more than 5,000 m^3 of water during the 12-step sequence whereas Sequence II requires injection and extraction of only approximately 500 m^3 of fluid (including the treatment chemical and water). Thus Sequence I requires considerably more energy and handling of fluids at a correspondingly higher cost. Also, throughout Sequence II the contaminant plume remains within a distance of approximately 0.5 L around well O (Figs. 7 and 8) whereas during Sequence I the contaminant spreads throughout a much larger region (Fig. 4).

The selection of an effective remediation process design can depend on the degree to which the aquifer can be remediated, cost, duration of the process, size of the impacted area, and other tradeoffs. This example illustrates the need for multiobjective optimization in the design process, which is the subject of ongoing work.

The analysis conducted here assumed that ambient groundwater velocity is negligible compared to the velocities created through injection and extraction during EIE. This assumption allowed the focus to be on the effects of sorption and reaction properties on the contaminant degradation obtained with the two EIE sequences. If the ambient velocity were not negligible, the design would have to be adapted to ensure that the treatment chemical plume reached the outer edge of the contaminant plume everywhere, and that the plumes did not extend beyond the outer wells. Otherwise the possibility would exist for residual contaminant mass to remain in the aquifer. With non-negligible ambient groundwater flow, a larger value of λ_o would be required. Also the ideal placement of the four outer wells would likely not be equidistant from the origin but rather shifted in the direction of the ambient groundwater flow. The optimal parameter values and well locations would thus be dependent on the ambient velocity and the relationship between the injection rates, plume size, and the ambient velocity. Optimization of this system is the subject of ongoing work.

Conclusions

This work investigated the use of engineered injection and extraction (EIE) as a method for remediation of aquifers contaminated with sorbing solutes. For solutes that exhibit linear equilibrium sorption, this work developed an EIE strategy (the radial-flow Sequence II) that relies on the slower advection of sorbing contaminants relative to the nonsorbing treatment chemical, similar to the approach of Oya and Valocchi (1998). This EIE sequence can lead to nearly complete contaminant degradation if the reaction between the contaminant and the treatment chemical is instantaneous. For contaminants with linear equilibrium sorption and rate-limited reaction, nearly complete degradation can also be achieved if the duration of the remediation process is scaled with the inverse of the reaction rate constant such that the dimensionless rate constant, defined by Eq. (26), is approximately $k^* = 50$.

For solutes that exhibit linear kinetic sorption, Sequence II leads to nearly complete degradation if the reaction rate is relatively fast ($k_a \geq 10^2$ $m^3/mg/d$) and the sorption rate is sufficiently fast to approximate equilibrium sorption ($\alpha_s = 10$ d^{-1}). For slow sorption ($\alpha_s < 10$ d^{-1}), Sequence II does not achieve complete degradation, no matter what reaction rate is used; however, the stretching-and-folding Sequence I can achieve nearly complete degradation when the sorption rate is sufficiently fast to approximate equilibrium sorption ($\alpha_s = 10$ d^{-1}) and the reaction rate is relatively fast ($k_a \geq 10^2$ $m^3/mg/d$). The increased degradation in Sequence II has higher energy requirements, fluid volumes, and cost. Evaluation of these sequences is the subject of ongoing work using multiobjective optimization.

Acknowledgments

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Notation

The following symbols are used in this paper:

b = aquifer thickness;
C_{jb} = aqueous concentration of species j in bin b;
C_1 = aqueous contaminant concentration;
C_2 = treatment chemical concentration;
C_1' = initial aqueous contaminant concentration;
F = stoichiometric ratio;
k_a = reaction rate constant for the aqueous contaminant;
K_d = linear equilibrium partition coefficient;
k_s = reaction rate constant for the sorbed-phase contaminant;
k^* = dimensionless reaction rate;
L = distance between an outer well and the origin;
m = total particle mass;
m_a = aqueous particle mass;
m_s = sorbed phase particle mass;
$m_{aj\ell}$ = aqueous mass of the ℓth particle of species j;
$m_{s1\ell}$ = sorbed mass of the ℓ particle of the contaminant;
M_1 = initial mass of the contaminant;
M_2 = total mass of the treatment chemical;
M^* = ratio of initial mass of the contaminant to total mass of the treatment chemical;
n = porosity;
N_s = number of transport steps in each EIE step;
S_{jb} = sorbed phase concentration of species j in bin b;
T_i = duration of the ith EIE step;
T_{inj} = duration of the injection step;
T_{inj}' = duration of the treatment chemical injection;
T_{wa} = random waiting time of a particle in the aqueous phase;
T_{ws} = random waiting time of a particle in the sorbed phase;
V = volume of fluid injected;
V_b = volume of a bin;
V_2 = volume of treatment chemical injected;
α_L = longitudinal dispersivity;
α_s = sorption rate constant;
α_T = transverse dispersivity;
Δt = duration of the EIE step;
Δt_a = time that a particle spends in the aqueous phase;
Δt_i = duration of transport step;
λ_o = r_f^t / r_f;
Λ^2 = dimensionless number relating flow rate, duration of an EIE step, aquifer properties, and well spacing;
v_r = radial groundwater velocity; and
ρ_b = bulk density.

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