Comparison of Effective Active Spreading Designs for In-Situ Groundwater Remediation

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ABSTRACT

During in-situ remediation of contaminated groundwater, a chemical or biological amendment is introduced into the contaminant plume to react with the contaminant. Reactions occur only where the amendment and contaminant are in contact with each other, so active spreading has been proposed to increase the contact area between the two reactants. With active spreading, wells are installed in the vicinity of the contaminant plume and are operated in a pre-defined sequence of injections and extractions to create a spatio-temporally varying flow field that changes the shapes of the reactant plumes, generally leading to an increase in contact area and therefore an increase in reaction. The design of the active spreading system depends on the reaction chemistry of the contaminant. This study considers active spreading scenarios for contaminants with three different types of reactions: (1) non-sorbing aqueous contaminant, *A*, that degrades irreversibly to a benign chemical, *C*, through reaction with a non-sorbing aqueous amendment, *B*; (2) sorbing contaminant, *A,* the degrades irreversibly to a benign chemical, *C*, through reaction with a non-sorbing aqueous amendment, *B,* where sorption of *A* is independent of the concentration of *B*; and (3) contaminant, *A,* that exhibits reversible equilibrium surface complexation with concentrations in the mobile and immobile phases dependent on the concentration of the amendment, *B*. We compare the active spreading strategies for these three types of reactions and identify the characteristics each strategy that lead to enhanced removal of groundwater contaminants.

INTRODUCTION

During in situ remediation of contaminated groundwater, a chemical amendment can be introduced into the contaminant plume to react with and degrade the contaminant. Degradation occurs where the contaminant and the amendment are sufficiently close so that the chemical reaction can occur. The amount of reaction is controlled by two related processes – spreading and mixing. Mixing is the process of molecular diffusion and small-scale dispersion that occurs at the plume boundary (Dentz et al., 2011), which increases the volume occupied by the plume and leads to smoothing of concentration gradients at the plume boundary. Thus, mixing at the interface between the contaminant and amendment plumes brings the two species together to react. Spreading is the reconfiguration of the plume geometry as a result of spatial or spatio-temporal velocity variations. Spreading can lead to elongation of the of the plume boundary and sharpening of concentration gradients along the plume boundary, both of which promote mixing.

Mixing, and therefore reaction, can be enhanced by strategically reconfiguring the plume interfaces through a process called active spreading, which involves the operation of injection and extraction wells to create a pre-defined pattern of spatial or spatio-temporal velocity variations. The optimal injection and extraction patterns, hereafter called "active spreading protocols", depend on the reaction chemistry of the contaminant and amendment.

In this study, we use numerical simulation to investigate an active spreading protocol for three different models of reaction chemistry: (1) non-sorbing aqueous contaminant, A, that degrades irreversibly to a benign chemical, C, through reaction with a non-sorbing aqueous amendment, B; (2) sorbing contaminant, A, the degrades irreversibly to a benign chemical, C, through reaction with a non-sorbing aqueous amendment, B, where sorption of A is independent of the concentration of B; and (3) contaminant, A, that exhibits reversible equilibrium surface complexation, with concentrations in the aqueous and non-aqueous phases dependent on the pH which can be controlled by the introduction of amendment, B. Because the reaction chemistry and transport behavior are different among these three cases, the strategy for active spreading must be different. In the present work, we take the first step of demonstrating that the ideal active spreading strategy for one reaction model is not necessarily effective for other reaction models. Although reaction chemistry at a remediation site may be much more complex than the reactions considered herein, the active spreading strategies needed to promote degradation in each of the different cases considered here may serve as components of a more complicated active spreading remediation system.

MODELING APPROACH

In this work, we consider a two-dimensional confined aquifer that is homogeneous and isotropic. We assume that a circular plume of contaminant A was present in the aquifer, and that amendment B was introduced into the center of the plume of contaminant A immediately before the start of the active spreading remediation protocol. Thus, the introduction of the amendment is not considered to be part of the active spreading protocol.

Rather than modeling the reactive transport of all species, we instead define conservative components comprised of the reactive species, following the approach of Sole-Mari et al. (2021). Modeling the non-reactive transport of the conservative species provides a substantial savings in computational resources. During post-processing, the concentrations of the conservative components are unpacked into the concentrations of the reactive species. The governing equation of (non-reactive) transport of conservative species U_i is given by

$$R_i \frac{\partial C_{U_i}}{\partial t} = -\nabla \cdot \left(\mathbf{v} C_{U_i} \right) + \nabla \cdot \mathbf{D} \nabla C_{U_i} \tag{1}$$

where $C_{Ui}(x,y,t)$ is the molar concentration of species U_i as a function of spatial position $\mathbf{x} = (x,y)$ and time t, R_i is the retardation coefficient of species U_i, $\mathbf{v}$ is groundwater velocity, and $\mathbf{D}$ is the dispersion tensor given by

$$\mathbf{D} = \begin{bmatrix} D_{xx} & D_{xy} \\ D_{yx} & D_{yy} \end{bmatrix} \tag{2}$$

where

$$\begin{aligned} D_{xx} &= \alpha_L \frac{v_x^2}{|\mathbf{v}|} + \alpha_T \frac{v_y^2}{|\mathbf{v}|} \\ D_{yy} &= \alpha_T \frac{v_x^2}{|\mathbf{v}|} + \alpha_L \frac{v_y^2}{|\mathbf{v}|} \\ D_{xy} &= D_{yx} = \left(\alpha_L - \alpha_T\right) \frac{v_x v_y}{|\mathbf{v}|} \end{aligned} \tag{3}$$

where α_L and α_T are longitudinal and transverse dispersivity, respectively, and $\mathbf{v} = [v_x \; v_y]^T$ is the groundwater velocity.

Table 1 shows the relationship between the reactive species and the conservative components for each of the three reaction chemistry models. For Model 1, all species are aqueous and the reaction is irreversible, so $R_1 = R_2 = 1$. The concentrations of species A, B, and C can be found from the concentration of U_1 and U_2 as (Sather et al., 2021)

$$\begin{aligned} C_A(x,y,t) &= C_{U_1}(x,y,t) - C_C(x,y,t) \\ C_B(x,y,t) &= C_{U_2}(x,y,t) - C_C(x,y,t) \\ C_C(x,y,t) &= \min\left[C_{U_1}(x,y,t), C_{U_2}(x,y,t)\right] \end{aligned} \tag{6}$$

For Model 2, species A partitions between then aqueous phase A^{aq} and the sorbed phase A^s with an equilibrium constant of K_{eq}. Thus, conservative species U_1, which is comprised of A^{aq}, A^s, and C sorbs with a retardation coefficient that is depends on the concentrations of A^s and U_1. The relationship between the conservative components and the species concentrations are

$$\begin{aligned} C_{A^{aq}}(x,y,t) &= \frac{C_{U_1}(x,y,t) - C_C(x,y,t)}{1+K_{eq}} \\ C_{A^s}(x,y,t) &= \frac{K_{eq}}{1+K_{eq}}\left[C_{U_1}(x,y,t) - C_C(x,y,t)\right] \\ C_B(x,y,t) &= C_{U_2}(x,y,t) - C_C(x,y,t) \\ C_C(x,y,t) &= \min\left[C_{U_1}(x,y,t), C_{U_2}(x,y,t)\right] \end{aligned} \tag{7}$$

Table 1. Details of the three reaction chemistry models.

Model No.	Reactions	Conservative Components	Retardation coefficients	Equilibrium constants
1	$A + B \rightarrow C$	$U_1 = A+C$ $U_2 = B+C$	$R_1 = 1$ $R_2 = 1$	NA
2	$A^{aq} + B \rightarrow C$ $A^{aq} \rightleftharpoons A^{s}$	$U_1 = A^{aq} + A^{s} + C$ $U_2 = B+C$	$R_1 = \dfrac{C_{U_1}}{C_{U_1} - C_{A^s}}$ $R_2 = 1$	K_{eq}
3	$S\_OH + AO_2^{2+} \rightleftharpoons S\_OAO_2^{+} + H^{+}$ $H^{+} + OH^{-} \rightleftharpoons H_2O$	$U_1 = C_{AO_2^{2+}} + C_{S\_OAO_2^{+}}$ $U_2 = C_{S\_OH} + C_{S\_OAO_2^{+}}$	$R_1 = C_{U_1} / C_{AO_2^{2+}}$ $R_2 \rightarrow \infty$	K_s K_{H2O}

For Model 3 (adapted from Lu et al, 2015), species A partitions between the mobile phase, AO_2^{2+}, and the immobile phase, $S\_OAO_2^{+}$, where the partitioning is dependent on the pH of the water ("S" represents stationary surface complexation sites). Thus, there are two equilibrium reactions – one for the surface complexation reaction of species A, with equilibrium constant K_s, and one for the ionization of water with equilibrium constant K_{H2O}. The two conservative components are the moles of species A (U_1) and the surface complexation sites (U_2). The surface complexation sites are immobile, which can be interpreted as having an infinite retardation coefficient, so the retardation coefficient for U_2 is $R_2 \rightarrow \infty$. Component U_1 is partially mobile, because AO_2^{2+} is mobile while $S\_OAO_2^{+}$ is immobile. Since the retardation coefficient of a sorbing solute is the ratio of the total concentration to the aqueous (mobile) concentration, this partial mobility of AO_2^{2+} can be represented using a retardation coefficient that is the ratio of the total concentration of the component to the concentration of the mobile species is the component, given by

$$R_1 = \frac{C_{U_1}}{C_{AO_2^{2+}}} = \frac{C_{AO_2^{2+}} + C_{S\_OAO_2^{+}}}{C_{AO_2^{2+}}} \tag{8}$$

which varies from $R_1 = 1$ if $C_{U_1} \approx C_{AO_2^{2+}}$ to $R_1 \rightarrow \infty$ if $C_{U_1} \approx C_{S\_OAO_2^{+}}$. Since U_2 is stationary, only the transport of U_1 must be modeled. The relationship between C_{U_1}, C_{U_2}, and all other species is found by using the two equilibrium relationships in Table 1 along with charge balance, which leads to

$$
\begin{aligned}
&C_{AO_2^{2+}} + C_{U_1} + \frac{K_s C_{AO_2^{2+}}\left(C_{U_2} - C_{U_1} + C_{AO_2^{2+}}\right)}{C_{U_1} - C_{AO_2^{2+}}} - \frac{K_{H2O}\left(C_{U_1} - C_{AO_2^{2+}}\right)}{K_s C_{AO_2^{2+}}\left(C_{U_2} - C_{U_1} + C_{AO_2^{2+}}\right)} = 0 \\
&C_{S\_OAO_2^{2+}} = C_{U_1} - C_{AO_2^{2+}} \\
&C_{S\_OH} = C_{U_2} - C_{U_1} + C_{AO_2^{2+}} \\
&C_{H^+} = \frac{K_s C_{S\_OH} C_{AO_2^{2+}}}{C_{S\_OAO_2^{2+}}} \\
&C_{OH^-} = \frac{K_{H2O}}{C_{H^+}}
\end{aligned}
\tag{9}
$$

The first equation in (9) has one unknown, $C_{AO_2^{2+}}$, which can be obtained numerically. Once that value is known, the remaining concentrations can be obtained directly from the remaining equations.

RESULTS

We demonstrate here that the effectiveness of the active spreading protocol depends on the reaction chemistry. Neupauer and Mays (2015) demonstrated that active spreading induced by radial flow is an ideal active spreading scenario for the degradation of a sorbing contaminant (Model 2). Thus, we use a radial flow active spreading protocol in this work with the three reaction models shown in Table 1. With radial flow, velocity is a function of radial distance, *r*, from an injection well, given by

$$
\mathrm{v}(r) = \frac{Q}{2\pi n r} \tag{10}
$$

where *Q* is the injection rate per unit aquifer thickness. We use particle tracking to solve (1), with the particle position at time step *k* given by

$$
r_{i,j}^{k} = r_{i,j}^{k-1} + \frac{Q\Delta t}{2\pi n r R_i} + \varepsilon_{i,j}\sqrt{\frac{\alpha_L Q \Delta t}{\pi n r R_i}} \tag{11}
$$

where $r_{i,j}^{k}$ is the radial position of the j^{th} particle of U_i at the k^{th} time step, Δt is the time step, and $\varepsilon_{i.j}$ is a random number drawn from a standard normal distribution.

We solve (11) using the parameter values shown in Table 2, along with the retardation coefficients in Table 1 and the relationships between concentration of conservative components and reactive species shown in (6), (7), and (9) to obtain the temporal evolution of the spatial distributions of species concentration over a 25-day period, shown in Figures 1 – 3 for Models 1 – 3, respectively. The initial distributions (shown in subplot a in the figures) represents

Table 2. Parameter values used in the simulations.

Parameter	Value		
	Model 1	Model 2	Model 3
Injection rate, Q (m^3/d/m)	2.5	2.5	2.5
Porosity, n	0.3	0.3	0.3
Longitudinal dispersivity, α_L (m)	0.01	0.01	0.01
Equilibrium coefficients		$K_{eq} = 2$	$K_s = 0.1$ $K_{H2O} = 10^{-14}$
Molar mass of a particle (mol)	9.2 x10^{-5}	9.2 x10^{-5}	

concentric circles of an amendment plume (inner circle) and contaminant plume (outer circle) with concentrations approximately uniform within each plume. Figure 4 shows the percentage of the initial contaminant that was degraded over time for Models 1 and 2.

With Model 1, both species A and B are non-sorbing, so they move radially outward at equal rates, and reaction only occurs at the interface between the two plumes, where the two species are brought together by dispersion. Thus, the amount of A that is degraded is relatively low (see Figure 4). With Model 2, species A sorbs, so although it moves radially outward, species A moves more slowly than the non-sorbing species B, leading to overlapping plumes of A and B. When plumes of A and B overlap, they occupy the same space and therefore can react readily and degrade. Eventually, the plume of B completely passes through the plume of A (starting around $t = 25$ d), leading to complete degradation of species A (see Figure 4) based on our model of instantaneous irreversible reaction. With Model 3, no contaminant is degraded. At any location, the mass of A is partitioned between the mobile phase ($C_{AO_2^{2+}}$) and the immobile phase ($C_{S\_OAO_2^{+}}$). If the goal is to immobilze A, the active spreading model must be designed to create conditions that are favorable for complexation. In this example, the goal would be to decrease the pH.

The spread of the plumes is controlled by the dispersivity. In Models 1 and 2, a higher dispersivity would lead to a larger overlapping region of the two plumes, and therefore more reaction; however, the relative amounts of reaction between Models 1 and 2 would not change.

CONCLUSION

These results show that the radial flow active spreading protocol is very effective at degrading a sorbing contaminant, but ineffective at degrading a non-sorbing contaminant. This demonstration supports the broader conclusion that the optimal design of active spreading remediation protocols is completely dependent on the chemical reaction model for the degradation of the contaminant.

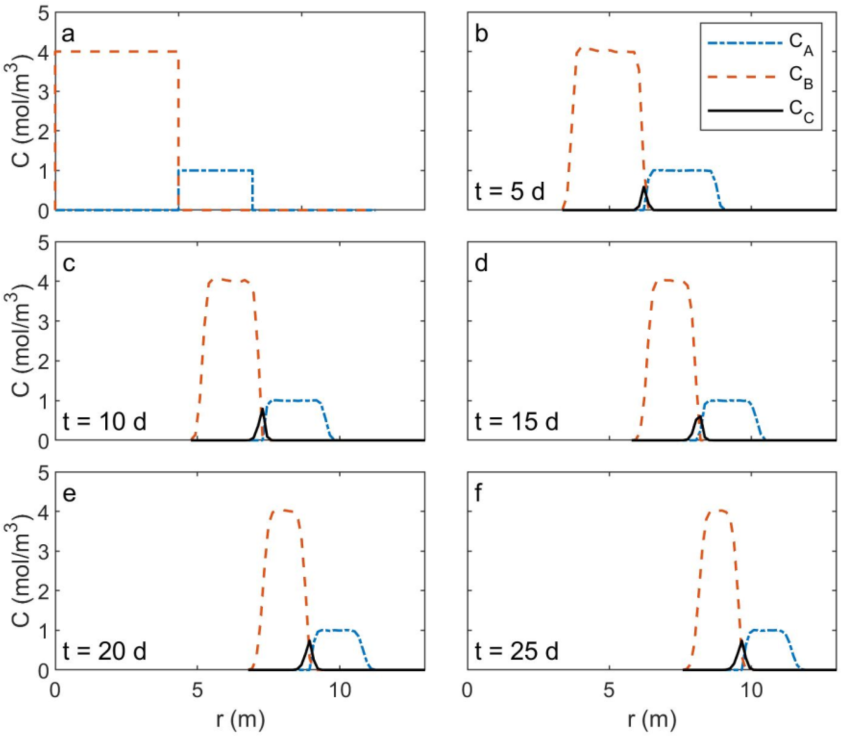

Figure 1. Spatial concentration distributions of species A, B, and C at various times for Model 1.

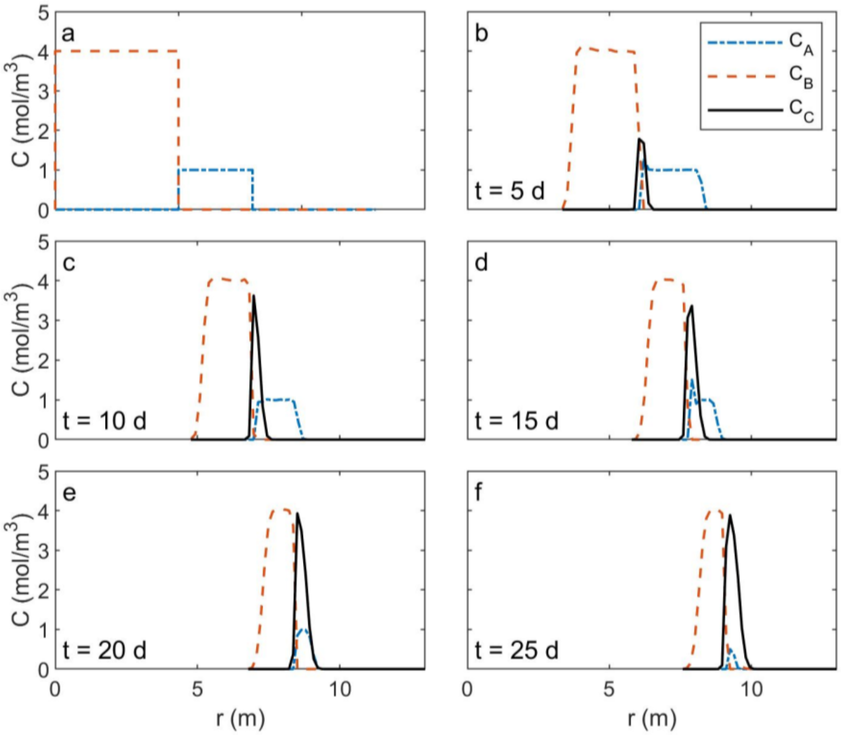

Figure 2. Spatial concentration distributions of species A, B, and C at various times for Model 2.

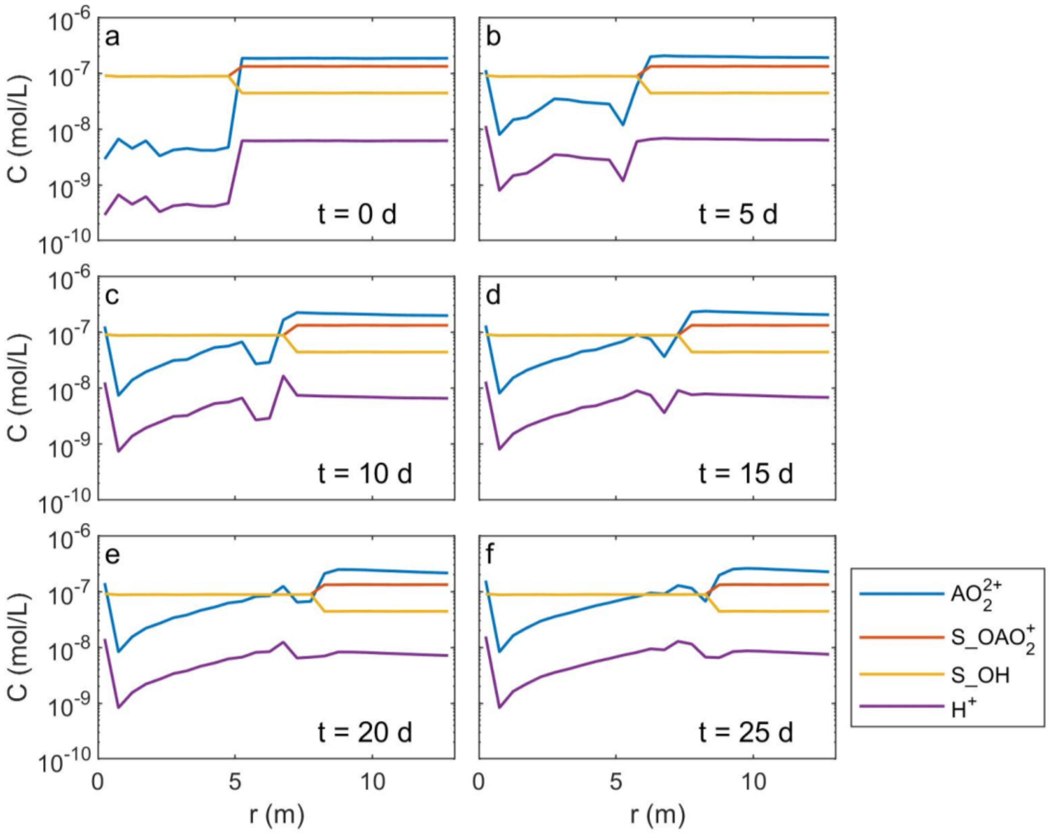

Figure 3. Spatial concentration distributions of species at various times for Model 3.

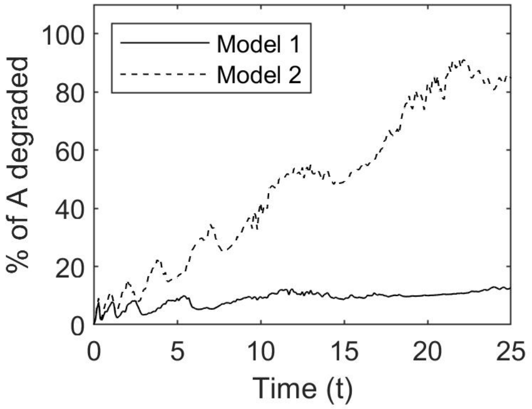

Figure 4. Cumulative contaminant mass degraded of time for Models 1 and 2.

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REFERENCES

Dentz, M., T. Le Borgne, A. Englert, and B. Bijeljic. (2005). Mixing, spreading, and reaction in heterogeneous media: A brief review. *J. Contam. Hydrol.*, *120-21*, 1-17, doi: 10.1016/j.jconhyd.2010.05.002, 2005.

Lu, D., M. Ye, and G.P. Curtis. (2015). Maximum likelihood Bayesian model averaging and its predictive analysis for groundwater reactive transport. *J. Hydrol.*, 529, doi:10.1016/j.jhydrol.2015.07.029.

Sather, L.J., R.M. Neupauer, D.C. Mays, J.P. Crimaldi, and E.J. Roth. (2021). Active spreading: Hydraulics for enhancing groundwater remediation, *Journal of Hydrologic Engineering,* in review.

Sole-Mari, G., M.J. Schmidt, D. Bolster, and D. Fernàndez-Garcia. (2021). Random-walk modeling of reactive transport in porous media with a reduced-order chemical basis of conservative components. *Water Resources Research*, 57, e2020WR028679. https://doi.org/10.1029/2020WR02867.