Chaotic Advection and Unsteady Flow in Groundwater Remediation - 17237

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ABSTRACT

This paper reviews an ongoing research program of numerical and laboratory studies on chaotic advection applied to groundwater remediation, including numerically simulated effects of sorption and heterogeneity, and experiments aimed at demonstrating chaotic advection in refractive index matched (*i.e.*, transparent) porous media. Additionally, this paper outlines a proposed approach to test chaotic advection at an appropriate field site. If shown to be successful in a field application, chaotic advection offers the possibility of better hydraulic control of contaminant plumes, accelerated remediation, consequent reduction in cost, and improvement in environmental health.

INTRODUCTION

Groundwater is an essential natural resource, but vulnerable to contamination, so groundwater remediation has cost billions of taxpayer dollars and has been a major focus of federal agencies [1] including the U.S. Department of Energy (DOE) and the U.S. Environmental Protection Agency, which reports that 87% of active Superfund sites have contaminated groundwater [2]. Once contaminated, groundwater aquifers can be difficult to remediate, largely because the required biochemical reactions are transport-limited. This difficulty stems, in large part, from the laminar flows associated with aquifers. Lacking the turbulent eddy structures that drive spreading, mixing, and reaction in open channel flows or engineered reactors, reactions in aquifers are limited by the rate at which reactants can be delivered and products can be removed. The resulting difficulty in spreading is a widely recognized, fundamental problem in groundwater remediation.

The research described here approaches this fundamental problem using a simple idea from the field of complex systems science: When turbulent mixing is not possible, the best way to spread one fluid into another is by chaotic flow, called chaotic advection [3]. The essence of chaotic advection in laminar flows is actually quite simple: One needs to impose plume stretching and folding, which generates an essential signature of chaos, sensitive dependence on initial conditions (Figure 1). In other words, chaotic advection imposes a velocity field in which the trajectory of fluid parcels depends on the minutest details of their initial position, much like two neighboring marbles taking on manifestly different trajectories after moving down opposite sides of a saddle point. In a chaotic flow, over time, initially adjacent particles will tend to move farther and farther apart.

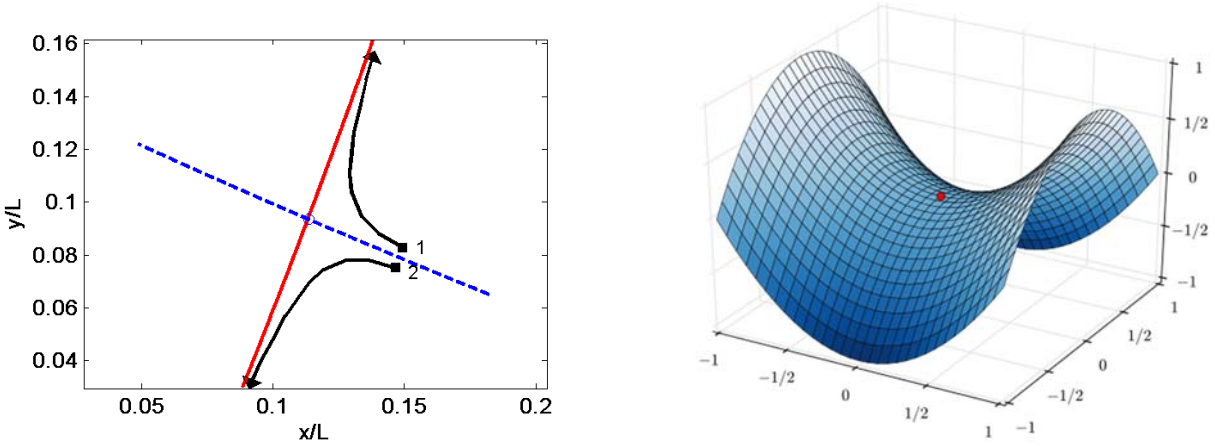

Figure 1: Plume spreading is enhanced by chaotic advection, which manifests sensitive dependence on initial conditions. Sensitive dependence on initial conditions is illustrated in the left panel, which shows the trajectory of neighboring fluid parcels 1 and 2 as they move, during successive iterations of a periodic chaotic flow, down a stable manifold (blue dashed line) near the intersection with an unstable manifold (red solid line). As they approach the intersection, the small distance between fluid parcels 1 and 2 grows rapidly, analogous to two adjacent marbles rolling down opposite sides of the saddle point in the right panel. Left panel is taken from Neupauer et al. [4] with permission from the American Geophysical Union (AGU). Right panel by Nicoguaro [5] from Wikimedia Commons.

This paper is structured as follows. The next section reviews ongoing simulations and experiments on chaotic advection applied to groundwater remediation, including numerically simulated effects of sorption and heterogeneity, and experiments aimed at demonstrating chaotic advection in refractive index matched (i.e., transparent) porous media. The following section outlines proposed field testing of chaotic advection at an appropriate field site, and the final section Discussion and Conclusions places this work in the broader context of environmental biogeochemistry.

SIMULATIONS and EXPERIMENTS

Building on previous applications of chaotic advection to groundwater remediation [6-9], Mays and Neupauer [10] proposed a new approach to generate chaotic advection using engineered injection and extraction, in which water is injected and extracted in a specified order through a manifold of wells surrounding the contaminated plume (Figure 2). Using an idealized model with homogeneous hydraulic conductivity and zero dispersion, this simulation showed how it is possible to transform a circular plume into a stretched and folded plume with a much larger circumference. This elongated circumference increases the area over which dispersion, diffusion, and reaction take place. Importantly, the pumping scheme in Figure 2 avoided re-injection, which provides practical and regulatory benefits.

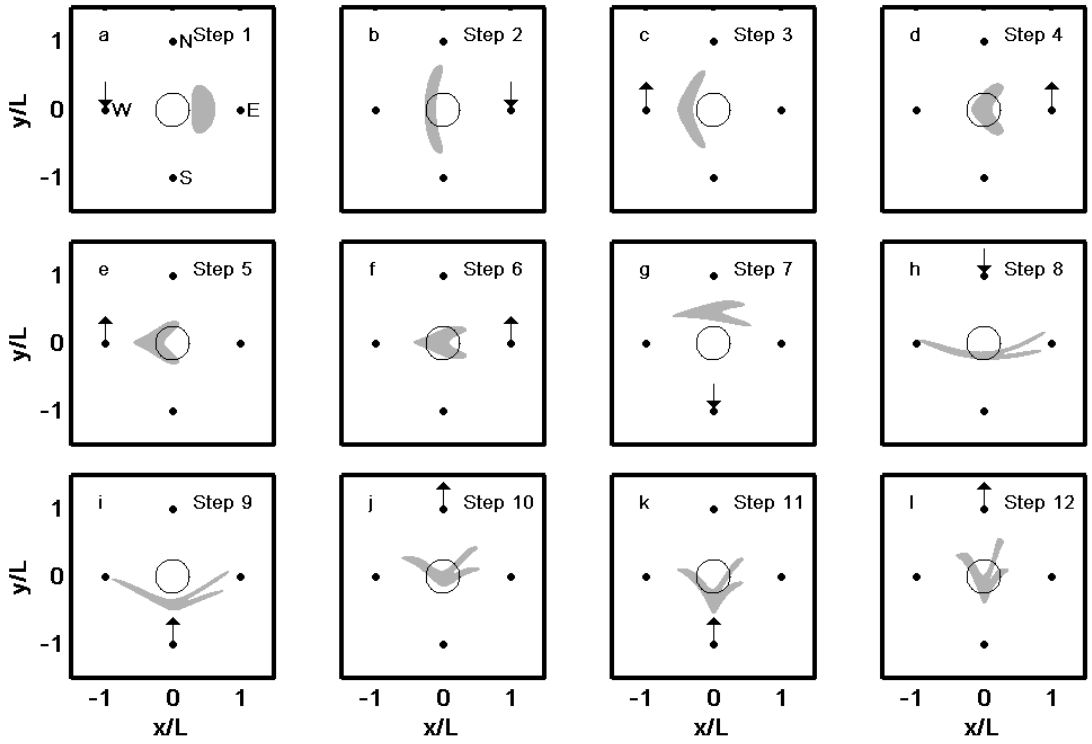

Figure 2: Plume stretching and folding by the 12-step engineered injection and extraction (EIE) pumping scheme of Mays and Neupauer [10]. The thin circle is the initial position of a plume in a homogeneous two-dimensional aquifer with zero dispersion, with wells installed *L* units away in each of the four cardinal directions. Downward arrows indicate injection, while upward arrows indicate extraction. Steps 1-6 generate the first fold in the west-east direction through balanced injections and extractions (*i.e.*, zero net injection), while steps 7-12 generate a second fold in the south-north direction by repeating the previous six steps with the south and north wells. The plume geometry after each step is shown in gray. An animation of this scheme is available at http://www.ucdenver.edu/dmays/research/spreading. Reproduced from Neupauer et al. [4] with permission from AGU.

As a practical matter, avoiding re-injection minimizes clogging by reaction byproducts at injection wells [11]. From a regulatory perspective, avoiding re-injection obviates the need to comply with groundwater injection regulations under the Safe Drinking Water Act [12] and the Resource Conservation and Recovery Act [13]. Simulations [14] predicted that chaotic advection accelerates contaminant degradation (Figure 3). Reaction was also amplified by the presence of heterogeneous hydraulic conductivity, but this effect was less important than that of chaotic advection. Later simulations [4] showed that heterogeneity changed the nature of chaotic advection itself (Figure 4), by generating additional intersections of stable and unstable manifolds (*i.e.*, saddle points), and making manifolds more tortuous than the homogeneous case. This additional complexity renders finer spatial structure in the plume geometry, generating additional mixing and reaction at the cost of increased risk of contaminant extraction and re-injection.

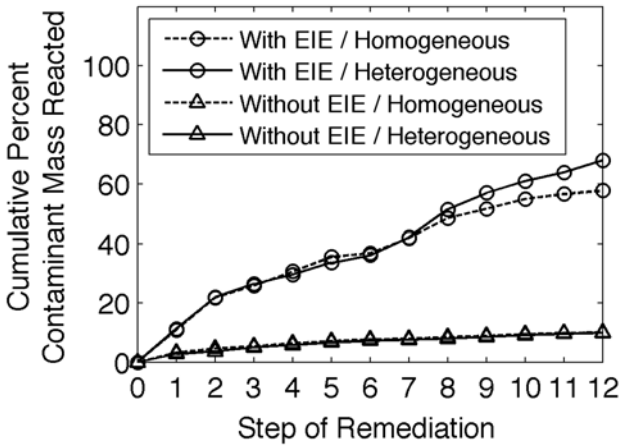

Figure 3: Simulations predict approximately six-fold increases in contaminant mass reacted with EIE (circles) compared to a base case without EIE (triangles), assuming instantaneous reaction in a homogeneous two-dimensional aquifer without sorption. Reproduced from Piscopo et al. [14] with permission from AGU.

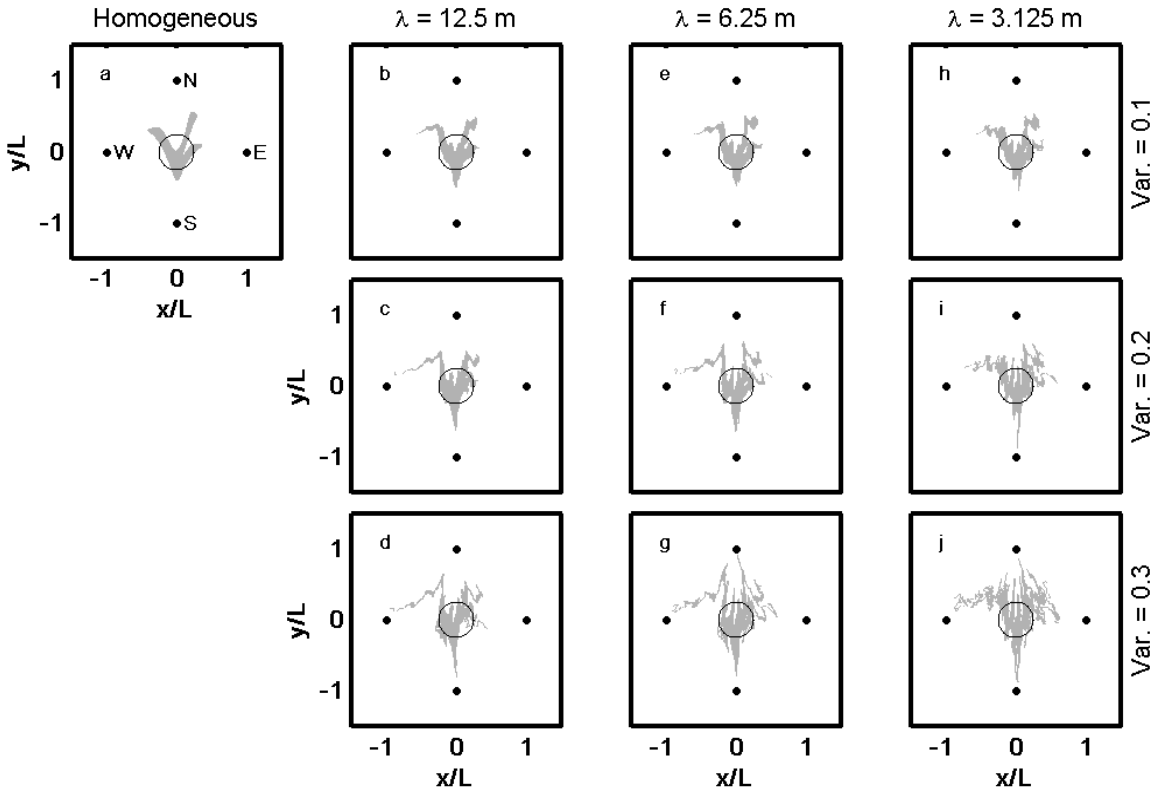

Figure 4: Aquifer heterogeneity generates more complex chaotic advection. The upper-left panel is the final frame of Figure 2. The other panels show corresponding plume geometry with heterogeneity increasing to the right with decreasing correlation length scale λ, and increasing downward with larger variance of the natural logarithm of the transmissivity. Reproduced from Neupauer et al. [4] with permission from AGU.

The results in Figures 2-4 are all based on the same pumping scheme that was developed heuristically. Two approaches have led to alternative pumping schemes. First, simulations indicate that when the contaminant or the treatment solution or both sorb to aquifer materials, qualitatively different pumping schemes may be required [15]. Second, when designing pumping schemes using more realistic assumptions (such as heterogeneity, sorption, and dispersion), the power of multi-objective evolutionary algorithms can be brought to bear [16]. For example, Figure 5 shows one of many possible pumping schemes designed with the aid of evolutionary algorithms, along with its position (in objective space) among many other possible pumping schemes. In sum, simulations to date have shown that (1) one can generate chaotic advection without re-injection, (2) chaotic advection increases contaminant degradation, and (3) this approach can be generalized using a formal optimization framework. Extension of these modeling results is underway.

In parallel, proof-of-principle laboratory experiments have confirmed the potential feasibility of chaotic advection via engineered injection and extraction. Briefly, a circular plume of black dye was injected into glycerin in the center of a Hele-Shaw apparatus, a pair of flat plates separated by a nominal aperture of 100 μm (Figure 6ab). Glycerin was injected and extracted through the four wells surrounding the central plume following the scheme of Figure 2. After the 12-step pumping scheme, the final plume geometry manifested stretching and folding qualitatively similar to that of the theoretical results in Figure 2, but with additional complexity from Taylor dispersion within the 100 μm aperture and certain experimental artifacts.

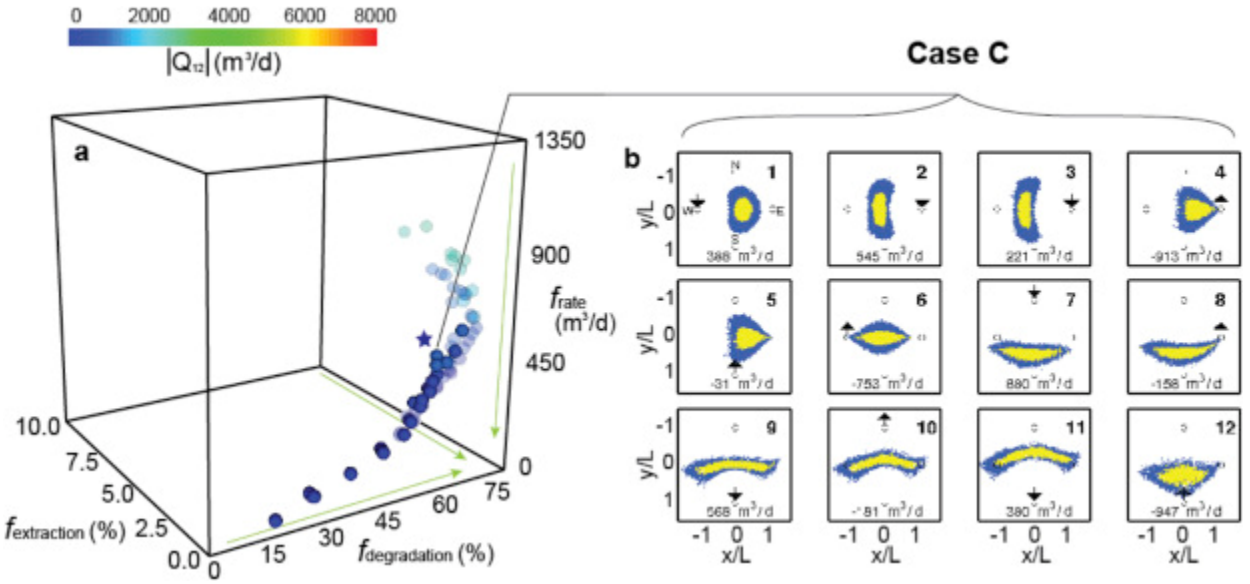

Figure 5: Engineered injection and extraction (EIE) pumping schemes can be optimized using multi-objective evolutionary algorithms. The left panel compares solutions generated under the constraints of zero net injection, ≤10% extraction of treatment solution, and keeping the plume within the square bounding box shown at right. The right panel shows the optimized EIE sequence, where the outer blue plume is non-sorbing contaminant and the inner yellow plume is treatment solution. Reproduced from Piscopo et al. [16] with permission from Elsevier.

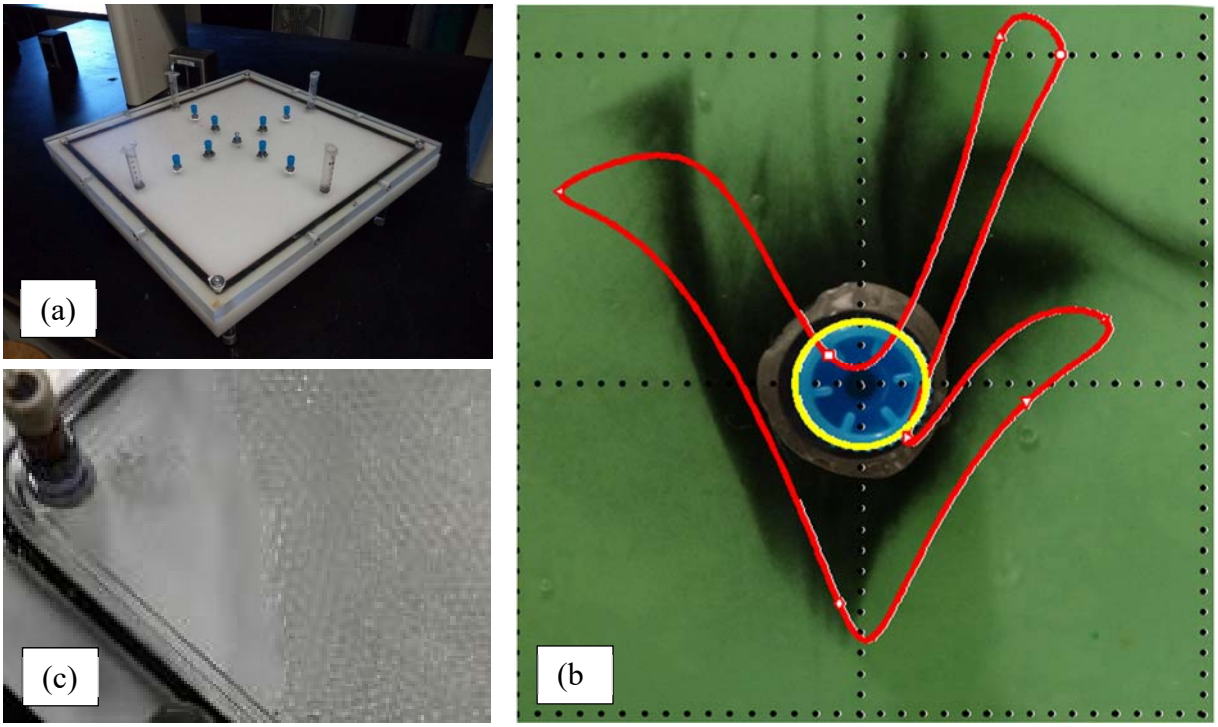

Figure 6: Clockwise from upper left, (a) Hele-Shaw apparatus for experimental demonstration of plume stretching and folding using engineered injection and extraction. (b) Final plume geometry after the 12-step EIE pumping scheme of Figure 2, with the theoretical geometry superimposed in red. (c) When glycerin saturates Pyrex beads, the beads disappear because of refractive index matching. Experiments are underway to study plume stretching and folding using planar laser-induced fluorescence in refractive index matched media.

Building on these proof-of-principle experiments, current laboratory efforts are aimed at studying plume stretching and folding within porous media. In this approach, plume geometry and solute concentrations are tracked using the optical technique of planar laser-induced fluorescence [17]. To make this optical technique possible within porous media, the porous media and the working fluid are selected such that each has an identical index of refraction, which effectively renders transparent porous media (Figure 6c). When coupled with the ongoing experiments described above, it is hoped that this approach will lead to a solid theoretical and practical understanding of how to impose chaotic advection.

PROPOSED FIELD TESTING

The simulations and experiments described above, and additional simulations and experiments currently underway, have demonstrated that chaotic advection offers a new approach to the hydraulics of groundwater remediation. The proposed next step in this work is to test the hypothesis that engineered injection and extraction

accelerates groundwater remediation through faster and more spatially extensive delivery of treatment solutions.

Prospective field sites include those with an aqueous contaminant, such as hexavalent uranium or methyl tert-butyl ether (MTBE), in a shallow alluvial aquifer whose velocity field could be manipulated by engineered injection and extraction. The rationale for testing chaotic advection at a field site is as follows: Remediation is transport-limited, so faster and more spatially extensive delivery of treatment solutions should improve remediation efficacy, duration, and sustainability. Testing chaotic advection is unconventional, but the design of the envisioned field test itself is straightforward, comprising parallel injections of treatment solution in forced-gradient tests without (*i.e.* the base case) and with (*i.e.*, the test case) engineered injection and extraction (Figure 7). The base case would inject bromide as a conservative tracer for plume tracking and an appropriate treatment solution to stimulate contaminant remediation. The test case would additionally impose an unsteady velocity field using injections and extractions through wells surrounding the contaminant plume, using an optimized pumping sequence such as that shown in Figure 5. The proposed experimental design depends on several considerations:

- To allow comparison between the base case and the test case, the experimental plot should be large enough to accommodate both cases.
- The diameter of the injected plume of bromide and treatment solution should be similar to the saturated thickness of the unconfined aquifer in order to maintain quasi-2D flow, that is, flow that is not primarily dominated by 3D effects.
- The radius of the injected plume to treatment solution should be small enough to allow manipulation of the plume geometry within the circle inscribed by the wells used for engineered injection and extraction. For example, the simulations in Figure 2 assumed an initial plume radius of $L/4$, where L is the distance from the plume center to the wells.
- After manipulation by the unsteady velocity field, the lobes resulting from stretching and folding should be large enough to be detected in monitoring wells. Accordingly, a densely-instrumented field site would be ideal for the proposed field test.

By way of illustration, Figure 7 shows a conceptual experimental design based on the DOE's Old Rifle site, which is an alluvial aquifer contaminated with hexavalent uranium on the banks of the Colorado River [18]. This site is large enough to accommodate both the base case and the test case. Using an injected plume radius of 1.0 m would render quasi-2D flow, and using an array of injection-extraction wells with a radius of 4.0 m would render an initial radius of $L/4$, which is small enough to be manipulated by engineered injection and extraction. As shown in Figure 2, the lobes resulting from stretching and folding are approximately $L/10$ thick, which is about 40% of the initial plume radius, which in this case corresponds to approximately 0.4 m, which could be detected using an existing array of densely-spaced wells. A field test along these lines would answer two key questions.

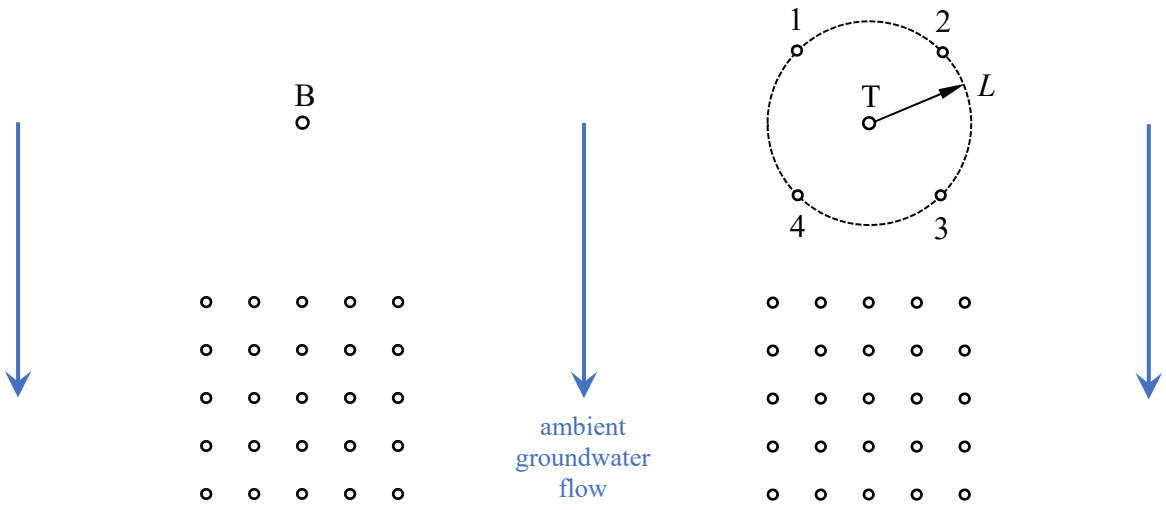

Figure 7: Plan view of a conceptual experimental design to field test chaotic advection for improved groundwater remediation. Ambient groundwater flow is from top to bottom. In the base case at left, treatment solution is injected at well B, and contaminant degradation is monitored downstream through an array of densely-spaced wells. In the test case at right, the treatment solution is injected at well T, manipulated by injections and extractions through wells 1-4 surrounding well T on a circle of radius L = 4 m, and then monitored downstream through a second array of densely-spaced wells.

First, interpolation of measured tracer concentrations will provide field validation for plume stretching and folding resulting from a quasi-2D engineered injection and extraction scheme such as that in Figure 5. Second, comparison of contaminant removal between the base case and the test case will determine whether chaotic advection improves groundwater remediation.

DISCUSSION and CONCLUSIONS

The biogeochemical complexity of the subsurface environment and the consequent challenge of groundwater remediation are well known. Within this framework, the research described here asks the question: To what extent can we advantageously manipulate subsurface conditions using hydraulic control through wells? This approach is complementary to existing biogeochemical models for reactive transport in alluvial aquifers, such as those developed by the DOE for the Old Rifle site in Colorado [19] or the Hanford site in Washington [20]. This approach is also complementary to the extensive work linking plume evolution, spreading, mixing, and reaction resulting from heterogeneous hydraulic conductivity being performed by various groups around the world [21-25]. The simulations and experiments discussed here show the potential feasibility of imposing chaotic advection within groundwater remediation, and set the stage for a proposed field test. The authors would be interested to hear from colleagues interested in collaboration on such a field test.

REFERENCES

1. National Research Council (2009), *Advice on the Department of Energy's Cleanup Technology Roadmap: Gaps and Bridges*. Washington, DC: National Academies Press.
2. Environmental Protection Agency (2009), Search Superfund Site Information, http://cfpub.epa.gov/supercpad/cursites/srchsites.cfm (accessed November 20, 2009).
3. Stremler, M.A., F.R. Haselton, and H. Aref (2004), Designing for chaos: applications of chaotic advection at the microscale*. Philos T R Soc A*, **362**(1818): 1019-1036.
4. Neupauer, R.M., J.D. Meiss, and D.C. Mays (2014), Chaotic advection and reaction during engineered injection and extraction in heterogeneous porous media*. Water Resour Res*, **50**(2): 1433-1447.
5. Nicoguaro (2016), A saddle point on the graph of $z = x^2 - y^2$ (in red), https://commons.wikimedia.org/w/index.php?curid=20570051 (accessed October 20, 2016).
6. Bagtzoglou, A.C. and P.M. Oates (2007), Chaotic advection and enhanced groundwater remediation*. J Mater Civil Eng*, **19**(1): 75-83.
7. Lester, D.R., G. Metcalfe, M. Telfry, A. Ord, B. Hobbs, and M. Rudman (2009), Lagrangian topology of a periodically reoriented potential flows: Symmetry, optimization, and mixing*. Phys Rev E*, **80**: 036298, doi:10.1103/PhysRevE.80.036208.
8. Sposito, G. (2006), Chaotic solute advection by unsteady groundwater flow*. Water Resour Res*, **42**(6): W06D03, doi:10.1029/2005WR004518.
9. Zhang, P.F., S.L. DeVries, A. Dathe, and A.C. Bagtzoglou (2009), Enhanced mixing and plume containment in porous media under time-dependent oscillatory flow*. Environ Sci Technol*, **43**(16): 6283-6288.
10. Mays, D.C. and R.M. Neupauer (2012), Plume spreading in groundwater by stretching and folding*. Water Resour Res*, **48**: W07501, doi:10.1029/2011WR011567.
11. Mays, D.C. and R.M. Neupauer (2013), Reply to comment by D.R. Lester et al. on "Plume spreading in groundwater by stretching and folding"*. Water Resour Res*, **49**(2): 1192-1194.
12. 42 U.S.C. 300f–300j–9 *Safe Drinking Water Act*. Washington, DC: as amended through P.L. 107–377, December 31, 2002, U.S. Government Printing Office.
13. 42 U.S.C. 6901–6992k *Resource Conservation and Recovery Act*. Washington, DC: as amended through P.L. 107–377, December 31, 2002, U.S. Government Printing Office.
14. Piscopo, A.N., R.M. Neupauer, and D.C. Mays (2013), Engineered injection and extraction to enhance reaction for improved in situ remediation*. Water Resour Res*, **49**(6): 3618-3625.
15. Neupauer, R.M. and D.C. Mays (2015), Engineered Injection and Extraction for In Situ Remediation of Sorbing Solutes in Groundwater*. J Environ Eng*, **141**(6): 04014095, doi:10.1061/(ASCE)EE.1943-7870.0000923.
16. Piscopo, A.N., J.R. Kasprzyk, and R.M. Neupauer (2015), An iterative approach to multi-objective engineering design: Optimization of engineered injection and

extraction for enhanced groundwater remediation. *Environ Modell Softw*, **69**: 253-261.
17. Crimaldi, J.P. (2008), Planar laser induced fluorescence in aqueous flows. *Exp Fluids*, **44**(6): 851-863.
18. Anderson, R.T., H.A. Vrionis, I. Ortiz-Bernad, C.T. Resch, P.E. Long, R. Dayvault, K. Karp, S. Marutzky, D.R. Metzler, A. Peacock, D.C. White, M. Lowe, and D.R. Lovley (2003), Stimulating the in situ activity of Geobacter species to remove uranium from the groundwater of a uranium-contaminated aquifer. *Appl Environ Microbiol*, **69**(10): 5884-5891.
19. Yabusaki, S.B., M.J. Wilkins, Y.L. Fang, K.H. Williams, B. Arora, J. Bargar, H. Beller, N. Bouskill, E. Brodie, J. Christensen, M. Conrad, R. Danczak, E. King, N. Spycher, C. Steefel, T. Tokunaga, R. Versteeg, S.R. Waichler, and H. Wainwright (2015), *Floodplain Water Table Dynamics: Biogeochemical Cycling and Uranium Mobility*, in *Fall Meeting*, American Geophysical Union: San Francisco, California.
20. Zachara, J.M., P.E. Long, J. Bargar, J.A. Davis, P. Fox, J.K. Fredrickson, M.D. Freshley, A.E. Konopka, C.X. Liu, J.P. McKinley, M.L. Rockhold, K.H. Williams, and S.B. Yabusaki (2013), Persistence of uranium groundwater plumes: Contrasting mechanisms at two DOE sites in the groundwater-river interaction zone. *J Contam Hydrol*, **147**: 45-72.
21. Bolster, D., M. Dentz, and J. Carrera (2009), Effective two-phase flow in heterogeneous media under temporal pressure fluctuations. *Water Resour Res*, **45**: W05408, doi:10.1029/2008WR007460.
22. Cirpka, O.A., G. Chiogna, M. Rolle, and A. Bellin (2015), Transverse mixing in three-dimensional nonstationary anisotropic heterogeneous porous media. *Water Resour Res*, **51**(1): 241-260.
23. Dentz, M. (2016), Mixing in Heterogeneous Media Across Spatial and Temporal Scales. *InterPore News*, **17**(2 September 2016).
24. Engdahl, N.B., D.A. Benson, and D. Bolster (2014), Predicting the enhancement of mixing-driven reactions in nonuniform flows using measures of flow topology. *Phys Rev E*, **90**(5): 051001(R), doi:10.1103/PhysRevE.90.051001.
25. Jha, B., L. Cueto-Felgueroso, and R. Juanes (2011), Quantifying mixing in viscously unstable porous media flows. *Phys Rev E*, **84**(6): 066312, doi:10.1103/PhysRevE.84.066312.

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