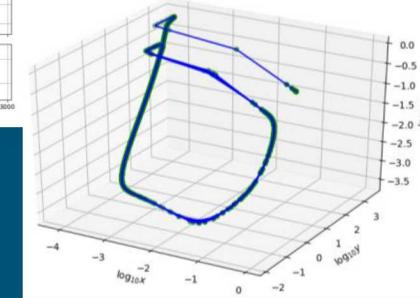
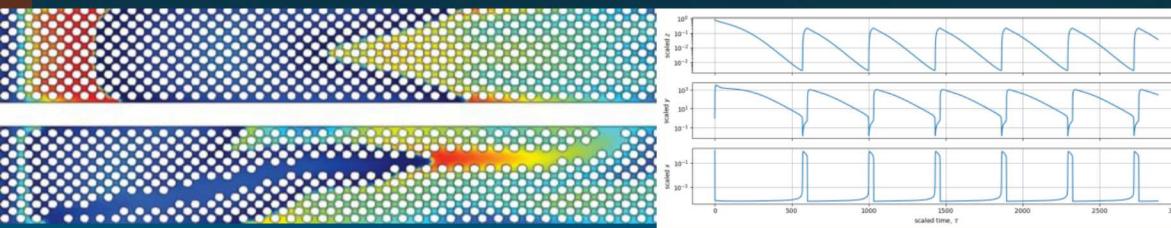




# Subsurface Sensing of Fault and Fracture Networks with Nonlinear Chemical Wave Tracing



## PRESENTED BY

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<sup>1</sup>Nuclear Waste Disposal Research and Analysis

<sup>2</sup>Geomechanics

<sup>3</sup>Applied Systems Analysis and Research

# Overview and Acknowledgements



- Background
- Microfluidic Experiments
- CFD Numerical Experiments
- Examples:
  - characterization
  - fracture aper. “mapping”
  - detection of contaminants
- Further Musings
- Conclusions

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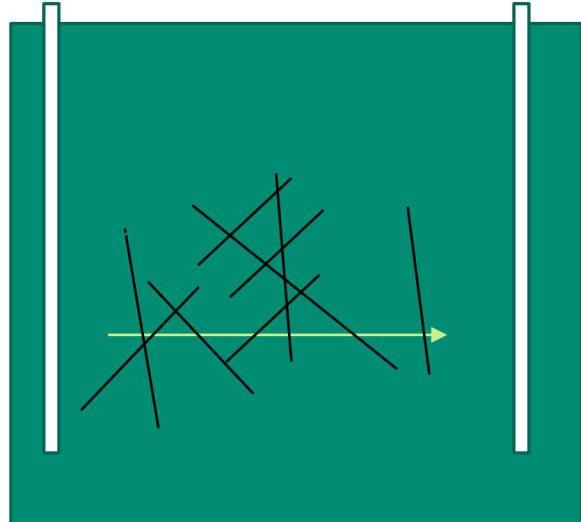
# Subsurface Sensing with Chemical Waves

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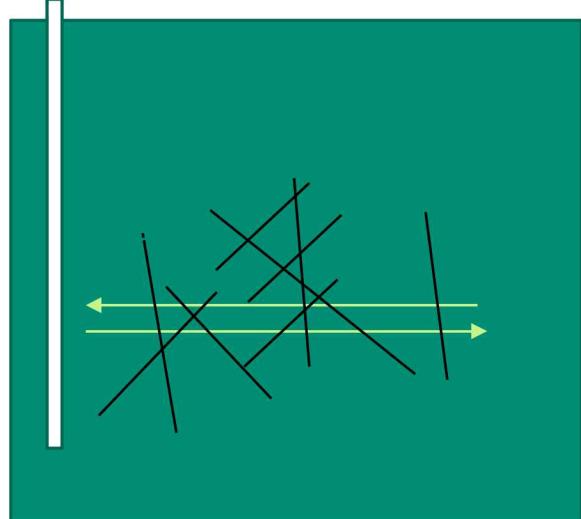
- **Central premise:** Chemical kinetics systems with multiple stationary states coupled to transport can support *chemical waves* with the ability to provide information on spatial networks through which they propagate
- Chemical waves are self-sustaining disturbances in chemical or other variables that propagate over distance with or without attenuation (Ortoleva, 1992) arising from *nonlinear coupling* of chemical reaction and transport under far-from equilibrium conditions (Nicolis and Prigogine, 1977).
- Use of chemical waves for subsurface sensing are termed here “*nonlinear tracers*” to discern from usual linear tracers, such as isotopes, conservative tracers such as Cl or Br, temperature, etc.
- Chemical waves involved in ore deposits such as uranium roll fronts.



Cross-Well Tracer

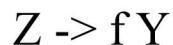
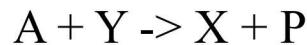


Push-Pull Tracer

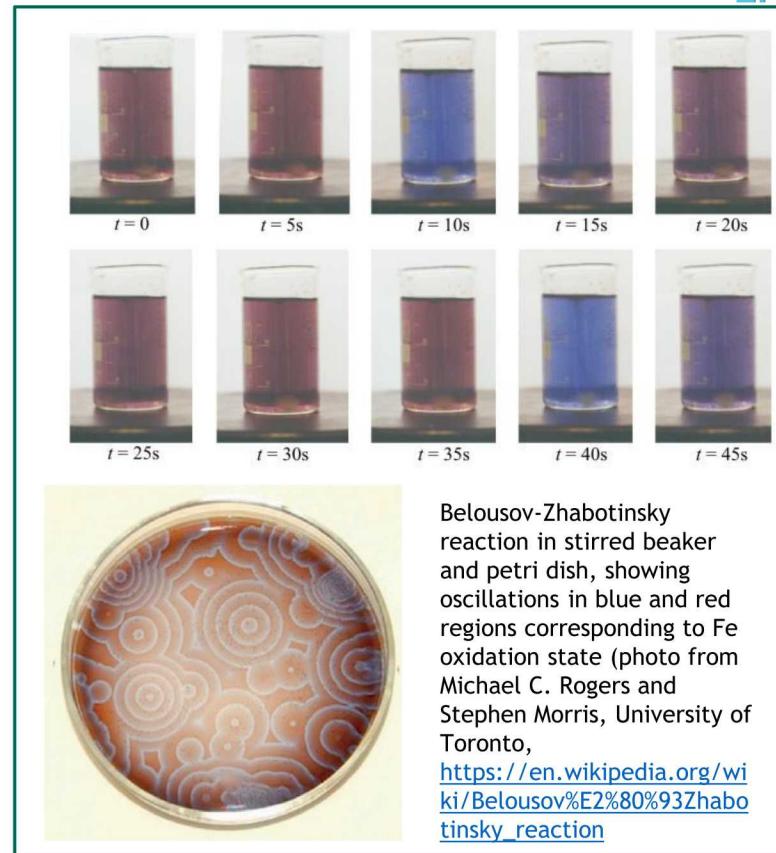


## Belousov-Zhabotinsky Reaction

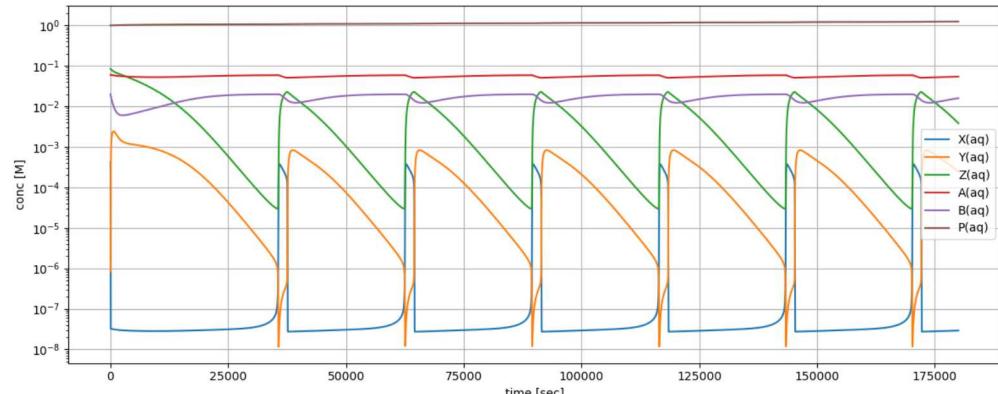
- Canonical oscillatory reaction is the oft-studied Belousov-Zhabotinsky (BZ) reaction
- Organic substrate (malonic acid) oxidized by bromate in acidic solution with metal (Fe) catalyst
- Complex kinetic steps. A simple model is the *Oregonator* (Field et al., 1972) in which the autocatalytic step is made clear (X is  $\text{HBrO}_2$ , or bromous acid; Y is  $\text{Br}^-$ , and Z is  $\text{Fe}^{3+}$  or other catalyst; A and P are “pool” concentrations):



\*autocatalytic step



Belousov-Zhabotinsky reaction in stirred beaker and petri dish, showing oscillations in blue and red regions corresponding to Fe oxidation state (photo from Michael C. Rogers and Stephen Morris, University of Toronto, [https://en.wikipedia.org/wiki/Belousov-Zhabotinsky\\_reaction](https://en.wikipedia.org/wiki/Belousov-Zhabotinsky_reaction))

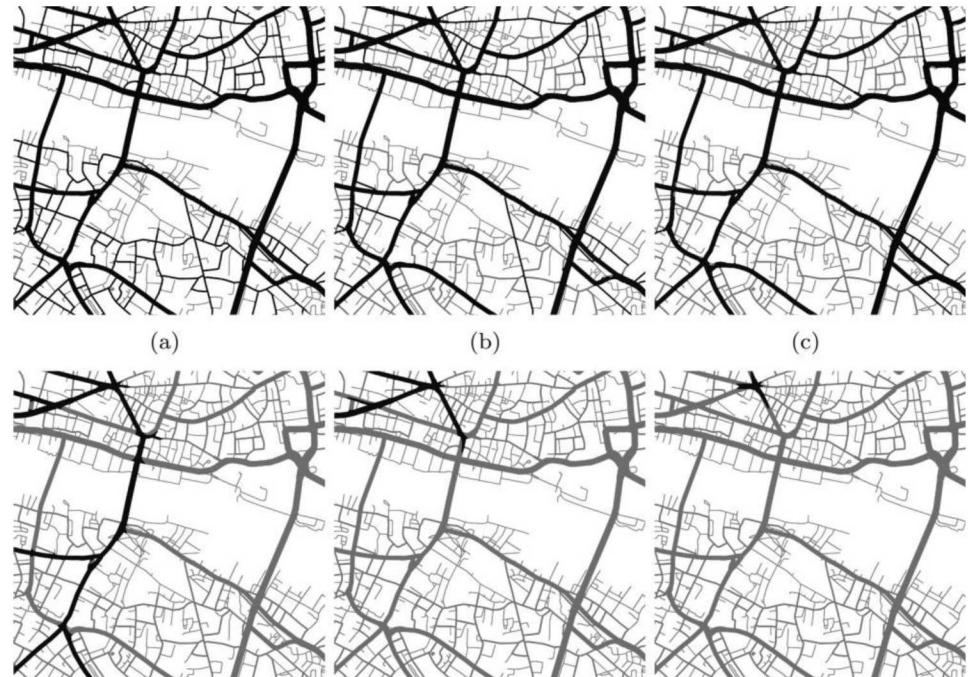


Numerical solution of *Oregonator* reaction scheme using PFLOTRAN

# Unconventional Computing Examples with BZ

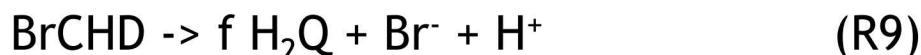
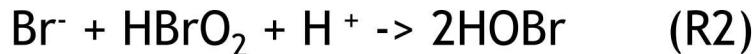


- “Liquid chemical computing”: chemical waves interacting with a geometrical medium can be used as chemical switches (Rossler, 1974); logic gates (Hjelmfelt and Ross, 1995; Steinbock et al., 1996; Toth et al., 2009); chemical neural networks (Gorecki et al., 2015); Turing machines (Hjelmfelt et al., 1991); and chemical clocks (Winfree, 1982).
- Microfreight delivery by chemical waves, coupling chemical reaction with vectoral motion in analogy with bi-motility (Ichino et al., 2008)
- Soft robotics and embedded organic electronics (Adamatsky, 2016).



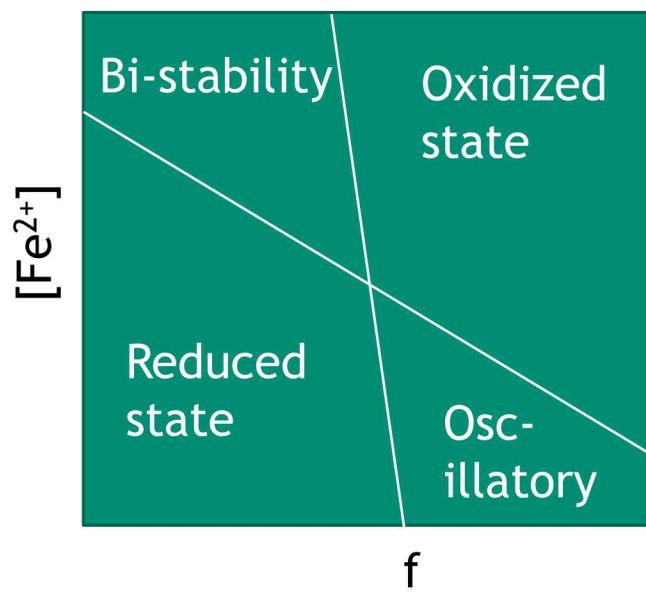
Tunable BZ-like dynamics show selective propagation top to bottom thru street network according to size/wavelength (from Adamatsky et al., 2018)

# CFD Modeling: “Skeleton Model” of CHD-Br-Fe System



$f$  = stoichiometric factor in decomposition of BrCHD

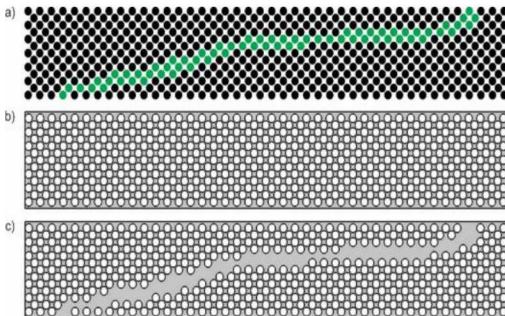
- Reaction network from Szalai et al., 2002; 2003
- Uses 1,4-Cyclohexandione (CHD) as organic substrate ( $\text{CO}_2$  generated remains in solution)
- Similar autocatalytic step as original BZ



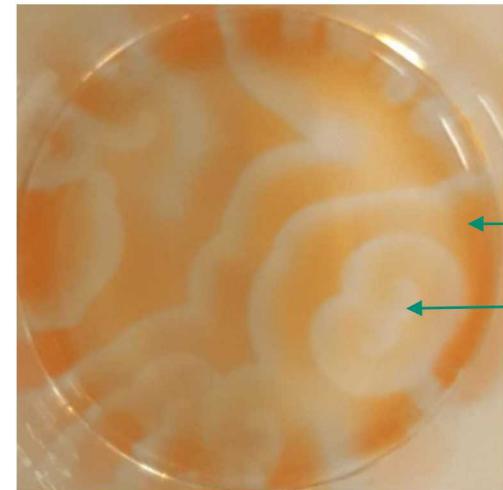
## 7 Microfluidics Experiments



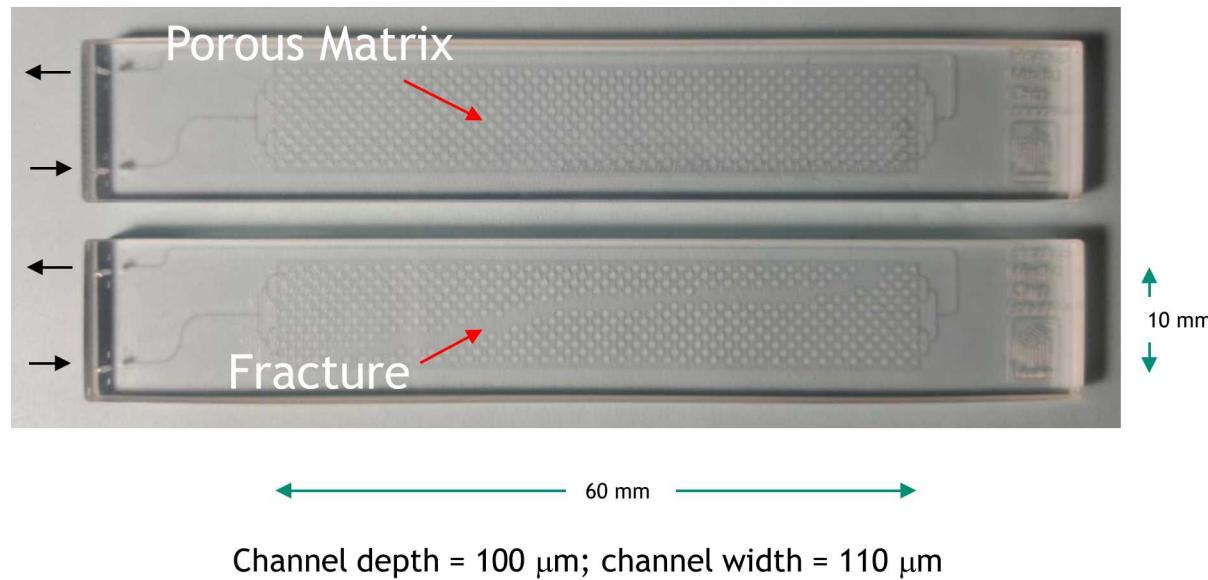
- Two soda-glass microfluidic cells (Dolomite Centre, Ltd.) are used to examine excitability of BZ media coupled with advection/diffusion/ dispersion in porous media
- Use CHD as organic substrate to avoid bubbles in microfluidic cells
- Influent fed from well mixed BZ media



Schematics of micromodel columns in a 60 mm long by 10 mm tall domain. Black and green circles represent the full regular packing of columns. Green represents columns to be removed for fracture modeling.

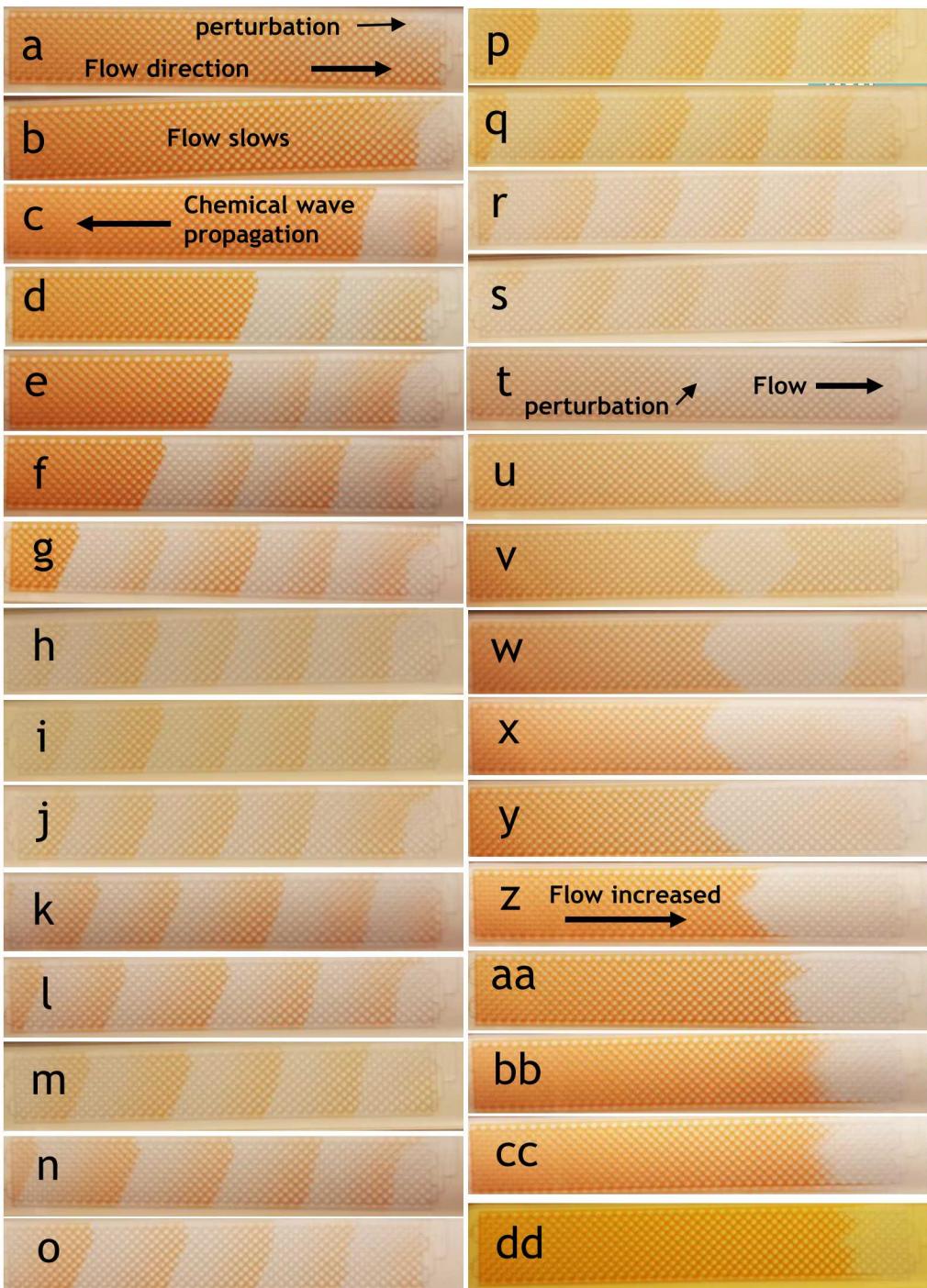


Chemical waves in CHD-Br-Fe system in beaker



## Microfluidics Results

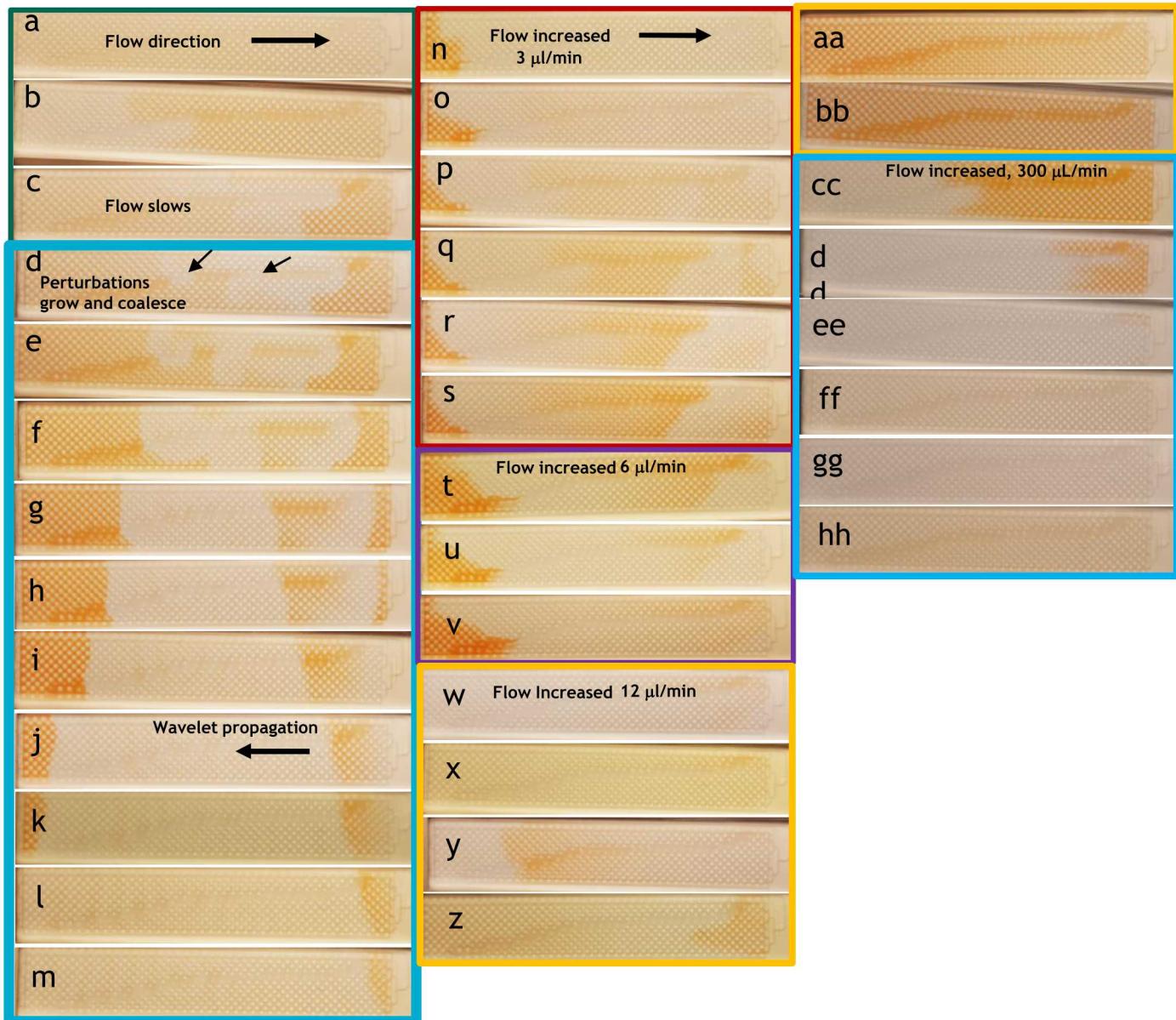
- Volumetric flow uses Optos Eldex HPLC pump
- Flow rate ranges from 300 to 0.1 microliters/s
- Flow rate is stepped down and stepped up
- Variety of chemical wave propagation observed



# Microfluidics Results: Fracture-Matrix Interaction



- Examples with “fracture”
- Wave generation and propagation vary from previous example
- Chemical wave tracers could be used to characterize porous media
- Sensitivity to advection velocity

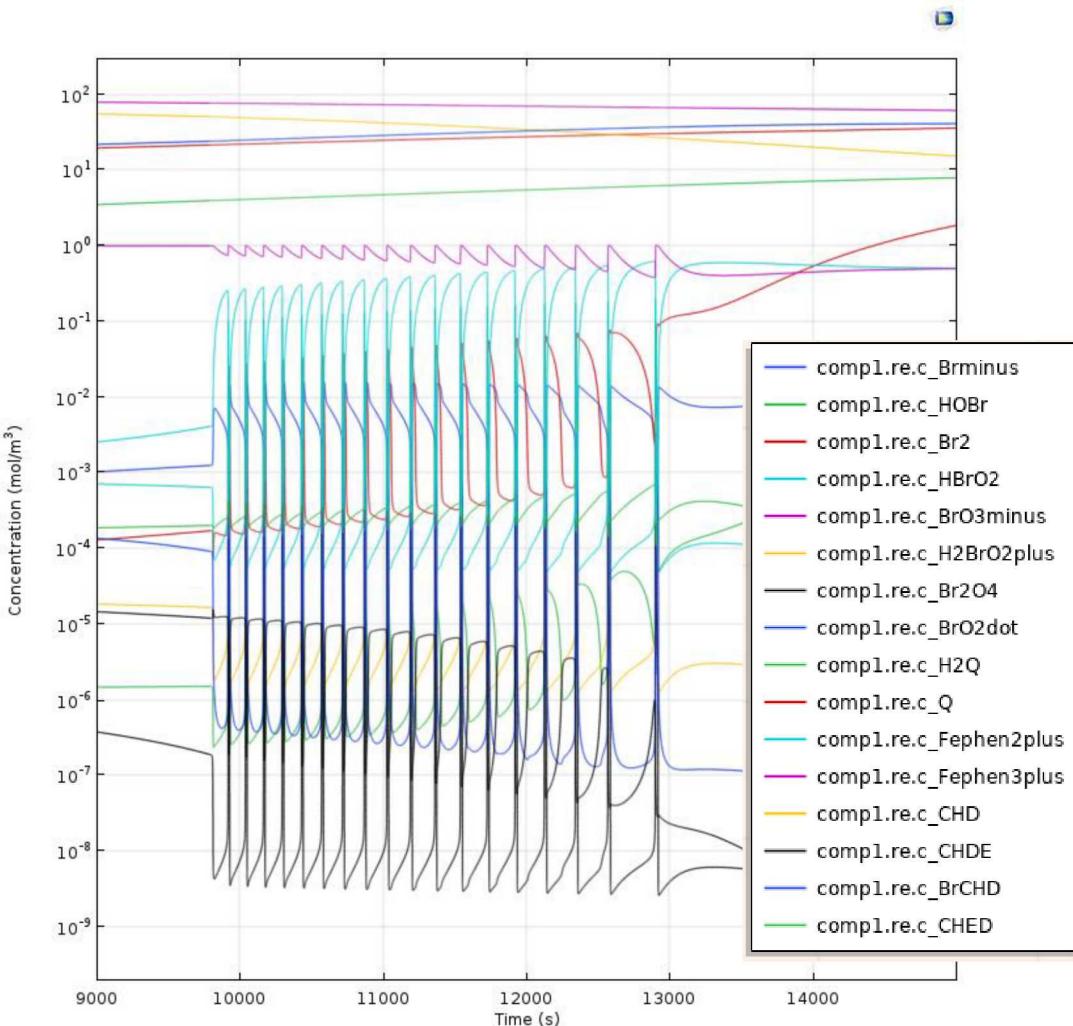


## Summary of Experimental Observations



- Spatio-temporal chemical waves will advance from spatial perturbations, but will not initiate in an initially spatially homogeneous concentration field
- Wave trains of advancing zones of alternating redox state are initiated and sustained, with period/wavelength sensitive to the properties of the porous media
- Wave trains are sensitive to flow conditions. In the absence of flow, waves advance at rates faster than diffusion rates through the cells. In low flow conditions, waves can remain spatially stagnant or even migrate against the advective gradient
- At higher rates of flow, chemical wave trains can be swept along at rates commensurate with the advective velocity, and the instability leading the spatio-temporal oscillatory behavior is damped
- At sufficiently high advective flow rates, any spatial variability is wiped out, but the pore solution can still exhibit chemical clock behavior in a manner uninfluenced by the porous texture

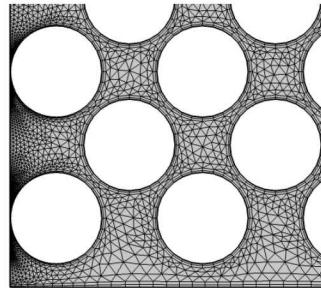
# CHD-Br-Fe System: Numerical Examples



- Model of Salazai et al., (2002) with complex kinetics involving ~49 steps
- Solution of a simpler 19-step “skeleton model” in batch mode shown at left, a good approximation of the Salazai et al. (2002) experimental behavior
- ~20 minute induction time required, after which the system develops complex oscillations

# Computational Fluid Dynamics Modeling

- Coupled Navier-Stokes equations with species continuity equations (keeping inertial terms) and assuming incompressible flow
- Shallow channel approximation for microfluidic cell thickness
- Nonlinearly coupled reaction network with (pseudo) mass action kinetics
- Triangular mesh:



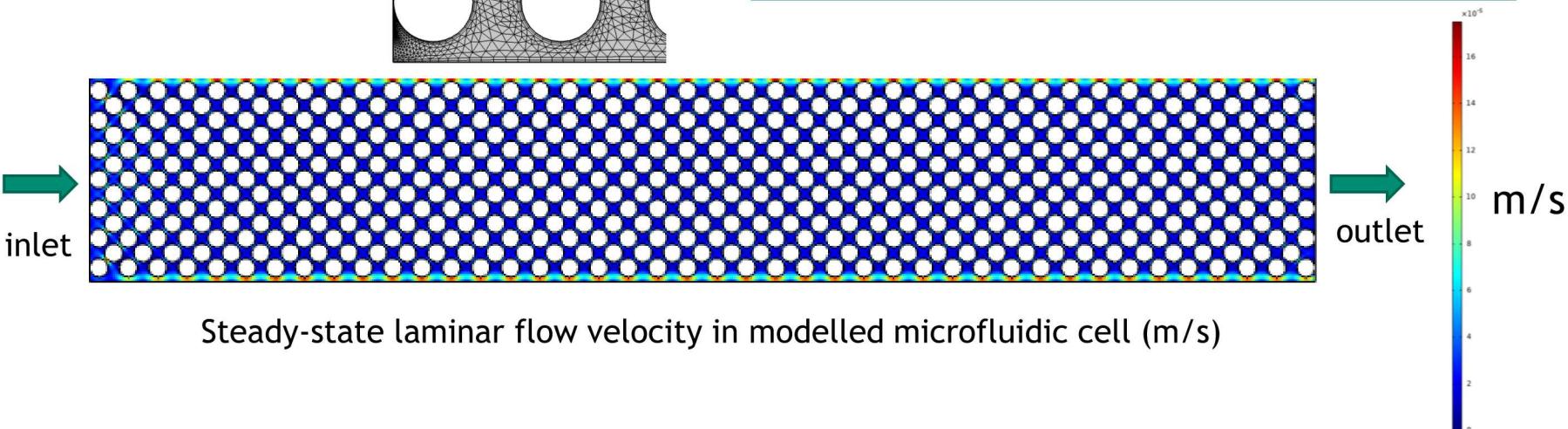
$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mathbf{K}] - \frac{\mu \mathbf{u}}{d_z^2}$$

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i + \mathbf{u} \cdot \nabla c_i = R_i$$

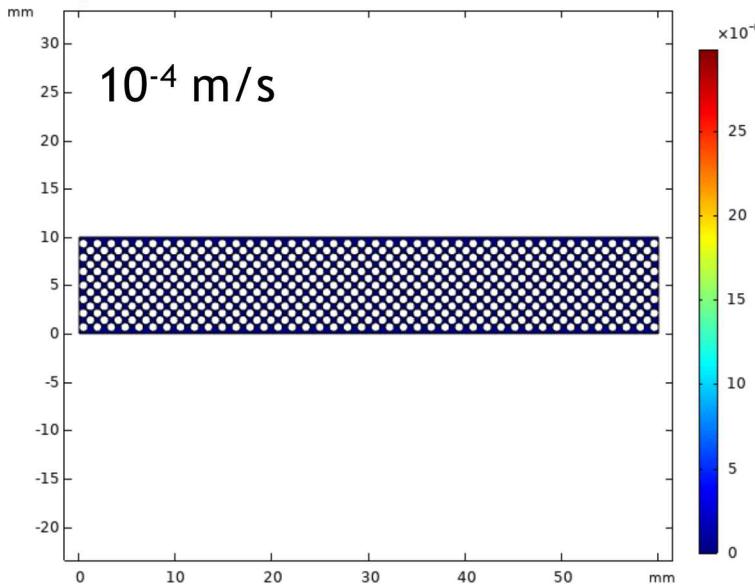
$$\rho \nabla \cdot \mathbf{u} = 0 \quad \mathbf{K} = \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)$$

$$\mathbf{J}_i = -D_i \nabla c_i$$

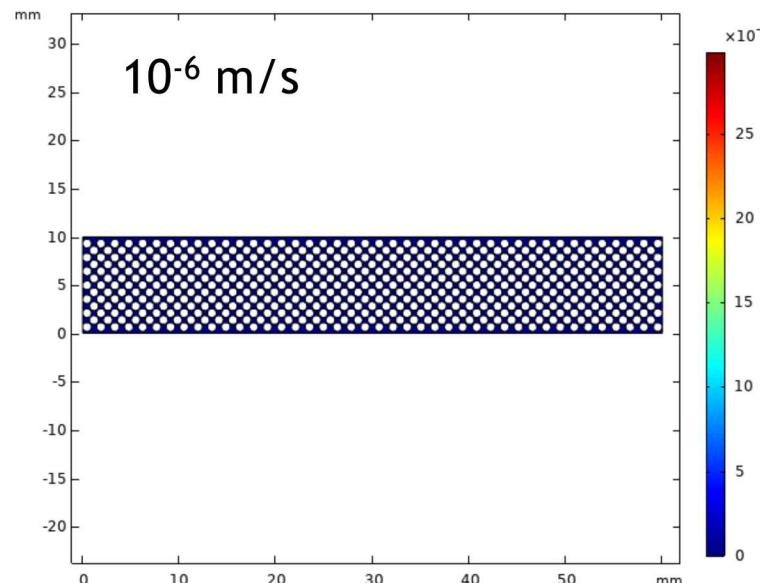
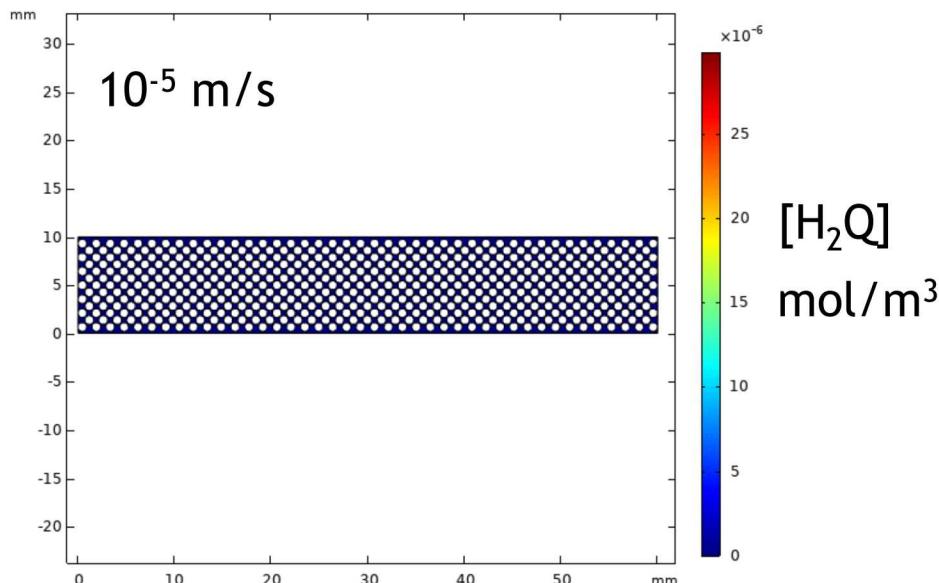
$$R_i = \vartheta_i r \quad r_j = k_j^f \prod_i c_i^{-\vartheta_{ij}}$$



# CFD Animations of Full CHD-Br-Fe: Advective gradient



- Waves influenced by advection
  - $>10^{-4}$  m/s- wipes out organized wave
  - $10^{-4}$  m/s: standing wave
  - $10^{-5}$  m/s: waves propagating upstream and downstream
  - $10^{-6}$  m/s: wave propagating against advective gradient

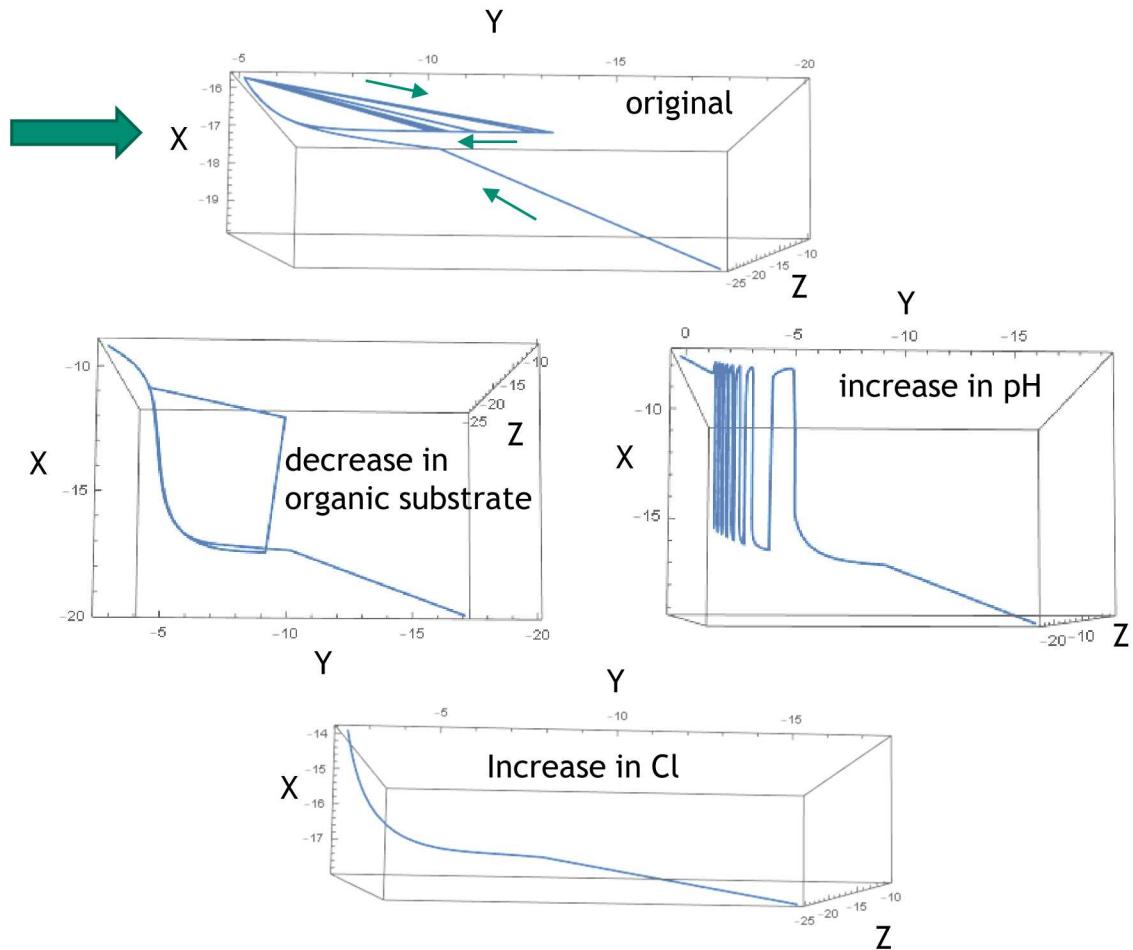
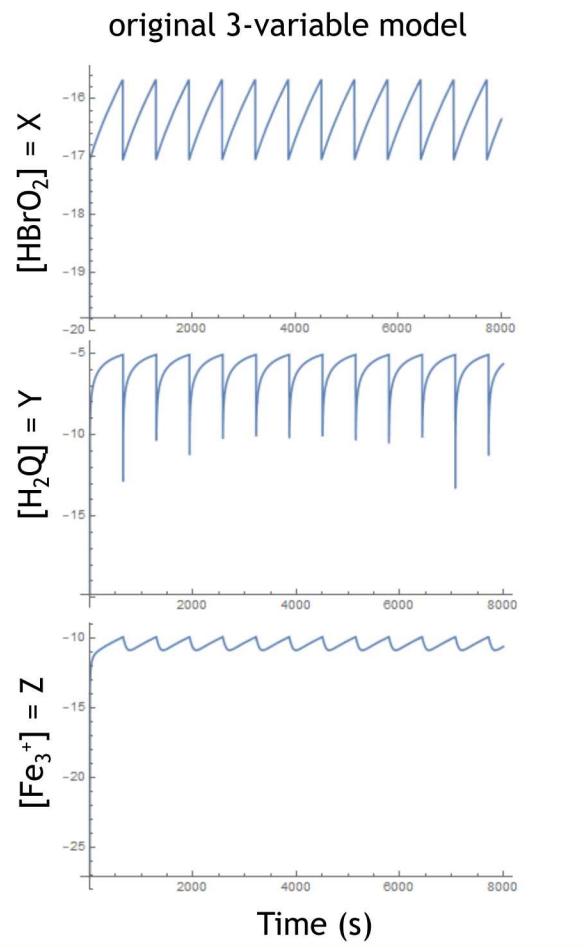


$\text{H}_2\text{Q} = 1,4$  hydroquinone

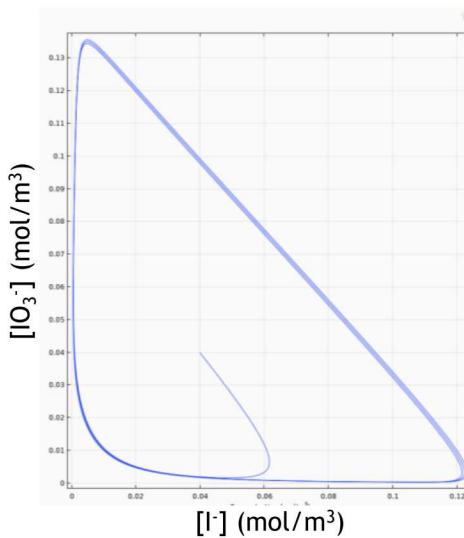
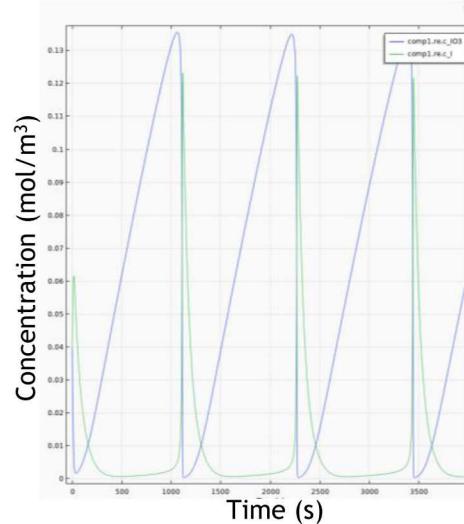
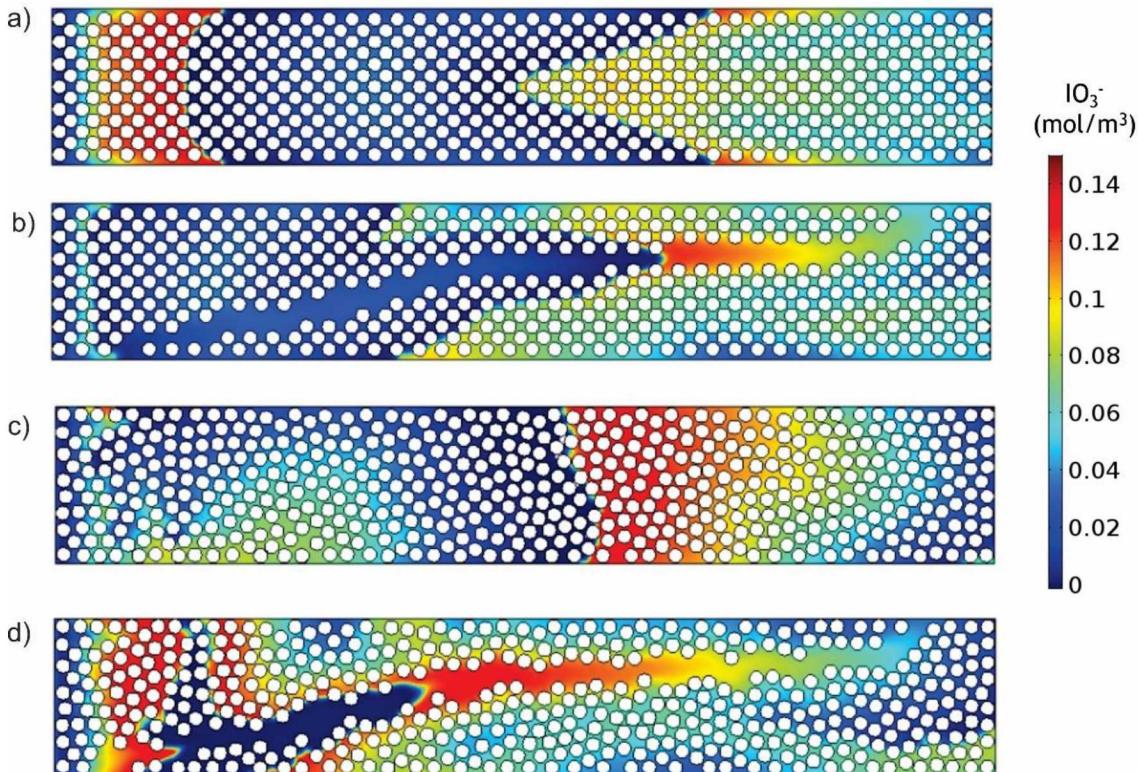
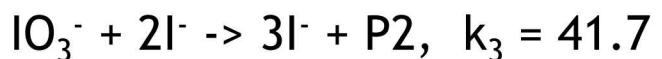
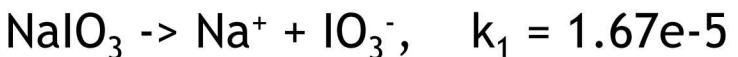
# Applications – Contaminant Detection



- Reduce CHD-Br-Fe reaction network to Oregonator-like dynamics
- Solve system in 1D moving reference frame
- Perturb kinetics and examine phase space behavior
- Quite sensitive to environmental variations in pH, Cl-, organic substrate



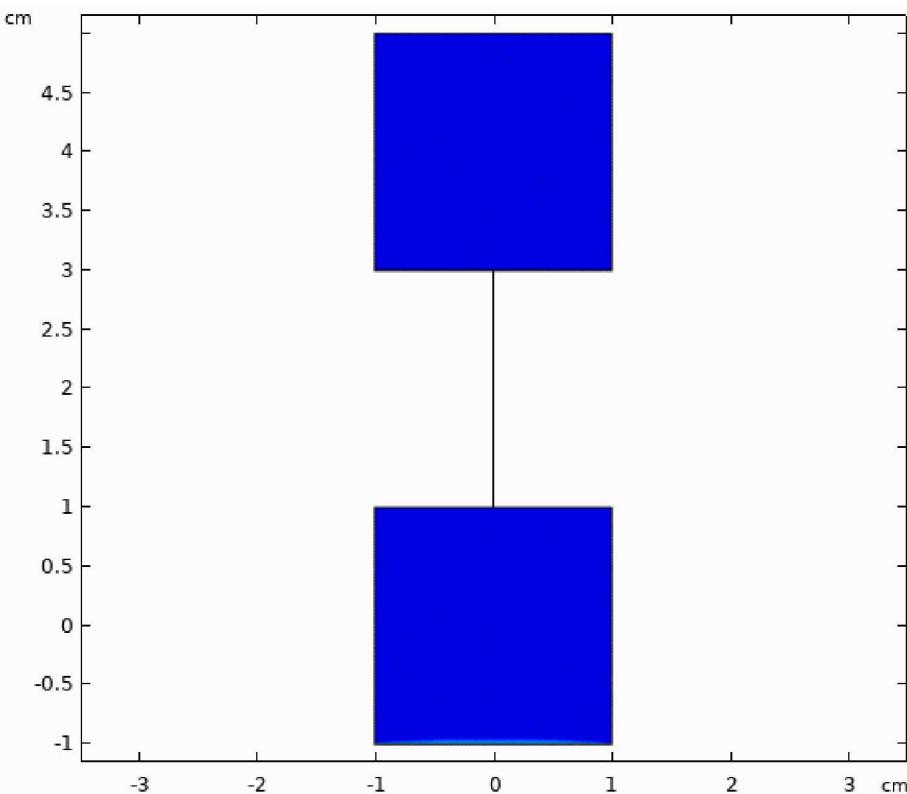
# Applications: Other Chemical Systems



Model system from:  
 M.M.C. Ferreira, W.C. Ferreira Jr., A.C.S. Lino, and M.E.G. Porto, *J. Chem. Education*, vol. 76, p. 861, 1999;

H.S. Fogler and M.N. Gurmen,  
[http://www.engin.umich.edu/~cre/web\\_mod/oscil/module.htm](http://www.engin.umich.edu/~cre/web_mod/oscil/module.htm)

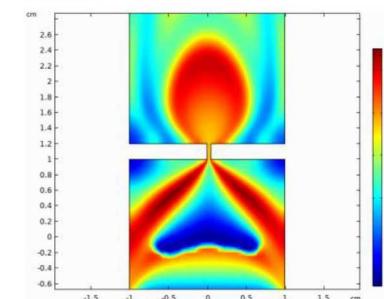
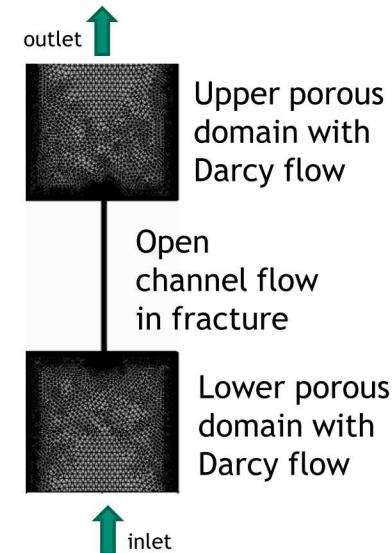
# Applications: Interaction with Fractures and Leakage in Engineered Barriers



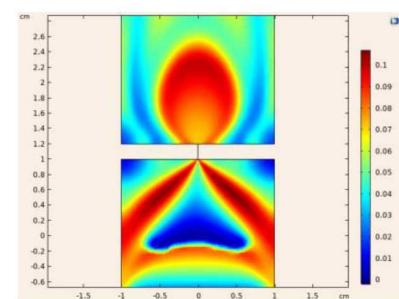
$\text{IO}_3^-$  model; 50 micron aperture,  $10^{-5}$  m/s

*Iodate chemical waves passing through fracture-like leakage pathways show lack of sensitivity to fracture aperture*

## 2D Forscheimer model for fracture flow



500 micron aperture, 5000 s

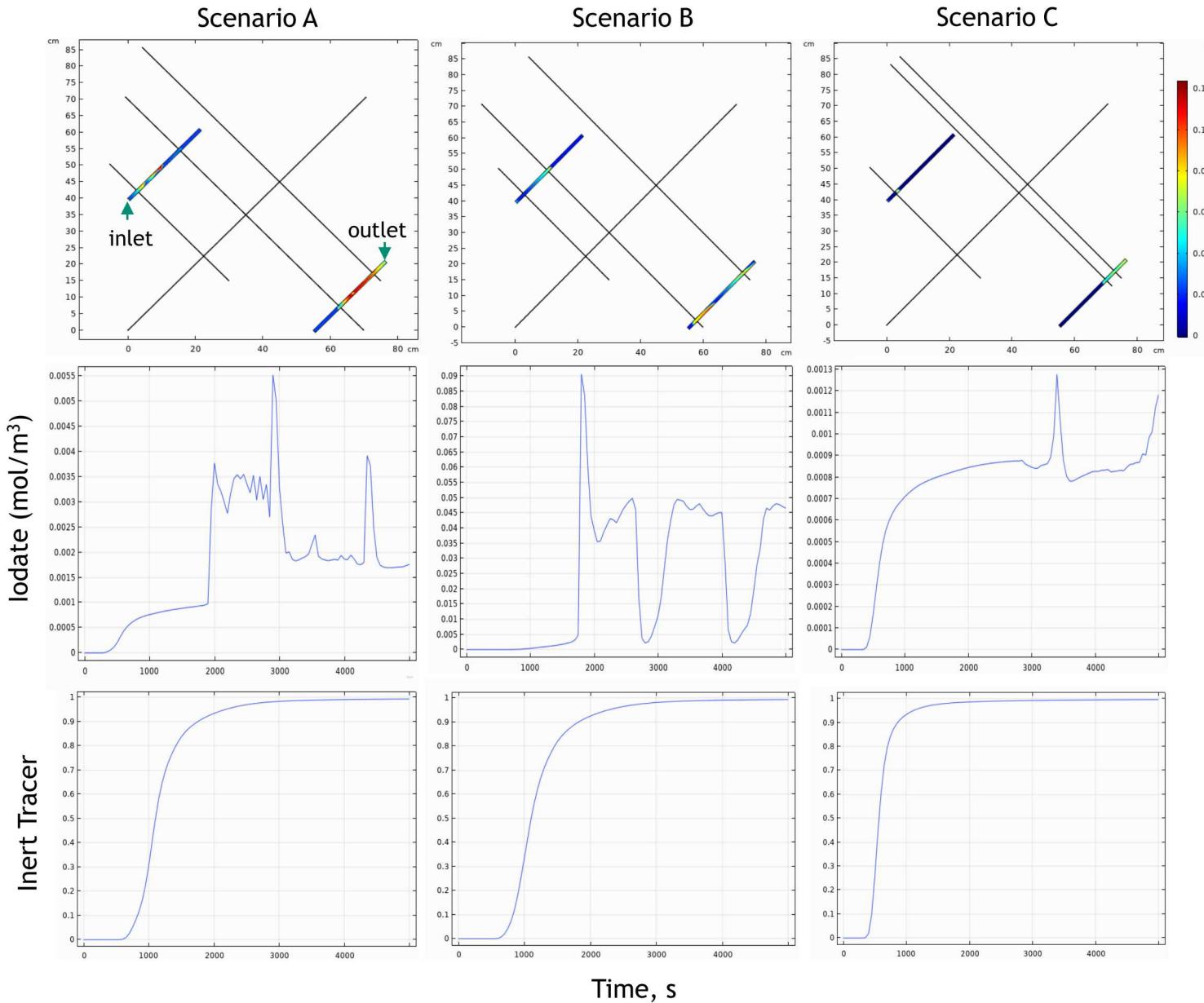


5 micron aperture, 5000 s

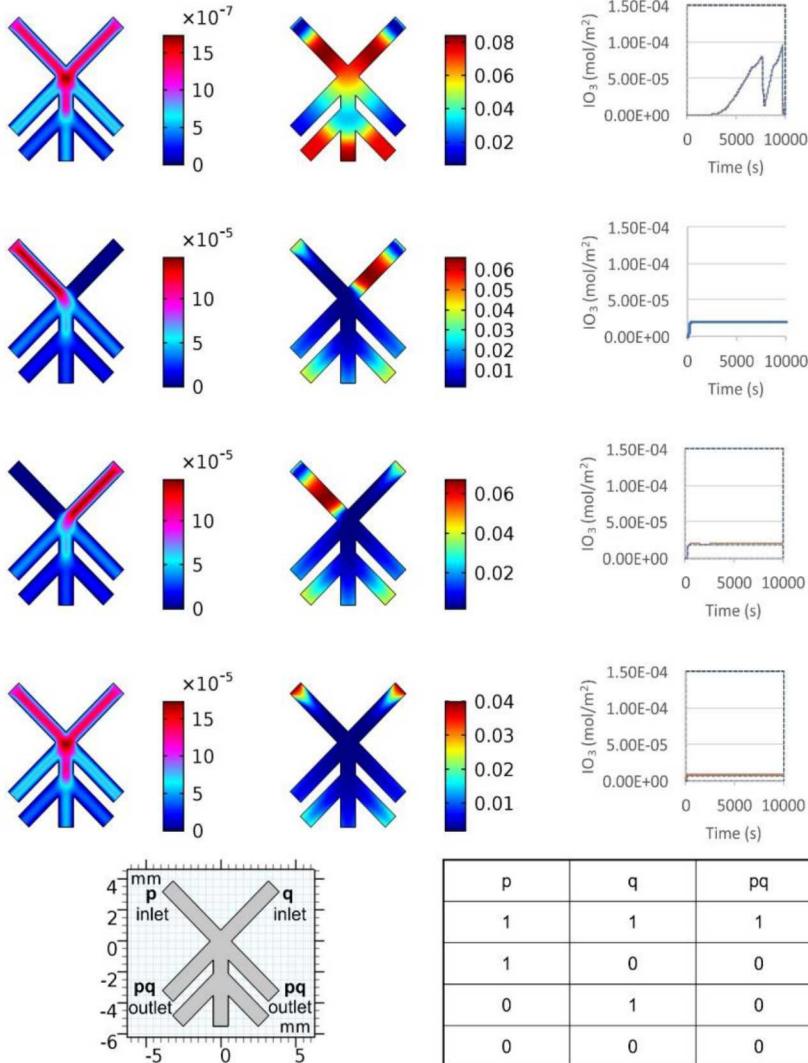
# Non-Linear vs Linear Tracers in 2D Fracture Networks



- Non-linear tracer informs on fracture connectivity and aperture
- Wave arrival and amplitude describes interaction of flow pathways
- Conservative tracer shows typical breakthrough on same network scenario



# Applications: Liquid Logic Gates in Fractured Media



$p = 1$  if: inlet has low vel.; outflow has significant oscillations  
 $q = 1$  if: inlet has low vel.; outlet has significant oscillations

CFD Models for Iodate system in simple 2D fracture network mimics Boolean functions of diodes, transistors, fluidic logic, etc.

- Flow, chemical concentrations, and logic gate design for an AND logic gate.
- Left column: velocity ( $m/s$ ). Middle column: iodate concentration ( $mol/m^3$ ). Right column: line integral of outflow concentration for the left pq outlet (orange-solid line) and right pq outlet (blue-dashed line).
- The image and table gives the geometry and labels of inlets/outlets and the truth table.

## Further Musings on Applications



*A variety of autocatalytic chemical systems are known (e.g. Noyes, 1990; Orba'n et al., 2015) that could help design analogous systems that could serve as nonlinear chemical tracers in the subsurface:*

- Bray-Liebhafsky reaction involving disproportioning of  $\text{H}_2\text{O}_2$  by iodate
- Briggs-Rauscher reaction with iodate, hydrogen peroxide, and carboxylic acids
- Oscillatory dehydration of formic acid involving carbon monoxide
- Destruction of ozone by CFCs

*We suggest that appropriately engineered chemical waves could serve other purposes in subsurface sensing:*

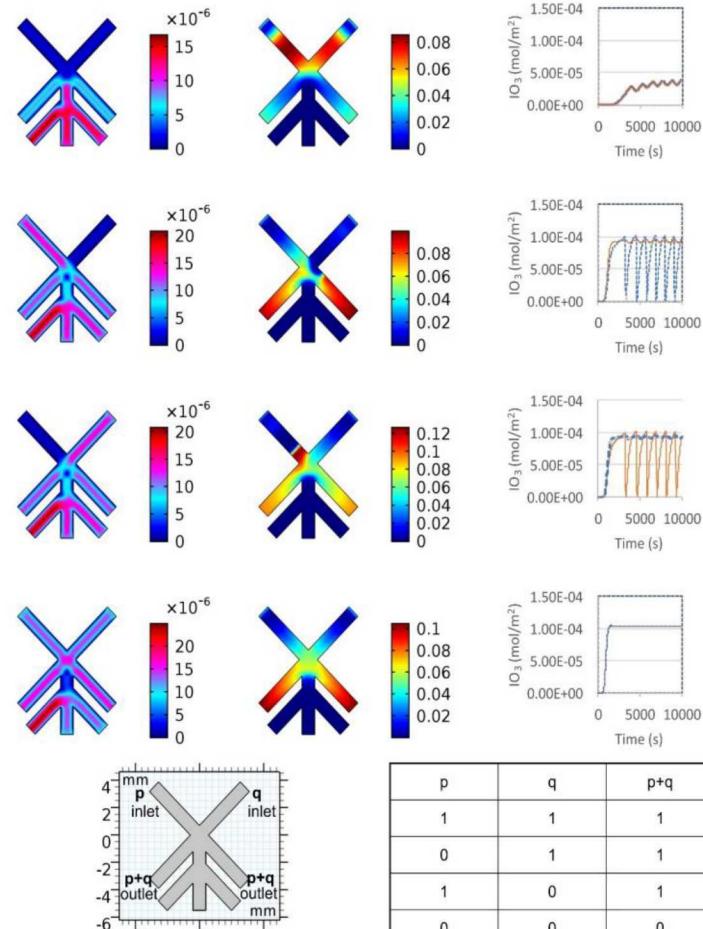
- Information or power delivery to or from embedded electronic sensors
- Swelling clays as chemo-mechanical pumps
- Interacting with microbial populations to track migrating contaminant plumes.
- Inasmuch as the kinetics of chemical waves can be fine-tuned, chemical waves can alternatively overcome temporal and spatial limitations of other subsurface sensing mechanisms, increasing resolutions below that of seismic imaging, or overcoming attenuation of electronic sensors.

# Conclusions

*We suggest that simple autocatalytic reaction networks could serve as “chemical wave” or “nonlinear” tracers for subsurface sensing*

*A combination of microfluidic experimentation and CFD modeling of nonlinear tracing demonstrates sensitivity to flow path geometries and advective gradients, displaying excitability and a variety of wave behavior*

*Nonlinear tracers could prove useful for leakage and contaminant detection at sub-seismic resolutions, expanding the role of chemical tracing in subsurface sensing*



$p = 1$  if: inlet has low vel.; outflow has significant oscillations  
 $q = 1$  if: inlet has low vel.; outlet has significant oscillations

Simple “OR” logic gates in iodate oscillator system