From Solute Transport to Chemical Weathering

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Objective: to predict \( W(t; z = h) \) called the distribution of arrival times.
Problem

• Given the condition of an incompressible fluid flowing at constant speed through a disordered, finite, porous medium:
• How do we predict solute arrival time distributions?
RELEVANCE?

Predicting solute spreading in porous media is relevant to
• remediation and monitoring of toxic wastes in groundwater,
• cellular mitosis,
• blood perfusion in the brain,
• chromatography,
• filtration,
• secondary oil recovery,
• catalysis,
• behavior of packed bed reactors,
• degradation of building materials,
• tissue physiology,
• migration and epidemiology,
• heat dispersion in foams,
• the internal dynamics of the atom.


And chemical reaction rate scaling in porous media (Ghanbarian et al., 2013; submitted)
Our Solution

• Use realistic models of actual media,
• Use percolation theoretical concepts to classify solute transport paths through the medium – i.e., according to minimum conductance values,
• Percolation theory is related to finding the statistical occurrence of these paths,
• Find the times for solute transport along such paths.
Simplified, it’s really about counting paths with given flow velocity and length

- Minimum conductance values relate to flow velocity.
- Time is length divided by velocity summed up over all the pores on each path – relates to cumulative resistance.

The standard approach uses the advection-diffusion equation, (ADE).

Thermodynamic analogy

\[
\text{ADE} \quad \frac{\partial C}{\partial t} = -\nu \cdot \nabla C + D_h \nabla^2 C
\]
Features of Our Results
Statistical Mechanics approach

• Long-tailed (nearly power-law) arrival time distributions, (not Gaussian as in ADE)
• Long tails can cause divergent mean arrival time (in Gaussian, all moments exist)
• Distribution shape is nearly independent of transport distance, (Gaussian narrows)
• Dispersivity \( \frac{\sigma^2}{x} \propto x \) \( \frac{\sigma^2}{x} = \text{const} \)
• Solute velocity, \( v_s \), is typically less than water velocity, \( v_w \), and ratio diminishes with transport distance, (For Gaussian \( v_s = v_w \))
Our resulting distributions ever noticed before?

TIME-SCALE INVARIANCE IN TRANSPORT AND RELAXATION

Important, and often puzzling, features of transport and relaxation in disordered systems can be attributed to the long-tailed distributions of the times between events that limit the motion.

Harvey Scher, Michael F. Shlesinger and John T. Bendler

Physics Today, January 1, 1991

Yes, but never derived before.

Article features dispersive transport in polymers and a-semiconductors, but authors present only a description, the Continuous Time Random Walk!
Outline of approach

1. Discretize flow network and define local conductances

2. Use cluster statistics of percolation theory to find probability that there exists a cluster with a specified minimum conductance value that spans the system.

3. Use knowledge of flow through resistances in series and topology of percolation theory to find the time of solute transport across the cluster

Background: define a few quantities from percolation theory
Percolation on a square lattice

Bonds emplaced at random with probability $p$

$p > p_c = 0.5$

Dead ends
Terminology

Dead ends (gone)

Loops

Backbone cluster

The fractal dimensionality, $D_b$, of the backbone cluster will be important to tortuosity of solute paths.
Cluster statistics of percolation theory

\[ n_s = s^{-\tau} \exp\left(-s^\sigma (p-p_c)^2\right) \]

\[ \frac{\tau - 1}{\sigma} = \frac{187/91 - 1}{36/91 \cdot 4/3} = d = 2 \]

\[ \tau = 187/91, \quad \sigma = 36/91 \]
\[ g = \text{conductance} \]

\[ \int_{0}^{\infty} W(g')dg' = 1 \]

\[ \int_{g_c}^{\infty} W(g')dg' = p_c \]

\[ \int_{g_{\text{min}}}^{\infty} W(g')dg' = p \]

\[ s \propto N^{\sigma \nu} \]

\[ n_s = s^{-\tau} \exp(-[s^\sigma(p-p_c)]^2) \]
2. We applied above procedure to a power-law distribution of pore-sizes (and conductances), with $D$ the fractal dimension of the pore space and found,

$$N^d n_N = \frac{N^d}{N^{d+1}} \exp \left\{ -\left[ \left( \frac{Nl}{L} \right)^{\frac{1}{\nu}} \right] - \left( \frac{g_{\text{min}}}{g_c} \right)^{\frac{3-D}{3}} \right\}^2$$

$W_p(g_{\text{min}})$ is obtained by integrating the above expression over all volumes larger than or equal to size of system.

$$W_p(g_{\text{min}}) \propto \frac{1}{\beta} Ei \left[ \alpha \left( \frac{x}{L} \right)^{\beta} \right]$$

NOT a power law

$$\alpha = \left| 1 - \left( \frac{g_{\text{min}}}{g_c} \right)^{\frac{3-D}{3}} \right|^2$$

and

$$\beta = \frac{2}{\nu}$$
Minimum conductance, $g_{\text{min}} / g_c$
Now we need the time it takes for solute to traverse such a cluster

- This time has two distinct contributions:
  - From the resistance distribution in the medium,
  - From the tortuosity.

- Effects of the resistance distribution can be calculated by assuming a 1-D arrangement of resistances, i.e., water flows through a series arrangement of resistances smaller than $g_{\text{min}}^{-1}$.

- Paths constructed with $g_{\text{min}}$ near $g_c$ are more tortuous, as are longer paths (larger system sizes).
The fractal dimensionality, $D_b$, of the backbone cluster will be important to tortuosity of solute paths.
Even more complicated result includes effects of porosity and relative saturation – not shown, and difference is not critical.

This contains a power-law divergence, which controls the long-time behavior of the arrival-time distribution \((D_b-1)\nu\).

IMPORTANT exponent \(D_b\) is not universal, but takes distinct values of 1.87 or 1.46 in 3-D and 1.64 or 1.22 in 2-D. \(\nu\) is 0.88 in 3-D and 1.33 in 2-D.
$D = 2.5, \ \theta_t = 0.05$
Apply probabilistic transformation

• $W(t)dt = W(g)dg$

• $W(t) = \frac{W(g)}{(dt/dg)}$
Note relative insensitivity of results to significant changes in porous medium characteristics.
2-D Navier-Stokes simulations (blue) in small simplified system. Choose (red) appropriate 2-D percolation exponents and reasonable values of system parameters to fit $X = 10$; same parameters make prediction for $X = 50$

*Philosophical Magazine, 2008*
Same set of parameters yields both the shape of the curves and the scaling of the absolute time with saturation. PRE 2012.
Extract physical parameters for model description by fitting our model to experimental data for water content.
Make predictions for solute dispersion
Make predictions for solute dispersion PRE 2012
Analogous procedure yields spatial distribution at any instant in time

\[ t = \left( \frac{x}{L} \right)^{D_b} \frac{t_0}{3-D} \frac{g_c}{g_{\text{min}}} \left( \frac{1}{1-\theta_t} \right)^{D_b \nu-\nu} \left[ \left( 1 + \frac{\theta_t}{1-\theta_t} \right) \left( \frac{g_c}{g_{\text{min}}} \right)^{1-D/3} - 1 \right] \left( \frac{g_{\text{min}}}{g_c} \right)^{1-D/3} - 1 \]

using \( x(t) \), then:

\[ W(x) = W(g) / (dx/dg) \]
The longitudinal dispersion coefficient is written most simply as

\[ D_l(t) = \frac{\sigma^2}{t} \frac{\langle x^2 \rangle - \langle x \rangle^2}{t} \]

Most of our comparisons are with the dispersivity, written as,

\[ \alpha_l(x) = \frac{D_l(t)}{v} = \frac{\langle x^2 \rangle - \langle x \rangle^2}{v t} \]

The velocity, \( v \), cannot be calculated from an arrival time distribution (why?), so it has to be calculated from the spatial distribution as \( \langle x \rangle / t \). Thus,

\[ \alpha(x) = \frac{\langle x^2 \rangle - \langle x \rangle^2}{\langle x \rangle} \]
Our results for the scaling of the typical system crossing time with system length imply the following velocity function:

\[
v(t) = \frac{L}{t_0} f \left( \frac{t}{t_0} \right) \approx v_0 \left[ \frac{t}{t_0} \right]^{(1-D_b)/D_b}
\]

If chemical reaction rates, \( R \), are limited by the velocity of solute transport (removal of products and/or delivery of reagents, then \( R \) should scale as:

\[
R(t) = \frac{R_0}{v_0} \frac{L}{t_0} f \left( \frac{t}{t_0} \right) \approx R_0 \left[ \frac{t}{t_0} \right]^{(1-D_b)/D_b}
\]
Brantley and White (2005) report weathering rates of silicate minerals are proportional to the power -0.51 at short times and -0.63 over periods up to 10 million years.

“Slow dissolution of minerals on land and formation of biogenic calcite in the oceans also maintains atmospheric CO$_2$ concentrations and therefore plays an important role in maintaining global temperatures at levels optimal for the presence of liquid water (Berner, 1992). In Earth's past, major changes in rock weathering have coincided with periods of mass extinction (Algeo and Scheckler, 1998; Sheldon, 2006) and reorganization of global biogeochemical cycles (Raymo, 1994; Vance et al., 2009).” (From Maher, 2010)
\[ y = -0.6338x - 0.708 \]

\[ R^2 = 0.9886 \]

\[ y = -0.4695x - 0.6899 \]

\[ R^2 = 1 \]

\[ y = -0.5171x - 0.6228 \]

\[ R^2 = 0.9967 \]

\[ y = -0.6338x - 0.708 \]

\[ R^2 = 0.9886 \]

\[ y = -0.6135x - 0.6443 \]

\[ R^2 = 0.9972 \]
log \[t \text{ (yr)}\]

- D=1.5
- D=2.95

- K-feldspar
- Hornblende
- Plagioclase
- Biotite
- FPP
- Volcanic
Experiments (Maher, 2010)

Theory (D=2.95, 3D Rand. Percolation)
D = 2.95
D = 1.50

- Field (Maher, 2010)
- 2000-8000 μm (Du et al., 2012)
- <2000 μm (Du et al., 2012)
- 500-2000 μm (Du et al., 2012)
- 75-500 μm (Du et al., 2012)
- <75 μm (Du et al., 2012)
First BTC (Liu et al., 2009)
Second BTC (Liu et al., 2009)
Third BTC (Liu et al., 2009)
Fourth BTC (Liu et al., 2009)
Theory (D=2.95, 3D Rand. Percolation)
First BTC (Liu et al., 2008)

Theory (D=2.95, 2D Rand. Percolation)

Theory (D=2.95, 2D Inv. Percolation)
First BTC (Liu et al., 2008)

Theory (D=2.95, 2D Inv. Percolation)
Fe(II)=0 mmol/g (Zhong et al., 2005)

Fe(II)=0.02 mmol/g (Zhong et al., 2005)

Theory (D=2.95, 3D Rand. Percolation)
Conclusions: It works – everywhere we’ve tried it.