COLUMN TRACER EXPERIMENTS

We will determine retardation factor and sorption distribution coefficient, and dispersion coefficient and dispersivity using breakthrough curves obtained from miscible displacement experiments using a laboratory column.

Equipment

(1) laboratory column;
(2) piston pump;
(3) fraction collector;
(4) ion selective electrodes (Cl and Cu);
(5) pH meter (room 230D, ask Tim Shanahan, 621-4072 or shanahan@hwr.arizona.edu).

Experiments

Make tracer solutions for each tracer (100 ppm for Cl and 10 ppm for Cu). Make enough to finish the experiments.

Ideal tracer (Cl\(^{-}\))

Pumping the background solution to establish steady flow. Switch to a 100 ppm Cl tracer and let the flow continue. Collect samples using fraction collector. Measure Cl concentration using the Cl electrode. Continue until the outlet concentration is the same as the tracer concentration (here, 100 ppm). (This approach is called step input because we changed from 0 ppm to 100 ppm and continued until the end of experiment) Switch back to the background (matrix) solution.

Plot the data as a breakthrough curve (pore volumes (=vt/x) versus C/C\(_0\)). Analyze the curve and calculate the longitudinal dispersion coefficient and longitudinal dispersivity.

Sorbing tracer (Cu\(^{2+}\))

Repeat the above experiment with two changes:

1. use 10 ppm Cu solution (remember that Cl is an interfering species for Cu electrode, so make sure that all Cl is flushed out of the system; use non-Cl background solution, e.g., Na\(_2\)SO\(_4\));
2. do a pulse input instead of step input (create a pulse and trace it at the column outlet); the pulse duration depends on the sorption properties of the system, but because we do not know these properties, we should use about one pore volume; after one pore volume, switch back to the background solution. Continue collecting samples and measure Cu concentrations until you have defined the peak and the concentration of Cu came back to near zero.

Plot the data as a breakthrough curve (pore volumes (=vt/x) versus C/C\(_0\)). Analyze the curve and calculate the retardation factor and sorption distribution coefficient.
Data analysis

The transport equation is

\[
R \frac{dc}{dt} = D \frac{d^2 c}{dx^2} - v \frac{dc}{dx}
\]

where:

\( R = 1 + \rho K / Q \) is the retardation factor [-] (\( \rho \) is the bulk density of soil [M L^{-3}], \( K \) is the linear sorption distribution coefficient [L^3 M^{-1}], \( \Theta \) is the volumetric water content [-]);

\( C \) is the solute concentration in effluent [M L^{-3}];

\( D = v \alpha \) is the longitudinal hydrodynamic dispersion coefficient [L^2 T^{-1}] (\( \alpha \) is the longitudinal dispersivity [L], \( v \) is the velocity [L T^{-1}]);

\( v = q / \Theta \) is the pore velocity [L T^{-1}] (\( q \) is the specific discharge [L T^{-1}]);

\( x \) is the length of soil column [L];

Assumptions behind the above equation:

(1) linear and reversible sorption;
(2) constant retardation factor;
(3) constant dispersion coefficient;
(4) constant pore velocity;
(5) no sources/sinks of solute;
(6) constant water content (porosity).

For boundary conditions:

BC1: \( C(0,t) = C_0 \) (first type)

BC2: \( x = \infty, \ \frac{\partial c}{\partial x} = 0 \) (second type)

the solution is:

\[
\frac{C}{C_0} = \frac{1}{2} \text{erfc} \left( \frac{Rx - vt}{2(DRt)^{\frac{1}{2}}} \right) + \frac{1}{2} \exp \left( \frac{vx}{D} \right) \text{erfc} \left( \frac{Rx - vt}{2(DRt)^{\frac{1}{2}}} \right)
\]
for, in terms of the column Peclet number \( P_n = \frac{vx}{D} \) and column pore volume \( P_v = \frac{vt}{x} \):

\[
\frac{C}{C_0} = \frac{1}{2} \text{erfc}\left(\left(\frac{P_n}{4RP_v}\right)^{1/2} (R - P_v)\right) + \frac{1}{2} \exp(P_n) \text{erfc}\left(\left(\frac{P_n}{4RP_v}\right)^{1/2} (R - P_v)\right)
\]

For large Peclet number \( P_n > 10 \), the influence of boundary conditions on analytical solutions becomes negligible and the solution for step input is:

\[
\frac{C}{C_0} = \frac{1}{2} \text{erfc}\left(\left(\frac{P_n}{4RP_v}\right)^{1/2} (R - P_v)\right)
\]

Use the above solutions as a guide in the analysis of the results. One possible approach is trial and error with the aid of a simple computer program of your design (vary R and D until you fit the observed data). Another possibility is to use a standard program (such as CXTFIT) to analyze column data. I have an old copy (download from our web site: http://quebec.hwr.arizona.edu/classes/hwr432/s00/cxtfit.zip), but ask around for a newer version.

**Report**

In the report, include the following:

- description of the experiments
- results and their interpretations
- discussion (compare the two experiments)
- any problems encountered and potential solutions
- improvements and recommendations

Answer the following questions:

1. Is the recovery of Cu complete (i.e., has 100% of mass been accounted for)? What processes might cause the recovery of Cu to differ from 100%?
2. How does the position and shape of the Cl breakthrough curve (BTC) compare with what we would expect for an ideal tracer?
3. What does the shape of the Cu BTC suggest about Cu sorption and desorption in this soil?
4. What problems in the experimental design might lead to different transport characteristics in the column as compared to those for the same soil in the field?
5. Given more resources, how could the experimental design be improved to give a more realistic simulation of field behavior?
Electrode calibration

To prepare standards, use these tracer solutions to do successive gravimetric dilutions and make at least five calibration standards for each tracer. I suggest the following:

For Cl: 100 ppm (tracer solution), 50 ppm, 20 ppm, 5 ppm and 2 ppm.

For Cu: 10 ppm (tracer solution), 2 ppm, 0.5 ppm, 0.05 ppm and 0.01 ppm.

Follow the instructions in the electrode manuals to make calibration curves (but write a spreadsheet program rather than use graphical method to determine concentrations of the unknown samples).

References


Note: this book is available in my office.