Goal: Model the PFM elution curve assuming retardation of the tracer on the PFM sorbent is governed by a) linear and b) Freundlich partitioning processes. The elution curve represents dimensionless mass remaining in the PFM as a function of time t [T], and shall be designated $\Omega(t)$. This will be accomplished by calculating $\Omega(t)$ at discrete points in time. Time shall be discretized using

$$t = (k-1)dt + t_{start} \quad ,$$

where k is a temporal counter starting from 1, and t_{start} is the starting time. For $\Omega(t)$, $t_{start} = 0$, and that term is omitted hereafter. Note that

$$t_{end} = (k_{end} - 1)dt$$

where k_{end} is the counter ending value and t_{end} is the end time. Therefore $k = [1, 2, ..., k_{end}]$ is an array of integers, and $t = [0, dt, ..., t_{end}]$ is an array of real numbers. For each point in time, Ω must be calculated, such that an array of Ω values are creating, starting from 1 at $t = 0$, and having the same number of elements as the k and t arrays.

The PFM is cylindrical, therefore its shape is described by its radius r [L] and height Z [L]. Following Hatfield et al (2004), the solution will be based on advective flow within a stream tube (i.e., dispersion is neglected), and the PFM cross section shall be divided into $s_{\max}$ stream tubes. Let s be an integer counter representing each stream tube, therefore $1 \le s \le s_{\max}$. Since the PFM is cylindrical, stream tube lengths and therefore travel times vary from a maximum corresponding to the PFM diameter to zero at the circumference (see Hatfield et al., [2004] for the treatment of stream tube dimensions as a function of the cylindrical PFM). Tracer is assumed to be uniformly distributed in the

PFM at a concentration of C_0 [ML^{-3}] at $t = 0$. Groundwater entering the PFM is assumed to be tracer free.

For linear partitioning, each stream tube can be divided into two segments: a region with zero concentration (i.e., tracer-free region), and a region with tracer at concentration $C = C_0$ (i.e., tracer-ladened region). For any time t, the position of the front x_f separating these two regions in a given stream tube is given by

$$x_f = \frac{vt}{R}$$

where v is seepage velocity [LT^{-1}] (equal to the ratio of Darcy flux q [LT^{-1}] and PFM porosity η [-]), and R is the retardation factor [-]; which for linear partitioning is given by

$$R = 1 + \frac{\rho_b k_d}{\eta},$$

where ρ_b is the PFM bulk density [ML^{-3}] and k_d is the tracer-sorbent partitioning coefficient [L^{3}M^{-1}]. Consequently, the tracer mass in both aqueous and sorbed phases remaining in stream tube s at time t can be expressed as

$$M_{R,s}(t) = \begin{cases} RC_0\eta Zdy\left(x_d - \frac{vt}{R}\right) \text{ for } vt/R < x_d \\ 0 \text{ for } vt/R \geq x_d \end{cases}.$$

Therefore, the dimensionless mass remaining at time t is

$$\Omega(t) = \frac{\sum_{s=1}^{s_{\max}} M_{R,s}(t)}{M_0} ,$$

where M_0 is the PFM initial tracer mass in both aqueous and sorbed phases.

For Freundlich partitioning, R is now a function of C, and significant different transport behavior may result depending on the value to the exponent m in the Freundlich partitioning model:

$$q = KC^m ,$$

where q is sorbed concentration [MM-1] and K is the Freundlich partitioning coefficent. Sheng and Smith (1999) provide solutions to one dimensional advective transport with Freundlich partitioning. In particular, they present the following equation:

$$v_C = \frac{\eta v}{\eta + \rho_b KmC^{m-1}} , \qquad \text{(X)}$$

where v_C is the velocity at which fluid at concentration C travels under Freundlich partitioning. Consider the initial condition of tracer with $C = C_0$ in the region of $0 \le x \le x_D$, and $C = 0$ elsewhere. Groundwater is assumed to flow in the positive x direction. Initially, instantaneous changes in concentration are located at $x = 0$ and $x = x_D$. What happens under conditions of $m > 1$ and $m < 1$?

For $m > 1$ and $C = 0$, equation (X) results in $v_{C=0} = v$. At $x = 0$, it is useful to compare conditions for $x \to 0^-$ and $x \to 0^+$. For $x \to 0^-$, $v_{C=0} = v$ as noted. For

$x \to 0^+$, $C = C_0$ and $v_{C=C_0} < v$. As a result, the step change in concentration (i.e., shock front) in maintained as it propagates downstream. At $x = x_D$, the opposite condition is true and a self-spreading wave (area of rarefaction) is produced as described below for $x = 0$ when $m < 1$.

For $m < 1$ and $C = 0$, equation (X) yields $v_{C=0} = 0$. For $x = 0$, this result occurs more specifically for the condition $x \to 0^-$. For $x \to 0^+$, $C = C_0$ and $v_{C=C_0} > 0$. As a result, an area of rarefaction occurs in which $0 \le C \le C_0$, and the space over with the rarefaction occurs grows with time. At $x = x_D$, the opposite condition is true and a shock front is produced (i.e., the instantaneous change in concentration is maintained). Sheng and Smith (1999) provide the following equation for C in the rarefaction area:

$$C(x,t) = \left(\frac{\eta v t - \eta x}{\rho_b K m x} \right)^{\frac{1}{m-1}} \qquad \text{(Y)}$$

Consequently, the stream tube can be divided into two regions: in the first region defined by $0 \le x < x_b$, where $x_b = v_{C_0} t$, C is given by equation (Y), and in the region defined by $x_b \le x \le x_D$, $C = C_0$. Once $x_b \ge x_D$, then C in the entire region of $0 \le x \le x_D$ is given by equation (Y). Therefore, the mass in the stream tube is given by

$$M_{R,s}(t) = \begin{cases} Zdy \left[\int_0^{x_b} \left[\eta C(x,t) + \rho_b K C(x,t)^m \right] dx + \left[\eta C_0 + \rho_b K C_0^{\,m} \right] (x_D - x_b) \right] & \text{for } x_b < x_d \\ Zdy \int_0^{x_D} \left[\eta C(x,t) + \rho_b K C(x,t)^m \right] dx & \text{for } x_b \ge x_D \end{cases}$$

A trapezoidal approximation can be used to approximate the integrals above, as illustrated below using an arbitrary variable $\xi(x)$:

$$\int_0^{x_D} \xi(x)dx \cong \frac{dx}{2}\left\{\xi(0) + \xi\left((w_{\max}-1)dx\right)\right\} + dx\sum_{w=2}^{w_{\max}-1} \xi\left((w-1)dx\right)$$,

where w is a space counter ($w \geq 1$), similar to k for time. As such, we can write

$$x = (w-1)dx + x_{start}$$,

where dx is the spatial step size, x_{start} is the starting value (i.e., $x_{start} = 0$). Therefore, the ending spatial value x_{end} is related to the ending spatial counter w_{end} by

$$x_{end} = (w_{end}-1)dx$$.

QA Checks

1) Compare output from linear partitioning script to equation (14) from Hatfield et al (2004).
2) Compare output from linearized Freundlich script to equation (14) from Hatfield et al (2004).
3) Compare results for Freundlich partitioning for a single stream tube as estimated using an EXCEL worksheet to that from the script.
4) Compare output from linear partitioning script to Freundlich script with a Freundlich exponent of unity (or approximately unity).

5) Compare output from linearized Freundlich script to the Freundlich script. The early time data should be comparable, and the tailing behavior should be different.
6) Use script to produce Figure 4 from Hatfield et al (2004) for a qualitative comparison (note this Figure is for a single streamtube).
7) Compare output from Freundlich script to equation (19).

Applications

1) Explore elution curve sensitivity to Freundlich parameters. Use Freundlich script to generate elution curves for a range of values for the two Freundlich parameters.
2) Use Freundlich script (for a single stream tube) to estimate Freundlich parameters by matching data presented in figure 8 of Hatfield et al (2004) script output.
3) Create elution curve for alcohol applications using estimates of the two Freundlich parameters.
4) Create elution curve for hypothetical fluorescein applications using estimates of the two Freundlich parameters.
5) Explore what happens if the tracer and contaminant have different sorption properties.
6) Explore under what conditions the sorbent acts as an infinite capacity media