

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

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

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 $k = [1, 2, \dots, k_{end}]$ is an array of integers, and $t = [0, dt, \dots, t_{end}]$ is an array of real numbers. For each point in time, Ω must be calculated, such that an array of Ω values are created, starting from 1 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, and that varies from 1 to S_{max} . Note that 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 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 $C = C_0$ (i.e., tracer-laden 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^3M^{-1}]. Consequently, the tracer mass remaining in stream tube S at time t can be expressed as

$$M_{R,x}(t) = \begin{cases} C_0 \eta Z dy \left(x_d - \frac{vt}{R} \right) & \text{for } vt/R < x_d \\ 0 & \text{for } vt/R \geq x_d \end{cases} .$$

Therefore, the dimensionless mass remaining at time t is

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

where M_0 is the initial tracer mass in the PFM.

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. Assume $m < 1$. [Justification?] Sheng and Smith (1999) provide solutions to one dimensional advective transport with Freundlich partitioning. In particular, they present the following equation:

$$v_C = \frac{\eta v}{\eta + \rho_b K m C^{m-1}} , \quad (X)$$

where v_C is the velocity at which fluid at concentration C travels under Freundlich partitioning with a coefficient of K . Consider the initial condition of tracer with $C = C_0$ in the region of $0 \leq x \leq x_D$, 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 $x = x_D$. For $m < 1$ and $C = 0$, $v_{C=0} = 0$. For $x = 0$, this results occurs more specifically for the condition $x \rightarrow 0^-$. For $x \rightarrow 0^+$, $C = C_0$ and $v_{C=C_0} > 0$. As a result, an area of rarefaction occurs in which $0 \leq C \leq C_0$, 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., an instantaneous change in concentration is maintained). Sheng and Smith (1999) provide the following equation for C in the rarefaction area:

$$C(x, t) = \left(\frac{\eta v t - \eta x}{\rho_b K_{mx}} \right)^{\frac{1}{n-1}} \quad (Y)$$

Consequently, the stream tube can be divided into two regions: in the first region defined by $0 \leq x < x_b$, where $x_b = v_{c_0} t$, C is given by equation (Y), and in the region defined by $x_b \leq x \leq x_D$, $C = C_0$. Once $x_b \geq x_D$, then C in the entire region of $0 \leq x \leq x_D$ is given by equation (Y). Therefore, the mass in the stream tube is given by

$$M_{R,x}(t) = \begin{cases} \eta Z dy \left[\int_0^{x_b} C(x, t) dx + C_0 (x_D - x_b) \right] & \text{for } x_b < x_D \\ \eta Z dy \int_0^{x_D} C(x, t) dx & \text{for } x_b \geq x_D \end{cases}$$

A trapezoidal approximation for the second integral term is

$$\int_0^{x_D} C(x, t) dx = \frac{dx}{2} \left\{ C[0, t] + C[(w_{\max} - 1)dx, t] \right\} + dx \sum_{i=2}^{w_{\max}-1} C[(w-1)dx, t]$$

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