Appendix U. SSFL Sandstone Sorption and Diffusion Experiments

U-1. SSFL Sorption Experiments

The batch sorption experiments were carried out using a well-documented method (Ball and Roberts, 1991; Harmon and Roberts, 1994). The only deviations from the method were (1) carbon-14 labeled chemicals and (2) flame-sealed ampules (as opposed to screw-top vials) were used in the previous studies but were not used here. Both of these deviations lead to a less precise measurement relative to the methods cited, but also lower the cost of the measurement significantly.

Four replicate samples and two blanks (no solids) were prepared for each of four initial concentrations tested (specified below). All the vials along with the caps were weighed and weight was recorded. The vials were filled approximately to half their volumes with the crushed sandstone. The vial-cap system was reweighed and the weight of solids was recorded. Then the vials were filled with Nano-pure® water till the brim of the vial. The vials were then capped and shaken on a vortex mixer to ensure the removal of the air bubbles and left undisturbed for 12 hours. Later, the vials were filled with water to the top and recapped. The blanks were also filled with water. All the vials are reweighed and the final weight of the solids and the water is noted. These vials were then spiked with TCE spiking solutions of different concentrations, roughly 1170, 5840, and 117700 µg/L and shaken to insure instant mixing. The vials were remixed every 8-10 hours for approximately 24-36 hours. Then the samples were left undisturbed overnight to settle. This equilibration time was believed to be sufficient for crushed sand using previous results for crushed sand for reference (Ball and Roberts, 1991). At the end of 48h, 3 mL of the supernatant water was added to the 4 mL crimped-top vials, which also contained 1 mL of pentane. These vials were then manually shaken for 20 minutes to extract the TCE into the pentane. The pentane from the vials was then transferred to the 1 mL gas chromatograph (GC) sample vials and analyzed on a Hewlett-Packard 6890 GC equipped with an electron capture detector (ECD). Sample concentrations were quantified using a GC response curve generated using calibration standards prepared in pentane. From the initial and final aqueous TCE concentrations and the losses determined from the blanks, the sorbed TCE concentration was determined for each sample. The concentrations in the sorbed phase versus the final aqueous concentrations were then plotted and the value of K_d was obtained as the slope of this curve.

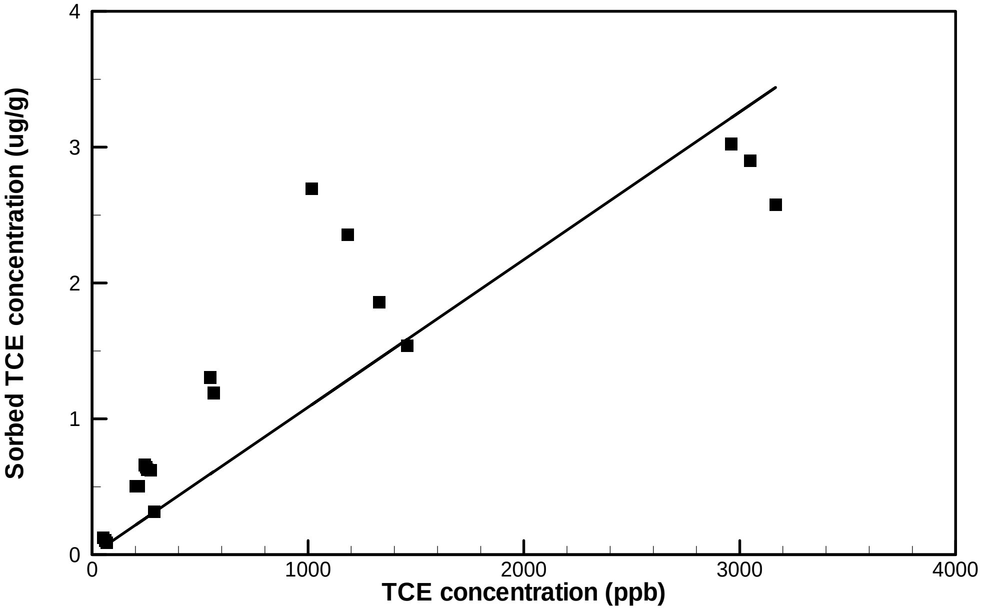

Figure U-1. SSFL sandstone sorption data with linear isotherm estimated for pulverized core material in batch tests (line indicates best-fitting distribution coefficient estimate K_d value of 1.1 mL/g).

U-2. Diffusion of Tritiated Water in SSFL Sandstone

The diaphragm-cell (Figure U.2) is a single unit containing two compartments (~ 40 cm^3 each) separated by a porous barrier. A sampling port, useful in filling and emptying the chambers as well, is connected to the side of each chamber.

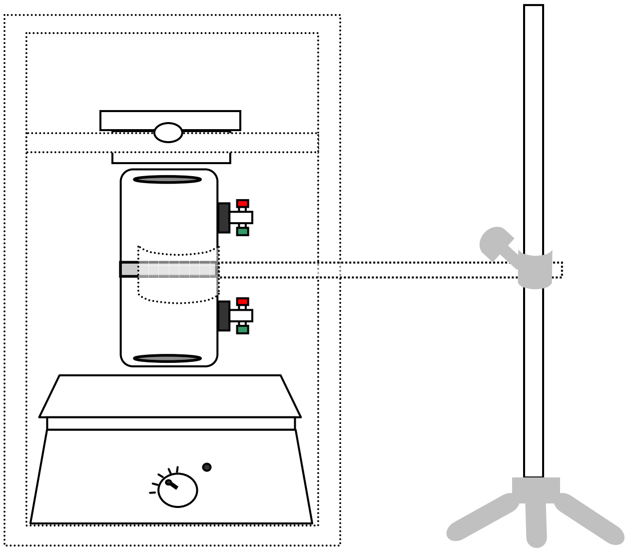

Figure U-2. The diffusion cell setup consisting of two chambers, each with a stop-go valve sampling port, separated by a porous barrier (sandstone) configured in the horizontal plane. Stirring plates atop and below the chambers provide mixing via stir bars.

Assuming that the concentration gradient through the porous barrier achieves steady state soon after the onset of the experiment, the flux across this barrier is can be approximated by the expression for diffusion through a membrane (Cussler, 1997):

$$j_1 = \left[\frac{DH}{l}\right]\left(C_{1,\text{lower}} - C_{1,\text{upper}}\right) \tag{U-1}$$

where *H* is the fraction of the area of the porous barrier in which diffusion occurs, *D* is the diffusion coefficient, *l* is the width of the porous barrier, and *C* is the concentration in each compartment (upper or lower) after the specified time. The flux can also be expressed as part of a mass balance between the two compartments:

$$\frac{d}{dt}\left(C_{1,\text{lower}} - C_{1,\text{upper}}\right) = A\left(\frac{1}{V_{\text{lower}}} + \frac{1}{V_{\text{upper}}}\right) j_1 \tag{U-2}$$

where *A* is the area of the porous barrier and *V* is the volume of each chamber. Equations (U-1) and (U-2) can then be combined to eliminate the flux term:

$$\frac{d}{dt}\left(C_{1,\text{lower}} - C_{1,\text{upper}}\right) = D\beta\left(C_{1,\text{upper}} - C_{1,\text{lower}}\right) \tag{U-3}$$

where the cell geometry constant (β) is given by:

$$\beta = \frac{AH}{l}\left(\frac{1}{V_{\text{lower}}} + \frac{1}{V_{\text{upper}}}\right). \tag{U-4}$$

This geometry constant describes the configuration of the diaphragm cell with the porous barrier; it is a characteristic of the specific diffusion cell and barrier system employed.

At the start of the experiment, the concentration of the solute is zero in the solvent chamber, and the initial condition for (U-3) can be expressed as:

$$C_{1,\text{lower}} - C_{1,\text{upper}} = C^0_{1,\text{lower}} - C^0_{1,\text{upper}} \qquad (t = 0) \tag{U-5}$$

Utilizing this condition (and letting *D* become D_p, signifying that the diffusion barrier poses resistance to the diffusion process), the solution to (U-3) becomes:

$$D_p = \frac{1}{\beta t}\ln\left(\frac{C^0_{j,\text{lower}} - C^0_{j,\text{upper}}}{C_{i,\text{lower}} - C_{i,\text{upper}}}\right) \tag{U-6}$$

This result describes the effective or pore diffusion coefficient for the solute-barrier system, obtained by measuring the concentrations in each compartment of the diaphragm-cell at a specified time.

Results from the SSFL sandstone diffusion cell test are shown in Figure U.3. The diffusion cell characteristics in this case are as follows: $H = 0.86$, $l = 1.4$ cm, $A = 4.9$ cm^2, $V_{\text{lower}} = 35$ cm^3, $V_{\text{upper}} = 40$ cm^3. C_{lower} and C_{upper} were measured by extracting 5 μL samples from the reservoirs at times ranging from 0 to 60 days. Steady measurements were achieved at around 20 days. Using the geometry above yields $\beta = 0.16$, and an observed effective diffusion coefficient (*D*) value of about 1.6×10^{-7} cm^2/s. Given that the self-diffusion coefficient for water is about 2.2 x

10^{-5} cm^2/s, and a porosity value of about 0.13, this implies that the tortuosity factor for tritiated water in the sandstone is about 18 for this core sample. Tortuosity factors depend on pore structure, molecular size, and (for molecular scale pores that are extremely restrictive) on steric effects. Thus, because TCE is a larger molecule than water, it will have a larger tortuosity factor for the same pore network. Using the ratio of the square root of molecular weights as a scaling factor (Schwarzenbach et al., 1993), the TCE tortuosity factor will be approximately 2.7 times greater than that for the tiritated water, or a value of 48. TCE will be retarded relative to tritiated water (by roughly a factor of 20, as estimated above). Estimating a free aqueous diffusion coefficient for TCE of 8.6 x 10^{-6} cm^2/s (Hayduk and Laudie, 1974), the value of the apparent diffusion coefficient value for TCE in the sandstone sample tested is about $(0.13*8.6 \times 10^{-6})/(20*48) = 1.15 \times 10^{-9}$ cm^2/s. These estimates are based on room temperature. If the temperature of the groundwater is lower, then this number will be slightly lower. Diffusion coefficients of this order of magnitude suggest that the rate of TCE propagation into the SSFL sandstone is extremely slow (on the order of a gram per square meter per year).

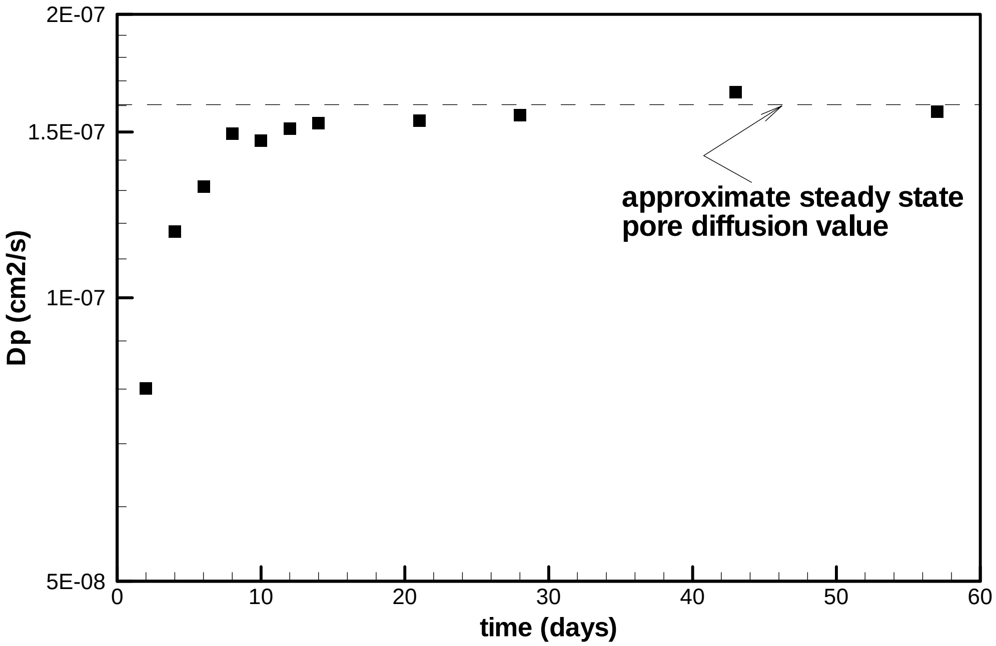

Figure U-3. Experimentally observed approach to steady state behavior for titrated water diffusion through an SSFL sandstone disk.

U-3. TCE Dissolved and Aqueous Mass Estimate for SSFL Plumes

There are three plume areas with different concentration ranges (see MW, 2000 a Fig. 5.1). The total contaminated volume V_i (including sandstone adsorption and dissolved water phase) would be for area plume i (i = 1,2,3)

$$V_i = A_i N 2 P_d \tag{U-7}$$

where A_i is the area (m^2), N is the number of fractures factored by 2 because for each fracture there would be and affected volume above and below, and P_d is the penetration depth.

Penetration depth was estimated using a one-dimensional transient diffusion calculation, where the diffusion model was parameterized using the results from the previous section. The number of fractures is given by $N=T/S$, where T is the assumed plume thickness and S the fracture spacing.

The mass of TCE dissolved in water (W_i) within the sandstone matrix is then

$$W_i = \phi V_i C_i \tag{U-8}$$

The mass of TCE in the solid part of the sandstone (SM_i) is given by

$$SM_i = (1-\phi) V_i C_i^{sm} = (1-\phi) V_i C_i \rho_s K_d \tag{U-9}$$

In these equations ϕ is porosity, C_i is concentration in the water phase and ρ_s is the density of the solid phase, taken as 2.65 g/mL. Total TCE in area i, then can be calculated adding the two previous equations

$$(Total\ TCE)_i = W_i + SM_i = V_i C_i \left[\phi + (1-\phi)\,\rho_s K_d\right] = V_i C_i \zeta \tag{U-10}$$

for the sorption coefficient (1.1 mL/g) and a matrix porosity of about 0.1:

$$\zeta = \phi + (1-\phi)\,\rho_s K_d = 0.1 + 0.9 * 2.65 * 1.1 = 2.72 \tag{U-11}$$

The analysis procedure described above was utilized to assess partition coefficient and retardation factor of TCE. This information was utilized to evaluate the partitioning of TCE between the aqueous solid matrix phase and its rate of diffusion in the soil subsurface (see Chapter 7.)