H11 (Fitts)

- A dense liquid (ρ > 1.00) that has low solubility would sink into hard-to-remove areas and persist. Higher solubility will cause rapid, high levels of contamination, but will lessen persistence. It should have toxicity at much lower concentrations (low MCL) compared to its solubility. It should be resistant to microbiologic decay and relatively nonreactive, so it persists. It should have low sorption (low Kow), so it can travel far. It should have a low vapor pressure, so it cannot be remediated easily with vapor extraction. Sounds like a recipe for 1,2-DCA, TCE, and PCE!
- 2) These are, in fact, DNAPLs. In general, chlorinated hydrocarbon NAPLs tend to be denser than water due to the heavy chlorine atoms.
- 3) There is only one isomer because there is only one chlorine atom and no matter which of the four bond positions it is located at, the same molecule results.
- Caq = 46 mg/L, Doing the same for ethylbenzene (molecular weight = 106.2 g/mol, S = 180 mg/L) results in caq = 3.5 mg/L, and for MTBE (molecular weight = 88.2 g/mol, S = 45,000 mg/L) results in caq = 1,040 mg/L.
- 5) The higher this ratio, the greater potential risk it poses to humans. A high ratio means that concentrations in water can be much higher than the concentration where health risks become significant. High solubility will make the contaminant less persistent as a NAPL, because it will dissolve into passing groundwater more rapidly.
- 6) S = 1330 mg/L. This is close to the listed solubility of 1100 mg/L. Note that there is easily this much variability in the experimental S, KH, and vapor pressure data reported in the literature.
- 7) To invade a smaller pore requires a smaller radius of curvature for the NAPL-water interface, which requires larger capillary pressure (see Eqs. 11.6 and 11.7). At first, there is not sufficient capillary pressure to enter the finer pores, but as NAPL piles up on the interface, capillary pressure increases and eventually the NAPL does invade the finer pores.
- 8) The greater pn is, the larger Pc is, and the more likely it is that the capillary pressure is high enough for DNAPL to invade pores and continue moving. Therefore, denser DNAPLs are more mobile.
- 9) At a given capillary pressure, water saturation is lower for a higher K material. The higher K material has larger pores and at a given Pc, more NAPL can invade the pores, displacing more water in the process.
- 10) Fax = -120 mg/day/m2, the flux through 15 m2 at this rate is $120 \times 15 = -1800 \text{ mg/day}$. The negative sign indicates flux in the negative x direction.
- 11) In this case, the retardation factor (see Eq. 11.11) for a reactive solute may be calculated with: $R = \Delta s$ chloride / Δs reactive solute where Δs is the distance traveled by the center of mass of the solute cloud. By manipulating Eq. 11.12, Kd may be calculated from R, n,

and ρb : Kd = (R – 1)n / ρb . Possible reasons for the differences include: 1) Diffusionlimited sorption that has greater affect at larger times, and 2) heterogeneity in the adsorptive properties of the materials such that the materials are more sorptive where the plume is after 350 days.

- 12) For this analysis, the retardation factor (see Eq. 11.11) for a reactive solute may be calculated with: $R = \Delta t$ reactive solute / Δt chloride where Δt is the time of the peak arrival. R values are smaller than those calculated in the previous problem. This is probably due to the fact that these data are closer to the source, which limits the effects of intragranular diffusion and introduces some error because the solute pulse occupied a finite volume, not a point, at its source.
- 13) It would be much higher in the peat because the fraction of organic carbon is so high. Organic carbon typically provides the bulk of sorption sites for nonpolar organic molecules (see section 10.9.2).
- 14) Use the following form of Eq. 10.77 to calculate Kd :
- Kd = (mg sorbed chemical / mg dissolved chemical)*($\rho b / \theta$). The ratio in parentheses can be inferred from the data of Figure 11.30, assuming that the sorbed mass = injected mass – mass in solution. Thus, mg sorbed chemical / mg dissolved chemical = 1–D / D where D is the ratio plotted in Figure 11.30. The Kd values calculated this way agree well with those calculated in Problem 11 for carbon tetrachloride and PCE, but not for bromoform. The bromoform Kd calculated this way is 2–4 times higher than the result calculated in Problem 11. This is most likely because bromoform was biodegraded significantly, and this lost mass is incorrectly attributed to sorption in this analysis.
- 15) Molecular diffusion can make a minor contribution to overall solute transport in a material where advective flux is much larger than diffusive flux. Examples include coarse gravels and porous basalts. However, molecular diffusion can still be an important transient solute transport process in materials with large advective flux, by moving solute mass in and out of low-K lenses, dead-end pores, etc.
- 16) A) $Fdx = 7.7 \times 10-6 \text{ mg/m2 /sec} = 0.66 \text{ mg/m2 /day}.$
 - b) Fax = 4500 mg/m2 /day.

c) The ratio Fax /Fdx \approx 6700; the advective flux is much larger than the molecular diffusion flux.

- 17) Fmx = 220 mg/m2 /day. Fmx /Fdx ≈ 330, Fax /Fmx ≈ 20. This transport is occurring in a sand where the dominant transport mechanisms are advection and mechanical dispersion caused by velocity variations (macrodispersion).
- 18) A zone of depressed O2 levels coincides with the core of the plume where there is the most active aerobic decomposition (respiration) of hydrocarbon solutes. There is elevated CO2 in the core of the plume near the source, probably the byproduct of respiration. Unlike the pattern of depressed O2, the pattern of elevated CO2 does not

persist in the downgradient portion of the plume. The CO2 is probably reacting with water to form bicarbonate (section 10.8.2).

- 19) In this case, there is only molecular diffusion and Dmx = Tx *D.
- 21) The average linear velocity of the chloride solute cloud from Figure 11.29 is v = 0.09 m/day. The dispersion coefficients are (m, day units): Dmx = $\alpha |v| = (0.36)(0.09) = 0.0324 \text{ m} 2 / \text{day}$, Dmy = $\alpha \text{th} |v| = (0.039)(0.09) = 0.0035 \text{ m} 2 / \text{day}$, Dmz = $\alpha \text{tv} |v| = (0.023)(0.09) = 0.0021 \text{ m} 2 / \text{day}$. The injected mass of chloride is M = 10, 700 g and the time is t = 462 days.
- 22) t= 21 yrs to dissolve away all the TCE. In an actual situation, the water flowing through the cylinder will probably leave with concentrations somewhat below the solubility concentration due to kinetic effects and irregular NAPL distributions, so F will be smaller than calculated and t will be larger than calculated.
- 23) A) The mass of NAPL per square meter is 37.0 kg, the mass of benzene per square meter is 591 g
 - b) caq = 37.2 mg/L
 - c) F = 18.6 g/yr
 - d) t = 31.8 yr

e) Benzene would persist longer than MTBE because MTBE's solubility is about 25 times larger than benzene's, which overwhelms the fact that there is about 4 times as much MTBE as benzene in the NAPL.

f) The calculation ignores biodegradation, which would accelerate disappearance of benzene. It also assumes that the mole fraction of benzene remains constant through time. The mole fraction actually evolves with time as NAPL constituents dissolve at different rates and degrade at different rates.