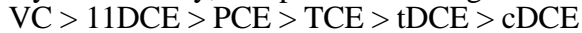


HW7 and 8 - CAC-Contaminated Site Remediation SOLUTION

1. [5 pts] Given the following reactor descriptions, state the order in which you believe the compounds would be removed from the system (fastest to slowest, each compound). justify your response, list the specific compounds, and distinguish biotic/abiotic losses

a. mono through tetra chlorinated ethenes from water in a stirred, open flask containing aerobic bacteria

in this case, losses can occur by both volatilization out of water and aerobic biodegradation based only on volatility, compounds with highest H will exit system first, therefore:

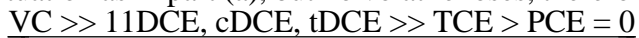


however, based on aerobic biodegradation, only VC can be used as a growth substrate, and the DCE's can be cometabolically degraded by the VC degraders; TCE has not been shown to be degraded under these conditions (without methane, phenol, etc. cosubstrate); PCE is NEVER aerobically degraded.

Therefore, propose: VC > 11DCE > tDCE > cDCE > PCE > TCE

b. mono through tetra chlorinated ethenes from water in a stirred, closed flask (to which oxygen is added) containing aerobic bacteria

same situation as in part (a), but no volatile losses, therefore:



c. a mixture of mono through tetra chlorinated ethanes in water (a stirred, closed flask to which oxygen is added, containing aerobic bacteria)

mono and dichloroethanes can be used as aerobic growth substrates, and commonly lower chlorinated compounds more readily degraded aerobically; therefore:



(assuming potential cometabolic aerobic degradation for 2-4 chloro ethanes)

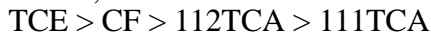
d. mixture of tetra chlorinated-methane, -ethene, and -ethanes in water in a closed, stirred flask with aerobic bacteria to which O₂, CH₄ supplied

fully chlorinated compounds NEVER aerobically degraded, therefore CT and PCE not potential for cometabolic degradation of TeCA's by methanotrophs, OB3b for example



e. mixture of trichlorinated-methane, -ethene, and -ethanes in water in a closed, stirred flask with aerobic bacteria to which O₂ and CH₄ supplied

based on the methanotroph OB3b, and that generally methanotrophs degrade ethenes faster than methanes, and sometimes ethanes:



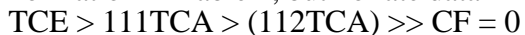
f. mixture of trichlorinated-methane, -ethene, and -ethanes in water in a closed, stirred flask with aerobic bacteria to which O₂, propane supplied

based on work by Keenan



g. a mixture of trichlorinated-ethanes, CF, and TCE in water in a closed, stirred flask containing anaerobic bacteria, and sulfate

given information in Table 4, but no rate data



2. [5 pts] An anaerobic continuously stirred-tank reactor (CSTR) is operated to treat PCE-contaminated water, and is at “steady state” conditions. The reactor contains a bioconsortia (mixed cultures of different anaerobic bacteria). Given the following information, predict the effluent concentrations of CACs from the reactor.

**total reactor volume = 2000-L; liquid volume = 1800-L
(gas collection system attached)**

reactor solids retention time = hydraulic retention time = 20 days

total biomass concentration = 1000 mg/L; Temp. 30 °C

Influent Water 80 L/day containing 0.2 mg/L PCE

Add liquid to reactor at 10 L/d containing nutrients and organic substrates glucose, acetate, benzoate, phenol, methanol

Biokinetics for each reductive dechlorination, 30°C, K mg/g-d, Ks mg/L:

PCE K 0.035, Ks 0.01; TCE K 0.035, Ks 0.01; cDCE K 0.020, Ks 0.02; VC 0.015, 0.04

Assume no volatilization losses of CACs, and biosorption of CACs not significant
Assume that the organic substrates and bioconsortia generate the necessary Hydrogen pool needed for electron donor to drive the reductive dehalogenation reactions

At steady state, assuming no competition, do a mass balance for PCE:

inflow - outflow - biodegradation = 0

$(0.2 \text{ mg/L} * 80 \text{ L/d}) - (P * 90 \text{ L/d}) - (KPXV/Ks + P) = 0$

where P is conc of PCE in CSTR; K, Ks are PCE biokinetics; V = liq vol; X = bio

substitute known values leaves P as only unknown, rearrange to get in quadratic form and solve for P: P = 0.0033 mg PCE/L effluent

Then the mass balance for TCE (which is formed from PCE biotransformation):

formation rate - degradation rate - outflow = 0

$(KPXV/Ks + P)*(MW \text{ TCE}/MW \text{ PCE}) - (KTXV/Ks + T) - (T * 90 \text{ L/d}) = 0$

where TCE formation rate = PCE degradation rate, when corrected for the 1:1 conversion on a MOLAR basis using the molecular weights (MW) of each compound

(therefore PCE K and Ks in formation equation)

TCE degradation rate uses TCE K and Ks

T only unknown, rearrange to quadratic form and solve: T = 0.0024 mg/L effluent

Using same procedure for cDCE and VC, get:

D = 0.0062 mg DCE/L, M = 0.0084 mg VC/L

(but, since the CACs quite volatile, significant partitioning out of liquid would likely occur) also, there may be some inhibition between the compounds

if inhibition between the compounds (competing electron acceptors) is considered, the effluent concentrations will increase. The greatest increases will occur in the DCE and VC effluent concentrations, since these compounds have higher Ks values and will be more strongly effected by competition than the compounds with lower Ks values (lower enzyme affinity).

Approx. concs with competition: 6, 6, 22, 33 µg/L PCE, TCE, DCE, and VC, respectively

3. If a sequential anaerobic : aerobic treatment scheme was used to treat the waste stream from Question 2, what system SRT could be used in the anaerobic part, and size the aerobic CSTR reactor (size and SRT). Assume a cosubstrate is added to the aerobic reactor to serve as an enzyme inducer and growth substrate (what, how much added?). Assume that all CACs must be less than EPA MCL drinking water standard in the final effluent. also: write any assumed biokinetics used in your calculations

1. CAC effluent standards are 5 µg/L for PCE, TCE, 70 µg/L cDCE, 2 µg/L VC therefore, from previous anaerobic alone, VC is too high
2. PCE can only be degraded anaerobically; if set effluent at 4.5 µg/L what is biomass and reactor volume needed? assume same biokinetics as from Question 2
 $16 \text{ mg/d influent} - 0.405 \text{ mg/d effluent} = \text{biodegraded } 15.6 \text{ mg/d}$
 $15.6 \text{ mg/d} = K_S X V / (K_S + S) = 0.035 * 0.0045 * X V / 0.0145 \Rightarrow X V = 1436 \text{ mg bio}$

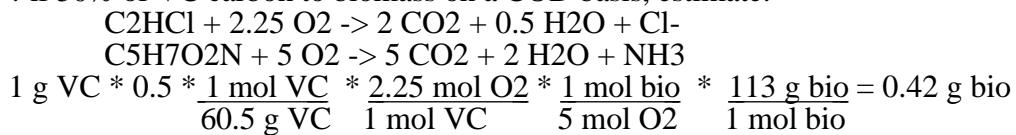
if assume that biogrowth on fed substrates stays the same, previously:
 $\text{growth} = \text{loss} = 1 \text{ g/L} * 90 \text{ L/d} = 90 \text{ g/d}$, with total biomass in system of 1800 g
 now: $\text{growth} = \text{loss} = 90 \text{ g/d} = 90 \text{ L/d} * X \Rightarrow 1 \text{ g/L}$
 then $V = 1436 \text{ L}$, can have smaller reactor! SRT = 16 days

IF 4.9 µg/L, then: $V = 1350 \text{ L}$, SRT = 15 days \Rightarrow reactor is 75% of original size :)

3. Calculate effluent TCE, DCE, and VC concentrations from anaerobic reactor assuming final scenario of 15 d SRT and 1350 L liquid volume, using same method used in Q2
 $\text{PCE} = 4.91 \text{ µg/L}$ less than 5 µg/L std
 $\text{TCE} = 3.41 \text{ µg/L}$ less than 5 µg/L std
 $\text{cDCE} = 8.57 \text{ µg/L}$ less than 70 µg/L std
 $\text{VC} = 10.66 \text{ µg/L}$ exceeds 2 µg/L std !

These are the influent concentrations to the aerobic reactor

4. Since only VC exceeds the DW std, only VC degradation in the aerobic reactor would be needed. VC can serve as a growth substrate for some bacteria, so seed these into the reactor. Assume biokinetics of VC $K = \text{growth substrate}$, assume 0.5 mg/mg-d, $K_S = 0.2 \text{ mg/L}$,
 $\text{yield} = ?$ if 50% of VC carbon to biomass on a COD basis, estimate:



then $Y = 0.42 \text{ g bio / g VC}$ (estimate)
 assume $k_d = 0.01 \text{ /d}$ (typical for endogenous cell death)

write mass balances:

where $M = \text{conc mono-chloroethene (aka VC)}$; unknown = X, V ,
 $(M = 1.8 \text{ µg/L}$ which meets MCL effluent requirement)

for biomass:

$$\begin{aligned} \text{growth on VC} &= \text{loss due to wasting} + \text{endogenous decay} \\ \text{biodeg VC} * Y &= X * 90 \text{ L/d} + X * k_d * V \\ \text{MKXV}/(K_S+M) * Y &= 90X + 0.01XV \\ & \text{(assume endogenous decay negligible at this stage, then...)} \\ \text{AND } \text{MKXV}/(K_S+M) &= 90X/Y \end{aligned}$$

combining two equations:

$$3.294 \text{ mg VC/d} = 90 \text{ L/d} * X / 0.42 \text{ mg bio/mg VC}$$
$$X = 0.01537 \text{ mg/L} <- \text{this is VERY low!! but so little VC substrate!}$$

solve for the reactor volume:

$$0.0018 \text{ mg/L} * 0.5 \text{ mg/mg-d} * 0.01537 \text{ mg/L} * V / (0.2 \text{ mg/L} + .0018 \text{ mg/L}) = 3.294 \text{ mg/d}$$
$$6.8548 \times 10^{-5} * V = 3.294 \text{ mg/L}$$
$$V = 48,054 \text{ L} !!! \quad 48 \text{ m}^3 \leq \text{TOO BIG! (even larger if endogenous decay included)}$$

Therefore, must use co-substrate to increase biomass so a smaller reactor can be used!

Options: methane, propane, ammonia

Assume use methane

Biodegradation kinetics of CACs by methane-oxidizing filament (some intermediate toxicity from TCE degradation, also competition between CACs and CACs vs methane):

Biokinetics, based on OB3b work by Tsien and others, VC and cDCE degraded faster than TCE. If temp still 30°C from the anaerobic reactor:

$$\text{TCE } K = 3.8 \text{ mg/mg-d}, K_s = 3.8 \text{ mg/L (mixed TCE deg, Chang/Alv-Cohen)}$$
$$\text{cDCE } K = 4 \text{ mg/mg-d}, K_s = 3 \text{ mg/L (estimated)}$$
$$\text{VC } K = 4 \text{ mg/mg-d}, K_s = 3 \text{ mg/L (estimated)}$$
$$\text{Methane } K = 2 \text{ g/g-d (from 1 g/g-d at 20°C)}, K_s = 0.5 \text{ mg/L}, Y = 0.4 \text{ g cells/gCH}_4$$

First, assume TCE competition and intermediate toxicity negligible since concentration is so low.

Then, degradation rate of VC, in mass per time:

$$M * K V X / (K_s I + M), \text{ where } I = 1 + S / K_s + D / K_s$$

S = substrate conc, methane; K_s for respective compounds

at worst case, D will be 0.0086 mg/L, and we need VC to be approx. 0.0018 mg/L
BUT S (methane conc) is not known!

Therefore, too many unknowns!

SELECT a Reactor Liquid Volume = 900 L, therefore SRT is 10 days

Estimate a methane concentration in the liquid of 0.5 mg/L

Solve for X:

$$\text{VC Mass Balance: } \text{VC in} - \text{VC out} - \text{VC biodegraded} = 0$$
$$(0.01066 \text{ mg/L} - 0.0018 \text{ mg/L}) * 90 \text{ L/d} - X * \text{deg VC} = 0$$
$$\text{VC biodeg} = X * 0.0018 \text{ mg/L} * 4 \text{ mg/mg-d} * 900 \text{ L} / (3 * I + 0.0018)$$
$$I = 1 + (0.0086/3) + (0.5/0.5) = 2.003$$
$$\text{VC biodeg} = X * 1.078$$

$$\text{AND } 0.7974 \text{ mg VC/d} - 1.078 * X = 0 \quad \Rightarrow X = 0.74 \text{ mg/L (VERY LOW)}$$

Due to low biomass, try a 5 day SRT = 450 L liquid reactor, then X = 1.48 mg/L bio

Again, quite low, try a 2 day SRT = 180 L liquid reactor, then X = 3.7 mg/L bio

How much methane needed to get this amount of biomass?

bio growth on methane = washout + endogenous decay

$$Y * \text{biodeg methane} = (90 \text{ L/d} * 3.7 \text{ mg/L}) + (0.01/\text{day} * 3.7 \text{ mg/L} * 180 \text{ L})$$

$$\text{biodeg methane} = 2 \text{ mg/mg-d} * 0.5 \text{ mg/L} * 3.7 \text{ mg/L} * 180 \text{ L} / (0.5 * I + 0.5)$$

$$I = 1 + 0.0018/3 + 0.0086/3 = 1.005, \text{ negligible CAC effect on methane}$$

$$\text{Biodeg methane} = 666 \text{ mg/d}$$

$Y * 666 = 340 \Rightarrow$ if $Y = 0.51$, then OK, and this is reasonable Y !

Amount of methane needed = $666 \text{ mg/d} = 0.7 \text{ g/d}$, can use methane in air to supply both methane and oxygen needed to the reactor

Due to explosion risk, 5% methane in air \Rightarrow

$1 \text{ L air} * 0.05 \text{ CH}_4/\text{air} * 1 \text{ mol CH}_4/24.6\text{L} * 16 \text{ g/mol} = 0.0325 \text{ g CH}_4/\text{L air}$

$0.7 \text{ g/d} / 0.0325 \text{ g/L air} = 21.5 \text{ L air/day}$ supplied to 180 L reactor, significant stripping losses

With very low VC concentrations, could be more cost effective to air strip and treat off gas with activated carbon!

4. A plume of CAC-contaminated groundwater exists below a former “evaporation pit” into which used solvents were disposed. Assuming that the plume contains the “full spectrum” of CACs, propose further sampling/site characterization and a **conceptual** strategy to minimize the risks posed by the site (address each contaminated media; justify your design in terms of advantages over alternatives). Basic site map and available data below:

Water Table Aquifer: lab permeameter test with water found $K = 80 \text{ cm/d}$;
dry specific gravity of soil solids = 2.5; porosity 0.5

	SV-1	SV-2	SV-3	SV-4	SV-5	SV-6
5' TVH, mg/L	0	42	48	5	2	0
% O ₂	20.5	6	7	12	11	17
% CO ₂	0.5	11	12	5	6	1
% CH ₄	0	0	0	0	0	0
% H ₂ S	0	0	0	0	0	0
*TH, g/g	0	0.056	0.058			
15' TVH, mg/L	0	45	52	12	15	8
% O ₂	20	0	0	5	4	14
% CO ₂	0.5	15	16	10	11	2
% CH ₄	0	0	0	0	0	0
% H ₂ S	0	1	1	0	0	
*TH, g/g	0	0.048	0.046			0

Lower Aquifer: porosity 0.3, dry specific gravity of soil solids = 2.5
time for tracer compd to get from GW2 to GW3 = 2 yrs

	GW1	GW2	GW3	GW4
Water level, ft bgs	19.70	20.00	20.15	20.37
TH, mg/L	0	10,000	10,000	3000
DO, mg/L	4	0.2	0.1	0.0
NO ₃ , mg/L	40	41	40	39.5
SO ₄ , mg/L	250	250	251	249
Redox, V	0.7	0.2	0.1	-0.25
*TH, g/g dry soil	0	0.060	0.030	0.002

* based on soil sample taken during monitoring well construction;
TH = total hydrocarbons in g mass/g dry soil; will include “intrapore” NAPLs

a. List three PRIMARY potential risk pathways associated with the site (remember: pathway consists of source, release, travel, receptor, exposure) Justify your response as necessary

surface soils contaminated with sorbed CACs -> volatile losses to air -> migration in air -> inhalation by workers at the industrial site and people doing on-site sampling,

soils contaminated with sorbed CACs and residual NAPLs in vadose zone -> direct on-site dermal contact by people involved in on-site activities

surface soils contaminated with sorbed CACs -> become wind-borne particulates -> transported off-site by wind -> dermal contact by children in nearby neighborhoods

DNAPLs which have migrated down to the Lower Aquifer serve as source of dissolved contaminants to groundwater -> gw migrates to city drinking water wells -> volatilization of compounds into air during water treatment processes -> inhalation by workers at the DW tmt plant

DNAPLs which have migrated down to the Lower Aquifer serve as source of dissolved contaminants to groundwater -> gw migrates to city drinking water wells -> city residents ingest the CACs by drinking the water

others also possible...

b. List the contaminated phases where remediation must be considered.

contaminants sorbed to soil in the vadose zone, and aquifer material in the saturated zone (also the clay in the impermeable layer)

contaminants present in the soil gas

contaminants dissolved in the water in the unsaturated zone, and water table aquifer, and potentially in the Lower Aquifer

residual pure phase DNAPL trapped in the soil pores in the vadose zone, also residual within the saturated zone, and also “potential pools” (pores saturated with DNAPL) on the clay lens or on the bedrock.

c. How will your selected strategy address each of these phases?

d. Conceptual design should include approximate well locations, substrates or nutrients added and approximate amounts, monitoring frequency, etc.

** There were two general approaches to this problem:

1. Using what we have learned in class about biodegradation and looking at the site data, determine if some intrinsic bioremediation is occurring. Then determine whether it is worthwhile to attempt to enhance these processes, through bioventing, biosparging, etc. However, this strategy will only address the volatilized contaminants in the vadose zone (and to some extent sorbed compounds on the soil) and the solubilized compounds in the groundwater. Your discussion should include some mention of the possibility of DNAPLs, and if present that these remedial strategies will not address that problem.

from approximate radius of influence, a single air extraction well sunk into the center of the former pit and screened in the vadose zone from 5' to 19' bgs could be used for bioventing (either air injection or air extraction; with off-gas treatment if air is extracted)

due to migration of contaminants down-gradient in the groundwater and smaller radius of influence of an air injection well in the saturated zone, may need two air injection wells. screen in the upper aquifer from 29' to 39' bgs.

we are currently unsure of contamination in the lower aquifer. Therefore, need to sample groundwater and soil there, with the particular goal of looking for DNAPL. Also, sampling directly on top of clay lens to look for a DNAPL pool. Additional wells located: near center of former pit (by GW well 2) screened at 37' to 39' bgs and another screened at 55' to 65' bgs (when drilling deep well must be careful not to provide a point for downward migration through the clay lens!). Also a deeper well near well3 at the down-gradient edge of the pit (screened 55'-65' bgs).

along with the air injection (in the sat and unsat zone if used), more monitoring is necessary to ensure no off-site migration of contaminants. Therefore, bot monitoring

points are needed. These could be vadose-zone gas sampling points screened just above the water table (16' to 19' bgs) around the perimeter of the former pit (on N, W, and S side).

Due to likely presence of DNAPLs as a continuous source of contamination, would likely need a series of cut-off wells or a bioreactive barrier to control and/or intercept contaminated groundwater. Some form of surface treatment of this extracted water would be necessary.

2. Using the fact that DNAPLs are present and would serve as a continual source of contamination, determine that remediation of the site itself is not feasible. Therefore, attempt to "remove the source", by excavation of highly contaminated areas in the pit and using barriers to prevent groundwater migration through the contaminated area. (this approach is something that would likely have been learned in a hazardous waste class).

Cap area to prevent infiltration through contaminated soils...

5. [3 pts] A surface spill of 50 gallons pure PCE and TCE mix (50% each) occurs on the ground surface. The ground is bare sandy loam, the season is rainy with some site run-off and some infiltration. Soil permeability (k-horiz) calculated from a liquid constant-head permeameter test is 1 darcy (assume vertical permeability 80% of the horizontal permeability, therefore 0.8 darcy). The total porosity of the aquifer (both above and below water table) is 0.3. The typical water saturation in the vadose zone is 20%. The groundwater table varies seasonally between 15' to 18' below ground level. The hydraulic gradient (dh/dl) is 0.001 m water head/m horizontal distance. At 30 ft below ground level is a bedrock formation. The average temperature of the subsurface varies from 5°C to 15°C.

Considering the fate and partitioning between different phases, estimate:

- what will be the concentration of compounds in the subsurface 1 month after the spill?
- what will be the concentration of compounds in the subsurface 1 year after the spill?

Both TCE and PCE are DNAPLs and will migrate down into the subsurface. The total mass of each compound spilled which must be accounted for is:

$$25 \text{ gallons PCE} * 3.785 \text{ L/gal} * 1.63 \text{ kg/L} = 154.24 \text{ kg PCE}$$

$$25 \text{ gallons TCE} * 3.785 \text{ L/gal} * 1.46 \text{ kg/L} = 138.15 \text{ kg TCE}$$

(assuming that at the ground surface at the time of the spill the NAPLs were 25°C).

When the material is spilled on the surface, the immediate fate will be:

- * some volatilization from the pure compound to the air
 - speed of volatilization will depend on temperature, surface area, wind speed
 - in addition, the “equilibrium” vapor pressure and H of the compounds
 - * some will “run-off” over the ground surface dissolved in the rainwater
 - speed of “dissolution” into rain runoff dependent on temperature, rainfall time and quantity, water characteristics, water:NAPL interfacial area, ...
 - in addition, the equilibrium solubility of the compounds
 - * some of the compounds will dissolve into the rainwater and infiltrate into the subsurface
 - * some of the compounds will sorb to the surface soil
 - * some pure DNAPL will penetrate into the soil
 - penetration will depend on temperature, viscosity of NAPL, density of NAPL, pore structure of the soil, ...
 - and of this DNAPL some will remain trapped as ganglia in the unsaturated zone,
- some of the compounds will sorb to the soil, DNAPL will eventually migrate to the water table, saturated zone, and bedrock unless it is fully trapped at residual saturation in the vadose zone
- * some of the compounds may be transformed
 - primary process likely anaerobic degradation of PCE and TCE, but will only occur in an anaerobic zone in the subsurface (therefore, unlikely to be significant biotransformation on the surface or in the vadose zone)

AFTER 1 MONTH...

For this case, the “equilibrium” partitioning behavior of the compounds is less critical than the rate of partitioning.

in this case, estimate the vertical penetration “NAPL conductivity”

$$K_{\text{-pce}} = k * \frac{\rho_w}{\mu} = 0.8 \times 10^{-8} \text{ cm}^2 * 1.63 \text{ g/cm}^3 * 981 \text{ cm/s}^2 / 0.009 \text{ g/cm-s} \\ = 0.00142 \text{ cm/s} = 122.8 \text{ cm/d} \Rightarrow 3684 \text{ cm/month} = 36.84 \text{ m/mo}$$

but also consider: “head”

for Darcy’s Law the velocity is $K * dh/dl$

vertical head gradient in the unsaturated zone -> related to capillary forces and amount of pooling on the ground surface => if assume 2 cm deep ~ 0.004 m/m,
 then max velocity ~ 0.15 m/mo (if fully saturated pores) => max penetration 150 cm
 therefore, will not reach water table within the first month

“spread” horizontally of contaminants and retention of NAPL in the pores will also effect location of DNAPL after 1 month.

assuming saturated pores in the vadose zone, such that all the air and none of the water are displaced from the soil, then:

$$0.8 * 0.3 = 0.24 \text{ L NAPL per L soil}$$

and if assume that PCE and TCE are comingled and maintain a 50:50 volumetric ratio, then can determine the amount of soil volume which would be saturated with DNAPL

Significant surface losses of DNAPL mass from volatilization and run-off would likely occur, however, to be conservative assume all DNAPL penetrates into ground and that no pool of DNAPL remains on the surface, then:

$$50 \text{ gallons} = 189 \text{ L DNAPL} / 0.24 \text{ L DNAPL per L soil} = 790 \text{ L contam soil}$$

To determine vertical depth of DNAPL must assume a “surface spill area”:

Pool Depth, cm	Area, m ²	Depth of DNAPL, cm
1	18.9	4.2
2	9.45	8.4
4	4.725	16.7

all of these are within the theoretical “max vertical depth” based on the velocity calc. Therefore, all of the contamination will be in the vadose zone.

Also, these calculations assumed that most of the mass of PCE and TCE were associated with the pure phase, rather than sorbed, dissolved, or volatilized.

When these other phases are taken into account:

$$\text{per unit volume of soil: } 0.3 * 0.2 = 0.06 \text{ L water per L vadose zone}$$

Rauolt’s Law: sol TCE = X * Indiv Sol

$$\text{TCE} = \text{L TCE} * 1.46 \text{ g/mL} / 131 \text{ g/mol} = 11.145 \text{ mol TCE/L}$$

$$\text{PCE} = \text{L PCE} * 1.63 \text{ g/mL} / 165 \text{ g/mol} = 9.88 \text{ mol PCE/L}$$

$$X\text{-tce} = 11.145 / (11.145 + 9.88) = 0.53$$

$$X\text{-pce} = 1 - 0.53 = 0.47$$

$$C\text{l-tce max} = 0.53 * 1100 \text{ mg/L} = 583 \text{ mg/L TCE in vadose zone pore water}$$

$$C\text{l-pce max} = 0.47 * 150 \text{ mg/L} = 70.5 \text{ mg/L PCE in vadose zone pore water}$$

$$\text{per unit volume of soil: } 0.7 \text{ L soil} * 2.5 \text{ g/mL (assumed specific gravity of solids)} \\ = 1.75 \text{ kg solids per L vadose zone}$$

$$\text{if } 1\% \text{ foc, then } K_p = \text{foc} * K_{oc} = 0.01 * 364 \text{ mL/g} = 3.64 \text{ mL/g for PCE}$$

$$= 0.01 * 126 \text{ mL/g} = 1.26 \text{ mL/g for TCE}$$

$$K_p = \text{Conc Soil/Conc Water}$$

use above liquid concs and K_p to get sorbed quantities

$$C\text{s-tce} = C\text{l} * K_p = 583 \text{ mg/L} * 1.26 \text{ mL/g} = 0.735 \text{ mg TCE/g soil}$$

$$C\text{s-pce} = C\text{l} * K_p = 70.5 \text{ mg/L} * 3.64 \text{ mL/g} = 0.257 \text{ mg PCE/g soil}$$

Soil Vapor Concentrations - “around” DNAPL-contaminated vadose zone

$$C_{g-tce} = H * C_l = 0.35 * 583 \text{ mg/L} = 204 \text{ mg/L}$$

$$C_{g-pce} = H * C_l = 0.51 * 70.5 \text{ mg/L} = 36.0 \text{ mg/L}$$

mass in the “non-NAPL” phases is by comparison negligible

After 1 year, the DNAPL has likely migrated its maximum extent. Assume that the vadose zone soils are now at the “residual saturation” of DNAPL, determined by the trapping of the NAPL in the soil pores. Will any contamination have reached the water table?

Area, m ²	Resid. Sat, %	Depth DNAPL, m -> ft	
18.9	10	0.416	1.36
	5	0.83	2.73
	2	2.08	6.82
9.45	10	0.83	2.73
	5	1.66	5.46
	2	4.15	13.6
4.725	10	1.66	5.46
	5	3.32	10.9
	2	8.30	27.3

Therefore, only in the most conservative scenario tested did the DNAPL penetrate into the saturated zone. Residual saturation in the saturated zone is less than in the vadose zone due to the necessity to displace water which is the wetting fluid and therefore preferred.

Given the final scenario of 4.725 m² area and 2% resid sat in vadose zone, if the water table is at 15' deep, then 55% of the DNAPL is in the sat zone -> 104 L DNAPL
 if the residual saturation in the sat zone is then 1% (less than vadose zone)
 0.0024 L DNAPL per L soil -> 43.3 m³ contam sat soil -> 9.16 m deep = 30 ft
 since the “sat zone” only extends 15', this indicates that a pool of DNAPL will exist on the bedrock formation which consists of approx. 52 L DNAPL

Note that based on your assumptions for spill area and residual saturation of DNAPL, you may predict that the DNAPL doesn't reach the water table...or that it fully penetrates through the saturated zone and pools on the bedrock. Significantly different answers! This further neglects subsurface heterogeneity that may result in pools on lower permeability lenses.

FINALLY, BASED ON THE ABOVE DISCUSSION THE UNCERTAINTY OF PREDICTING THE FATE OF CONTAMINANTS IN THE SUBSURFACE WHEN DEALING WITH DNAPLS IS CLEAR!

6. [2.5 pts] Given the following table of information, fill in the specified blanks. Assume a 1-L CSTR, with inflow 100 mL/d containing 2 mg/L TCE concentration.

Substrate	Phenol	Propane
Active Biomass, mg/L	200	190
Substrate Fed, mg/d	<u>46</u>	XXXXX
Substrate Conc, mg/L	1	<u>1.3</u>
Substrate K, g/g-d	0.41	0.25
Substrate Ks, mg/L	0.80	0.05
Substrate Y*, g/g	0.55	0.6
TCE Conc, mg/L	0.1	0.3
TCE K, g/g-d	0.5	0.45
TCE Ks, mg/L	<u>23.3</u>	5.22
Tc, g TCE/g bio	<u>0.036</u>	0.0065
Ty, g TCE/g substrate	0.02	<u>0.0039</u>

* this is "observed yield" which includes endogenous decay loss of cells

First, it is easy to calculate Tc or Ty using the formula:

$$T_y = T_c * Y$$

Next, calculate Ks for TCE from a mass balance for TCE and the competitive inhibition Michaelis-Menten Equation:

$$\text{Inflow} - \text{Outflow} = \text{Biodegradation}$$

$$(2 \text{ mg/L} * 0.1 \text{ L/d}) - (0.1 * 0.1 \text{ L/d}) = K_S X V / (K_S I + S)$$

$$I = 1 + \text{conc phenol} / K_S \text{ phenol} = 1 + 1 / 0.8 = 2.25$$

$$0.19 \text{ mg/d} = 0.5 * 0.1 * 200 * 1 / (K_S * 2.25 + 0.1)$$

$$K_S = 23.3 \text{ mg/L}$$

Similar procedure used to find the Substrate concentration with the propane bacteria, by using the competitive inhibition equation for TCE.

$$\text{Inflow} - \text{Outflow} = \text{Biodegradation}$$

$$(2 \text{ mg/L} * 0.1 \text{ L/d}) - (0.3 \text{ mg/L} * 0.1 \text{ L/d}) = K_S X V / (K_S I + S)$$

$$I = 1 + P / 0.05 \text{ where } P = \text{propane concentration in reactor (and effl. fr. reactor)}$$

$$0.17 \text{ mg/d} = 0.45 * 0.3 * 190 * 1 / (5.22 * I + 0.3)$$

$$P = 3.75 \text{ mg/L}$$

Finally, found out how much phenol must be fed to achieve the stated biomass conditions in the reactor :

Total phenol = phenol to grow cells wasted per day + phenol to grow cells killed by TCE toxicity per day

$$= QX/Y + (TCE_{in} - TCE_{out})Q/T_y$$

$$= 0.1 \text{ L/d}(200 \text{ mgBio/L}) / 0.55 \text{ gBio/g phe} + (2-0.1)\text{mgTCE/L} * 0.1\text{L/d} / 0.02 \text{ gTCE/g phe}$$

$$= 36.36 \text{ mg phenol/d} + 9.5 \text{ mg phenol/d}$$

$$= 45.9 \text{ mg phenol/d}$$

Alternatively, a mass balance could be done on phenol, and should give the same value.