

1.725 Chemical Fate and Transport in the Environment

Quiz #2

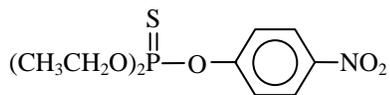
Dec. 14, 2004 9am-12am.

1) (15 pts) Wind from over the ocean has a temperature of 17 degrees C and a relative humidity of 85 %. Orographic effects direct this air to rise to a maximum altitude 2500 meters, after which it descends to an altitude of 500 meters on the lee side of the coastal mountains.

a) If this is typical of average conditions, at what altitude do you expect to see the beginning of the rainforest on the windward side of the mountain range?

b) What is the temperature of air as it reaches the 500 meter level in the desert located on the lee side of the mountains?

2) (10 pts) The tanker Ever Reward is leaking its cargo of the pesticide Parathion. The attending Coast Guard official (who has taken a few environmental science classes) says not to worry about the pesticide; it will undergo hydrolysis in the water and be degraded within a few weeks. The company representative says not to worry, photolysis will quickly degrade the pesticide. Does either (or both) mode of degradation seem likely, based on the chemical structure of Parathion? (explain)



Parathion

3. (15 pt) The compound, dichloromethylacetate, $\text{Cl}_2\text{CHCOOCH}_3$, undergoes hydrolysis with rate constants as follows: k_a is $2.3 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$, k_n is $1.5 \times 10^{-5} \text{ s}^{-1}$, and k_b is $2.8 \times 10^{+3} \text{ M}^{-1}\text{s}^{-1}$.

a) What is the hydrolysis half-life of dichloromethylacetate in water at pH 7.8?

b) A mole of the compound, together with a mole of a tracer, sodium bromide, are spilled into a canal whose average velocity is 0.91 m/s (3 ft/s) and discharge is $0.84 \text{ m}^3/\text{s}$ ($30 \text{ ft}^3/\text{s}$). If the Manning coefficient is .020 and width is 3 m (10 ft.), determine the slope of the rectangular channel. (note- this Manning coefficient of 0.20 works with the traditional engineering units, not SI units)

c) What is u^* for the canal?

d) What are maximum bromide and dichloromethylacetate concentrations expected 0.5 km downstream, assuming pH = 7.8?

4. (15 pt) An aquifer cleanup program requires that you design a well that will create a hydraulic gradient of 0.009 at a distance of 45 m from the well at steady state. Assume a radius of influence of 200 m. (This gradient will assure the capture of a cloud of perchloroethylene.)

a) What is the necessary pumping rate of the well, if aquifer transmissivity is $15 \text{ m}^2/\text{day}$ and aquifer thickness is 16 m?

b) The simple form of the Theim equation assumes that drawdown is small everywhere compared to saturated zone thickness. In this case you have decided to use an eight-inch-diameter (20 cm) well. What is calculated drawdown at the radius of the well casing?

c) Your objective is to clean the aquifer of perchloroethylene (sometimes called perc, or PCE). Consider that the organic content of the soil is 1.2%, and $\log K_{ow}$ of PCE is 2.88. How long will it take perchloroethylene to reach the capture well? Express as a ratio relative to the time it would take if instead of perc the contaminant were sodium bromide, which is often used as a conservative tracer in groundwater studies. Assume reasonable values for any aquifer parameters that may be needed and are not given.

5) (15 pt) Carbon disulfide (CS_2) is released to the air in the process of rayon manufacturing. Due to the toxic nature of carbon disulfide, the Occupational Safety and Health Administration (OSHA) has set a limit of CS_2 concentration in the air of 20ppm(v). A local rayon plant steadily releases 220 kg CS_2 per year to the indoor air. Knowing that CS_2 degrades by reaction with OH radical, the owner of the plant considers adding OH radical (produced photochemically on-site) to the factory air to keep the concentration of CS_2 below the OSHA standard.

a) Given a second order rate constant of OH radical with CS_2 of $2.9 \times 10^{-12} \text{ cm}^3 / (\text{molecule} \cdot \text{sec})$ and a factory volume of 3800 m^3 , how much OH radical (expressed in molecules/ cm^3) must be maintained in the factory air to meet the OSHA standard for CS_2 in the factory air? The density of CS_2 in air is 3.12 kg/m^3 .

b) Can you think of any possible adverse effects of the CS_2 control strategy? If so, please explain.

6) (15 pts) You are chief biologist aboard a research submarine, and are observing a rare giant squid. Unfortunately, however, the sub's cryogenic air purifier has failed, and the partial pressure of CO_2 in the air of the sub has risen to 10^{-3} atm . The captain is ready to surface, but you do not want to cut short this exciting mission.

The chief chemist has an idea - she will pour strong base into the bilge water, and this water will then absorb CO_2 from the air.

There are 500L of somewhat acidic (pH 5) bilge water sloshing around in the ship. The chemist begins to pour in Liquid Drano (a strong solution of NaOH used by plumbers to clean pipes) until the pH rises to 8.3. She will maintain this pH by adding Drano until it is all used up.

a) Assume the bilgewater is in equilibrium with the air. Given $PCO_2 = 10^{-3}$ Atm, what is $[H_2CO_3^*]$?

b) What is $[H_2CO_3^*]$ immediately after raising the pH to 8.3 (note that the acid-base chemistry is very fast)?

c) As carbon dioxide dissolves, the pH drops, requiring more Drano to be added. A total of 15 moles of NaOH are added before it runs out, pH starts to drop, and PCO_2 rises again. It's time to abandon the squid and surface the ship. What is C_T at this time? (assume pH is 8.3 and air is nearly in equilibrium with the bilge water).

7) (10 pts) A 10-g (dry weight) mouse is accidentally bottled in a 25-liter jug of spring water that initially contains 10 mg/liter of O_2 . Assume that 70% of the mouse's dry weight is CH_2O .

a) Write the relevant reaction for O_2 consumption.

b) Does the jug become anaerobic?

c) If 2 ppm NO_3^- (mol. wt = 62) and 15 ppm SO_4^{2-} (mol. wt = 96) are in the spring water, how much NO_3^- and SO_4^{2-} will be left when the jug reaches equilibrium?

8) (10 pts) Benzene, at an initial concentration of 10^{-4} mol/L, undergoes aerobic biodegradation in river water. Given a density of benzene-degrading bacteria of 10^5 cells/ml, a V_{\max} of $10^{-15} \frac{\text{mol}}{\text{cell} \cdot \text{s}}$, and K_s of $7.8 \times 10^{-2} \frac{\text{mol}}{\text{L}}$, estimate the initial rate of benzene degradation.

9) (15pts) A certain residential home has a typical air change rate (ACH) of 0.45/hour during the winter heating season. Due to seepage of radon through the basement floor and walls, the wintertime radon concentration averages 3.1 pCi/L, below EPA's action level of 4 pCi/L.

a) What fraction of the radon atoms entering the house are lost to the outdoors before they undergo radioactive decay? Radon has a half-life of 3.8 days.

b) The residents of the house are persuaded by Homeland Security announcements to seal off one bedroom of the house using duct tape and sheets of plastic. By doing this, they decrease the ventilation rate of the bedroom to 0.1 ACH. Bedroom volume is 28 cubic meters. Assume that the radon source strength to the bedroom, expressed in pCi per hour per unit volume of indoor space, is not changed by this action. What is the new steady-state radon concentration in the bedroom's air?

c) Guests are visiting, and the plastic-sealed bedroom is to be used as a guest room. However, the room is now too cold because the heating ducts have been sealed off with plastic, so a small kerosene heater is put in the room. This heater uses 200 grams of fuel per hour (assume it is $C_{12}H_{26}$), and is fairly clean-burning; only 0.1 % of the carbon atoms in the fuel are released as CO, the rest being burned to carbon dioxide. What is steady state CO concentration in the room with the heater is turned on?

10) (15 pts) An offshore oil platform is venting natural gas (assume it is all methane) at a rate of 150 L/sec through a stack with diameter 15 cm at a height of 45 meters above the sea. The wind is blowing at 4 m/s. Because the ocean is relatively cool, the atmosphere can be regarded as having neutral stability despite the strong sunlight.

a) Neglecting plume rise, what is methane concentration 500 meters downwind i) at sea level, and ii) 50 m above the water?

b) A helicopter is ferrying oil workers to the platform. A spark plug wire is loose on the engine, making the aircraft a possible source of ignition (thanks to dual ignition, the engine is running fine). The helicopter approaches the oil platform from directly downwind, coming to within 100 m of the platform. Is this safe, or could the plume ignite? The lower flammability limit of methane in air is 5%.

c) (Extra Credit) Estimate plume rise at 100 m downwind. Note that the expression

$\left[\frac{T_s - T_a}{T_s} \right]$ can be thought of as a measure of density relative to air. (i.e., $\rho_{air} \propto \frac{1}{T_{air}}$):

thus for the dimensionless quantity $\left[\frac{T_s - T_a}{T_s} \right]$ you can use $\left[\frac{1/\rho_{gas} - 1/\rho_{air}}{1/\rho_{gas}} \right]$

In the case of methane (mw=16), the difference in density arises not from the temperature but molecular weight. The net result, though, is still buoyant plume rise. (Hint- density of the gas is proportional to its molecular weight. Air has average molecular weight of about 29.9)

(Note—in practice, there are also other concerns. In particular, H₂S often associated with venting natural gas is highly toxic. As a result there are specific regulations that must be followed for landing helicopters on oil platforms)

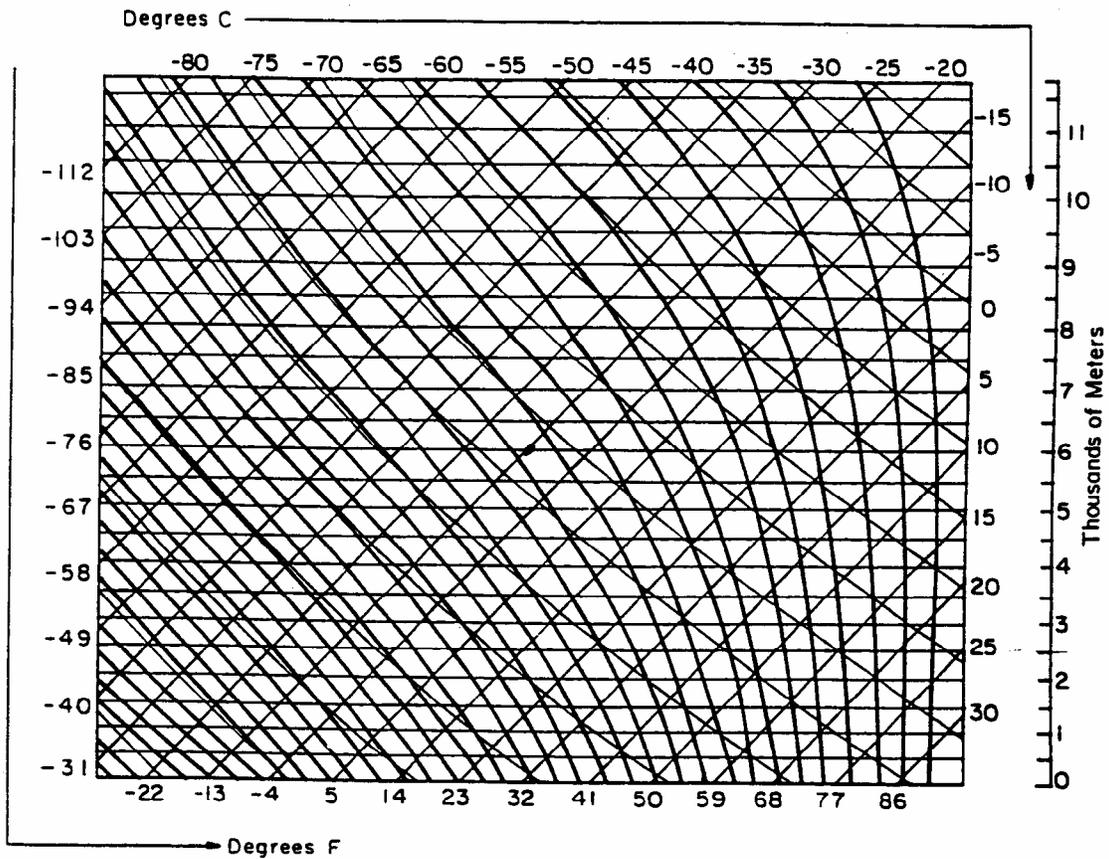


TABLE 4-2 Vapor Pressure of Water^a

Temperature (°C)	V.P. (mm Hg)	Temperature (°C)	V.P. (mm Hg)
-5	3.16	16	13.63
-4	3.41	17	14.53
-3	3.67	18	15.48
-2	3.96	19	16.48
-1	4.26	20	17.54
0	4.58	21	18.65
1	4.93	22	19.83
2	5.29	23	21.07
3	5.68	24	22.38
4	6.10	25	23.76
5	6.54	26	25.21
6	7.01	27	26.74
7	7.51	28	28.35
8	8.04	29	30.04
9	8.61	30	31.82
10	9.21	31	33.70
11	9.84	32	35.66
12	10.52	33	37.73
13	11.23	34	39.90
14	11.99	35	42.18
15	12.79	36	44.56

^aSource: Weast (1990).

Pasquill Stability Categories

Surface wind speed (m/sec) ^c	Insolation ^d			Night ^b	
	Strong ^d	Moderate ^d	Slight	Thinly overcast or $\geq 4/8$ low cloud	$\leq 3/8$ cloud
<2	A	A-B	B	—	—
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

^aStrong insolation corresponds to sunny midday in midsummer in England; slight insolation to similar conditions in midwinter.

^bNight refers to the period from 1 hr before sunset to 1 hr after sunrise.

^cThe neutral category D should also be used, regardless of wind speed, for overcast conditions during day or night and for any sky conditions during the hour preceding or following night as defined in footnote b.

^dFor A-B, interpolate between values in Fig. 4-25 for A and B, etc.

Source: Pasquill, 1974.

Formulae for σ_y and σ_z Recommended by Briggs^{a,b}

Pasquill stability category	σ_y (m)	σ_z (m)
Open country conditions		
A	$0.22 x(1 + 0.0001 x)^{0.5}$	$0.20 x$
B	$0.16 x(1 + 0.0001 x)^{0.5}$	$0.12 x$
C	$0.11 x(1 + 0.0001 x)^{0.5}$	$0.08 x(1 + 0.0002 x)^{0.5}$
D	$0.08 x(1 + 0.0001 x)^{0.5}$	$0.06 x(1 + 0.0015 x)^{0.5}$
E	$0.06 x(1 + 0.0001 x)^{0.5}$	$0.03 x(1 + 0.0003 x)$
F	$0.04 x(1 + 0.0001 x)^{0.5}$	$0.016 x(1 + 0.0003 x)$
Urban conditions		
A, B	$0.32 x(1 + 0.0004 x)^{0.5}$	$0.24 x \cdot (1 + 0.001 x)^{0.5}$
C	$0.22 x(1 + 0.0004 x)^{0.5}$	$0.20 x$
D	$0.16 x(1 + 0.0004 x)^{0.5}$	$0.14 x(1 + 0.0003 x)^{0.5}$
E, F	$0.11 x(1 + 0.0004 x)^{0.5}$	$0.08 x(1 + 0.0015 x)^{0.5}$

^a x is the downwind distance in meters; valid only for $100 \text{ m} < x < 10,000 \text{ m}$.

^bGifford (1976).

