- 1) At an experimental watershed, you have received permission to carry out experiments in which small amounts of several radionuclides are introduced into a small river as tracers. In one experiment you introduce an 85 mCi pulse of arsenic-76 ($t_{1/2}=26.4h$) in the chemical form of sodium arsenate into the river. Flow at the time is 2.7 m³/s, and the relatively uniform but winding natural channel has a cross-section of 19 m² and average depth of 1.2 meters. u* is 0.3 m/sec.
- a) Estimate a longitudinal dispersion coefficient for this river.
- b) Determine the distance from injection point to point of maximum concentration of arsenic-76, as well as spatial standard deviation of the radionuclide, 8 hours after the spill.
- c) What is the activity of the radionuclide at this time and location (expressed as mCi/L), assuming no sorption occurs?

5 pts. a)
$$D_{L} = 0.011 V^{2} W^{2}$$

 $d_{U,*}$
 $V = 2.1 m^{3} IS = 0.142 m IS$
 $W = \frac{A}{d} = \frac{19m^{2}}{1.2m} = 15.8m$
 $= 0.011 (0.142m IS)^{2} (15.8m)^{2}$
 $= 0.15m^{3} IS$

5 pts. b) distance = velocity * time
 $= 0.142m$, $8hr \times 3\omega00s = 14090m$
 $6^{2} = 2D_{L}t$
 $G = \sqrt{2(a.15m^{3}}S)(28,800s) = 193m$
10 pts. c) $C(X,t) = \frac{M}{14TD_{L}t} e^{-(X-Vt)^{2}} HD_{L}t} e^{-kt}$
neglect this because at point of max concentration,
 $X = Vt$ $(e^{0} = 1)$
 $M = moss = W 85 mCi} = 4.41mCi/m^{2}$
 $k = ln2 = 0.020h^{-1}$

 $C(x,t) = \frac{4.47 \text{ mci}/\text{m}^2}{\sqrt{4\pi}(0.15 \text{ m}^3\text{s}X_{28,8005})} e^{-0.02 \text{ u} \text{h}^3(8\text{h})} = \frac{0.01 \text{ u} \text{ m}^2}{\text{m}^3} = \frac{1.0 \times 10^{-5} \text{ mci}/\text{L}}{1000 \text{ L}}$

(part c)

· ..

.....

This was tricky - you had to recognize that activity can be treated like concentration, and that you need to account for dispersion as well as radioactive decay. Since dispersion causes the plume to spread out, the maximum activity decreases with time even if there is no decay.

Cmax = <u>M</u> We can see that as t increases, Cmax decreases. HTDLt

+3 for the activity calculation

+ 2 (additional) for recognizing that you were asked for mcile, and introducing a volume somehow

2) Several large tanks of water are to be adjusted to different pH values in order to test fish survival under conditions of acidification. Well water with an initial Alk of 6×10^{-4} eq/L and pH of 6.5 is pumped into open storage tanks and amended with H₂SO₄ to make waters having pH values of 6.0, 5.0, and 4.0, respectively.

- a) How much $H_2CO_3^*$ is initially present in the well water?
- b) How much sulfuric acid (in equivalents/L) must be added to the well water to adjust it to pH 6.0?
- c) A day after the storage tanks are filled and adjusted to their correct pH, it is found that the pH 6 tank has risen to pH 6.5! How could this happen, if nobody has made any further additions of chemicals to the tanks?

10 pts.
a) from Deffeyes diagram: Alk =
$$b \times 10^{-4} \text{ eg}[L \implies C_T = 10^{-3} \text{ M}$$

(4 for Cr,
u for H_2COS*)
 $C_T = EH_2COS*] + EHCOS^{-1} + ECOS^{2-1}$ (can neglect $ECOS^{2-1}$] at this pH)
 $H_2COS* \Rightarrow HCOS^{-1} H^{+} K = 10^{-0.5}$
 $EHCOS^{-1}EH^{+1}] = 10^{-0.5}$ $EHCOS^{-1} = 10^{-0.5} EH_2COS^{+1} = 10^{0.2} [H_2COS^{+}]$
 $EH_2COS^{+1} = 10^{-0.5}$
 $EH_2COS^{+1} = 10^{-3}$
 EH_2COS^{+1}

5 pts. () The water must have been oversaturated with co2 (as H2CO3*), so some of the CO2 would have escaped to the atmosphere. This would lower CT; since Alk doesn't change (no strong acids or bases are involved), we can see on the diagram that pit would increase.

- 3) A pond has depth d (cm) and area A. Propane gas is added as tracer; propane is inexpensive, non-toxic, has large Henry's constant, and is easily measured at low concentrations.
- a) What is the expected concentation of propane in the pond as a function of time, expressed in terms of initial concentration ([C₃H₈]_o) and depth d? (Use k_w (cm/sec) = 4 x 10⁻⁴ + 4 x 10⁻⁵u₁₀² to estimate gas exchange velocity). Wind is 0.5 m/s. Assume bulk [C₃H₈] is uniform throughout the pond. As always, be clear about units.
- b) An experiment is carried out in which methane (CH₄) is added along with propane. Methane is more likely than propane to experience significant oxidation (by methanotrophic bacteria), as well as tend to escape to the atmosphere. If there is no bacterial oxidation, and methane and propane are initially added in equal concentrations, what is the expected ratio methane to propane concentration in the pond as a function of time?

a)
$$C = C_0 e^{-K_T T}$$

 $K_W = 4 \times 10^{-4} + 4 \times 10^{-5} (0.6)^2 = 4.1 \times 10^{-4} \text{ cm}/\text{s}$
 $K_T = K_N = 4.1 \times 10^{-4} \text{ s}^{-1}$
 $\overline{a} = \overline{d}$
 \overline{d}
 $\overline{C_0 + K_T} = C_0 + 8]_0 e^{-(4.1 \times 10^{-4} T/d)}$
 $T = C_0]$

thin film =>
$$\frac{kp}{km} = \sqrt{MWm}$$
 CH+: 16 glmol
 $\frac{kp}{km} = \sqrt{MW}p$ Cate: 44 glmol
 $\frac{kp}{km} = \sqrt{16}$ $km = 1.658 kp = 6.8 \times 10^{-4} cmls$
 $\frac{CCH+3}{CCaHa3} = \frac{CCH+3_0 e^{-4.8 \times 10^{-4} cld}}{CCaHa3_0 e^{-4.1 \times 10^{-4} cld}} = e^{C-6.8 \times 10^{-4} cld + 4.1 \times 10^{-4} cld 3}$

4) Sediment oxygen demand (or benthic oxygen demand as it may be called) is the rate at which oxygen is consumed by the bottom sediments of a river or lake. It is often expressed as a flux density having no dependency on the exact oxygen concentration of the overlying water (this is obviously an approximation that can not be true for very low overlying oxygen concentration). One way to estimate benthic oxygen demand is to put sediment in the bottom of a tank and observe the rate of oxygen consumption from the water.

In such a test, you put a layer of sediment in the bottom of a cylindrical tank (crosssectional area = 0.5 m²) and cover the sediment with a layer of water. The tank is open to the atmosphere (T = 25°C, Po₂ = 0.2 atm), and you observe that at steady state the bulk water overlying the sediment in the tank arrives at a constant [O₂] of 6 mg/L. The only source of O₂ to the water is atmospheric gas exchange. The Henry's constant for O₂ is 774 $\frac{atm}{(mol \cdot L^{-1})}$ at 25°C, and you may use a gas exchange velocity (note: it is *water side controlled*) of 4x10⁻⁴ (^{cm}/_s) under the test conditions.

a) Calculate the oxygen demand of the sediment $\left(\frac{mg}{m^2 \cdot s}\right)$. Water-side control: $\frac{y}{z} = \frac{c_{a}|H}{c_{w}}$ $J = k(c_{w}-c_{a}|H)$ $k = 4 \times 10^{-4} \text{ cm/s}$ given $\frac{c_{a}}{H} = \frac{0.2 \text{ atm}}{714 \text{ atm}} \text{ mol } \text{s}^{-1} \times \frac{32 \text{ g}}{\text{mol }} \times \frac{1000 \text{ mg}}{\text{g}} = 8.27 \text{ mg/s}$ plug it all in: $J = 4 \times 10^{-4} \text{ cm/s} (\text{bmg/s} - 8.27 \text{ mg/s})$ $= 4 \times 10^{-4} \text{ cm/s} (\text{bmg/s} - 8.27 \text{ mg/s})$

at steady state (constant [02]), so flux in = flux out oxygen demand from sediment = rate of gas exchange = [9.1×10-3 mg/m2.s 5) Estimate the rate of sediment accumulation (in cm/year) in the following lake (the result will be essential for purposes such as calculating the associated fluxes of contaminants to the bottom). Measurements of Lead-210 (t $\frac{1}{2} = 22.3$ y) activity yield the following table and graph. (ignore the excessive sig figs in ln (activity)!)

Depth range (cm)	Mean depth	Activity (DPM/g)	In (Activity)
0 to 2	1	4	1.38629436
2 to 4	3	2.7	0.99325177
4 to 6	5	2.1	0.74193734
6 to 8	7	1.4	0.33647224
8 to 10	9	0.9	-0.10536052
10 to 12	11	0.7	-0.35667494
12 to 14	13	0.51	-0.67334455
14 to 16	15	0.33	-1.10866262
16 to 18	17	0.25	-1.38629436
18 to 20	19	0.17	-1.77195684



taking the endpoints (1 cm. 4 DPM/g and 19 cm., 0.17 DPM/g) because it's pretty linear (can also estimate a best-fit line and use that)

Ad = Ao $e^{-\lambda t}$ $\lambda = \ln 2 = 0.093 = 0.031 y^{-1}$ $\frac{0.17}{4} = e^{-0.031t}$ $-\ln \left(\frac{0.17}{4}\right) = 0.031t$ rate = 18 cm = 0.18 cm/yrt = 102 yr 1. (24 pts.) The owner of a small factory has installed a new well to supply process water. The well is 0.3 m in diameter, and it is fully screened for the entire 12-m depth of the aquifer, which is composed of coarse sand having an estimated bulk density of 2 g/cm³, K of 0.1 cm/s, porosity of 0.25, and organic content of 0.5%. The radius of influence of this well can be taken as approximately 3,000 meters.

a) What is steady state drawdown, in the well, if the average water use of the factory is 360 L/min?

b) A plume of TCE – contaminated groundwater lies at a distance of 800 m from the well. What is the average seepage velocity of this groundwater due to well pumping?

c) How fast is the TCE plume moving toward the well? Neglect any movement that may result from regional aquifer flow, plume density, etc. and consider only dissolved TCE under the influence of well pumping at hydraulic steady state. Note that log K_{ow} of TCE is 2.42, suggesting that log K_{oc} is about 2.26 according to regression equations compiled by Lyman et al.

- 2). (16 pts.) A vulture is circling in a "thermal" above a plowed, open field in which he has spotted some attractive carrion. While waiting for a party of hunters to depart, the vulture wants to circle as high as possible (to avoid possibly becoming additional carrion) while keeping lunch in sight (i.e. remaining below the clouds). Temperature of air above the plowed field is 18°C and RH is 70%.
- a) What is the dew point at ground level? Estimate how high the bird can go before reaching the altitude of the lowest clouds.

3). (20 pts.) The "inventor extraordinaire" has a new idea, namely to mitigate solvent vapor in the air of automotive spray-painting booths using OH radicals. Your job as her technical assistant (the inventor is mostly into marketing) is to determine the performance of the proposed system. The OH generator would need to generate a high enough OH concentration to maintain solvent vapor concentrations at the same level or lower than produced by the commonly-used ventilator fans. A suggested "model" for a spray booth is a box measuring 3 m x 4 m x 8 m, whose volume is 96 m³, or 96 x 10⁶ cm³. Assume ventilator fans provide 5 air changes/hour, and solvent input is about 80 moles/hr (= 4.8 x 10^{25} molecules/hr = 1.3×10^{22} molecules/sec) while painting is in progress.

a) What is steady-state vapor concentration during car painting with the ventilators running (and no OH generator)?

b) What is the necessary OH concentration needed to maintain the above solvent vapor concentration with ventilators off (assume the air in the room is nonetheless well-mixed). Assume the average rate constant for reaction of OH with various paint solvents is approximately 4×10^{-13} cm³/(molecule/sec).

c) Are there any problems with this invention (assuming that it is economically viable and appears to be marketable to potential users)?

4). (20 pts). A plane is flying at an altitude of 2,500 meters, in clouds. Outside air temperature is -3 degrees C, and the pilot has noticed the beginning of icing on the wings. She calls air traffic control to ask for a different altitude, to avoid the ice.

a) How low would she have to fly to get out of the ice, if the atmosphere in the cloud were of neutral stability?

b) Due to terrain clearance issues, the altitude of part a) is not good, so she instead asks for clearance to climb out of the cloud to avoid further icing. Although the cloud tops are at 3000 meters, she is instructed to climb to 3700 meters to avoid other air traffic. What is the temperature at this altitude? Again assume neutral stability.

5. (20 pts) You have invented a very accurate, lightweight instrument to measure carbon dioxide in the atmosphere; it can detect as small as a 1 mg per cubic meter change in concentration over a period of a few seconds. One of your customers wants to use this instrument to locate moonshine stills hidden in the backwoods, by detecting their carbon dioxide plumes. For this purpose your detector will be mounted on a robotic blimp, which will traverse an area of interest.

Grandpa Smith has a distillery that burns 25 kg of dry hickory wood (CH₂O) each hour, and combustion products are vented via a 10 meter high chimney; however the effective height is 40 m due to plume rise. The blimp is 50 m above ground and passes 100 m downwind of Smith's still. What maximum carbon dioxide concentration (in mg/m³) does it detect? Assume it is nighttime (of course), with cloudy sky and a 2.5 meter per second wind.

6) (6 pts) Give brief answers:

a) What is the principal mode of formation of stratospheric ozone? How does this pathway contrast with that for the formation of urban ozone?

b) In what two processes is nitrous oxide naturally formed in ecosystems?

c) Describe why the deposition velocities for ozone and for sulfur dioxide often follow diurnal cycles in a vegetated region.

7) (2 points Thanksgiving bonus) As discussed in class, when roasting a turkey, roasting time should be enough to bring the coldest part of the meat up to 180 degrees F. Recalling that heat and mass both obey the diffusion equation, what scaling rule would you use to estimate cooking time for a large turkey, if the correct time is known for a small turkey? (specifically we posed the question: if a 3 lb turkey cooks in an hour, how long do you cook 20 pound turkey?)

TABLE 4-2 Vapor Pressure of Water"

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

TABLE 4-5 Pasquill Stability Categories

Surface wind speed (m/sec) ^c	Insolation*			Night [*]		
	Strong	Moderate	Slight	Thinly overcast or ≥ ⁴ / _n low cloud	≤ ≟ cloud	
< 2	٨	A-B	8			
2-3	A-B	В	Ĉ	· E	F	
3-5	В	B-C	С	D	E	
56	С	C-D	D	D	Ď	
> 6	с	D·	D	Ď	D	

Strong insolation corresponds to sunny midday in midsummer in England; slight insolation to similar conditions in midwinter. *Night refers to the period from 1 hr before sunset to 1 hr after sunrise.

The 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 above. Source: Stern *et al.* (1984).

⁴Source: Weast (1990).



1.725 Fate+ Transport

Fall 2003 Quiz #2 (12/3/03)

1. aquifer: b = 12m well. d = 0.3m $p_{b} = 2.91cm^{3}$ R= 3000m k = 0.7 cm/s n = 0.25fue = 0.5%

a) find drawdown in well if Qw= 3404min

 $S = Qw \ln \left(\frac{P}{r}\right) \text{ where } r = 0.15 \text{ m} (radius ef weil)$ $Qw = \frac{3401}{min} \times \frac{min}{4005} = \frac{min}{1000 L} \text{ min}^{3} \text{ ls}$ $S = \frac{.00 \text{ m}^{3}\text{ ls}}{2\pi (.001 \text{ m}\text{ ls})(2m)} \ln \left(\frac{3000 \text{ m}}{0.15 \text{ m}}\right) = \boxed{0.188 \text{ m}}$

b) seepage relacity soom from well

 $Q = Q \cdot A$

Water flows across this area Nell 800m $Q = Q = .006m^{3}ls$ $2\pi rb$ $2\pi (800m)(12m)$ $V = Q = .9.95 \times 10^{-8} m/s$ V = 0.25 $10^{-8} m/s$ $10^{-1} m/s$

can also use $\frac{ds}{dr} = \frac{Qw}{2\pi krb}$ and then $q = k \frac{dh}{dx}$ (notice that k cancels out)

c) velocity of TCE plume (log Koc = 2.26)
Kd = foc Koc = .005(10^{2.24}) = 0.91 mLlg
R = 1 + Kd Po = 1 + 0.91 mLlg (2gicm³) = 8.28
N
VTCE = Vwater =
$$4.0 \times 10^{-7}$$
 mls = 4.8×10^{-2} mls
R
R
R
R

2. at ground level, T= 18°C and RH=70%

 $[:0H] = 5hr^{-1}(hr|3w00s) = 3.5 \times 10^{9} molec|cm^{3}]$ $4 \times 10^{-13} cm^{3}|molec.sec$

c) The required E-oit] is very high (1000x more than atmospheric). Since oit, is very reactive, it can lead to harmful byproducts in the spray booth, potentially and would be directly harmful to human health.

4. conditions: 2500m, in clouds, T= -3°C

a) follow wet adiabat until T=0°C (should really go to T>0°C)

-=] ~ 2000mj

b) find T at 3700m, cloud tops at 3000m

- follow wet adiabat to 3000m, then dry adiabat (which slopes upward to the left) to 3700m

5. Pasquill-Gifford model H= 40m night, cloudy, 2.5mls wind => x=100m, y=0; 2= 50m

category E at 100m (10-1 km) 0-0 000

$$U = \frac{g_{1}g_{2}}{2\pi6y6z}$$

$$G_{y} = 6m, 6z = 3.4m$$

$$g_{1} = e^{-0.5(y^{2}/6y^{2})} = 1$$

$$g_{2} = e^{-0.5(z-H)^{2}/6z^{2}} + e^{-0.5(z+H)^{2}/6z^{2}} = .013$$

$$Q = 25kg CH_{20} + 44glmul CO_{2} + hr = 3000cs + \frac{100cg}{kg} = 10.2glsec$$

 $= 4.1 \times 10^{-4} \text{ g/m}^3 = 0.41 \text{ mg/m}^3$ c = 10.2 gls (.013) 2.6m/s 217(um)(3.4m)

Since the detection limit is a change of I mglm3 from background, Grandpa smith does not get caught.

a) stratospheric: oz hit with UV light (to form O, which reacts with 4. another 02)

urban: Noz hit with light calso produces 0 to react with 02)

b) nitrification (NH++ -> NO3 in the presence of 02) denitrification (NO3 -> N2)

These are both multi-electron overall reactions; N20 (Nis+I) is an intermediate or side product.

c) stomates on the leaf surface open during the day to let in co2, allowing ozone and sulfur dioxide to enter as well.

Extra Credit:

Scaling rule for turkey cooking (does cooking time depend linearly on turkey weight, on square root of weight, or what?)

Back-of-the-envelope (very simple) estimate:

- neat needs to go through thickest part of turkey
- simplest model: everything within 10 has reached 180 °F



combining the two, we have .

$$Wa(t^{1/2})^3 = taW^{2/3}$$

$$\frac{t}{1} = \left(\frac{20}{31b}\right)^{2/3} \quad t \approx 3.5 \text{ hours}$$