

## Chapter 1

1.1

(a) In water "ppb" refers to a mass fraction:

$$\text{ppb (water)} = \frac{\text{mass of contaminant} \times 10^9}{\text{mass of (water + contaminant)}}$$

In air "ppb" refers to a mole or, equivalently, volume fraction:

$$\text{ppb (air)} = \frac{\text{moles (or volume) of contaminant} \times 10^9}{\text{moles (or volume) of (air + contaminant)}}$$

Since the mass and moles of a contaminant are usually much lower than the mass of water and moles of air, respectively, the contaminant is usually left out of the denominator.

(b) 35 ppm is equal to  $\frac{35 \times 10^{-6} \text{ moles CO}}{\text{mole air}}$

To convert this to a mass concentration, we first need to determine what volume is taken up by 1 mole of air. We can use the IDEAL GAS LAW:

$$PV = nRT ; \frac{V}{n} = \frac{RT}{P}$$

Assuming  $P = 1 \text{ atm}$  and  $T = 293 \text{ K}$ , and using  $R = 82.05 \times 10^{-6} \frac{\text{atm m}^3}{\text{mol K}}$ :

$$\frac{V}{n} = \frac{(82.05 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1} \text{ K}^{-1})(293 \text{ K})}{1 \text{ atm}}$$
$$= 0.024 \text{ m}^3 \text{ mol}^{-1}$$

We also need to know what mass is contained in 1 mole of CO:

$$\text{MW}_{\text{CO}} = 12 \text{ g mol}^{-1} + 16 \text{ g mol}^{-1} = 28 \text{ g mol}^{-1}$$

Thus, the conversion is:

$$\left( \frac{35 \times 10^{-6} \text{ mol CO}}{\text{mole air}} \right) \left( \frac{28 \text{ g CO}}{\text{mol}} \right) \left( \frac{10^3 \text{ mg}}{\text{g}} \right) \left( \frac{1 \text{ mol air}}{0.024 \text{ m}^3 \text{ air}} \right)$$
$$= [41 \text{ mg m}^{-3}]$$

(c) The conversion is:

$$\left( \frac{0.005 \text{ mg Cd}}{1 \text{ L H}_2\text{O}} \right) \left( \frac{1 \text{ L H}_2\text{O}}{1000 \text{ g H}_2\text{O}} \right) \left( \frac{1 \text{ g Cd}}{10^6 \text{ mg Cd}} \right) (10^6) = [0.005 \text{ ppm}]$$

to convert to ppm

1.2

1.2

(a) As in problem 1.1(b) above, we use the ideal gas law and the molecular weight of the contaminant, in this case  $\text{CHCl}_3$ , to make the conversion. Recall:

$$PV = nRT ; \frac{V}{n} = \frac{RT}{P}$$

With  $P = 1 \text{ atm}$  and  $T = 293 \text{ K}$ , and using  
 $R = 82.05 \times 10^{-6} \frac{\text{atm m}^3}{\text{mol K}}$ :

$$\frac{V}{n} = \frac{(82.05 \times 10^{-6} \frac{\text{atm m}^3 \text{ mol}^{-1} \text{ K}^{-1}}{1 \text{ atm}})(293 \text{ K})}{= 0.024 \text{ m}^3 \text{ mol}^{-1}}$$

The molecular weight of  $\text{CHCl}_3$  is:

$$\begin{aligned} \text{MW}_{\text{CHCl}_3} &= 12 \text{ g mol}^{-1} + 1 \text{ g mol}^{-1} + 3(35.5 \text{ g mol}^{-1}) \\ &= 119.5 \text{ g mol}^{-1} \end{aligned}$$

The conversion is:

$$\begin{aligned} (0.4 \frac{\mu\text{g CHCl}_3}{\text{m}^3 \text{ air}}) &\left( \frac{0.024 \text{ m}^3 \text{ air}}{\text{mol air}} \right) \left( \frac{1 \text{ g}}{10^6 \mu\text{g}} \right) \left( \frac{1 \text{ mol CHCl}_3}{119.5 \text{ g CHCl}_3} \right) (10^9) \\ &= \boxed{0.08 \text{ ppb CHCl}_3} \end{aligned}$$

(b) We use the fact that the density of water is 1 g/mL to make the conversion:

$$\begin{aligned} \left( \frac{42 \mu\text{g CHCl}_3}{1 \text{ L H}_2\text{O}} \right) &\left( \frac{1 \text{ L}}{10^3 \text{ mL}} \right) \left( \frac{1 \text{ mL H}_2\text{O}}{1 \text{ g H}_2\text{O}} \right) \left( \frac{1 \text{ g}}{10^6 \mu\text{g}} \right) (10^9) \\ &= \boxed{42 \text{ ppb CHCl}_3} \end{aligned}$$

(c) The exposures to  $\text{CHCl}_3$  through inhalation and ingestion:

	Inhalation	Ingestion
Amount consumed	$20 \text{ m}^3 \text{ day}^{-1}$	$2 \text{ L day}^{-1}$
$\text{CHCl}_3$ concentration	$0.4 \mu\text{g m}^{-3}$	$42 \mu\text{g L}^{-1}$
$\text{CHCl}_3$ exposure	$8 \mu\text{g day}^{-1}$	$84 \mu\text{g day}^{-1}$

1.2 (continued)

(d) The exposures to  $C_2Cl_4$  through inhalation and ingestion:

	Inhalation	Ingestion
Amount consumed	$20 \text{ m}^3 \text{ day}^{-1}$	$2 \text{ L day}^{-1}$
$C_2Cl_4$ concentration	$2.1 \mu\text{g mL}^{-3}$	$0.10 \mu\text{g L}^{-1}$
$C_2Cl_4$ exposure	$42 \mu\text{g day}^{-1}$	$0.20 \mu\text{g day}^{-1}$

(e) Ingestion is more important than inhalation for chloroform (by a factor of 10), while inhalation is more important for  $C_2Cl_4$ .

1.3 (a) The conversion in water is:

$$\left( \frac{80 \times 10^{-9} \text{ g } C_2H_3Cl}{\text{g H}_2\text{O}} \right) \left( \frac{10^6 \mu\text{g}}{\text{g}} \right) \left( \frac{10^3 \text{ g}}{\text{kg}} \right) \left( \frac{1 \text{ kg H}_2\text{O}}{1 \text{ L H}_2\text{O}} \right) \\ = [80 \mu\text{g L}^{-1} C_2H_3Cl]$$

Note: In general,  $[ppb] = \left[ \frac{\mu\text{g}}{\text{L}} \right]$  in water.

(b) The conversion in air is:

$$\left( \frac{80 \times 10^{-9} \text{ mol } C_2H_3Cl}{\text{mol air}} \right) \left( \frac{62.5 \text{ g } C_2H_3Cl}{\text{mol}} \right) \left( \frac{10^6 \mu\text{g}}{\text{g}} \right) \left( \frac{1 \text{ mol air}}{0.024 \text{ m}^3} \right) \left( \frac{1 \text{ m}^3}{10^3 \text{ L}} \right) \\ = [0.2 \mu\text{g L}^{-1} C_2H_3Cl]$$

Note: See problems 1.1 and 1.2 for a calculation of what volume is occupied by a mole of air.  $P = 1 \text{ atm}$  and  $T = 293 \text{ K}$  are assumed.

1.4

We want to convert mass concentration to molarity and normality for five ions in drinking water. Recall that the definitions of molarity and normality are as follows:

$$\text{MOLARITY} = M = \frac{\# \text{ of moles of solute}}{\text{volume of solution}} = \left[ \frac{\text{mol}}{\text{L}} \right]$$

1.5

**1.4 (continued)**

$$\text{NORMALITY} = N = \frac{\# \text{ of equivalents of solute}}{\text{volume of solution}} = \frac{\text{eq.}}{L}$$

where

$$\text{eq.} = |\text{net charge}| \times \text{moles}$$

Therefore

$$N = |\text{net charge}| \times M$$

Our conversions are as follows:

Species	Mass Concentration (mg L <sup>-1</sup> )	Atomic weight (g mole <sup>-1</sup> )	Net charge	M (mol L <sup>-1</sup> )	N (eq L <sup>-1</sup> )
Fe <sup>3+</sup>	0.02	56	3	3.6 × 10 <sup>-7</sup>	1.1 × 10 <sup>-6</sup>
Ca <sup>2+</sup>	9.8	40	2	2.5 × 10 <sup>-4</sup>	4.9 × 10 <sup>-4</sup>
Mg <sup>2+</sup>	1.8	24	2	7.5 × 10 <sup>-5</sup>	1.5 × 10 <sup>-4</sup>
K <sup>+</sup>	0.6	39	1	1.5 × 10 <sup>-5</sup>	1.5 × 10 <sup>-5</sup>
Na <sup>+</sup>	4.6	23	1	2.0 × 10 <sup>-4</sup>	2.0 × 10 <sup>-4</sup>

**1.5**

We first want to find the total mass of CO<sub>2</sub> in the atmosphere, given:

$$\begin{aligned} M_{\text{atm}} &= 5.1 \times 10^{18} \text{ kg} \\ Y_{\text{CO}_2} &= 350 \text{ ppm} \end{aligned}$$

We also know that

$$M_{\text{W air}} = 28.9 \text{ g mole}^{-1}$$

$$M_{\text{W CO}_2} = 44 \text{ g mole}^{-1}$$

Therefore, the total mass of CO<sub>2</sub> is:

$$M_{\text{CO}_2} = \left( \frac{350 \text{ mol CO}_2}{10^6 \text{ mol air}} \right) \left( \frac{1 \text{ mole air}}{29.8 \text{ g}} \right) \left( \frac{10^3 \text{ g}}{\text{kg}} \right) \left( 5.1 \times 10^{18} \text{ kg air} \right)$$

$$M_{\text{CO}_2} = \left( 6.18 \times 10^{16} \text{ mol CO}_2 \right) \left( \frac{44 \text{ g CO}_2}{\text{mol CO}_2} \right) \left( \frac{1 \text{ metric tons}}{10^6 \text{ g}} \right)$$

$$M_{\text{CO}_2} = 2.72 \times 10^{16} \text{ metric tons}$$

The rate of mass accumulation, then, is:

$$\text{Rate} = \left( 2.72 \times 10^{16} \text{ metric tons} \right) \left( 0.5 \frac{\%}{\text{year}} \right) = \boxed{1.4 \times 10^{10} \frac{\text{metric tons}}{\text{year}}}$$

1.6

(a) To find the  $\text{CO}_2$  emission rate from private automobiles in the US, simply multiply:

$$\begin{aligned} & (1.2 \times 10^8 \text{ cars}) \left( \frac{10^4 \text{ miles}}{\text{car yr}} \right) \left( \frac{1 \text{ gal C}_8\text{H}_{18}}{18 \text{ miles}} \right) \left( \frac{3785 \text{ cm}^3 \text{ C}_8\text{H}_{18}}{1 \text{ gal C}_8\text{H}_{18}} \right) \\ & \quad \times \left( \frac{0.72 \text{ g C}_8\text{H}_{18}}{1 \text{ cm}^3 \text{ C}_8\text{H}_{18}} \right) \left( \frac{96 \text{ g C}}{114 \text{ g C}_8\text{H}_{18}} \right) \left( \frac{44 \text{ g CO}_2}{12 \text{ g C}} \right) \left( \frac{1 \text{ metric tonne}}{10^6 \text{ g}} \right) \\ & = \boxed{\frac{5.6 \times 10^8 \text{ metric tonnes CO}_2}{\text{yr}}} \end{aligned}$$

(b) Of the total mass accumulation of  $\text{CO}_2$  in the atmosphere, US private automobiles account for  $\frac{5.6 \times 10^8}{1.4 \times 10^{10}} \times 100 = 4\%$ . Thus, if US auto  $\text{CO}_2$  emissions were reduced to 0 through regulation, global  $\text{CO}_2$  mass accumulation would still be 96% of our current estimates. However, automobiles worldwide may also be significant contributors to  $\text{CO}_2$  accumulation and so fuel efficiency regulations may reduce emissions.

1.7

First we want to find out how much PCE waste is produced each month:

$$\begin{aligned} \frac{\text{PCE waste produced}}{\text{month}} &= \frac{\text{PCE purchased}}{\text{month}} (1 - 0.3) \\ &= \frac{250 \text{ L}}{\text{month}} (0.7) = 175 \frac{\text{L PCE}}{\text{month}} \end{aligned}$$

Now find out how long for the  $0.7 \text{ m}^3 (=700 \text{ L})$  disposal container to fill:

$$T = \frac{700 \text{ L}}{175 \text{ L/month}} = \boxed{4 \text{ months}}$$

←  
Container will have to be emptied this often

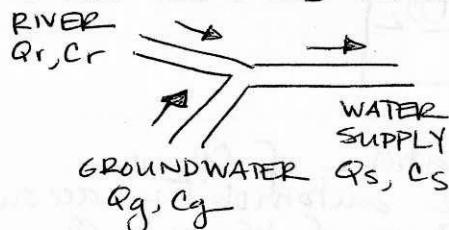
1.8

1.8

We want to determine the relative amounts of river water and groundwater to be used for Ecocity's water supply, given the following:

Barium drinking water standard =  $2 \text{ mg L}^{-1}$   
Barium concentration in river =  $0.5 \text{ mg L}^{-1}$   
Barium concentration in groundwater =  $9 \text{ mg L}^{-1}$   
Water supply needs for Ecocity =  $10 \text{ m}^3 \text{ day}^{-1}$

We can use the mass balance concept to solve:



Let  $Q_s = 10 \text{ m}^3 \text{ day}^{-1}$   
 $C_s = 5 \text{ mg L}^{-1}$   
 $C_r = 0.5 \text{ mg L}^{-1}$   
 $C_g = 9 \text{ mg L}^{-1}$

Mass balance on water:  $Q_r + Q_g = Q_s$   
mass balance on barium:  $C_r Q_r + C_g Q_g = C_s Q_s$   
Therefore:

$$Q_r + Q_g = 10 \text{ m}^3 \text{ day}^{-1}$$
$$(0.5 \text{ mg L}^{-1}) Q_r + (9 \text{ mg L}^{-1}) Q_g = (2 \text{ mg L}^{-1}) (10 \text{ m}^3 \text{ day}^{-1})$$

Setting  $Q_r = 10 - Q_g$ , substituting into the second equation and solving for  $Q_g$ :

$$0.5(10 - Q_g) + 9Q_g = 20$$

$$5 - 0.5Q_g + 9Q_g = 20$$

$$8.5Q_g = 15$$

$$Q_g = 1.76 \text{ m}^3 \text{ day}^{-1}$$

$$\text{and } Q_r = 10 - Q_g = 8.24 \text{ m}^3 \text{ day}^{-1}$$

So Ecocity should use:

$1.8 \text{ m}^3 \text{ day}^{-1}$  (47%) groundwater  
 $8.2 \text{ m}^3 \text{ day}^{-1}$  (53%) river water

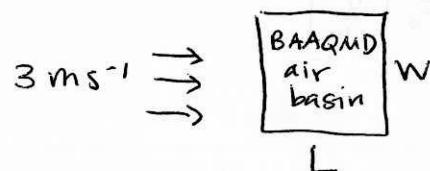
Note: We can check to make sure this combination of flows will give us the desired barium concentration:

$$C_s = \frac{0.5 \times 8.2 + 9 \times 1.8}{10} = 2.0 \text{ mg L}^{-1} \checkmark$$

1.9

- (a) We want to find the characteristic residence time of air in the BAAQMD air basin, given that the basin encompasses  $6094 \text{ mi}^2$  and a steady wind of  $3 \text{ m s}^{-1}$  blows from the west.

Consider a generic rectangular air basin:



Let's start with the simplest case, with  $L = W$ :

$$L = \sqrt{6094} = 78.06 \text{ miles}$$
$$L = (78.06 \text{ miles})(1609 \text{ m mile}^{-1}) = 125600 \text{ m}$$

Thus, the residence time is:

$$\tau = \frac{125600 \text{ m}}{3 \text{ m s}^{-1}} = 41900 \text{ s}$$

$$\tau = (41900 \text{ s})\left(\frac{1 \text{ min}}{60 \text{ s}}\right)\left(\frac{1 \text{ hr}}{60 \text{ min}}\right) = 11.6 \text{ hr}$$

$$\boxed{\tau = 10 \text{ hrs}} \quad (\text{keeping the same number of significant figures as we were given})$$

More generally, for any  $L$  or  $W$ :

$$L = \sqrt{\frac{6094}{\text{aspect ratio}}}, \text{ where "aspect ratio"} = \frac{W}{L}$$

Therefore

$$\tau = \frac{\sqrt{\frac{\text{area}}{\text{aspect ratio}}}}{\text{wind velocity}}$$

For example, with an aspect ratio of 2, we would get  $\tau = 8 \text{ hrs}$ , which is not that different than what we found for the square.

- (b) We want to find  $t$ , the time required for restoration of the air basin to a pristine state. We simply want to select any  $t$ , such that  $t \gg \tau$ . So,  $\boxed{t = 1 \text{ day to 1 week}}$  is sufficient. This assumes that the wind itself is pristine.

1.10

1.10

To find the characteristic time needed for the contaminant to return to its pre-spill level, we need to express the stock and flows in terms of known variables. Our system looks like:



So our stock is actually  $V$ , the lake volume, since the characteristic time required for flushing  $M$  from the lake is the same as the characteristic time required for flushing water from the lake.

Our flows can be written as either the inflow ( $= F_i$ ) or the outflow ( $= F_E + F_o$ ). We assume that the inflow equals the outflow.

Therefore, our characteristic time is:

$$T = \frac{V}{F_i} = \frac{V}{F_E + F_o}$$

1.11

Let's first find the number of democrats in the Senate after two years (i.e. one election). Of the 33.33 (= 1/3 of the Senate) senators replaced or reelected, 2/3, or 22.22, are democrats. Therefore the number of the democrats after the first election is:

$$50 - \underbrace{16.665}_{\begin{array}{l} \# \text{ to} \\ \text{start} \\ \text{with} \end{array}} + \underbrace{22.22}_{\begin{array}{l} \# \text{ at end} \\ \text{of 6-year} \\ \text{term} \end{array}} = \underbrace{55.555}_{\begin{array}{l} \# \text{ put} \\ \text{into office} \end{array}} \text{ democrats}$$

This assumes that of the 33.33 senators who are at the end of their 6-year term, half are democrats.

1.11 (Continued)

Using the same assumption (that half of the seats put up for election were held by democrats) let's find the number of democrats after the second election.

$$\underbrace{55.555}_{\text{\# to start with}} - \underbrace{16.665}_{\text{\# at end of 6-yr term}} + \underbrace{22.22}_{\text{\# put into office}} = 61.11 \approx 61 \text{ democrats}$$

1.12

Find the stock of water in the body first:

$$\text{STOCK} = (70 \text{ kg body}) (0.9 \frac{\text{kg H}_2\text{O}}{\text{kg body}}) = 63 \text{ kg}$$

Now find the flows. Since the body's water content is constant over time, the inflow equals the outflow. The inflow is:

$$\text{FLOW} = \left( \frac{1500 \text{ g}}{\text{day}} + \frac{700 \text{ g}}{\text{day}} + \frac{300 \text{ g}}{\text{day}} \right) \frac{1 \text{ kg}}{10^3 \text{ g}} = 2.5 \frac{\text{kg}}{\text{day}}$$

The characteristic time is:

$$T = \frac{\text{STOCK}}{\text{FLOW}} = \frac{63 \text{ kg}}{2.5 \frac{\text{kg}}{\text{day}}} = 25 \text{ days} \approx 1 \text{ month}$$

1.13

We are given that the capacity of the Shasta reservoir is 4,552,000 acre-feet and that the average annual inflow is 5,439,000 acre-feet.

(a) The conversions are:

$$\text{CAPACITY: } (4,552,000 \text{ a-f}) (43,560 \frac{\text{ft}^3}{\text{a-f}}) \left( \frac{1 \text{ m}^3}{35.31 \text{ ft}^3} \right) = 5.6 \times 10^9 \text{ m}^3$$

$$\text{INFLOW: } (5,439,000 \text{ a-f}) (43,560 \frac{\text{ft}^3}{\text{a-f}}) \left( \frac{1 \text{ m}^3}{35.31 \text{ ft}^3} \right) = 6.7 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$$

1.13

113 (continued)

(b) The characteristic time of a water molecule is found by:

$$T = \frac{\text{STOCK}}{\text{FLOW}} = \frac{\text{CAPACITY}}{\text{INFLOW}} = \frac{5.6 \times 10^9 \text{ m}^3}{6.7 \times 10^9 \text{ m}^3/\text{yr}} = 0.836 \text{ yr}$$

$$T = (0.836 \text{ yr}) (365 \frac{\text{days}}{\text{yr}}) = \boxed{305 \text{ days}}$$

(c) Because the chemical mixes thoroughly with the reservoir water and because it is inert, the characteristic time needed for the water to return to its pre-spill condition is the same as the characteristic time for a water molecule in the reservoir. Therefore:

$$T = \boxed{305 \text{ days}}$$

(d) The time is found by:

$$t = (5.6 \times 10^9 \text{ m}^3) \left( \frac{1 \text{ person-day}}{1400 \text{ L}} \right) \left( \frac{10^3 \text{ L}}{\text{m}^3} \right) \left( \frac{1}{30 \times 10^6} \text{ persons} \right)$$

$$\boxed{t = 133 \text{ days}}$$

(e) Use the concept of material balances to find how long it will take for the reservoir to go dry. Using a material balance on water:

$$\frac{\Delta S}{\Delta t} = f_{in} - f_{out}$$

where

$\Delta S / \Delta t$  = change in (water) stock with time

$f_{in}$  = flow in

$f_{out}$  = flow out

If the reservoir goes dry, then  $\Delta S = -5.6 \times 10^9 \text{ m}^3$ . Since the reservoir level is currently unchanging, then  $f_{in} = f_{out}$ . If we reduce the inflow by 50%, then  $f_{in} = \frac{1}{2} f_{out}$ . Now we can solve for  $\Delta t$ :

$$\Delta t = \frac{\Delta S}{\frac{1}{2} f_{out} - f_{out}} = \frac{\Delta S}{-\frac{1}{2} f_{out}} = \frac{-5.6 \times 10^9 \text{ m}^3}{-\frac{1}{2} (6.7 \times 10^9 \frac{\text{m}^3}{\text{yr}})} = \boxed{1.7 \text{ yrs}}$$

$\approx 620 \text{ days}$