Chapter 1

$\boxed{1.1}$

(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 $\frac{35\times10^{-6}\text{ moles CO}}{\text{mole air}}$

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:

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

Assuming $P = 1$ atm and $T = 293$ 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:

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

Thus, the conversion is:

$$\left(\frac{35\times10^{-6}\text{ mol CO}}{\text{mol air}}\right)\left(\frac{28\text{ g CO}}{\text{mol}}\right)\left(\frac{10^3\text{ mg}}{\text{g}}\right)\left(\frac{1\text{ mol air}}{0.024\text{ m}^3\text{ air}}\right)$$

$$= \boxed{41\text{ mg m}^{-3}}$$

(c) The conversion is:

$$\left(\frac{0.005\text{ mg Cd}}{\text{L H}_2\text{O}}\right)\left(\frac{1\text{ L H}_2\text{O}}{1000\text{ g H}_2\text{O}}\right)\left(\frac{1\text{ g Cd}}{10^3\text{ mg Cd}}\right)\underset{\text{to convert to ppm}}{(10^6)} = \boxed{0.005\text{ ppm}}$$

$\boxed{1.2}$

(a) As in problem 1.1(b) above, we use the ideal gas law and the molecular weight of the contaminant, in this case $CHCl_3$, to make the conversion. Recall:

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

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

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

The molecular weight of $CHCl_3$ is:

$$MW_{CHCl_3} = 12 \text{ g mol}^{-1} + 1 \text{ g mol}^{-1} + 3(35.5 \text{ g mol}^{-1})$$
$$= 119.5 \text{ g mol}^{-1}$$

The conversion is:

$$\left(\frac{0.4 \, \mu g \; CHCl_3}{m^3 \text{ air}}\right)\left(\frac{0.024 \, m^3 \text{ air}}{\text{mol air}}\right)\left(\frac{1 \text{ g}}{10^6 \, \mu g}\right)\left(\frac{1 \text{ mol } CHCl_3}{119.5 \text{ g } CHCl_3}\right)(10^9)$$
$$= \boxed{0.08 \text{ ppb } CHCl_3}$$

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

$$\left(\frac{42 \, \mu g \; CHCl_3}{L \; H_2O}\right)\left(\frac{1 \text{ L}}{10^3 \text{ mL}}\right)\left(\frac{1 \text{ mL } H_2O}{g \; H_2O}\right)\left(\frac{1 \text{ g}}{10^6 \, \mu g}\right)(10^9)$$
$$= \boxed{42 \text{ ppb } CHCl_3}$$

(c) The exposures to $CHCl_3$ through inhalation and ingestion:

	Inhalation	Ingestion
Amount consumed	$20 \text{ m}^3 \text{ day}^{-1}$	2 L day^{-1}
$CHCl_3$ concentration	$0.4 \, \mu g \text{ m}^{-3}$	$42 \, \mu g \text{ L}^{-1}$
$CHCl_3$ exposure	$8 \, \mu g \text{ day}^{-1}$	$84 \, \mu g \text{ day}^{-1}$

1.2 (continued)

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

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

(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:

$$\left(\frac{80\times10^{-9}\ g\ C_2H_3Cl}{g\ H_2O}\right)\left(\frac{10^6\ \mu g}{g}\right)\left(\frac{10^3\ g}{kg}\right)\left(\frac{1\ kg\ H_2O}{L\ H_2O}\right)$$

$$= \boxed{80\ \mu g\ L^{-1}\ C_2H_3Cl}$$

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

(b) The conversion in air is:

$$\left(\frac{80\times10^{-9}\ mol\ C_2H_3Cl}{mol\ air}\right)\left(\frac{62.5\ g\ C_2H_3Cl}{mol}\right)\left(\frac{10^6\ \mu g}{g}\right)\left(\frac{1\ mol\ air}{0.024\ m^3}\right)\left(\frac{1m^3}{10^3 L}\right.$$

$$= \boxed{0.2\ \mu g\ L^{-1}\ C_2H_3Cl}$$

Note: See problems 1.1 and 1.2 for a calculation of what volume is occupied by a mole of air. $P = 1$ atm and $T = 293$ 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:

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

1.4 (continued)

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

where

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

Therefore

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

Our conversions are as follows:

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

1.5

We first want to find the total mass of CO_2 in the atmosphere, given:

$$M_{atm} = 5.1\times10^{18}\ kg$$
$$Y_{CO_2} = 350\ ppm$$

We also know that

$$MW_{air} = 28.9\ g\ mole^{-1}$$
$$MW_{CO_2} = 44\ g\ mole^{-1}$$

Therefore, the total mass of CO_2 is:

$$M_{CO_2} = \left(\frac{350\ mol\ CO_2}{10^6\ mol\ air}\right)\left(\frac{1\ mole\ air}{29.8\ g}\right)\left(\frac{10^3 g}{kg}\right)\left(5.1\times10^{18}\ kg\ air\right)$$

$$M_{CO_2} = \left(6.18\times10^{16}\ mol\ CO_2\right)\left(\frac{44\ g\ CO_2}{mol\ CO_2}\right)\left(\frac{1\ \text{metric tons}}{10^6\ g}\right)$$

$$M_{CO_2} = 2.72\times10^{16}\ \text{metric tons}$$

The rate of mass accumulation, then, is:

$$\text{Rate} = \left(2.72\times10^{16}\ \text{metric tons}\right)\left(0.5\ \frac{\%}{\text{year}}\right) = \boxed{1.4\times10^{10}\ \frac{\text{metric tons}}{\text{year}}}$$

1.6

(a) To find the CO_2 emission rate from private automobiles in the US, simply multiply:

$$\left(1.2\times10^{8}\,\text{cars}\right)\left(\frac{10^{4}\,\text{miles}}{\text{car yr}}\right)\left(\frac{1\,\text{gal}\,C_8H_{18}}{18\,\text{miles}}\right)\left(\frac{3785\,\text{cm}^3\,C_8H_{18}}{\text{gal}\,C_8H_{18}}\right)$$

$$\times\left(\frac{0.72\,\text{g}\,C_8H_{18}}{1\,\text{cm}^3\,C_8H_{18}}\right)\left(\frac{96\,\text{gC}}{114\,\text{g}\,C_8H_{18}}\right)\left(\frac{44\,\text{g}\,CO_2}{12\,\text{gC}}\right)\left(\frac{1\,\text{metric tonne}}{10^{6}\,\text{g}}\right)$$

$$=\boxed{5.6\times10^{8}\,\frac{\text{metric tonnes }CO_2}{\text{yr}}}$$

(b) Of the total mass accumulation of CO_2 in the atmosphere, US private automobiles account for $\frac{5.6\times10^{8}}{1.4\times10^{10}}\times100=\underline{4\,\%}$. Thus, if US auto CO_2 emissions were reduced to 0 through regulation, global CO_2 mass accumulation would still be 96% of our current estimates. However automobiles worldwide may also be significant contributers to 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:

$$\frac{\text{PCE waste produced}}{\text{month}}=\frac{\text{PCE purchased}}{\text{month}}\,(1-0.3)$$

$$=\frac{250\,\text{L}}{\text{month}}\,(0.7)=175\,\frac{\text{L PCE}}{\text{month}}$$

Now find out how long for the 0.7 m³ (=700 L) disposal container to fill:

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

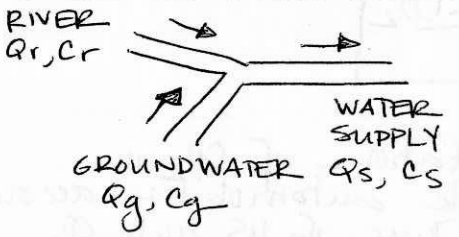
container will have to be emptied this often

$\boxed{1.8}$

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 mg L^{-1}
Barium concentrantion in river = 0.5 mg L^{-1}
Barium concentration in groundwater = 9 mg L^{-1}
Water supply needs for Ecocity = 10 $m^3\,day^{-1}$

We can use the mass balance concept to solve:



Let $Q_s = 10\ m^3\ day^{-1}$
$C_s = 5\ mg\ L^{-1}$
$C_r = 1.5\ mg\ L^{-1}$
$C_g = 9\ mg\ L^{-1}$

Mass balance on water: $Q_r + Q_g = Q_s$
Mass balance on barium: $C_rQ_r + C_gQ_g = C_sQ_s$
Therefore:

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

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

$$0.5(10 - Q_g) + 9Q_g = 20$$
$$5 - 0.5\,Q_g + 9\,Q_g = 20$$
$$8.5\,Q_g = 15$$
$$Q_g = 1.76\ m^3\ d^{-1}$$
$$\text{and}\quad Q_r = 10 - Q_g = 8.24\ m^3\ d^{-1}$$

So Ecocity should use:

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

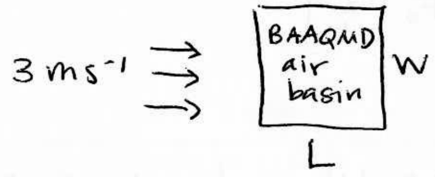
Note: We can check to make sure this combination of flows will give us the desired barium concentration:

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

$\boxed{1.9}$

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

$$\tau = \frac{125600 \text{ m}}{3 \text{ m s}^{-1}} = 41900 \text{ s}$$
$$\tau = (41900 \text{ s})\left(\frac{1 \text{ min}}{60 \text{ s}}\right)\left(\frac{1 \text{hr}}{60 \text{min}}\right) = 11.6 \text{ hr}$$

$\boxed{\tau = 10 \text{ hrs}}$ (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

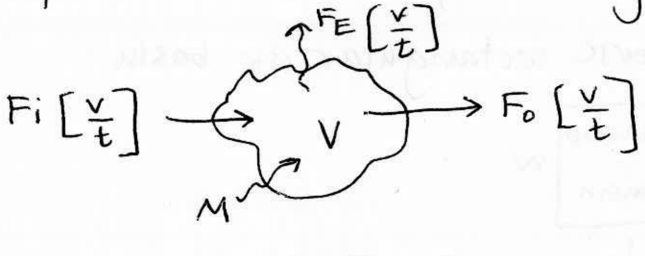
$$\tau = \frac{\sqrt{\frac{\text{area}}{\text{aspect ratio}}}}{\text{wind velocity}}$$

For example, with an aspect ratio of 2, we would get τ = 8 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, $\boxed{t = 1 \text{ day to } 1 \text{ week}}$ is sufficient. This assumes that the wind itself is pristine.

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:

$$\boxed{\tau = \frac{V}{F_i} = \frac{V}{F_e + F_o}}$$

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:

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

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

$\boxed{1.11}$ (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

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

$\boxed{1.12}$

Find the stock of water in the body first:

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

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

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

The characteristic time is:

$$\tau = \frac{\text{STOCK}}{\text{FLOW}} = \frac{63 \text{ kg}}{2.5 \text{ kg/day}} = \boxed{25 \text{ days}} \simeq 1 \text{ month}$$

$\boxed{1.13}$

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:

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

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

$\boxed{1\,13}$ (continued)

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

$$\tau = \frac{\text{STOCK}}{\text{FLOW}} = \frac{\text{CAPACITY}}{\text{INFLOW}} = \frac{5.6\times10^{9}\,m^{3}}{6.7\times10^{9}\,m^{3}/yr} = 0.836\,yr$$

$$\tau = (0.836\ yr)\left(365\,\frac{days}{yr}\right) = \boxed{305\ days}$$

(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:

$$\tau = \boxed{305\ days}$$

(d) The time is found by:

$$t = (5.6\times10^{9}\,m^{3})\left(\frac{1\ \text{person-day}}{1400\,L}\right)\left(\frac{10^{3}\,L}{m^{3}}\right)\left(\frac{1}{30\times10^{6}\ \text{persons}}\right)$$

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

(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 $\Delta S = -5.6\times10^{9}\,m^{3}$. 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 Δt:

$$\Delta t = \frac{\Delta S}{\frac{1}{2}f_{out} - f_{out}} = \frac{\Delta S}{-\frac{1}{2}f_{out}} = \frac{-5.6\times10^{9}\,m^{3}}{-\frac{1}{2}\left(6.7\times10^{9}\,\frac{m^{3}}{yr}\right)} = \boxed{1.7\ yrs}$$

≈ 620 days