

## Practice Introductory Problems

1. Using the data in the diagram of the water cycle to estimate the residence time of water in the atmosphere, rivers and the oceans.
2. Using the data from the table *Inputs and Residence times of common ions in seawater* (handout), estimate the volume of water in the oceans.
3. The concentration of lead in the blood of an adult male was 140 micrograms per liter ( $\mu\text{g/L}$ ) and the blood volume was 4.8 L. The net transfer of lead into the bones was estimated at  $7.5 \mu\text{g/day}$  and the net excretion rate at  $24 \mu\text{g/day}$ . Calculate the residence time of lead in the blood of this individual.
4. The residence time of water in Lake Erie is 2.7 yrs. The concentration of phosphorous in L. Erie in 1983 was  $15 \mu\text{g L}^{-1}$  and the volume of the lake is  $484 \text{ km}^3$ . Calculate the average rate of input of phosphorous into Lake Erie at that time.
5. Convert the data in table *Typical concentration of common ions in river and seawater* (handout) to  $\text{mg/L}$  and calculate the total dissolved solids in river water. Compare this to the average total dissolved solids of the oceans, which is about  $35 \text{ g/L}$ .
6. Convert the concentrations in table *Typical concentration of common ions in river and seawater* (handout) to equivalents per liter and check for charge balance.
7. In freshwater the units of  $\text{mg/L}$  and ppm are often used interchangeably, whereas this is not the case in seawater. Explain.
8. Why are the major freshwater ions  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  yet the major seawater ions are  $\text{Na}^+$  and  $\text{Cl}^-$ ?

## Solutions to Practice Intro Problems

1. Residence Time ( $\tau$ ) =  $\frac{\text{amount}}{\text{rate input/output}}$

Therefore, residence time for water in the atmosphere

$$= \frac{14 \times 10^{15} \text{ kg}}{(350 + 70) \times 10^{15} \text{ kg yr}^{-1}} = 0.033 \text{ yr}$$

or

$$0.033 \text{ yr} \times \frac{365 \text{ d}}{1 \text{ yr}} \approx 12 \text{ days}$$

*note: the rate output = 320 + 100 = 420 x 10<sup>15</sup> kg yr<sup>-1</sup>, which is the same as the rate of input*

Similarly for rivers and oceans,

$$\tau(\text{rivers}) \sim 15 \text{ days}$$

$$\tau(\text{oceans}) \sim 4000 \text{ yr}$$

2. Using any data set from the table (eg Cl<sup>-</sup>), we have;

$$\tau(\text{Cl}^-) = \text{amount Cl}^- / \text{rate input of Cl}^-$$

Where amount of Cl<sup>-</sup> = 0.55 mol/L x Volume(ocean)

$$\text{Rate of input of Cl}^- = 720 \times 10^{10} \text{ mol yr}^{-1}$$

$$\text{Since } \tau(\text{Cl}^-) = 1 \times 10^8 \text{ yr}$$

$$1 \times 10^8 \text{ yr} = \frac{0.55 \text{ mol L}^{-1} \times V_{\text{ocean}}}{720 \times 10^{10} \text{ mol yr}^{-1}}$$

Rearranging yields,

$$V_{\text{ocean}} = \frac{1 \times 10^8 \text{ yr} \times 720 \times 10^{10} \text{ mol yr}^{-1}}{0.55 \text{ mol L}^{-1}} \sim 1.4 \times 10^{21} \text{ L}$$

Since, 1 km<sup>3</sup> = 10<sup>12</sup> L

$$V_{\text{ocean}} \sim 1.4 \times 10^9 \text{ km}^3 \quad (\text{check this against other estimates})$$

3.  $\tau(\text{Pb in blood}) = (\text{amt of Pb in blood}) / (\text{rate of loss of Pb from blood})$

$$\text{Amt Pb} = 140 \mu\text{g/L} \times 4.8 \text{ L} = 672 \mu\text{g}$$

$$\text{Rate of loss} = 7.5 \mu\text{g d}^{-1} + 24 \mu\text{g d}^{-1} = 31.5 \mu\text{g d}^{-1}$$

$$\text{Therefore, } \tau \sim (672 \mu\text{g}) / (31.5 \mu\text{g d}^{-1}) = 21 \text{ days}$$

4.  $\tau_{\text{water}}(\text{Erie}) = V_{\text{water}}(\text{Erie})/\text{Rate water input} = 2.7 \text{ yr}$

Since,  $V_{\text{Erie}} \sim 484 \text{ km}^3$ ,

Rate water input =  $484\text{km}^3/2.7 \text{ yr} = 180 \text{ km}^3/\text{yr}$

Since,  $[\text{P}] = 15 \text{ }\mu\text{g/L}$ ,

Rate of P input =  $15 \text{ }\mu\text{g/L} \times 180 \text{ km}^3/\text{yr} \times 1 \text{ kg}/10^9 \text{ }\mu\text{g} \times 10^{12} \text{ L}/1 \text{ km}^3$   
 $= 2.7 \times 10^6 \text{ kg P yr}^{-1}$  (assuming well mixed reservoir)

5 and 6. Converting M to mg/L, involves multiplying the molar concentration by the molar mass in mg/mol (i.e.,  $2.2 \times 10^{-4} \text{ mol Cl}^-/\text{L} \times 35,450 \text{ mg Cl}^-/\text{mol Cl}^- = 7.8 \text{ mg Cl}^-/\text{L}$ )  
 Converting M to N involves multiplying molar concentration by the unit charge on the ion.

Similarly, for the ions below.

| Ion                | Molarity             | mg/L ~ ppm | Normality (equiv/L)  |
|--------------------|----------------------|------------|----------------------|
| $\text{Cl}^-$      | $2.2 \times 10^{-4}$ | 7.8        | $2.2 \times 10^{-4}$ |
| $\text{Na}^+$      | $2.7 \times 10^{-4}$ | 6.2        | $2.7 \times 10^{-4}$ |
| $\text{Mg}^{2+}$   | $1.7 \times 10^{-4}$ | 4.1        | $3.4 \times 10^{-4}$ |
| $\text{SO}_4^{2-}$ | $1.2 \times 10^{-4}$ | 12         | $2.4 \times 10^{-4}$ |
| $\text{K}^+$       | $5.9 \times 10^{-5}$ | 2.3        | $5.9 \times 10^{-5}$ |
| $\text{Ca}^{2+}$   | $3.8 \times 10^{-4}$ | 15         | $7.6 \times 10^{-4}$ |
| $\text{HCO}_3^-$   | $9.5 \times 10^{-4}$ | 58         | $9.5 \times 10^{-4}$ |
|                    |                      |            |                      |

5. The total dissolved solids (TDS) in this sample can be estimated by adding all the numbers in the third column above; TDS ~ 105 mg/L. Seawater has a TDS of ~ 35,000 mg/L (~ 350x more saline)

6. The charge balance can be checked by summing all the equivalents of positive charge and comparing this to the sum of the negative charges in the forth column (table above).

$\Sigma + = 1.4 \times 10^{-3} \text{ equiv/L}$

$\Sigma - = 1.4 \times 10^{-3} \text{ equiv/L}$

(therefore, the solution is charge balanced)

7. The equivalency between mg/L and ppm is based on the density of pure water at 20°C, which is 1.00 g/mL or 1.00 kg/L. This is generally true for dilute solutions and most freshwater applications.

$$\frac{1 \text{ mg}}{\text{L}} \times \frac{1 \text{ L}}{1.00 \text{ kg}} = \frac{1 \text{ mg}}{\text{kg}} = 1 \text{ ppm}$$

The density of seawater, brines and certain wastewaters is greater than 1.00 and in these cases concentrations in mg/kg = ppm and mg/L  $\neq$  ppm.

Consider the concentration of **Cl<sup>-</sup>** in seawater (which has a density of 1.035 kg/L),

$$0.55 \text{ mol/L} \times 35,450 \text{ mg/mol} = 19,500 \text{ mg/L}$$

Using the density to convert volume of solution (L) to mass of solution (kg), we calculate

$$0.55 \text{ mol/L} \times 35,450 \text{ mg/L} \times 1 \text{ L}/1.035 \text{ kg} = 19,000 \text{ mg/kg} = 19,000 \text{ ppm}$$

8. The answer to this apparent contradiction can be summed by in a word: *solubility*. The oceans are long-term reservoirs, which receive inputs of dissolved solids from freshwater rivers etc. and lose water (not dissolved solids) by evaporation. Therefore, the concentration of all ions increases slowly over time due to continental weathering. At some point, ion concentrations will approach their saturation limit and may begin to precipitate from solution. This is particularly true for the ions which combine to form less soluble solids, such as **CaCO<sub>3</sub>(s)** ( $K_{sp} \sim 10^{-8}$ ).

Sodium chloride is extremely soluble and the aqueous concentrations in the oceans are not anywhere near the saturation limit. On the other hand, the concentrations of the calcium and carbonate ions are essentially at the saturation limit in surface ocean waters. Much of the calcium carbonate is deposited in sedimentary materials and the exoskeletons of some marine organisms.

Consistent with this description are the estimated residence times for various ions in the oceans, which are much longer for **Na<sup>+</sup>** and **Cl<sup>-</sup>** than those for **Ca<sup>2+</sup>** and **HCO<sub>3</sub><sup>-</sup>**.