Provide solutions to the following questions in a neat and well organized manner. Clearly state assumptions and reference sources for any constants used. 
Due date: November 18th

1. Methane and carbon dioxide are produced under anaerobic conditions by the fermentation of organic matter, approximated by the following equation:

\[ 2 \text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2 \]

As gas bubbles are evolved at the sediment interface at 5 m depth and remain in contact with water at the sediment surface long enough so that equilibrium is attained. The total pressure at this depth is 148 kPa. If the pH is 8.20, calculate the total carbonate concentration in the interstitial water at 25°C. How would you expect your answer to change if these gas bubbles were present at 500 m depth?

**Strategy:** The total pressure inside the gas bubble must be equal to the total pressure on the outside of the gas bubble (or else it would either explode or collapse). Furthermore, the total pressure inside that gas bubble is equal to the sum of the partial pressures of CH\(_4\) and CO\(_2\). We can then use the partial pressure of CO\(_2\) inside the gas bubble and the corresponding Henry’s law constant to calculate the concentration of aqueous CO\(_2\) at equilibrium. Given the pH of the solution and the expressions for K\(_{a1}\) and K\(_{a2}\), we can determine the concentration of HCO\(_3^-\) and CO\(_3^{2-}\). (see textbook pgs 241-242; Chap 11, Q9)

**Solution:**

The total carbonate concentration is given by:

\[
[\text{CO}_3^{2-}]_T = [\text{CO}_2(aq)] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]
\]

From the pH speciation diagram (Fig. 1.2 text), we can see that at pH 8.2, the vast majority of the inorganic carbon present is in the form of the bicarbonate ion (i.e., [HCO\(_3^-\)] \gg [CO\(_2(aq)\)] \approx [CO\(_3^{2-}\)]).

So we can write,

\[
[\text{CO}_3^{2-}]_T \approx [\text{HCO}_3^-]
\]

In order to ‘solve’ this problem, we need find the partial pressure of CO\(_2\), which is in equilibrium with the surrounding water. Since this reaction is occurring under anaerobic conditions, these are the only gases likely to be presence at appreciable concentrations and they are produced with 1:1 stoichiometry. Therefore,

\[
P_T = 148 \text{ kPa} = P_{CO_2} + P_{CH_4}
\]

and

\[
P_{CO_2} = P_{CH_4} = 74 \text{ kPa}
\]

To calculate the total carbonate, we will first need the [CO\(_2(aq)\)].
From the Henry’s Law expression;

\[ [\text{CO}_2(aq)] = K_H P_{\text{CO}_2} \]

Using the \( K_H \) value in Table 11.1 (textbook) yields;

\[ [\text{CO}_2(aq)] = 3.3 \times 10^{-7} \text{ M Pa}^{-1} \times 74,000 \text{ Pa} = 2.44 \times 10^{-2} \text{ M} \]

Using this value in the \( K_{a1} \) expression and substituting in the \([H^+] = 10^{-8.2} \text{ M}\), allows us to calculate the \([\text{HCO}_3^-]\) as follows;

\[
\begin{array}{c|c|c|c}
\text{CO}_2(aq) & + & \text{H}_2\text{O} & \rightleftharpoons \text{HCO}_3^- & + & \text{H}^+ \\
\hline
\text{I} & 2.44 \times 10^{-2} \text{ M} & 0 & 0 \\
\text{C} & 0 & +x & 0 \\
\text{E} & 2.44 \times 10^{-2} \text{ M} & x & 10^{-8.2} \text{ M} \\
\end{array}
\]

\[ K_{a1} = \frac{[H^+][\text{HCO}_3^-]}{[\text{CO}_2(aq)]} = \frac{(4.5 \times 10^{-7})(2.44 \times 10^{-2})}{10^{-8.2}} = 1.75 \text{ M} \]

So, \([\text{CO}_3^{2-}]_T \approx [\text{HCO}_3^-] = 1.75 \text{ M}\)

*Note: this represents an upper limit, since the assumption is that the supply of \( \text{CO}_2 \) is inexhaustible (i.e., the change in \([\text{CO}_2(aq)]\) as the acid dissociation reaction proceeds is assumed to be negligible). This is clearly not the case here since the \( \text{CO}_2 \) in the gas bubble is consumed as the reaction proceeds. In order to correct for this, we would need additional information such as the size of the gas bubble so that we could determine the number of moles of \( \text{CO}_2 \) molecules present.*

At 500 m depth in the water column, the partial pressure inside the gas bubbles would necessarily be much greater and the calculated total carbonate concentration would be huge. Again, this results in an unrealistically high value.
2. Use the following chemical equilibrium for a water sample in equilibrium with atmospheric CO\(_2\)(g) and limestone (CaCO\(_3\)). In such a system, the concentrations of H\(^+\) and Ca\(^{2+}\) are coupled to each other and to the partial pressure of CO\(_2\).

\[
\text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2 \text{HCO}_3^-
\]

Calculate the solubility of CaCO\(_3\) in equilibrium with P\(_{CO2}\) = 390 ppmv. What effect will a doubling of the atmospheric concentration of CO\(_2\) have on your result?

*Strategy:* The solubility of CaCO\(_3\)(s) will be given by the concentration of Ca\(^{2+}\) in equilibrium with solid calcium carbonate and an inexhaustible supply of atmospheric carbon dioxide. If we can determine the value of the equilibrium constant for the above reaction and independently determine the concentration of HCO\(_3^-\), we can rearrange the expression and calculate the [Ca\(^{2+}\)]. Alternatively, we can write the solubility product expression for CaCO\(_3\) and rearrange for [Ca\(^{2+}\)]. Making the appropriate substitutions, we can derive an expression for [Ca\(^{2+}\)] in terms of a series of equilibrium constants and the [H\(^+\)]. Since we have two variables and two unknowns, we use a second independent expression (i.e., charge balance) to solve for both [H\(^+\)] and [Ca\(^{2+}\)]. (see textbook pgs 242-244)

*Solution:* The solubility of calcium carbonate and thus the concentration of Ca\(^{2+}\), will vary with changes in the P\(_{CO2}\) and [H\(^+\)]. To derive an expression for the [Ca\(^{2+}\)] as a function of P\(_{CO2}\), we must first determine the [H\(^+\)].

Rearranging the K\(_{sp}\) expression for CaCO\(_3\), we can write;

\[
[\text{Ca}^{2+}] = K_{sp}/[\text{CO}_3^{2-}]
\]

Remembering that we wish to express the [Ca\(^{2+}\)] in terms of P\(_{CO2}\) and [H\(^+\)], we look for an appropriate substitution for [CO\(_3^{2-}\)].

Rearranging the K\(_{a2}\) expression gives;

\[
[\text{CO}_3^{2-}] = K_{a2} [\text{HCO}_3^-]/[\text{H}^+]
\]

and we can substitute for [HCO\(_3^-\)] using the K\(_{a1}\) expression;

\[
[\text{HCO}_3^-] = \{K_{a1}[\text{CO}_2(aq)]/[\text{H}^+]\}
\]

and we can substitute for [CO\(_2(aq)\)] using the K\(_{H}\) expression;

\[
[\text{CO}_2(aq)] = K_{H} P_{CO2}
\]

Making these substitutions into the expression for [Ca\(^{2+}\)] gives;
\[[Ca^{2+}] = \frac{K_{sp}[H^+]^2}{K_{a1}K_{a2}K_{H^+}P_{CO2}}\]

From this expression we can see that the concentration of calcium depends not only on the \(P_{CO2}\), but also on the equilibrium concentration of \([H^+]\) – which we know will also depend on the \(P_{CO2}\).

To derive an expression for the \([H^+]\) as a function of \(P_{CO2}\), we will need an additional independent relationship – the charge balance equation. Since all solutions are electrically neutral, we can write that the sum total of positive charges is equal to the sum total of negative charges.

Thus;

\[2[Ca^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]\]

For most natural water in contact with solid CaCO\(_3\) (pH ranges 5-9), this simplifies to;

\[2[Ca^{2+}] = [HCO_3^-]\]

since \([Ca^{2+}] >> [H^+]\)

and

\([HCO_3^-] >> [CO_3^{2-}]\) and \([OH^-]\)

So from the charge balance, we can write; \([Ca^{2+}] = \frac{1}{2} [HCO_3^-]\)

Using the \(K_{a1}\) and \(K_H\) expressions to substitute for the \([HCO_3^-]\) in terms of \([H^+]\) and \(P_{CO2}\) (as before), yields;

\[[Ca^{2+}] = \frac{K_{a1}K_H^2P_{CO2}}{2[H^+]^2}\]

Since we now have two expressions for the concentration of \(Ca^{2+}\) (one derived from the \(K_{sp}\) expression and the other from the charge balance), we can set them equal to each other and solve for \([H^+]\) as a function of only the \(P_{CO2}\).

Thus;

\[\frac{K_{sp}[H^+]^2}{K_{a1}K_{a2}K_H^2P_{CO2}} = \frac{K_{a1}K_H^2P_{CO2}}{2[H^+]^2}\]

Rearranging and solving for \([H^+]\) yields;
Thus, we have an expression to calculate the $[H^+]$ at any $P_{CO_2}$. We can use this and then substitute both the $[H^+]$ and the $P_{CO_2}$ into the expression for $[Ca^{2+}]$ above and calculate the equilibrium concentration of calcium.

$$[H^+] = \sqrt[3]{\frac{K_{a1}^2 K_H^2 K_{a2} P_{CO_2}^2}{2K_{sp}}}$$

$$[H^+] = \sqrt[3]{\frac{(4.5 \times 10^{-7} M)^2 (3.3 \times 10^{-7} M Pa^{-1})^2 (4.7 \times 10^{-11} M)(39.5 Pa)^2}{2 (5 \times 10^{-9} M^2)}}$$

$$= 5.45 \times 10^{-9} M \quad \text{(i.e., pH = 8.26)}$$

$$[Ca^{2+}] = \frac{K_{sp}[H^+]^2}{K_{a1} K_{a2} K_H P_{CO_2}} = \frac{(5 \times 10^{-9} M^2)(5.45 \times 10^{-9} M)^2}{(4.5 \times 10^{-7} M)(4.7 \times 10^{-11} M)(3.3 \times 10^{-7} M Pa^{-1})(39.5 Pa)}$$

$$\therefore \ [Ca^{2+}] = 5.39 \times 10^{-4} M$$

In other words, 0.54 millimoles of CaCO$_3$(s) dissolves in 1 L of water in equilibrium with atmospheric CO$_2$ at 390 ppmv.

Doubling of the $P_{CO_2}$ from 390 ppmv to 780 ppmv yields the following;

$$[H^+] = 8.65 \times 10^{-9} M \quad \text{(i.e., pH = 8.06)}$$

and

$$[Ca^{2+}] = 6.78 \times 10^{-4} M$$

In other words, the solubility of CaCO$_3$ increases by 25% if $P_{CO_2}$ doubles.

Note: For gases, a ppm is defined as a volume ratio (hence ppmv) and since the partial pressure of a gas is directly proportional to its partial volume (via $P = nRT/V$), we can write:

$$P_{CO_2} = (390 \times 10^6) P_T, \text{ where } P_T \text{ at sea-level is } 101,300 \text{ Pa}$$

Hence, $P_{CO_2} @ 390 \text{ ppmv} = 39.5 \text{ Pa}$
3. Sulfur dioxide is soluble in water, $K_H = 1.8 \times 10^{-5}$ mol L$^{-1}$ Pa$^{-1}$ at 25°C. Calculate the equilibrium aqueous concentration of SO$_2$ in raindrops, if the air contains 2.0 ppmv of SO$_2$(g). Calculate the pH of this rain. How would your answer change if the dissolved sulfur dioxide is oxidized to sulfur trioxide? Justify your answer.

**Strategy:** The concentration of aqueous SO$_2$ in equilibrium with an inexhaustible supply of atmospheric SO$_2$(g) will be given by the partial pressure of sulfur dioxide and the value of the corresponding Henry’s law constant. To calculate the pH of the solution, we will need the value of the acidic dissociation constant for sulfurous acid. (see textbook pgs 241-242; Chap 11 Q6)

**Solution:**
We will need to consider both the dissolution of SO$_2$(g) into water ($K_H$) and the subsequent dissociation to produce protons ($K_{a1}$ and $K_{a2}$). These equilibria are summarized below.

\[
\begin{align*}
\text{SO}_2(g) & \rightleftharpoons \text{SO}_2(aq) \quad K_H = 1.8 \times 10^{-5} \text{ M Pa}^{-1} \text{ (text, Table 11.1)} \\
\text{SO}_2(aq) + \text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{HSO}_3^- \quad K_{a1} = 1.72 \times 10^{-2} \text{ (text, App. B1)} \\
\text{HSO}_3^- & \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-} \quad K_{a2} = 6.43 \times 10^{-8} \text{ (text, App. B1)}
\end{align*}
\]

Assuming a total pressure of one atmosphere, the $P_{SO_2} = 2.0 \times 10^{-6}$ atm. Converting the given $K_H$ into atmospheres yields;

\[1.8 \times 10^{-3} \text{ M Pa}^{-1} \times 101,300 \text{ Pa atm}^{-1} = 1.82 \text{ M atm}^{-1}\]

Thus, $[\text{SO}_2(aq)] = K_H \times P_{SO_2} = (1.82 \text{ M atm}^{-1}) (2.0 \times 10^{-6} \text{ atm}) = 3.64 \times 10^{-6} \text{ M}$

Using the $K_{a1}$ expression and assuming no further dissociation of HSO$_3^-$ (i.e., ignoring $K_{a2}$), yields;

\[K_{a1} = \frac{x^2}{[\text{SO}_2(aq)]},\]

where $x = [\text{H}^+] = [\text{HSO}_3^-]$ and we assume that the atmosphere provides an inexhaustible supply of SO$_2$(aq)

\[\therefore [\text{H}^+]^2 = (1.72 \times 10^{-2}) (3.64 \times 10^{-6})\]

so

\[ [\text{H}^+] = 2.50 \times 10^{-4} \text{ M}\]

\[\therefore \text{pH} = 3.60\]

If the SO$_2$(aq) is oxidized to SO$_3$(aq), the pH will be even lower since the resulting sulfuric acid (H$_2$SO$_4$) is stronger than sulfurous acid (H$_2$SO$_3$). See further the $K_{a1}$ and $K_{a2}$ values for H$_2$SO$_4$. 
Note 1: A much lower pH results from a smaller amount of SO\textsubscript{2} than for CO\textsubscript{2}. This is the result of two factors $K_{H}(\text{SO}_2)$ is larger and $K_{a1}(\text{SO}_2)$ is larger.

Note 2: If we consider the second dissociation using the $K_{a2}$ expression, we solve for an additional $[H^+] = (K_{a2} \times [\text{HSO}_3^-])^{1/2} = 3.6 \times 10^{-6}$ M, which makes a relatively insignificant contribution to the pH when added to the $3.05 \times 10^{-4}$ M already present from the first dissociation, $[H^+] \sim 2.05 \times 10^{-4} + 3.6 \times 10^{-6} = 2.09 \times 10^{-4}$ M, so $pH = 3.68$. 
4. Estimate the fraction of lead complexed to fulvic acid in a sample containing 3.6 µg/L of lead and 12 mg/L of DOM (as fulvic acid) at pH 5. Assume a $[\text{FA}_{\text{CO}_2^-}] = 4.5 \text{ mmol g}^{-1}$ of DOM and that lead is the only metal ion in solution. $K_f (\text{Pb}^{2+} - \text{FA}) = 1.1 \times 10^4$

**Strategy:** The fraction of lead complexed to FA relative to the total amount of lead can be determined if we calculate the concentration of lead complexed to FA. We approach this by writing the chemical equilibrium for the complexation of lead by FA and the corresponding formation constant expression ($K_f$). Distinguishing between ‘free’ and ‘complexed’ forms of both Pb and FA$_{\text{CO}_2^-}$, allows us to complete this calculation. (see textbook pgs 265-266, 283-286, Chap 13 Q5)

**Solution:**
This question requires some knowledge of the association constant ($K_f'$) between Pb$^{2+}$ and fulvic acid, given in Table 13.3 in your textbook and some assumption about the average concentration of carboxylate groups ($C_{\text{CO}_2^-} \sim 4.5 \text{ mmol/g}$) given in the question.

We need to calculate the fraction of lead bound to FA, which we can define as follows;

$$\text{Fraction Pb - FA} = \frac{[\text{Pb - FA}_{\text{CO}_2^-}]}{[\text{Pb}]}$$

where $[\text{Pb-FA}_{\text{CO}_2^-}]$ represents the concentration of lead complexed to fulvics and $[\text{FA}_{\text{CO}_2^-}]_T$ represents the total concentration of fulvic acid carboxylates. We will further define the following terms; $[\text{Pb}^{2+}]_T$, $[\text{Pb}^{2+}]_{\text{free}}$ and $[\text{FA}_{\text{CO}_2^-}]_{\text{free}}$

Such that

$[\text{Pb}^{2+}]_T = [\text{Pb}^{2+}]_{\text{free}} + [\text{Pb-FA}_{\text{CO}_2^-}]$

and

$[\text{FA}_{\text{CO}_2^-}]_T = [\text{FA}_{\text{CO}_2^-}]_{\text{free}} + [\text{Pb-FA}_{\text{CO}_2^-}]$

From the information provided in the question;

$[\text{Pb}^{2+}]_T = 3.6 \times 10^{-6} \text{ g/L x 1 mol/207.2 g} = 1.74 \times 10^{-8} \text{ M}$

$[\text{FA}_{\text{CO}_2^-}]_T = (12 \times 10^{-3} \text{ g/L x (4.5 x 10^{-3} mol/g}) = 5.4 \times 10^{-5} \text{ M}$

Since $[\text{Pb}^{2+}]_T \ll [\text{FA}_{\text{CO}_2^-}]_T$

$[\text{FA}_{\text{CO}_2^-}]_T \sim [\text{FA}_{\text{CO}_2^-}]_{\text{free}}$

(i.e., the vast majority of $\text{FA}_{\text{CO}_2^-}$ is not complexed to Pb)

The relevant reaction is given by;

$$\text{Pb}^{2+} + \text{FA}_{\text{CO}_2^-} \rightleftharpoons \text{Pb-FA}_{\text{CO}_2^-} \quad K_f' = 1.12 \times 10^4$$
$1.1 \times 10^4 = \frac{[\text{Pb-FA}_{\text{CO}_2}^-]}{[\text{Pb}^{2+}]_{\text{free}}[\text{FA}_{\text{CO}_2}^-]_{\text{free}}}$

If we let $x$ represent the concentration of complexed fulvic acid ([Pb-FA$_{\text{CO}_2}$-]), then 

$[\text{Pb}^{2+}]_{\text{free}} = 1.74 \times 10^{-8} \text{M} - x$

Further, we can assume that the $[\text{FA}_{\text{CO}_2}^-]_{\text{free}} \sim [\text{FA}_{\text{CO}_2}^-]_T = 5.4 \times 10^{-5} \text{M}$

so

$1.1 \times 10^4 = \frac{x}{(1.74 \times 10^{-8} - x)(5.4 \times 10^{-5} \text{M})}$

$x = (5.4 \times 10^{-5})(1.74 \times 10^{-8} - x)(1.1 \times 10^4) = 1.034 \times 10^{-8} - 0.594x$

and $1.594x = 1.034 \times 10^{-8}$

so $x = 6.487 \times 10^{-9} \text{M} = [\text{Pb-FA}_{\text{CO}_2}]$

Therefore the fraction of lead complexed = $(6.49 \times 10^{-9} / 1.74 \times 10^{-8}) = 0.373$

In other words, under the stated conditions, roughly 37% of the lead is bound to fulvic acid.
5. What fraction of NTA is uncomplexed after $H_2T^-$ has been brought to equilibrium with solid PbCO$_3$ at pH 7 in aqueous solution with $[HCO_3^-] = 1.25 \times 10^{-3}$ M.

\[
PbCO_3(s) + HT^2- \rightleftharpoons PbT^- + HCO_3^-
\]

\[
\log K_{sp}(PbCO_3) = -13.13 \quad \log K_f(PbT^-) = 11.34
\]

**Strategy:** We want to solve for the fraction of free NTA to the total NTA in solution, which will include some NTA complexed to Pb$^{2+}$ ions. Since at pH 7, the predominant form of NTA is HT$^2-$, this fraction we are interested in is $[HT^2-]/([HT^2-] + [PbT^-])$. To solve this, we will write out the expression for the equilibrium above and rearrange to isolate $[PbT^-]$. (see textbook pgs 293-296, Chap 13 Q4)

**Solution:**

\[
PbCO_3(s) \rightleftharpoons Pb^{2+} + CO_3^{2-} \quad K_{sp} = 10^{-13.13} = 7.41 \times 10^{-14}
\]
\[
Pb^{2+} + T^{3-} \rightleftharpoons PbT^- \quad K_f = 10^{11.34} = 2.19 \times 10^{11}
\]
\[
HT^2- \rightleftharpoons H^+ + T^{3-} \quad K_{a3} = 10^{-10.28} = 5.25 \times 10^{-11} \text{ (pg 294)}
\]
\[
H^+ + CO_3^{2-} \rightleftharpoons HCO_3^- \quad K_{a2}^{-1} = (4.7 \times 10^{-11})^{-1} = 2.13 \times 10^{10}
\]

\[
PbCO_3(s) + HT^2- \rightleftharpoons PbT^- + HCO_3^- \quad K_{eq} = \frac{K_{sp}K_fK_{a3}}{K_{a2}} = 0.0181
\]

Since,

\[
K_{eq} = \frac{[PbT^-][HCO_3^-]}{[HT^2-]}
\]

rearranging for $[PbT^-] = \frac{K_{eq}[HT^2-]}{[HCO_3^-]}$

and substituting into the fractional abundance expression;

\[
\alpha_{HT^2-(free)} = \frac{[HT^2-]}{[HT^2-] + [PbT^-]} = \frac{[HT^2-]}{[HT^2-] + \frac{K_{eq}[HT^2-]}{[HCO_3^-]}} = \frac{1}{1 + \frac{K_{eq}}{[HCO_3^-]}}
\]

Substituting in for the value of $K_{eq}$ (above) and the concentration of bicarbonate ion given in the question, yields;

**Fraction of free NTA = 0.0645 (or ~ 6.5%)**
In the “Times Beach” incident, a waste oil hauler removed 18,500 US gallons of oil contaminated by 33 ppm of ‘dioxin’ from a 2,4,5-T manufacturing plant.

a) What mass of dioxin was involved? (assume the oil density is ~ 1 g/mL)

b) Some horse arenas that were sprayed with this waste oil had solid matter concentrations of 1750 ppb (µg/kg). What mass of this solid matter needs to be ingested by a 25 g mouse to reach the LD$_{50}$ of 114 µg per kg?

**Strategy:** We know the concentration of ‘dioxin’ as a mass ratio (i.e., ppm = mg/kg) and we can convert the volume of oil to a corresponding mass, therefore the total mass of ‘dioxin’ can be determined.

For the second part, we scale the LD$_{50}$ given as µg per kg to the mass of a mouse and determine the mass of solid matter that contains an equivalent mass of ‘dioxin’.

**Solution:**

a) Mass of dioxin involved =

\[
\frac{33 \text{ mg}}{\text{kg}} \times \frac{18,500 \text{ US gallons}}{1 \text{ US gallon}} \times \frac{3.78 \text{ L}}{1 \text{ L}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 2.3 \text{ kg}
\]

b) Mass of dioxin to reach LD$_{50}$ in 25 g mouse = 114 µg/kg x 0.025 kg = 2.85 µg.

Mass of contaminated solid matter containing 1750 µg/kg =

\[
2.85\mu\text{g} \times \frac{1 \text{ kg}}{1750 \mu\text{g}} = 1.63 \times 10^{-3} \text{ kg} \text{ (or 1.6 g of contaminated solid matter)}
\]
7. Report the octanol-water partition coefficients and bioconcentration factors for the pesticides hexachlorocyclohexane (HCH) and isopropyl N-phenylcarbamate (IPA). Draw their structures and illustrate how they may associate with dissolved organic matter in aqueous solution. Suggest where these compounds will distribute in the environment on a triangular air-soil-water distribution plot.

**Strategy:**
(see further textbook pgs 267-269 and Chap 20; various websites including,
and
http://logkow.cisti.nrc.ca/logkow/index.jsp)

**Physical and biological properties:**
*hexachlorocyclohexane – gamma isomer (CAS# 58-89-9)*
Log Kow = 3.55; log BCF = 3.10 (fish)

*Isopropyl N-phenylcarbamate (CAS# 122-42-9)*
Log Kow = 2.60; log BCF 1.43 (species not specified)

**Chemical Structures:**

\[
\begin{align*}
\gamma\text{-HCH} & \\
\text{IPA} &
\end{align*}
\]

**Types of humic interactions possible:**
*HCH* (see Fig 12.7, text)
Non-polar contaminant will have affinity for hydrophobic portions of humate.

*IPA* (see Fig 12.5, text)
Carbamates can act as both H-bonding acceptors on the oxygens and H-bonding donors on the N-H group.
Environmental distributions;

HCH
smaller size, non-polar weaker IMFs
therefore more volatile and
less water soluble than IPA

IPA
larger size, more polar, stronger IMFs
therefore less volatile and more water
soluble than HCH
8. Given the equilibria below, what fraction of lead species is present as Pb\(^{2+}\) at pH 7.

\[
\begin{align*}
Pb^{2+} + OH^- & \rightleftharpoons PbOH^+ \quad K = 2.0 \times 10^6 \\
PbOH^+ + OH^- & \rightleftharpoons Pb(OH)_2 \quad K = 4.0 \times 10^4
\end{align*}
\]

**Strategy:**

We will need an expression for the fractional abundance of Pb\(^{2+}\) as a function of pH. We can approach this in several ways, but to will consistent with out previous discussions on pH speciation, I will re-write these complex ion formations as ‘acid dissociations’. (see textbook pgs 276-278, Chap 13 Q2)

**Solution:**

\[
\alpha_{Pb^{2+}} = \frac{[Pb^{2+}]}{[Pb^{2+}] + [PbOH^+] + [Pb(OH)_2]}
\]

Converting given equilibria to acid dissociations by adding the auto-ionization of water yields;

\[
\begin{align*}
Pb^{2+} + OH^- & \rightleftharpoons PbOH^+ \quad K_{f1} = 2.0 \times 10^6 \\
H_2O & \rightleftharpoons H^+ + OH^- \quad K_w = 1.0 \times 10^{-14} \\
Pb^{2+} + H_2O & \rightleftharpoons PbOH^+ + H^+ \quad K_{a1} = K_{f1} \times K_w = 2.0 \times 10^{-8}
\end{align*}
\]

\[
\begin{align*}
PbOH^+ + OH^- & \rightleftharpoons Pb(OH)_2 \quad K_{f2} = 4.0 \times 10^4 \\
H_2O & \rightleftharpoons H^+ + OH^- \quad K_w = 1.0 \times 10^{-14} \\
PbOH^+ + H_2O & \rightleftharpoons Pb(OH)_2 + H^+ \quad K_{a2} = K_{f2} \times K_w = 4.0 \times 10^{-10}
\end{align*}
\]

Therefore, \(pK_{a1} = 7.7\) and \(pK_{a2} = 9.4\)

Given the magnitude of the \(pK_a\) values, it is reasonable to assume that the concentration of Pb(OH)\(_2\) will be negligible at pH 7, hence we can simplify the fractional abundance expression as;

\[
\alpha_{Pb^{2+}} = \frac{[Pb^{2+}]}{[Pb^{2+}] + [PbOH^+]} \]

Rearranging the \(K_{a1}\) expression for \([PbOH^+] = (K_{a1} [Pb^{2+}])/[H^+]\) and substituting into the fractional abundance expression yields;

\[
\alpha_{Pb^{2+}} = \frac{[Pb^{2+}]}{[Pb^{2+}] + [PbOH^+]} = \frac{[Pb^{2+}]}{[Pb^{2+}] + K_{a1} [Pb^{2+}]/[H^+]} = \frac{1}{1 + K_{a1} [Pb^{2+}]/[H^+]} = \frac{[H^+]}{[H^+] + K_{a1}}
\]

**Hence at pH = 7, the fractional abundance of Pb\(^{2+}\) = 0.833**