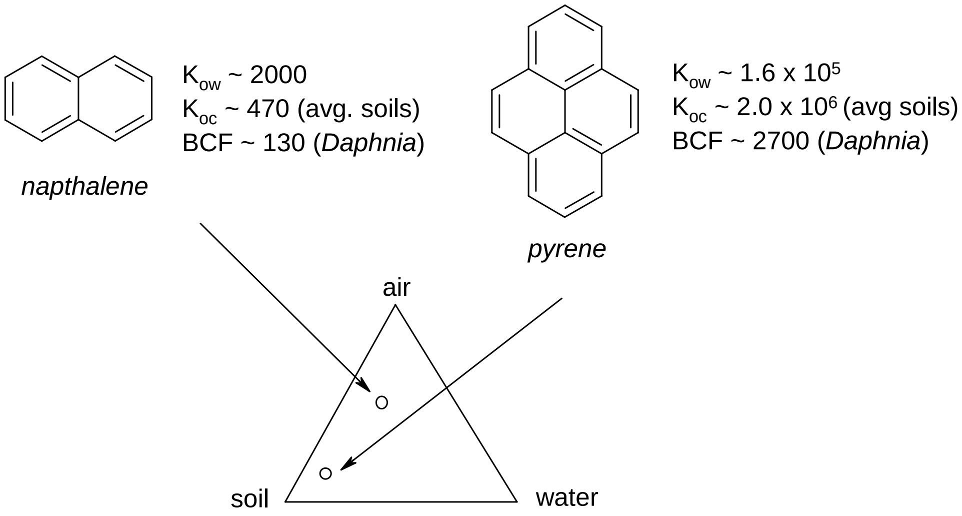
CHEM 301 – Aqueous Environmental Chemistry
Solutions Assignment #3

1. What are **PAH**'s ? Give an example of at least one member of this class of compounds. Define the following terms and report their values for the **PAH** that you have choosen.

K_{ow} K_{oc} BCF

Solution: Polyaromatic Hydrocarbons, referred to as PAH's are a class of organic compounds that contain fused aromatic (benzene) rings. Two examples of PAH's are shown below. Although there is a range of properties associated with PAH's, they are non-polar and therefore relatively insoluble in water. They are characterized by relatively high K_{ow}, K_{oc} and K_{om} values and therefore a high affinity for organic matter. The small PAH's have a relatively high vapour pressure and therefore tend to be transported in the atmosphere. PAH's in the environment are associated with organic matter and tend to be distributed among DOM, POM, sediments and soils. PAH's may be transported in the atmosphere as fine particulates or adsorbed onto particulate surfaces and are often released into the environment as the result of incomplete combustion processes.



napthalene

K_{ow} ~ 2000
K_{oc} ~ 470 (avg. soils)
BCF ~ 130 (*Daphnia*)

pyrene

K_{ow} ~ 1.6×10^5
K_{oc} ~ 2.0×10^6 (avg soils)
BCF ~ 2700 (*Daphnia*)

K_{ow} is known as the 1-octanol-water partition co-efficient and is a ratio of the equilibrium concentration of a species in 1-octanol to that in water. K_{ow} is a measure of the relative '*hydrophobicity*' of a molecule.

K_{oc} is known as the organic carbon partition co-efficient and is a ratio of the equilibrium concentration of a species in the organic component of soil or sediment to that in water. In general, K_{ow}'s are correlated with K_{oc}'s.

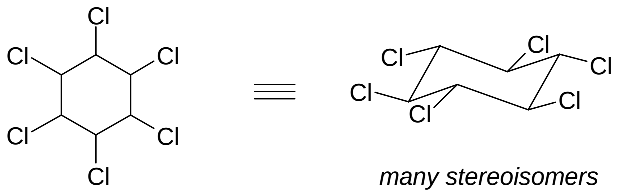
BCF is known as the bioconcentration factor and is defined as the ratio of the concentration of a chemical species in a specific organism to that in the surrounding water. In general, high K_{ow}'s are correlated with a high tendency to bioconcentrate. (To be meaningful, the organism must be specified).

Note: *Biomagnification* is a measure of the tendency of a chemical species to concentrate between trophic levels in the food chain.

2. Draw the structure of the pesticides hexachlorocyclohexane (HCH) and isopropyl N-phenylcarbamate (IPA) and illustrate how they may associate with dissolved organic matter in aqueous solution. Suggest a location for each of these pesticides on a triangular air-soil-water plot.

Solution: The structures and predicted interactions are outlined below.

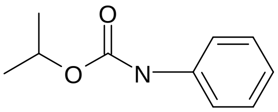
Hexachlorocyclohexane (aka Lindane): non-polar hydrophobic interactions with DOM



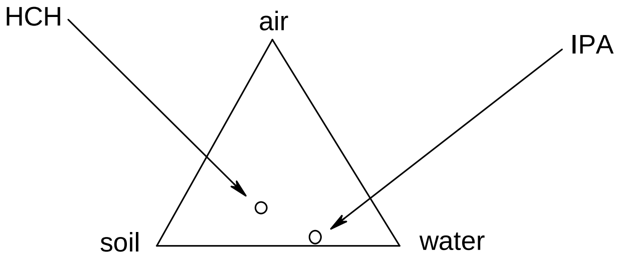
HCH

many stereoisomers

Isopropyl N-phenylcarbamate: polar with H-bonding capability, dipole interactions with DOM



IPA



3. 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?

***Solution*:**

a) 1 US gallon = 3.8 L

Therefore volume of oil is 7.0×10^4 L ~ 7.0×10^4 kg (assuming density of 1 g/mL)

Mass of dioxin = 33 mg/kg x 7.0×10^4 kg = 2.3×10^6 mg (or 2.3 kg)

b) Mass of dioxin required to reach the LD_{50};

(114×10^6 g/kg) x (25 g x 1kg/1000 g) = 2.9×10^{-6} g dioxin

concentration of dioxin in the solid matter = 1750×10^{-6} g dioxin/kg solid matter

= 1750×10^{-9} g dioxin/g solid matter

mass of solid matter required;

(2.9×10^{-6} g dioxin)/(1750×10^{-9} g dioxin/g solid matter) = 1.6 g of solid

4. Calculate the percent of fulvic acid bound to calcium in a lake sample containing 36 mg/L of calcium and 12 μg/L of DOM (as fulvic acid). Assume **Ca^{2+}** is the only metal present in significant concentration and a pH of 5.

Solution: This question requires some knowledge of the association constant (K_f') between Ca^{2+} and fulvic acid, given in Table 13.3 in your textbook and some assumption about the average concentration of carboxylate groups (C_{CO2}- ~ 4.5 mmol/g) given on page 250.

We need to calculate the percent of fulvic acid bound to calcium.

$$\%boundFA = \frac{[Ca - FA_{CO2-}]}{[FA_{CO2-}]_T} x100$$

where [Ca-FA_{CO2}-] represents the concentration of calcium complexed to fulvics and [FA_{CO2}-]$_T$ represents the total concentration of fulvic acid carboxylates. We will further define the following terms; $[Ca^{2+}]_T$, $[Ca^{2+}]_{free}$ and [FA_{CO2}-]$_{free}$

Note: $[Ca^{2+}]_T = [Ca^{2+}]_{free}$ + [Ca-FA_{CO2}-]
and
[FA_{CO2}-]$_T$ = [FA_{CO2}-]$_{free}$ + [Ca-FA_{CO2}-]

From the information provided in the question;
$[Ca^{2+}]_T$ = 36 mg/L x 1 mol/40,080 mg = 9.0 x 10^{-4} M
[FA_{CO2}-]$_T$ = (12 x 10^{-6} g/L) x (4.5 x 10^{-3} mol/g) = 5.4 x 10^{-8} M

Since $[Ca^{2+}]_T$ >> [FA_{CO2}-]$_T$
$[Ca^{2+}]_T \sim [Ca^{2+}]_{free}$

The relevant reaction is given by;

Ca^{2+} + FA_{CO2}- ==== Ca-FA_{CO2}- K_f' = 1.2 x 10^3

$$1.2x10^3 = \frac{[Ca - FA_{CO2}{}^-]}{[Ca^{2+}]_{free}[FA_{CO2}{}^-]_{free}}$$

If we let *x* represent the concentration of complexed fulvic acid ([Ca-FA_{CO2}-]),
then the [FA_{CO2}-]$_{free}$ = [FA_{CO2}-]$_T$ - *x* = 5.4 x 10^{-8} - *x*
so

$$1.2x10^3 = \frac{x}{(9.0x10^{-4})(5.4x10^{-8} - x)}$$

x = (9.0 x 10^{-4}) (5.4 x 10^{-8} – *x*) (1.2 x 10^3) = 5.8 x 10^{-8} – 1.08 *x*
and 2.08 *x* = 5.8 x 10^{-8}
so *x* = 2.9 x 10^{-8} M

Therefore the % bound fulvic = (2.9 x 10^{-8}/5.4 x 10^{-8}) x 100% = 54%
In other words, under the stated conditions, roughly 54% of the fulvic acid carboxylate sites are bound to calcium.

5. Using the information given in Table 13.2 (text), predict the principle inorganic aqueous species for **Al**, **Cu** and **Pb** in freshwater and seawater, respectively. Predict the same for **Cd**.

Solution: See Table 13.2

Metal Ion	**Electronic Configuration**	**Type**	**Major Species Freshwater**	**Major Species Seawater**
Al^{3+}	[Ne]	A	$Al(OH)_2^+$ $Al(OH)_3^o$	$Al(OH)_4^-$
Cu^{2+}	$[Ar]3d^9$	borderline	Cu^{2+} $CuOH^+$ $CuHCO_3^+$	$CuCl^+$ $CuCl_2^o$ $CuCl_3^-$
Pb^{2+}	$[Xe]6s^24f^{14}5d^{10}$	B	Pb^{2+} $PbOH^+$ $PbHCO_3^+$	$PbCl^+$ $PbCl_2^o$ $PbCl_3^-$ $PbSO_4^o$
Cd^{2+}	$[Kr]4d^{10}$	B	Cd^{2+} $CdOH^+$ $CdHCO_3^+$	$CdCl^+$ $CdCl_2^o$ $CdCl_3^-$ $CdSO_4^o$

6. Given the equilbria below, what fraction of lead species is present as Pb^{2+} at pH 7.

$$\mathbf{Pb^{2}+ \quad + \quad OH^- \quad ====== \quad PbOH^+} \qquad K = 2.0 \times 10^6$$
$$\mathbf{PbOH^+ \quad + \quad OH^- \quad ====== \quad Pb(OH)_2} \qquad K = 4.0 \times 10^4$$

Solution: The fraction of Pb^{2+} is given by;

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

One strategy to solve this problem is to rearrange the equilibria expressions to solve for both $PbOH^+$ and $Pb(OH)_2$ in terms of $[Pb^{2+}]$ and substitute these into the fractional abundance expression above.

From the equilibria provided;

$$K_1 = \frac{[\mathrm{PbOH}^+]}{[Pb^{2+}][OH^-]}$$

at pH 7, $[OH^-] = 10^{-7}$ M and therefore, $[PbOH^+]/[Pb^{2+}] = K_1 \times 10^{-7} = 0.20$

Thus, $[PbOH^+] = 0.20\ [Pb^{2+}]$

$$K_2 = \frac{[\mathrm{Pb(OH)}_2]}{[\mathrm{PbOH}^+][\mathrm{OH}^-]}$$

at pH 7, this yields $[Pb(OH)_2]/[PbOH^+] = K_2 \times 10^{-7} = 4.0 \times 10^{-3}$

Thus, $[Pb(OH)_2] = 4.0 \times 10^{-3}\ [PbOH^+]$

And substituting the above expression for $[PbOH^+]$ yields, $[Pb(OH)_2] = 8.0 \times 10^{-4}\ [Pb^{2+}]$

Substituting these terms into the fractional abundance expression gives;

$$\alpha_{Pb^{2+}} = \frac{[\mathrm{Pb}^{2+}]}{[Pb^{2+}] + 0.20\,[\mathrm{Pb}^{2+}] + 8.0 \times 10^{-4}[\mathrm{Pb}^{2+}]} = 0.83$$

An alternative strategy involves converting the given equations into the more familiar Ka reactions. This can be accomplished by adding the auto-dissociation of water as follows.

$Pb^{2+} + OH^- ==== PbOH^+$ K
$H_2O ==== H^+ + OH^-$ K_w

$Pb^{2+} + H_2O ==== PbOH^+ + H^+$ $K_{a1} = K\,K_w = 2.0 \times 10^{-8}$

Similarly, $K_{a2} = 4.0 \times 10^{-10}$

Now the alpha expressions will appear in the same form as those of other polyprotic acids.

i.e., $$\alpha_{Pb^{2+}} = \frac{1}{1 + \frac{K_{a1}}{[H^+]} + \frac{\mathrm{K}_{a1}\,\mathrm{K}_{a2}}{[\mathrm{H}^+]^2}} = 0.83$$

7. What fraction of NTA is uncomplexed after $\mathbf{H_2T^-}$ has been brought to equilibrium with solid $\mathbf{PbCO_3}$ at pH 7 in aqueous solution with [$\mathbf{HCO_3^-}$] = 1.25 x 10^{-3} M.

$$\mathbf{PbCO_3(s) \quad + \quad HT^{2-} \quad ====== \quad PbT^- \quad + \quad HCO_3^-}$$

log K_{sp} ($\mathbf{PbCO_3}$) = -13.13
log K_f $\mathbf{PbT^-}$ = 11.34

Solution:
The fraction of uncomplexed NTA is given by the expression $[NTA]_u/[NTA]_T$
where at neutral pH, $[NTA]_u = [HT^{2-}]$ and the $[NTA]_T = [HT^{2-}] + [PbT^-]$

We need to calculate the equilibria constant for the overall reaction by the combination of appropriate reactions with known equilibrium constants.

$PbCO_3(s) \quad ==== \quad Pb^{2+} \quad + \quad CO_3^{2-}$	log K_{sp} = -13.13
$Pb^{2+} \quad + \quad T^{3-} \quad ==== \quad PbT^-$	log K_f = 11.34
$H^+ \quad + \quad CO_3^{2-} \quad ==== \quad HCO_3^-$	log $\{1/K_{a2}\}$ = 10.33
$HT^{2-} \quad ==== \quad H^+ \quad + \quad T^{3-}$	log K_{a3} = -10.28
$PbCO_3(s) \quad + \quad HT^{2-} \quad ==== \quad PbT^- \quad + \quad HCO_3^-$	log K = -1.74 and K = 0.0182

$$K = \frac{[PbT^-][HCO_3^-]}{[HT^{2-}]} = 0.0182$$

Rearrange and solve for $[HT^{2-}] = ([PbT-][HCO_3^-])/K$

So $[HT^{2-}] = 0.0687\,[PbT^-]$

Thus, fraction of NTA uncomplexed is given by;

$$\alpha_{NTAfree} = \frac{[HT^{2-}]}{[HT^{2-}] + [PbT^-]} = \frac{0.0687\,[PbT^-]}{0.0687\,[PbT^-] + [PbT^-]} = 0.0642$$

So ~ 6.4% of the NTA is uncomplexed.

Alternatively, rearranging K expression to isolate $[PbT^-] = K\,[HT^{2-}]/[HCO_3^-]$ and substituting into the $\alpha_{NTAfree}$ equation yields;

$$\alpha_{NTAfree} = \frac{[HT^{2-}]}{[HT^{2-}] + \frac{K\,[HT^{2-}]}{[HCO_3^-]}} = \frac{1}{1 + \frac{K}{[HCO_3^-]}} = 0.0642$$

8. Using the pKa values below for the aluminium aquo complexes, plot a pH speciation diagram for the $\mathbf{Al^{3+}}$ **-** $\mathbf{Al(OH)^{2+}}$ **-** $\mathbf{Al(OH)_2^+}$ **-** $\mathbf{Al(OH)_3}$ **–** $\mathbf{Al(OH)_4^-}$ system over the pH range of 0 to 14. Use a spreadsheet program (such as Excel) for repetitive calculations and to plot curves for fractional abundance of each species. What is the distribution of aluminium species at pH 5?

$pK_{a1} = 5.00$ $pK_{a2} = 5.10$ $pK_{a3} = 6.80$ $pK_{a4} = 5.80$

Solution: The relevant equilibria are given below;

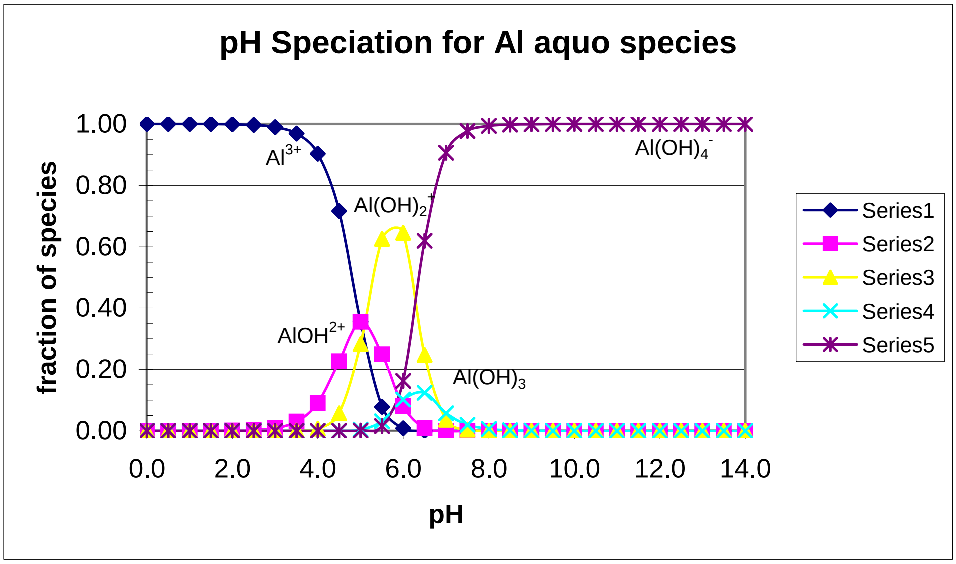
$Al^{3+} + H_2O \;{=}{=}{=}{=}\; AlOH^{2+} + H^+$	K_{a1}
$AlOH^{2+} + H_2O \;{=}{=}{=}{=}\; Al(OH)_2^+ + H^+$	K_{a2}
$Al(OH)_2^+ + H_2O \;{=}{=}{=}{=}\; Al(OH)_3 + H^+$	K_{a3}
$Al(OH)_3 + H_2O \;{=}{=}{=}{=}\; Al(OH)_4^- + H^+$	K_{a4}

$$\alpha_{Al^{3+}} = \frac{[\mathrm{Al}^{3+}]}{[Al^{3+}]+[AlOH^{2+}]+[Al(OH)_2{}^+]+[Al(OH)_3]+[Al(OH)_4{}^-]}$$

Rearranging the K_a expressions and substituting into the alpha equation as before, leads to the following for Al^{3+}

$$\alpha_{Al^{3+}} = \frac{1}{1+\frac{K_{a1}}{[\mathrm{H}^+]}+\frac{K_{a1}K_{a2}}{[H^+]^2}+\frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3}+\frac{K_{a1}K_{a2}K_{a3}K_{a4}}{[H^+]^4}}$$

A plot of the pH speciation appears below.



pH	[H+]	alpha Al3+	alpha AlOH2+	alpha Al(OH)2+	alpha Al(OH)3	alpha Al(OH)4-
0.0	1.00E+00	1.0000	0.0000	0.0000	0.0000	0.0000
0.5	3.16E-01	1.0000	0.0000	0.0000	0.0000	0.0000
1.0	1.00E-01	0.9999	0.0001	0.0000	0.0000	0.0000
1.5	3.16E-02	0.9997	0.0003	0.0000	0.0000	0.0000
2.0	1.00E-02	0.9990	0.0010	0.0000	0.0000	0.0000
2.5	3.16E-03	0.9968	0.0032	0.0000	0.0000	0.0000
3.0	1.00E-03	0.9900	0.0099	0.0001	0.0000	0.0000
3.5	3.16E-04	0.9686	0.0306	0.0008	0.0000	0.0000
4.0	1.00E-04	0.9026	0.0903	0.0072	0.0000	0.0000
4.5	3.16E-05	0.7163	0.2265	0.0569	0.0003	0.0000
5.0	**1.00E-05**	**0.3560**	**0.3560**	**0.2828**	**0.0045**	**0.0007**
5.5	3.16E-06	0.0787	0.2489	0.6253	0.0313	0.0157
6.0	1.00E-06	0.0081	0.0813	0.6459	0.1024	0.1622
6.5	3.16E-07	0.0003	0.0098	0.2467	0.1236	0.6196
7.0	1.00E-07	0.0000	0.0005	0.0361	0.0572	0.9063

Fraction at pH 5	**Formulas:**	
35.6%	**alpha Al3+**	([H+]^4)/(([H+]^4)+(Ka1*[H+]^3)+(Ka1Ka2*[H+]^2)+(Ka1Ka2Ka3*[H+])+(Ka1Ka2Ka3Ka4))
35.6%	**alpha AlOH2+**	(Ka1*[H+]^3)/(([H+]^4)+(Ka1*[H+]^3)+(Ka1Ka2*[H+]^2)+(Ka1Ka2Ka3*[H+])+(Ka1Ka2Ka3Ka4))
28.3%	**alpha Al(OH)2+**	(Ka1Ka2*[H+]^2)/(([H+]^4)+(Ka1*[H+]^3)+(Ka1Ka2*[H+]^2)+(Ka1Ka2Ka3*[H+])+(Ka1Ka2Ka3Ka4))
0.5%	**alpha Al(OH)3**	(Ka1Ka2Ka3*[H+])/(([H+]^4)+(Ka1*[H+]^3)+(Ka1Ka2*[H+]^2)+(Ka1Ka2Ka3*[H+])+(Ka1Ka2Ka3Ka4))
0.1%	**alpha Al(OH)4-**	(Ka1Ka2Ka3Ka4)/(([H+]^4)+(Ka1*[H+]^3)+(Ka1Ka2*[H+]^2)+(Ka1Ka2Ka3*[H+])+(Ka1Ka2Ka3Ka4))