# Exercise 1: Contaminated wetland



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Consider a contaminated wetland soil containing $Sr^{2+}$, $Co^{2+}$, and $Hg^{2+}$. Soil flooding results in soil reduction and in the release of bicarbonate ($HCO_3^-$) and sulfide ($HS^-$) into soil solution.

a. Which of the metals would you expect to mainly interact via complexation and precipitation with bicarbonate and which one predominantly with sulfide?

b. For which trace metal is it most difficult to anticipate its preference for one of the two anions?

# Exercise 1: Solution

a. Use the hard-soft concept

$Sr^{2+}$: hard cation

$Co^{2+}$: intermediate cation

$Hg^{2+}$: soft cation

$HCO_3^-$: hard ligand

$HS^-$: soft ligand

We would expect $Sr^{2+}$ to preferentially react with $HCO_3^-$ and $Hg^{2+}$ to primarily react with $HS^-$.

b. For $Co^{2+}$, it is most difficult to anticipate a preference for one of the two ions.

# Exercise 2: Silver speciation

For a system with $Ag^+$ and $NH_3$, what is the silver speciation at pH 7?

We know: $[Ag^+]_{tot} = 10^{-6}$ M, $[NH_4^+]_{tot} = 10^{-2}$ M, $K_1 = 10^{3.2}$, $K_2 = 10^{3.83}$, $K_a = 10^{-9.3}$

1. Identify species present at equilibrium
2. Write out equilibrium equations
3. List mass balance equations
4. Solve equations
5. Apply simplifications
6. Calculate silver speciation

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# Exercise 2: Solution



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1. Species at equilibrium:
   $Ag^+$, $Ag(NH_3)^+$, $Ag(NH_3)_2^+$, $NH_3$, $NH_4^+$

2. Equilibrium equations

$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+$

$$K_1 = \frac{[Ag(NH_3)]}{[Ag^+][NH_3]} \quad \text{eq.1}$$

$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+$

$$K_2 = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+][NH_3]} \quad \text{eq. 2}$$

$$\beta_2 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} \quad \text{eq. 3}$$

$NH_4^+ \rightleftharpoons NH_3 + H^+$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} \quad \text{eq. 4}$$

3. Mass balance equations

$$[Ag^+]_{tot} = Ag^+ + Ag(NH_3)^+ + Ag(NH_3)_2^+ \quad \text{eq. 5}$$

$$[NH_4^+]_{tot} = [NH_3] + [NH_4^+] \quad \text{eq. 6}$$

# Exercise 2: Solution

4. Use eqs. 1-6 to obtain an expression of $[Ag^+]$ as a function of given values

   Express eq. 5 by substituting $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ using eqs. 1-3:

   $$[Ag^+]_{tot} = [Ag^+]\,(1 + [NH_3]K_1 + [NH_3]^2\beta_2) \qquad \text{eq. 7}$$

   Express $NH_3$ as a function as a function of $[NH_4^+]_{tot}$ and $K_a$ using eq. 6:

   $$[NH_3] = \frac{K_a[NH_4^+]_{tot}}{10^{-pH}+K_a} \qquad \text{eq. 8}$$

   Solve eq. 7 for $[Ag^+]$ and substitute $[NH_3]$ using eq. 7 to get

   $$[Ag^+] = \frac{[Ag^+]_{tot}}{1 + \left(\frac{K_a[NH_4^+]_{tot}}{10^{-pH}+K_a}\right) K_1 + \left(\frac{K_a[NH_4^+]_{tot}}{10^{-pH}+K_a}\right)^2 \beta_2} \qquad \text{eq. 9}$$

5. Apply simplifications: ligand is in excess, we do not consider complexes in the total ligand concentration

6. Calculate silver speciation

   for $[Ag^+]$: fill numbers into eq. 9

   for $[Ag(NH_3)^+]$: use $[Ag^+]$ and eq. 1 with $[NH_3]$ from eq. 8

   for $[Ag(NH_3)_2^+]$: use mass balance eq. 5

# Exercise 3: Zn(II) speciation in the presence of several ligands



Consider a system with Zn(II). Zn forms both hydroxo-complexes and carbonato-complexes. You have the following information:

- pH 8.5
- $Zn_{tot} = 10^{-8}$ M
- Total carbonate: $C_{tot} = 2 * 10^{-3}$ M

Calculate the concentrations of $Zn^{2+}$, $Zn(OH)^{+}$, $Zn(OH)_2$ and $ZnCO_3$

$Zn^{2+} = Zn(OH)^{+} + H^{+}$ $\quad K_1 = 10^{-9.1}$

$Zn^{2+} = Zn(OH)_2 + 2\,H^{+}$ $\quad \beta_2 = 10^{-17}$

$Zn^{2+} + CO_3^{2-} = ZnCO_3$ $\quad K_2 = 10^{4.52}$

$HCO_3^{-} = CO_3^{2-} + H^{+}$ $\quad K_a = 10^{-10.2}$

# Exercise 3: Solution



$[Zn_{tot}] = [Zn^{2+}] + [Zn(OH)^{+}] + [Zn(OH)_2] + [ZnCO_3]$

$= [Zn^{2+}] + \frac{K_1}{[H^+]}[Zn^{2+}] + \frac{\beta_2}{[H^+]^2}[Zn^{2+}] + K_2\,[CO_3^{2-}]\,[Zn^{2+}]$

$= [Zn^{2+}]\,(1 + \frac{K_1}{10^{-pH}} + \frac{\beta_2}{10^{-2pH}} + K_2\,[CO_3^{2-}])$ eq. 1

Find expression for $[CO_3^{2-}]$

$C_{tot} = [CO_3^{2-}] + [HCO_3]$, i.e., $[HCO_3] = C_{tot} - [CO_3^{2-}]$

$K_a = \frac{[CO_3^{2-}][H^+]}{C_{tot}-[CO_3^{2-}]}$, thus $[CO_3^{2-}]\,(K_a + [H^+]) = K_a\,C_{tot}$

$[CO_3^{2-}] = \frac{K_a C_{tot}}{K_a + [H^+]}$ eq. 2

Fill eq. 2 into eq. 1 and solve for $[Zn^{2+}]$ to get $\underline{[Zn^{2+}] = 2.8 * 10^{-9}\ M}$

Calculate the concentrations of $Zn(OH)^+$, $Zn(OH)_2$ and $ZnCO_3$ using the equilibrium constants.

$Zn(OH)^+ = \frac{K_1}{[H^+]}[Zn^{2+}]$, $Zn(OH)_2 = \frac{\beta_2}{[H^+]^2}[Zn^{2+}]$, $ZnCO_3 = K_2\,[CO_3^{2-}]\,[Zn^{2+}]$