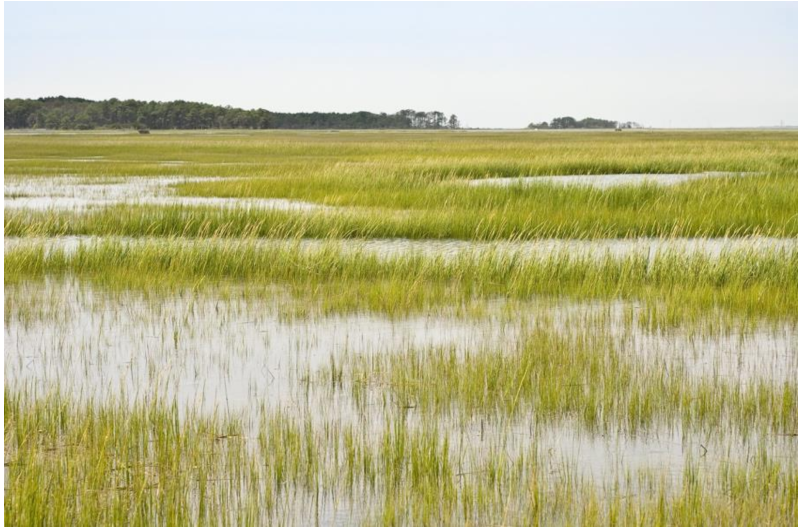
Exercise 1: Contaminated wetland

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

Meret Aeppli

Exercise 2: Solution

Meret Aeppli

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

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

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

Meret Aeppli

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:

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

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

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

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 $ZnCO_3$

$Zn^{2+} = Zn(OH)^{+} + H^{+}$	$K_1^{*} = 10^{-9.1}$
$Zn^{2+} = Zn(OH)_2 + 2H^{+}$	$\beta_2^{*} = 10^{-17}$
$Zn^{2+} + CO_3^{2-} = ZnCO_3$	$K_2 = 10^{4.52}$
$HCO_3^{-} = CO_3^{2-} + H^{+}$	$K_a = 10^{-10.2}$

Exercise 3: Solution

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

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

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

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