Copper – NTA problem

- **NTA:** nitrilotriacetate
  - Used as a substitute “builder” in place of phosphate
  - Good example of moderately strong ligand
- **Research interests:** 70’s & 80’s
  - **General Review**
    - Perry et al., 1984 [Wat. Res., 18(3)255]
  - **Other Aspects**
    - Photochemistry: e.g., Langford et al., 1973 [ES&T 7(9)820]
    - Biodegradation: e.g., Kuhn et al., 1987 [Wat. Res. 21(10)1237], Vanbiesen et al., 2000 [ES&T 34(6)3346]
    - Bioavailability of bound metals: e.g., Bressan & Brunetti, 1988 [Wat. Res. 22(5)553]

See: [Knud-Hansen Paper](#)
Cu-NTA II

- Thermodynamics (20ºC)
  - Acid/Base
    - \( H_3NTA = H^+ + H_2NTA^- \)  \( pK_1 = 1.6 \)
    - \( H_2NTA^- = H^+ + HNTA^{2-} \)  \( pK_2 = 3.0 \)
    - \( HNTA^{2-} = H^+ + NTA^{3-} \)  \( pK_3 = 10.3 \)
  - Cu complex
    - \( Cu^{2+} + NTA^{3-} = CuNTA^- \)  \( \beta_1 = -13.0 \)
    - Others are rather weak
      - CuHNTA

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<p>| TABLE 5-10 Variation of Metal Complexation by NTA with NTA Concentration at pH 8 |
|---|---|---|---|---|
| <strong>From: Snoeyink &amp; Jenkins, 1980</strong> |</p>
<table>
<thead>
<tr>
<th>Total Concentration ( C_{NTA} ) M</th>
<th>Complex Species</th>
<th>Log Formation Constant of</th>
<th>Percentage of Total Metal Present as Indicated Complex at Stated NTA Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Cu^{II} = 2 \times 10^{-6} )</td>
<td>CuNTA^-</td>
<td>13</td>
<td>( NTA = 10^{-7} M )</td>
</tr>
<tr>
<td>( Pb^{II} = 3 \times 10^{-7} )</td>
<td>PbNTA^-</td>
<td>11.8</td>
<td>2</td>
</tr>
<tr>
<td>( Ni^{II} = 2 \times 10^{-7} )</td>
<td>NiNTA^-</td>
<td>11.9</td>
<td>1</td>
</tr>
<tr>
<td>( Fe^{III} = 2 \times 10^{-6} )</td>
<td>Fe(OH)_{3}NTA^{3-}</td>
<td>10.8</td>
<td>0.4</td>
</tr>
<tr>
<td>( Zn^{II} = 1.5 \times 10^{-6} )</td>
<td>ZnNTA^-</td>
<td>10.4</td>
<td>0.2</td>
</tr>
<tr>
<td>( H^+ = 10^{-8} )</td>
<td>HNTA^-</td>
<td>10.3</td>
<td>0</td>
</tr>
<tr>
<td>( Mn^{II} = 2 \times 10^{-8} )</td>
<td>MnNTA^-</td>
<td>7.4</td>
<td>0</td>
</tr>
<tr>
<td>( Cu^{II} = 10^{-9} )</td>
<td>CuNTA^-</td>
<td>6.4</td>
<td>0</td>
</tr>
<tr>
<td>( Mg^{II} = 2.5 \times 10^{-4} )</td>
<td>MgNTA^-</td>
<td>5.4</td>
<td>0</td>
</tr>
<tr>
<td>( Sr^{II} = 2 \times 10^{-6} )</td>
<td>SrNTA^-</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>( Ba^{II} = 1.5 \times 10^{-7} )</td>
<td>BaNTA^-</td>
<td>4.8</td>
<td>0</td>
</tr>
<tr>
<td>( Na^+ = 5 \times 10^{-4} )</td>
<td>NaNTA^-</td>
<td>2.2</td>
<td>0</td>
</tr>
</tbody>
</table>

Cu-NTA III

- Specific problem
  - $\text{Cu}_T = 10^{-4}$ M: 6.35 mg/L
  - $\text{NTA}_T = 10^{-4}$ M: 19.1 mg/L

- Notes:
  - this is a much higher concentration of NTA than is generally found, but it can be used to represent background natural organic matter
  - Copper concentrations may sometimes be this high when used as an algicide
  - We are ignoring other complexes such as copper hydroxides or carbonates

Cu-NTA IV

- Mass Balance Equations
  - $\text{Cu}_T = [\text{Cu}^{+2}] + [\text{CuNTA}^{-}]$
  - $\text{NTA}_T = [\text{CuNTA}^{-}] + [\text{H}_3\text{NTA}] + [\text{H}_2\text{NTA}^{-}] + [\text{HNTA}^{-2}] + [\text{NTA}^{-3}]$

- Definition: total free concentration (TF) is that which is unbound to any metal except $\text{H}^+$
  - $\text{NTA}_T = [\text{CuNTA}^{-}] + \text{NTA}_{TF}$
Cu-NTA V

- Equilibria
  \[ \alpha_3 = \frac{[NTA^-]}{NTA} \]

- Acid/base
  \[ \beta_1 = \frac{[CuNTA^-]}{[Cu^{+2}] [NTA^-]} \]

- Complexation
  \[ \beta_1 = \left( 1 + \frac{[H^+]}{K_3} + \frac{[H^+]^2}{K_2 K_3} + \frac{[H^+]^3}{K_1 K_2 K_3} \right)^{-1} \]

Cu-NTA VI

- Substitute mass balance and alpha equations into the beta equation

\[ \beta_1 = \frac{Cu_T - [Cu^{+2}]}{[Cu^{+2}] \alpha_3 [NTA_T - [CuNTA^-]]} = \frac{Cu_T - [Cu^{+2}]}{[Cu^{+2}] \alpha_3 [NTA_T - (Cu_T - [Cu^{+2}])]} \]
Cu-NTA VII

- Now solve, noting that $Cu_T = NTA_T$

$$\beta_1 = \frac{Cu_T - [Cu^{2+}]}{[Cu^{2+}] \alpha_3 (NTA_T - (Cu_T - [Cu^{2+}]))}$$

$$\beta_1 = \frac{Cu_T - [Cu^{2+}]}{[Cu^{2+}] \alpha_3 [Cu^{2+}]}$$

- Which gives us a quadratic which can be solved for a given pH

$$\alpha_3 \beta_1 [Cu^{+2}]^2 + [Cu^{+2}] - Cu_T = 0$$

Cu-NTA VIII

- Then determine other species from the free copper

$$[CuNTA^-] = Cu_T - [Cu^{2+}]$$

$$NTA_{TF} = NTA_T - [CuNTA^-]$$

$$[NTA^{-3}] = \alpha_3 NTA_{TF}$$

- Can use a spreadsheet to calculate $\alpha_3$ versus pH, and then calculate the other species
Cu-NTA IX

- Figure shows impact of ligand speciation on extent of complexation
- Same thing happens with fulvic acid
To next lecture