Updated: 24 March 2020

Print version

# CEE 680: Water Chemistry

Lecture #32

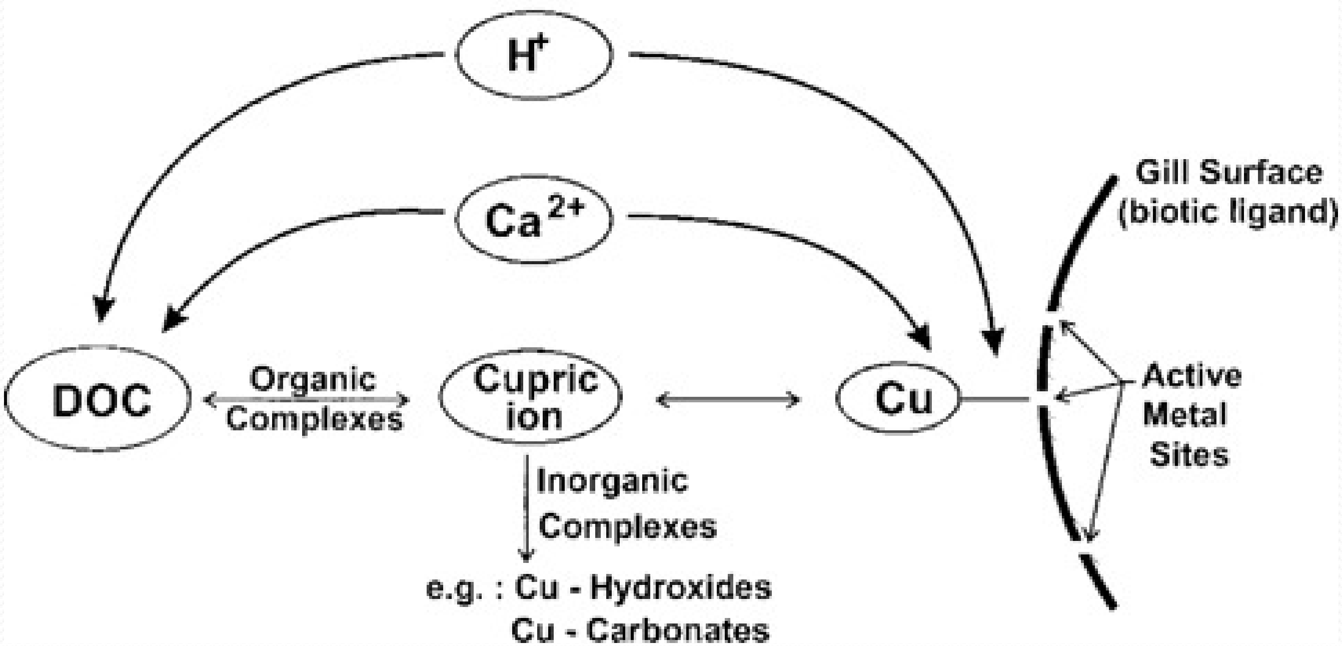
Coordination Chemistry: Case Studies: NTA (cont.)

(Stumm & Morgan, Chapt.6: pg.317-319)

Benjamin; Chapter 8.1-8.6

Biotic ligand model of the acute toxicity of metals. 2. Application to acute copper toxicity in freshwater fish and Daphnia

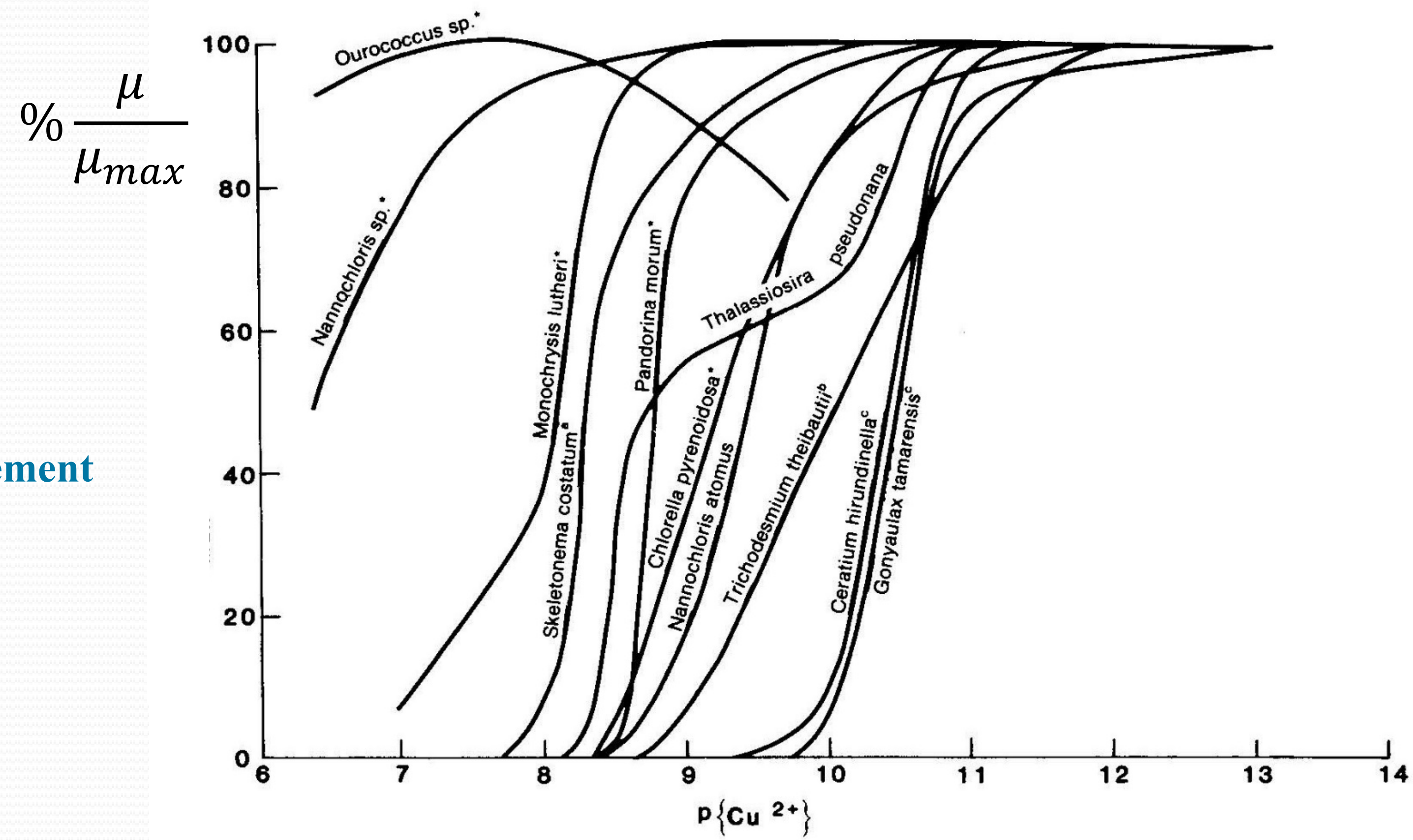
CONCEPTUAL DIAGRAM OF COPPER SPECIATION AND COPPER-GILL MODEL (After Pagenkopf [1])




Environmental Toxicology and Chemistry, Volume: 20, Issue: 10, Pages: 2397-2402

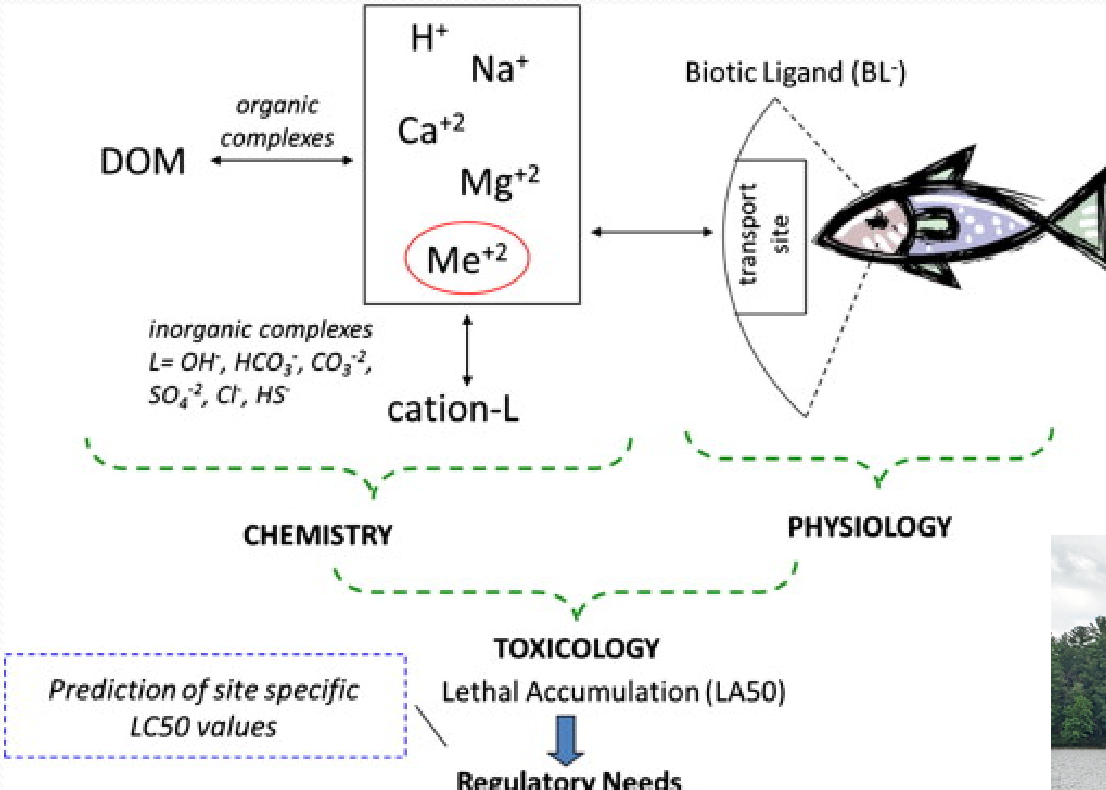
# Algae and Copper

- Fresh and salt water algae
- Depends on $Cu^{+2}$ ion: $10^{-7}$M seems to work for most

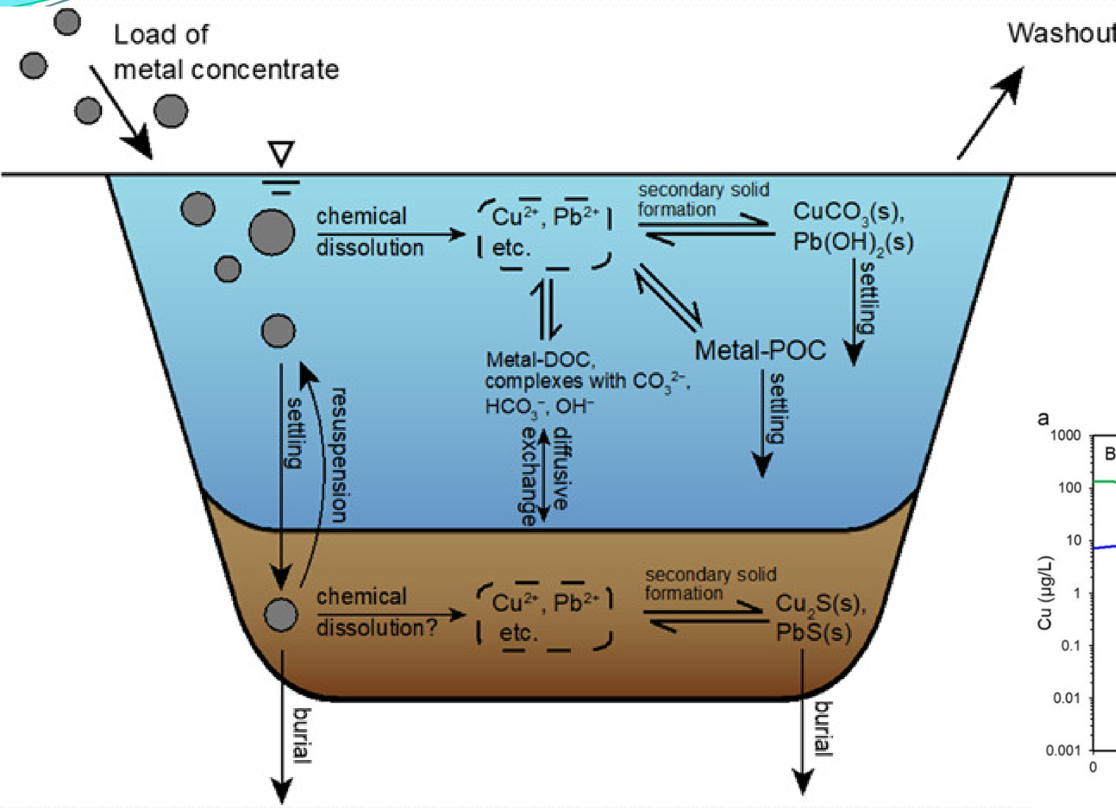


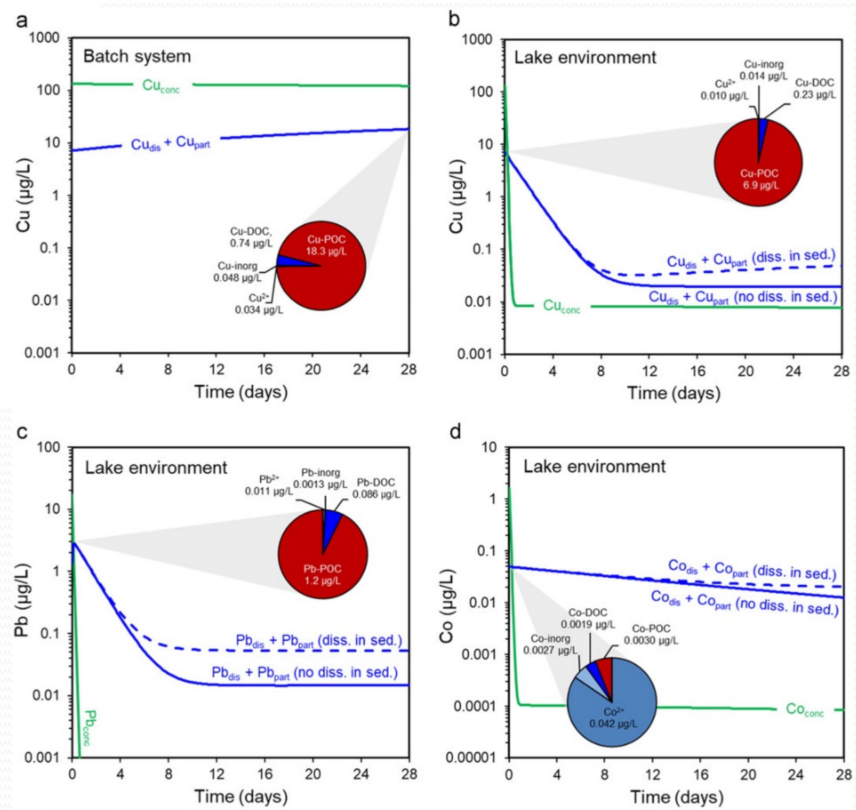

McKnight et al., 1983; Environmental Management 7(4)311-320

# Add $CuSO_4$




**Smith et al., 2015, Applied Geochemistry 57:55**



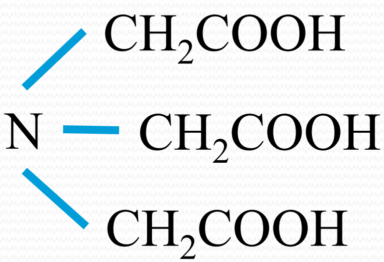




**Environmental Toxicology and Chemistry, Volume: 38, Issue: 6, Pages: 1256-1272, First published: 23 March 2019, DOI: (10.1002/etc.4417)**

# Copper – NTA problem

See: Knud-Hansen Paper

- 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], Vanbriesen et al., 2000 [ES&T 34(16)3346]
    - Bioavailability of bound metals: e.g., Bressan & Brunetti, 1988 [Wat. Res. 22(5)553]



# 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
    - $Cu^{+2} + NTA^{-3} = CuNTA^-$ $p\beta_1 = -13.0$
    - Others are rather weak
      - CuHNTA

TABLE 5-10 Variation of Metal Complexation by NTA with NTA Concentration at pH 8

**From: Snoeyink & Jenkins, 1980**

| Total Concentration $C_{T,x}$ *M* | Complex Species | Log Formation Constant of | Percentage of Total Metal Present as Indicated Complex at Stated NTA Concentration | | |
|---|---|---|---|---|---|
| | | | NTA = $10^{-7}$ *M* | NTA = $3 \times 10^{-6}$ *M* | NTA = $2 \times 10^{-4}$ *M* |
| Cu(II) = $2 \times 10^{-6}$ | $CuNTA^-$ | 13 | 4 | 82 | 100 |
| Pb(II) = $3 \times 10^{-7}$ | $PbNTA^-$ | 11.8 | 2 | 80 | 100 |
| Ni(II) = $10^{-7}$ | $NiNTA^-$ | 11.3 | 1 | 60 | 100 |
| Fe(III) = $2 \times 10^{-6}$ | $Fe(OH)NTA^-$<br>$Fe(OH)_2NTA^{2-}$ | 10.9<br>3.1 | 0.4 | 34 | 100 |
| Zn(II) = $1.5 \times 10^{-6}$ | $ZnNTA^-$ | 10.4 | 0.2 | 20 | 100 |
| $H^+$ = $10^{-8}$ | $HNTA^{2-}$ | 10.3 | 0 | 0 | 9 |
| Mn(II) = $2 \times 10^{-6}$ | $MnNTA^-$ | 7.4 | 0 | 0 | 100 |
| Ca(II) = $10^{-3}$ | $CaNTA^-$ | 6.4 | 0 | <0.1 | 17 |
| Mg(II) = $2.5 \times 10^{-4}$ | $MgNTA^-$ | 5.4 | 0 | 0 | 2 |
| Sr(II) = $2 \times 10^{-6}$ | $SrNTA^-$ | 5.0 | 0 | 0 | 0 |
| Ba(II) = $1.5 \times 10^{-7}$ | $BaNTA^-$ | 4.8 | 0 | 0 | 0 |
| Na(I) = $5 \times 10^{-4}$ | $NaNTA^{2-}$ | 2.2 | 0 | 0 | 0 |

*Source:* C. W. Childs, *Proc. 14th Conf. Great Lakes Res.*, 198–210 (1971). *Intl. Assoc. Great Lakes Res.* (Reprinted by permission of the International Association for Great Lakes Research.)

# Cu-NTA III

- Specific problem
  - $Cu_T = 10^{-4}$ M 6.35 mg/L
  - $NTA_T = 10^{-4}$ 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
  - $Cu_T = [Cu^{+2}] + [\ CuNTA^-]$
  - $NTA_T = [CuNTA^-] + [H_3NTA] + [H_2NTA^-] + [HNTA^{-2}] + [NTA^{-3}]$
- Definition: total free concentration (TF) is that which is unbound to any metal except $H^+$
  - $NTA_T = [CuNTA^-] + NTA_{TF}$

# Cu-NTA V

- Equilibria
  - Acid/base
  - Complexation

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

$$= \left(1 + \frac{[H^+]}{K_3} + \frac{[H^+]^2}{K_2K_3} + \frac{[H^+]^3}{K_1K_2K_3}\right)^{-1}$$

$$\beta_1 = \frac{[CuNTA^-]}{[Cu^{+2}][NTA^{-3}]}$$

# Cu-NTA VI

- Substitute mass balance and alpha equations into the beta equation

$$\beta_1 = \frac{[CuNTA^-]}{[Cu^{+2}][NTA^{-3}]} = \frac{Cu_T - [Cu^{+2}]}{[Cu^{+2}]\alpha_3 NTA_{TF}}$$

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

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

# Cu-NTA VII

- Now solve, noting that $Cu_T$ = $NTA_T$

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

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

- 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

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

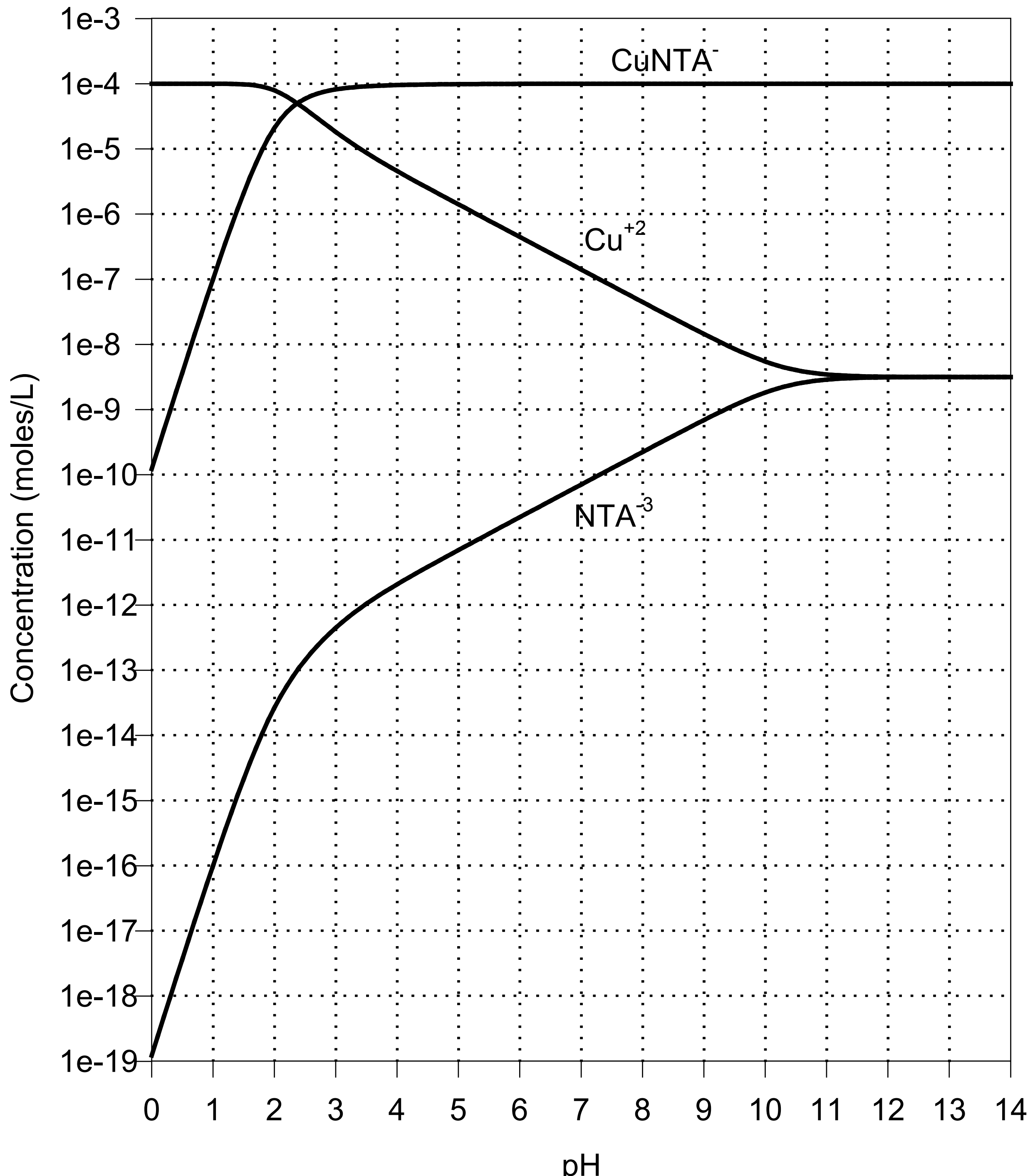
$$NTA_{TF} = NTA_T - [CuNTA^{-}]$$

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

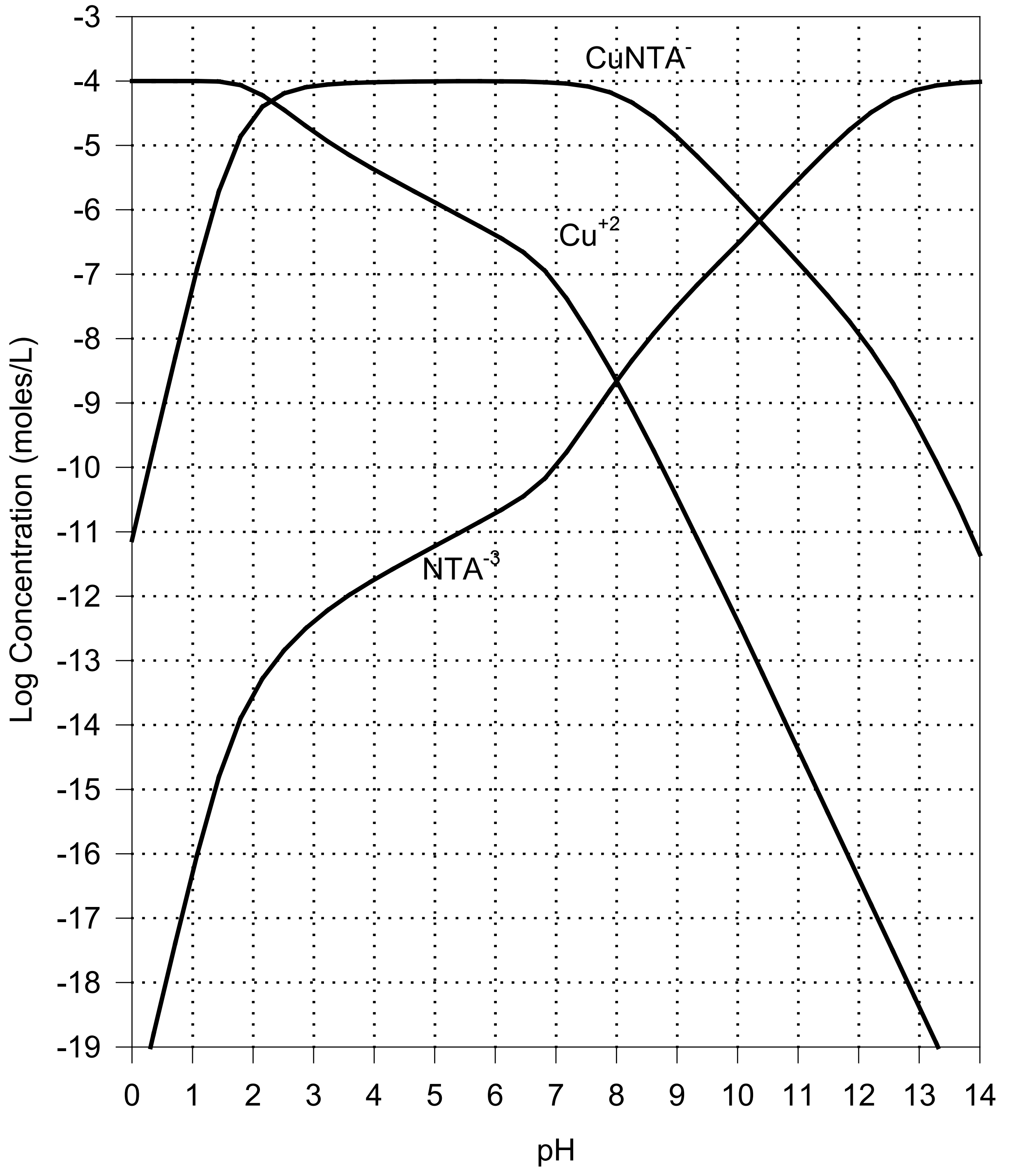
- Can use a spreadsheet to calculate $\alpha_3$ versus pH, and then calculate the other species

# Cu-NTA IX

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

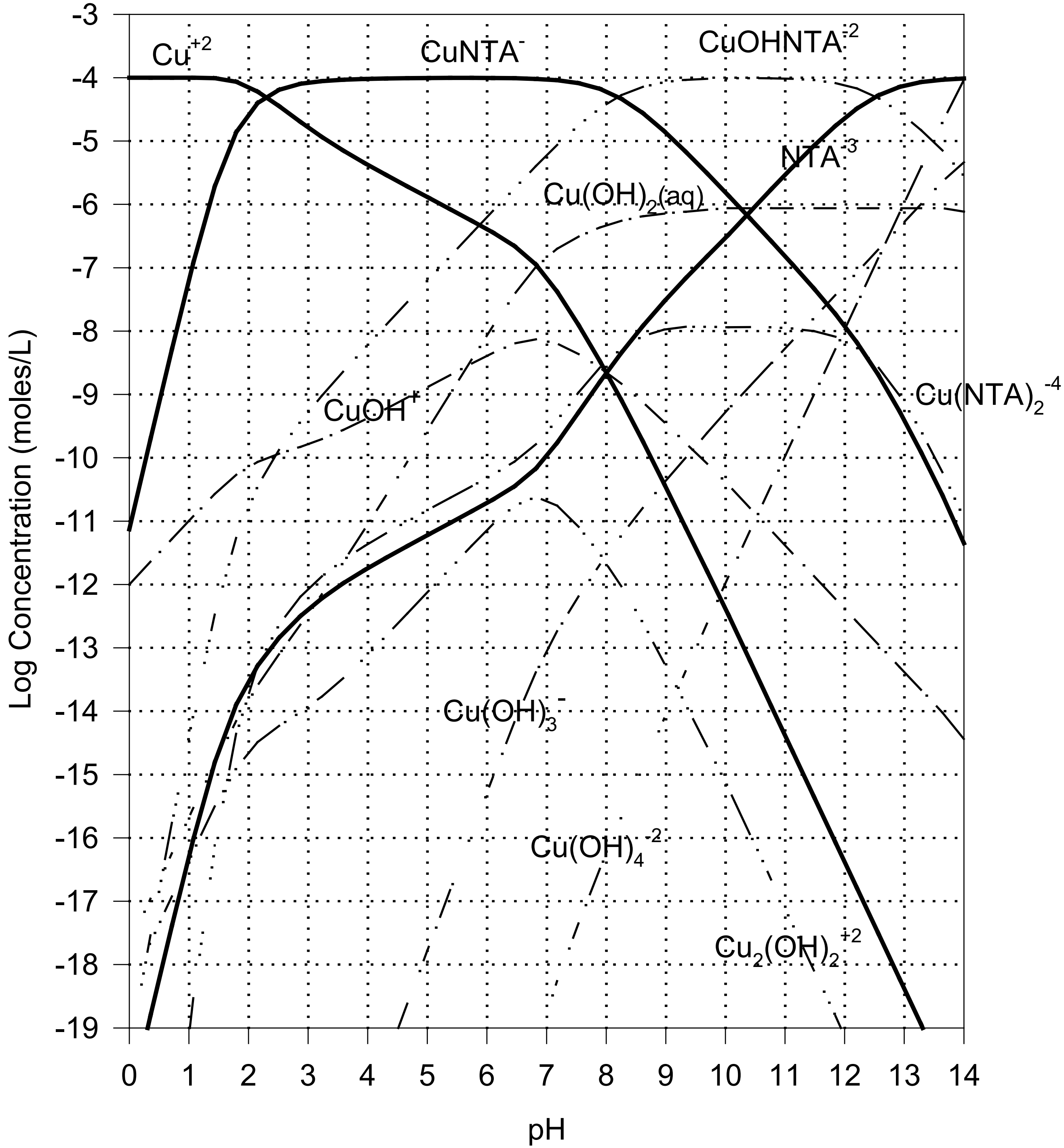


# CuNTA X



CuNTA-
Cu+2
NTA-3
Log Concentration (moles/L)
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15
-16
-17
-18
-19
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH

# CuNTA XI



Cu+2
CuNTA-
CuOHNTA-2
NTA-3
Cu(OH)2(aq)
CuOH+
Cu(NTA)2-4
Cu(OH)3-
Cu(OH)4-2
Cu2(OH)2+2
Log Concentration (moles/L)
pH
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15
-16
-17
-18
-19
0
1
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- To next lecture