Updated: 25 March 2020

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CEE 680: Water Chemistry

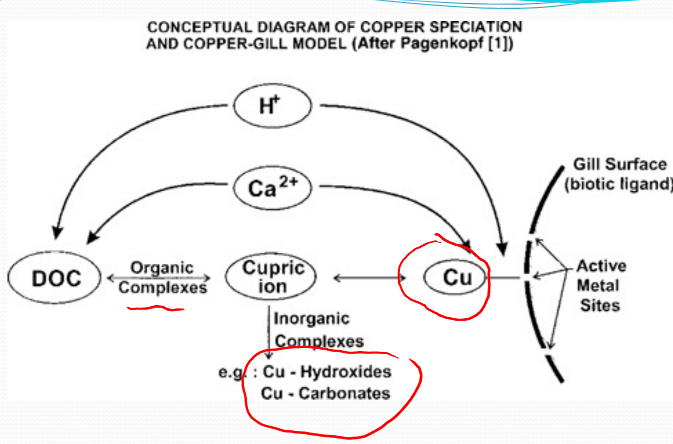
Lecture #32

Coordination Chemistry: Case Studies: NTA (cont.)

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

Benjamin; Chapter 8.1-8.6

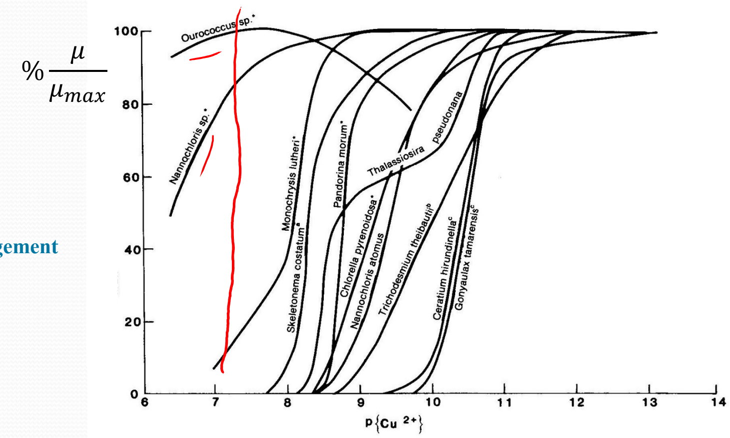
Biotic ligand model of the acute toxicity of metals. 2. Application to acute copper toxicity in freshwater fish and Daphnia



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

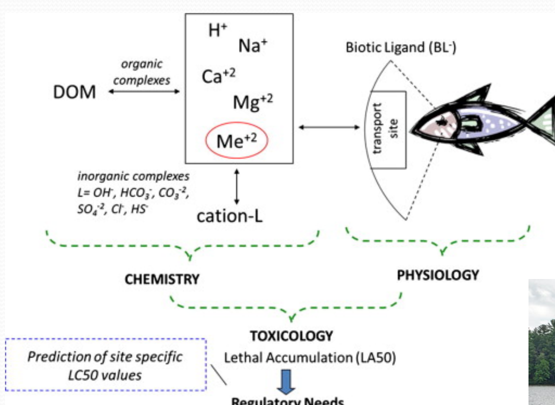
Algae and Copper

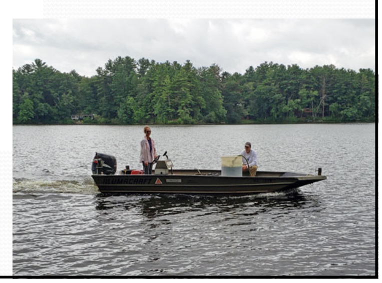
- Fresh and salt water algae
- Depends on Cu^{+2} ion: 10^{-7}M seems to work for most



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

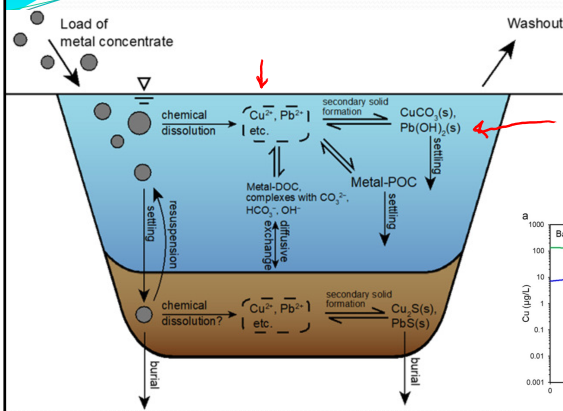
Add $CuSO_4$

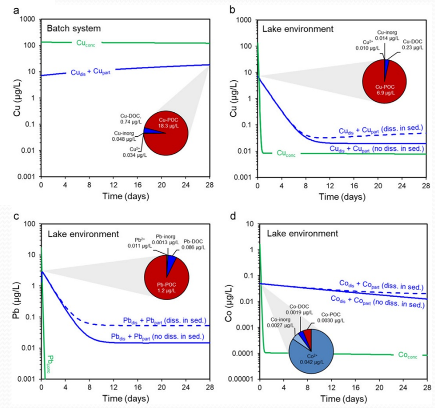




Smith et al., 2015, Applied Geochemistry 57:55

Modeling the Fate of Metal Concentrates in Surface Water



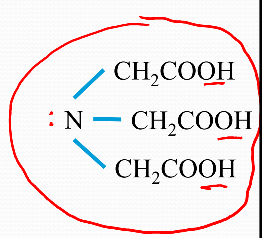


Environmental Toxicology and Chemistry, Volume: 38, Issue: 6, Pages: 1256-1272, First published: 23 March 2019, DOI: (10.1002/etc.4417)

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 = 3×10^{-6} M	NTA = 2×10^{-4} M
Cu(II) = 2×10^{-6}	$CuNTA^-$	13	4	82	100
Pb(II) = 3×10^{-7}	$PbNTA^-$	11.8	2	80	100
Ni(II) = 10^{-7}	$NiNTA^-$	11.3	1	60	100
Fe(III) = 2×10^{-6}	$Fe(OH)NTA^-$ $Fe(OH)_2NTA^{2-}$	10.9 3.1	0.4	34	100
Zn(II) = 1.5×10^{-6}	$ZnNTA^-$	10.4	0.2	20	100
$H^+ = 10^{-8}$	$HNTA^{2-}$	10.3	0	0	9
Mn(II) = 2×10^{-6}	$MnNTA^-$	7.4	0	0	100
Ca(II) = 10^{-3}	$CaNTA^-$	6.4	0	<0.1	17
Mg(II) = 2.5×10^{-4}	$MgNTA^-$	5.4	0	0	2
Sr(II) = 2×10^{-6}	$SrNTA^-$	5.0	0	0	0
Ba(II) = 1.5×10^{-7}	$BaNTA^-$	4.8	0	0	0
Na(I) = 5×10^{-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

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

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Cu-NTA V

- Equilibria
  - Acid/base
  - Complexation

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

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

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

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Cu-NTA VI

- Substitute mass balance and alpha equations into the beta equation

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

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

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

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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

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

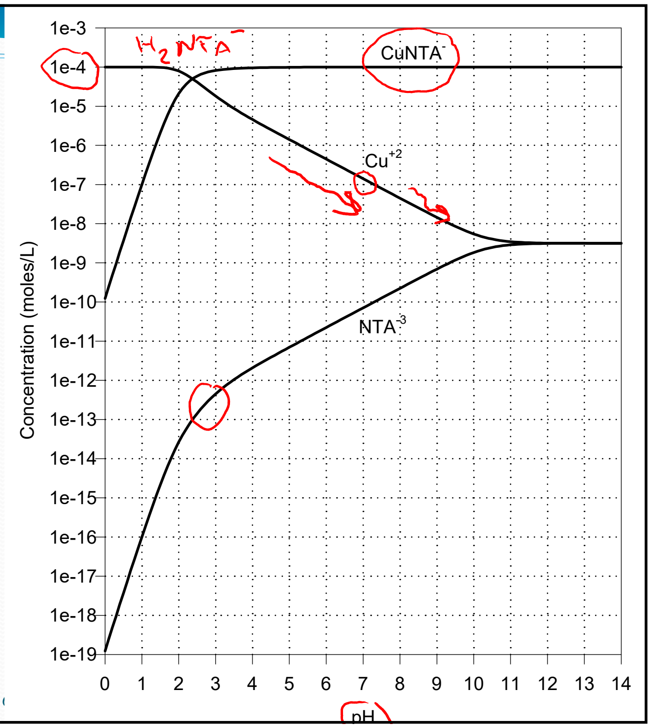
$$NTA_{TF} = NTA_T - [CuNTA^-]$$

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

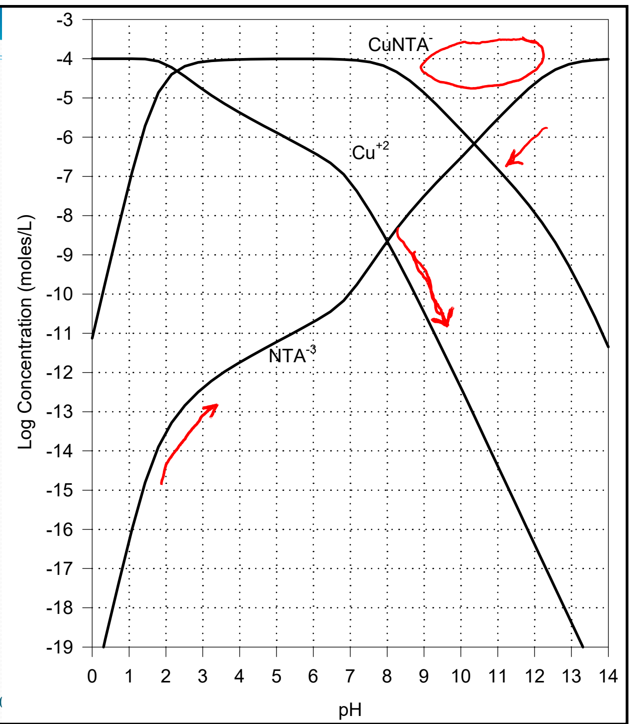
- Can use a spreadsheet to calculate α_3 versus pH, and then calculate the other species

Cu-NTA IX

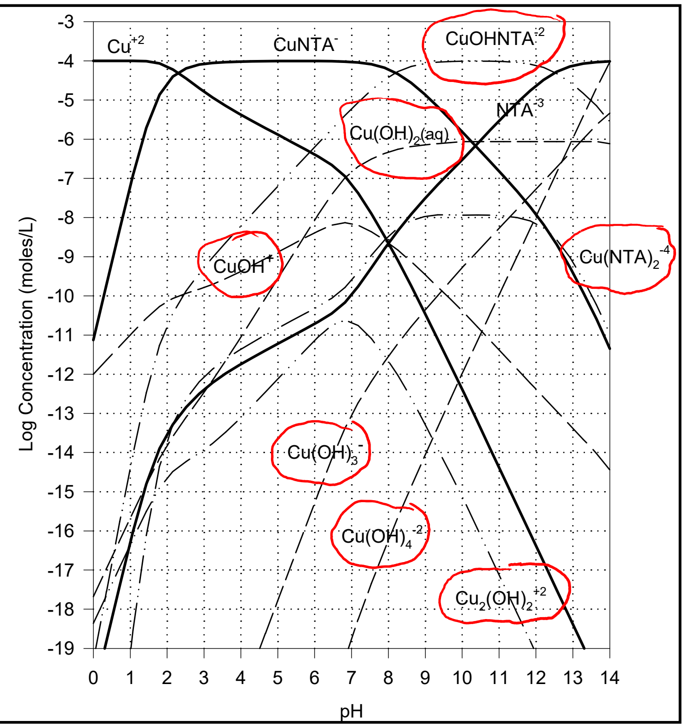
- Figure shows impact of ligand speciation on extent of complexation
- Same thing happens with fulvic acid



CuNTA X



CuNTA XI



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- To next lecture

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