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Aquatic Chemistry of Metals

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Aquatic Chemistry of Metals

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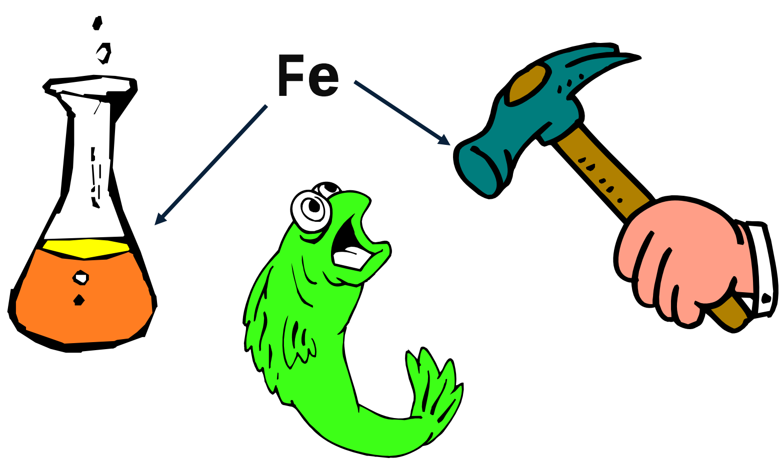
Speciation is Important



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Metal Speciation

- Water chemistry is critically important in terms of the toxicity of metal ions to aquatic organisms
- Equally important is knowledge about the speciation of the metal in the water of interest
- pH is often a factor determining speciation
- Metals bind to many ligand sites (carbon, suspended particles, metal hydroxides of Al and Fe, algae, etc.)
- Different metal species have different binding affinities

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Metal Speciation

- Knowing the metal species in solution is important – toxicity is a function of speciation
- Speciation: Distribution of an element among its possible chemical and physical forms
- Speciation can refer to an analytical measured value or a value derived by chemical equilibrium calculation

For example: Cu^0, Cu^{+1}, Cu^{+2}, CuOH, $CuCo_3$

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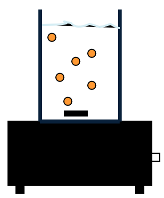
Does Metal Form Matter?

- **Transformation/ dissolution**



Example

Cu^0 solubility = ~ <0.1 µg/L at pH 6.0

Cu0 solubility = ~ 10 µg/L at pH 6.0

Cu_20 solubility = ~30 µg/L at pH 6.0

$CuSO_4$ solubility = > 1 mg/L, pH 6.0

Speciation
- Function of pH and ionic composition

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Theoretical Basis: Metals

- **Metals frequently occur as charged ions in aqueous solutions and require active transport to facilitate uptake for both essential and non-essential elements**
- **Active transport mechanisms exhibit saturable kinetics (i.e., rate limited)**

In contrast:

- **Neutral lipophilic organics**
  - Uptake via passive diffusion across lipid bilayer
  - Not active transport and not kinetically hindered

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Metal Solubility Issues

- Toxicity tests are most often performed with soluble metal salts (chloride, nitrates, sulfates)
- While these are sold in the market they are a very small part of the market
- Most metals are sold in the massive form as ingots or large particle and are sparingly soluble
- Toxicity tests with a metal salt represent the potential for toxicity once a small portion of the massive form goes into solution
- A translator is needed between the massive form and the soluble form

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Metal Transformation/Dissolution

- An approach to assess the dissolution of massive metal and sparingly soluble metal compounds was developed under OECD
- The Transformation Dissolution Protocol (TDP) is now a standard OECD test for assessing metal solubility as function of pH, and time (7 versus 28 days)
- Results of the 7 and 28 day dissolution studies (i.e., amount in solution) is compared with standard acute and chronic toxicity results, respectively

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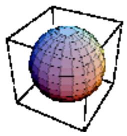
Methodology for Massive Classification



Sphere of 1 mm in diameter

Surface = 3.1416 mm^2
$Mass_{Cu}$ = 4.83 mg

Solvent needed to reach cut off values

Vol for 1mg/L = 4.83 L
Vol for 10 mg/L = 0.483 L
Vol for 100 mg/L = 0.0483 L

From TD test

Copper released at different cut off values (loading) = µg/L
Specific surface area = mm^2/mg
Released copper per surface unit at different loading = µg/mm^2

Normalized Critical Surface Loading (NCLS) at each Cut off values

$NCLS_{1mg/L}$ = 3.1416 mm^2 / 4.83 L = 0.67 mm^2/L
$NCLS_{10mg/L}$ = 6.7 mm2/L
$NCLS_{100mg/L}$ = 67 mm2/L

Normalized concentration values (NCV) in ug/L = NCSL in mm^2/L @ X loading * ug/mm^2 @ X loading

If NCV / LC(E)50 >1 substance is classified

If NCV / LC(E)50 < 1 substance is not classified

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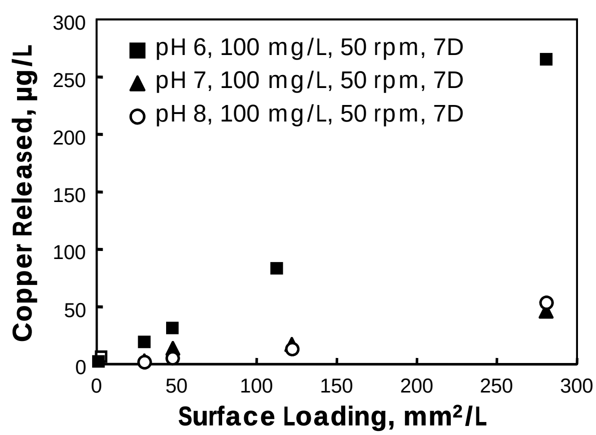
Comparison of dissolved released copper after 7 days of transformation dissolution of different copper surface loadings at pH 6, 7 and 8



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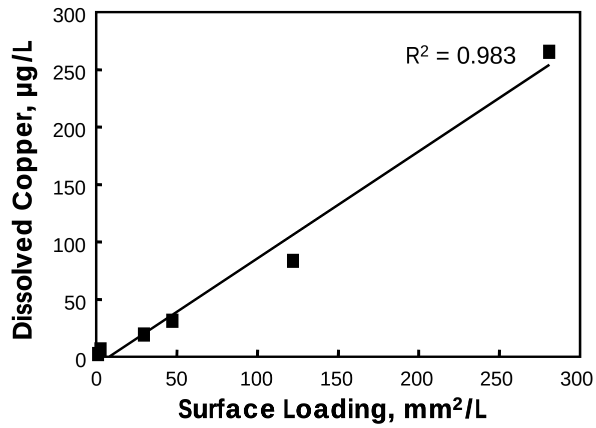
Linear relationship of the released dissolved copper at pH 6.0 for 7 days and the surface loading



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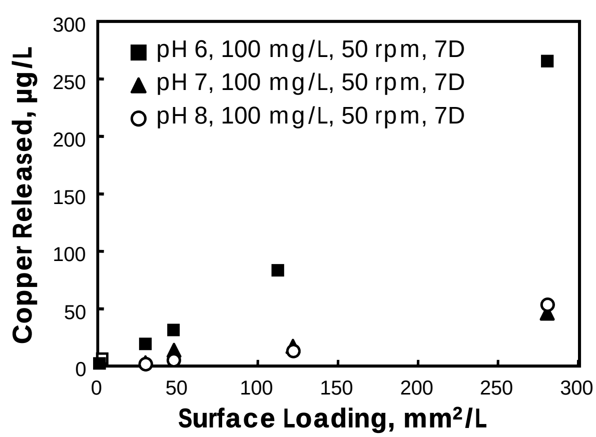
Comparison of dissolved released copper after 7 days of transformation dissolution of different copper surface loadings at pH 6, 7 and 8



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Transformation Conclusions

- This demonstrates the importance of using surface area when assessing the dissolution of a massive metal
- It is proposed that the surface area is an intrinsic property of a substance and should be considered as such within the guidance to perform TD testing
- This makes it possible to apply the data obtained for massive metals to metals powders when the metal released from the massive is expressed per surface area

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Toxicity Tests

- Toxicity tests (acute and chronic) are typically performed to standard protocols available from OECD, ISO and ASTM
- Tests are typical 24–96 hours for acute tests and 7–90 days for Chronic tests depending upon species
- Metals are typically tested using soluble metal salts
- Tests with Cu, Cd, Ni, Pb, Zn are frequently performed with numerous species. These are the metals which create less problems in testing
- Many metals have properties which make them difficult to test in fresh and marine waters

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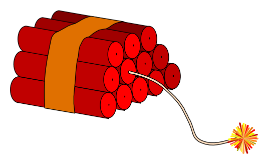
Behaviour of Difficult to Test Metal Substances

- **Difficulties have arisen in aquatic testing with some metal compounds**
  - Aluminium, iron, lead, manganese and tin
- **Each of these substances form insoluble compounds in standard Toxicity tests**
- **At circumneutral pH each of these metals form insoluble metal hydroxides (carbonates in the case of lead) which come out of solution**
- **precipitation varies with metal, pH and the ions in the test solution**
  - this is not good……



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Examples of The Solubility Ranges Obtained in Screening Simulations

Metal	Calculated solubilities (M) at pH 7			
	MINEQL		MINTEQ	
	minimum	maximum	minimum	maximum
Al(III)	1.78×10^{-9}	1.50×10^{-4}	9.69×10^{-10}	8.19×10^{-6}
Fe(III)	5.72×10^{-13}	4.55×10^{-9}	3.64×10^{-14}	2.95×10^{-10}
Pb(II)	2.56×10^{-6}		2.29×10^{-6}	
Sn(IV)	1.25×10^{-15}	6.13×10^{-9}	1.25×10^{-15}	6.18×10^{-9}
Sn(II)		1.24×10^{-5}	2.65×10^{-39}	1.26×10^{-5}

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Solid Phases Most Likely to Form Under the Conditions of a Typical Aquatic Toxicity Test (Al, Fe, Pb, Sn)

Metal		Suggested Solid Phase(s)
Aluminum	-	Microcrystalline gibbsite or amorphous $Al(OH)_3$
Iron(III)	-	Ferrihydrite ($Fe(OH)_3$
Lead	-	$Pb(OH)_2$; Hydrocerrusite ($Pb_3(OH)_2(CO_3)_2$) or Cerrusite ($PbCO_3$)
Tin(II)	-	$Sn(OH)_2$
Tin(IV)	-	$Sn(OH)_4$

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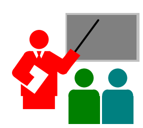
Behaviour of Difficult to Test Metal Substances



- **Reported test concentrations vary significantly**
- **Precipitation occurs in standard tests used to evaluate the metal effects (100–1000 µg/L)**
- **Results are reported as total, soluble, labile, bioactive, monomeric (single polymer), etc.....**
- **Kinetics of formation of insoluble species are not considered**
- **Test solutions are not checked for stability over time (i.e., aging)**
- **Metal species in solution are not tested; tests are conducted as if the substance is a stable soluble compound**

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Aquatic Toxicity of Metals Difficult to Test

Practical issues:

- Both Al and Fe occur in natural systems at levels that occur from 10 to 10,000 µg/L
- When low pH water (4.5–6.5), enters into streams with some what higher pH, hydroxides are formed that result in mixing zones where sensitive species can accumulate Al/Fe on their gills can impair osmoregulatory functions. This may be unique to select species in some environments.
- Examples are where acid rock drainage enters a pH neutral stream

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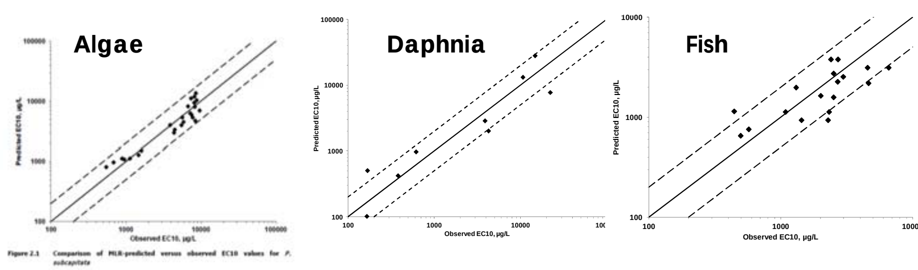
Development of Models to Predict the Effects of Iron on Aquatic Organisms

Test Organism	Range of DOC (mg/L)	Range of Hardness (mg/L as $CaCO_3$)	Range of pH
P. subcapitata	0.3–9.9	26–255	6.3–8.0
C. dubia	0.3–4	11–252	6.3–8.0
P. promelas	<0.5–4	10–82	6.0–8.0



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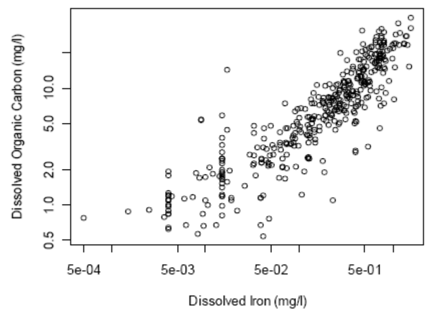
Iron and Water Chemistry Parameters

- Rate of iron oxidation and precipitation increases with increasing pH
- Co-variation observed between dissolved iron and dissolved organic carbon

This highlights the importance of any protective effect of DOC on iron toxicity



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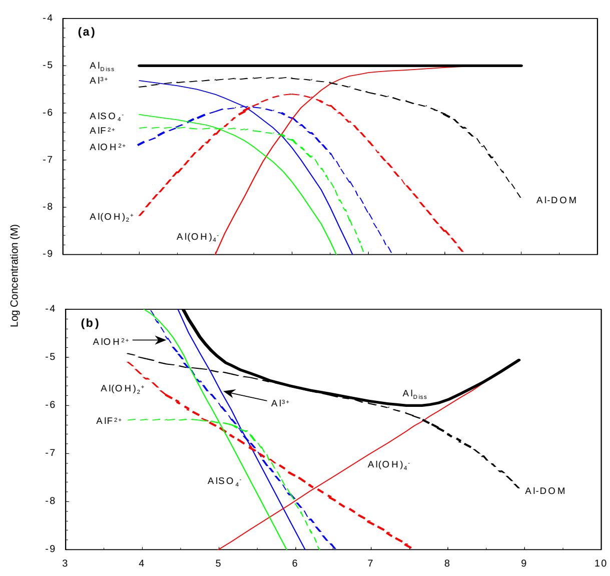
Al speciation in US EPA very soft water
Al = 10 um, DOC = 2 mg/L a) no solid phase b) Gibbsite present



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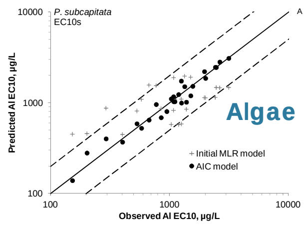
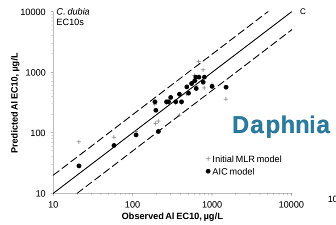
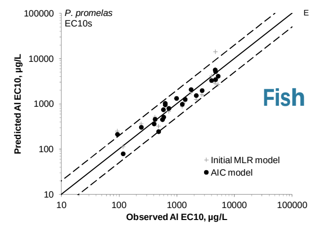
Predicted Versus Measured Toxicity of Aluminium







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Metals Bonded to Oxygen (Oxyanionic Metals)

- **Many metals (metalloids) exist covalently bonded to oxygen**
- **As, B, Cr, Mo, Se, V, U (iron and aluminum form oxides)**
- **Characteristics of most of these metals/metalloids are that they are quite soluble in water, they have multiple valence states depending upon redox of the system**

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Metals Bonded to Oxygen (Oxyanionic Metals)

- Metal Oxyanions tend to be less toxic than cationic metals and their toxicity is not moderated by DOC, hardness or suspended solids
- Toxicity can be influence by nitrate, nitrite, phosphate and sulfate

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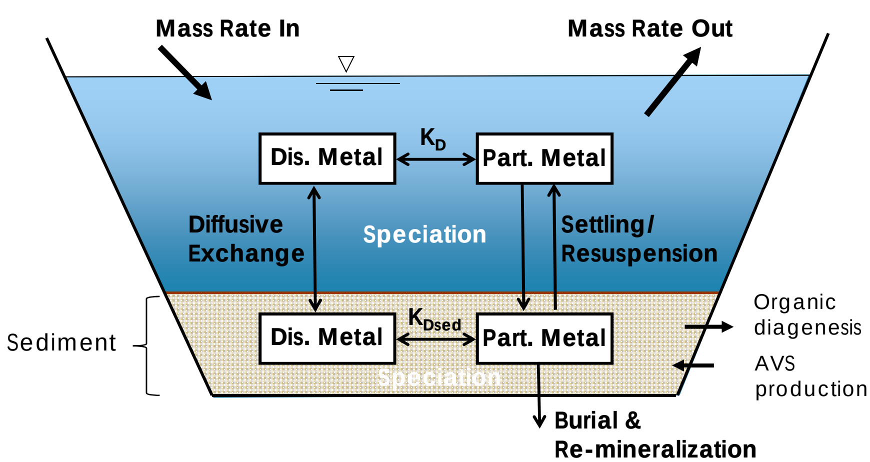
Development of a UWM Model for Lakes



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Unit World Model

- UWM "estimates rate at which a metal or Metal substance enters an ecosystem before reaching a concentration in one of the compartments that causes effects to biota."
- Most of the efforts to date have focused on soluble metal entering the unit world—
a worst case scenario
- Substances other than soluble metal compounds can be assessed by the model by utilizing transformation/ dissolution data

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Solubility Comparison of Metals Salts with Metal Massives, Oxides and Powders

Metal	Relative Solubility Resistance
Cd salt	1
Cu salt	1
Zn salt	1
Pb salt	1
Ni salt	1
Dicopper oxide	6
Curpic oxide	45
Iron powder	22
Copper powder	50
Zinc Massive	92*
Nickel powder	163
Cobalt tetraoxide	324
Copper massive	1,988
Nickel massive	216,500*

Relative Solubility Resistance
= Soluble salt / TdP value
Derived at pH 6

* Dissolution data derived at pH 8

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UWM Concluding Remarks

- UWM model has been developed as a means to assessing the fate and transport of metals in a model freshwater system
- Sensitivity analyses have been performed, model has been compared to real world systems and the results have been published

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Concluding Remarks

- Speciation is important
- Models exist to predict speciation as a function of water chemistry
- Metals which form metal hydroxides or insoluble carbonates are difficult to test and require special attention
- An OECD protocol has been developed to measure the solubility of Sparingly soluble metals (TDP protocol)
- A unit world model has been developed to estimate metal transport/fate and toxicity in freshwater systems

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