Aquatic Chemistry of Metals

Submitted by: Rio Tinto
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Speciation is Important
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

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\(_3\)
Does Metal Form Matter?

- Transformation/dissolution

**Example**
- $\text{Cu}^0$ solubility $\approx 0.1 \, \mu\text{g/L at pH 6.0}$
- $\text{CuO}$ solubility $\approx 10 \, \mu\text{g/L at pH 6.0}$
- $\text{Cu}_2\text{O}$ solubility $\approx 30 \, \mu\text{g/L at pH 6.0}$
- $\text{CuSO}_4$ solubility $> 1 \, \text{mg/L, pH 6.0}$

Speciation
- Function of pH and ionic composition

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
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

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
Methodology for Massive Classification

Sphere of 1 mm in diameter

Surface = 3.1416 mm²
MassCu = 4.83 mg

Solvent needed to reach cutoff values
Vol for 1 mg/L = 4.83 L
Vol for 10 mg/L = 0.483 L
Vol for 100 mg/L = 0.0483 L

Normalized Critical Surface Loading (NCLS) at each cutoff values

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

Copper released at different cutoff values (loading) = µg/L
Specific surface area = mm²/mg
Released copper per surface unit at different loading = µg/mm²

Normalized concentration values (NCV) in µg/L:
NCV in mm²/L @ X loading * µg/mm² @ X loading

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

Comparison of dissolved released copper after 7 days of transformation dissolution of different copper surface loadings at pH 6, 7 and 8
Linear relationship of the released dissolved copper at pH 6.0 for 7 days and the surface loading

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

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
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......

Examples of The Solubility Ranges Obtained in Screening Simulations

<table>
<thead>
<tr>
<th>Metal</th>
<th>Calculated solubilities (M) at pH 7</th>
<th>MINEQL</th>
<th>MINTEQ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>minimum</td>
<td>maximum</td>
<td>minimum</td>
</tr>
<tr>
<td>Al(III)</td>
<td>1.78×10^{-9}</td>
<td>1.50×10^{-4}</td>
<td>9.69×10^{-10}</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>5.72×10^{-13}</td>
<td>4.55×10^{-9}</td>
<td>3.64×10^{-14}</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>2.56×10^{-6}</td>
<td>2.29×10^{-6}</td>
<td></td>
</tr>
<tr>
<td>Sn(IV)</td>
<td>1.25×10^{-15}</td>
<td>6.13×10^{-9}</td>
<td>1.25×10^{-15}</td>
</tr>
<tr>
<td>Sn(II)</td>
<td>1.24×10^{-5}</td>
<td>2.65×10^{-5}</td>
<td>1.26×10^{-5}</td>
</tr>
</tbody>
</table>
### Solid Phases Most Likely to Form Under the Conditions of a Typical Aquatic Toxicity Test (Al, Fe, Pb, Sn)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Suggested Solid Phase(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Microcrystalline gibbsite or amorphous Al(OH)₃</td>
</tr>
<tr>
<td>Iron(III)</td>
<td>Ferrihydrite (Fe(OH)₃)</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb(OH)₂; Hydrocerrusite (Pb₃(OH)₂(CO₃)₂) or Cerrusite (PbCO₃)</td>
</tr>
<tr>
<td>Tin(II)</td>
<td>Sn(OH)₂</td>
</tr>
<tr>
<td>Tin(IV)</td>
<td>Sn(OH)₄</td>
</tr>
</tbody>
</table>

### 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
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 somewhat 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

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

<table>
<thead>
<tr>
<th>Test Organism</th>
<th>Range of DOC (mg/L)</th>
<th>Range of Hardness (mg/L as CaCO₃)</th>
<th>Range of pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>P. subcapitata</td>
<td>0.3–9.9</td>
<td>25–255</td>
<td>6.3–8.0</td>
</tr>
<tr>
<td>C. dubia</td>
<td>0.3–4</td>
<td>11–252</td>
<td>6.3–8.0</td>
</tr>
<tr>
<td>P. promelas</td>
<td>&lt;0.5–4</td>
<td>10–82</td>
<td>6.0–8.0</td>
</tr>
</tbody>
</table>

Algae

Daphnia

Fish
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
Predicted Versus Measured Toxicity of Aluminium

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
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 influenced by nitrate, nitrite, phosphate and sulfate.

Development of a UWM Model for Lakes

[Diagram showing mass rate in and out, Diffusive Exchange, Speciation, Settling/Resuspension, Burial & Re-mineralization, Organic diagenesis AVS production]
**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**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Relative Solubility Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd salt</td>
<td>1</td>
</tr>
<tr>
<td>Cu salt</td>
<td>1</td>
</tr>
<tr>
<td>Zn salt</td>
<td>1</td>
</tr>
<tr>
<td>Pb salt</td>
<td>1</td>
</tr>
<tr>
<td>Ni salt</td>
<td>1</td>
</tr>
<tr>
<td>Dicopper oxide</td>
<td>6</td>
</tr>
<tr>
<td>Cupric oxide</td>
<td>45</td>
</tr>
<tr>
<td>Iron powder</td>
<td>22</td>
</tr>
<tr>
<td>Copper powder</td>
<td>50</td>
</tr>
<tr>
<td>Zinc Massive</td>
<td>92*</td>
</tr>
<tr>
<td>Nickel powder</td>
<td>163</td>
</tr>
<tr>
<td>Cobalt tetraoxide</td>
<td>324</td>
</tr>
<tr>
<td>Copper massive</td>
<td>1,988</td>
</tr>
<tr>
<td>Nickel massive</td>
<td>216,500*</td>
</tr>
</tbody>
</table>

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

*Dissolution data derived at pH 8*
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

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 Sparsely soluble metals (TDP protocol)
- A unit world model has been developed to estimate metal transport/fate and toxicity in freshwater systems