ENVIRONMENTAL RISKS OF INORGANIC METALS AND METALLOIDS – A CONTINUING, EVOLVING SCIENTIFIC ODYSSEY

Bioavailability / Toxicity

Exposure

Risk

Hazard

Receptor

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METALS / METALLOIDS ARE UNIQUE

Henceforth, the term ‘metals’ is used to refer to both metals and metalloids.

- Neither created nor destroyed; transformed from one chemical species to another.
- Variable solubility (solubility based on soluble salts → overestimates of bioavailability / toxicity).
- Both essential (Cu, Cr, Zn, Se) and non-essential elements (Pb, As, Hg).
- Organisms regulate metals, especially essential metals.
- Each metal species unique (fate / transport, bioavailability, bioaccumulation, toxicity).

DO NOT USE INCORRECT TERM ‘HEAVY METALS’
Essential metals can be toxic due to both too little (deficiency) and too much bioavailable metal (toxicity).
We Know

Metal Risks Moderated by Speciation

- Measurements of total concentrations of metals and metalloids do not provide definitive information about their mobility, bioavailability, and potential toxicity to ecological systems or biological organisms.

- Without knowledge of speciation, the toxicology and bioavailability of metals tend to be markedly overestimated (total concentrations of metals are not equivalent in any sense to bioavailable metals).
<table>
<thead>
<tr>
<th>Tool</th>
<th>Date</th>
<th>Description</th>
<th>Comments</th>
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</thead>
<tbody>
<tr>
<td><strong>Total recoverable metals</strong></td>
<td>Pre-1985</td>
<td>Dissolved metals + easily dissolved solid metals; hard mineral acid digestion</td>
<td>Highly conservative for metals in effluent that may become environmentally active</td>
</tr>
<tr>
<td><strong>Acid soluble metals</strong></td>
<td>1985</td>
<td>Less aggressive digestion procedure</td>
<td>Not much improvement</td>
</tr>
<tr>
<td><strong>Dissolved metals</strong></td>
<td>1993</td>
<td>&lt;0.45 micron, pH 6.5-9.0, TOC/TSS &lt; 5 mg/L</td>
<td>Improved approximation, but not ideal</td>
</tr>
<tr>
<td><strong>BLM</strong></td>
<td>2003</td>
<td>Model based on water chemistry</td>
<td>Continuing research focus</td>
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</table>
Stop-gap (time consuming, expensive) option for normalizing dissolved metals measures after hardness adjustment, prior to the BLM.

**Water Effect Ratio (WER)**

Sample Determination of a Water-Effect Ratio, WER

Site water LC50 = 350 μg/L copper

Toxicity in site water with added copper.

WER = \( \frac{350 \ \mu g/L}{100 \ \mu g/L} \) = 3.5

Laboratory water LC50 = 100 μg/L copper

Toxicity in laboratory water with added copper.
BIOTIC LIGAND MODEL

Can be any relevant surface on an organism

Accepted in US, EU, Canada, Australia,…

Originally developed for freshwater acute exposures

Extending chronic applicability to deal with mixtures

Extending to terrestrial and marine environments

Chemistry

Physiology

Toxicology

Regulatory Needs
Physiology Rules in Sea Water

and dietary metals uptake alters metals bioavailability in fresh or salt water

e.g., Galvez et al. 2007. Aquat Toxicol 84: 208-214


“...physiology rather than chemistry explains much of the variation in Cu toxicity seen across salinities”.
Limitations of Chemical Analyses

- We can’t measure everything
- Chemical analyses provide no information on *bioavailability* of contaminants or on factors that modify bioavailability

**BLM predictions an improvement**

- Chemical analyses provide no information on *effects*, let alone *impacts*
**Environmental Quality Guidelines (EQGs)**

*Use on the basis of common sense, not inflexibly*

<table>
<thead>
<tr>
<th>EQGs include sediment and water quality guidelines (SQGs and WQGs)</th>
<th>Limitations:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• Do not consider synergism between contaminants, biomagnification, or secondary poisoning</td>
</tr>
<tr>
<td></td>
<td>• Only based on toxicity to biological receptors</td>
</tr>
<tr>
<td></td>
<td>• Do not consider human health</td>
</tr>
<tr>
<td></td>
<td>• Not to be used alone for remediation decisions</td>
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</tbody>
</table>

**Uses:**

- To identify and describe contamination
- To identify and prioritize contaminants of potential concern (COPCs)
- *As part* of an ERA approach to decision-making
The Key Question(s)

So what?

➤ When does contamination (the presence of a substance at higher than natural concentrations) become pollution (contamination that results in adverse biological effects to individuals or, more importantly, in adverse biological impacts to populations)?

➤ And how does this occur (what are the sources and mechanisms)?
Effects vs Impacts

- **An effect:** a change to a valued ecosystem component (VEC) due to human activities – not necessarily negative (e.g., copper [Cu] and zinc [Zn] are essential elements)

- **An impact:** an effect to a VEC that adversely affects the utility or viability of that VEC (e.g., reduced productivity of aquatic communities due to Cu and/or Zn toxicity)
Scale Matters

- Laboratory
  - Pot
- Field
  - Test plot (site-specific)
- Regional
  - Landscape
- Continental

Terrestrial:
- Bioassay

Aquatic:
- Waterbody (site-specific)
- Watershed
Risk: risk comparisons are essential

Proposed tuna label:
Hey, I thought we were working with the same data!
The Different Forms of “Bio-”

**Bioaccessible:** Potentially available for uptake over the long-term. Fraction that may be available to an organism. Includes portion that is currently bioavailable + portion(s) that may become bioavailable over time (e.g., from matrices such as sediment, soil [food - for humans])

**Bioavailable:** Immediately available for uptake by organisms

**Bioabsorbed:** Actually taken up by an organism

**Bioreactive:** Actually able to cause toxicity (the bioabsorbed fraction minus the fraction that is depurated, internally sequestered, or used by the organism for its own needs)
Importance of “Bio-”

**BIOAVAILABLE**

No

Exposure?

Yes

Bioavailable fraction

Substance “A”

Non-bioavailable fraction

Not bioavailable

**BIOREACTIVE**

Yes

Essential?

No or excess

Bioreactive fraction

Internal transport and distribution

Detoxification, storage, elimination

Not bioreactive

**Site of toxic action**

**Toxic dose?**

No

Yes

TOXICITY
Metals and “Bio-”

- **Detoxified and not bioreactive**: metals bound to inducible metal-binding proteins such as metallothionein (MT) or precipitated into insoluble concretions consisting of metal-rich granules (MRG) – virtually unlimited potential for metal absorption.
- **Metabolically active and bioreactive**: metals in metal-sensitive fractions (MSF) such as organelles and heat-sensitive proteins.
- **Species-specific differences** in relative proportion of bioreactive metals.
- **Trophic transfer of metals to predators**: MSF and MT represent tropically available metal (TAM); MRG is not trophically available. Thus, total tissue burdens in prey will not directly relate to metal transfer to predators.
Metal Speciation, “Bio-”, and Toxicity

- The form, or species, of metal (or metalloid) in the environment will affect both bioavailability and toxicity (metal speciation).
- Environmental variables (e.g., pH, cation exchange capacity, hardness, DOM) modulate speciation (confounding variables).
- Metals in the environment bound to particulate matter may not be biologically available (bioavailability).
- Metals within organisms may be inert (e.g., detoxified) relative to the host organism and/or to predators (bioreactivity).
- Within “metalloregions” there may be selection for metal-resistant populations – normal responses by organisms to adjust boundaries of their ecological niches to maximize chances to survive and reproduce (tolerance).
“Bio-” and Organic Substances

Sorption of organic chemicals via “dual-mode sorption” – absorption in amorphous organic matter and to carbonaceous materials (e.g., black carbon)

Solid-phase concentrations bear little or no relation to actual concentrations in organisms – reconsider existing criteria

[Graph showing log Koc values for various carbon forms]

- Soil NOM
- Humic acid
- Coal tar pitch
- Kerogen
- Charcoal
- Coal
- Soot carbon
- Ac. carbon

[Images of various carbon forms]

- Wood
- Lignite
- Bituminous coal
- Anthracite coal
- Oxidized coal
- Coke
- Charcoal
- Cenosphere
- Soot carbon
- Coal tar pitch
Biological Tolerance

Tolerance to one metal can affect tolerance to other metals; need to understand previous exposure conditions.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Metabolic Cost?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acclimation</td>
<td>Yes</td>
</tr>
<tr>
<td>Non-genetic adaptation</td>
<td>Yes</td>
</tr>
<tr>
<td>Genetic adaptation</td>
<td>Possibly not</td>
</tr>
<tr>
<td>Metabolism</td>
<td>Possibly not</td>
</tr>
</tbody>
</table>
**Acclimation** (A) is physiological and an extension of an organism’s ecological range.

Genetic **adaptation** (B) comprises a new ecological range.
IMPORTANCE OF ERA

TO ANSWER THE “SO WHAT?” QUESTION – REGULATORY IMPLICATIONS

Risk

Default Uncertainty Factor

Margin of safety

Estimated risk

Actual risk (unknown)

Ecologically Relevant Knowledge

Chemical- and Site-Specific Assessment Factor
The Key Question(s)

So what?

1. Do metals accumulate in biota above background levels?
2. If so, are these metals biologically active (bioreactive)?
3. If so, are they likely to result in adverse effects to individuals either alone or in combination with other stressors?
4. If so, are they likely to result in adverse impacts to populations?

<table>
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<tr>
<th>Question</th>
<th>Chemical Tools</th>
<th>Biological Tools</th>
<th>Comments</th>
</tr>
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</table>
| **Do metals accumulate in biota above background levels?** | • Measured body burdens  
• Aqueous exposure estimates (Biotic Ligand Model [BLM], other models)  
• Dietary exposure estimates (gut digestive fluids, organisms) | | • Based on bioavailability (determined by speciation, site-specific conditions, and organism behaviour)  
• Dynamic models may provide better predictions for bioaccumulation and toxicity of some metals than equilibrium models  
• **BCFs and BAFs are not useful**  
• Metals accumulation in tissues does not necessarily relate to toxicity or trophic transfer |
Bioconcentration Factors (BCFs)

Example: If the contaminant concentration in the soil is 100 µg/kg and in a plant growing in the soil it is 10 µg/kg, the BCF = 0.1 (10 µg/kg)/(100 µg/kg)

BCFs are used to calculate expected concentrations in the tissues of receptor species.

A BCF is the ratio of the concentration of a contaminant in the source to the concentration in the receptor.

BCFs [and Bioaccumulation Factors (BAFs)] provide misleading data for metals (e.g., essential metals are taken up against the concentration gradient).
### Four Key ERA Metals Questions - #2

<table>
<thead>
<tr>
<th>Question</th>
<th>Chemical Tools</th>
<th>Biological Tools</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Are the metals biologically active?</td>
<td>• Metal fractionation within organisms</td>
<td>• Determination of food chains for predator-prey predictions</td>
<td>• Metals occur in two pools: biologically active and available; detoxified and unavailable</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Metals bioreactivity can vary by exposure route (water, diet)</td>
</tr>
<tr>
<td>Question</td>
<td>Chemical Tools</td>
<td>Biological Tools</td>
<td>Comments</td>
</tr>
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<td>-------------------------------------------------------------------------</td>
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</tr>
<tr>
<td><strong>Are the metals likely to result in adverse effects to individuals either alone or in combination with other stressors?</strong></td>
<td>• Predictions (BLM, biokinetics)</td>
<td>• Single species toxicity tests involving appropriate metals pre-exposure, and both aqueous and dietary exposures</td>
<td>• Predictions may also be possible using regression-based modeling involving toxicity data and DOC (dissolved organic carbon) measurements</td>
</tr>
<tr>
<td></td>
<td>• Predictions (Contaminant Body Residues [CBRs])</td>
<td>• Field data: organism responses to actual contamination</td>
<td>• Use of CBRs requires dose-response relationships between bioreactive metals and organism responses</td>
</tr>
<tr>
<td></td>
<td>• Predictions (environmental quality values)</td>
<td></td>
<td>• Contaminant interactions cannot at present be reliably predicted, nor can interactions with non-chemical stressors</td>
</tr>
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<td></td>
<td></td>
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<td>• Pulsed (intermittent) exposures need to be considered as well as continuous exposures</td>
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</table>
### Four Key ERA Metals Questions - #4

<table>
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<tr>
<th>Question</th>
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<th>Biological Tools</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Are the metals likely to result in adverse impacts to populations?</td>
<td>• Predictions from single-species data (Species Sensitivity Distributions [SSDs])</td>
<td>• SSDs presently less useful for chronic than acute responses</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Life-table response experiments</td>
<td>• Species extrapolations need to encompass appropriate sensitivities</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Multiple species toxicity tests involving appropriate metals pre-exposure, both aqueous and dietary exposures and, where appropriate, multi-generational studies</td>
<td>• Tolerance can be acclimation or adaptation; the latter may or may not have energetic costs (e.g., trade-offs of energy allowances)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Field data: community-level responses to actual contamination (structural and functional responses)</td>
<td>• Both direct and indirect effects need to be considered</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Direct effects may include chemosensory impairment</td>
<td></td>
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</table>
Use of Species Sensitivity Distributions (SSDs), not lowest available toxicity data divided by a safety factor

EPA Metals Framework – recognizes basic properties of metals, differences between metals and organics, and use of SSDs

Canadian 2007 Water Quality Guidelines recognize use of SSDs – example opposite is from that document (and essentiality, tolerance, speciation, modifying factors, etc)
MAJOR STRIDES HAVE BEEN MADE, BUT THE JOURNEY CONTINUES
Inter-relationships between Ecosystems and Chemicals are Complex

**ROPC** = Receptor of Potential Concern

**Processes**
1. Wet or dry deposition (e.g., rain, run-off, dust)
2. Settling/sorption
3. Resuspension (e.g., bioturbation, bioirrigation, scouring, desorption)
4. Burial/mixing
5. Burial

**ROPCs**
- Mammals/birds eating aquatic biota
- Fish
- Invertebrates
- Plants
- Algae

**Other Stressors**
- Climate change
- Habitat change
- Introduced species
- Eutrophication
A critical load is the highest acceptable input rate of a substance (e.g., a metal) into the environment (i.e., that will result in contamination but not in pollution).

The critical load concept is used to estimate acceptable current and future inputs of substances such as metals – it requires knowledge of sources, cycling, fate and effects to define acceptable inputs, often considered over different time scales.

Critical loads are intended to proactively prevent contamination accumulating to a degree that causes pollution. When pollution already exists, critical loads may be set to help reduce levels of contamination over time and ameliorate adverse effects / impacts.
Errors in current model estimates are at least an order of magnitude.
Assessing Potential Metal Effects

Answer the “So What?” question where it really matters:

1. Are there present or potential effects and impacts?
2. Is there present or potential pollution, not just contamination?
3. Conduct risk:risk comparisons (action versus no action) [all actions are not the same]
4. What good science is appropriate both proactively and reactively?
"One does not swat a gnat while being charged by elephants"

- Alvin Winberg (1987)

Focus on what really matters, the big picture, not the minutae
Global Environmental Threats (in order)

- Global Climate Change
- Habitat Change
- Exotic Species Introductions / Invasions
- Eutrophication
- Chemical (e.g., metals) Contamination

Interactions (e.g., metals and climate change) must also be considered.
Thank you for Listening!
Questions / Discussion?

pmchapman@golder.com
Additional Information re Metals RA
