ISSUES IN RISK ASSESSMENT OF METALS AND METALLOIDS

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ECOLOGICAL RISK ASSESSMENT (ERA)

A process that evaluates the potential for adverse ecological effects that *may occur* as a result of exposure to contaminants or other stressors

Advantages:

- A framework for gathering data and evaluating their sufficiency for decision-making.
- Recognizes, considers and reports uncertainties in estimating adverse effects of stressors

ERA Framework

Basic Risk Assessment Paradigm

Predicted Environmental Concentration (PEC)

Predicted No Effect Concentration (PNEC)

Risk Characterization
(PEC/PNEC)
[simple ☑ hazard quotient; more realistic, certain ☑ probabilistic approaches]

DETERMINING PEC (for metals and metalloids)

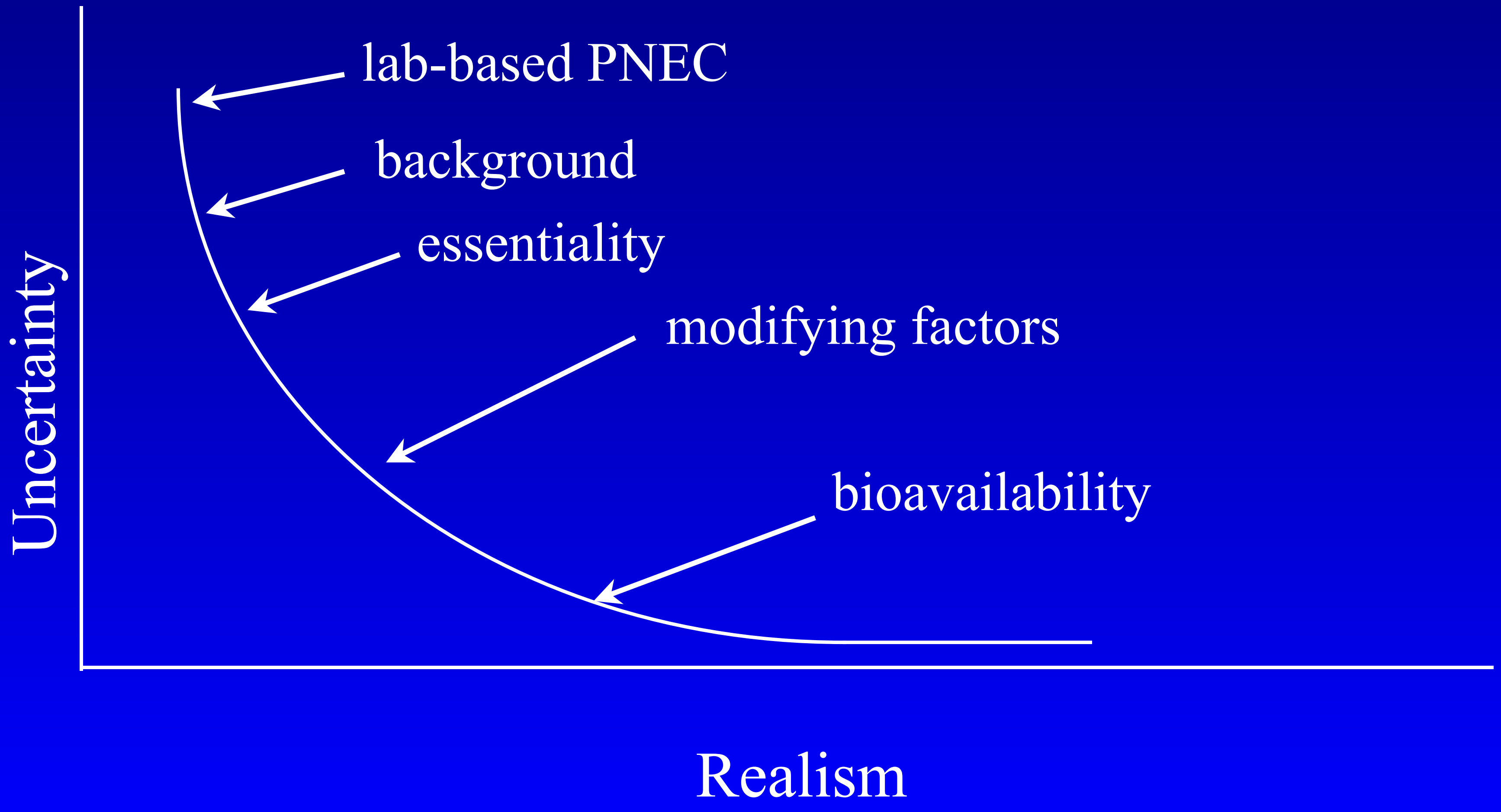
- Determine natural background
  - Geological processes, weathering
- Consider essentiality
- Measure concentrations (retrospective ERA)
  - Appropriate analytical methods
- Model concentrations (retrospective and prospective ERA)
  - Consider speciation
  - Allow for effects of modifying factors (e.g., hardness, pH, DOC)
  - Predict frequency, magnitude and duration
  - Evaluate non-point as well as point sources

DETERMINING PNEC (for metals and metalloids)

- Laboratory and field tests
  - Conservative uncertainty factors commonly applied
- Statistical extrapolations
  - e.g., Aldenberg-Slob method; U.S. EPA final acute value (FAV) approach
- Mechanistic approaches
  - e.g., Biotic Ligand Model (toxicity related to metal complexation and interaction at biotic receptor site)

[PNEC cannot be less than background, or below optimal levels for essential metals]

UNCERTAINTY vs. REALISM



Some Generic Differences: Screening Level Risk Assessment (SLRA) and Detailed Level Risk Assessment (DLRA)*

Parameter	SLRA	DLRA
relative level of effort	low	high
level of conservatism	high (over-protective)	decreased (reasonably protective)
level of uncertainty	high	decreased
hazard quotients (HQs)	generic	site-specifc
extrapolations	broad	limited

* Source: Hill R.A., Chapman P.M., Mann G.S., Lawrence G.S. 2000. Level of detail in ecological risk assessment. Marine Pollution Bulletin 40:471-474.

Information Provided by a Conservative SLRA

- If Hazard Quotients (HQs) <1
  - No Risk
- If HQs >1
  - A possible risk
  - Evaluate further (e.g., move from SLRA to DLRA)

RISK versus HAZARD

[Important for understanding ERA process and products]

- **Hazard** = *possibility* of a stressor causing adverse effects.
- **Risk** = *probability* of a stressor causing adverse effects.

ERA ISSUES SPECIFIC TO METALS AND METALLOIDS

1. Natural Occurrence

- Sources:
  - Physical and chemical weathering
  - Volcanic activities
- Highly variable
  - By environmental media (soils, sediments, water)
  - Different geological and environmental conditions
  - Baseline concentrations can vary by 5 orders of magnitude
- Overall concentrations constant over time
  - Releases between environmental media affected by humans, not overall concentrations

ERA ISSUES SPECIFIC TO METALS AND METALLOIDS (Continued)

2. Transformation

- Organic chemicals can be degraded
  - Into simple compounds such as CO_2
- Metals/metalloids generally do not degrade
  - Transformed into different chemical forms or species
  - Exceptions: organometallics; radioactive elements
  - *Categorization in terms of "persistence" is meaningless*

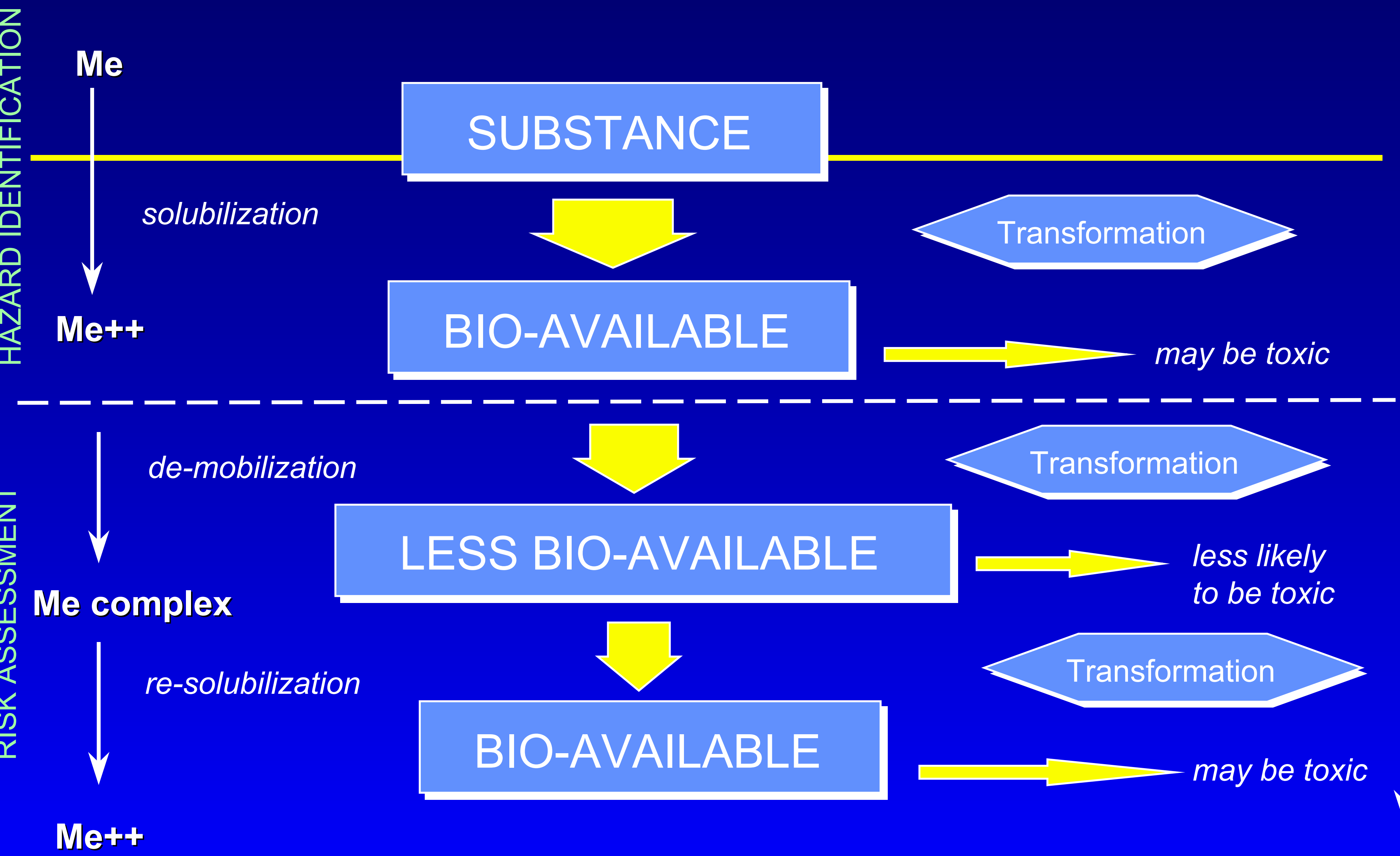
ERA ISSUES SPECIFIC TO METALS AND METALLOIDS (Continued)

3. Bioavailability

- Organic chemicals diffuse across lipid layer of biological membranes
  - log K_{ow} measurements
- Elemental metals and metalloids generally not bioavailable
- Dissolved metals and metalloids can be bioavailable
  - Facilitated diffusion through proteinaceous ionophores

Factors affecting bioavailability

Abiotic	Biotic
Dissolution	Organism
Metal/metalloid adsorption/desorption (pH)	Organism response
Kinetics	Endpoint measured
Complexion/speciation	Conditioning/tolerance/ stress/adaptation

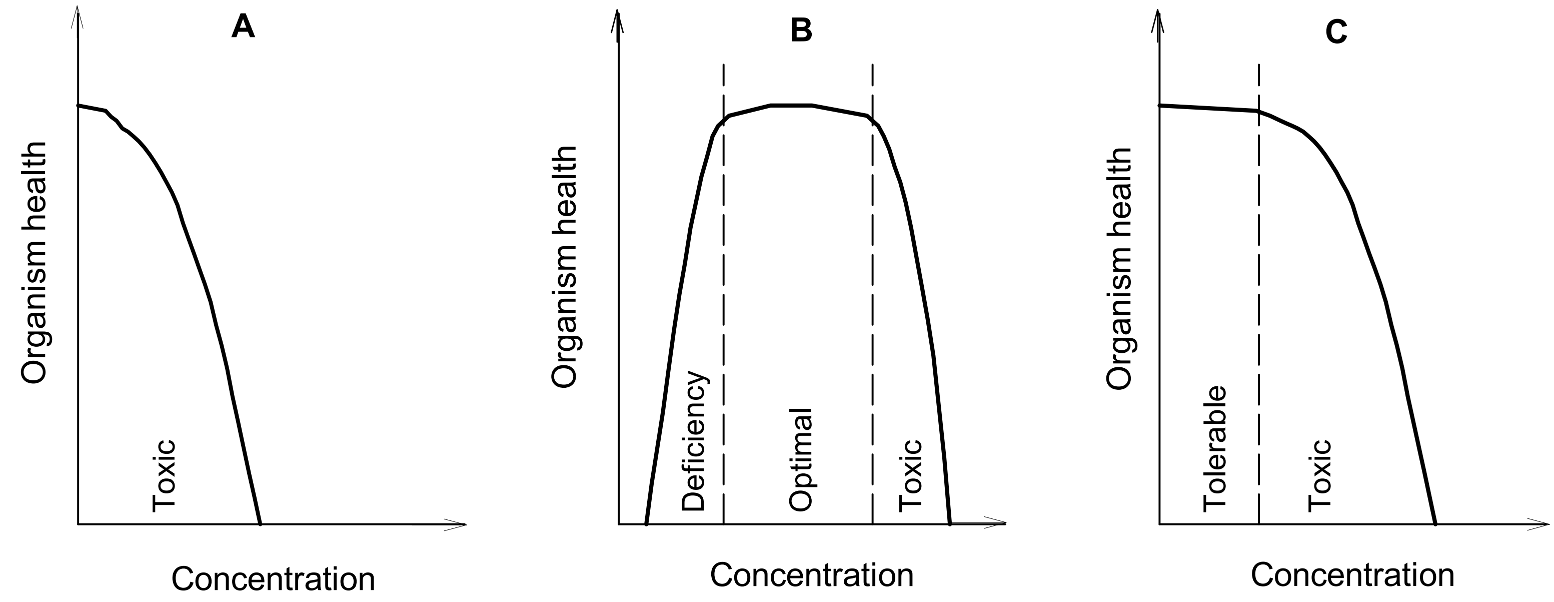

HAZARD IDENTIFICATION
RISK ASSESSMENT
Me
SUBSTANCE
solubilization
Transformation
Me++
BIO-AVAILABLE
may be toxic
de-mobilization
Transformation
LESS BIO-AVAILABLE
less likely to be toxic
Me complex
re-solubilization
Transformation
BIO-AVAILABLE
may be toxic
Me++

ERA ISSUES SPECIFIC TO METALS AND METALLOIDS (Continued)

4. Biological Effects

- Organic chemicals → no or negative effects
- Metals and metalloids
  - negative effects
  - positive effects (essential metals and metalloids – generally ignored in ERA)
  - no effects (tolerance and adaptation – generally ignored in ERA)

DOSE-RESPONSE RELATIONSHIPS



Implications of essentiality

Present Focus	Future Focus
Removing all chemicals	Determining appropriate amounts of some chemicals
Application of safety factors	No safety factors
High exposures	Both high *and* low exposures
Few exposures	More exposures
Assumption of monotonic/linear data pattern	No preconceived assumptions (or confining statistics)

Metals/metalloids vs synthetic organic chemicals

	Synthesized Organic Chemicals	Metals and Metalloids	
		Essential	Nonessential
Sources	Introduced by humans	Naturally-occurring; release can be enhanced by humans	
Fate	More or less degradable	Transformable but not degradable	
Effects			
Positive effects	No	Yes	No
No effects	Maybe	No	Yes
Adverse effects	Toxicity	Deficiency and toxicity	Toxicity

Differences between ERAs of metals/metalloids and organic chemicals

Step	Organic Chemicals	Metals and Metalloids
Hazard identification/Problem Formulation	Persistence; Bioaccumulation; Inherent toxicity.	Water solubility; Stability of dissolved forms; Inherent toxicity of the parent and dissociated compounds.
Exposure Analysis	Environmental concentration; Exposure duration.	Concentration added to background concentration; Bioavailability; Exposure duration.
Effects Analysis	Toxicity testing	Toxicity testing with organisms pre-acclimated to natural levels of metals and metalloids; Deficiency testing; Tolerance testing.
Risk Characterization	Integrating the above steps	

New Findings: MITE-RN

Metals in the Environment Research Network

- A network of collaborating institutions with participants from academia, government, and industry
- Conducts environmental research on metals within inter-disciplinary research domains
- Objective:
  - Advance understanding of risks to the environment posed by metals in the environment

[www.mite-rn.org]

MITE-RN Key Findings - Sources

Measurement of background metal/metalloid concentrations to assess natural versus anthropogenic influences:

- Methods development [tools for RA]
  - Weight of evidence approach
  - Separation of Hg species in atmospheric samples
  - Fingerprinting of smelter stack output
  - Assessing sediment aging methodologies
- Surficial sediment enrichment in remote lakes due to atmospheric deposition <u>and</u> diagenesis, and affected by forest fires, beaver activity
- Sulfate reduction may be sink for metals in lakes [measure]

MITE-RN Key Findings - Processes

Terrestrial, northern forest ecosystems:

- Tree and shrub species dominating plant community biomass control trace metal dynamics [conceptual diagrams, analyses]
- Root cycling, including rhizophere, more important than foliar for soil metals [conceptual diagrams, analyses]
- Lability of metals in soils influenced by source(s) [don’t lump/assume the same]
  - Atmosphere
  - Foliage
  - Roots

MITE-RN Key Findings – Processes (Continued)

Freshwater lakes:

- Dietary exposures can be predominant
  - Seasonal differences [snapshot not enough]
  - Selective feeding [don’t lump]
  - Species differences in metals bioaccumulation [don’t lump]
  - Consider food chains [conceptual diagrams]
  - Water only bioassays can be misleading [assess exposure routes]
- Food chain characteristics influence metal bioaccumulation and effects
  - Components [conceptual diagrams]
  - Length [conceptual diagrams]

MITE-RN Key Findings – Processes (Continued)

Freshwater lakes (Continued):

- Pharmacokinetics differ between water and dietary exposures [adjust BLM]
- Behaviour influences exposure, affecting bioaccumulation and toxicity [determine]
  - Burrowing and types of burrows
  - Irrigation
- Cd concentrations can decline along food chains (biodilution)
- Hg does not always biomagnify (also noted in Impacts)

MITE-RN Key Findings – Processes (Continued)

Freshwater lakes (Continued):

- Computer thermodynamic models revised - allow calculation of metal speciation with reduced sulfur species (RSS) [use revised models – HYDRQAL, WHAM]
- Metal-RSS (reduced sulfur species) complexes dominate metals speciation of many metals in anoxic waters (pore, hypolimnetic); also present in oxic surface waters [measure, using new methodology]

MITE-RN Key Findings – Processes (Continued)

Freshwater lakes (Continued):

- Zn-sulfide complexes relatively stable in oxic waters; may account for significant portion of measured dissolved zinc [measure, assess relative to bioavailability]
- Sediment sulfide very heterogeneous, laterally and vertically [measure/determine – changes due to manipulations may render the tools below inappropriate for ERA]
    - Bulk sediment chemistry/bioassay
    - Pore water chemistry/bioassay

MITE-RN Key Findings – Impacts

Freshwater lakes:

- Chronic toxicity of 10 metals/metalloids can be predicted from body burdens for *Hyalella* azteca [organism-specific CBRs useful screening-level predictors]
- Metals uptake and elimination by fish affected by nutritional status (may not be true for all invertebrates, e.g., *H.* azteca) [consider feeding regimes and growth rates]
- Mechanisms of metal uptake by different fish species appear common, but sensitivities differ [a single BLM inappropriate for ERA, but BLM can reasonably be adjusted for multiple species]

MITE-RN Key Findings – Impacts (Continued)

Freshwater lakes (Continued):

[consider bioenergetics and protection of key prey species]

- Food chains change in metal contaminated waters
  - Dietary Ca protects against Cd uptake
  - Dietary Na reduces Cu uptake
- Simplified food webs reduce efficiency of energy transfer
  - Reduced growth
  - Reduced reproduction

MITE-RN Key Findings – Impacts (Continued)

Freshwater lakes (Continued):

- Many implications to acute and chronic BLM for both fish and invertebrates [screening-level predictions]:
  - Dietary uptake
  - Water chemistry
  - Tissue burdens
  - Species differences
  - Dietary Na reduces Cu uptake

MITE-RN Key Findings – Impacts (Continued)

Freshwater lakes (Continued):

- Without knowledge of trophic status, tissue-specific bioaccumulation in fish not useful for ERA (confounding effects – food ration, growth rate) [tool utility]
- Metal additivity may be worst case; less than additivity also possible [assessment of metal/metalloid mixtures]
- No evidence for immunotoxicity of meHg to waterfowl
- Classic metallothionein spillover model may not apply to chronic exposures [utility of this biomarker]

SUMMARY

RA of Metals and Metalloids:

- Clear differences from "classical" organics
- Epistemic uncertainties (due to lack of knowledge/data) – MITE-RN and other research efforts are substantially reducing uncertainties
- Aleatory uncertainties (due to events without data, e.g., future human actions) – probabilities can only be defined through expert judgment / weight of evidence