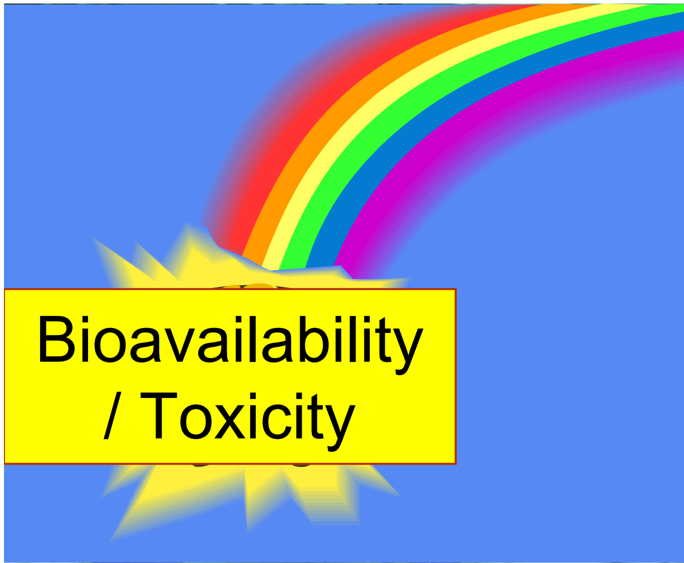
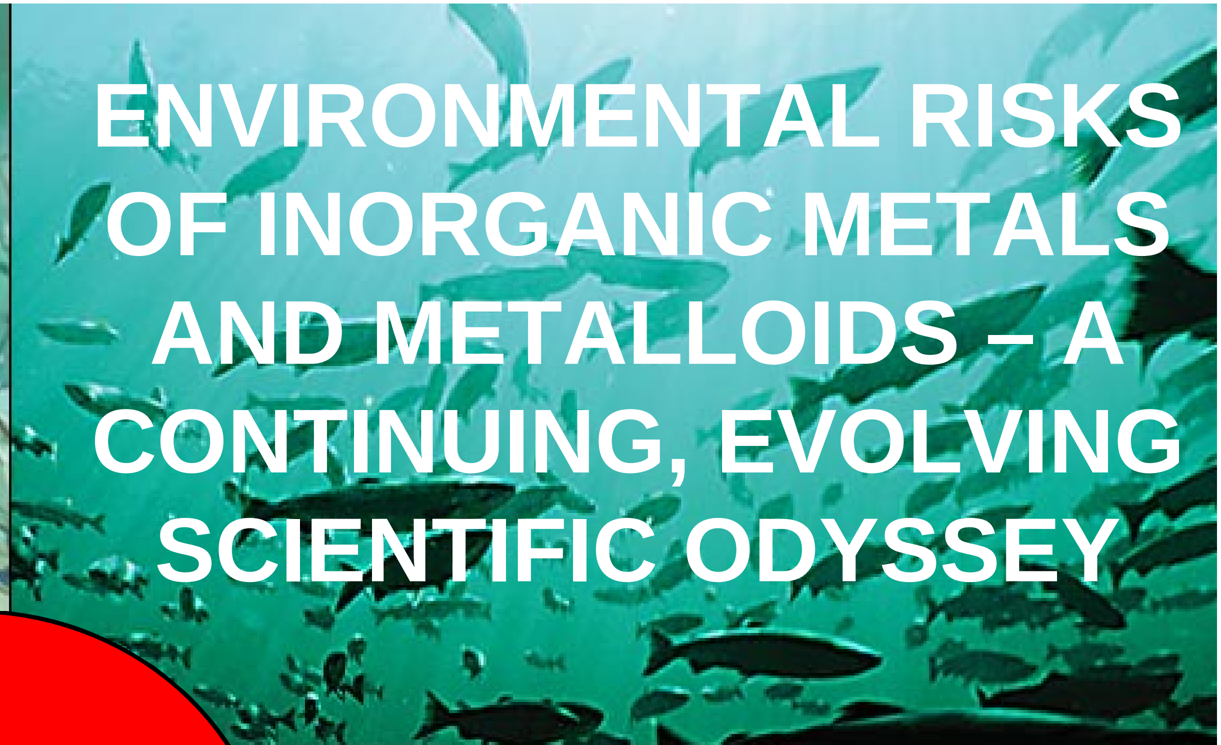
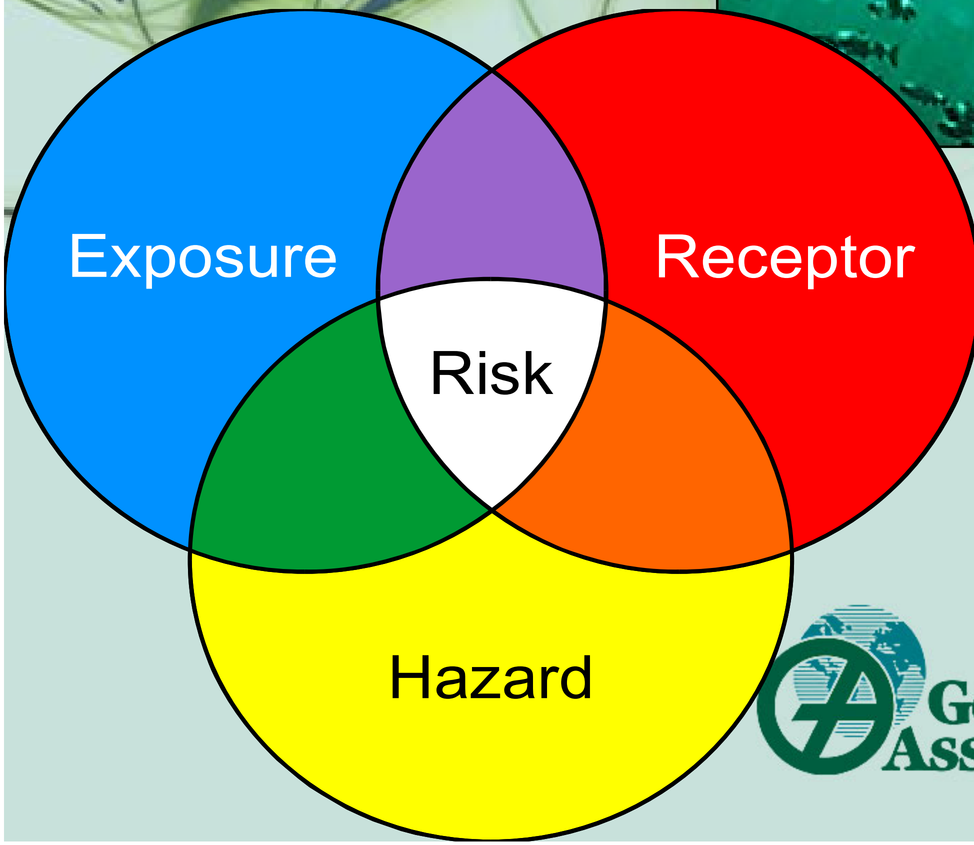




ENVIRONMENTAL RISKS OF INORGANIC METALS AND METALLOIDS – A CONTINUING, EVOLVING SCIENTIFIC ODYSSEY



Peter M. Chapman
Golder Associates Ltd.
North Vancouver, BC, Canada

October 24, 2007
Sudbury, Ontario

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METALS / METALLOIDS ARE UNIQUE

Henceforth, the term 'metals' is used to refer to both metals and metalloids

DO NOT USE INCORRECT TERM 'HEAVY METALS'

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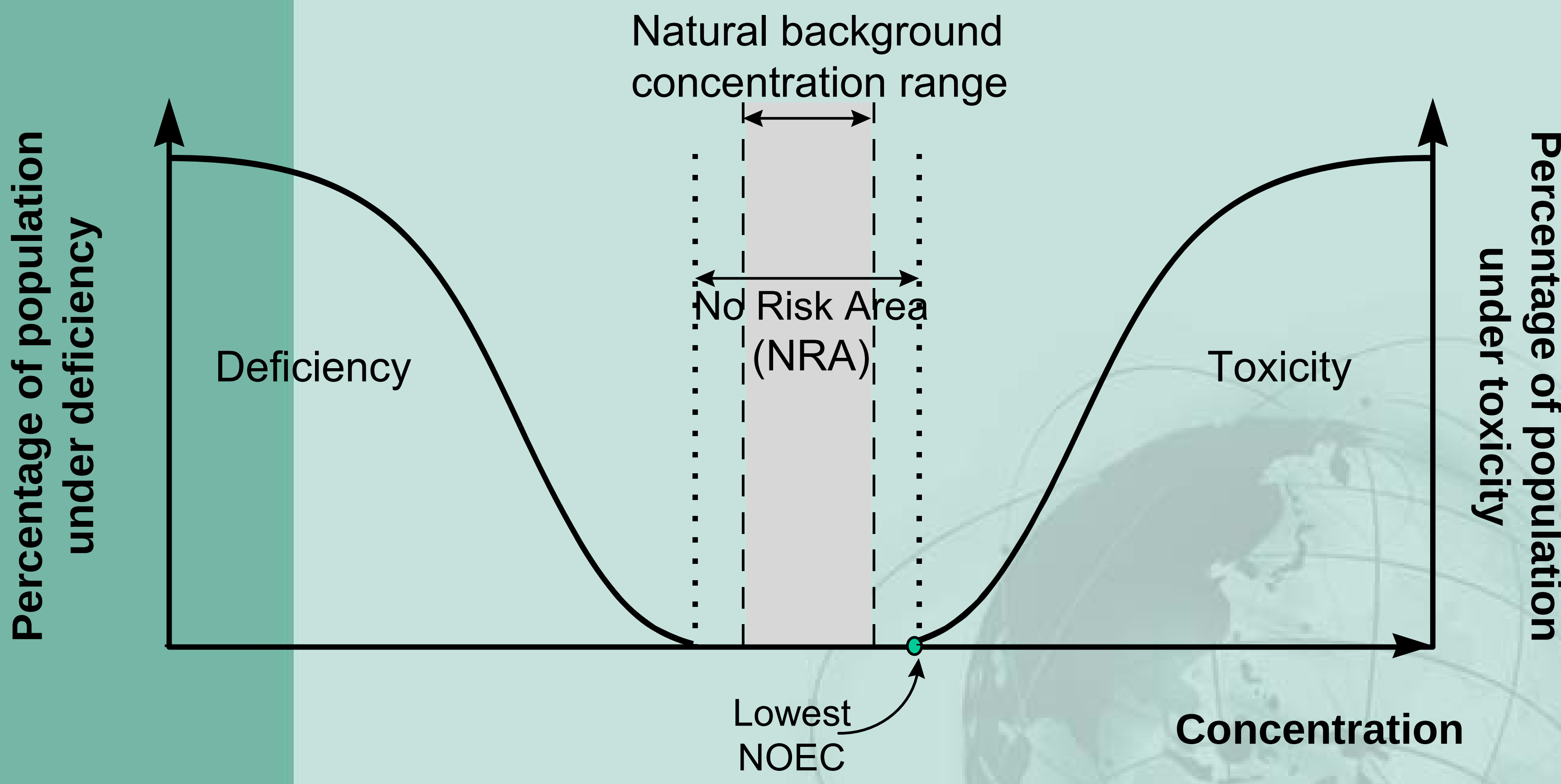
- Neither created nor destroyed; transformed from one chemical species to another
- Variable solubility (solubility based on soluble salts → overestimates of bioavailability / toxicity)
- Both essential (Cu, Cr, Zn, Se) and non-essential elements (Pb, As, Hg)
- Organisms regulate metals, especially essential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

Essential Metal Concentration-Response

Example issue: Micronutrients in fertilizer



Essential metals can be toxic due to both too little (deficiency) and too much <u>bioavailable</u> metal (toxicity)

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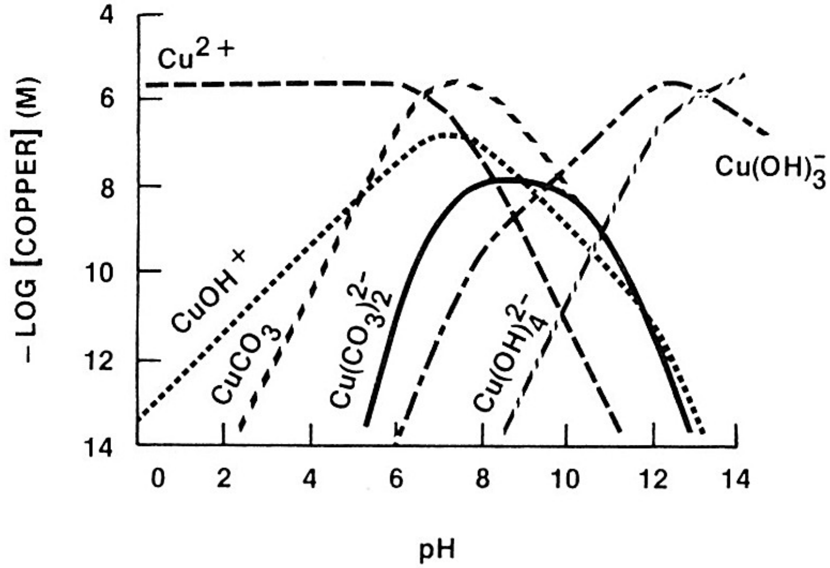

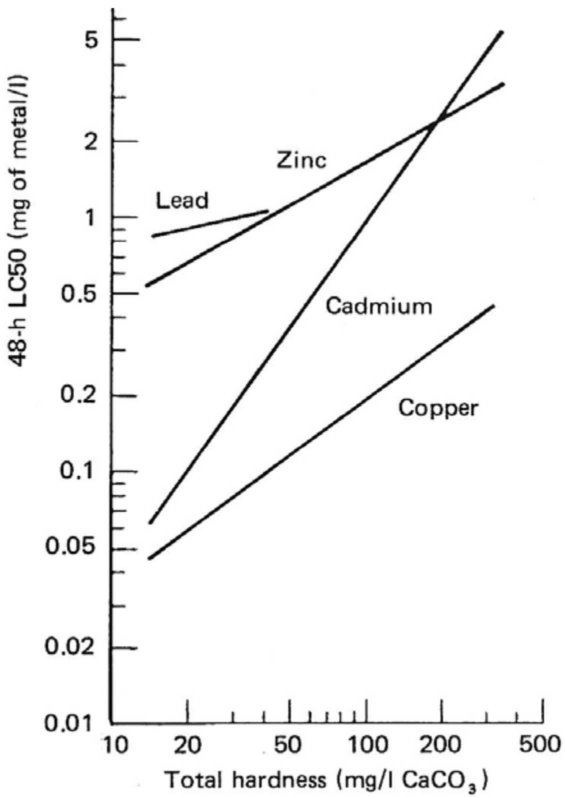

We Know

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*)**

HISTORIC METALS BIOAVAILABILITY TOOLS

Tool	Date	Description	Comments
Total recoverable metals	Pre-1985	Dissolved metals + easily dissolved solid metals; hard mineral acid digestion	Highly conservative for metals in effluent that may become environmentally active
Acid soluble metals	1985	Less aggressive digestion procedure	Not much improvement
Dissolved metals	1993	<0.45 micron, pH 6.5-9.0, TOC/TSS < 5 mg/L	Improved approximation, but not ideal
BLM	2003	Model based on water chemistry	Continuing research focus

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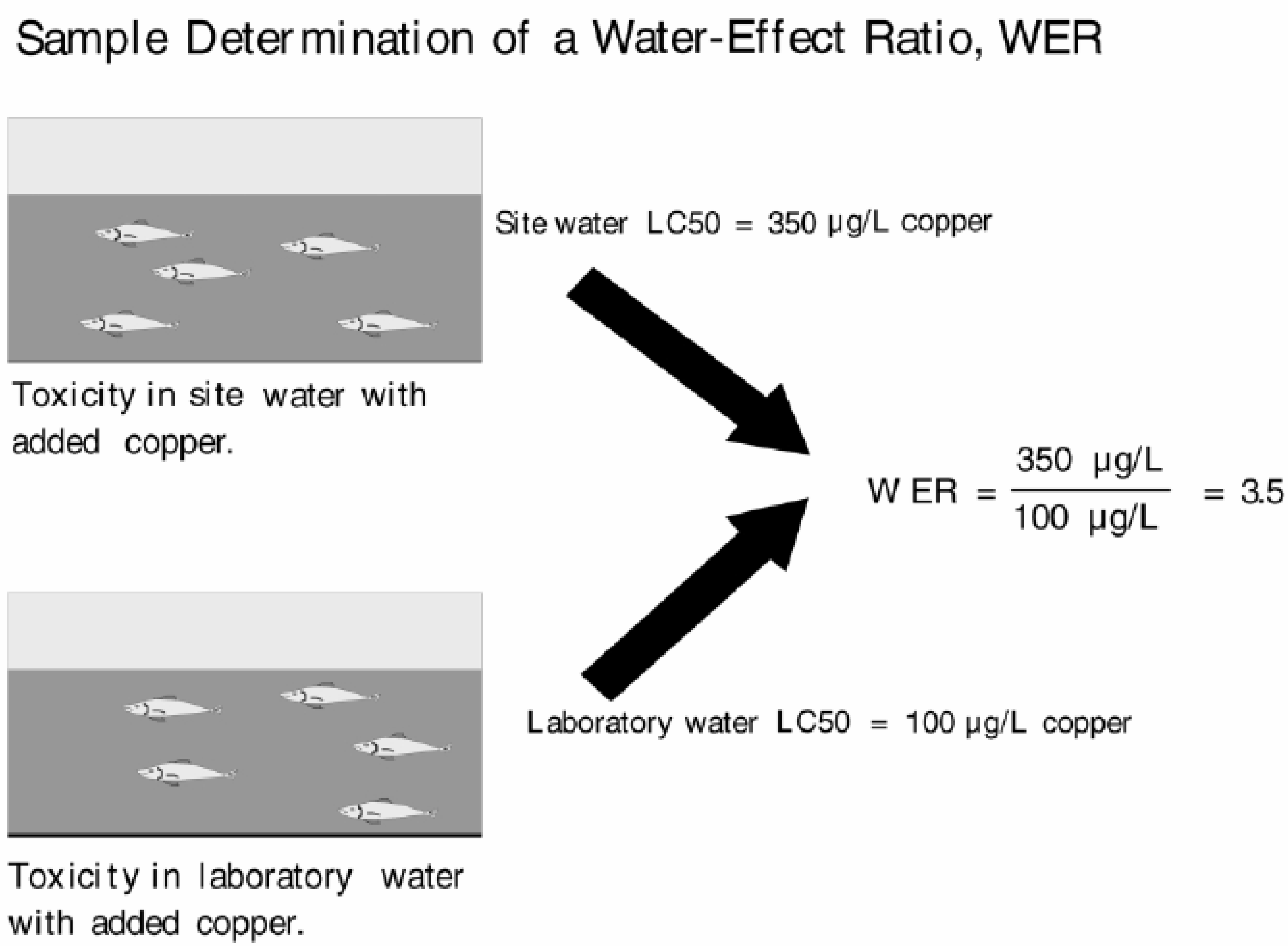
Water Effect Ratio (WER)

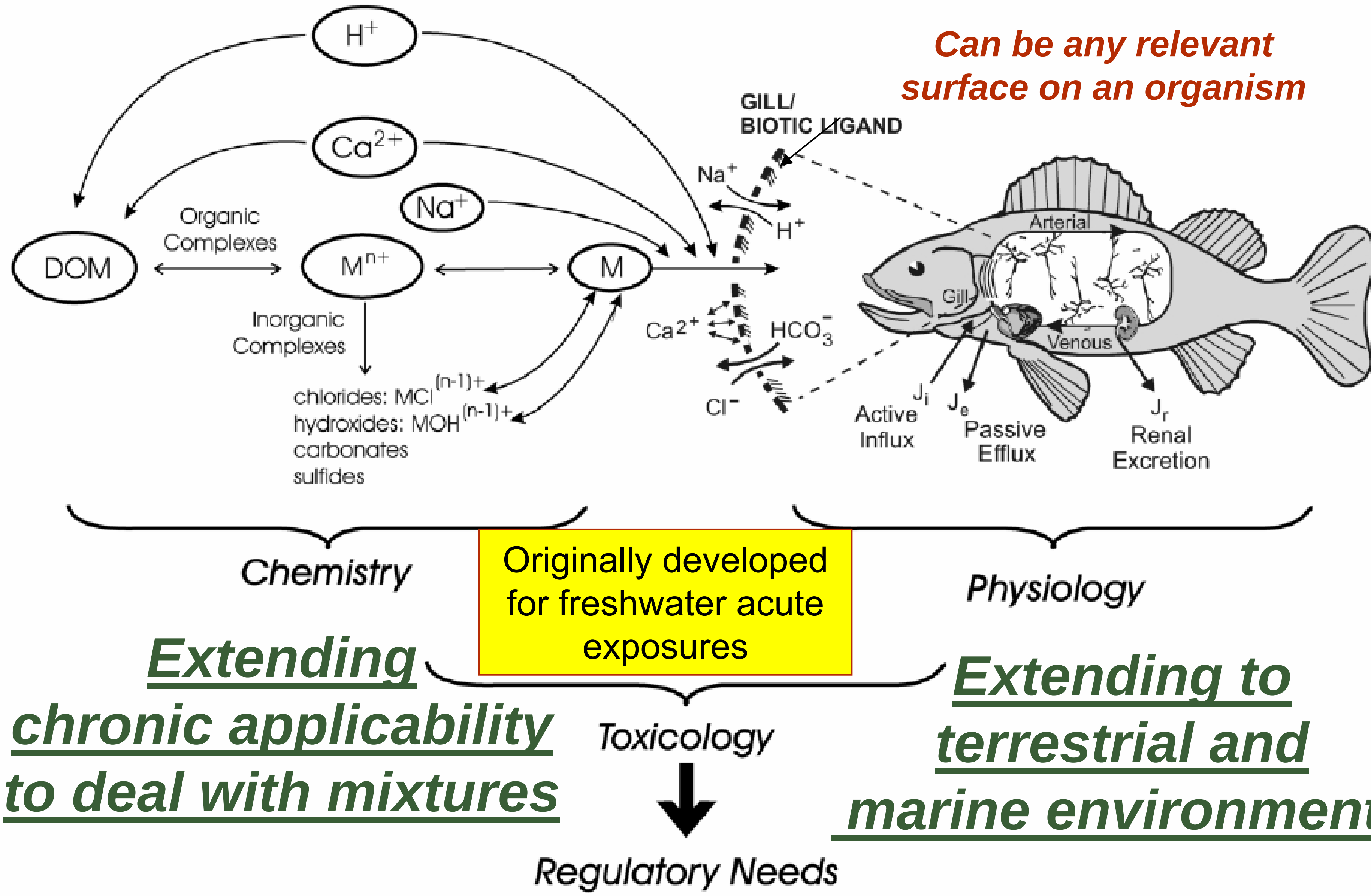
Stop-gap (time consuming, expensive) option for normalizing dissolved metals measures after hardness adjustment, prior to the BLM



BIOTIC LIGAND MODEL

Accepted in US, EU, Canada, Australia,…

Can be any relevant surface on an organism



Originally developed for freshwater acute exposures

Extending chronic applicability to deal with mixtures

Extending to terrestrial and marine environments

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

Blanchard J, Grosell M. 2006. Copper toxicity across salinities from freshwater to seawater in the euryhaline fish Fundulus heteroclitus: Is copper an ionoregulatory toxicant at high salinities? Aquat Toxicol 80: 131-139.

"…physiology rather than chemistry explains much of the variation in Cu toxicity seen across salinities".

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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***

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Environmental Quality Guidelines (EQGs)

Use on the basis of common sense, <u>not inflexibly</u>

EQGs include sediment and water quality guidelines (SQGs and WQGs)

Limitations:

- Do not consider synergism between contaminants, biomagnification, or secondary poisoning
- Only based on toxicity to biological receptors
- Do not consider human health
- Not to be used alone for remediation decisions

Uses:

- To identify and describe contamination
- To identify and prioritize contaminants of potential concern (COPCs)
- **As *<u>part</u>* of an ERA aproach to decision-making**

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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 <u>or, more importantly</u>, in adverse biological impacts to populations)?
- And how does this occur (what are the sources and mechanisms)?

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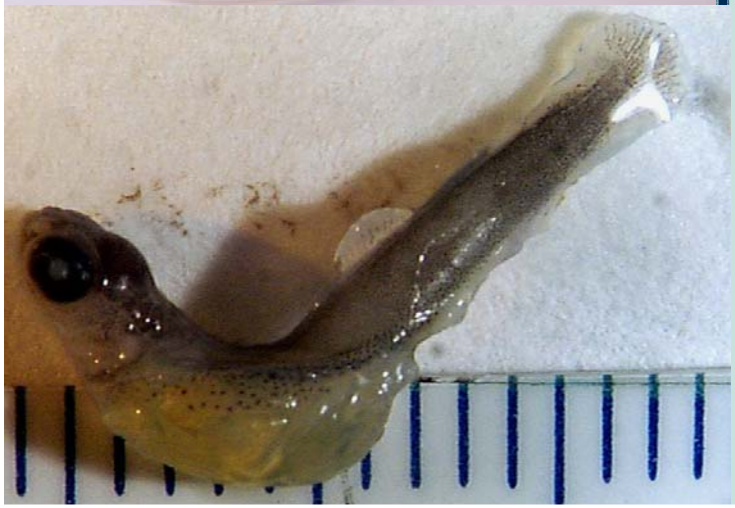
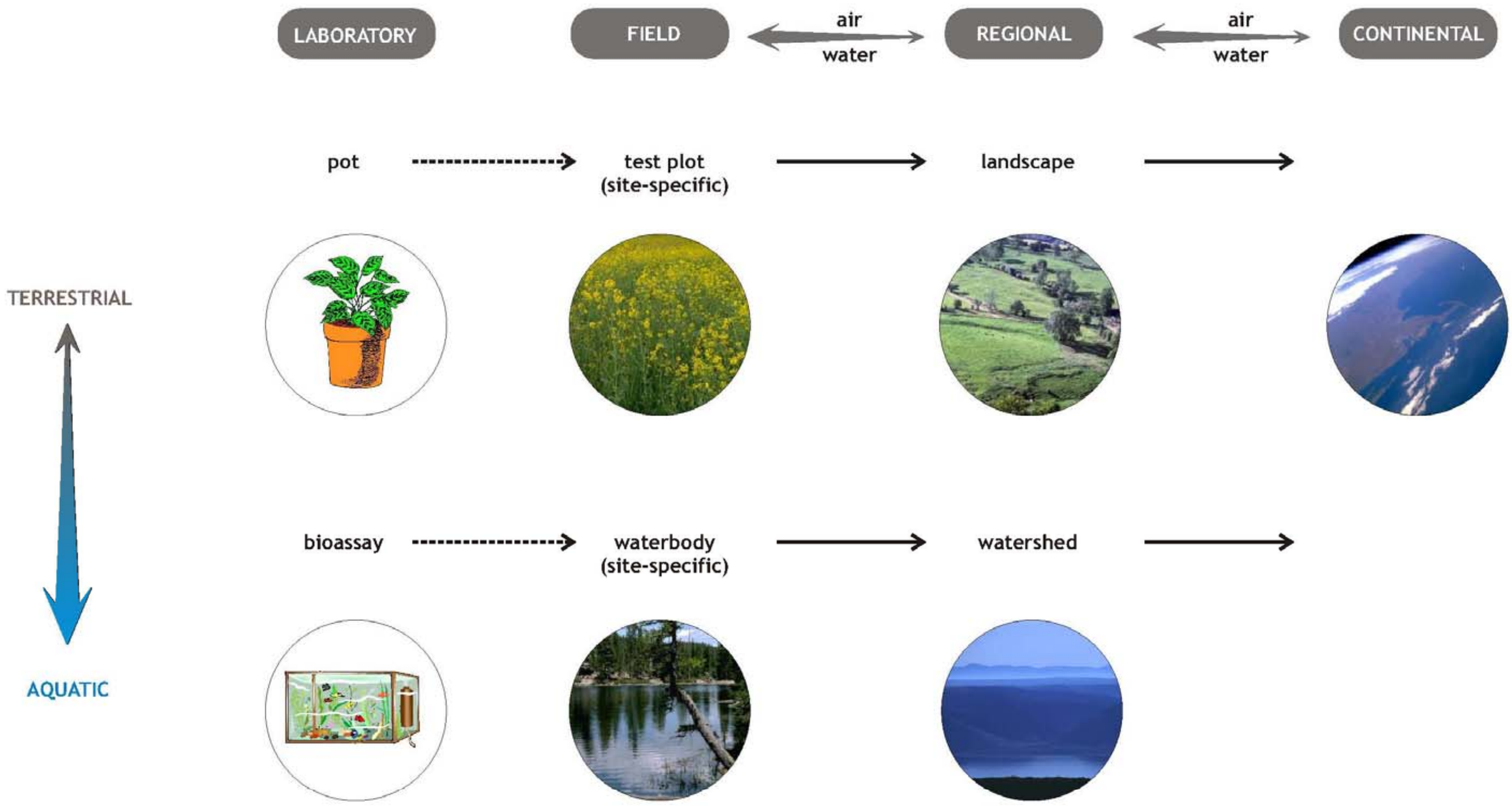


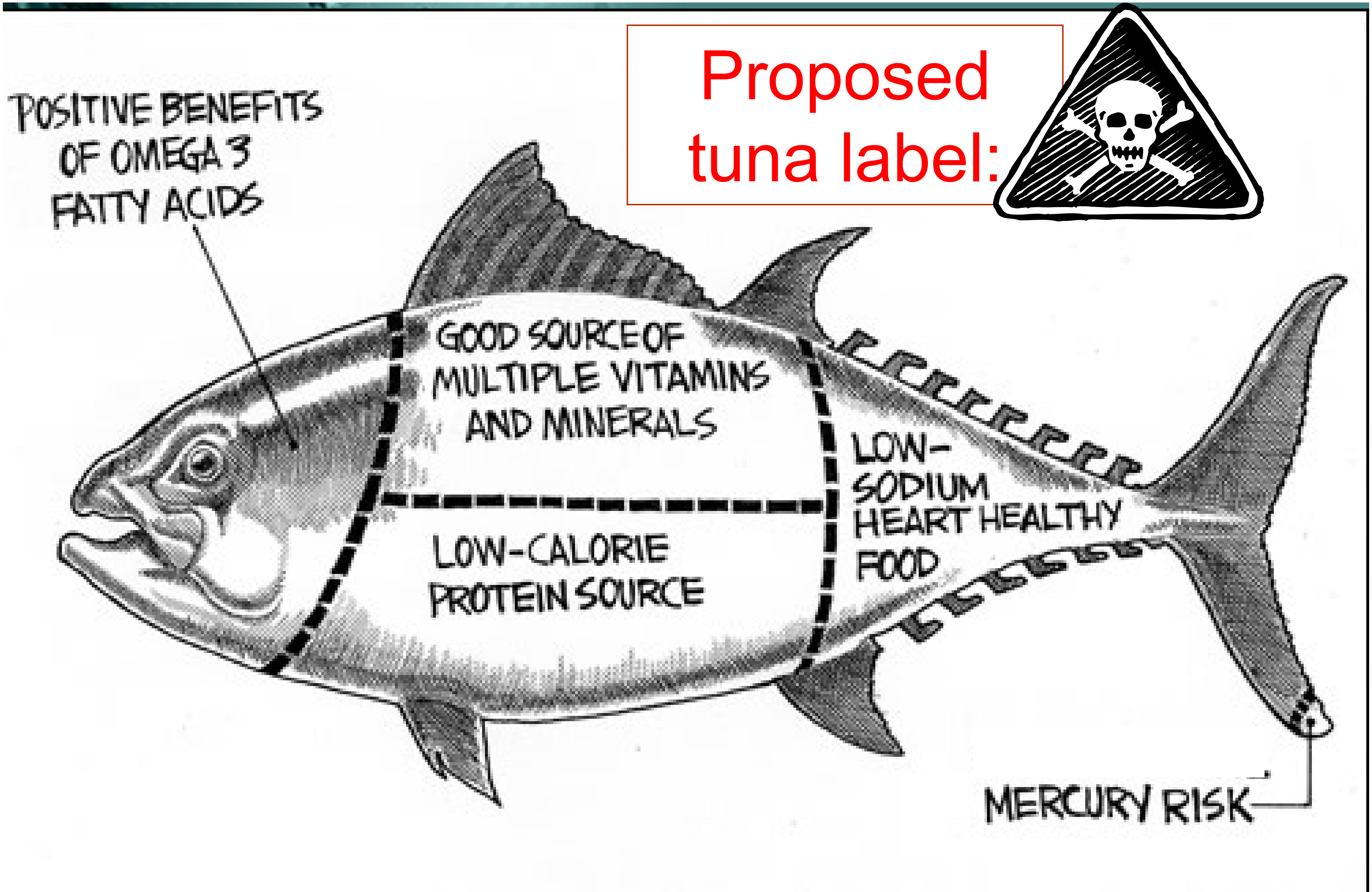
Effects vs Impacts

- **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)

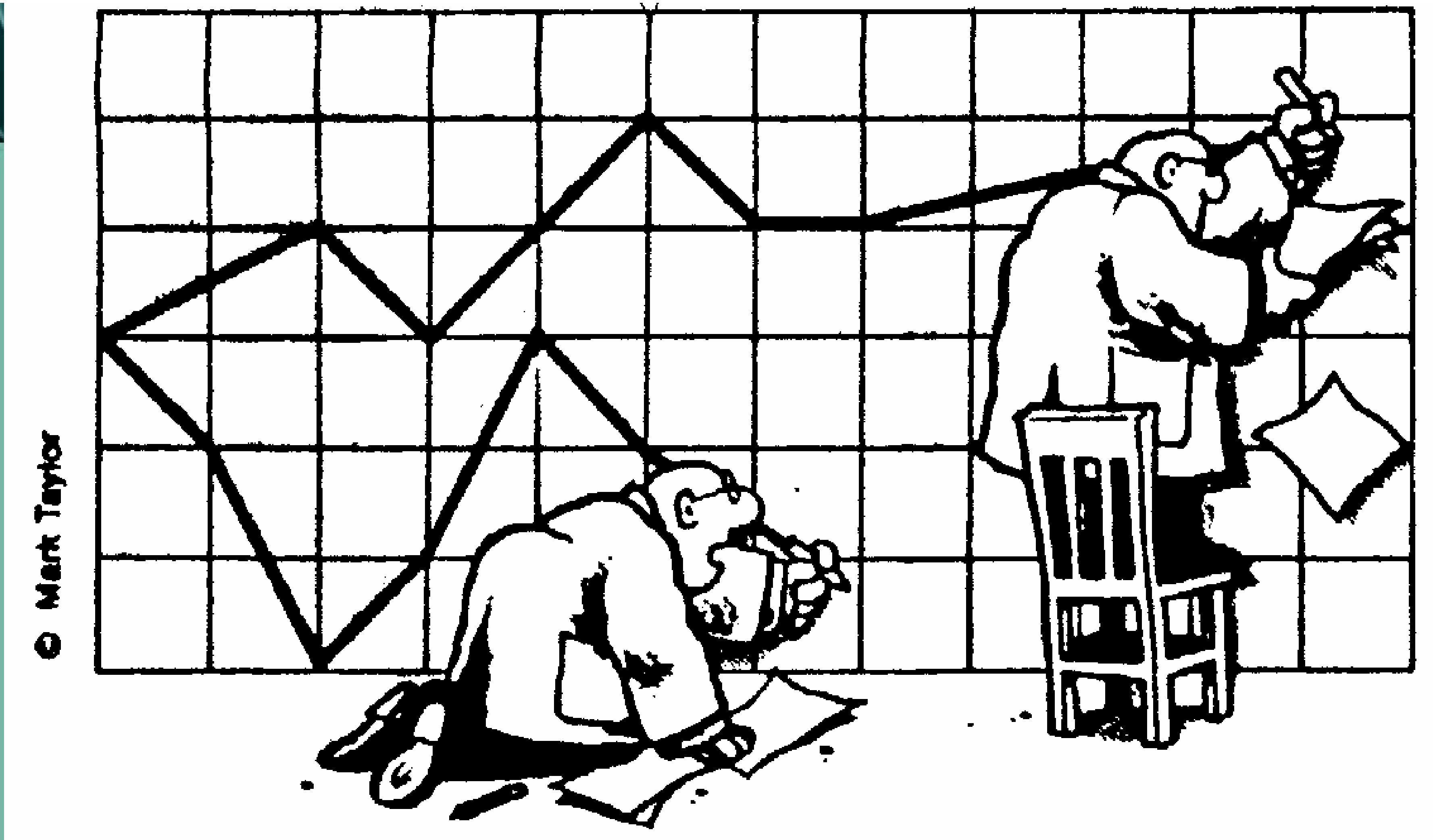
Scale Matters



Proposed tuna label:



Risk : risk comparisons are essential



Hey, I thought we were working with the same data!

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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)

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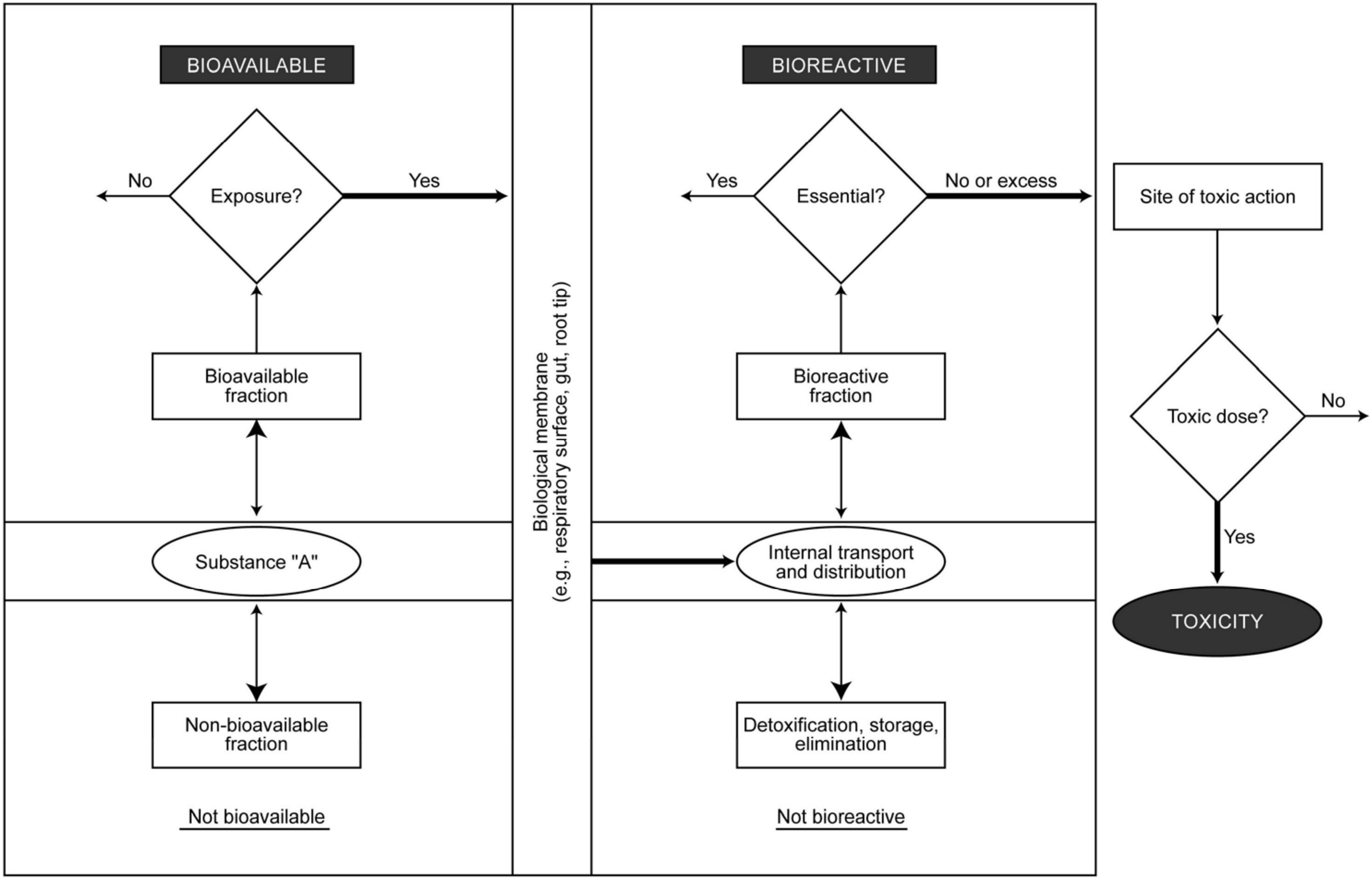
Importance of "Bio-"



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***

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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**)

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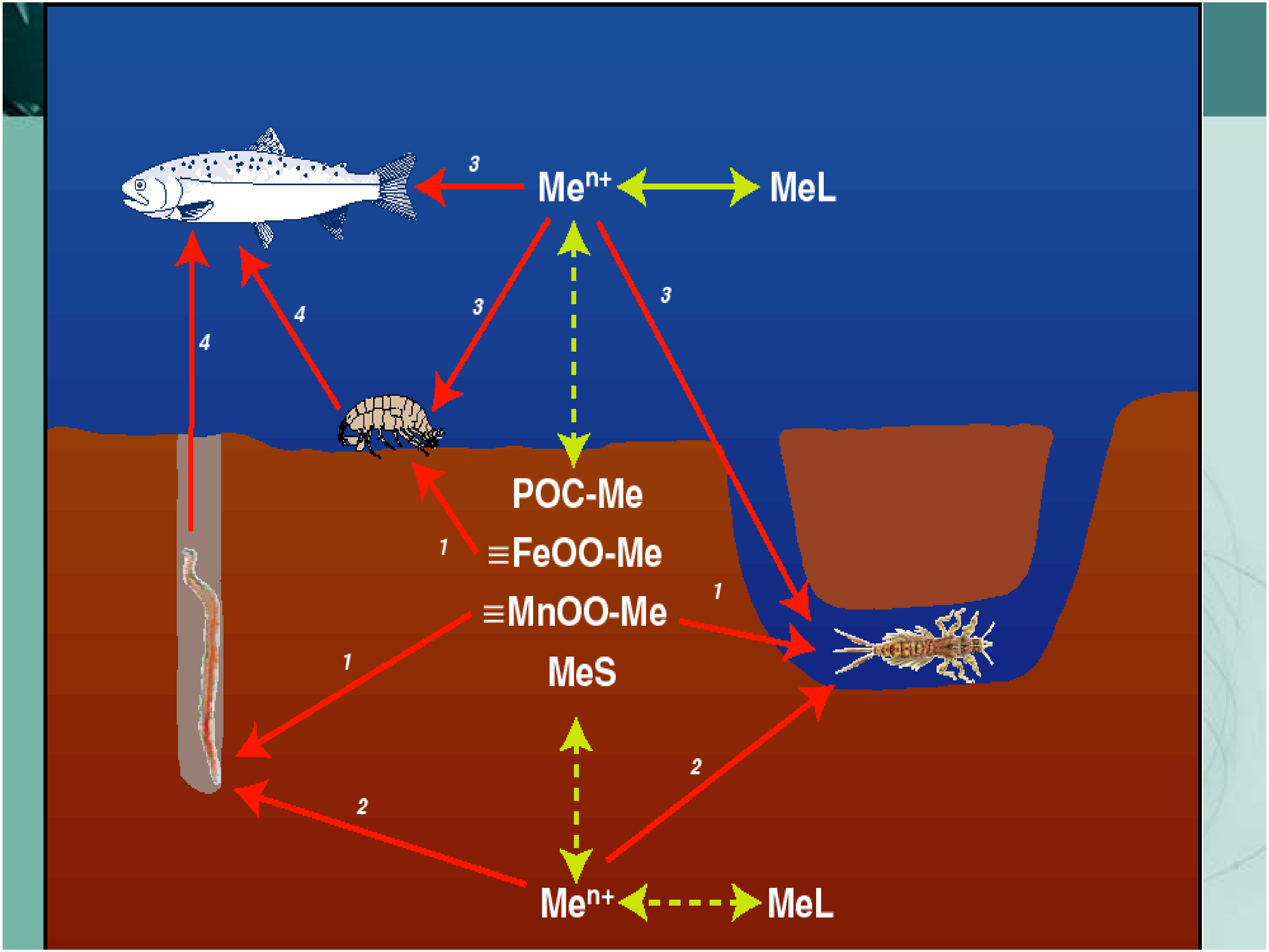
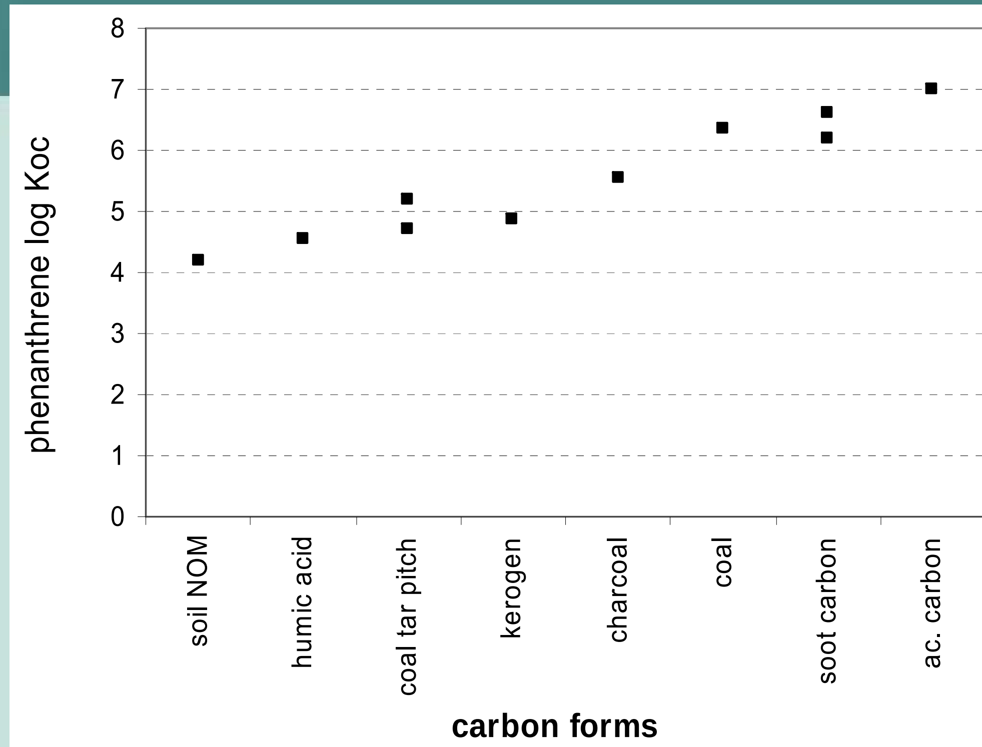
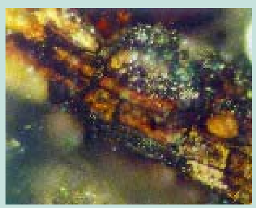


Me^n+
MeL
3
3
3
4
4
POC-Me
≡FeOO-Me
≡MnOO-Me
MeS
1
1
1
2
2
Me^n+
MeL

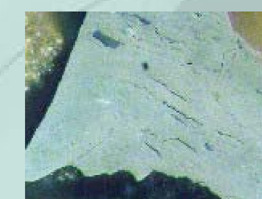
"Bio-" and Organic Substances

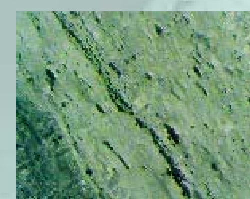
- **Sorption of organic chemicals via "dual-mode sorption" – absorption in amorphous organic matter and to carbonaceous materials (e.g., black carbon)**
- **Solid-phase concentrations bear little or no relation to actual concentrations in organisms – *reconsider existing criteria***



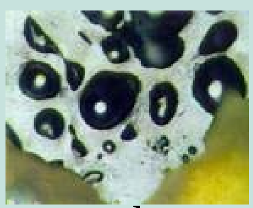

wood

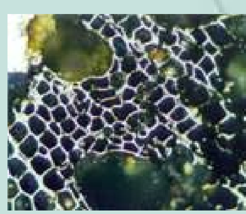

lignite


bituminous coal

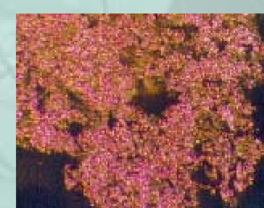

anthracite coal

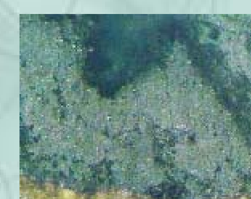

oxidized coal


coke


charcoal


cenosphere


soot carbon


coal tar pitch

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Biological Tolerance

Not generally considered in ERA

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

Mechanism	Metabolic Cost?
Acclimation	Yes
Non-genetic adaptation	Yes
Genetic adaptation	Possibly not
Metabolism	Possibly not

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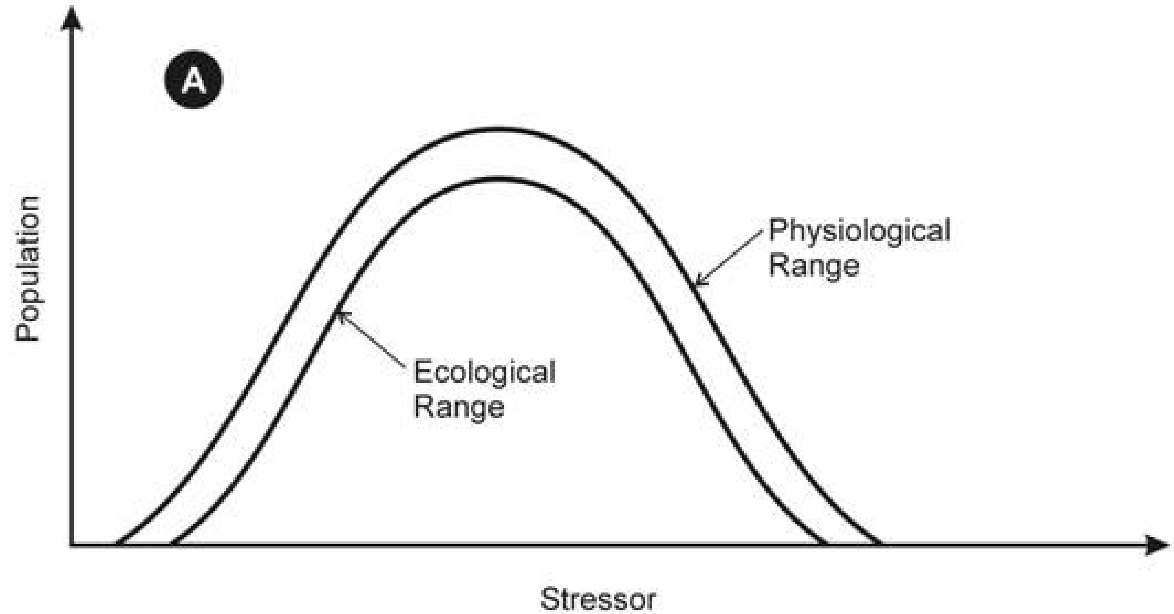
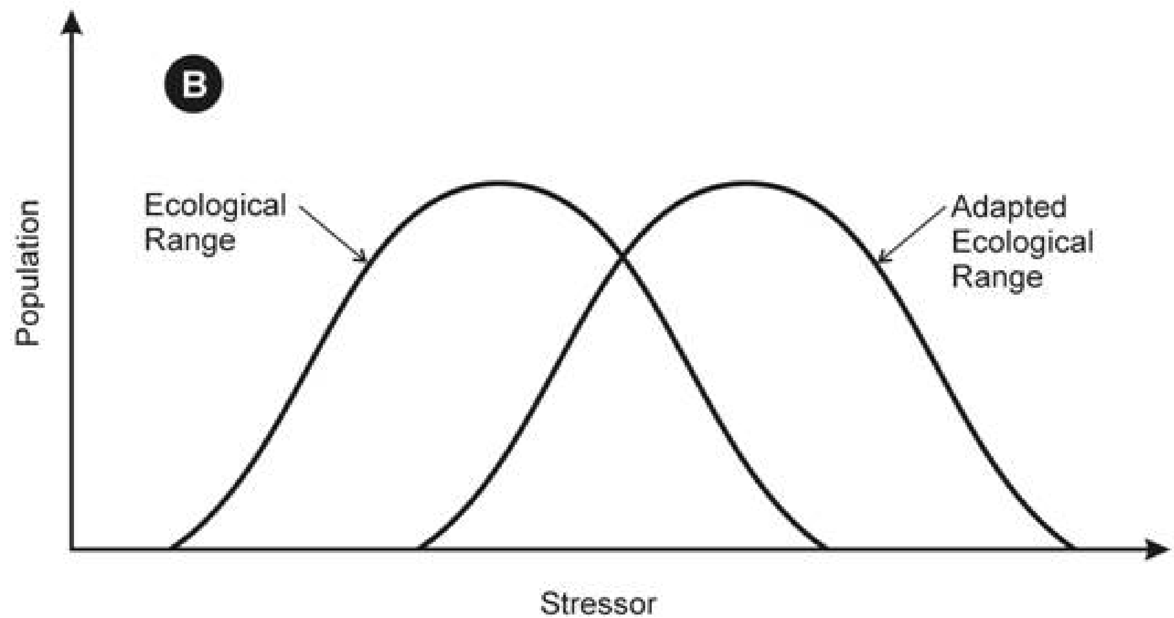
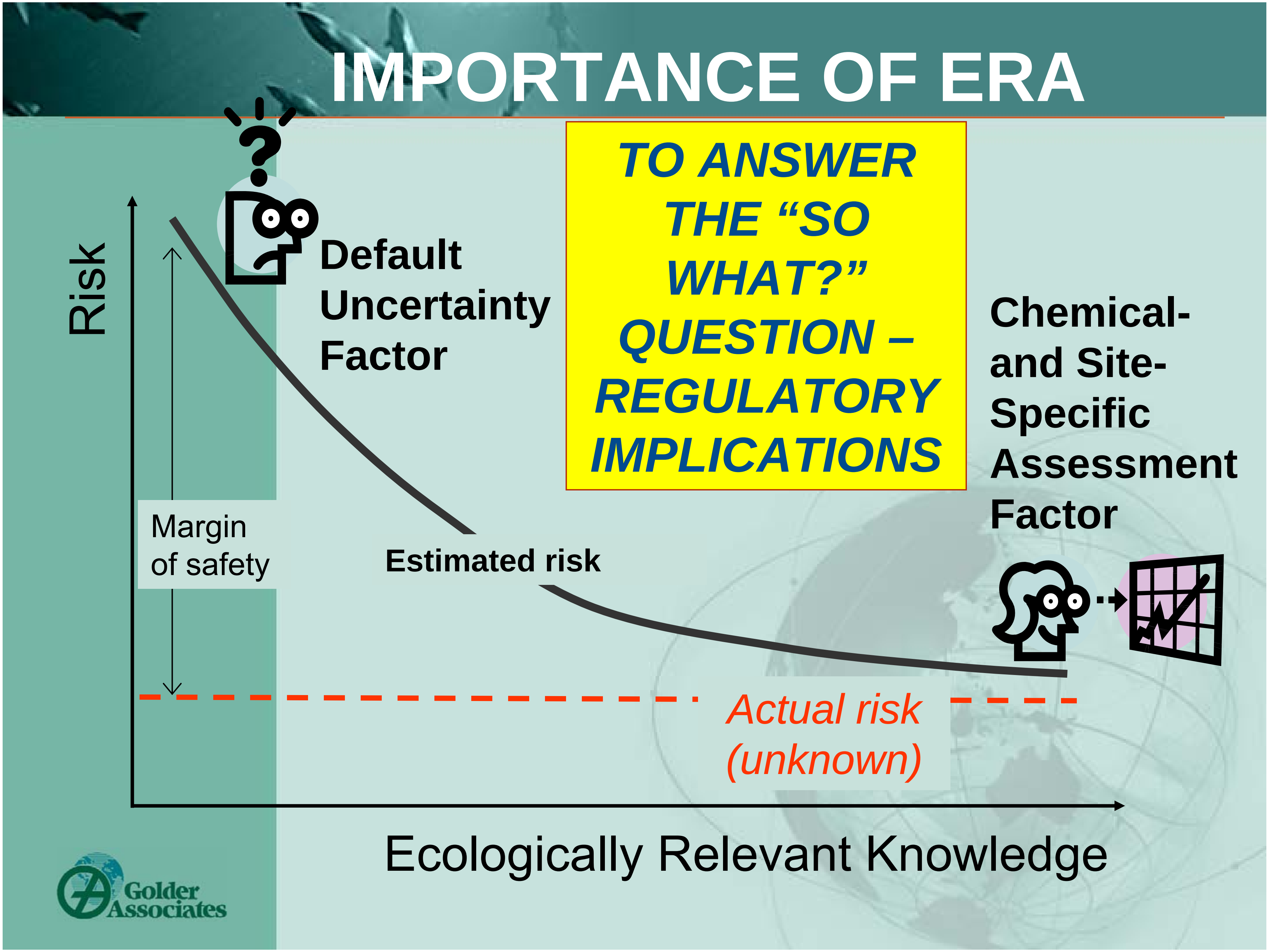
Acclimation **(A) is physiological and an extension of an organism's ecological range**

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
Chemical- and Site-Specific Assessment Factor
Actual risk (unknown)
Ecologically Relevant Knowledge
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The Key Question(s)

Chapman PM. 2008. Environmental risks of inorganic metals and metalloids: a continuing, evolving scientific odyssey. Human Ecol Risk Assess (in press)

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?

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Four Key ERA Metals Questions - #1

Question	Chemical Tools	Biological Tools	Comments
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

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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)

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Four Key ERA Metals Questions - #2

Question	Chemical Tools	Biological Tools	Comments
Are the metals biologically active?	• Metal fractionation within organisms	• Determination of food chains for predator-prey predictions	• Metals occur in two pools: biologically active and available; detoxified and unavailable • Metals bioreactivity can vary by exposure route (water, diet)

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Four Key ERA Metals Questions - #3

Question	Chemical Tools	Biological Tools	Comments
Are the metals likely to result in adverse effects to individuals either alone or in combination with other stressors?	• Predictions (BLM, biokinetics) • Predictions (Contaminant Body Residues [CBRs]) • Predictions (environmental quality values)	• Single species toxicity tests involving appropriate metals pre-exposure, and both aqueous and dietary exposures • Field data: organism responses to actual contamination	• Predictions may also be possible using regression-based modeling involving toxicity data and DOC (dissolved organic carbon) measurements • Use of CBRs requires dose-response relationships between bioreactive metals and organism responses • Contaminant interactions cannot at present be reliably predicted, nor can interactions with non-chemical stressors • Pulsed (intermittent) exposures need to be considered as well as continuous exposures

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Four Key ERA Metals Questions - #4

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

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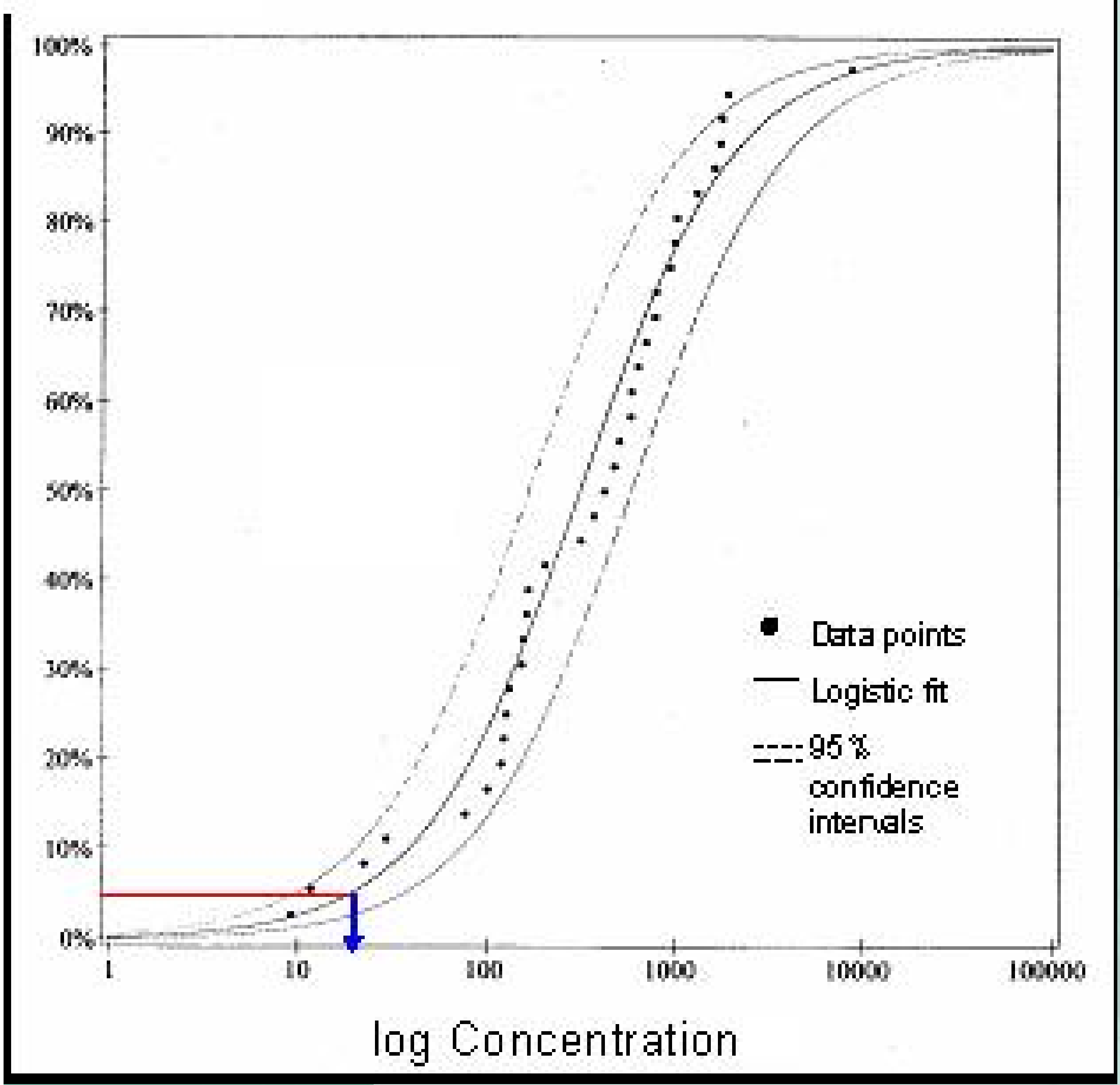
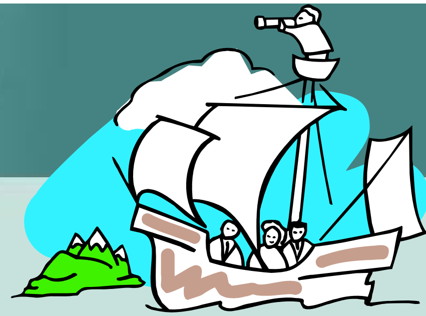
Species Sensitivity Distributions



- 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

Life-Cycle Assessment (LCA)

Biodynamics As a Unifying Concept

Non-Population Responses: Behavior

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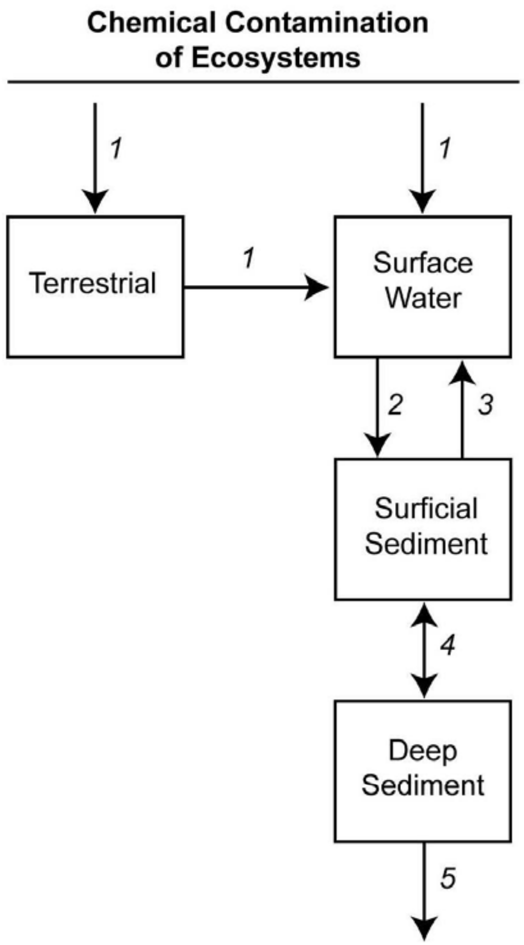
Pulsed Exposures

Metal-Containing Nanoparticles

Indirect Effects

Ecotoxico-genomics

Inter-relationships between Ecosystems and Chemicals are Complex



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

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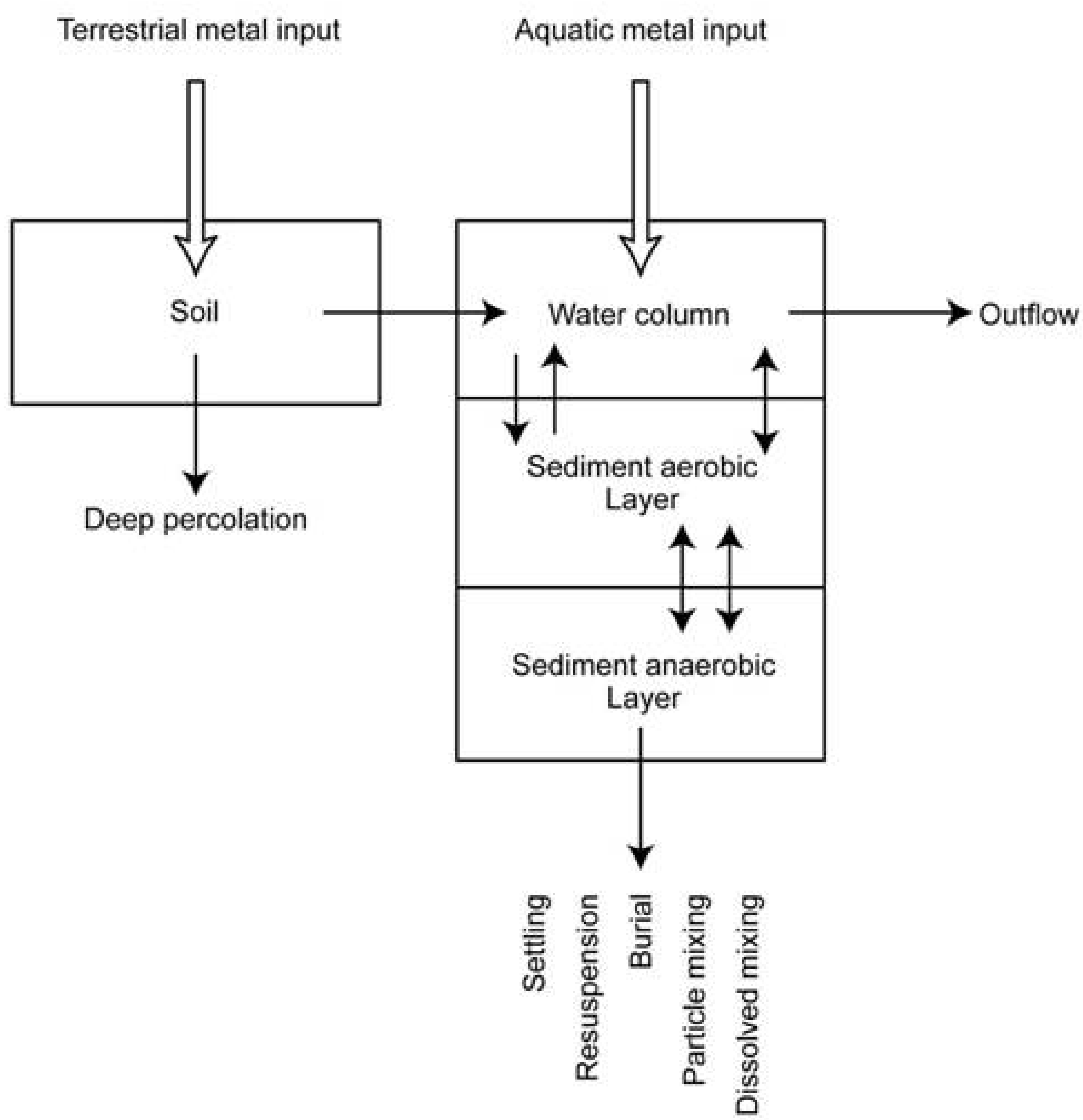
ROPC = Receptor of Potential Concern

Unit World Model

Adams WJ, Chapman PM (eds). 2006. Assessing the Hazard of Metals and Inorganic Metal Substances in Aquatic and Terrestrial Systems. SETAC Press, Pensacola, FL, USA



Critical Loads

- 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

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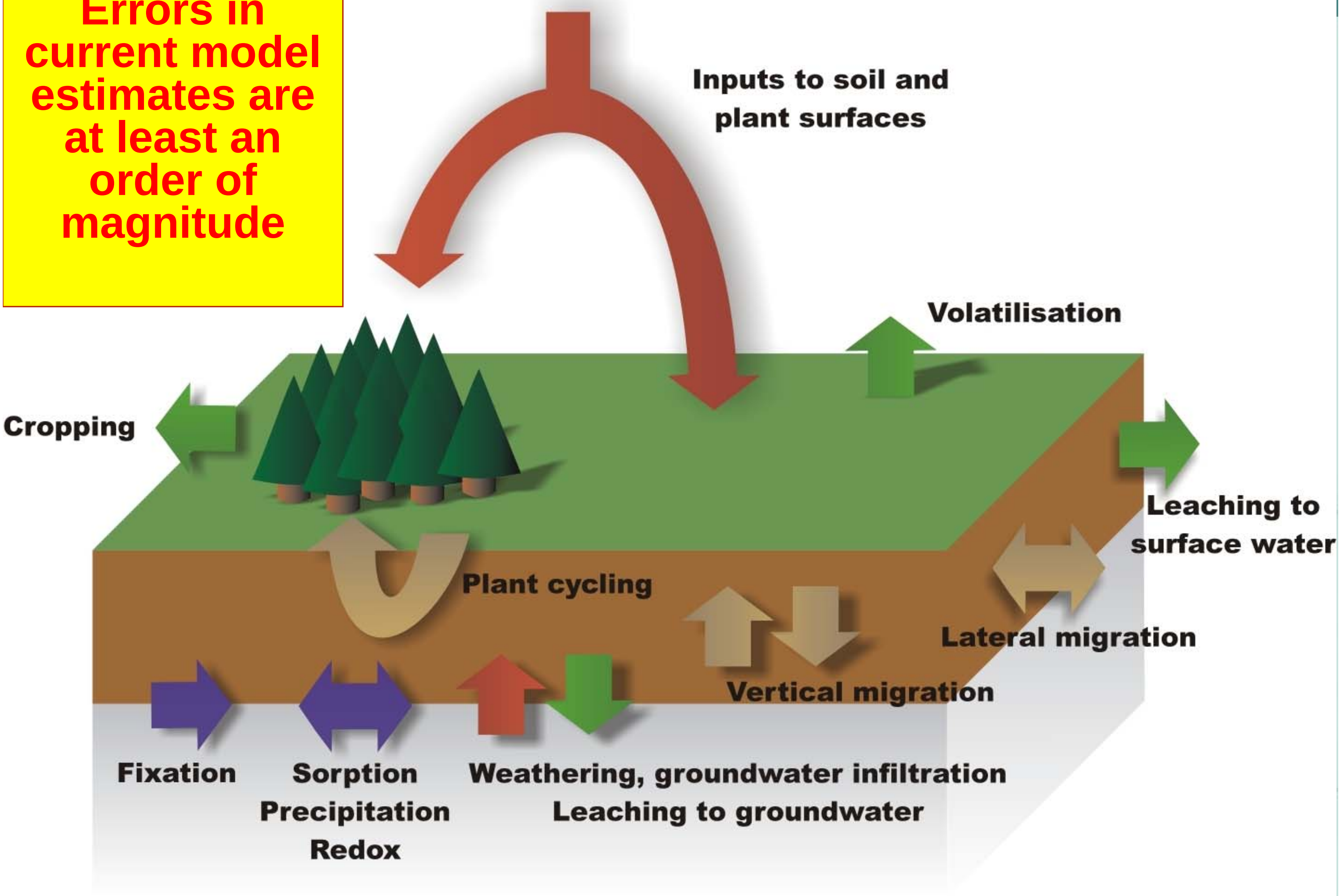
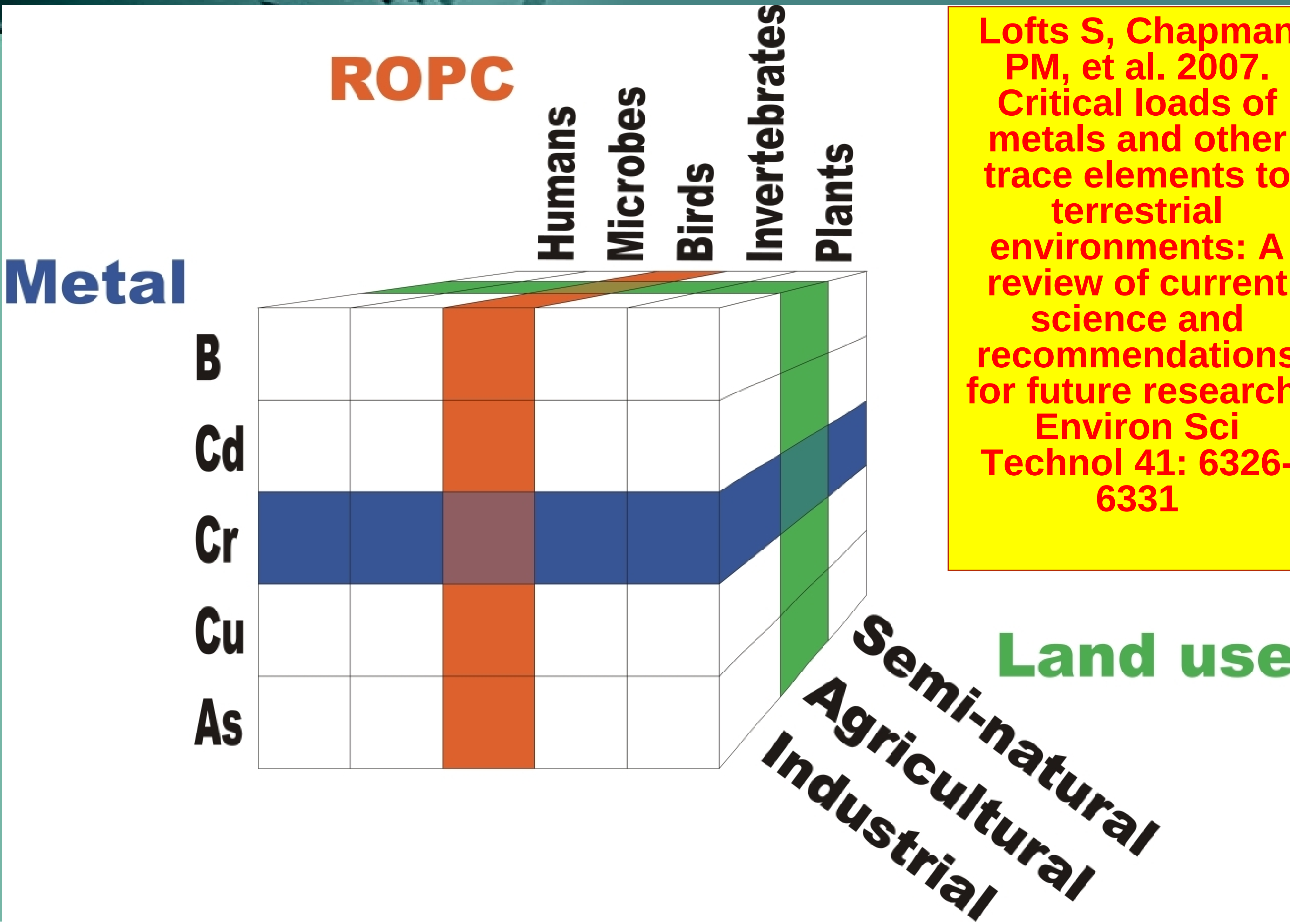
Major Terrestrial Metals Transformation and Transport Pathways

Errors in current model estimates are at least an order of magnitude

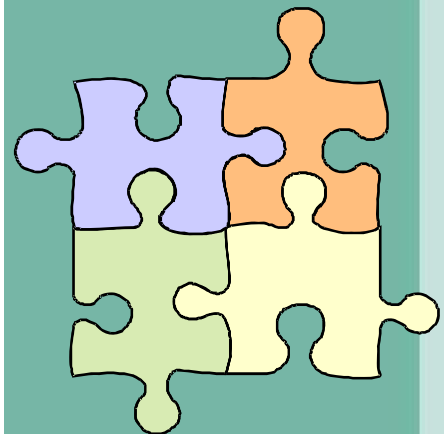


Assessing Potential Metal Effects



Lofts S, Chapman PM, et al. 2007. Critical loads of metals and other trace elements to terrestrial environments: A review of current science and recommendations for future research. Environ Sci Technol 41: 6326-6331

Overall Needs



Need to Address Reality ***and*** Perception

- Answer the **"So What?"** question where it really matters:

1. **Are there present or potential effects <u>and</u> impacts?**
2. **Is there present or potential pollution, <u>not just</u> 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?**

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"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)

Interactions (e.g., metals and climate change) must also be considered

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

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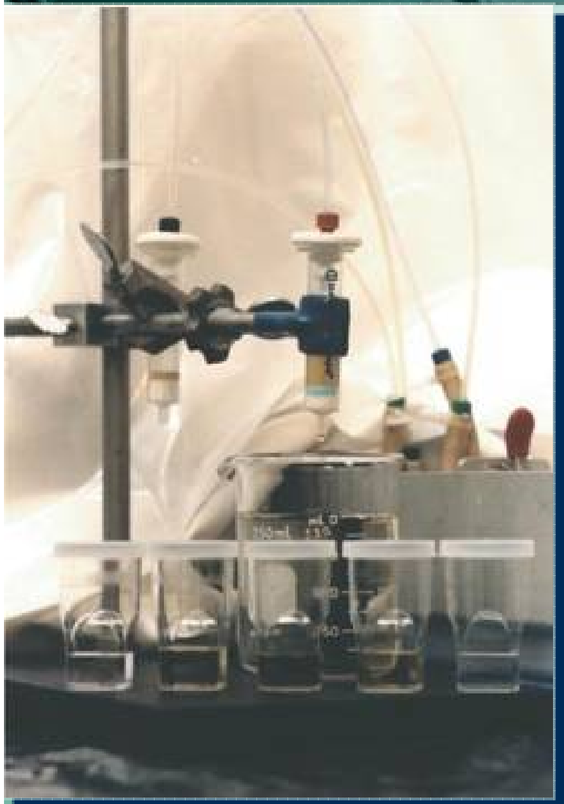

Thank you for Listening!

Questions / Discussion?

pmchapman@golder.com

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Additional Information re Metals RA

Fairbrother A, Wenstel R, Sappington K, Wood W. 2007. Framework for metals risk assessment. Ecotox Environ Saf 68: 145-227

USEPA. 2007. Framework for metals risk assessment. EPA 120/R-07/001 www.epa.gov/osa