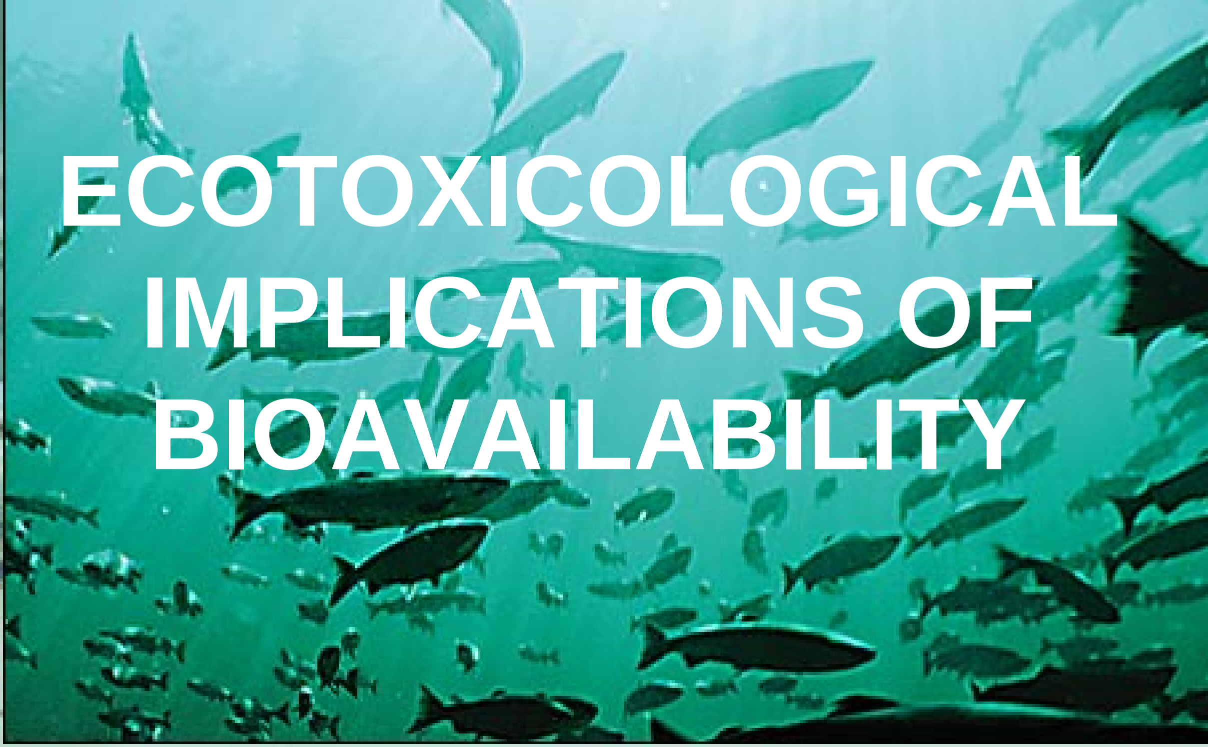

ECOTOXICOLOGICAL IMPLICATIONS OF BIOAVAILABILITY

Peter M. Chapman

Golder Associates Ltd.

North Vancouver, BC, Canada

November 9, 2005, Newark, NY

Two Considerations: First Consideration

BIOAVAILABILITY: WHAT WE WANT TO PROTECT

Human Toxicology:

- Protect 100% of one species

Ecological Toxicology (Ecotoxicology):

- Protect x% of many species
- Protect x% of individuals of each species
- Protect 100% of endangered species
- Protect populations / communities, not individuals

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Second Consideration:

Lewis Carroll: Alice’s Adventures in Wonderland

Key Terms

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

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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What is “Bioavailability”?

- A substance is bioavailable if it can be adsorbed or absorbed by an organism with the potential for distribution, metabolism, elimination and bioaccumulation
- Bioavailability simply means that a substance can be taken up by an organism; there are no implications regarding what may or may not occur once the substance enters biological tissues
- **Bioavailability is a prerequisite for toxicity**
- The next question is whether or not a bioavailable substance is also bioreactive

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What is “Bioreactivity”?

- A substance that is bioavailable to an organism is not necessarily bioreactive once it is within the organism
- Bioreactivity refers effectively to bioavailability within an organism
- Substances can be sequestered and rendered inert within organisms, which means they are not bioreactive
- Bioreactive substances are or can become active within an organism; they are not inert
- **Bioreactivity is a prerequisite for toxicity**

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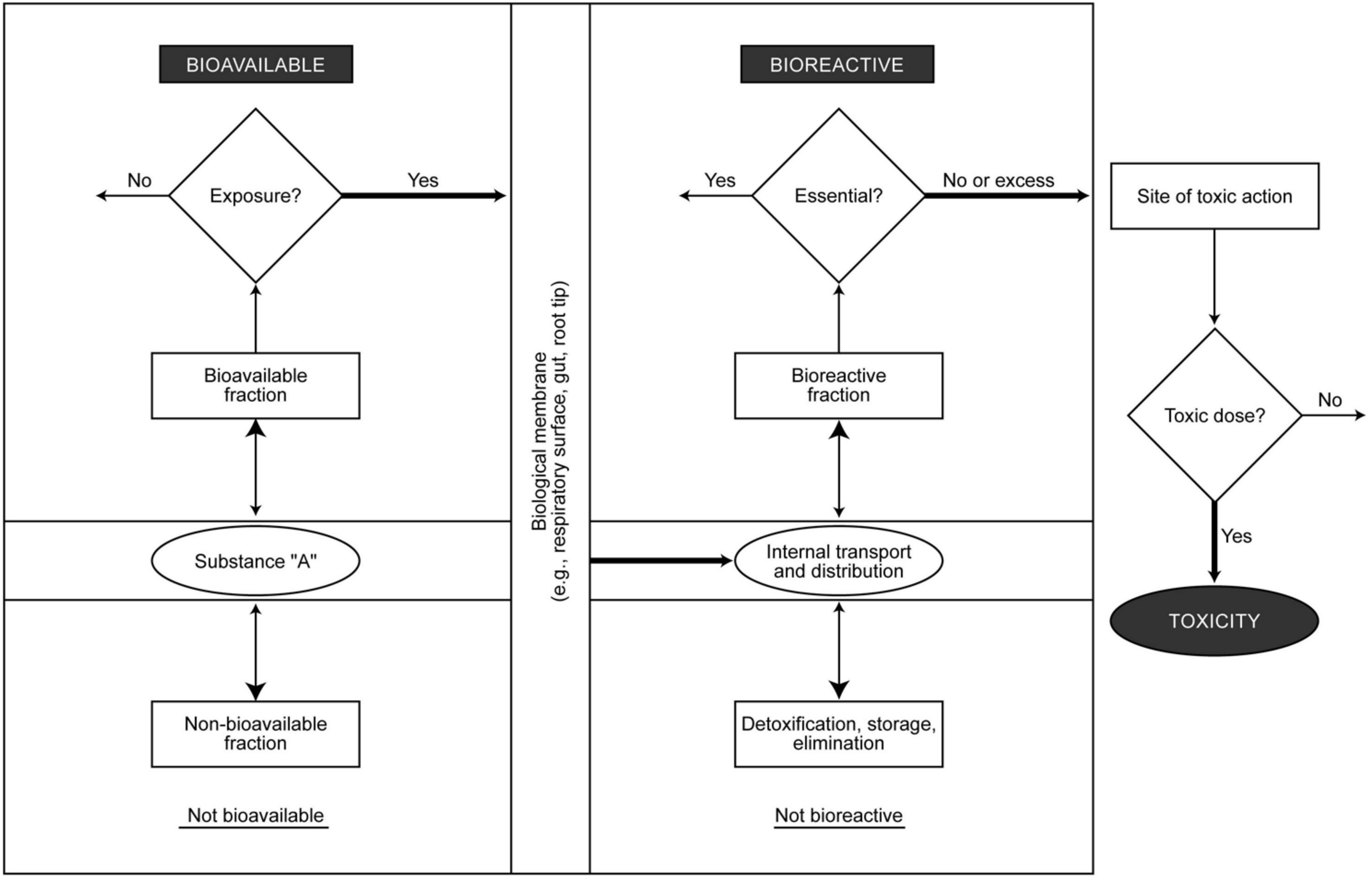
Three Compartment Model



Bioavailability is Affected By:

Chemistry

- Physico-chemical conditions
- Environmental compartment

Biology

- Route of exposure (e.g., via respiratory surfaces or via digestion)
- Biological interactions (including behavior)

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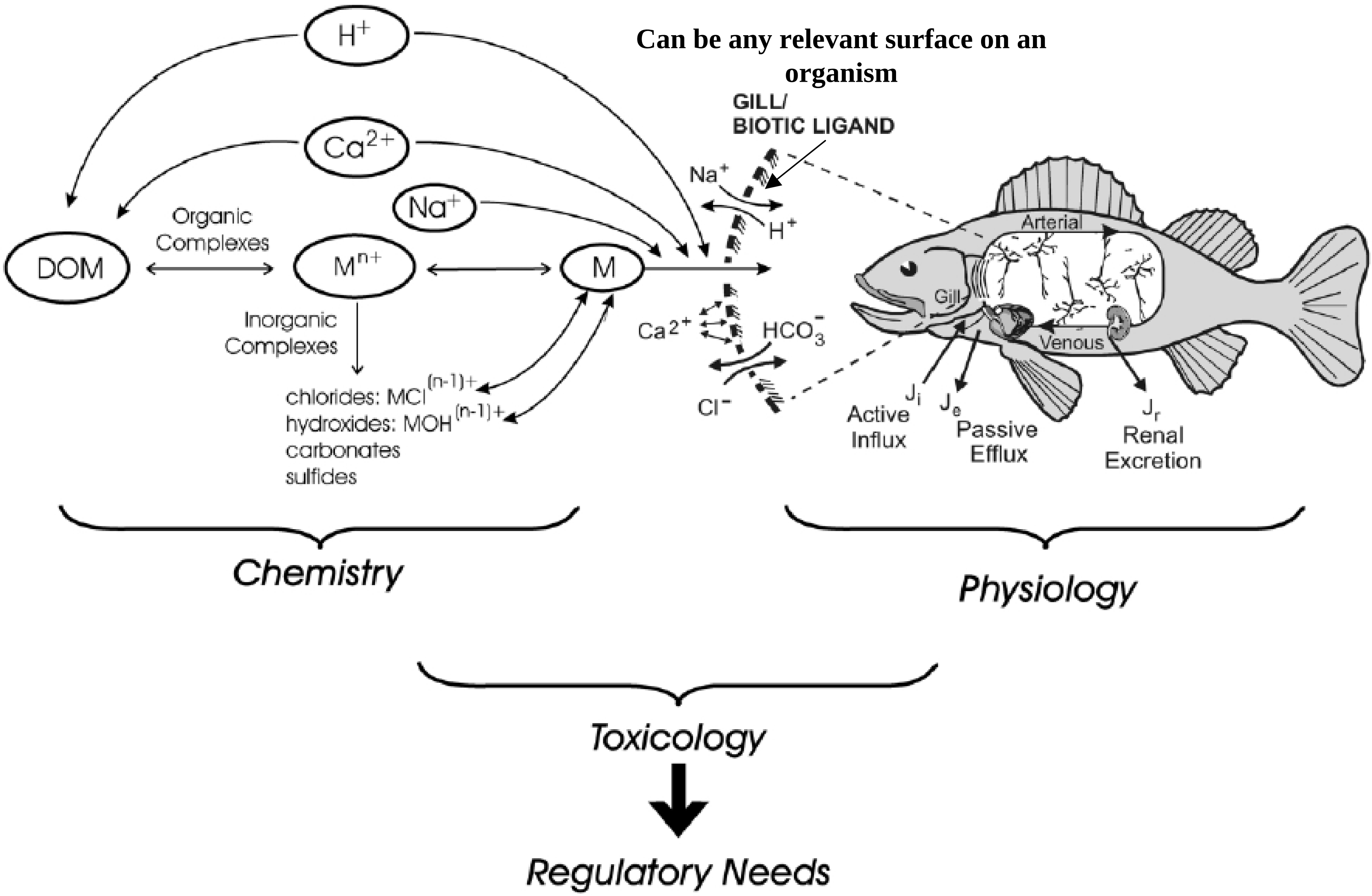
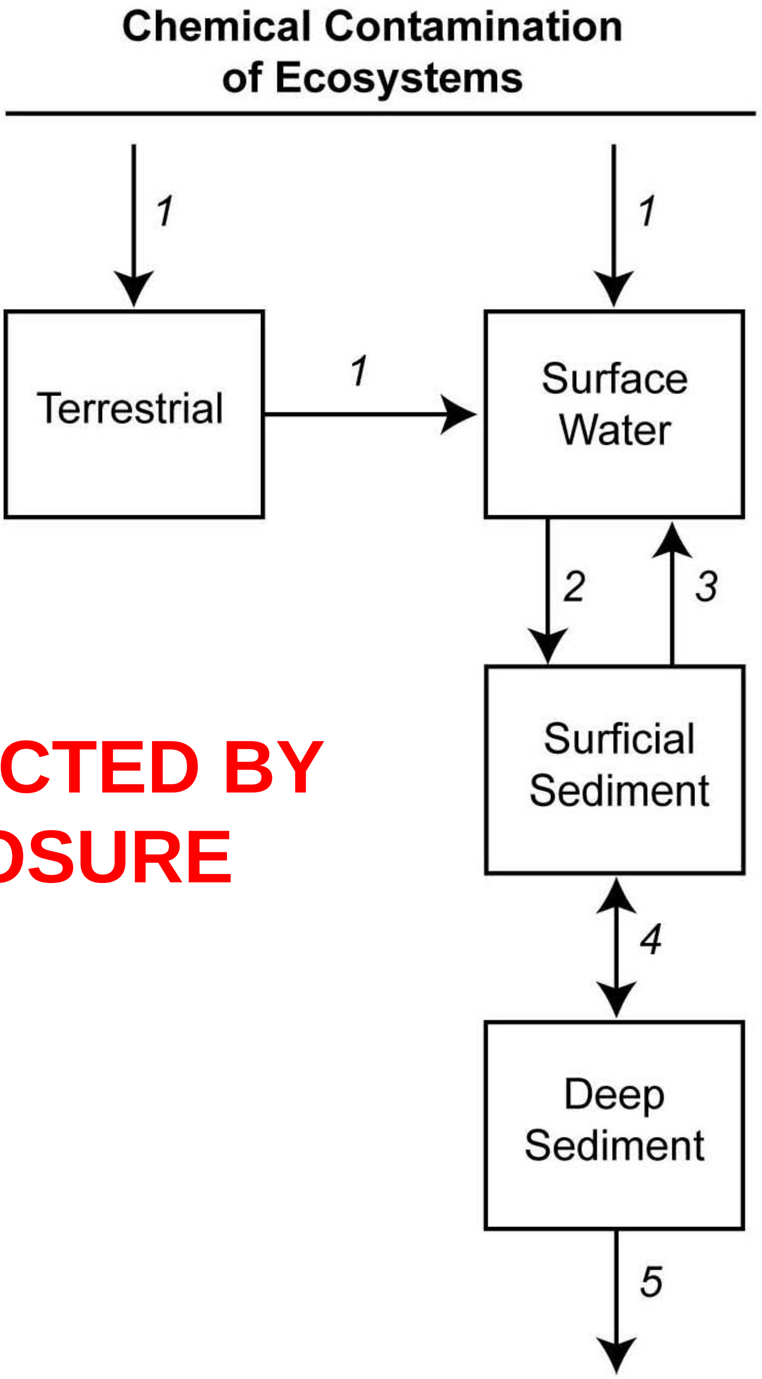
BLM: A Conceptual Model





BIOAVAILABILITY IS AFFECTED BY MODE OF ENTRY / EXPOSURE

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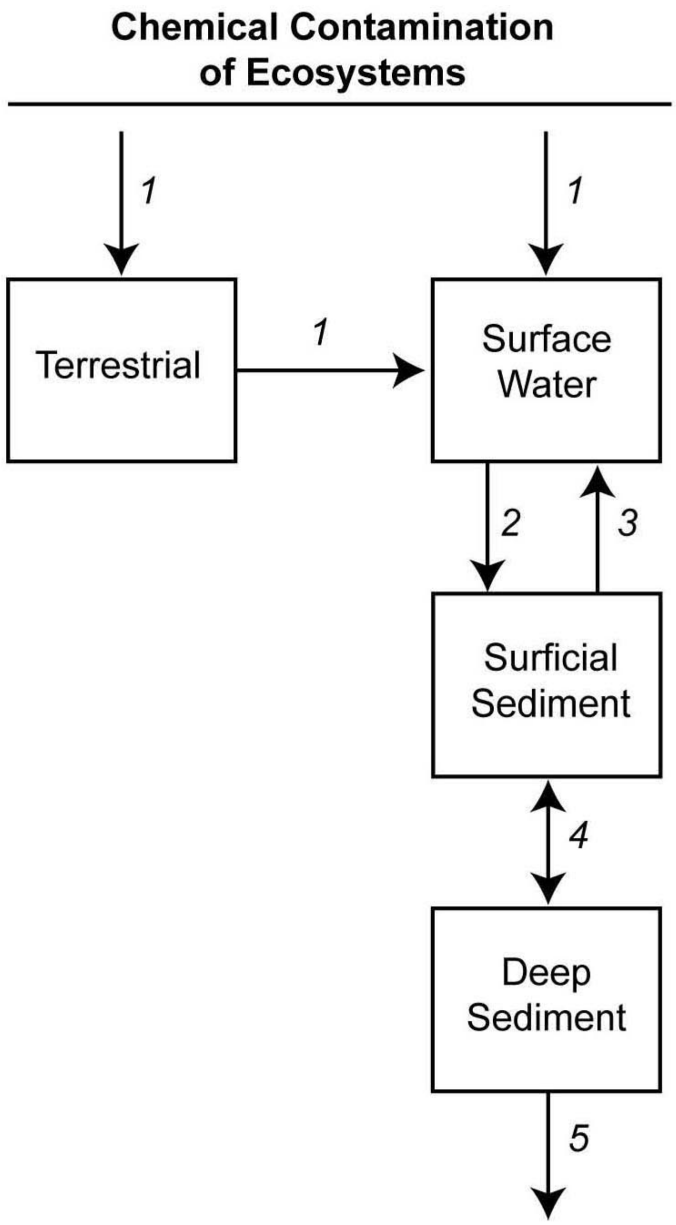
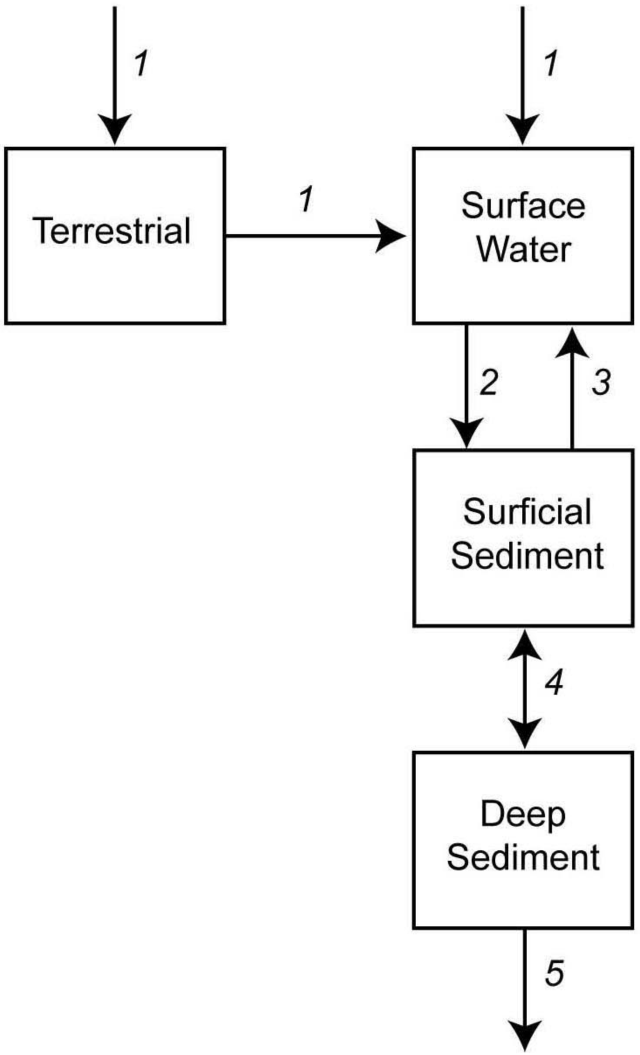


Processes

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

Chemical Contamination of Ecosystems



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ROPCs

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

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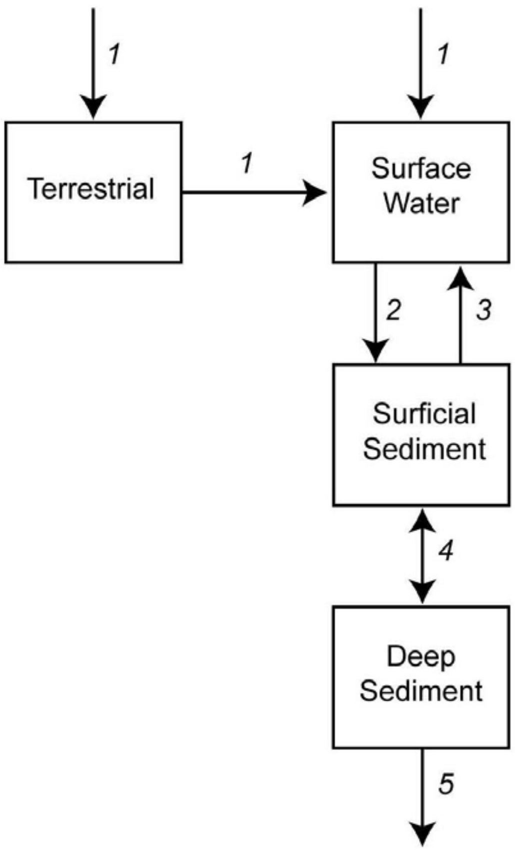

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ROPCs

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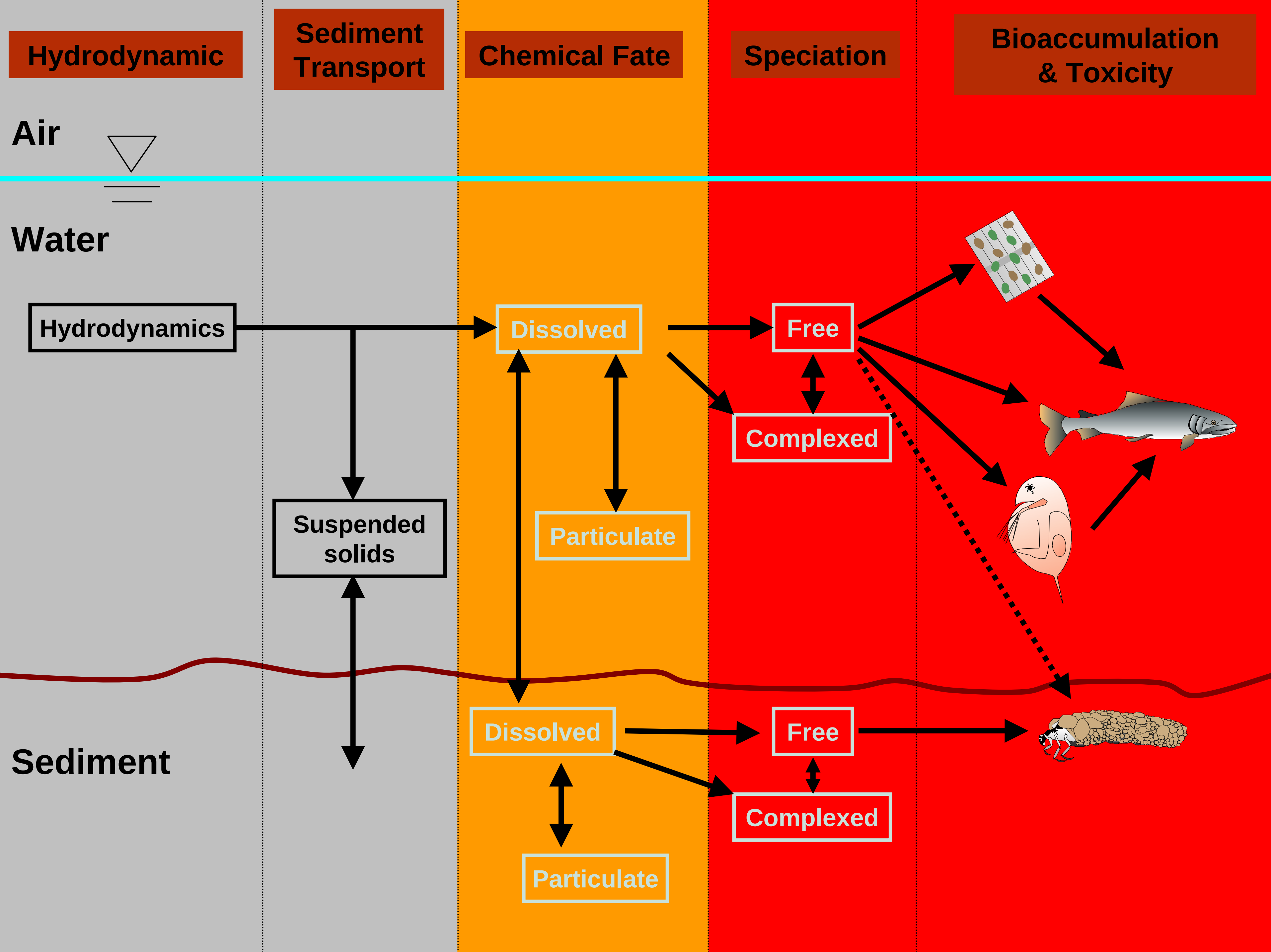
Other Stressors

Climate change

Habitat change

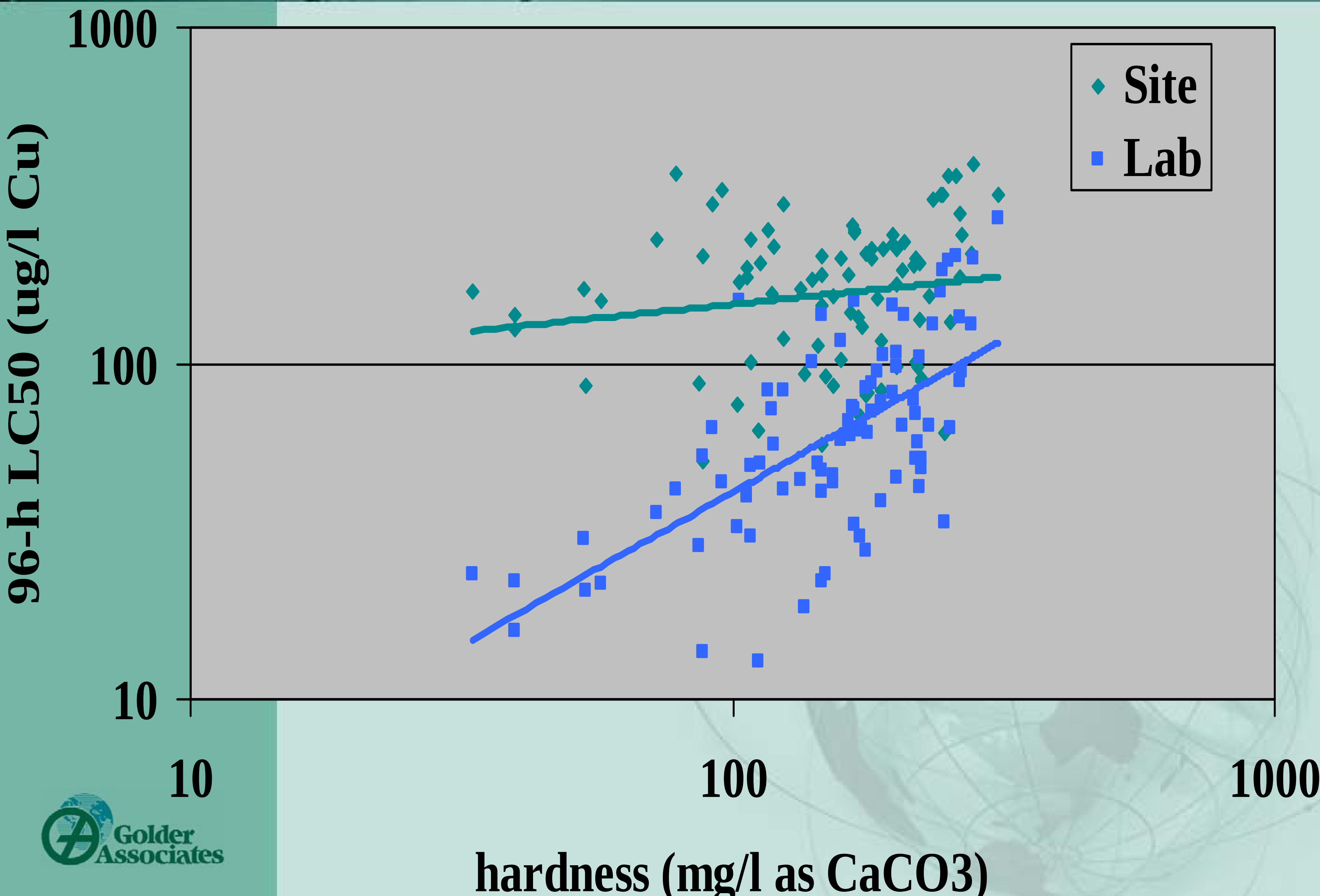
Introduced species

Eutrophication

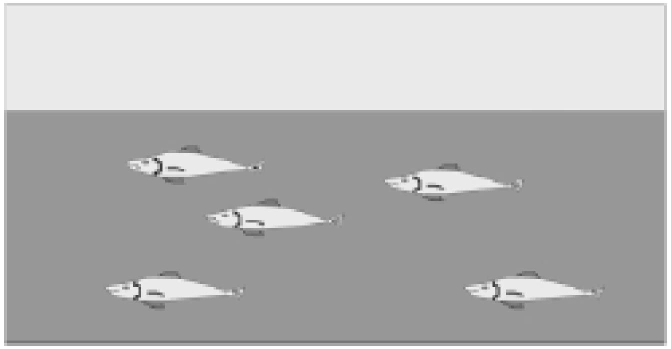


Hydrodynamic
Sediment Transport
Chemical Fate
Speciation
Bioaccumulation & Toxicity
Air
Water
Hydrodynamics
Dissolved
Free
Complexed
Particulate
Suspended solids
Sediment
Dissolved
Free
Complexed
Particulate

Environmental Conditions Affect Bioavailability



Sample Determination of a Water-Effect Ratio, WER

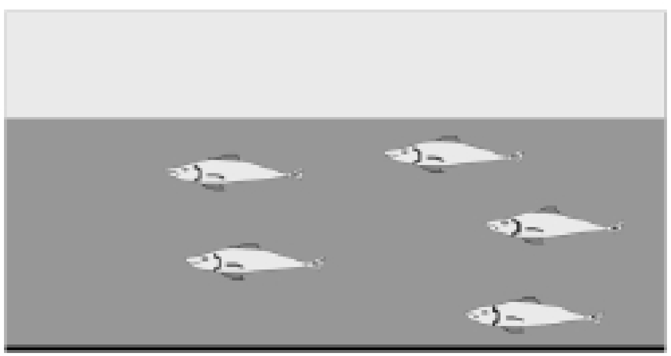


Toxicity in site water with added copper.

Site water LC50 = 350 µg/L copper

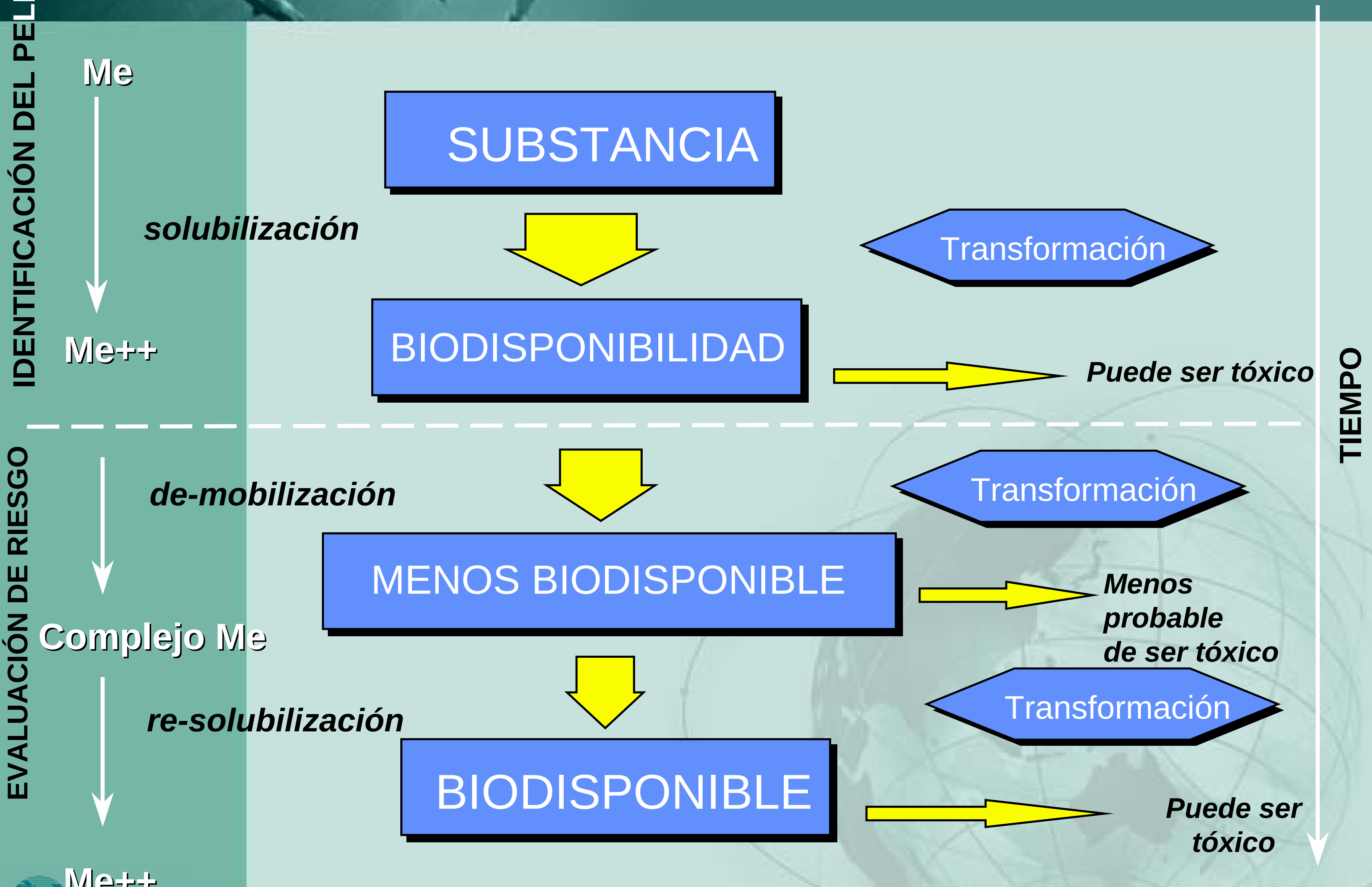
$$\text{WER} = \frac{350\ \mu g/L}{100\ \mu g/L} = 3.5$$

Laboratory water LC50 = 100 µg/L copper

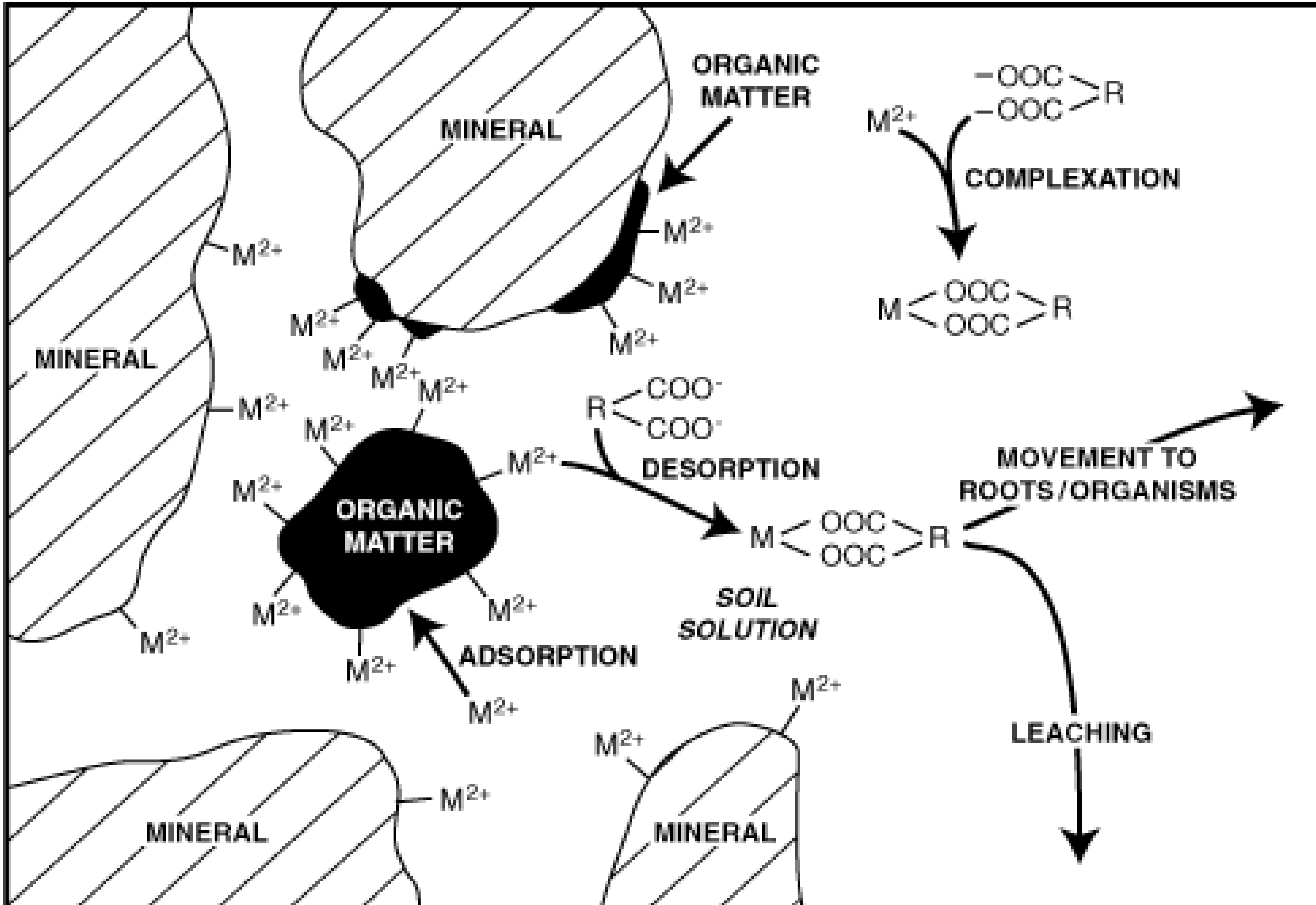


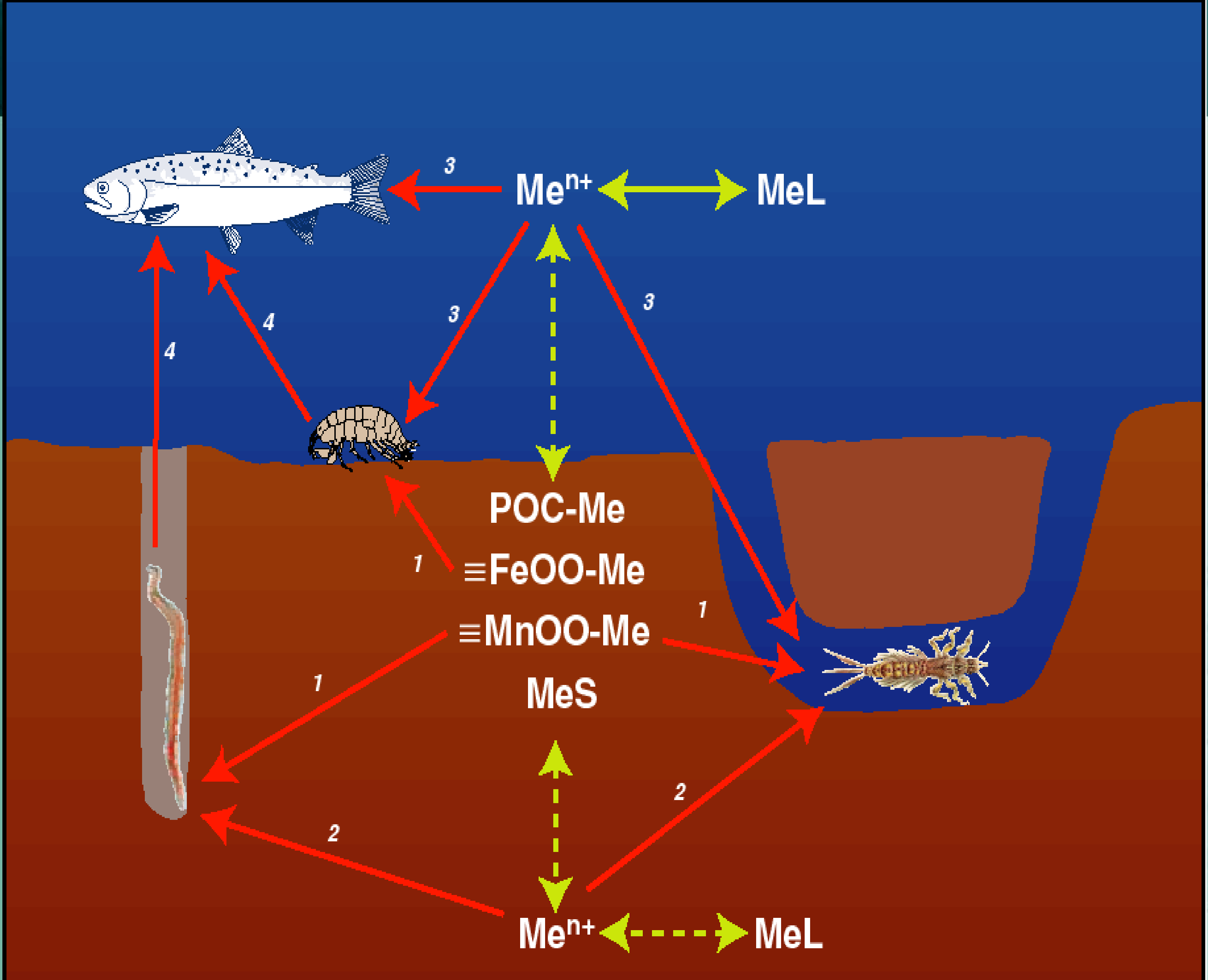
Toxicity in laboratory water with added copper.

Transformations Affect Bioavailability



Partitioning and Speciation Affect Bioavailability





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

Controls on Contaminant “Bioavailability”

- Chemical state
  - e.g., paint chips, lead shot, tar balls, metal ore, soot, pitch or coke globules
- Nature of sediment matrix
  - e.g., black carbon, peat, wood chips
- Biological degradation and tolerance (acclimation, adaptation) mechanisms, and biota behavior

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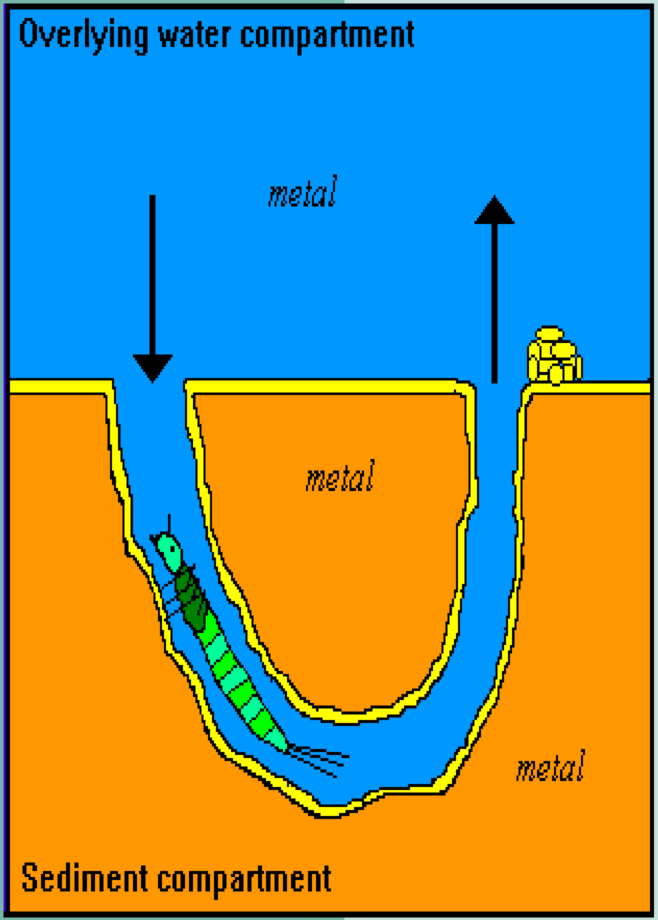
Bioavailability of Organic Substances

Cornelissen G, Gustafsson O, Bucheli TD, Jonker MTO, van Noort PCM. 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation and degradation. Environ Sci Technol 39(18): 6881-6895

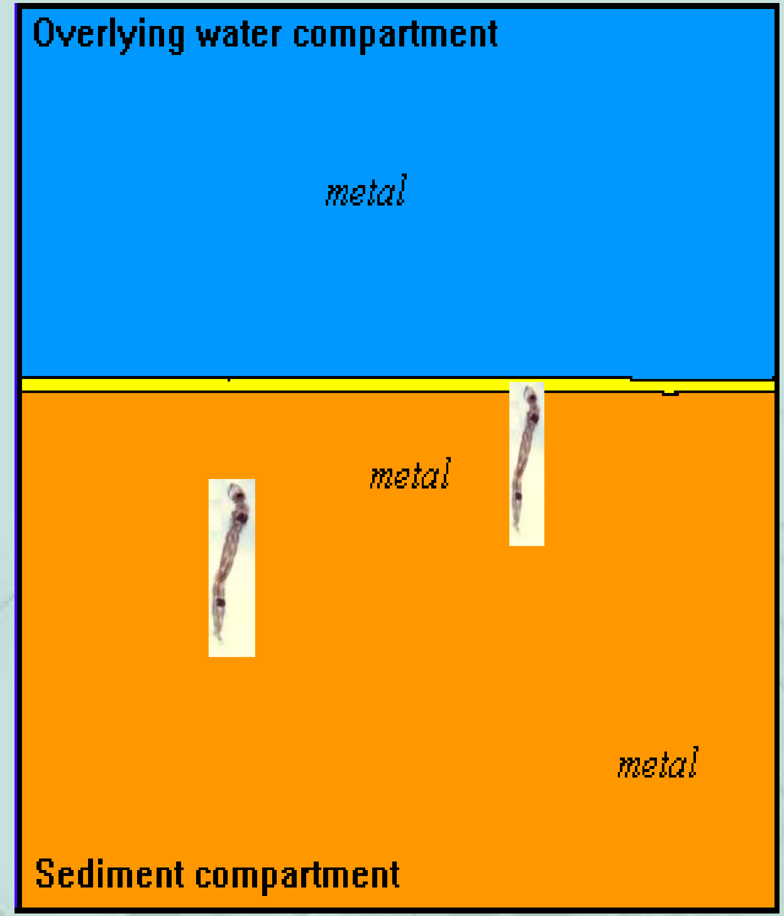
- Sorption of organic chemicals via “dual-mode sorption” – absorption in amorphous organic matter and to carbonaceous materials (e.g., black carbon)
- Solid-phase concentrations “bear little or no relation to actual concentrations in organisms” – reconsider existing sediment / soil criteria
- Freely dissolved concentrations most important

Organism Behavior Affects Bioavailability

These striking contrasts in behaviour…



vs.



have implications for bioavailability

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Plant Roots Affect Bioavailability

Metals

- Roots exude organic compounds that complex metals at the rhizosphere

Organics

- Roots influence the distribution of organochlorine pesticides and probably also other organic substances

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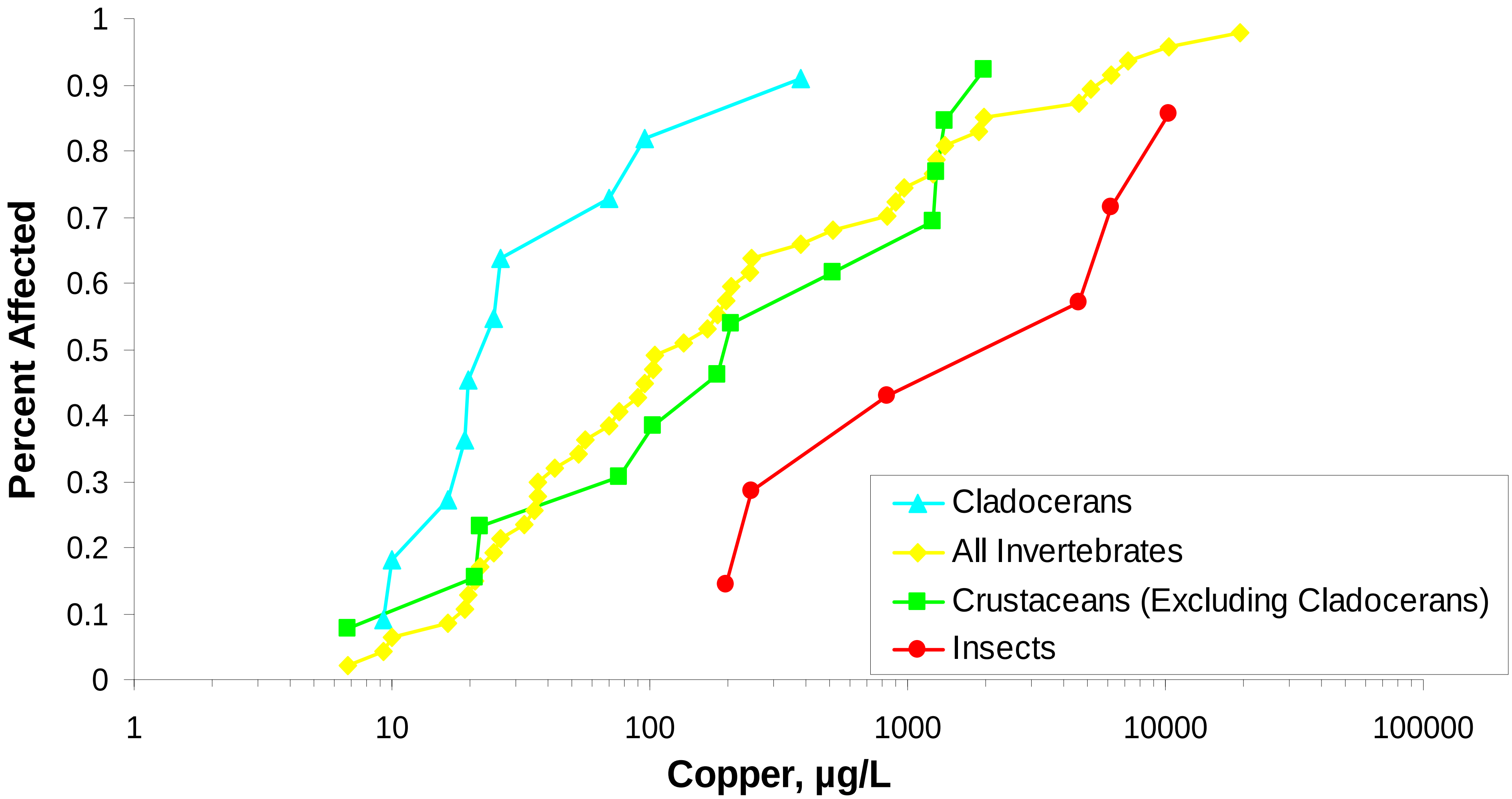
“Bioavailability” Differs Between Species



Bioavailability - Environmental Compartment

- Are deeper sediments contaminated and potentially toxic?

and

- Are deeper sediments likely to be uncovered under one or more reasonably possible set of circumstances?

If so, then contaminants in these sediments are potentially bioavailable

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Route 440 Exposure Pathways

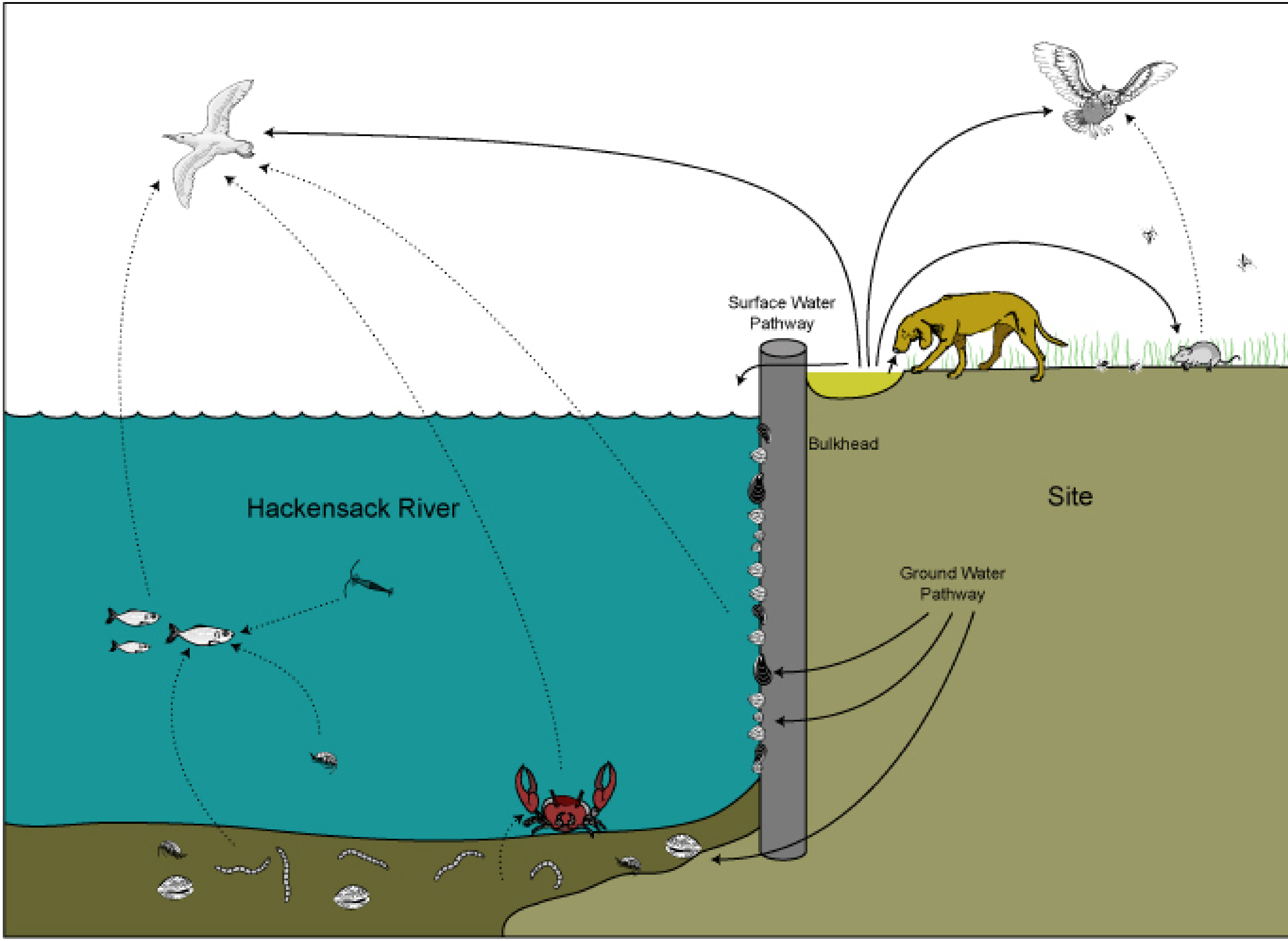
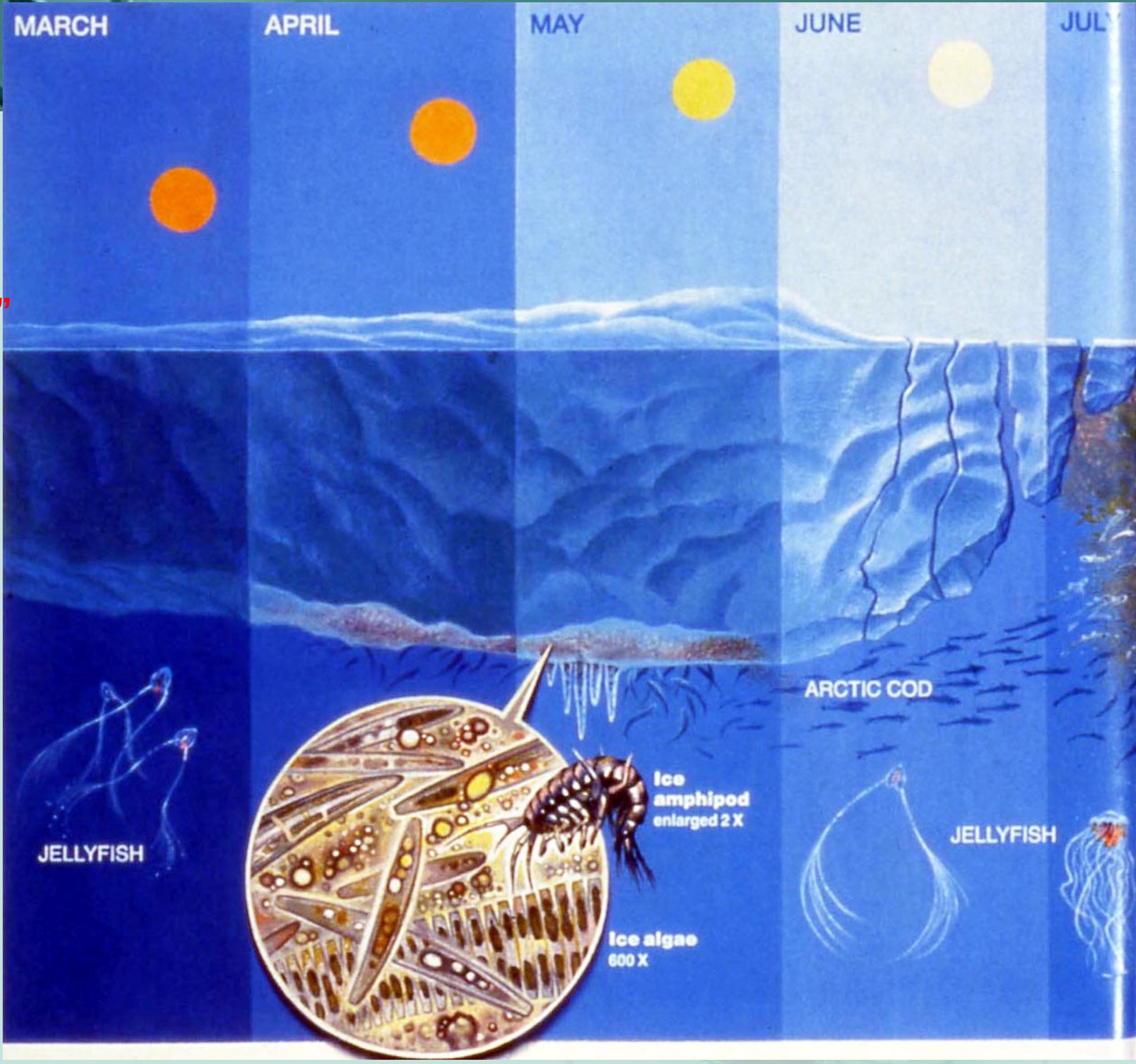


Figure 6: Total Chromium 2001, 5-10 cm

Figure 4: Amphipod Mortality 5-10 cm

“BIOAVAILABILITY” CAN VARY TEMPORALLY AND BETWEEN ECOSYSTEMS



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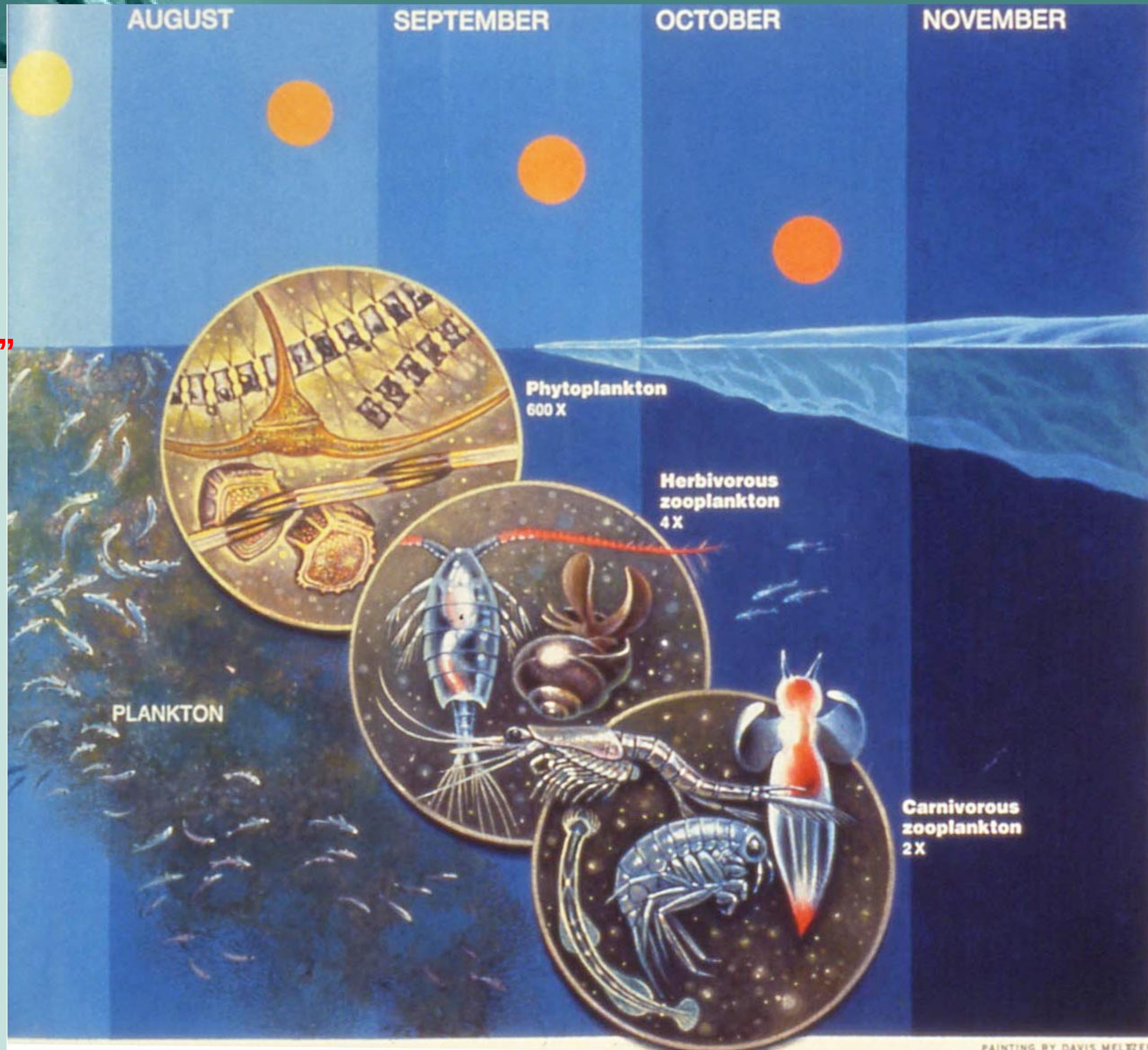

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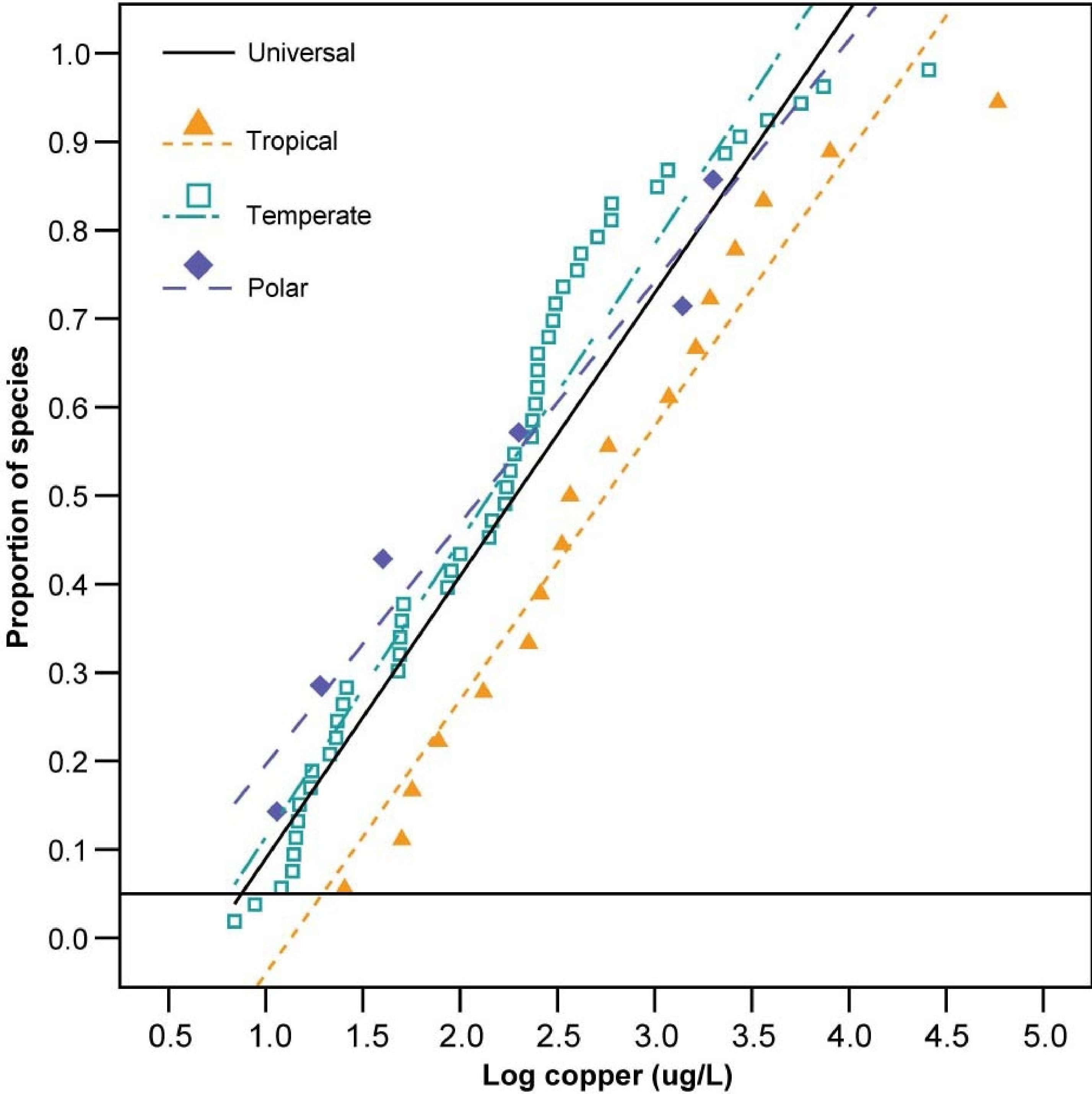
SPECIES SENSITIVITY DISTRIBUTIONS (SSDs)



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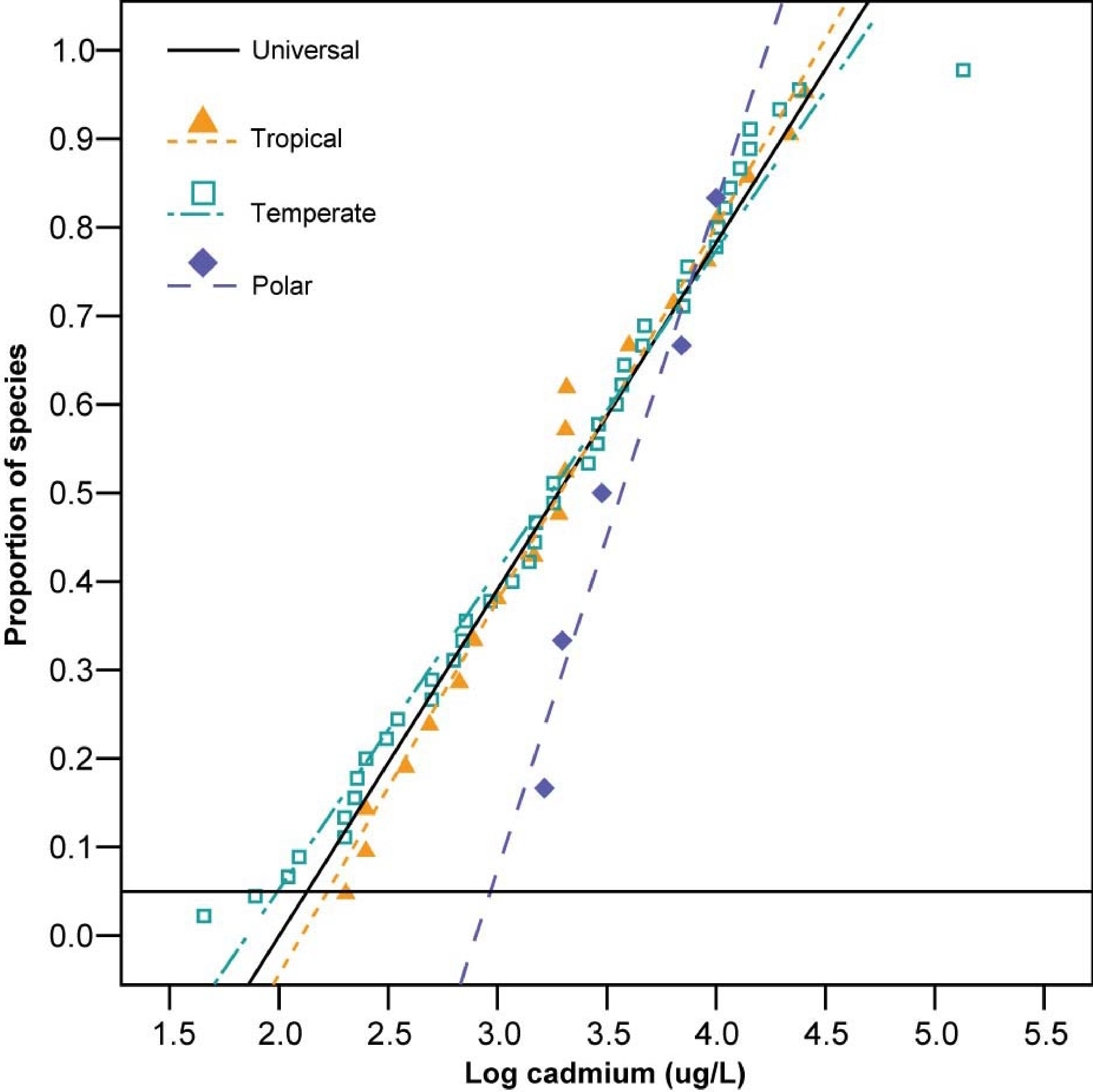

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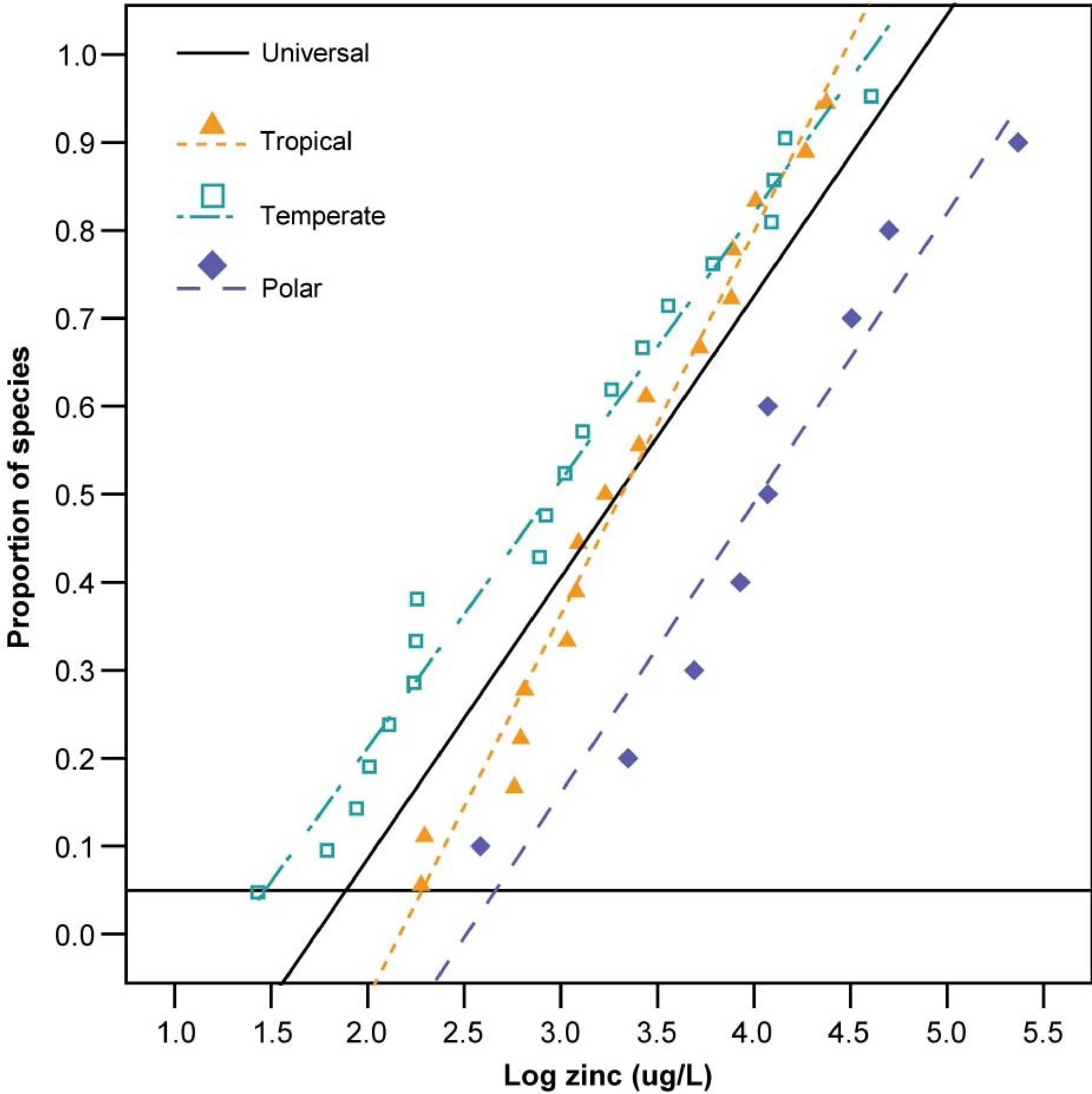

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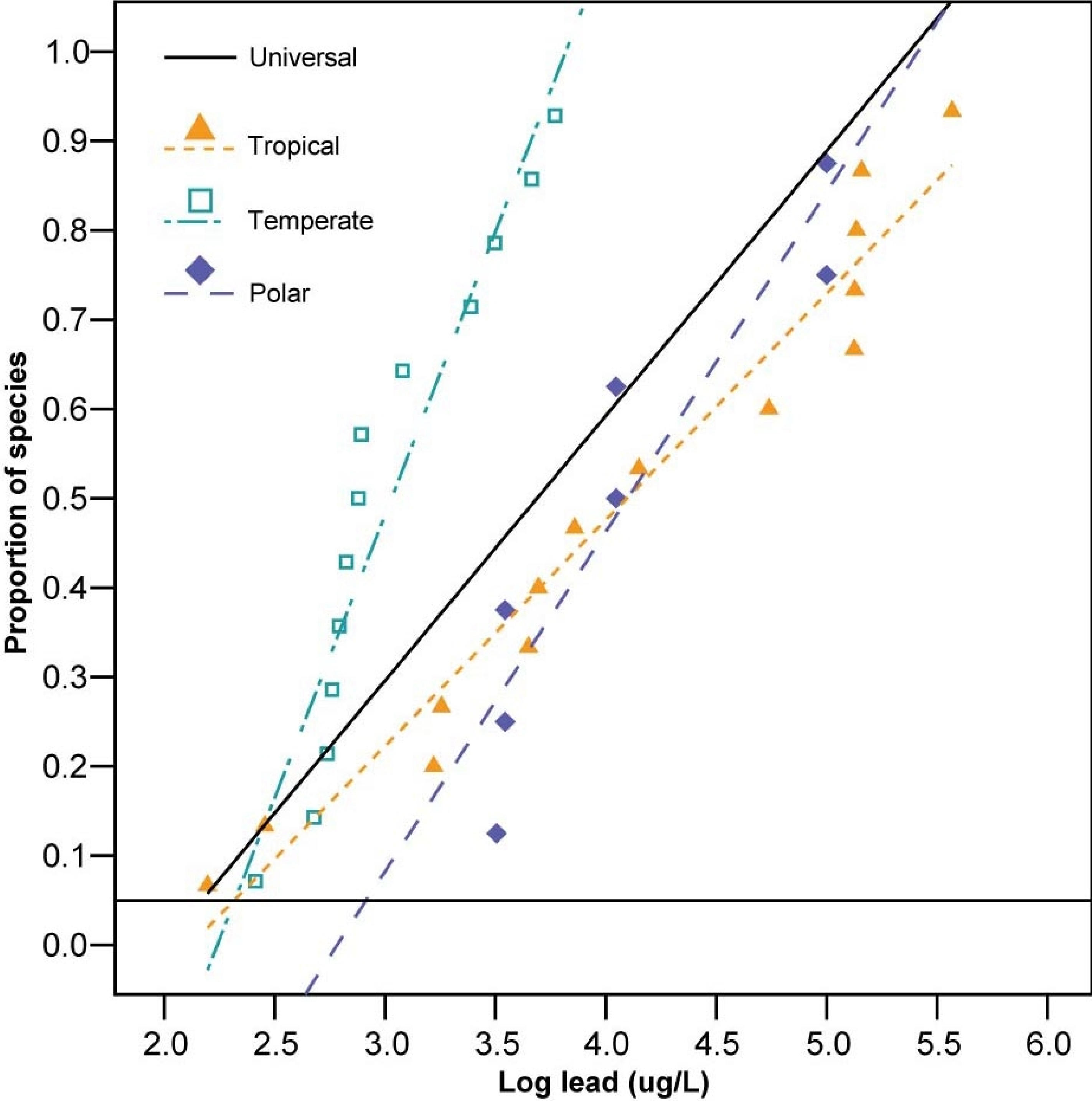

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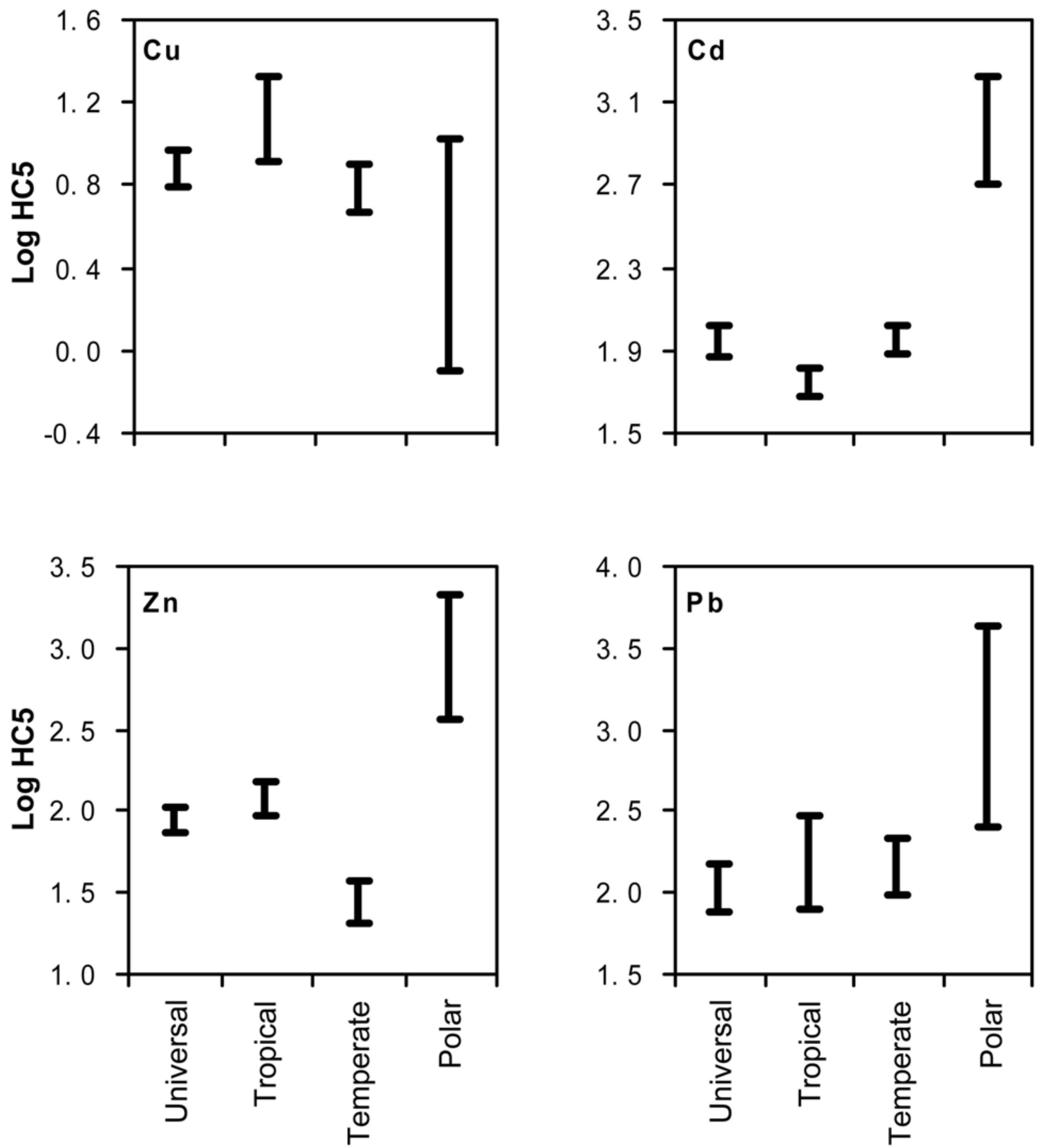
HC5 VALUES: 95% CL



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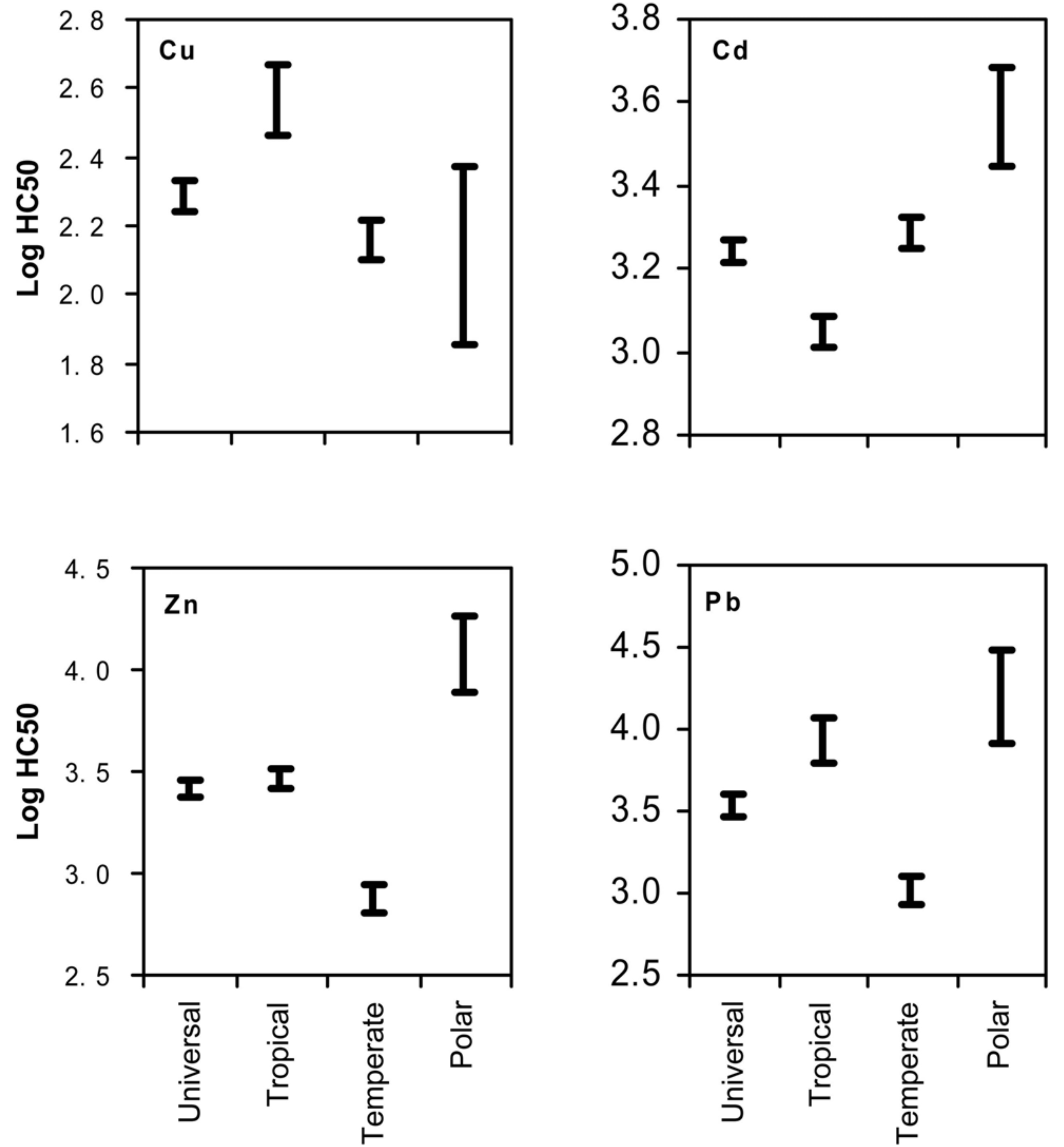

Relative Sensitivities (HC_{50} values)

METAL	MOST SENSITIVE	LEAST SENSITIVE
Cu	Polar/ Temperate	Tropical
Cd	Tropical	Polar
Zn	Temperate	Polar
Pb	Temperate	Polar

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Bioreactivity is affected by:

- **Route of exposure (gut vs gills)**
- **Depuration and sequestration mechanisms**
- **Concentrations of that substance already in the organism (e.g., spillover effect for metallothionein)**
- **Adaptation/acclimation** (if not behavioral, affects bioreactivity, not bioavailability)

Bioreactivity of Metals in Organisms

- **1. 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 for marine invertebrates
- **2. 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 may not directly relate to metal transfer to predators" (Wallace and Luoma 2003)

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Bioreactivity Affected by Uptake Route

Ball AL, Borgmann U, Dixon DG. In review. Toxicity of dietary cadmium to *Hyalella azteca*. Aquat. Toxicol.

- Growth more sensitive than survival (survival more sensitive for water exposures)
- No relationship between toxicity and Cd accumulation (relationship established for water exposures)

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Biological Strategies – Contaminant Exposure

Inducible Strategies	Constitutive Strategies
Changes in behaviour, physiology or biochemistry	Morphological, physiological or biochemical features
Occur only after exposure initiated	Persist irrespective of exposure
No performance trade-off	Possible fitness disadvantage in absence of stress
Often occur after a measurable time-lag	No time-lag
Example: avoidance (energetically easiest for fish)	Example: metallothionein to detoxify metals

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Bioavailability: We Can Get There From Here

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Questions / Discussion?