Influence of Dissolved Organic Matter on Aquatic Copper Toxicity in Iron-Rich Environments

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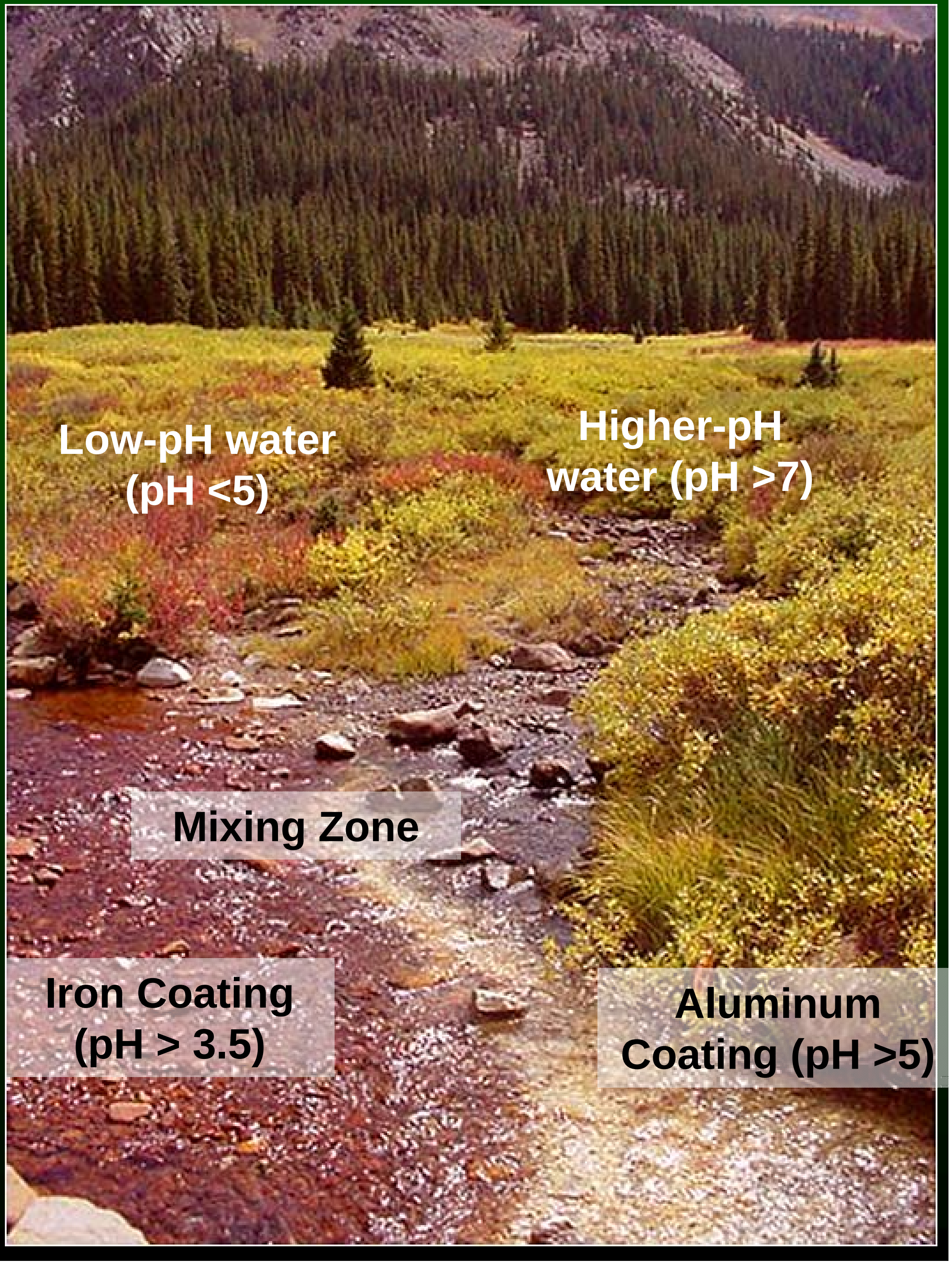
Mineralized areas commonly generate acidic water with elevated dissolved metal concentrations, especially iron and aluminum

At confluences with higher pH water, dissolved iron and aluminum precipitate



Fundamentals

- Chemical speciation of metals influences their potential toxicity to aquatic biota
- Dissolved free metals constitute the main bioavailable fraction of metals
- Presence of dissolved organic matter (DOM) decreases metal toxicity to aquatic biota by binding with dissolved metals

Dissolved Organic Matter Fractionation

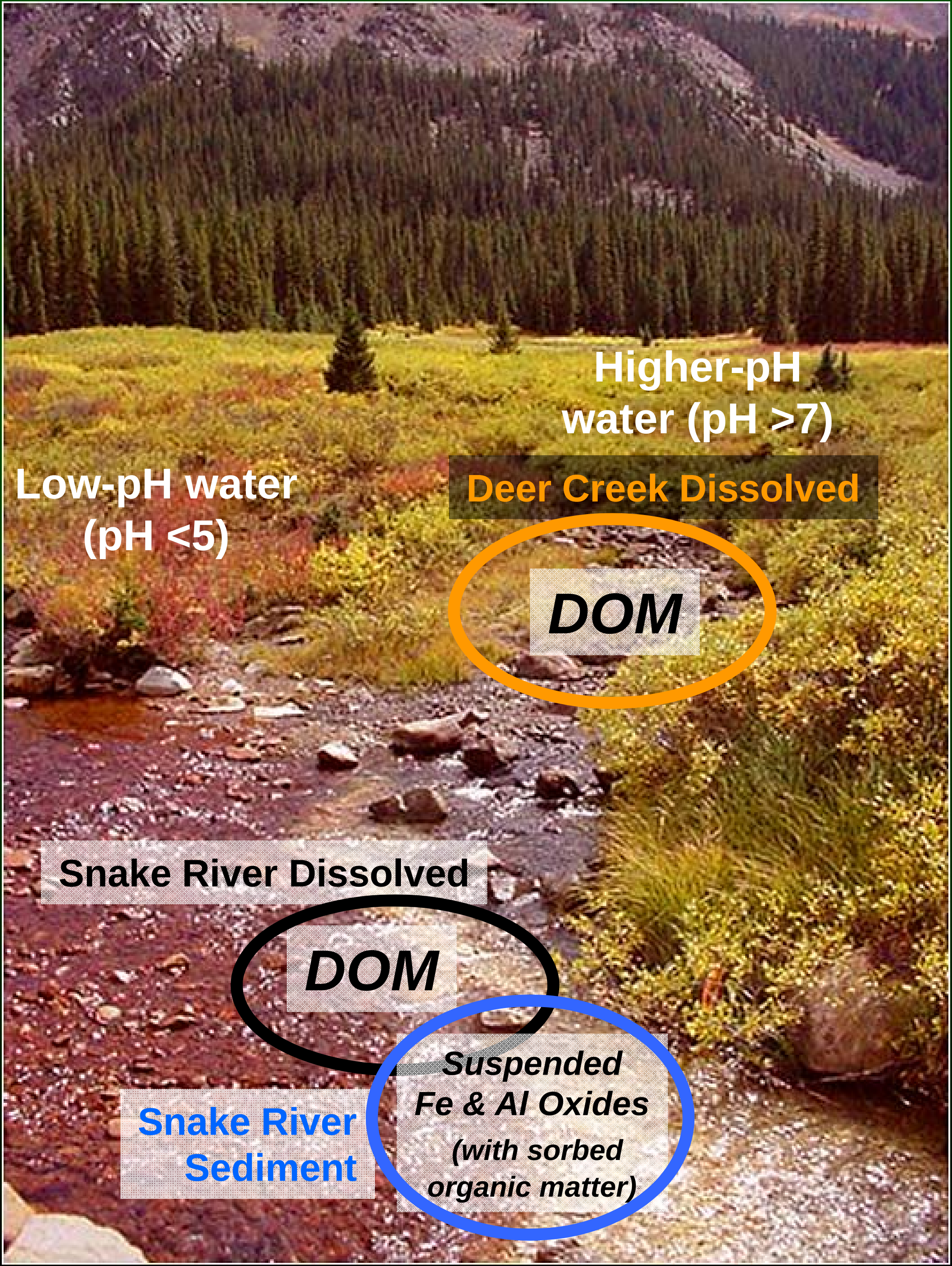
McKnight et al. (1992) demonstrated that DOM fractionates in the presence of precipitating iron and aluminum oxides

- ✓ Some DOM is removed from solution by sorption onto precipitating iron and aluminum oxides
- ✓ DOM sorption results in chemical fractionation
  - – Molecules with greater metal-binding affinities are preferentially sorbed
- ✓ Remaining DOM is depleted in constituents having greatest metal-binding affinity

Dissolved Organic Matter Isolation

McKnight et al., 1992

- Filtered stream water
- XAD-8 columns
- H^+ saturation
- Freeze dried



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Dissolved Organic Matter Collection Sites

1. Stream water from a pristine Colorado stream (Deer Creek Dissolved)
2. Stream water below the confluence of an acidic, metal-enriched stream with Deer Creek (Snake River Dissolved)
3. Suspended sediment (with sorbed organic matter) below the confluence of an acidic, metal-enriched stream with Deer Creek (Snake River Sediment)
4. Suwannee River Fulvic Acid (standard reference material)

Question

How does DOM fractionation in mineralized areas affect copper bioavailability to aquatic biota?

Ceriodaphnia dubia (Water Flea)

A sensitive fresh-water invertebrate commonly used in toxicity testing of contaminants

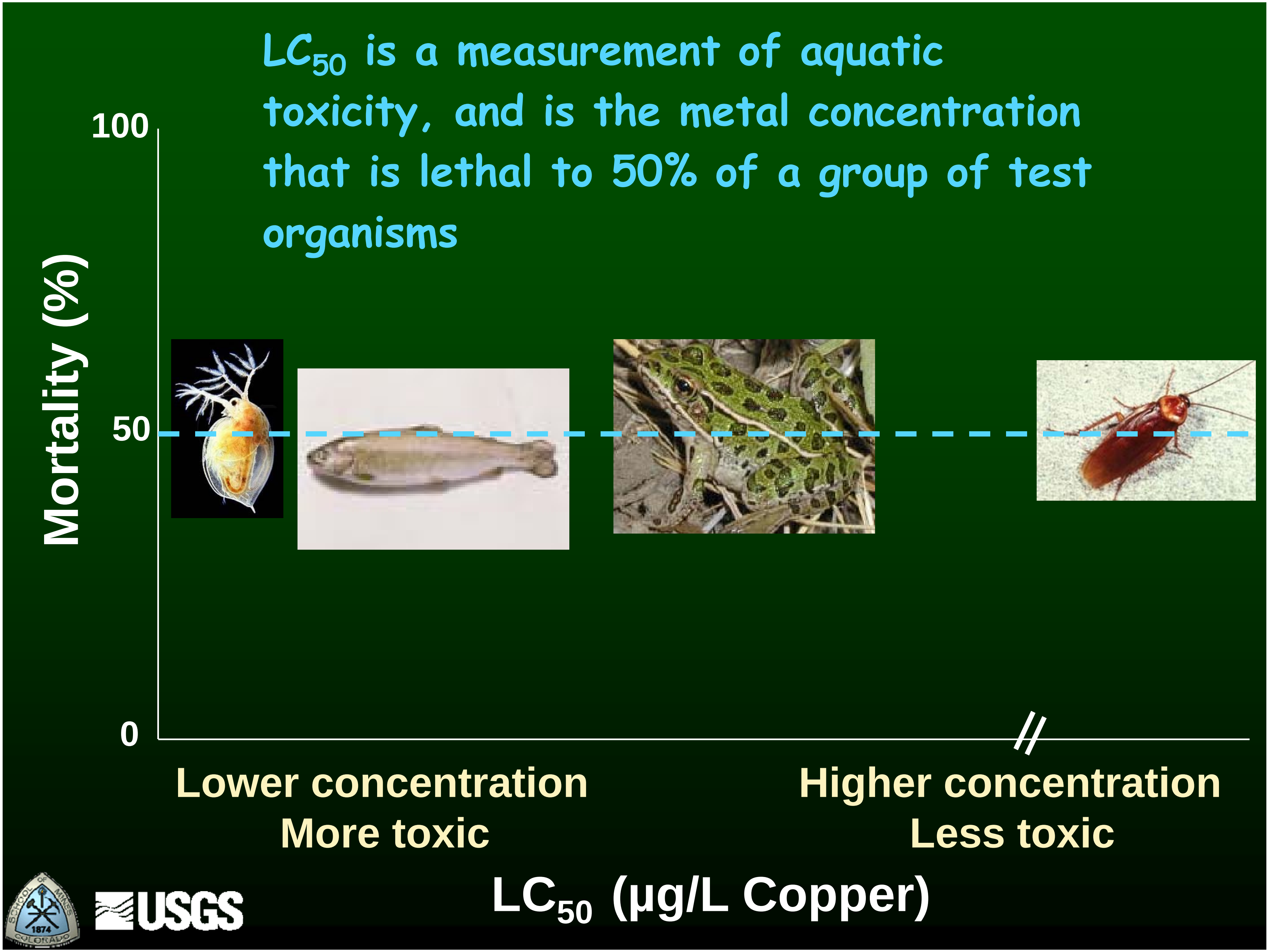
Toxicity Testing

Four replicate test cups
containing five organisms in each cup

Decreasing
copper
concentration

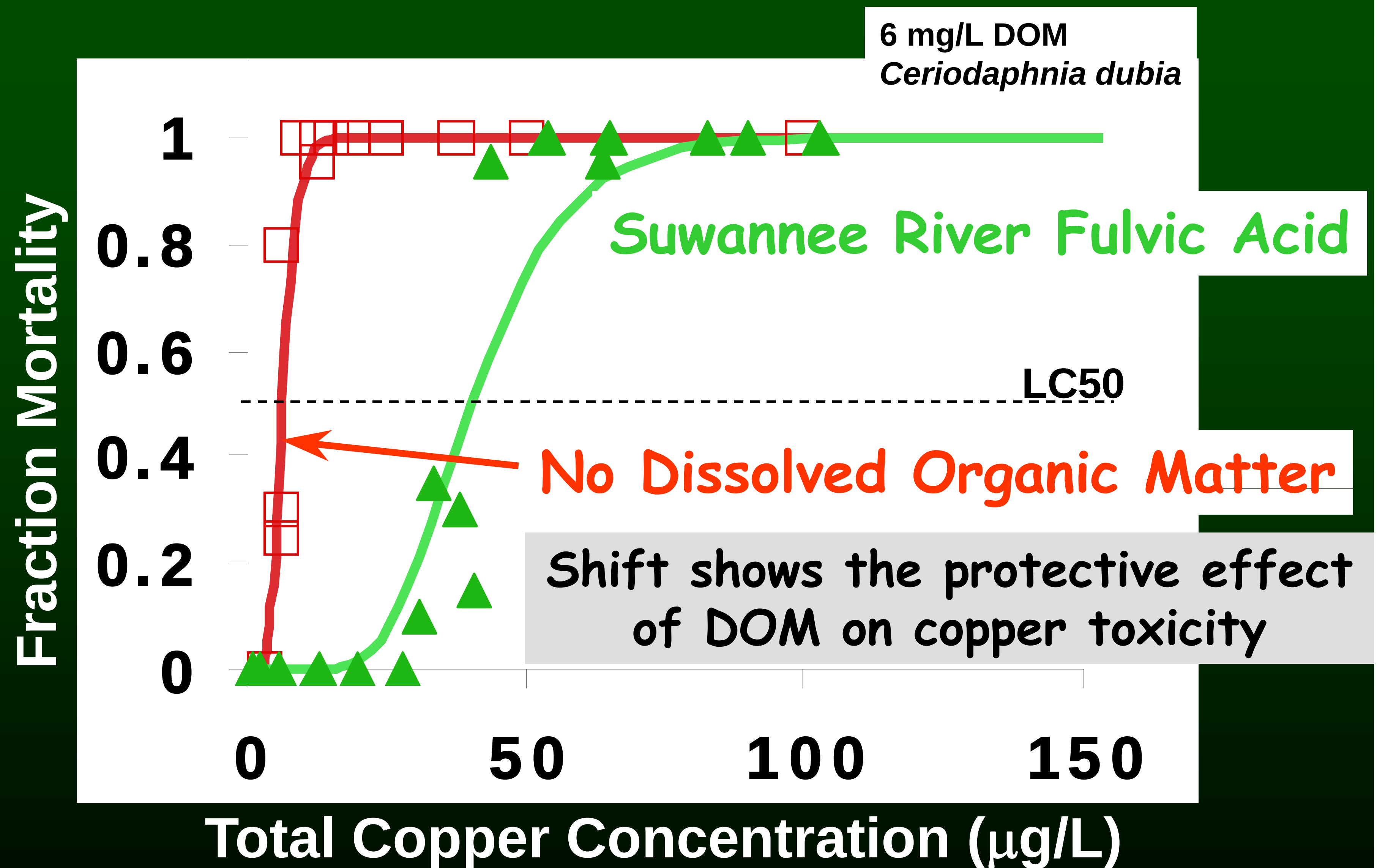
Laboratory Toxicity Tests

- One set with no DOM added (just EPA moderately hard water)
- Freeze-dried DOM (6 mg/L = 3 mg/L DOC) from the different sources was added to solutions containing different copper concentrations and allowed to equilibrate
- 48-hour static tests at 20°C were conducted with *Ceriodaphnia dubia*
- Determine mortality of test organisms (LC_{50})



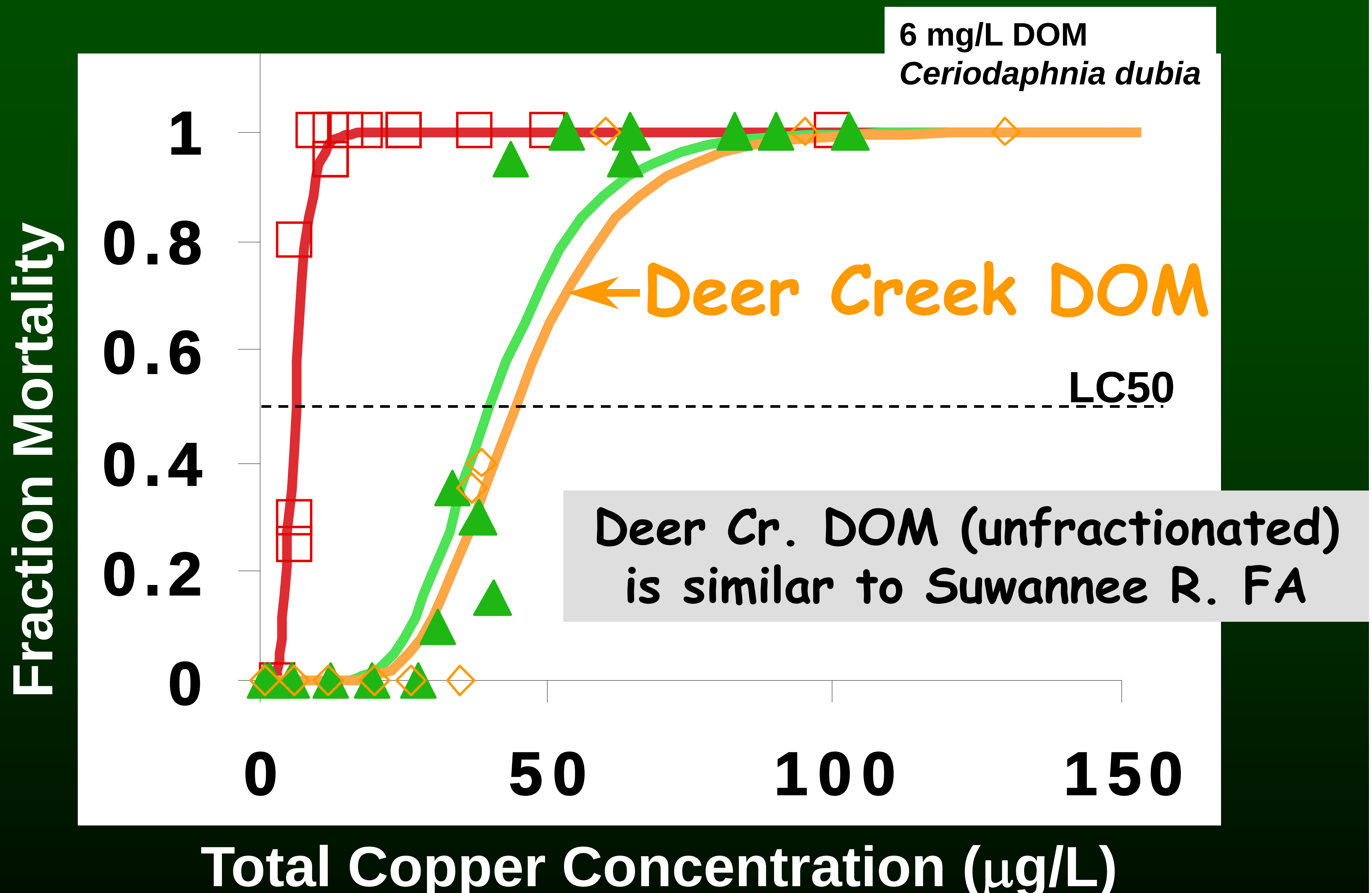
LC50 is a measurement of aquatic toxicity, and is the metal concentration that is lethal to 50% of a group of test organisms
100
50
0
Mortality (%)
Lower concentration
More toxic
Higher concentration
Less toxic
LC50 (µg/L Copper)
USGS

Toxicity Results



Shift shows the protective effect of DOM on copper toxicity

Toxicity Results



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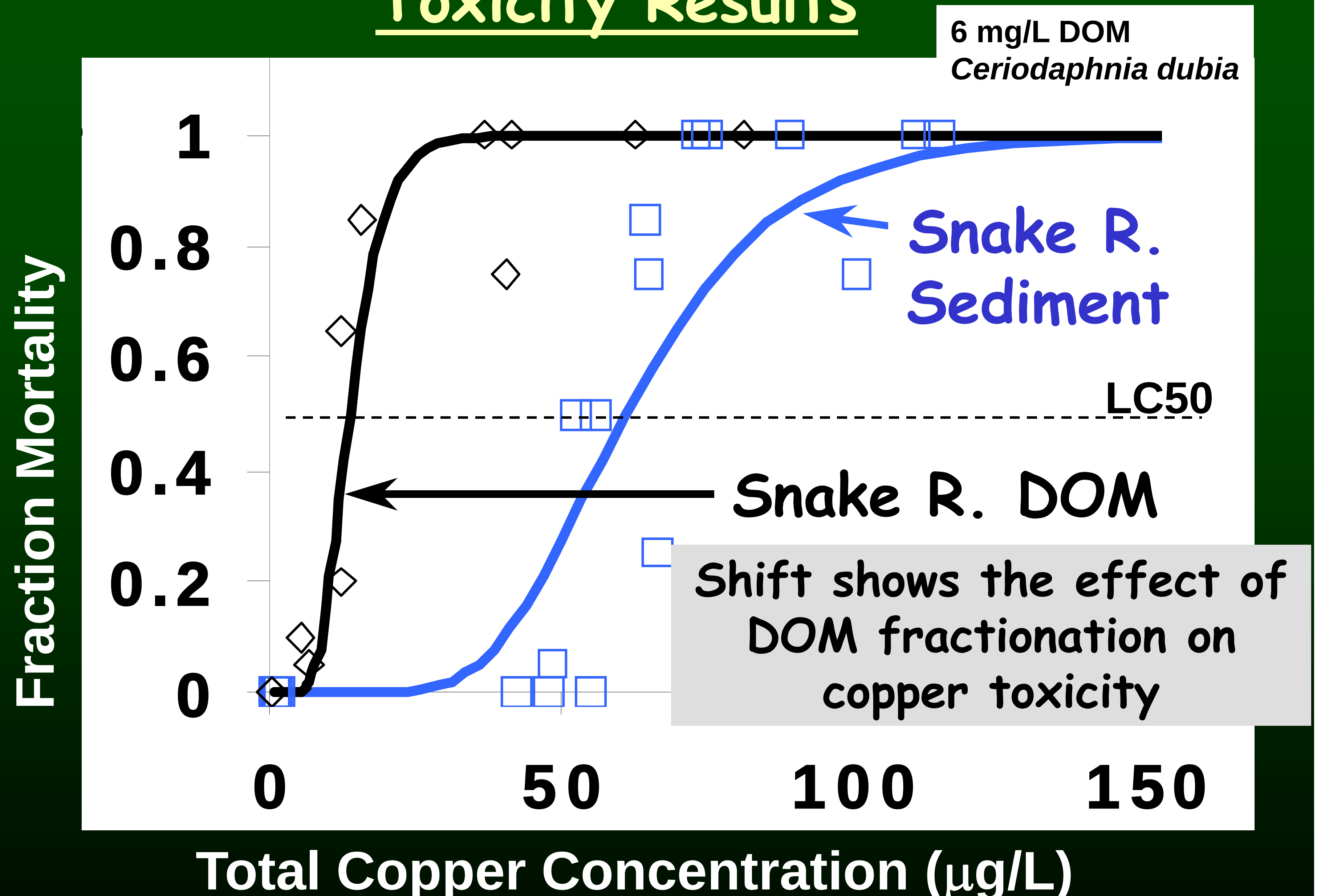
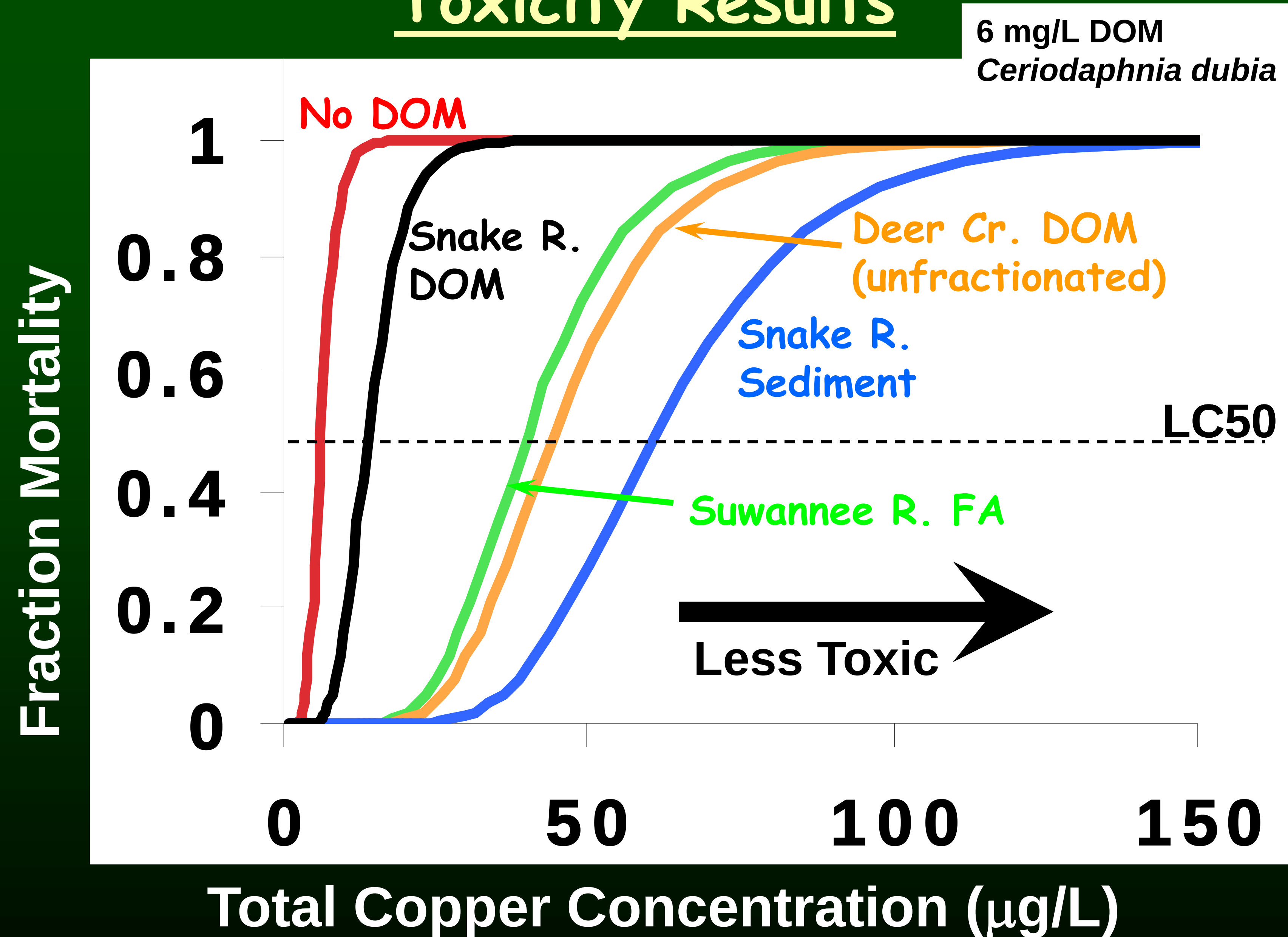
Toxicity Results



Toxicity Results



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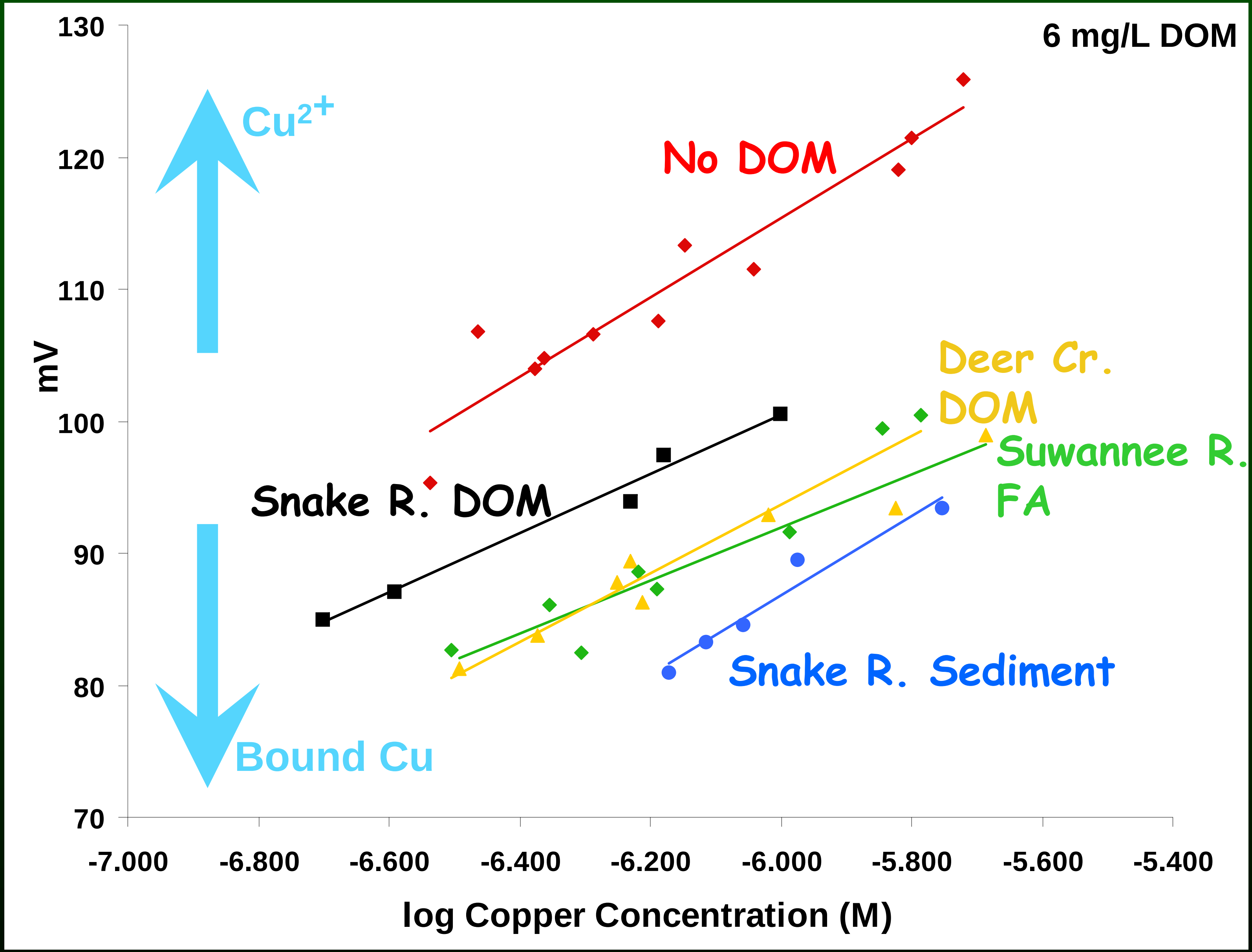
Free Copper Measured with a Cu ISE



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What does this mean for the Biotic Ligand Model?

(BLM…*not the agency*)

United States
Environmental Protection
Agency

Office of Water
4304T

EPA-822-R-07-001
February 2007

EPA

AQUATIC LIFE AMBIENT FRESHWATER QUALITY CRITERIA - COPPER

2007 Revision

The Biotic Ligand Model is incorporated into the U.S. Environmental Protection Agency 2007 Updated Aquatic Life Copper Criteria

SCHOOL OF MINES 1874 COLORADO

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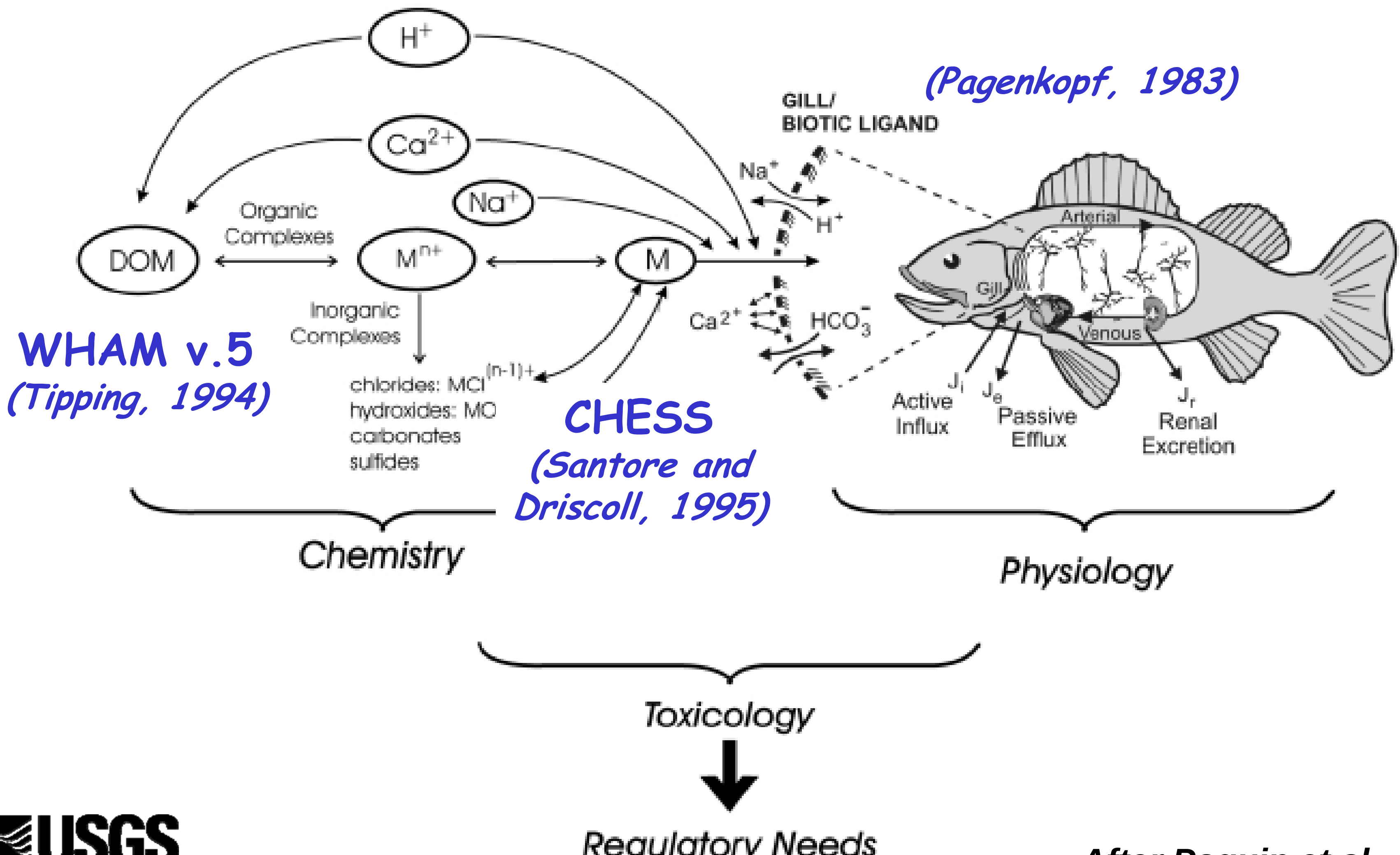
Biotic Ligand Model (BLM)

- Computational approach to estimate acute metal toxicity
- Considered to be an alternative to expensive and extensive toxicological testing to determine site-specific water-quality criteria
- Quantifies the "bioavailable" fraction

Biotic Ligand Model (BLM)

The BLM is an interface between the fields of aqueous geochemistry, physiology, and aquatic toxicology



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After Paquin et al., 2002

Use of the Biotic Ligand Model in Mineralized Areas

It is likely that a modified version of the BLM that incorporates the effects of iron and aluminum will need to be used to compute site-specific water-quality criteria and potential metal toxicity in many mineralized areas

Overall Summary

- DOM with greater affinity for metal binding tends to be preferentially sorbed to sediment phases in iron- and aluminum-rich streams
- DOM isolated from an iron- and aluminum-rich stream was 3 times <u>less</u> effective at reducing copper toxicity
- Fractionation of organic matter between dissolved and sediment phases in iron- and aluminum-rich streams can result in more bioavailable dissolved copper <u>and</u> greater potential for copper toxicity to aquatic biota

Overall Summary, cont.

- Stream ecosystems downstream of iron- and aluminum-rich streams may be more vulnerable to adverse effects from metal toxicity
- Modifications to the Biotic Ligand Model may be necessary for application to iron- and aluminum-rich environments

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Visit our websites at

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