Copper Fate and Effects: Use of Copper Formulations as Algaecides and Herbicides in Aquatic Systems

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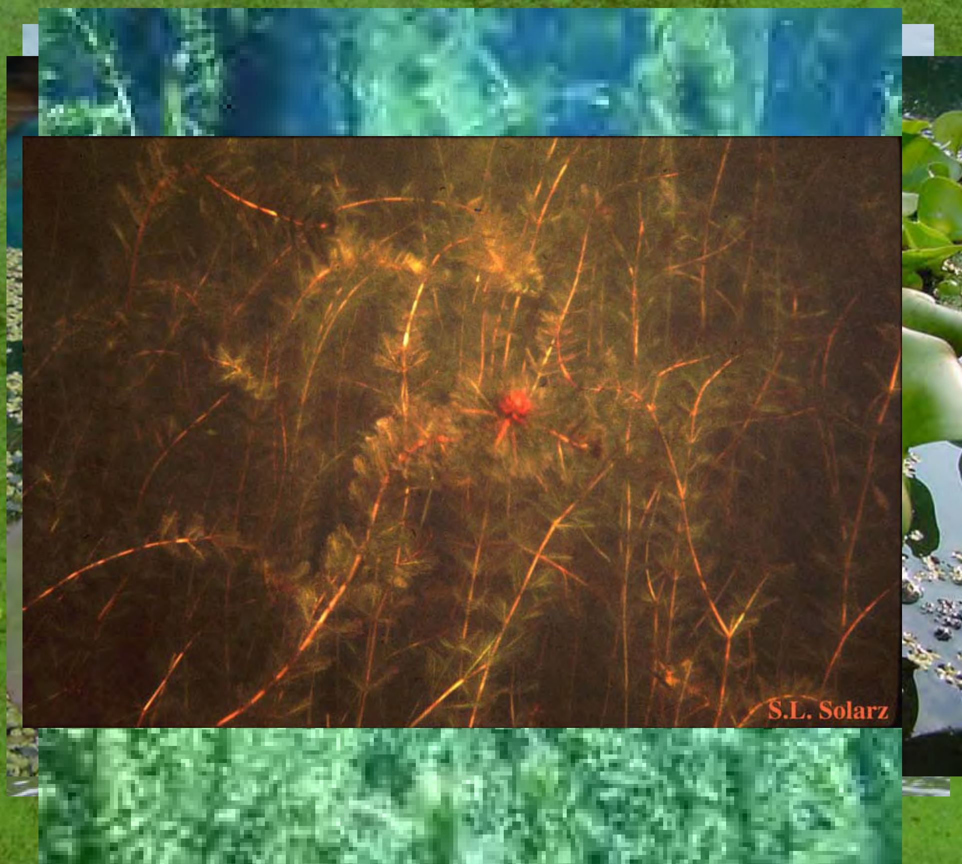
Why do we have problems?



- **Invasive and exotic species move at unprecedented rates.**
- **We have changed the landscape – e.g. canals, reservoirs, stormwater detention basins, etc.**
- **Human population increase – algae / plant - people interface.**
- **Changing climate – globally**
- **Pressure on water resources.**

Problems Caused by Vascular and Nonvascular (Algae) Plants

- Aesthetics
- Devalue property
- Disrupt transportation
- Taste and odor problems
- Impact fisheries and endangered species
- Impede irrigation
- Human health
- Interfere with water resource usages!

Problem or Not?

- **Aesthetics**
  (property value, tourism)
- **Alter Water Characteristics**
  (increase *p*H, decrease DO)
- **Taste and Odor Problems**
  (MIB, geosmin)
- **Hinder Recreational Activities**
  (swimming, fishing**)**
- **Toxin Production**
  (neurotoxins, hepatotoxins)


HEALTH ADVISORY
TOXIC ALGAE PRESENT IN THIS WATER.
NO Full Body Contact.
Avoid Ingesting Lake Water.
Monitor Small Children & Pets.
Avoid Concentrations of Algae.

Solutions for the problem

- **Risk assessment – problem or not?**
- **No decision / action vs. decision / action**
- **Consider all available options**
- **Implement viable option(s)**
- **Monitor results**
- **Modify approach if indicated**

Options for Remediation

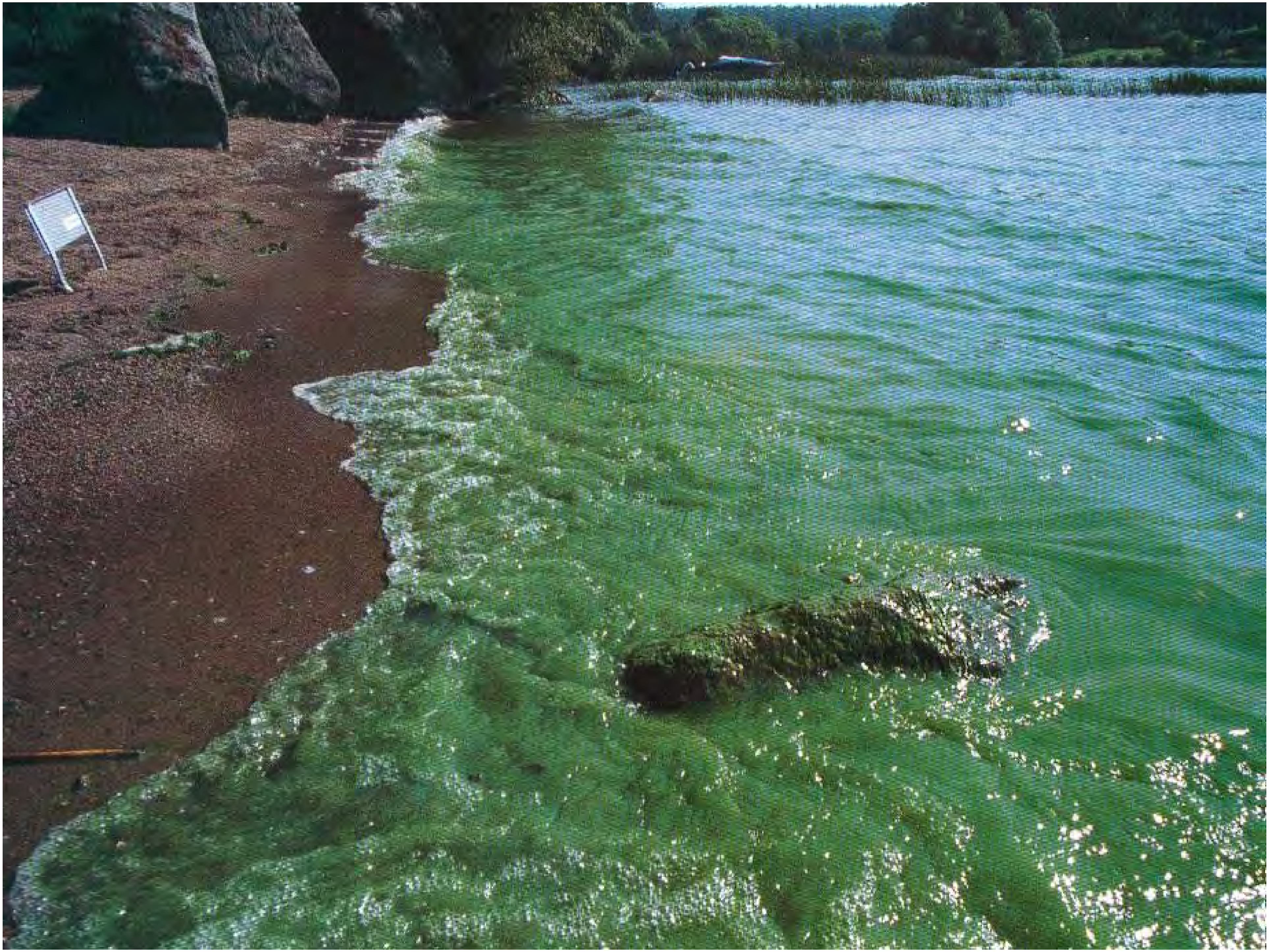
- **Physical**
  -dyes, aeration, precipitation

- **Mechanical**
  -rakes, filters, harvesters

- **Biological**
  -grass carp, filter feeding bivalves, insects

- **Chemical**
  -**Cu algaecides and herbicides**

Lyngbya wollei



Copper Fate Concerns / Questions?

- All copper is the same!
- Copper persists forever!
- Copper has a lithic biogeochemical cycle!
- Algaecide and herbicide applications are pulse exposures!
- All treatments are the same (area vs. whole lake treatments; application technique)!
- Copper partitions to cells and other ligands!

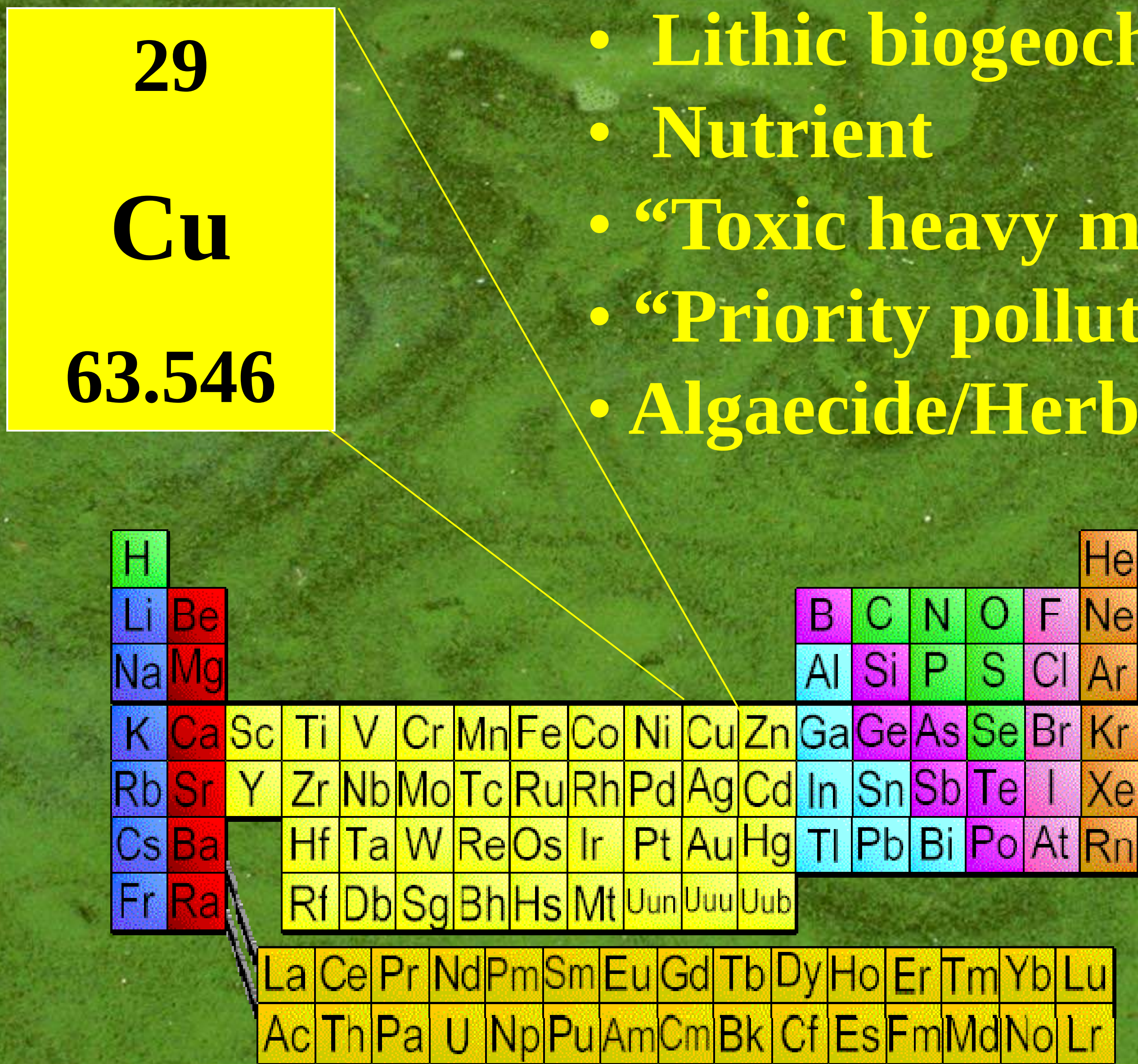
Copper <u>Effects</u> Concerns / Questions?

- Copper is an indiscriminant killer!
- Target species and assemblages vs. kill them all!
- Algae spill their guts – leaky cells happen!
- No margin of safety for nontarget species!
- Sensitive life stages and behaviors adversely affected (reproduction / spawning)!
- Copper bioconcentrates, bioaccumulates and biomagnifies!
- Algae become resistant to copper!

Copper Fate – All copper is the same!

Copper / Periodic Table

- Lithic biogeochemical cycle
- Nutrient
- "Toxic heavy metal"
- "Priority pollutant"
- Algaecide/Herbicide

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ONE CENT
CUTRINE-PLUS
ALGAECIDE/HERBICIDE

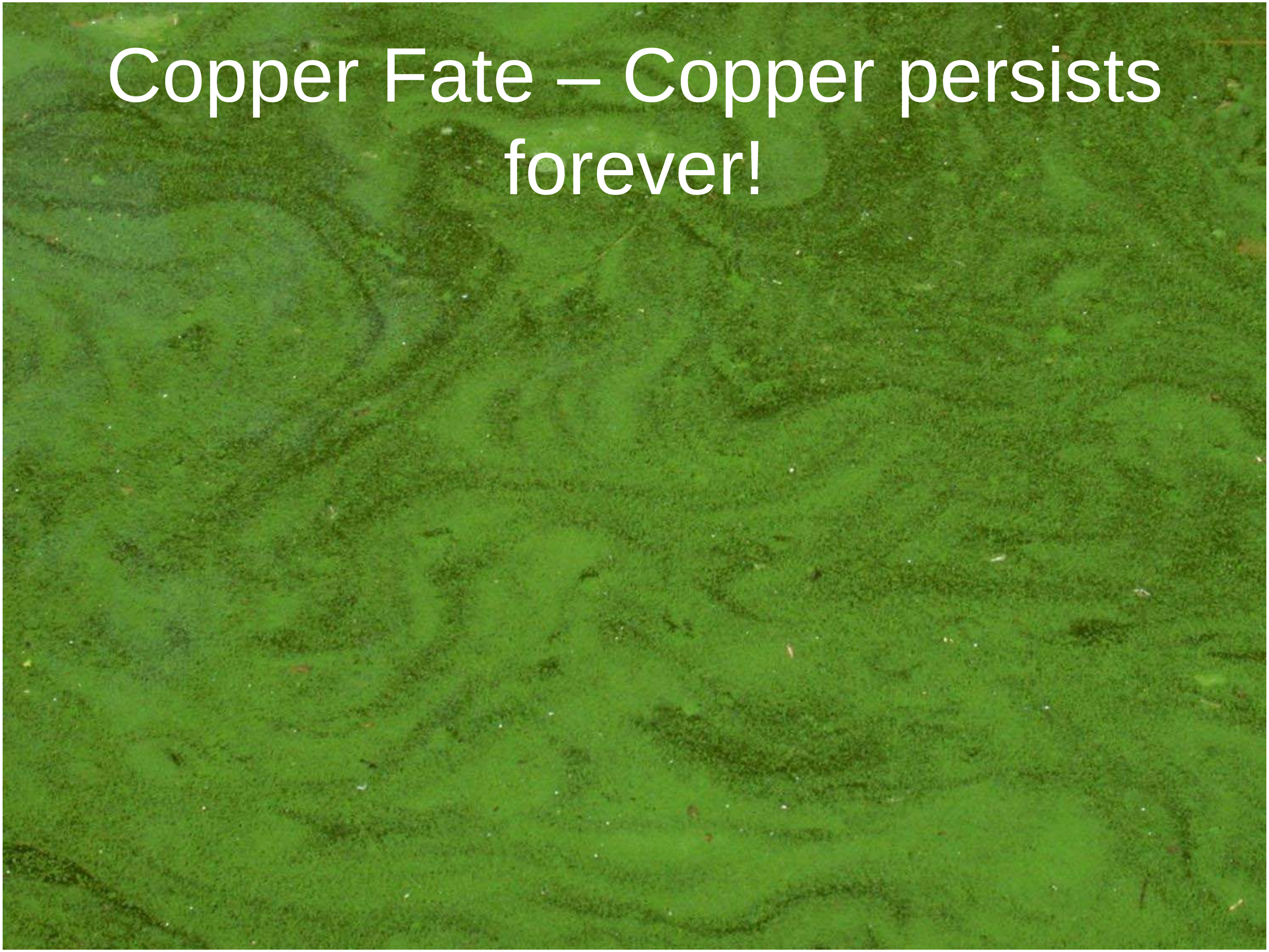
Copper sulfate

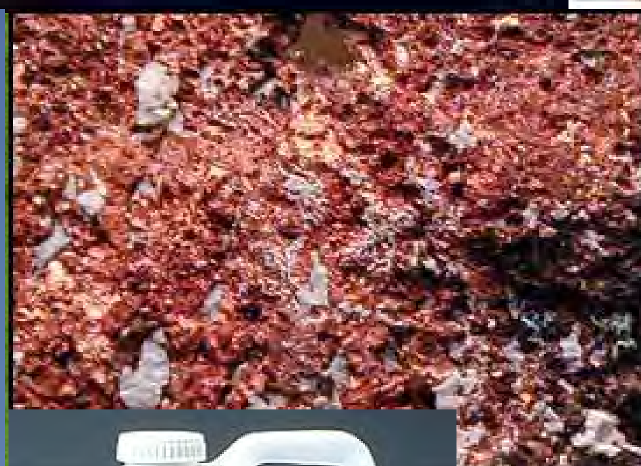
Copper-based Herbicides / Algaecides

Physical properties of Copper Sulfate Cutrine®-Plus, Cutrine®-Plus (Ultra), Algimycin ® and Clearigate.

	Copper Sulfate	Cutrine®-Plus	Cutrine® -Plus (Ultra)	Algimycin®	Clearigate®
% of Cu as elemental	25.4	9.0	9.0	5.0	3.8
Formulation	$CuSO_4 \bullet 5H_2O$	Copper ethanolamine complex	Copper triethanolamine complexes	Chelates of copper citrate and copper gluconate	Copper ethanolamine and D-limonene
Chemical class	copper salt	Chelated elemental copper (Cu_2CO_3)	Chelated elemental copper	Chelated copper	Chelated elemental copper (Cu_2CO_3)
Appearance	blue crystalline	blue viscous liquid	blue viscous liquid	blue viscous liquid	blue viscous liquid

Copper Fate – Copper persists forever!



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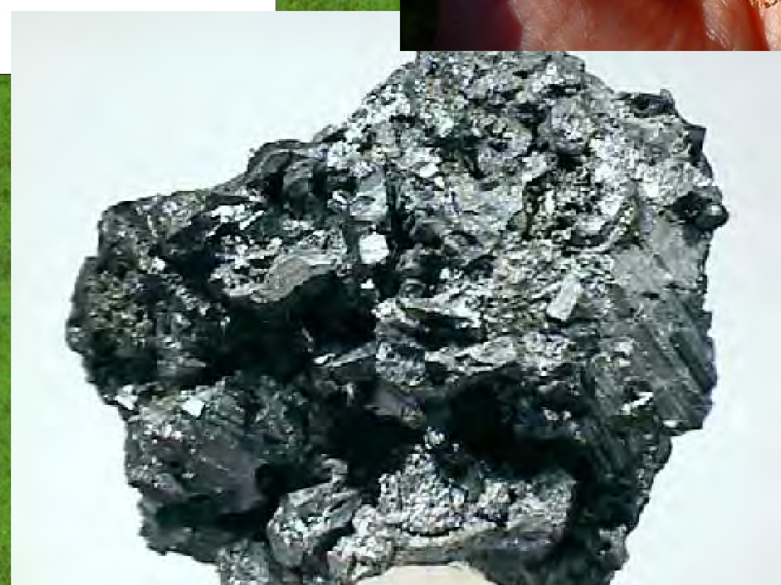
CUTRINE-PLUS
ALGAECIDE/HERBICIDE

Copper fate – Copper has a lithic biogeochemical cycle!

Copper Minerals



Copper Fate – Algaecide and herbicide applications are pulse exposures!

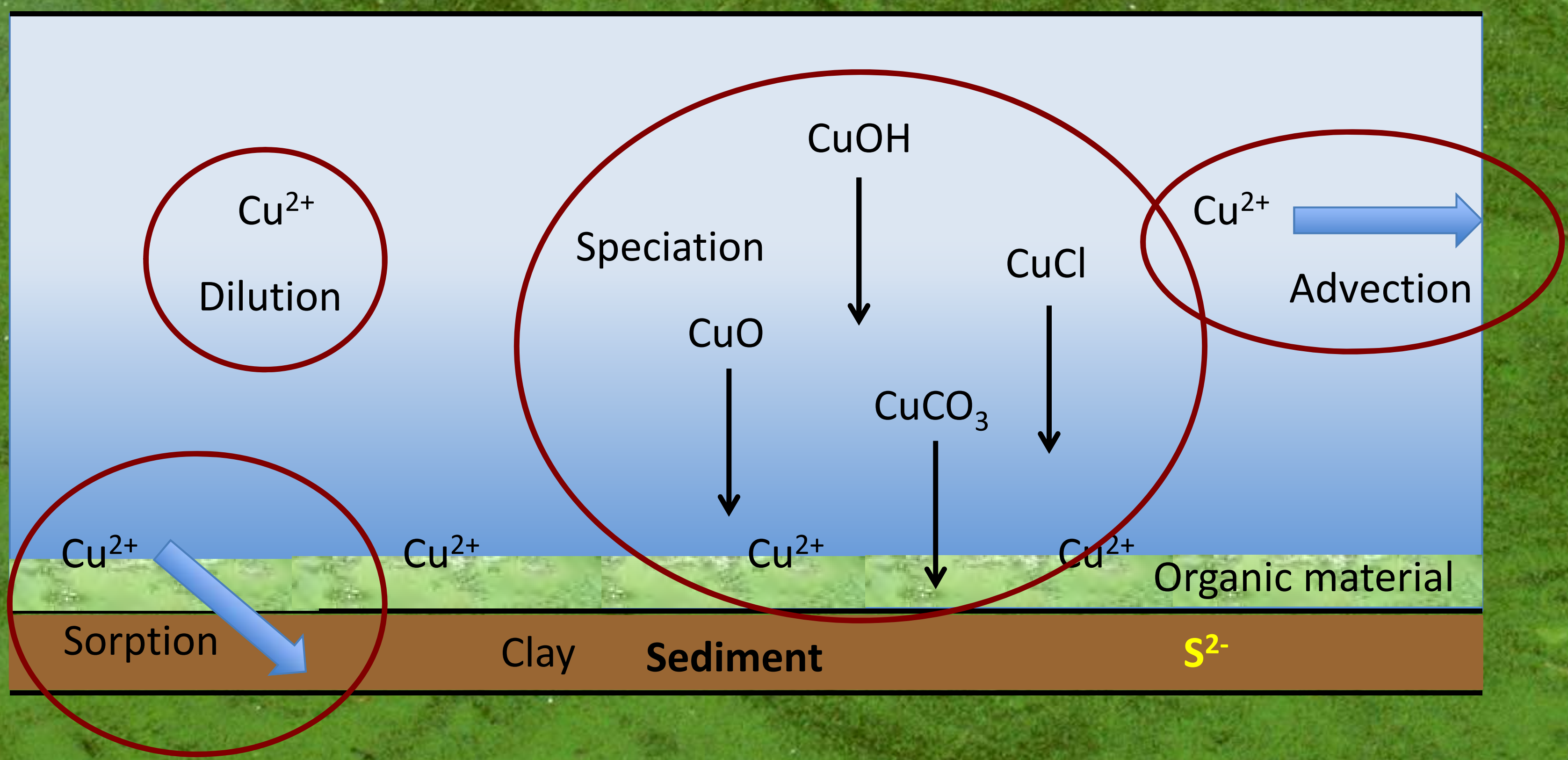

OCT
AL 1718 KF


OCT AL 1718 KF
G3
YAMAHA


ALABAMA
POWER
A SOUTHERN COMPANY

Copper Fate- All treatments are the same (area vs. whole lake treatments; application techniques)!

Copper in Aquatic Systems



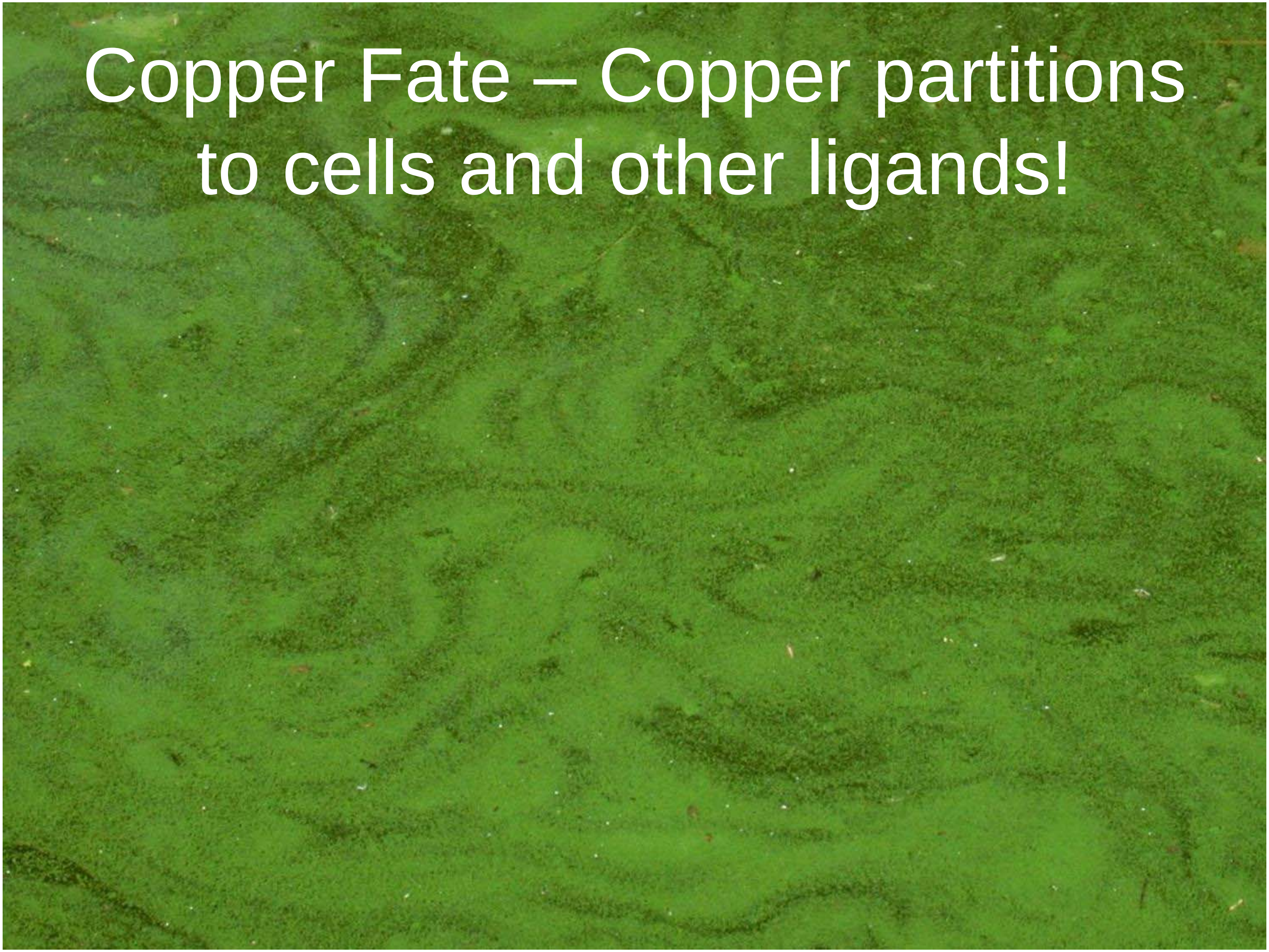
- Copper has a lithic biogeochemical cycle (US EPA 2006)
- Aqueous half-lives 1-7 days after application (Reinert and Rodgers 1987 and Murray-Gulde et al. 2002)

Copper Speciation

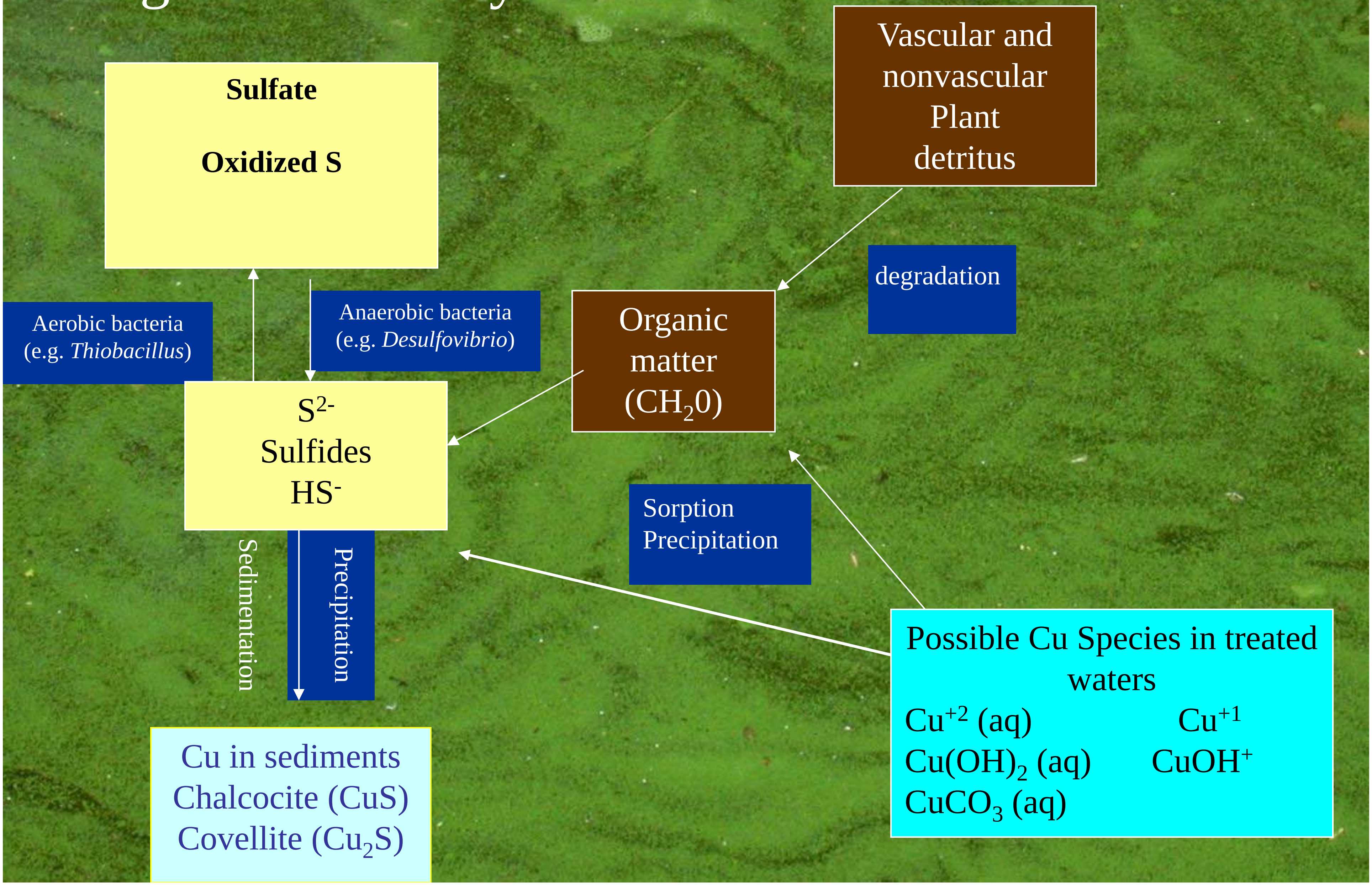
Several environmental factors influence speciation and bioavailability of copper in aquatic systems including:

- **pH**
- **alkalinity**
- **hardness**
- **ionic strength**
- **organic matter**
- **redox potential**

Copper Fate – Copper partitions to cells and other ligands!

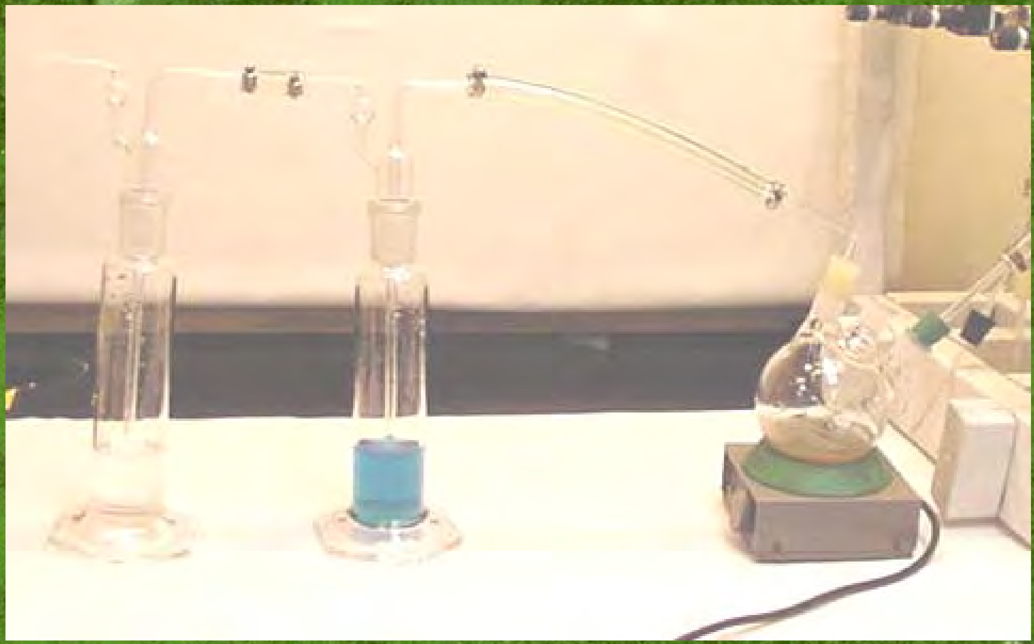


Coupling of copper, sulfur and carbon biogeochemical cycles



Acid Volatile Sulfides

Collect composite sediment samples from each wetland cell



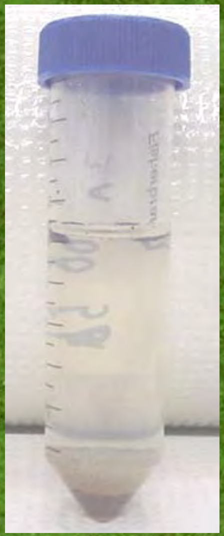
Digest 10 g sediment with 6M trace metal grade HCL

Collect Sulfides in 0.5M NaOH

Add Mixed Diamine Reagent and measure spectrophotometrically

Sequential Extractions

0.75g sediment sample



Shake sample 1-16 hr

Centrifuge sample

Collect supernate

Preserve with HNO_3 and analyze by AA

Rinse sample with DI

Centrifuge sample

Collect Rinse Supernate

Sequential Extractions

Soluble Fraction

⇩

Fraction 1: exchangeable – weakly sorbed

⇩

Fraction 2: bound to carbonates

⇩

Fraction 3: strongly bound to Mn and Fe oxides

⇩

Fraction 4: strongly bound to organic matter or other oxidizable species

⇩

Fraction 5: residual fraction

Hyalella azteca Toxicity Experiments

- 10-d static exposures
- 10 organisms/vessel
- Fed three 7-mm disks *Acer rubrum*
- Exposed to sediment samples collected from treated and untreated areas
- Water collected from untreated area used as overlying water

Copper in Sediments

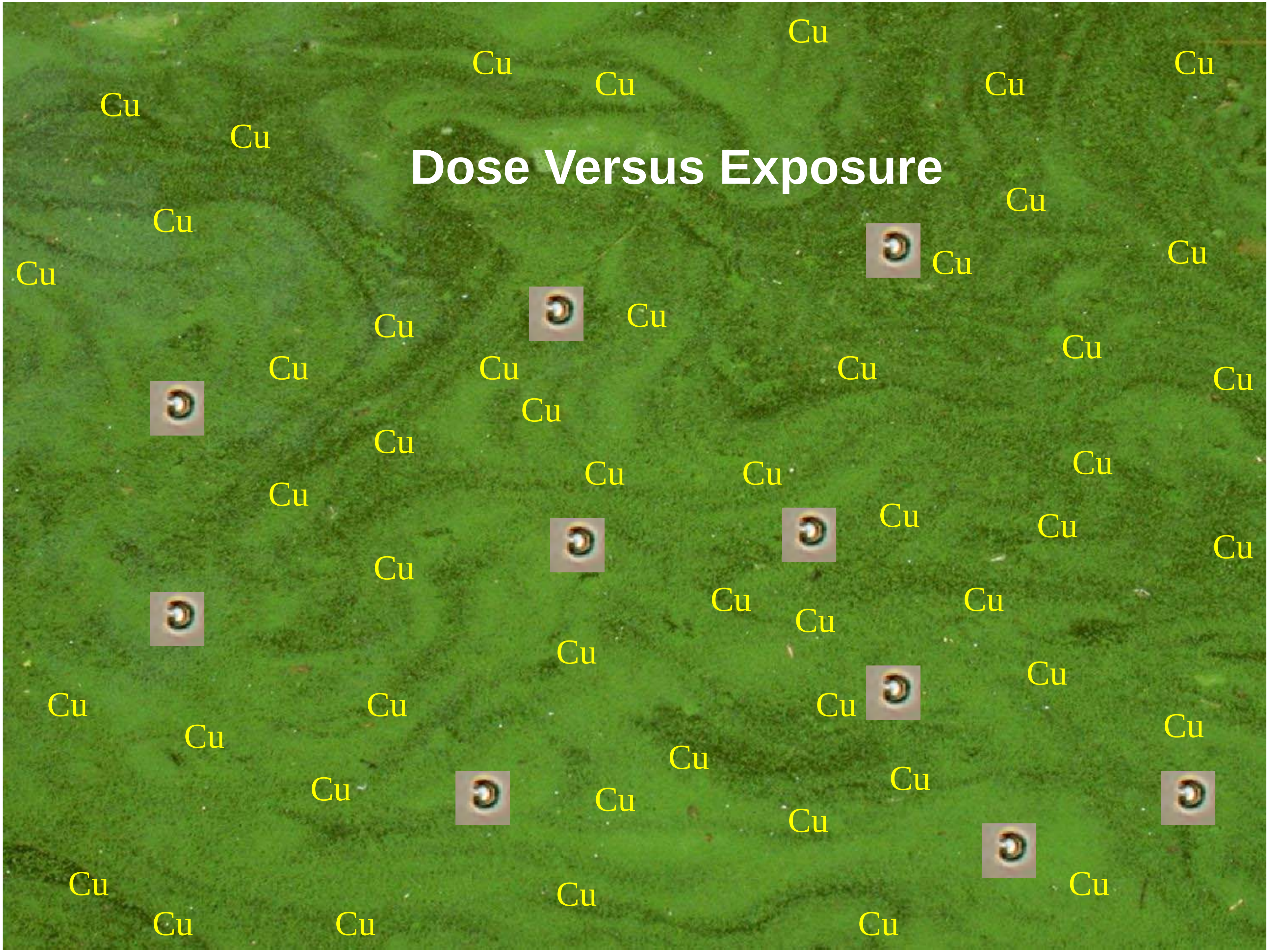
- found naturally in sediments and soils (~10-100 mg/kg)

In sediments that contain organic matter:

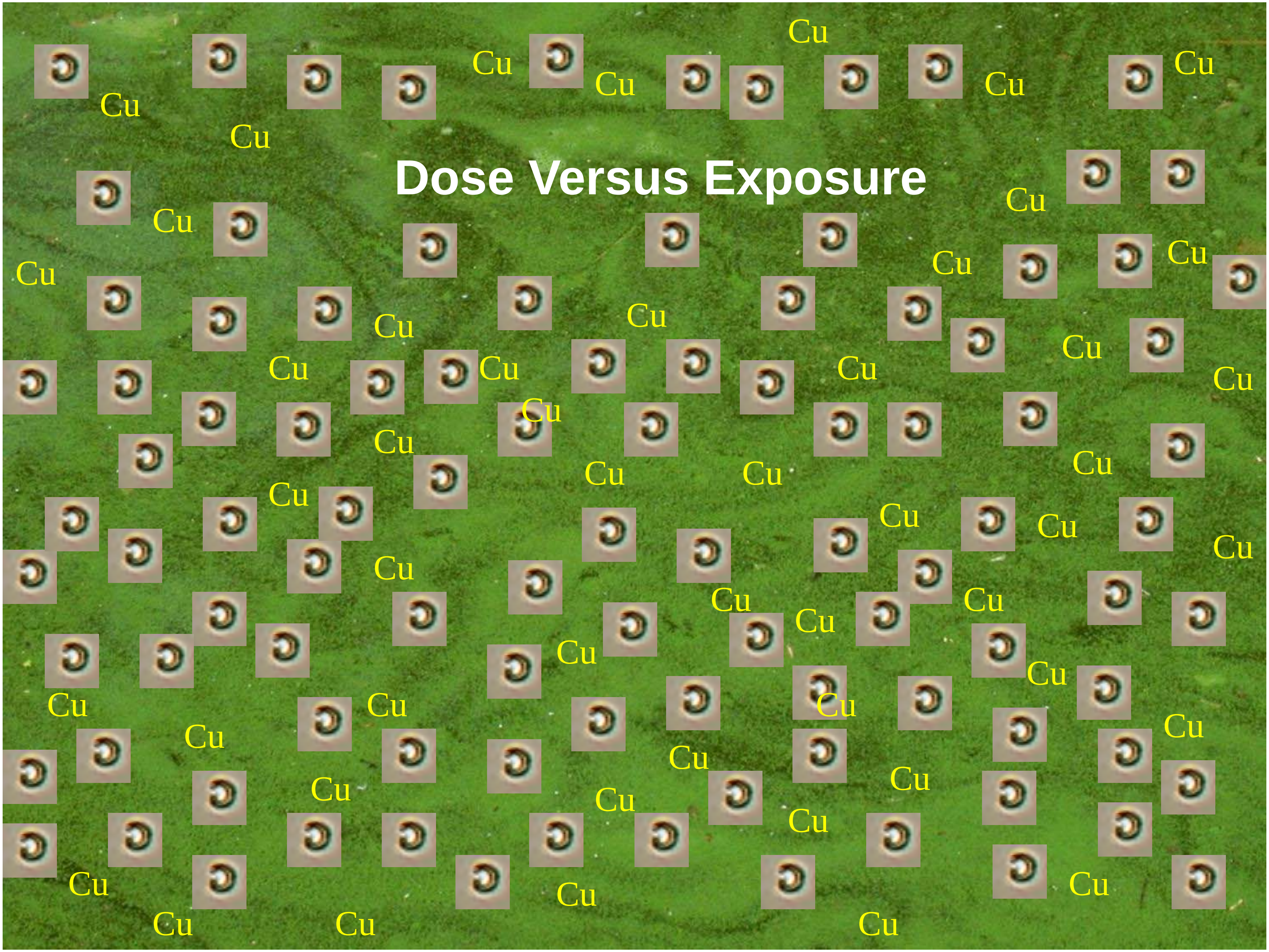
- bound Cu in sediments is generally not bioavailable to cause adverse effects on aquatic biota

Concentrations of Cu in sediments that can cause adverse effects are site dependent and can be best estimated through laboratory experimentation.

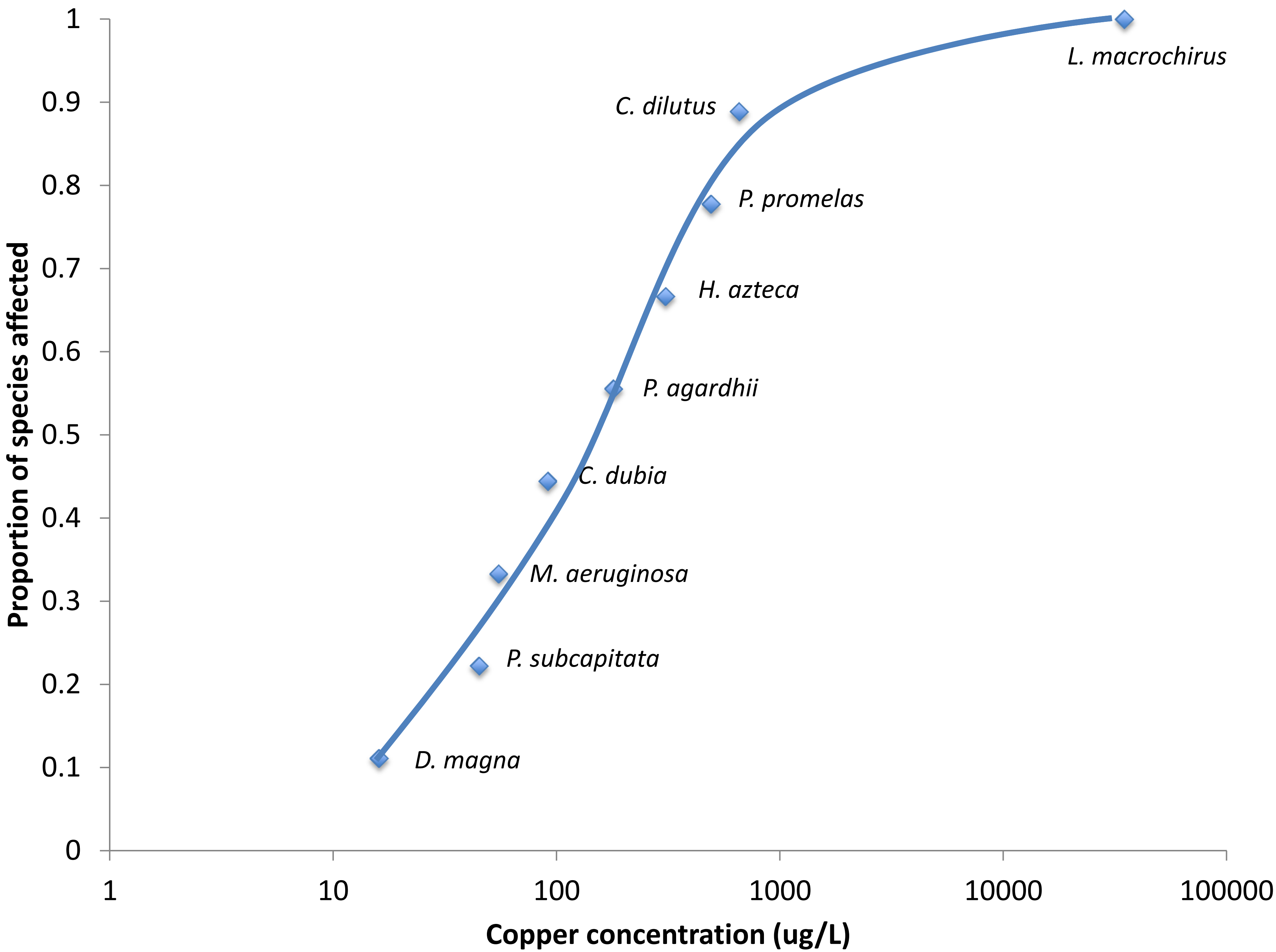
Dose Versus Exposure



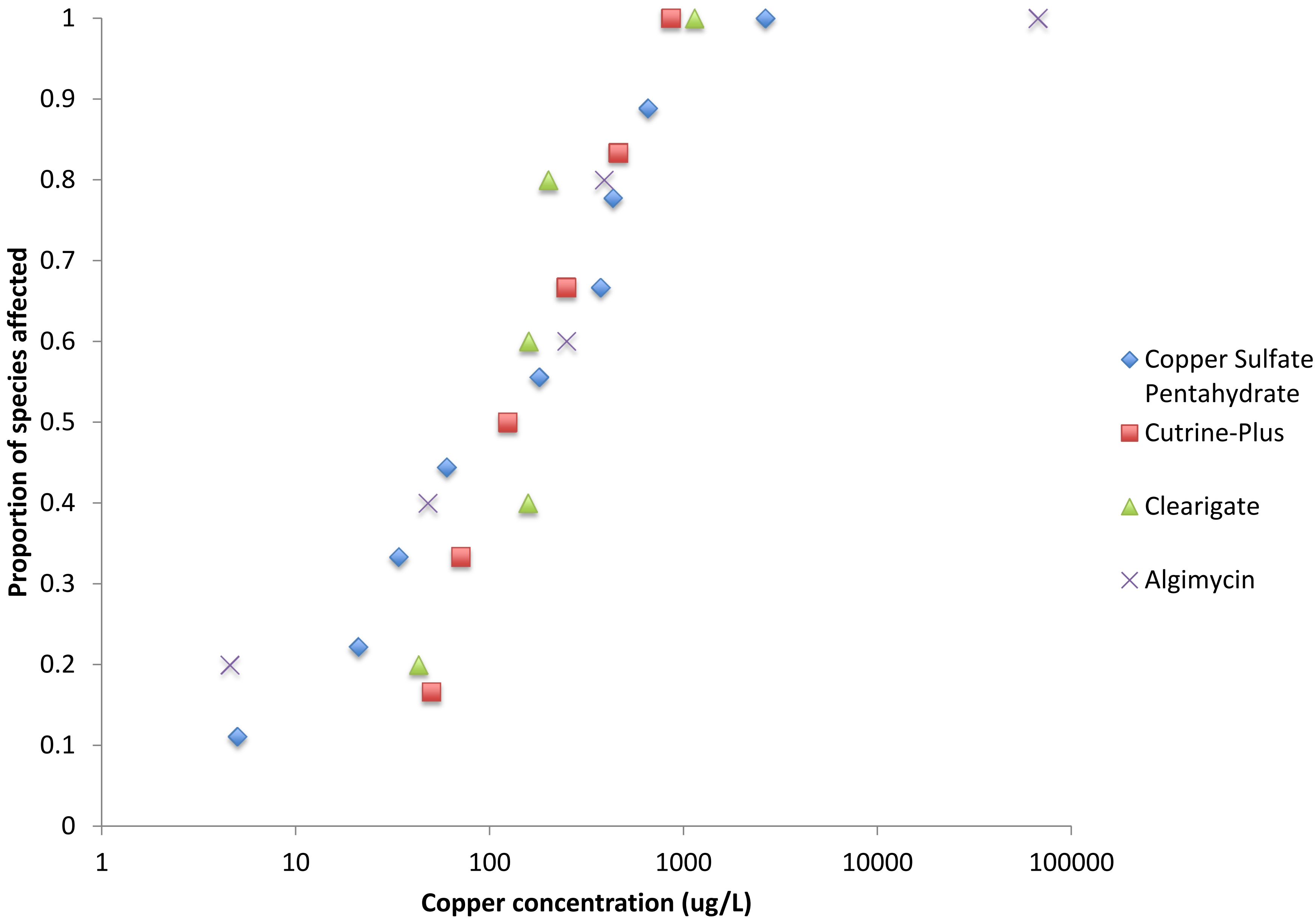
Dose Versus Exposure



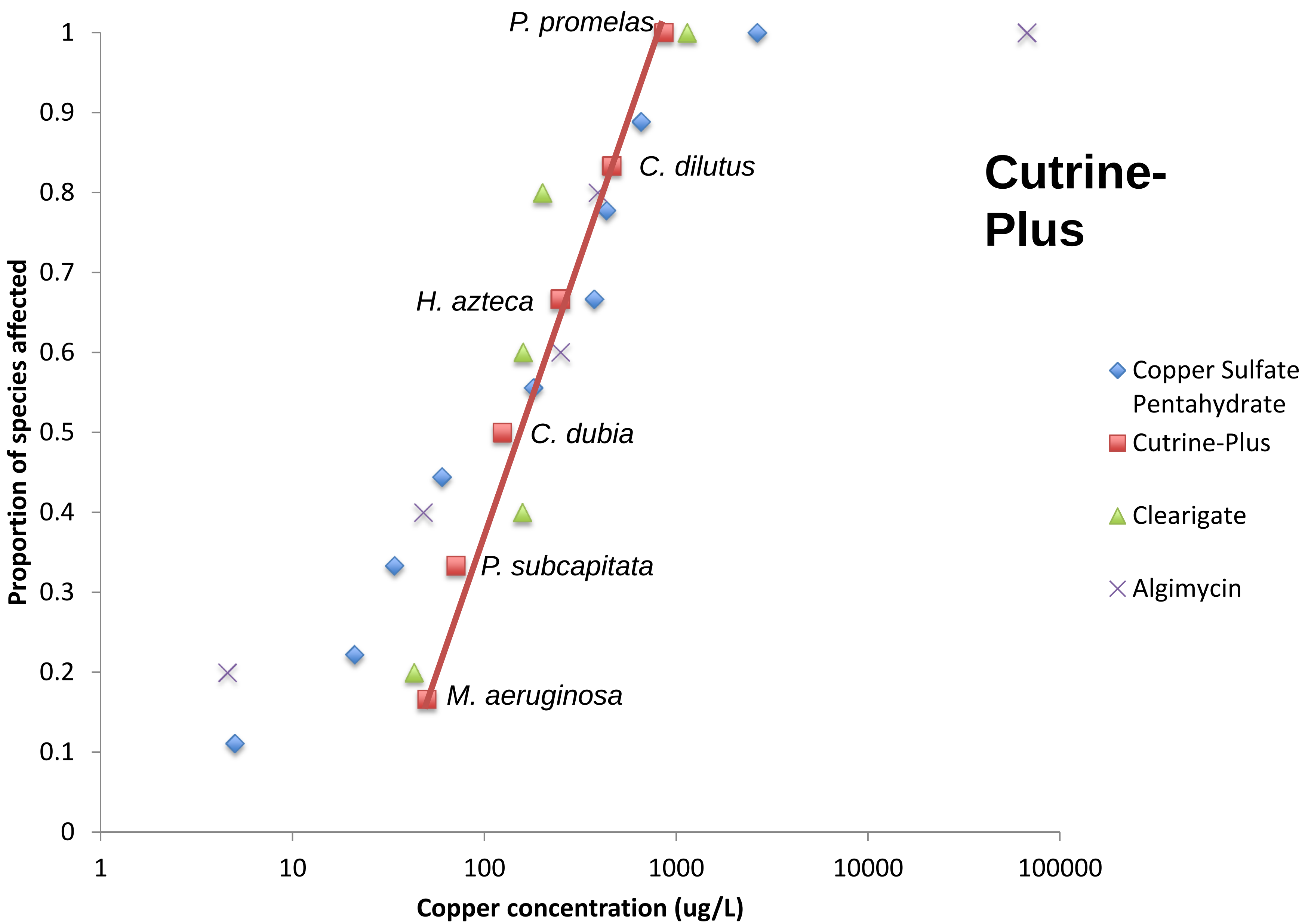
Copper Effects – Copper is an indiscriminant killer!

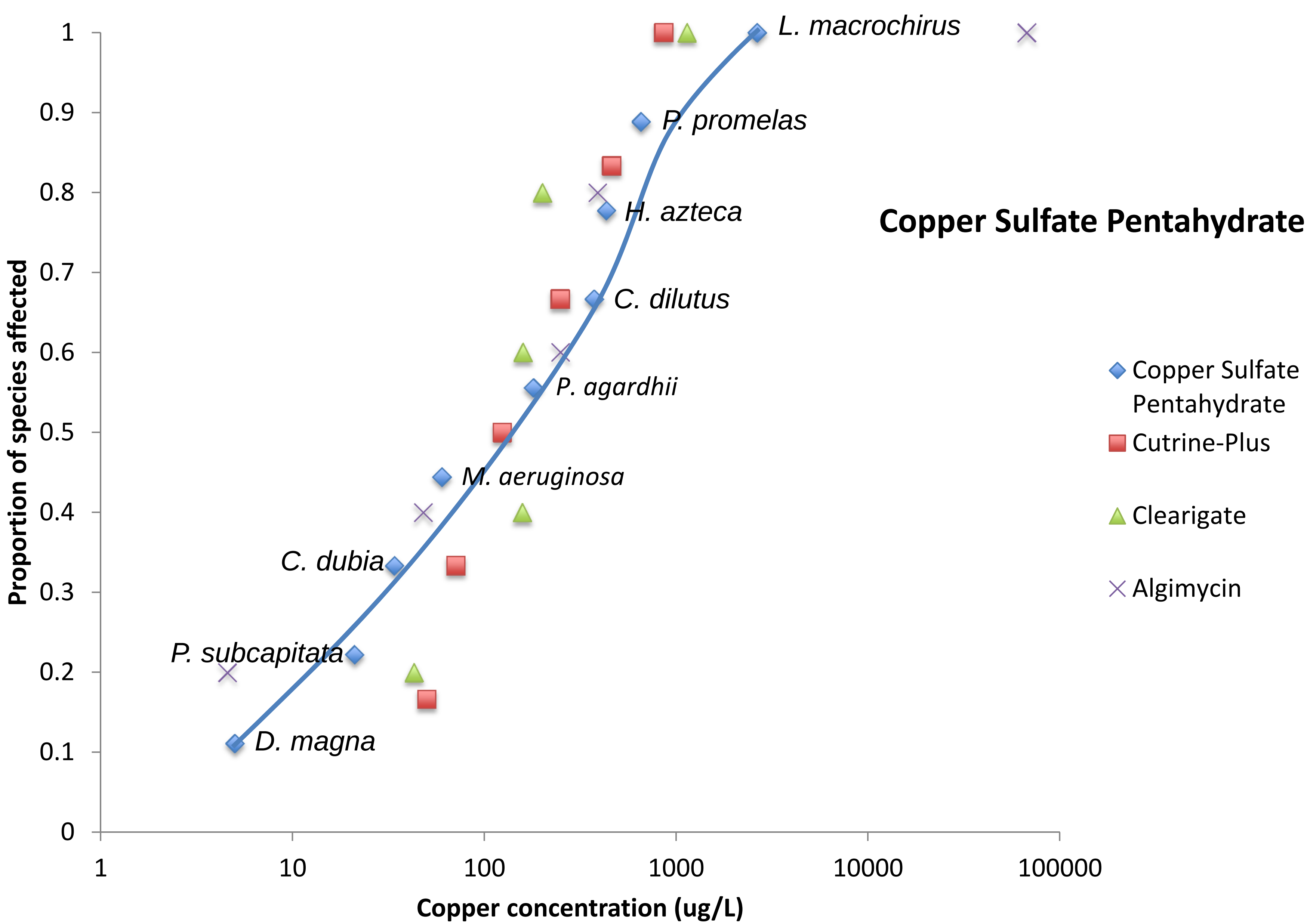


Proportion of species affected
Copper concentration (ug/L)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
10
100
1000
10000
100000
L. macrochirus
C. dilutus
P. promelas
H. azteca
P. agardhii
C. dubia
M. aeruginosa
P. subcapitata
D. magna

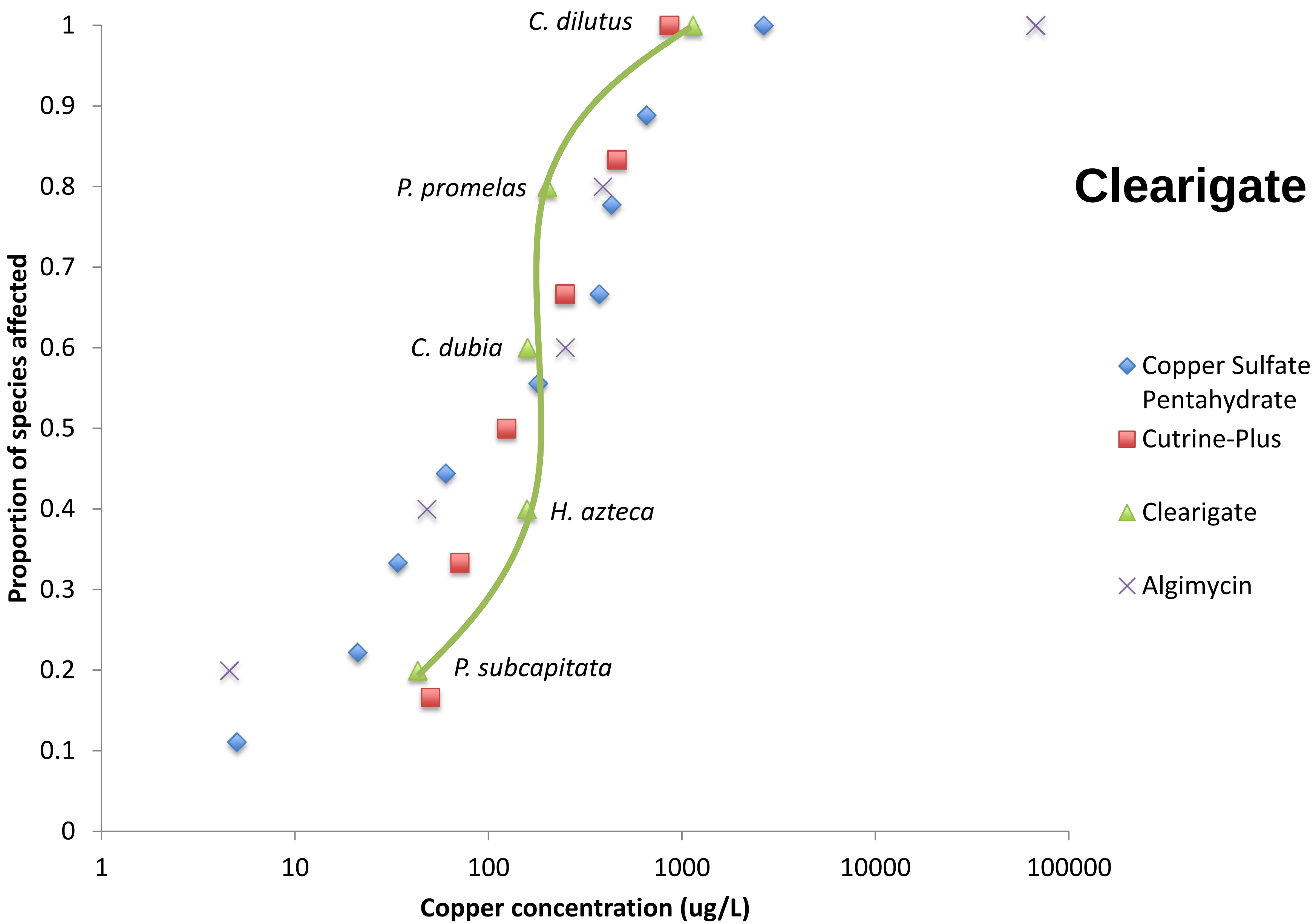


1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Proportion of species affected
1
10
100
1000
10000
100000
Copper concentration (ug/L)
Copper Sulfate Pentahydrate
Cutrine-Plus
Clearigate
Algimycin

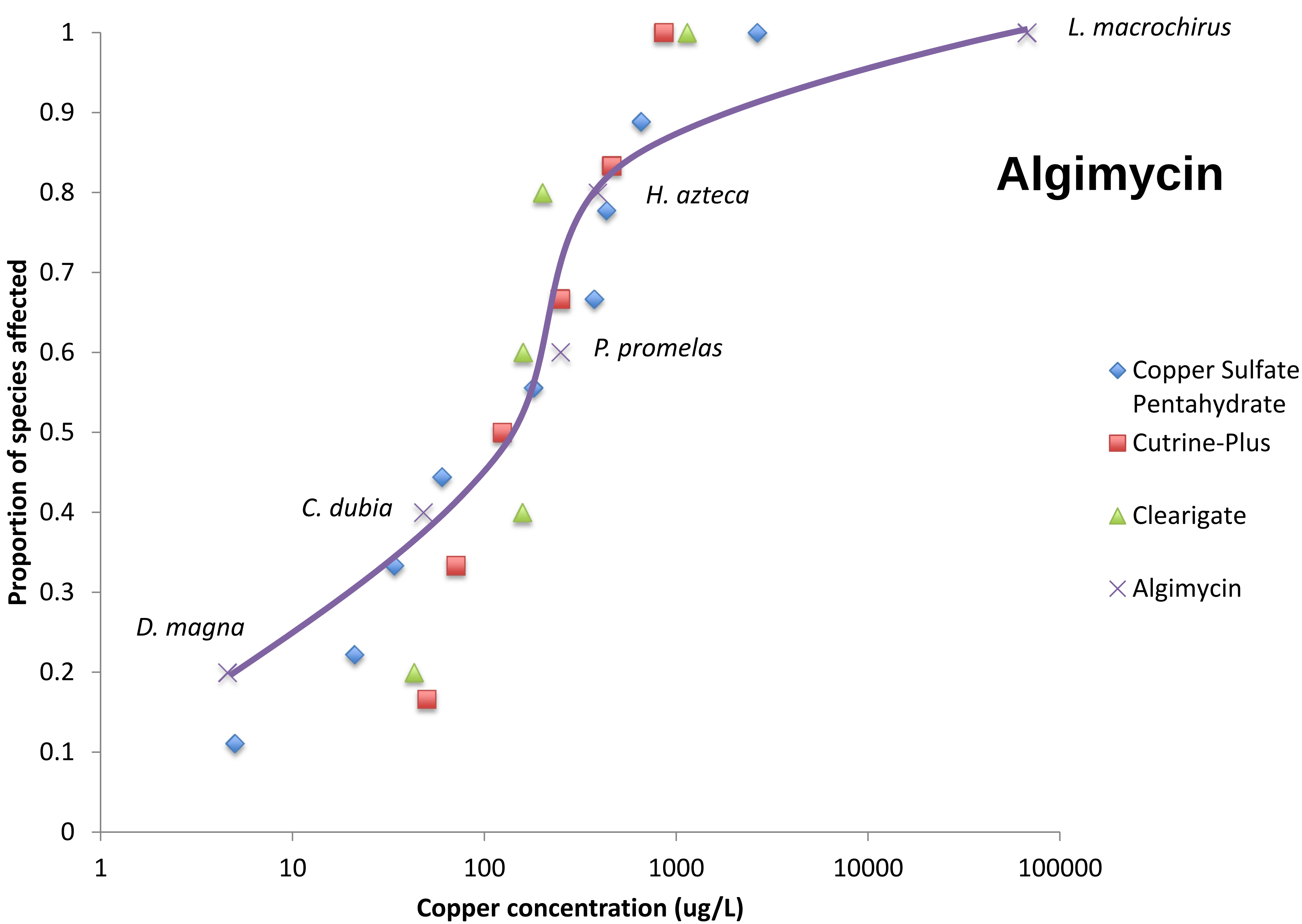

Cutrine-Plus
P. promelas
C. dilutus
H. azteca
C. dubia
P. subcapitata
M. aeruginosa
Proportion of species affected
Copper concentration (ug/L)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1
10
100
1000
10000
100000
Copper Sulfate Pentahydrate
Cutrine-Plus
Clearigate
Algimycin



Copper Sulfate Pentahydrate
Proportion of species affected
Copper concentration (ug/L)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
10
100
1000
10000
100000
L. macrochirus
P. promelas
H. azteca
C. dilutus
P. agardhii
M. aeruginosa
C. dubia
P. subcapitata
D. magna
Copper Sulfate Pentahydrate
Cutrine-Plus
Clearigate
Algimycin



Clearigate
Proportion of species affected
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
10
100
1000
10000
100000
Copper concentration (ug/L)
C. dilutus
P. promelas
C. dubia
H. azteca
P. subcapitata
Copper Sulfate Pentahydrate
Cutrine-Plus
Clearigate
Algimycin



Algimycin
L. macrochirus
H. azteca
P. promelas
C. dubia
D. magna
Proportion of species affected
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1
10
100
1000
10000
100000
Copper concentration (ug/L)
Copper Sulfate Pentahydrate
Cutrine-Plus
Clearigate
Algimycin

Considerations for using Copper Formulations as Algaecides/Herbicides

- margin of safety for nontarget aquatic species
- copper residence time in the water column
- the amount of copper that gets to algal cells or tissues of vascular plants
- quality control in production
- no human health risks with copper formulations when used according to label instructions

Copper Effects – Target species and assemblages vs. kill them all!

Algal Challenge “Test”

Water Sample →

Grow Algae →

“Challenge” Algae →

Observe Response →

Specific Recommendation


POND 3
2-27-02
Pond 4
2/27/02
POND
4
Control
A
Ctrl
A
POND
3


POND
4
A
POND
4
Cutrine
-Plus
1PPM
A
POND
4
1PPM
A
4
1PPM
B

Animal Species

Ceriodaphnia dubia

Pimephales promelas

Monitor Results

Measure:

- **Chlorophyll *a***
- **Mass (biomass)**
- **Density**
- **Oxygen production**
- **Respiration**
- **Responses of non-target species**
- **Residues**

Modify approach if indicated

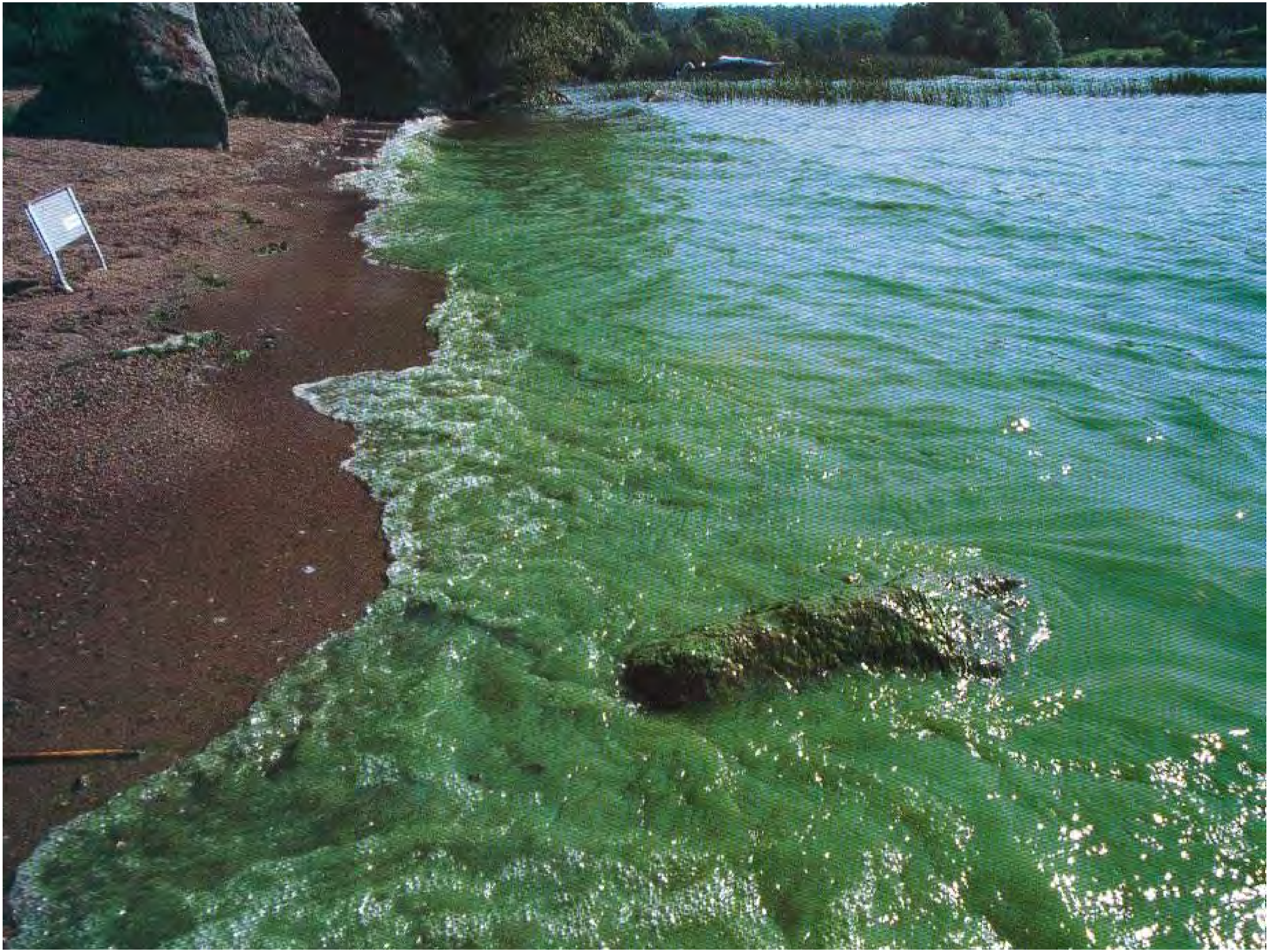
Copper Effects – Algae spill their guts / leaky cells happen!

“Leaky Cell” Hypothesis

- **Algae release intracellular contents (toxins) following exposure.**
  - **Copper sulfate, Algaecide (Coptrol®); water treatment chemicals (i.e. Chlorine, $KMnO_4$, $AlSO_4$, H_2O_2).**
- **Release following exposure not universal(?); however universally applied.**
  - ***Lyngbya*, *Cylindrospermopsis*, ***Microcystis*.**

Microcystin Producers

- ***Microcystis spp.***
- ***Anabaena spp.***
- ***Oscillatoria spp.***
- ***Planktothrix spp.***
- ***Nostoc spp.***
- ***Hapalosiphon spp.***
- ***Anabaenopsis spp.***



Kenefick *et al.*, 1993

- *Microcystis* concentrated from Coal Lake
- Unreplicated treatments (10.7 L) in the laboratory
- Copper sulfate at "higher chemical doses than commonly used in the treatment of surface waters." (unspecified concentrations)
- Laboratory culture
- Microcystin released?

Jones and Orr, 1994

- **“Copper-based algicides lyse cyanobacterial cells.”**
- ***Microcystis aeruginosa*** **– reservoir in Australia**
- **Microcystin concentration – 1,300 – 1,800 ug/L**
- **Algaecide treatment – Coptrol - “spot sprayed”**
- **Algae controlled 2-3 days after treatment.**
  - **“This is the first report of measurement *in situ* release and degradation of cyanobacterial microcystin following algicide treatment.”**

Peterson *et al.*, 1995

- *Aphanizomenon flos-aquae* in culture medium (steady state)
- Treated with chlorine, potassium permanganate, aluminum sulfate, ferric chloride, calcium hydroxide, hydrogen peroxide, copper sulfate.
- Ferric chloride, copper sulfate and potassium permanganate at high concentrations caused cell membrane damage, dissolved organic carbon release, and geosmin release.

Daly, Ho and Brookes, 2007

- *M. aeruginosa* cultured in laboratory
- Exposed to chlorine (8 – 20 mg/L)
- “Chlorine causes intact cells to lyse releasing intracellular toxin into solution.”
- “The soluble toxin (microcystin) can be destroyed by chlorine.”

Touchette, Edwards and Alexander, 2008

- **Samples of *Anabaena* and *Microcystis* evaluated in the laboratory.**
- **Treated with $CuSO_4$ and PAK-27 (SCP) at 0.15, 1.5 and 5.0 mg /L.**
- **Up to 1.8 ug microcystin/L was released in Cu treatments; measured release in PAK-27 up to 1.3 ug/L.**
- **“It is critical that cyanobacterial blooms be approached with caution when applying chemical treatments.”**

Pawnee Reservoir, NE

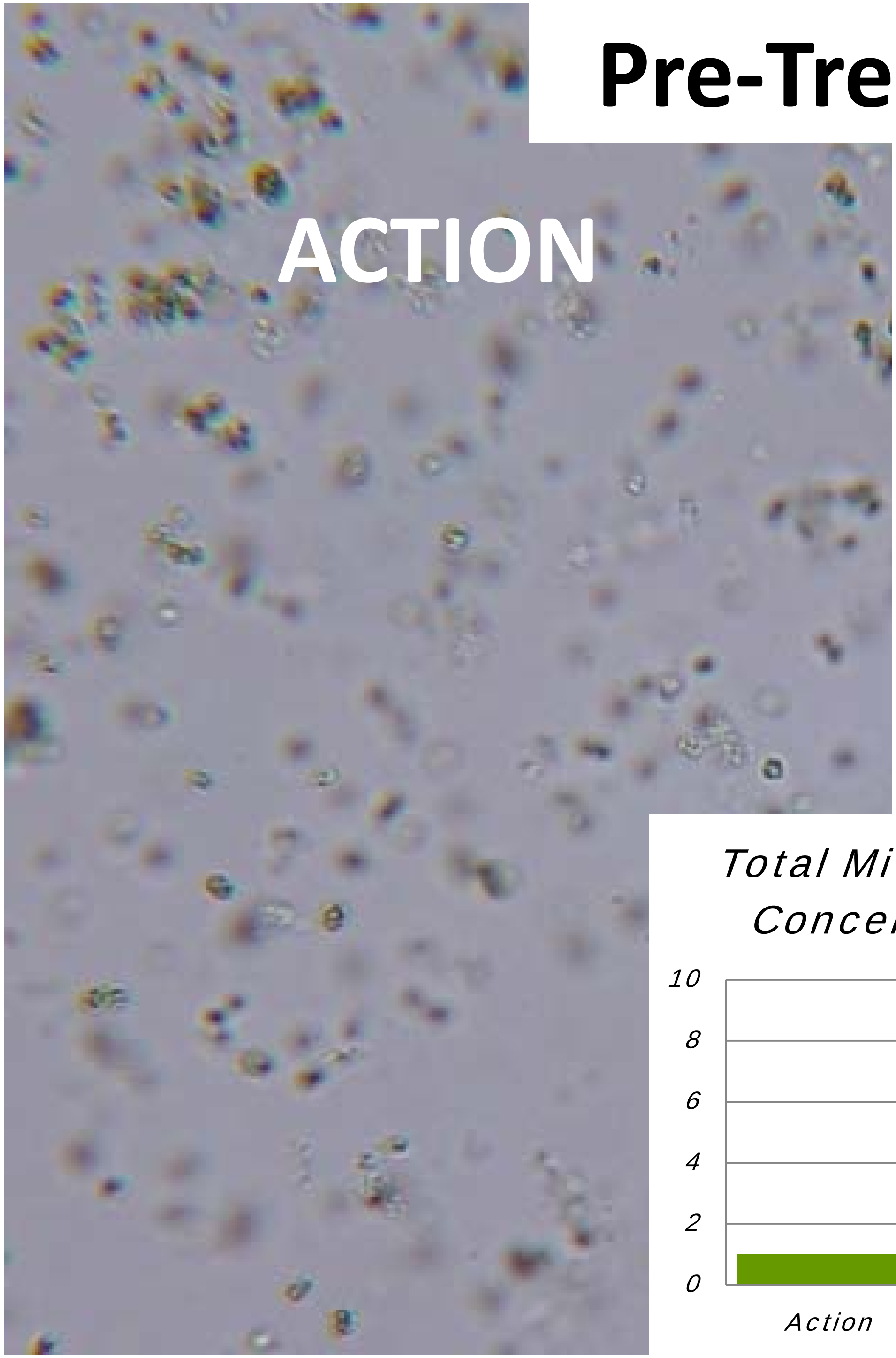
Pawnee Reservoir, NE June 2006

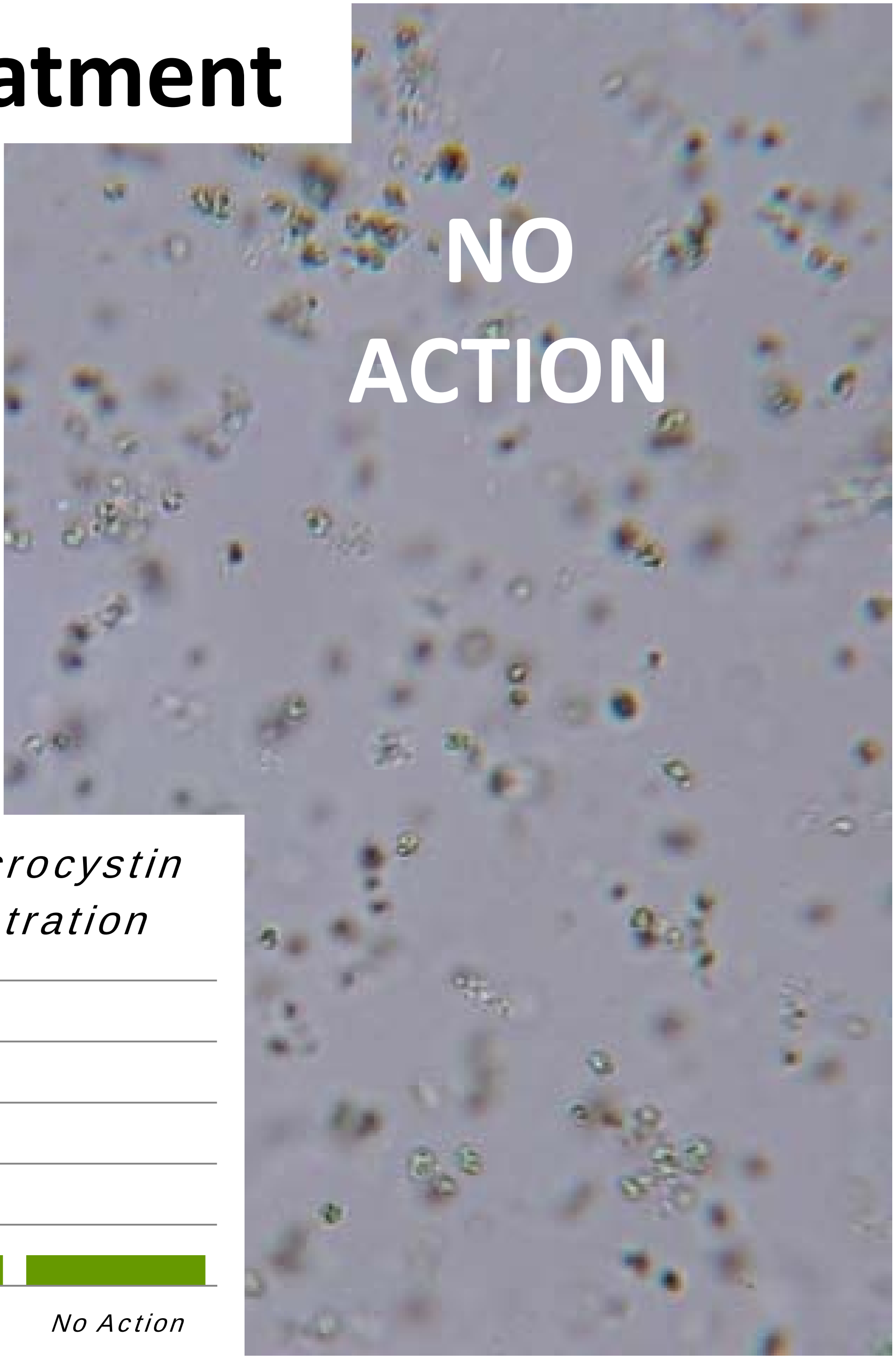
Treatment - 8 June 2006

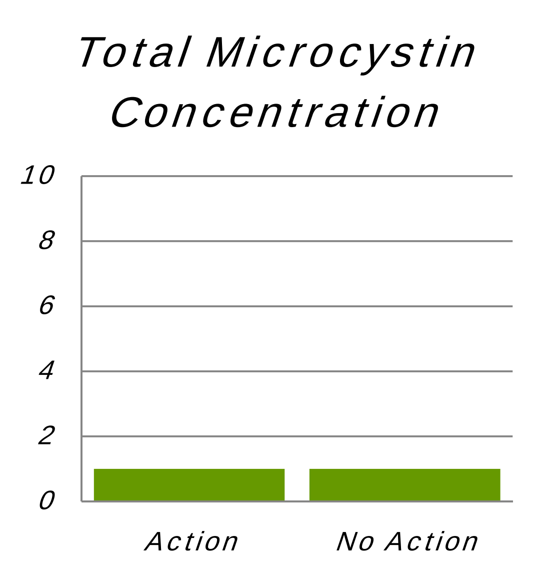
Cutrine - Ultra

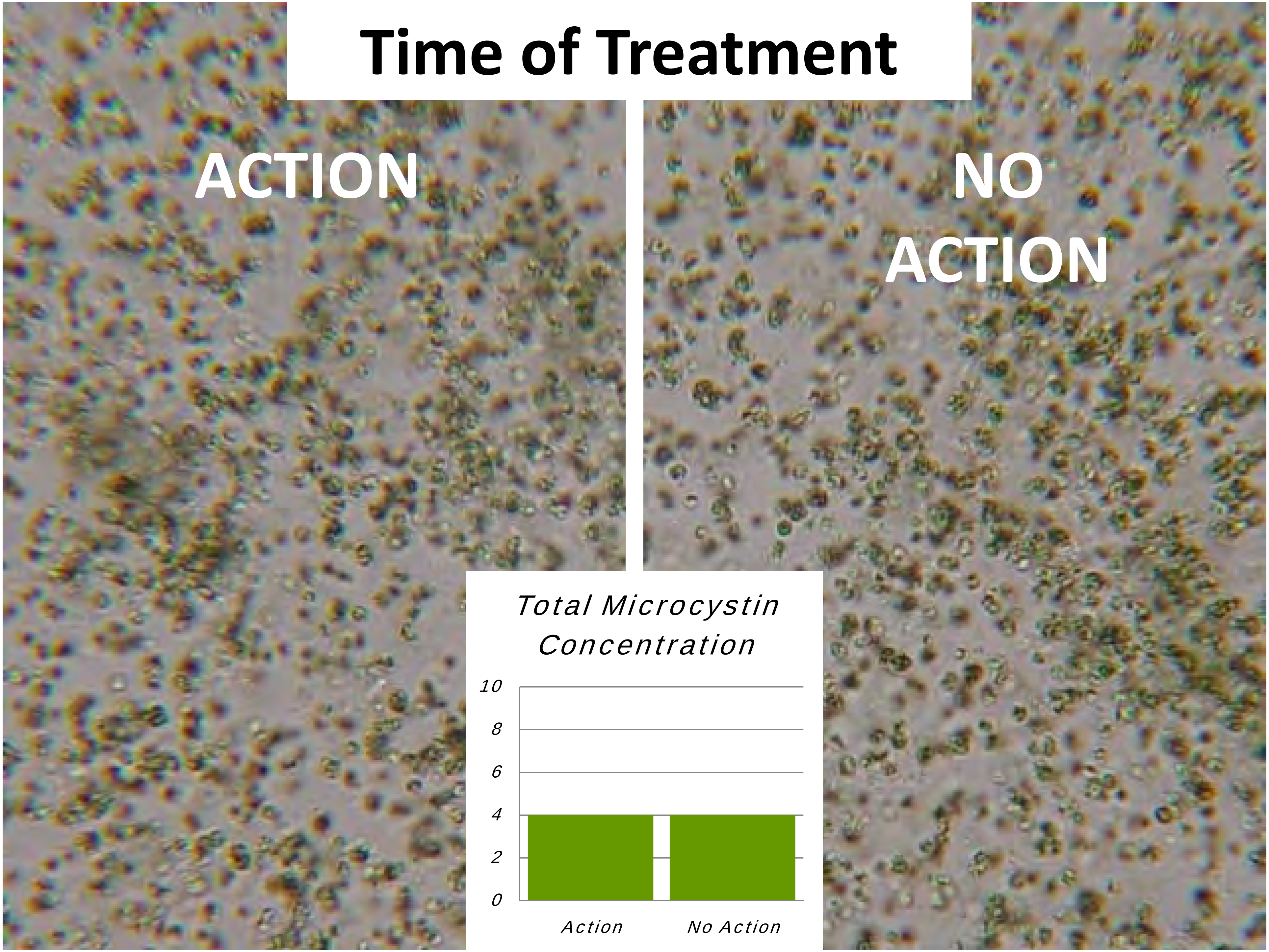
Pawnee Reservoir, NE
Post -Treatment

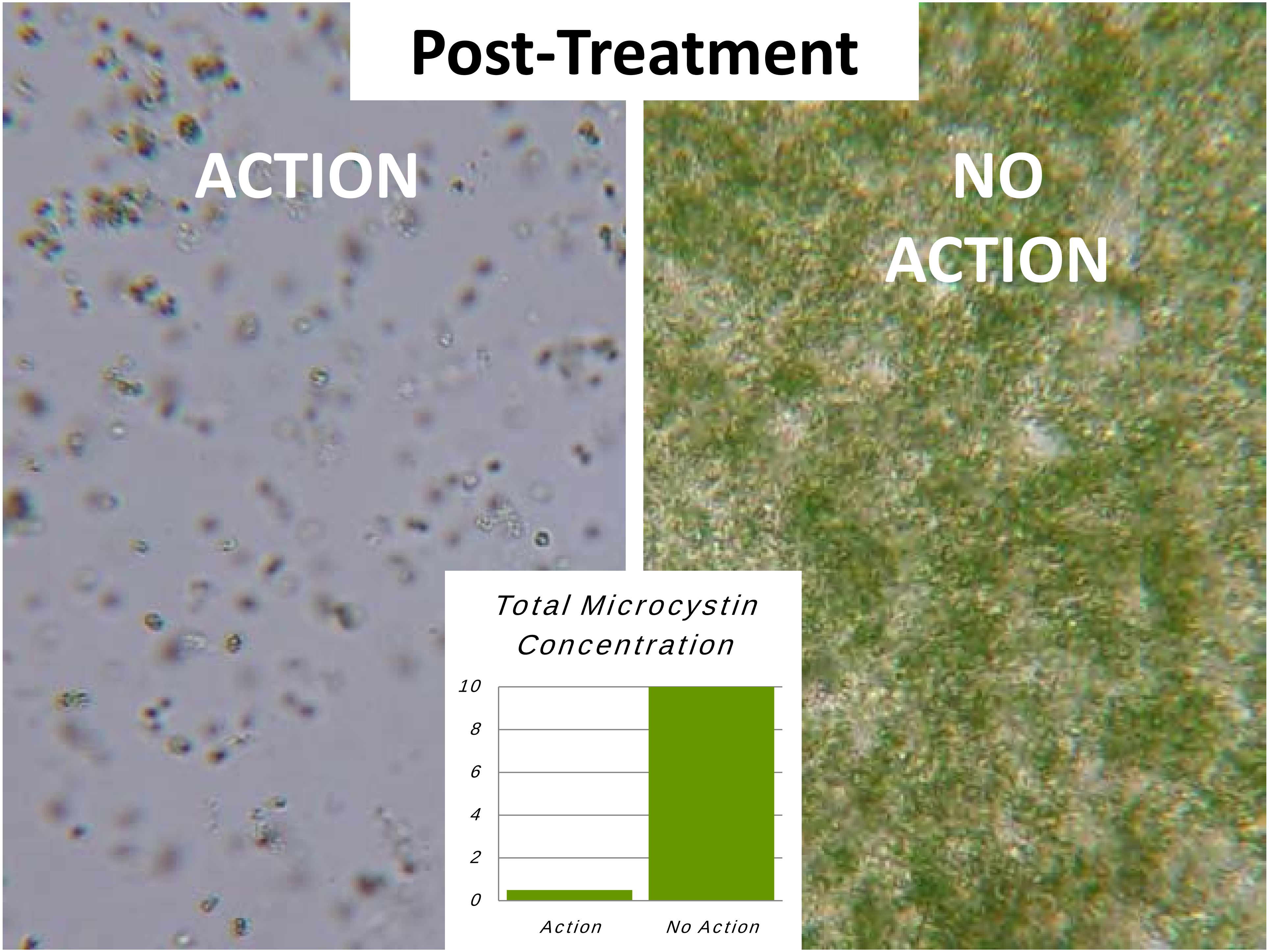
Pre-Treatment








Time of Treatment
ACTION
NO ACTION
Total Microcystin Concentration
10
8
6
4
2
0
Action
No Action



Post-Treatment
ACTION
NO ACTION
Total Microcystin Concentration
10
8
6
4
2
0
Action
No Action

Discussion/Conclusions

1. “Leaky cell” hypothesis is not generally applicable.
2. Even if treated cells leak toxins, risks can be avoided by treating before cell densities and toxin concentrations are excessive.
3. The decision and responsibility involves relative risk and site specific considerations.

- **Kenefick, S.L., S.E. Hrudey, H.G. Peterson, and E.E. Prepas. 1993. Toxin release from *Microcystis aeruginosa* after chemical treatment. Wat. Sci. Tech. 27(3-4): 433-440.**

- **Jones, G.J., Orr, P.T. 1994. Release and degradation of microcystin following algicide treatment of a *Microcystis aeruginosa* bloom in a recreational lake, as determined by HPLC and protein phosphatase inhibition assay. Water Research 28(4), 871-876.**

- **Peterson, H.G.; Hrudey, S.E.; Cantin, I.A.; Perley, T.R.; Kenefick, S.L. 1995. Physiological toxicity, cell membrane damage and the release of dissolved organic carbon and geosmin by *Aphanizomenon flos-aquae* after exposure to water treatment chemicals. Water Research 29(6), 1515-1523.**

- Daly, R.I., L. Ho, and J.D. Brookes. 2007. Effect of Chlorination on *Microcystis aeruginosa* Cell Integrity and Subsequent Release and Degradation. Environ. Sci. Technol. 41: 4447-4453.

- Touchette, B.W., C.T. Edwards and J. Alexander. 2008. A comparison of cyanotoxin release following bloom treatments with copper sulfate or sodium carbonate peroxyhydrate. In: H.K. Hudnell (ed.) Cyanobacterial Harmful Algal Blooms: State of the Science and Research Needs.Springer: New York. Pp.314-315.

Copper Effects – No margin of safety for nontarget species!

Copper Effects – Sensitive life stages and behavior adversely affected (reproduction / spawning)!

Copper Effects on Fish Spawning and Reproductive Success

- Limited Data from Field Studies

Field Studies - Herbicide Effects

- Maceina, M.J. and J.W. Slipke. 2004. The use of herbicides to control Hydrilla and the effects on young largemouth bass population characteristics and aquatic vegetation in Lake Seminole, Georgia. J. Aquat. Plant Manage. 42: 5-11.
- Sammons, S.M. and M.J. Maceina. 2005. Effect of Aquathol K treatments on activity patterns of largemouth bass in two coves of Lake Seminole. Georgia. J. Aquat. Plant Manage. 43: 17-24.
- Maceina, M.J. 2009. Spraying during the spawn. Bass Times: April 17, 2009. 3 pp.

Field Studies - Herbicide Effects

- Maceina, M.J. et al. 2015. Angling effort on an embayment of Lake Guntersville, Alabama, before and after herbicide application. J. Aquat. Plant Manage. 53: 141-143.
- Maceina, M.J. and J.W. Slipke. 2003. Response of adult largemouth bass and aquatic plants to small-scale applications of Aquathol K in Lake Seminole, Georgia. Proc. Conf. SE Assoc. Fish and Wildlife Agencies 57: 35-43.

Copper – Olfactory Effects on Fish

- Baldwin, D.H. et al. 2011. Copper-induced olfactory toxicity in salmon and steelhead: Extrapolation across species and rearing environments. Aquat. Tox. 101: 295-297.
- Tierney, K.B. et al. 2006. Relating olfactory neurotoxicity to altered olfactory-mediated behaviors inrainbow trout exposed to three currently-used pesticides. Aquat. Tox. 81: 55-64.
- Tierney, K.B. et al. 2009. Olfactory toxicity in fishes. Aquat. Tox. 96: 2-26.

Copper Effects – Copper bioconcentrates, bioaccumulates, and biomagnifies!

- YES
- And
- NO!

Copper Effects – Algae become resistant to copper!

- No evidence from the field!
- Unlikely
- Why?

Algal Resistance to Copper

- Garcia-Villada, L. et al. 2004. Occurrence of copper resistant mutants in the toxic cyanobacteria *Microcystis aeruginosa*: characterization and future implications in the use of copper sulphate as algaecide. Water Reaearch 38: 2207-2212.

- Rouco, M. et al. 2014. The limit of the genetic adaptation to copper in freshwater phytoplankton. Oecologia 175: 1179-1188.

Environmental Fate and Effects of Copper

- essential micronutrient for biota
- bioconcentrates and bioaccumulates when in a bioavailable form
- chemical speciation must be considered to predict fate and effects
- sensitive nontarget organisms include invertebrates and fish
- lithic biogeochemical cycle in aquatic systems

Some Issues Associated with Use of Copper Algaecides and Herbicides

Concerns vary among states and stakeholders:

- **fate and effects of copper**
- **potential effects on endangered or threatened species**
- **potential effects on species of economic concern**
- **accumulation of copper in sediments and bioavailability of copper residues**

Observations

- No decision is a decision. However, no decision does not = zero risk.
- Multiple treatments and monitoring are often required (management).
- Success of treatments often depends on applicator skill and equipment.
- Timing of treatments can be important (less density, higher dissolved oxygen, etc.)
- Risk assessment can help to focus decisions.

THANK YOU!

- **And a special thanks to AERF!**