Leaky Cyanobacterial Cells and Algaecide Treatments: A Look at the Data and Implications for Decision Making

John H. Rodgers, Jr., Alyssa Calomeni,
Kyla Iwinski, Ciera Kinley,
and Tyler Geer

Clemson University
Department of Forestry and Natural Resources

USEPA Cyanobacterial HABS Webinar
May 23, 2017

Drinking Water in the U.S.

- **Over 258 million U.S. residents obtain their drinking water from surface water.**
- **Every day, 30 billion gallons of water are used for public water use.**
- **In the past, leading causes of death (e.g. typhoid and cholera) were linked to drinking water.**
- **Source water protection and management are a high priority.**

Drinking Water in the U.S.

Surface water is the primary source of potable water for most US citizens.

Although about 90 percent of US public water systems obtain water from groundwater, these systems are usually much smaller than those served by surface waters.

Constituting about 66 percent of the potable water consumed, surface waters are periodically plagued by HABS producing toxins.

Harmful Algal Blooms (HABs)

- More prevalent in recent times.
- Occurring for billions of years.
- Pose special problems in critical water resources.
- Water resources are used for multiple purposes (e.g. potable water, recreation, etc.)
- When water resource usages are prohibited, water resource managers may be compelled to intervene.
- Often algaecides are the tactic of choice.

Decision to Intervene

- **Influenced by the “Leaky Cell” concept**
- **Risk assessment?**
- **Consequences of “action” vs. “no action”**

“Leaky Cell” Hypothesis

- **Algae release intracellular contents (toxins) following exposures.**
  - **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.**

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.**

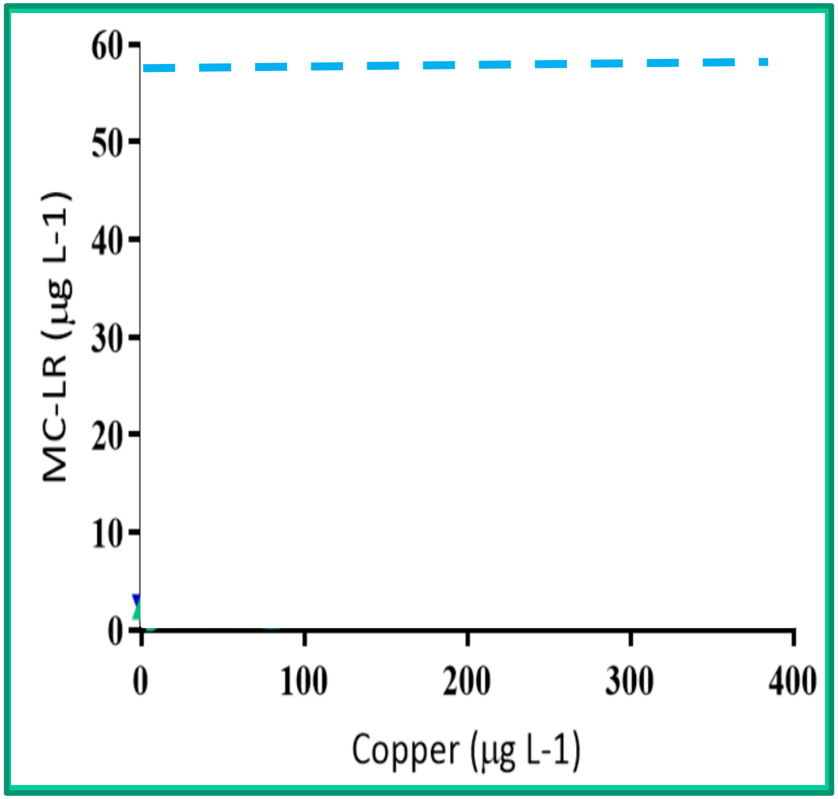
Daly, Ho and Brookes, 2007

- ***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.”**

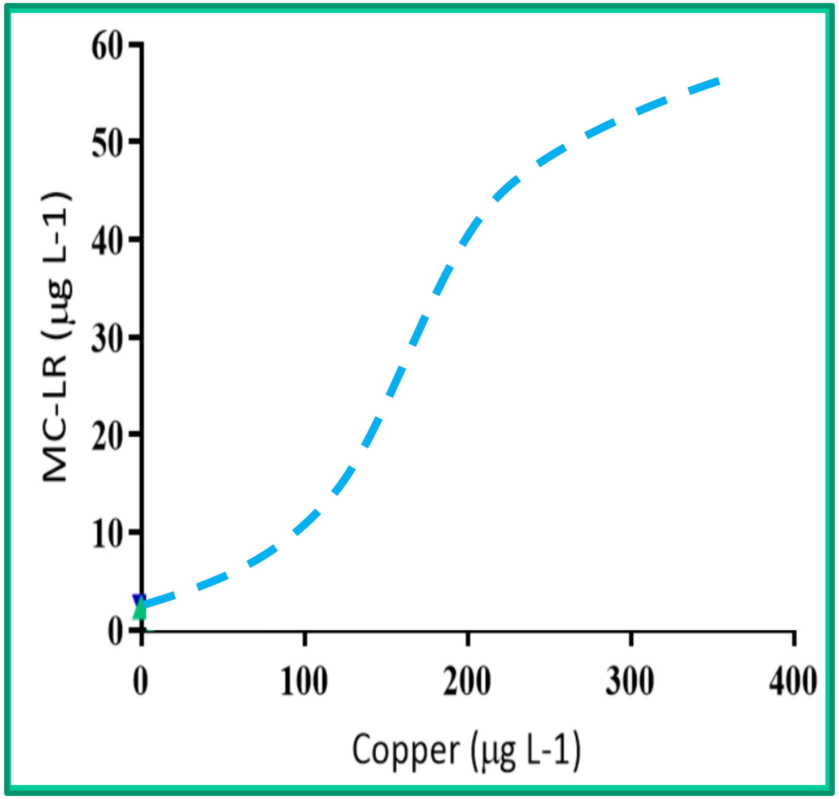
Touchette, Edwards and Alexander, 2008

- **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."**

”Leaky Cell Hypothesis”

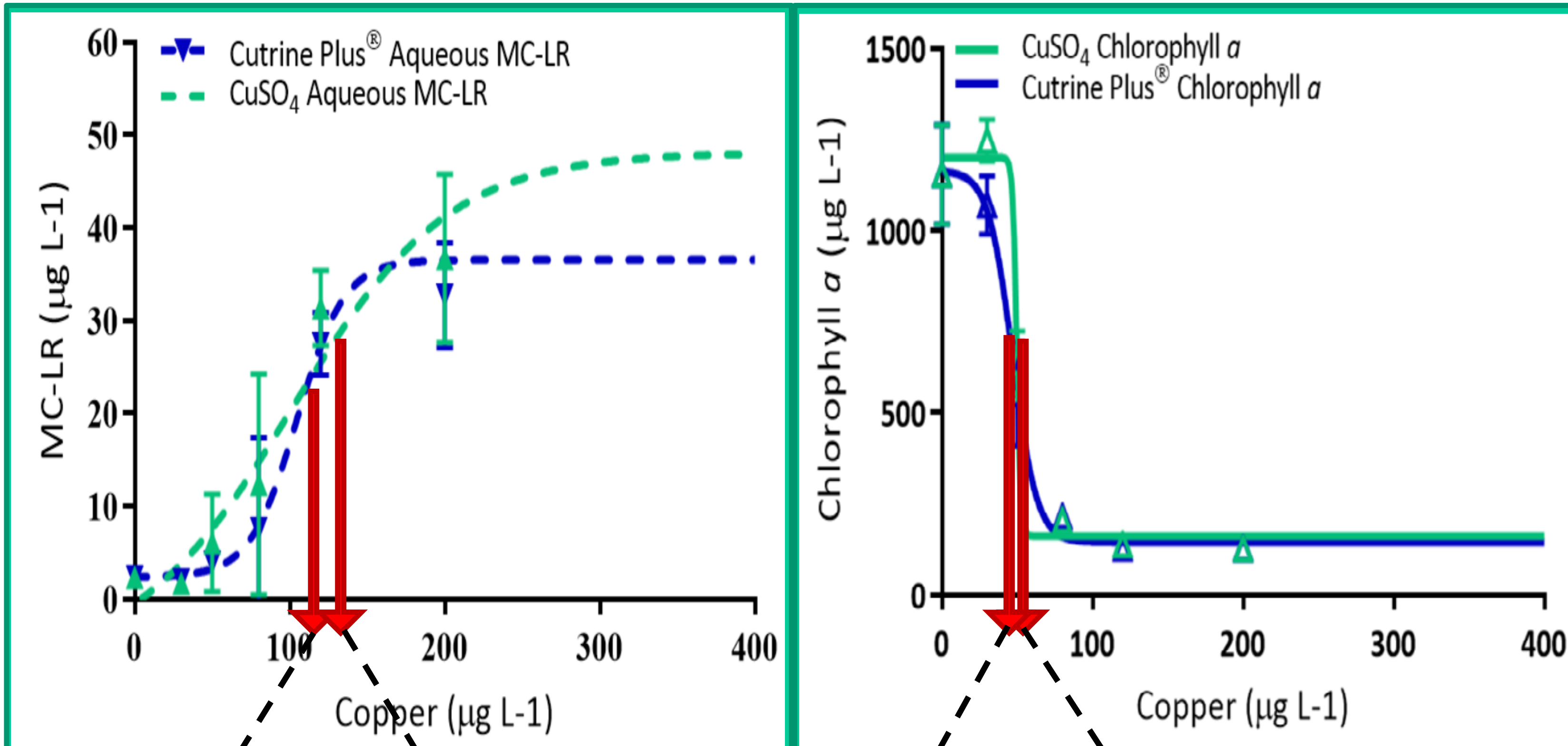


Hypothesized Response Based on Toxicological Principles



Results: Exposure-Response Relationships

- Microcystin-LR = 24h EC_{50}
- Chlorophyll *a* = 96h EC_{50}



EC_{50}= 0.105 mg Cu/L

EC_{50}= 0.107 mg Cu/L

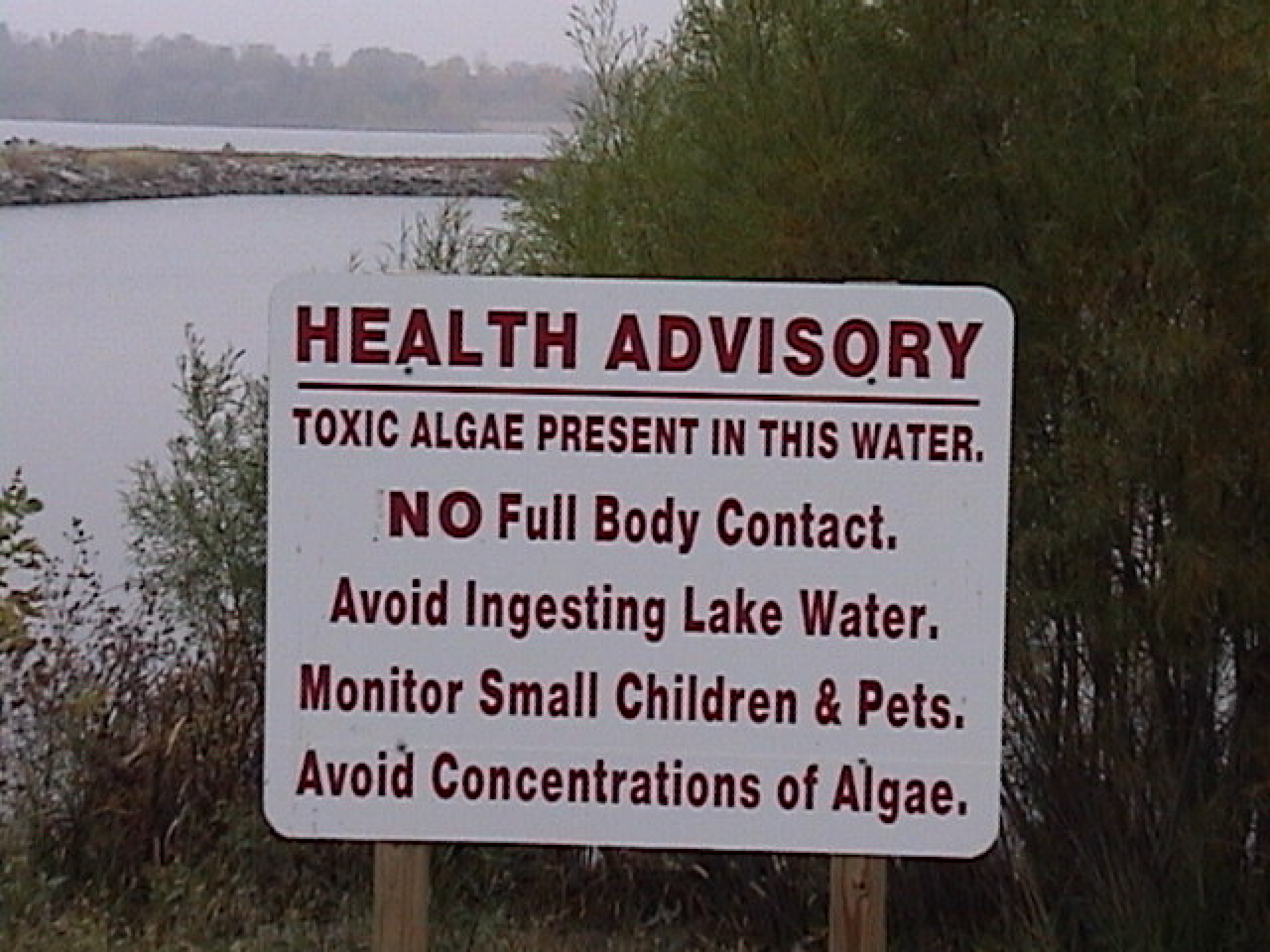
EC_{50}= 0.05 mg Cu/L

EC_{50}= 0.06 mg Cu/L

Exposure-Response Relationships

- Maximum microcystin-LR release 0.2-0.5 mg Cu/L
- Maximum decreases in chlorophyll <0.1 mg Cu/L
- Decreased copper exposures can minimize microcystin-LR release within effective concentration range

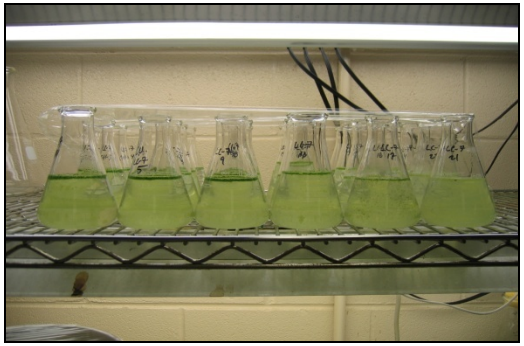
Pawnee Reservoir, NE


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

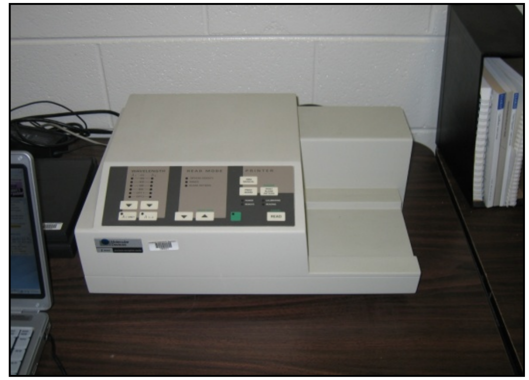
Experimental Objectives

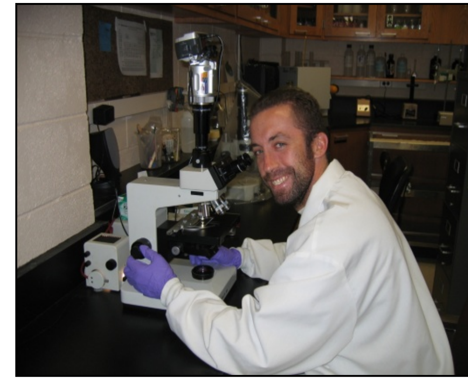
- **Determine effective [Cu] to control *M. aeruginosa.***
  - **Site water - Pawnee Reservoir, NE.**
- **Measure responses in terms of chl *a* and cell density.**
- **Measure responses in terms of microcystin concentrations.**
  - **Pre- and post- exposure.**
- **Confirm results in a field application.**

- **Exposure(s):**



- **Response(s):**





Algaecides

	Cutrine®- Ultra	Clearigate®	Algimycin® PWF	Copper Sulfate Pentahydrate
% Cu as elemental	9.0	3.8	5.0	25.4
Formulation	Copper-Triethanolamine Complexes and D-limonene	Copper-Ethanolamine and D-limonene	Chelates of Copper Citrate and Copper Gluconate	$CuSO_4 \bullet 5H_2O$
Chemical class	Chelated Elemental Copper	Chelated Elemental Copper (Cu_2CO_3)	Weakly Chelated Copper	Copper salt
Appearance	Blue Viscous Liquid	Blue Viscous Liquid	Blue Viscous Liquid	Blue Crystalline
Odor	Orange	Orange	Slight	Odorless
Water Solubility (mg/L)	Miscible	Miscible	Complete	316,000
pH	9.5-10.0	9.5-10.0	1.5-2.0	NA

Conclusions – Laboratory Experiment

- **Control of *Microcystis aeruginosa* was achieved:**
  - **[Cu] as algaecide to achieve the desired level of control**

    << 1 mg Cu / L.
    - **Cutrine®-Ultra = 0.2 mg Cu / L.**
  - **Statistically significant decrease in aqueous microcystin concentrations.**
  - **Site-specific algaecide treatment strategy.**

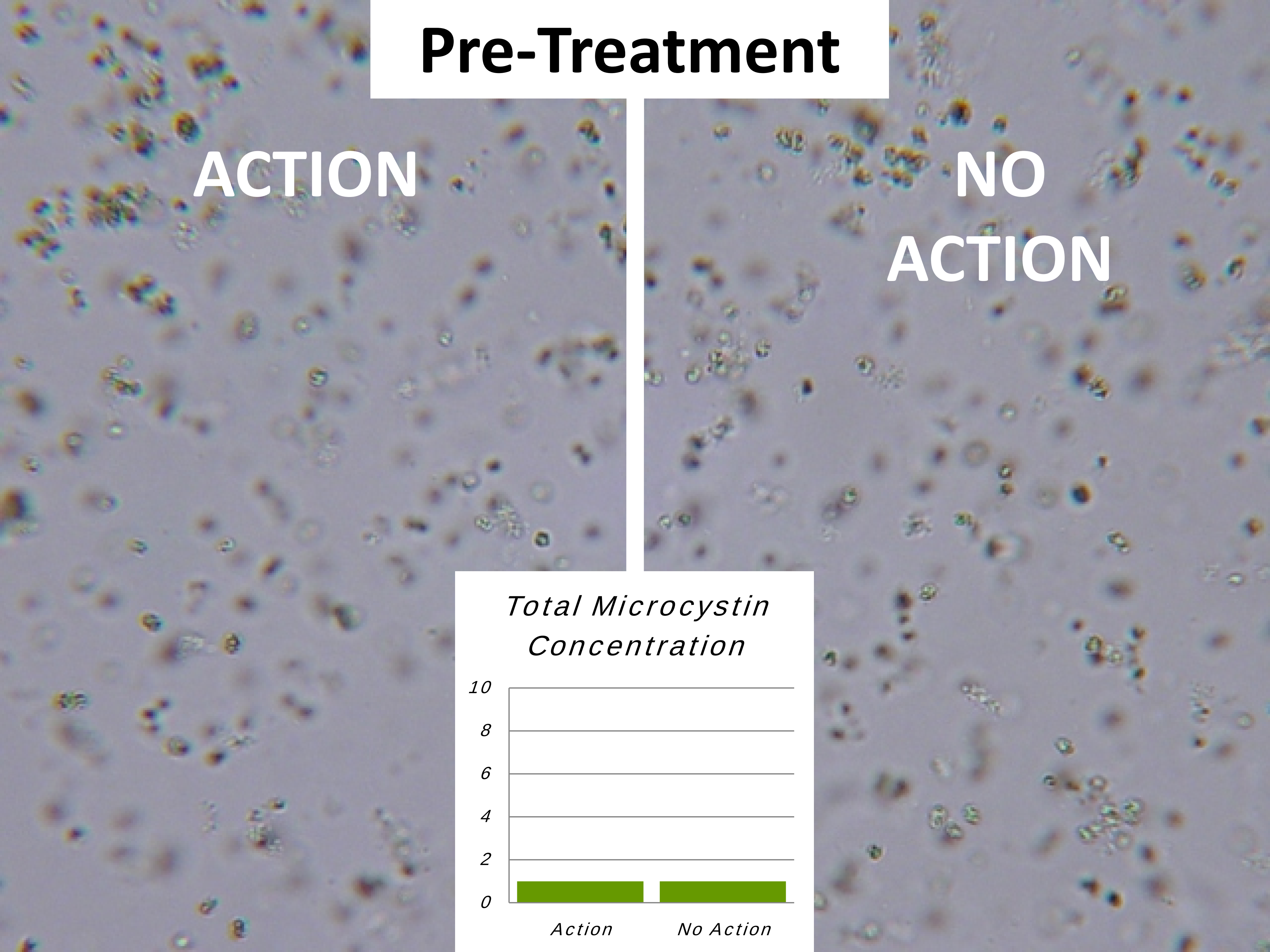
- **Different forms of Cu exposure ≠ same responses; same algae.**

Pawnee Reservoir, NE June 2006

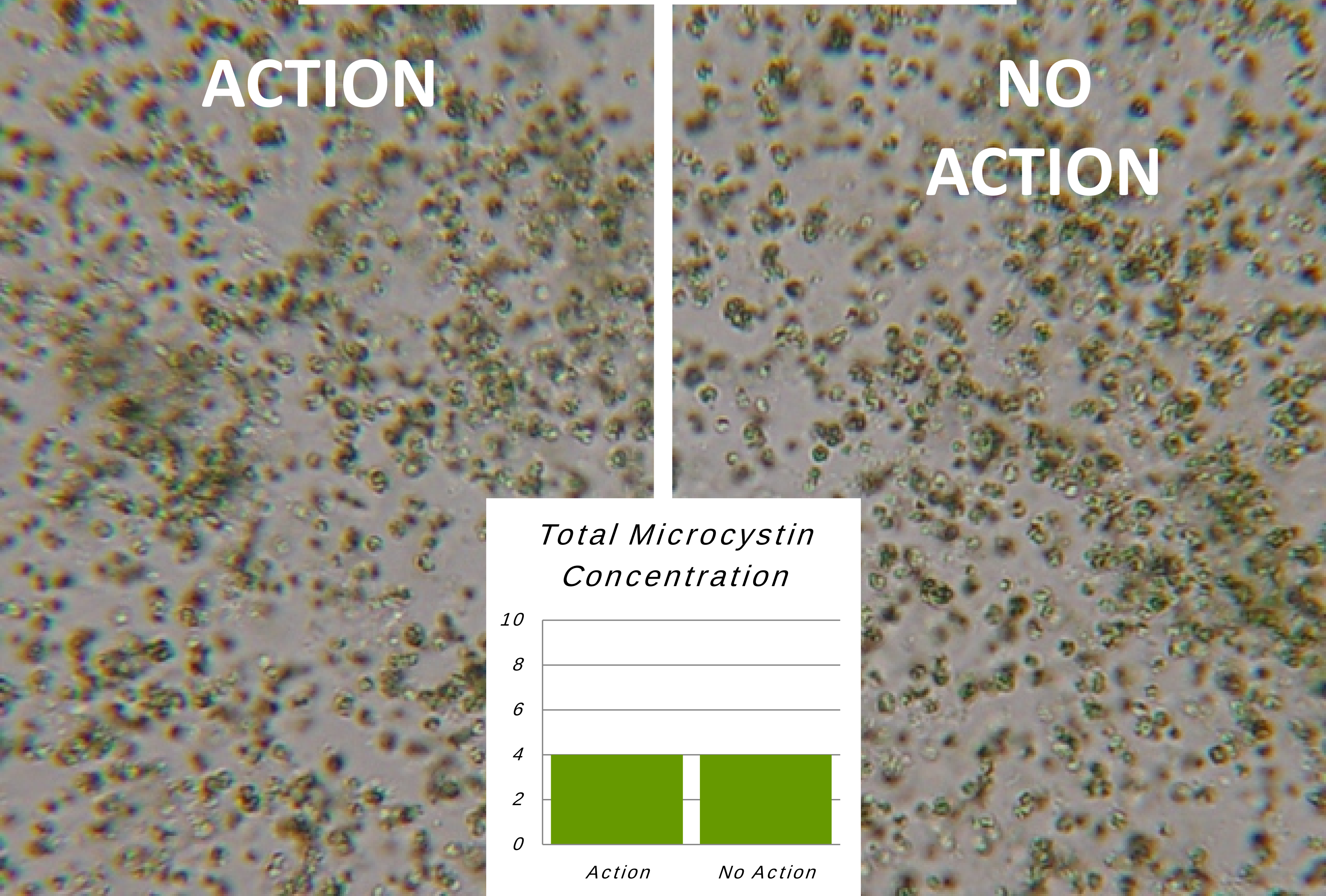
Treatment - 8 June 2006

Cutrine - Ultra

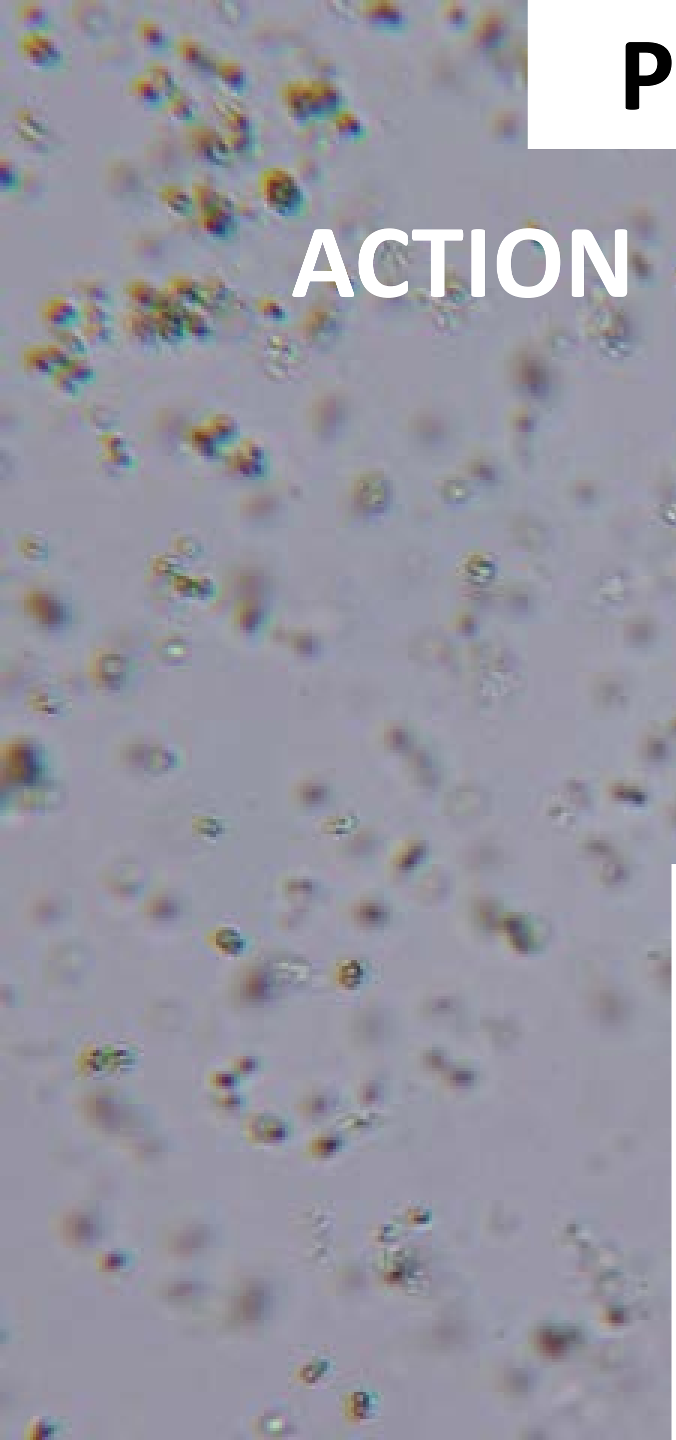
Pawnee Reservoir, NE
Post -Treatment

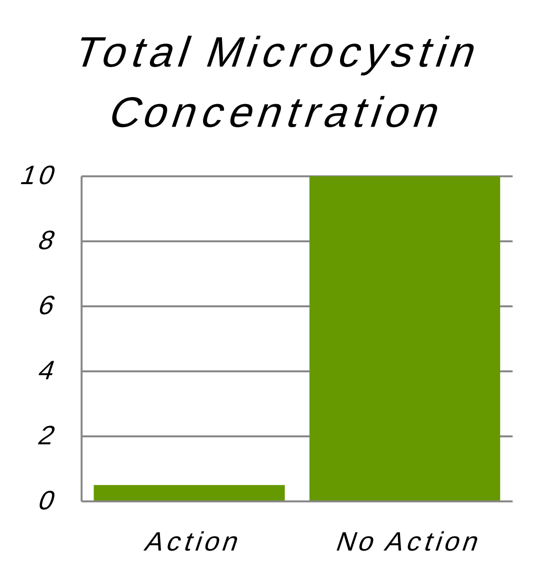

Pre-Treatment
ACTION
NO ACTION
Total Microcystin Concentration
10
8
6
4
2
0
Action
No Action

Time of Treatment



Post-Treatment





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.**

- **Iwinski, K.J. et al. 2016. Cellular and aqueous microcystin-LR following laboratory exposures of *Microcystis aeruginosa* to copper algaecides. Chemoshpere 147:74-81.**

- **Iwinski, K.J. et al. 2017. Influence of CuSO4 and chelated copper algaecide exposures on biodegradation of microcystin-LR. Chemosphere 174: 538-544.**

Questions?


KOMATSU
DUNCAN
DISPOSAL
972-225-5252
www.duncandisposal.com