



**EarthTec QZ:  
Protecting lakes and pipelines from invasive mussels**



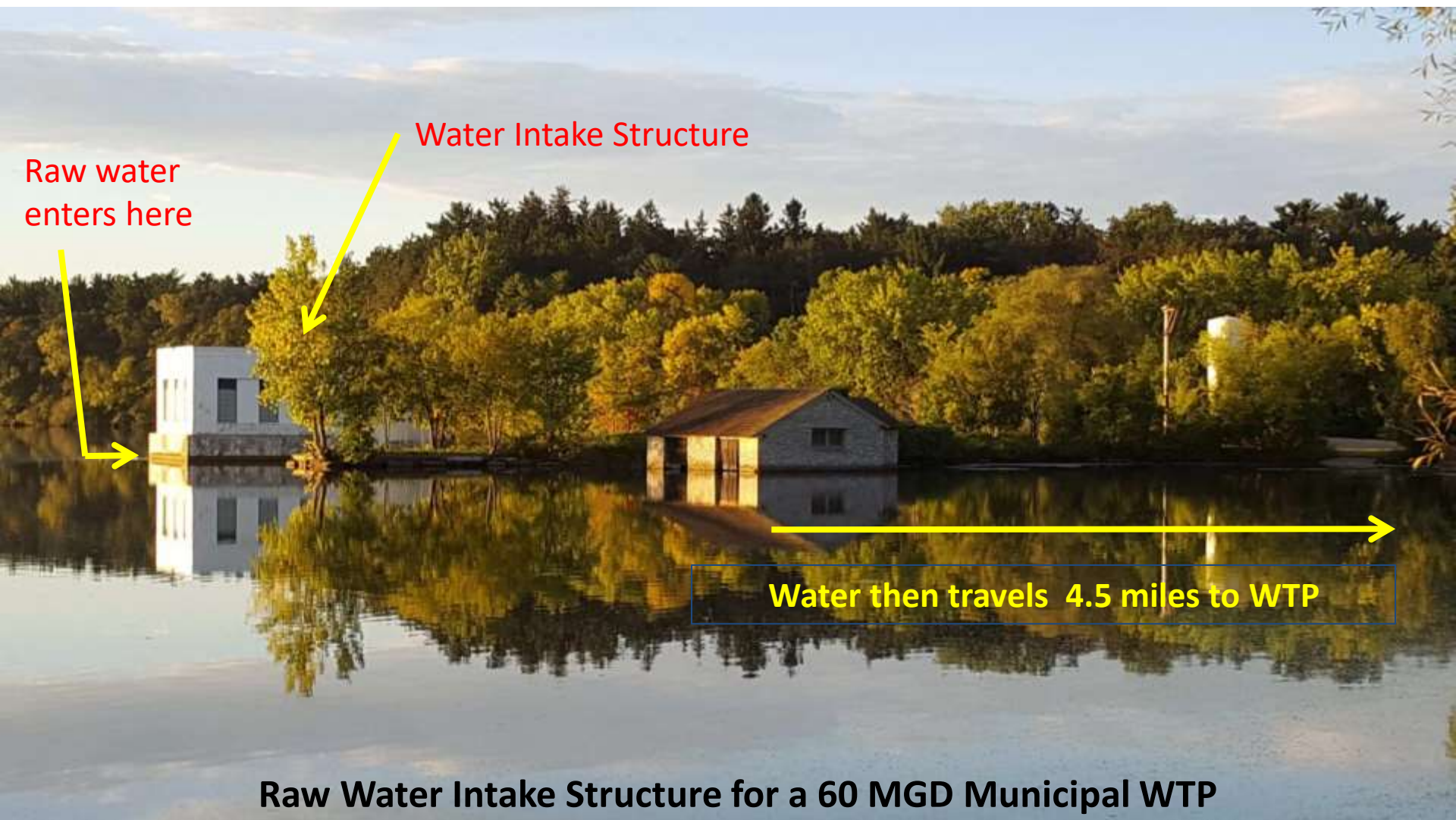
# Priority Sites for Mussel Control

- **Flowing Waters (pipelines, aqueducts)**
- **Open Waters (lakes)**
  - **Rapid Response**
  - **Full Lake**
  - **Fish Hatcheries**

3.5" = 9 cm



# Zebra mussels have historically infested the intake structure of a major municipal WTP in the Midwest 2015-16



**Raw Water Intake Structure for a 60 MGD Municipal WTP**



This is what the clean screens should look like

# Zebra mussels historically fouled the intake screens of the WTP 2015



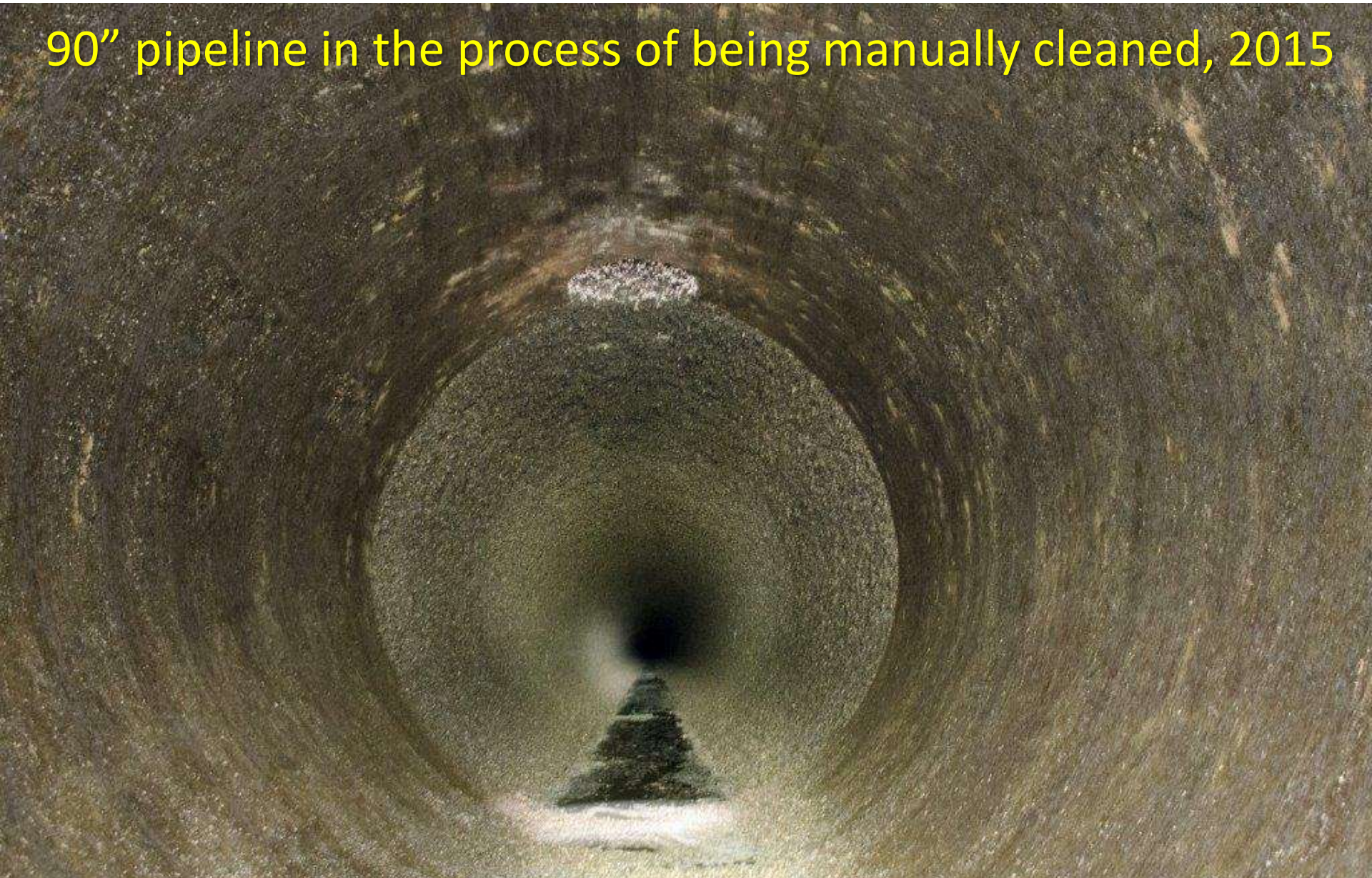
Screen fouled with  
zebra mussels, 2015



Screens and intake fouled with zebra mussels, 2015

**Zebra Mussels Infesting the 90" Raw Water Pipeline  
2015**

90" pipeline in the process of being manually cleaned, 2015





**Zebra Mussels Infesting the 90" Raw Water Pipeline  
2015**

**Manually scraped mussels to be removed, 1 foot deep, 2015**



# Zebra mussels being removed from the raw water pipeline 2015

Manual cleaning represents a worker safety hazard, requiring Tyvek suits and respirators



## Zebra mussels removed from the pipeline and screens



**Mussels are removed by the dumpster load**

# Metering pump and wall skid



Supply side

Delivery side

**Results of treatment with 1ppm QZ**  
**Ensured intake screens free of zebra mussels during height of the mussel season**  
September, 2016



**Treatment with 1ppm QZ ensured intake screens are free of zebra mussels**  
September, 2016



**EarthTec QZ successfully prevented biofouling in Summer-Fall of 2016**

**Treatment with 1ppm QZ ensured pipeline remained free of zebra mussels**  
September, 2016



**1 ppm dose as QZ  
= 60 ug/L as copper  
sufficient to achieve  
complete control**

**EarthTec QZ successfully prevented  
biofouling in Summer-Fall of 2016**

Treatment with 1ppm QZ ensured intake gates remained free of zebra mussels

September, 2016



6 ft x 4 ft intake gate

1 ppm dose as QZ  
= 60 ug/L as copper  
sufficient to achieve  
complete control

Note that mussels  
were only able to  
colonize a few spots  
within eddies of  
unmixed water,  
such as the feed  
line itself.

EarthTec QZ successfully prevented  
biofouling in Summer-Fall of 2016



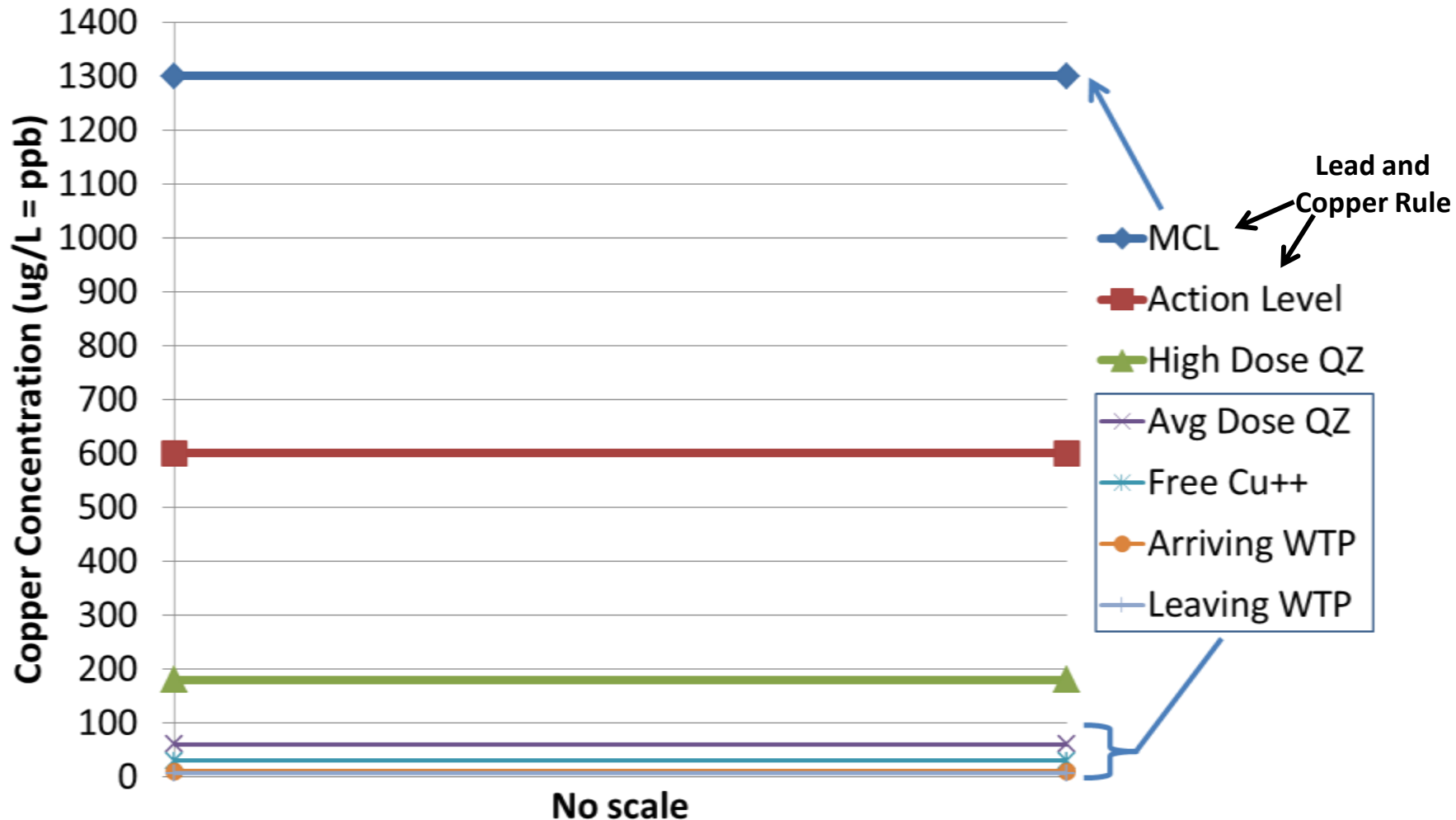
Zebra Mussel Control at City of St Paul, Minnesota  
**Copper Concentration (ug/L = ppb) in treated water  
reaching the St Paul WTP, summer of 2016**

**Dose applied at  
pipeline intake  
1 ppm as QZ  
= 60 ug/L as copper**

<b>Date</b>	<b>WTP</b>
6/14/2016	0
6/23/2016	2
6/30/2016	0
7/7/2016	3
7/14/2016	4
7/21/2016	1
7/28/2016	0
8/11/2016	0
8/18/2016	1
8/25/2016	0
8/31/2016	0
9/15/2016	0
<b>Average:</b>	<b>0.92</b>

**Copper is consumed by  
background demand  
in the pipeline**

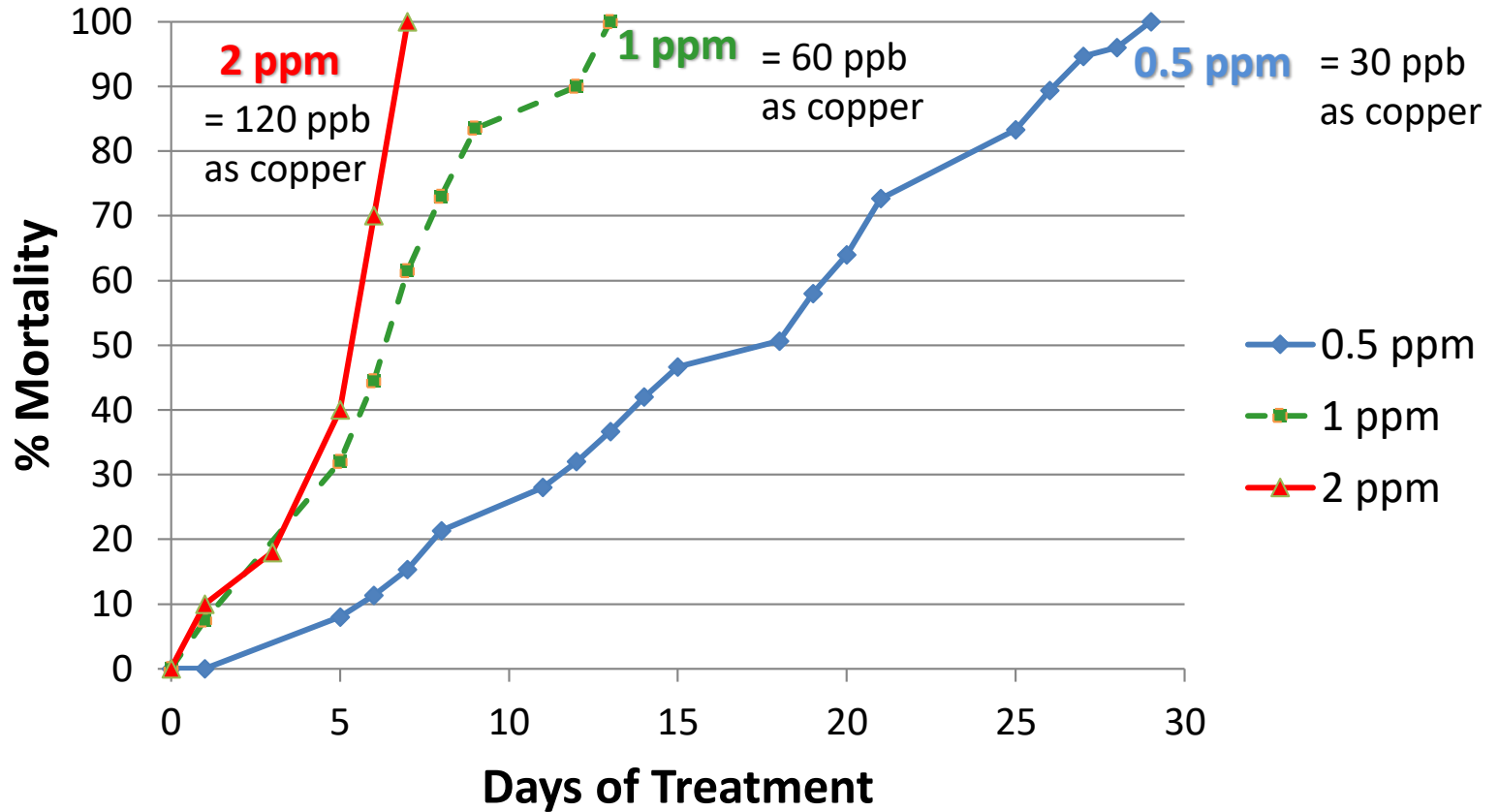
# Copper Concentrations in Drinking Water



The copper residual concentration arriving at a WTP is approximately 1/100<sup>th</sup> of the Lead and Copper Rule standard

# Ohio WTP

## Average Zebra Mussel Mortality, QZ Applied in Pipeline



100% mortality in 6 days at 2 ppm, in 12 days at 1 ppm, in 28 days at 0.5 ppm



# Priority Sites for Mussel Control

- Flowing Waters (pipelines, aqueducts)
- **Open Waters (lakes)**
  - Rapid Response
  - Full Lake
  - Fish Hatcheries

# Open Waters

## Mussel Eradication or Control using EarthTec QZ

### A. Rapid Response projects:

1. 2014: Christmas Lake
2. 2014: Independence Lake
3. 2015: Ruth Lake
4. 2016: Lake Minnewashta
5. 2017: Lake Marion

### B. Full-lake eradications:

6. 2016: Indiana private lake
7. 2017: Billmeyer PA
8. 2017: Minnesota Zoo

### C. Fish Hatchery eradications and decontaminations:

9. 2016: Indiana
10. 2017: Oklahoma
11. 2017: South Dakota



# Open Waters

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# Decontamination of Zebra Mussels from Oklahoma state fish hatchery



**Side benefits: Improved yields, healthier fish**

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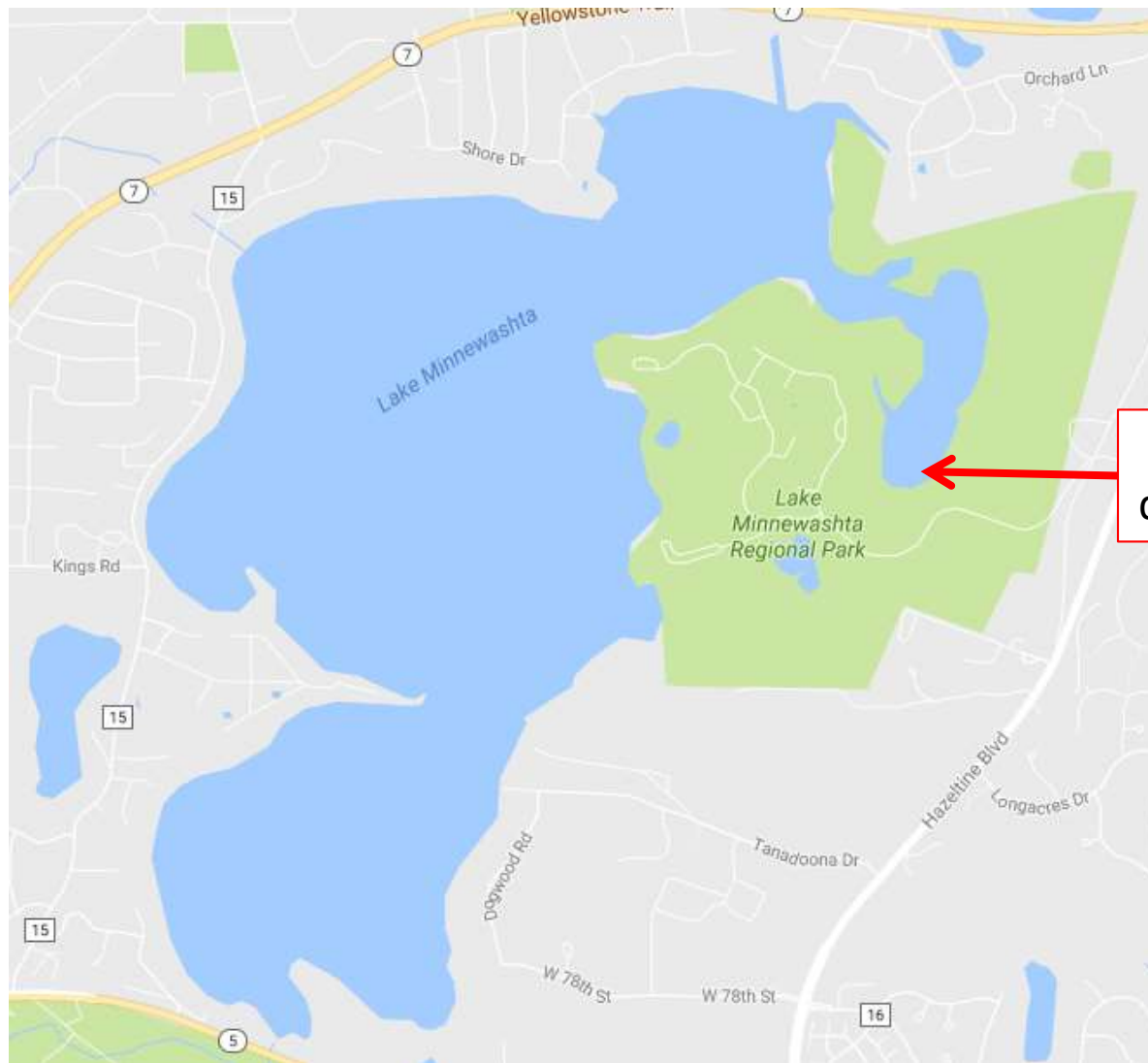
**Side benefits: Improved yields, healthier fish**



## RAPID RESPONSE

### Zebra Mussels discovered in Lake Minnewashta, Minnesota

August 18, 2016



Mussels discovered here

# Zebra Mussels discovered in Lake Minnewashta, Minnesota

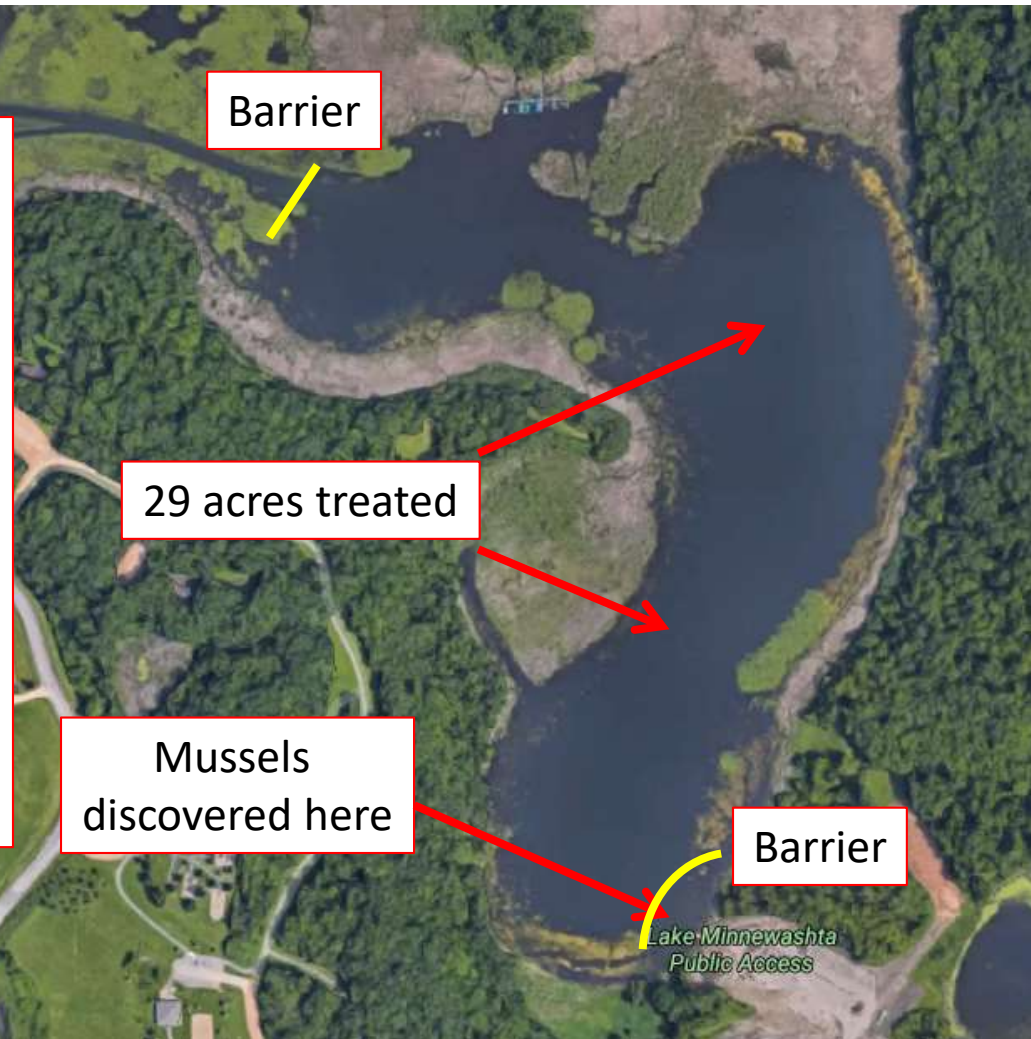
August 18, 2016

Mussel eradication led by:  
**Minnehaha Creek  
Watershed District**

Supported by:

- **Lake Preservation Association**
- **Carver County**

EarthTec QZ applied by:  
**PLM Lake and Land Mgt**

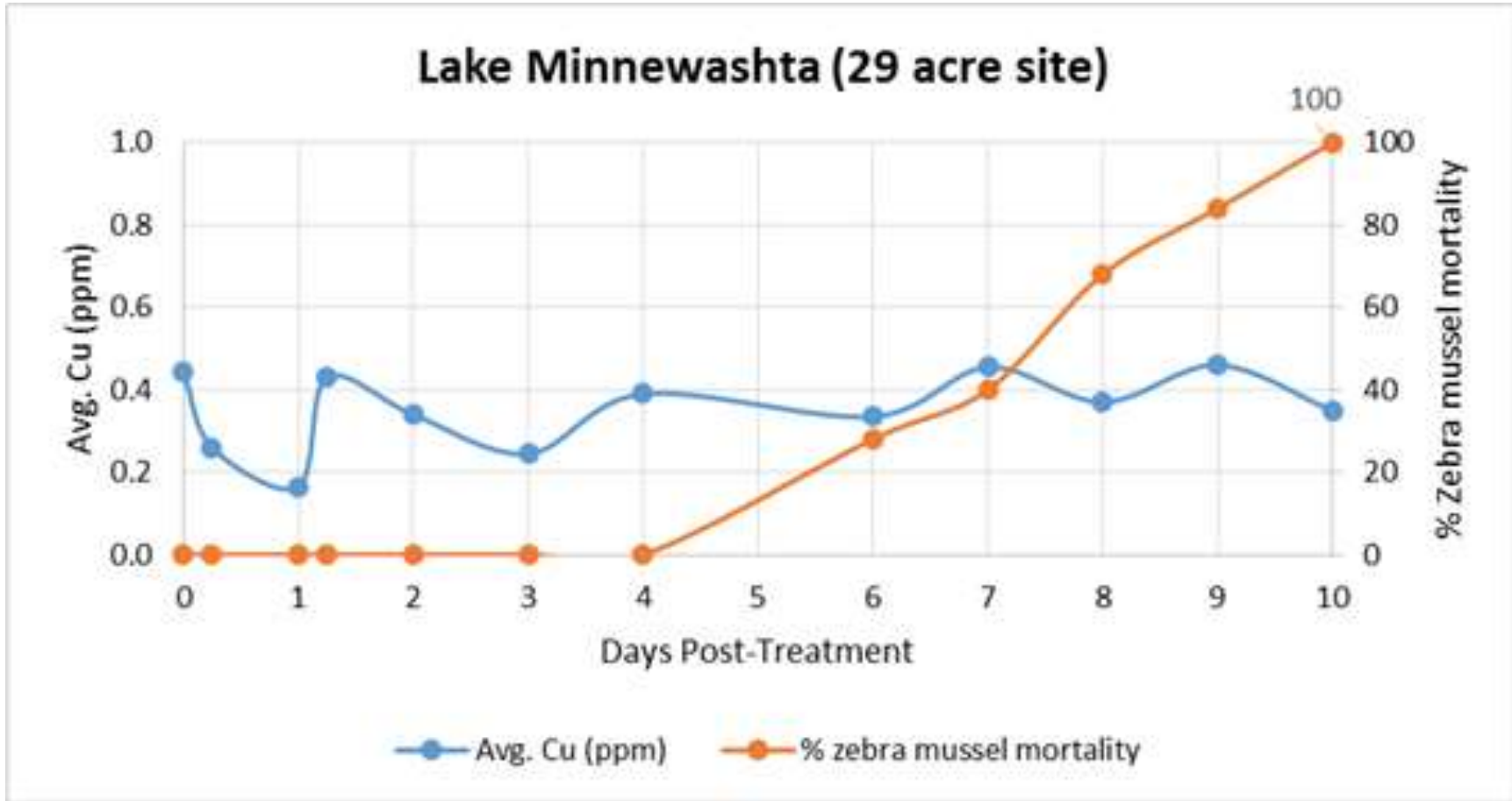




# Eradication of Zebra Mussels from Lake Minnewashta, Minnesota

Sept 13-23, 2016

Water Temperature 19°C = 66°F



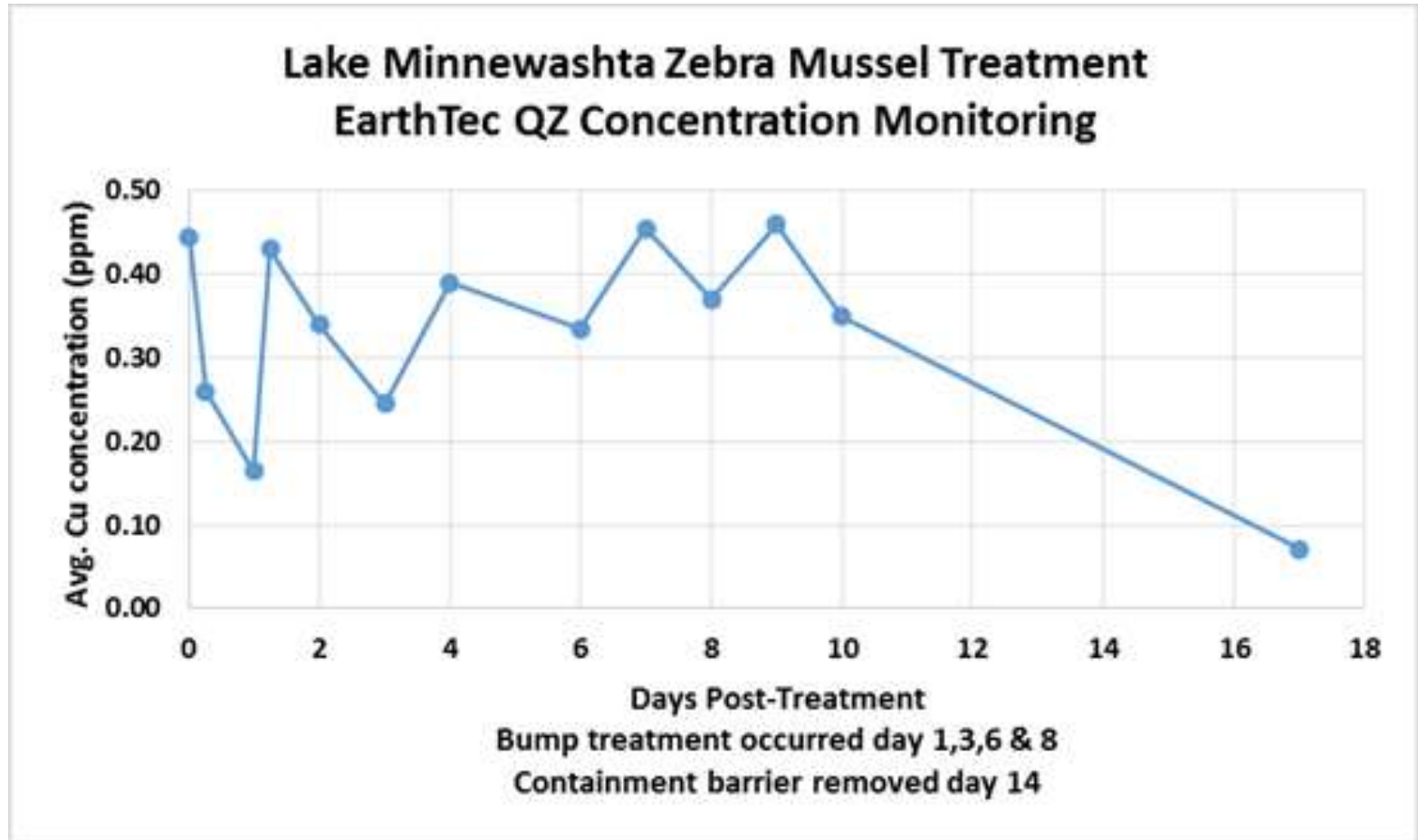
Source: Eric Fieldseth and Jill Sweet, Minnehaha Creek Watershed District



# Eradication of Zebra Mussels from Lake Minnewashta, Minnesota

Sept 13-23, 2016

Water Temperature 19°C = 66°F



*Source: Eric Fieldseth and Jill Sweet, Minnehaha Creek Watershed District*

# Eradication of Zebra Mussels from Lake Minnewashta, Minnesota

Sept 13-23, 2016

## Summary of QZ Dosing and Costs for Eradicating Invasive Mussels from Open Waters

Lake size, acres	29
Avg depth	9 ft
# of Applications	5
Treatment period	10 days
Sum of copper applied (5 doses)	1.06 mg/L
Chemical cost	\$22,500
Cost per acre	\$776
Cost per million gallons	\$265

Work performed by PLM Lake and Land Management, Inc.

# Unique to the EarthTec QZ Label

- **Repeat applications are permissible** if needed to maintain lethal concentrations of copper for sufficient time period.  
When re-applying, **do not exceed a resulting concentration of 1.0 mg/L** of metallic copper (background + applied copper) in the treated water.
- Pipelines are included



# Eradication of Quagga Mussels from Billmeyer Quarry Lake, Pennsylvania

Sept - Oct, 2017



**Billmeyer Quarry**

**Susquahanna River**

- **About 30 surface acres**
- **Max depth about 115 feet**
- **Quarry from 1846-1960's**
- **Scuba Diving School for 33 years, until 2015**
- **Quagga mussels now found throughout**
- **Consumptive Use Mitigation Plan**





## Billmeyer Quarry Lake, Pennsylvania

Full of Fish: Bluegill, Largemouth Bass, Catfish, Gizzard Shad



Collected quagga mussels for placement into cages





## Placing cages



# Eradication of Quagga Mussels from Billmeyer Quarry, Pennsylvania

Sept - Oct, 2017

## Summary of QZ Dosing and Costs for Eradicating Invasive Mussels from Open Waters

Lake size, acres	29
Max depth	115 ft
Avg depth	51 ft
Target copper conc (mg/L)	0.2 mg/L
# of Applications	3
Treatment period	37 days
Sum of copper applied (3 doses)	0.44 mg/L
Chemical cost	\$53,625
Cost per acre	\$1,849
Cost per million gallons	\$110



## The effective EarthTec dose for algae and invasive mussel control is safe for even the most sensitive fish

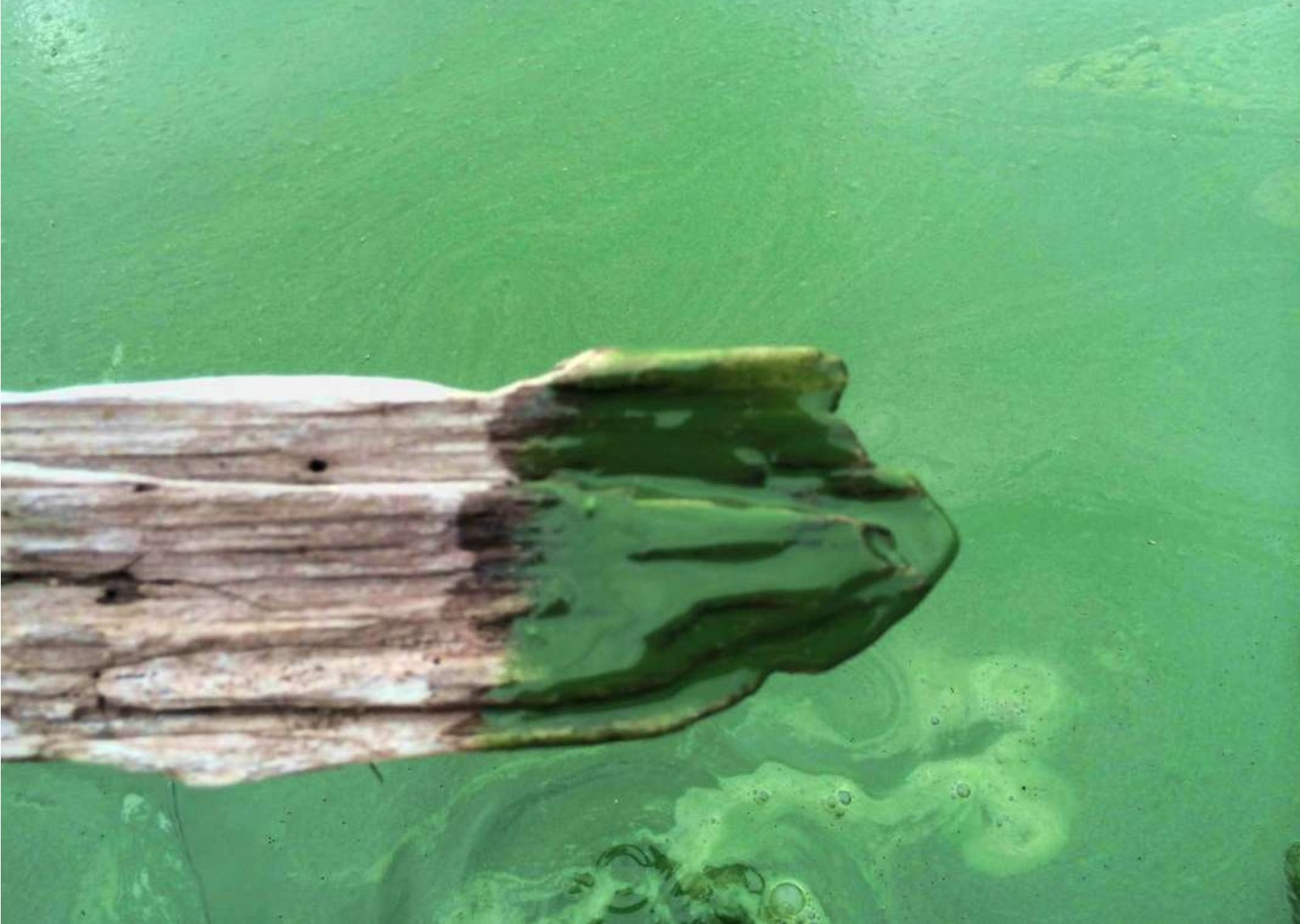
Recommended Dose of EarthTec according to Severity of Cyanobacterial Bloom

<b>Algal bloom conditions</b>	<b>μL/L, as EarthTec</b>	<b>ppm, as copper</b>	<b>ppb, as copper</b>
<b>Preventative dose</b>	0.5	0.030	30
<b>Mild bloom</b>	1	0.060	60
<b>Full bloom</b>	2	0.120	120
<b>Severe bloom</b>	3	0.180	180

Toxicity of EarthTec to Rainbow Trout (*Oncorhynchus mykiss*)

<b><u>Measured Effect</u></b>	<b><u>μL/L, as EarthTec</u></b>	<b><u>ppm, as copper</u></b>	<b><u>ppb, as copper</u></b>
<b>NOEC</b>	4.0	0.240	240
<b>LC25</b>	4.4	0.263	263
<b>LC50</b>	4.9	0.294	294

96-hour acute toxicity test performed by Aquatic Bioassay & Consulting, Inc.  
NOEC = No Observed Effect Concentration. Salmonids like rainbow trout are frequently used for toxicity testing because they are among the most environmentally sensitive fish.



**EarthTec and EarthTec QZ: A More Rational Use of Copper for Control of HABs, invasive mussels, and improving water quality**  
David Hammond, PhD and Fred Singleton, PhD

# EarthTec Chemistry

- **EPA Labeled** as an Algacide/Bactericide, Molluscicide
- Registered in **All 50 States** as Algacide/Bactericide, in 26+ States as Molluscicide
- Certified to **NSF** Standard 60
- Highly effective
- Reduces Costs



# Green Chemistry

1. Prevent waste
2. Maximize atom economy
3. Design less hazardous chemical syntheses
4. Design safer chemicals and products
5. Use safer solvents and reaction conditions
6. Increase energy efficiency
7. Use renewable feedstocks
8. Avoid chemical derivatives
9. Use catalysts, not stoichiometric reagents
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents

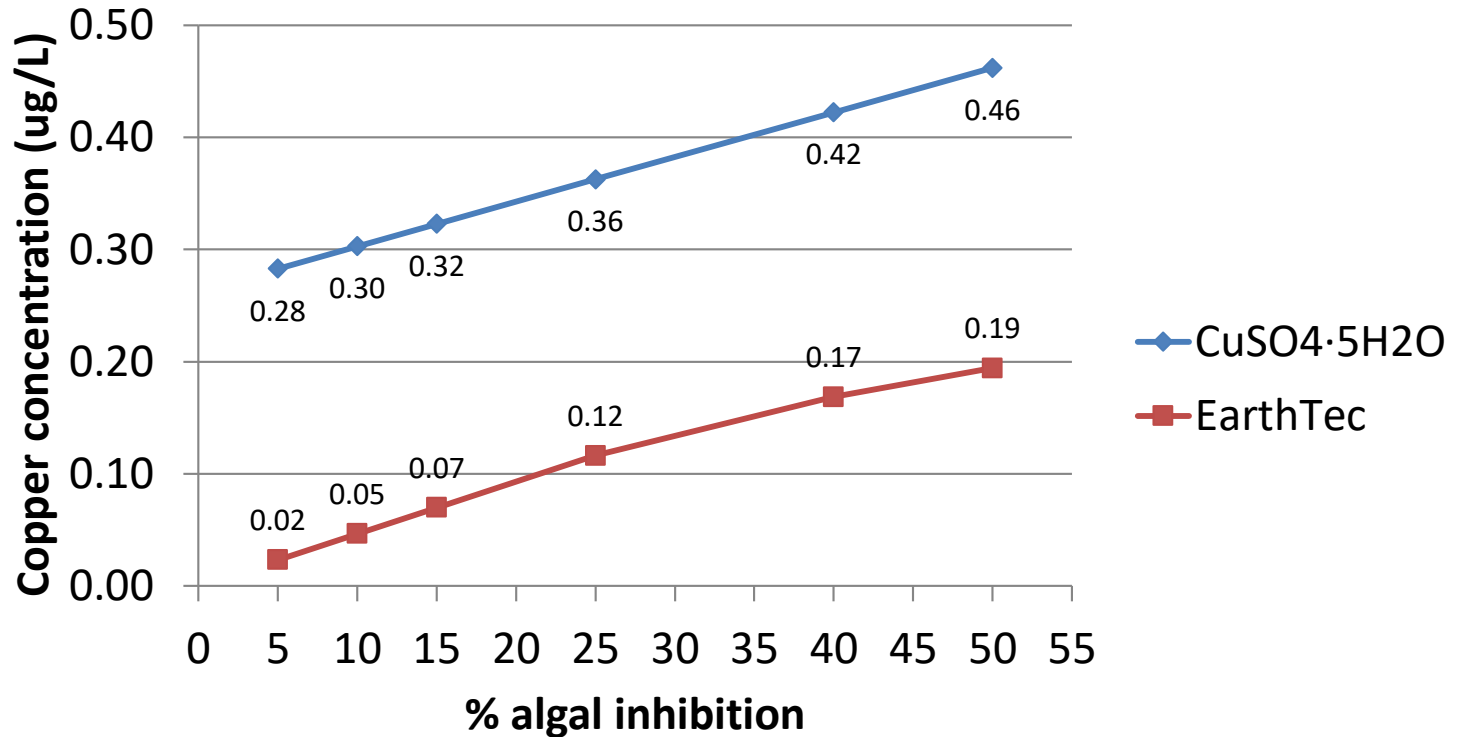
## EarthTec is an example of Green Chemistry:

- More efficient formulation
- Desired benefits at lower doses
- Safer
- Less waste



# Copper Sulfate vs EarthTec

% Inhibition of Algal Growth after 96h of exposure to copper delivered as conventional copper sulfate vs EarthTec



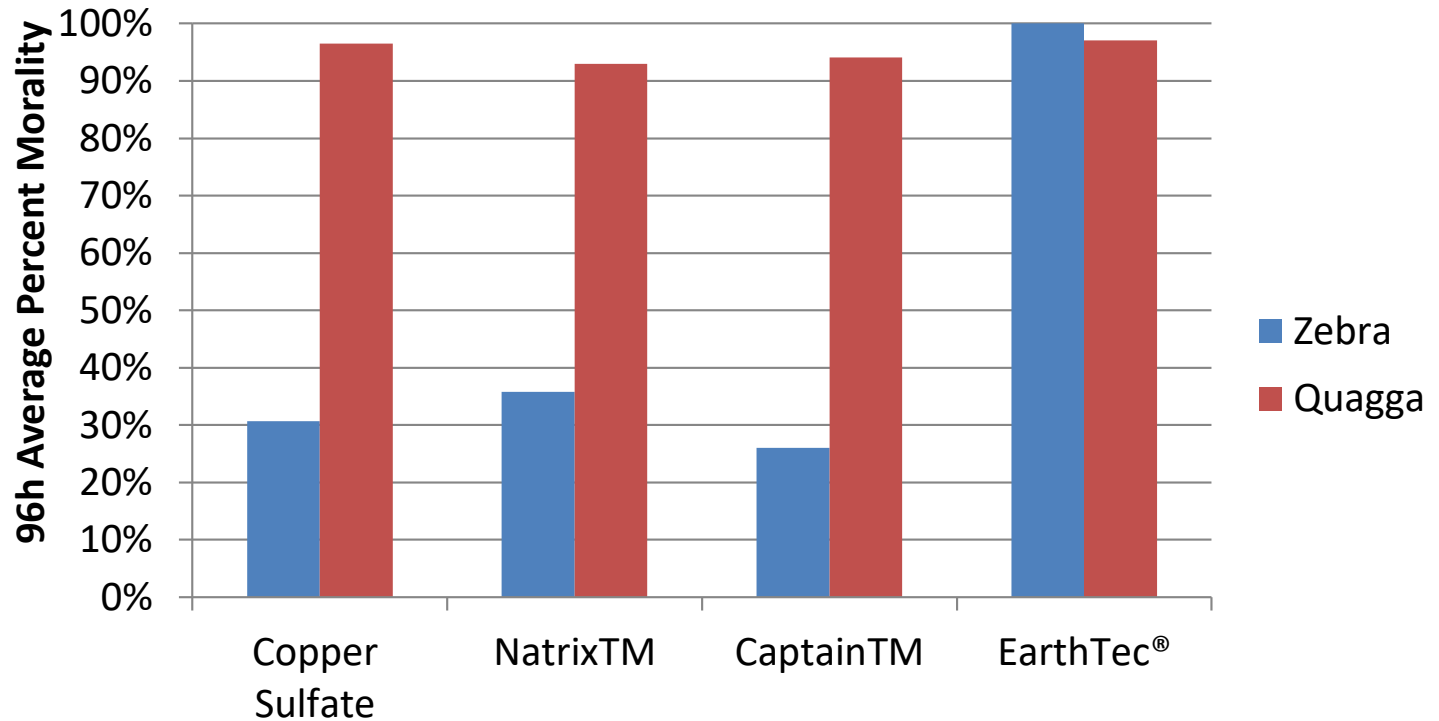
**The copper dose required to achieve a given % inhibition of algae is much lower if applied as EarthTec than if applied as copper sulfate**

Tests performed by **Aquatic BioAssay and Consulting Inc.**, against the indicator algal species, *Selenastrum capricornutum*, according to standard bioassays of chronic exposure, 96 hours.

## Copper Sulfate vs EarthTec

Average percent mortality after 96h of exposure to copper-based algaecides at 0.5 mg/L copper equivalent

0.5 mg/L copper equivalent



**Even at equivalent doses of active ingredient, EarthTec is more effective.**

**And we now know much lower doses of EarthTec are still effective against mussels.**

Renata Claudi M.Sc., T.H. Prescott P.Eng., Sergey Mastisky Ph.D. & Heather Coffey M.Sc., "Efficacy of Copper Based Algaecides for Control of Quagga and Zebra Mussels", January, 2014.

## Main message of this talk:

There is a new generation of liquid copper products that

- deliver copper entirely as cupric ions,  $\text{Cu}^{++}$
- are highly bioavailable,
- are effective at unprecedentedly low doses



# EarthTec Chemistry

EarthTec is:

- **Liquid** formulation containing **5% copper** by volume
- Made from copper sulfate + ET-3000
- Unique features:
  - **0.3 pH, yet won't burn your skin**
  - Copper is **99.99% cupric ion form (Cu<sup>++</sup>)** so it is **readily bioavailable**
  - **Self-dispersing**, so no need for mixing
  - Infinitely soluble in water, stays suspended, **will not settle** out
  - Low concentrations yield high performance: **30-200 ppb copper**
  - Adjuvant Properties: **Transport of Copper Across Cell Membrane**

## Recommended Dose of EarthTec according to Severity of Cyanobacterial Bloom

<b>Algal bloom conditions</b>	<b>μL/L, as EarthTec</b>	<b>ppm, as copper</b>	<b>ppb, as copper</b>
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EPA max for copper algaecides is 1 mg/L as copper  
= 1,000 ppb as copper  
(about 8x to 16x the usual dose of EarthTec)

# Product Comparison

Copper Sulfate vs EarthTec

## Norwalk, OH (2012 vs 2013)

Copper sulfate 2012	EarthTec 2013	
10	8	treatments per year
500	60	lbs or gallons per treatment
	10	lbs, weight per gal of EarthTec
5,000	4,800	lbs per year
25%	5%	fraction that is elemental copper
<b>1,250</b>	<b>240</b>	<b>elemental copper applied, lbs</b>
100%	19.20%	total copper applied, %

When Norwalk switched from copper sulfate to EarthTec, they had fewer total applications per year and applied <20% of the elemental copper used in previous years, even though their treatment season spanned a longer portion of the year.

# What about Harmful Algal Blooms?

## HABs in the N

Environment, US News

### Toxic Algae Rampant in California, Also Spreading Nationwide

Drought has helped cr

By Tara MacIsaac, Epoch Times

for algae's growth

SCIENTIFIC AMERICAN

### Toxic Algae Blooms Are

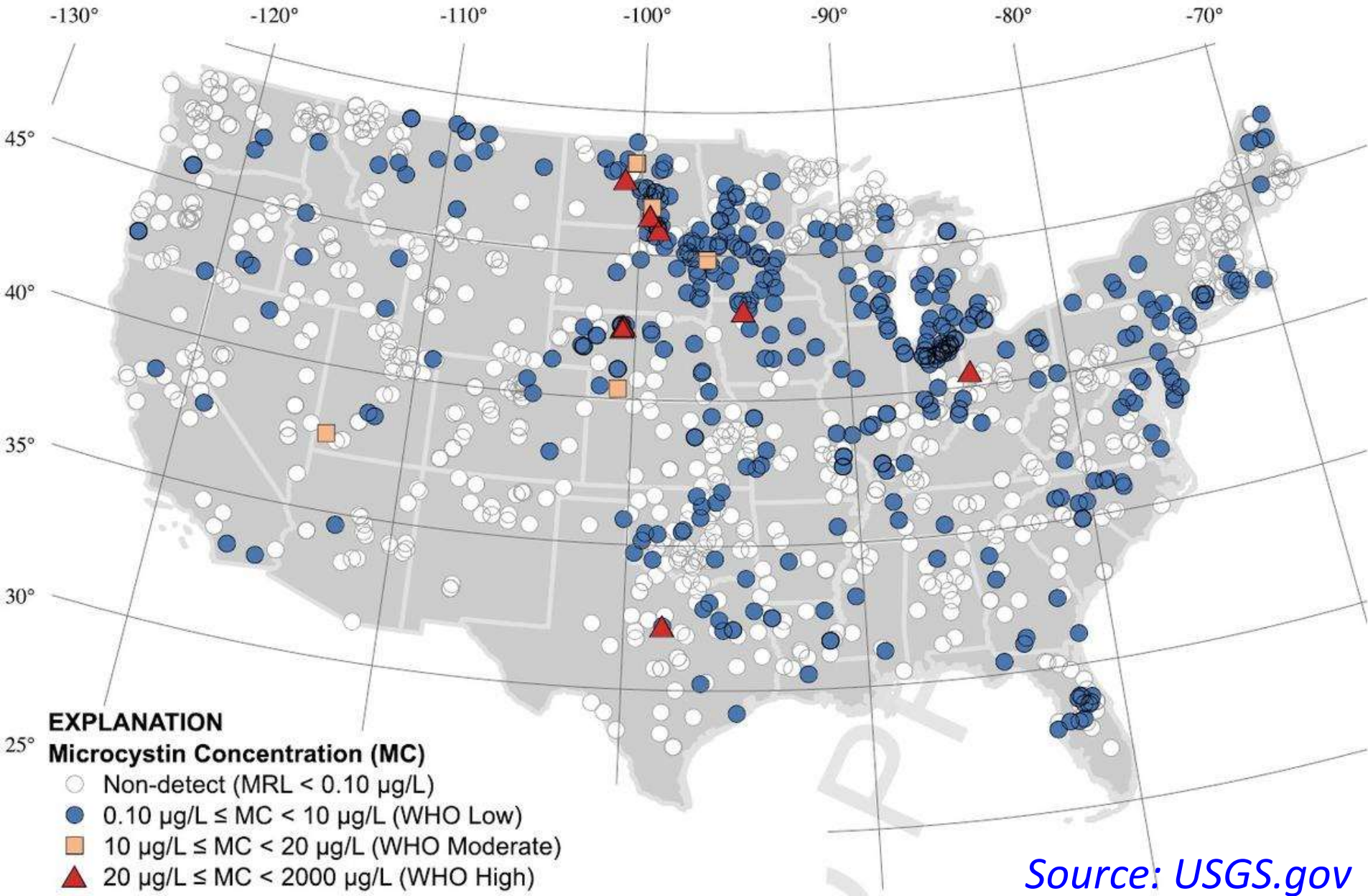
One Health Harm

The causes include incre

**CDC** Centers for Disease Control and Prevention  
CDC 24/7: Saving Lives, Protecting People™  
CDC launches updated Harmful Algal Bloom System OHHABS as hot weather h



# HABs are occurring nationwide





# Drinking Water Treatment Problems Associated with Harmful Algal Blooms

- **Increased Organic Load**
  - Total Organic Carbon (TOC)
  - Dissolved Organic Carbon (DOC)
- **Taste and Odor (T&O)**
  - Geosmin, MIB
- **Aesthetic concerns**
- **Cyanotoxins**

**Can and do algaecides help?**



# Harmful Algal Blooms and microcystins

## HAB in Norwalk, OH 2014



**Monday morning**

**Microcystin = 12 -22 ug/L**

**Treated with EarthTec Monday afternoon**



**Wednesday morning**

**36 h post-treatment.**

**Microcystin <1 ug/L by Friday**

Ohio EPA commended Norwalk on their appropriate management of the bloom.

# Harmful Algal Blooms and microcystins HAB in Herriman, Utah in Aug, 2015



Herriman responded by immediately applying 4 ppm EarthTec and two weeks later a follow-up dose of 2 ppm

# Harmful Algal Blooms and microcystins

## Herriman city officials say Blackridge Reservoir again safe for swimming

By Tori Jorgensen  
For the Deseret News  
Published: Wednesday, Sept. 2 2015 5:45 p.m. MDT

Print | Font [+][-] | [Leave a comment »](#)



[View 12 photos »](#)

The Blackridge Reservoir was closed due to an algae bloom in Herriman on Friday, Aug. 7, 2015.

Stacie Scott, Deseret News

### Summary

Herriman city officials say Blackridge Reservoir is now safe

**HERRIMAN** — City officials say Blackridge Reservoir is now safe for swimming after chemical algaecide treatment decreased contamination levels.

# Harmful Algal Blooms and microcystins

Badger 10/4 9am

**EARTHTEC**  
®



# Harmful Algal Blooms and microcystins

Badger 10/5 @9am

**EARTHTEC**  
®



# Harmful Algal Blooms and microcystins

Badger 10/6 @9am



# Harmful Algal Blooms and microcystins

Badger 10/9

**EARTHTEC**<sup>®</sup>





# Harmful Algal Blooms and microcystins

Badger 10/4 9am

**EARTHTEC**



# Harmful Algal Blooms and microcystins

Badger 10/5 @9am

**EARTHTEC**  
®



# Harmful Algal Blooms and microcystins

Badger 10/6 @9am

**EARTHTEC**  



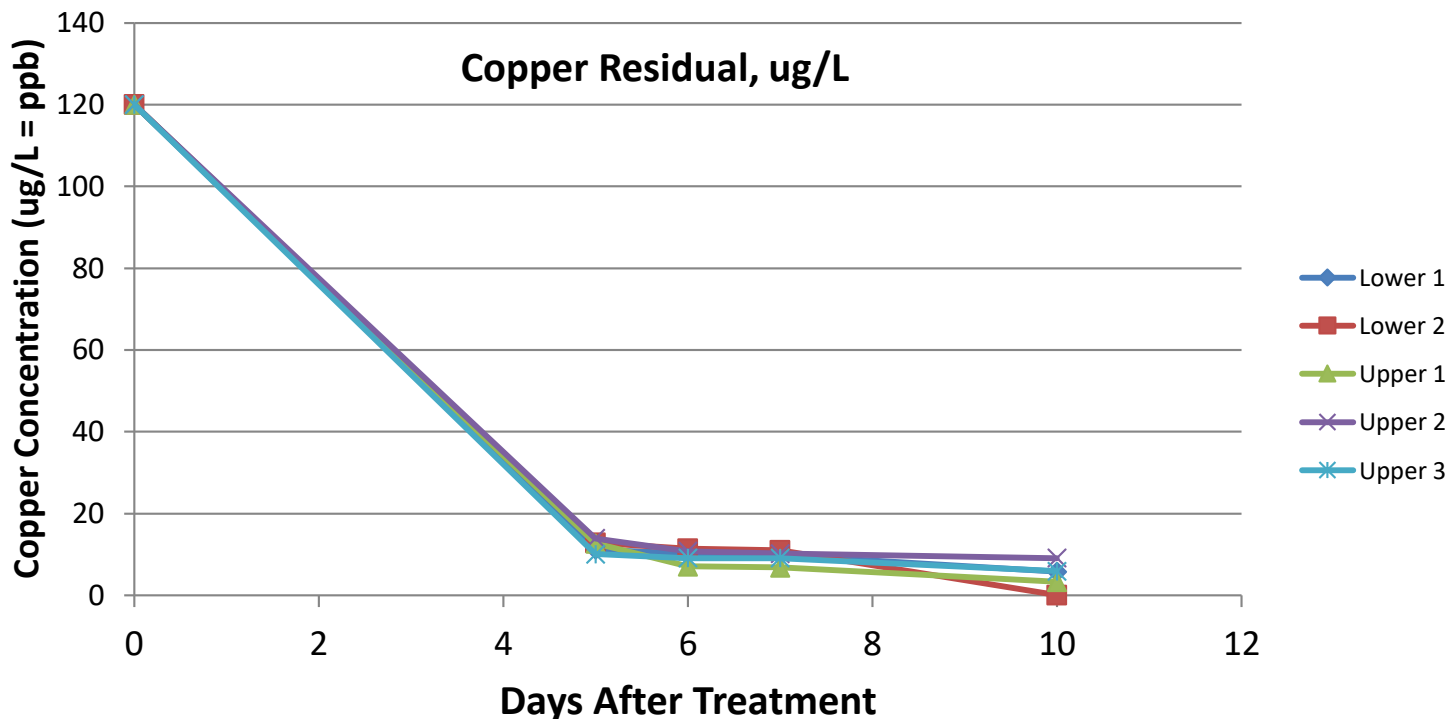

# Harmful Algal Blooms and microcystins

Badger 10/9

**EARTHTEC**  
®



## Copper residual concentration following treatment of algal bloom July 1, 2016 using EarthTec



### Copper residuals do not persist

**Figure:** Residual free copper in the days following algaecide application by boat of 2 gallons EarthTec per surface acre on two different reservoirs of the Norwalk, Ohio WTP, Upper and Lower. Samples taken at 6" depth at different locations around the reservoir shoreline.

# Current Biology

2011, Vol 21, Issue 21

Department of Pharmacology and Cancer Biology, Duke University School of Medicine,

## Primer

# Copper: An essential metal in biology

Richard A. Festa and Dennis J. Thiele\*

Life on Earth has evolved within a complex mixture of organic and inorganic compounds. While organic molecules such as amino acids, carbohydrates and nucleotides form the backbone of proteins and genetic material, these fundamental components of macromolecules are enzymatically synthesized and ultimately degraded. Inorganic elements, such as copper (Cu), iron and zinc, once solubilized from the

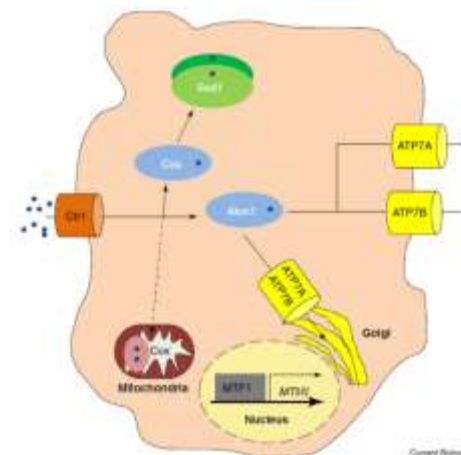
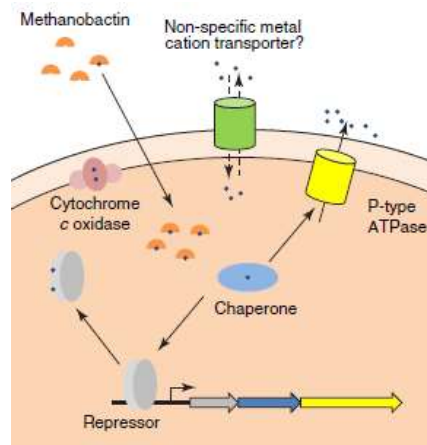


Table 1. Examples of Cu-dependent proteins and Cu homeostasis proteins.

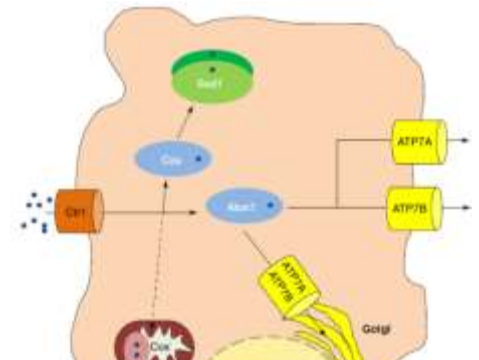
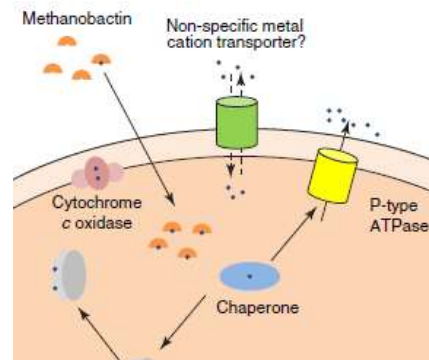
Protein	Function	Bacteria	Fungi	Animals	Plants
<b>Transcriptional regulators</b>					
Ace1	Transcriptional activation in high Cu conditions		X		
CopY	Bacterial Cu metalloregulatory repressor	X			
CsoR	Bacterial Cu metalloregulatory repressor	X			
Mac1	Transcriptional activator in low Cu conditions		X		
CueR	Bacterial Cu metalloregulatory repressor	X			
Mtf1	Metalloregulatory transcription factor			X	
Spl7	Transcriptional activator responding to Cu deficiency				X
<b>Chaperones/storage</b>					
Atx1	Metallochaperone delivering Cu to P-type ATPases		X	X	X
Ccs	Delivers Cu to the Cu/Zn SOD1		X	X	X
CopZ	Bacterial Cu chaperone	X			
Metallothionein	Low molecular weight, cysteine-rich metal-binding and detoxification	X	X	X	X
<b>Cell surface/secretory compartment transporters and receptors</b>					
P1B-type ATPases	Cu <sup>+</sup> -exporting proteins	X	X	X	X
Ctr	Cu <sup>+</sup> -importing proteins		X	X	X
Ethylene receptor	Uses Cu as a cofactor for ethylene signaling				X
<b>Oxidoreductases</b>					
Ascorbate oxidase	Reduction of L-ascorbate			X	
Dopamine-monoxygenase	Tyrosine metabolism			X	
Galactose oxidase	Reduction of galactose		X		
Amine oxidase	Oxidation of diamines	X	X	X	X
<b>Electron transfer/energy production/blue Cu proteins</b>					
Cytochrome c oxidase	Necessary for the last step of respiration	X	X	X	X
Plastocyanin	Electron transfer during photosynthesis	X			X
NADH dehydrogenase	Electron transfer from NADH to coenzyme Q	X	X	X	X
Nitrite reductase	Reduces nitrite to nitric oxide	X			
Amicyanin	Electron-accepting intermediate in the conversion of methylamine to formaldehyde and ammonia	X			
<b>Free radical scavenging</b>					
Cu/Zn SOD	Free radical scavenging	X	X	X	X
<b>Oxidase</b>					
Laccase	Melanine production	X	X	X	X
Lysyl oxidase	Catalyzes the formation of collagen and elastin precursors, extracellular			X	
Ceruloplasmin	MultiCu oxidase			X	
Hephaestin	Transmembrane ferroxidase, transports iron from the intestine to the circulatory system			X	
Multicopper ferroxidase	Cu-dependent iron uptake		X	X	X
<b>Monoxygenase</b>					
Methane monoxygenase	Oxidizes C-H bond in methane	X			
Phenylalanine hydrolase	Hydroxylation of the aromatic side chain of phenylalanine to generate tyrosine			X	
Tyrosinase	Monophenol monoxygenase, catalyzes the oxidation of phenols, melanin synthesis	X	X	X	X

## Primer

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**Copper is an essential micronutrient across all kingdoms and phyla, and participates in:**

- Photosynthesis
- Respiration
- Electron transport
- ATP synthesis
- Membrane transport
- Enzymatic activity
- Others

Hephaestin	Transmembrane ferroxidase, transports iron from the intestine to the circulatory system				X
Multicopper ferroxidase	Cu-dependent iron uptake		X	X	X
Monoxygenase					
Methane monooxygenase	Oxidizes C-H bond in methane	X			
Phenylalanine hydrolase	Hydroxylation of the aromatic side chain of phenylalanine to generate tyrosine			X	
Tyrosinase	Monophenol monooxygenase, catalyzes the oxidation of phenols, melanin synthesis	X	X	X	X

## Treatment Example in a large reservoir



## North Carolina

- Reservoir 1 - 750 acres, 12-16 MGD
- Reservoir 2 - 1,500 acres, 22-30 MGD
- Application - **Treat 275 Surface Acres on each Reservoir using 1-2 275-gallon totes every 2 weeks during the algae season**
- Treatment Dosage Dependent on Algae Cell Counts
- **Trigger for decision to treat = 50,000 cells per mL.**
- Results:
  - Algae counts greatly reduced
  - TOC Reduction Improved from 45% removal to 55%+
  - Manganese Reduced



# EarthTec use in WTPs



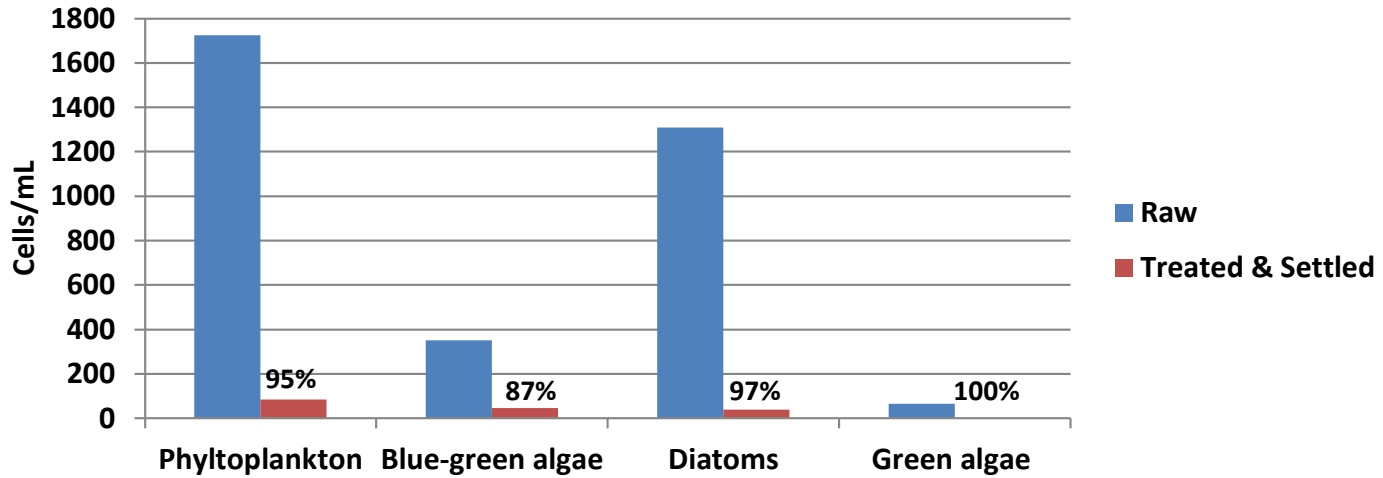
# EarthTec use in WTPs



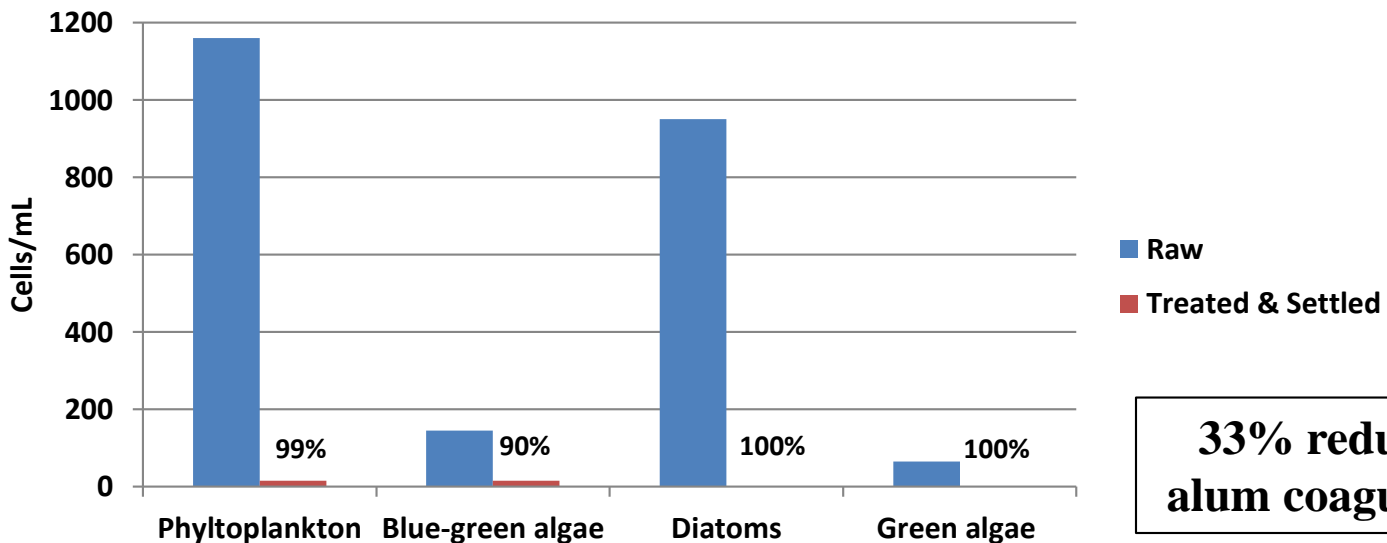
# EarthTec fed (1 ppm) at intake of two Calif WTPs, 2017



## Contra Costa - Bollman WTP



## Contra Costa - Randall-Bold WTP

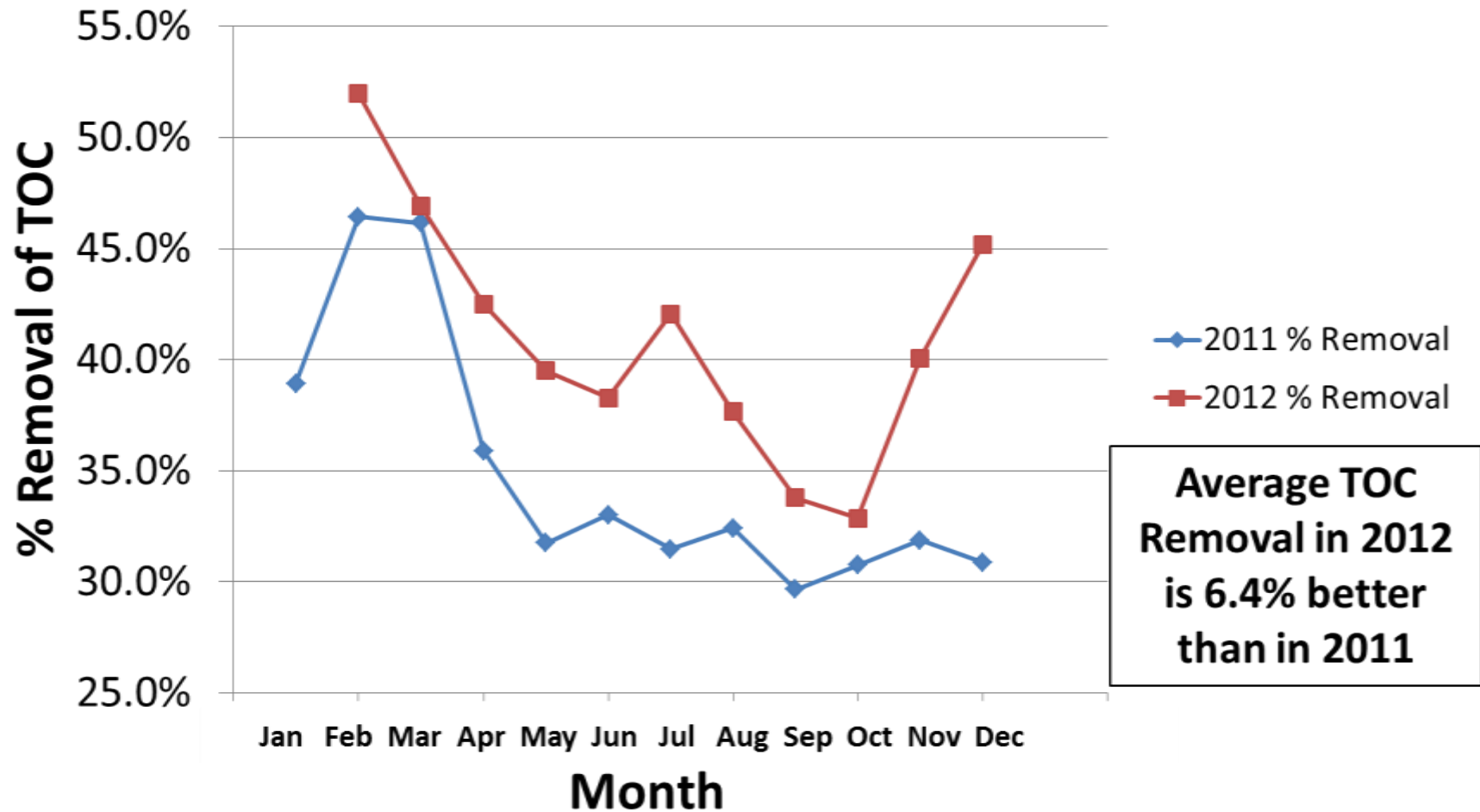


**33% reduction in alum coagulant dose**

# Treatment Example

## Texas WTP, 50 MGD

Average TOC Removal without (2011) and with (2012) EarthTec



## Treatment Example

# Texas, 50 MGD

### QUALITATIVE ASSESSMENT



#### Before EarthTec:

- Algae Mats Floating in Clarifiers
- Algae on Steel (Needed Skin Divers to Clean Framework)
- Algae present in Outdoor Filters (Short Filter Runs)
- Feeding Copper Sulfate Crystals
- Feeding 12 ppm PAC

#### With EarthTec:

- Clarifiers Clear of Algae
- Algae No Longer Adhered to Structural Steel
- Outdoor Filters Free of Algae and more regular filter runs
- Discontinued Copper Sulfate
- Only Feeding PAC when needed, <3 ppm



## Treatment Example

# Texas, 50 MGD

### COST-BENEFIT ASSESSMENT



- **Before EarthTec:**

- PAC at 12ppm,  $\$0.90/\text{lb} \times 5,000 \text{ lbs/d} = \$4,500/\text{d}$
- Copper sulfate at  $\$1.50/\text{lb} \times 100 \text{ lbs/d} = \$150/\text{d}$
- Total treatment for 50 MGD =  **$\$4,650/\text{d}$**

- **With EarthTec:**

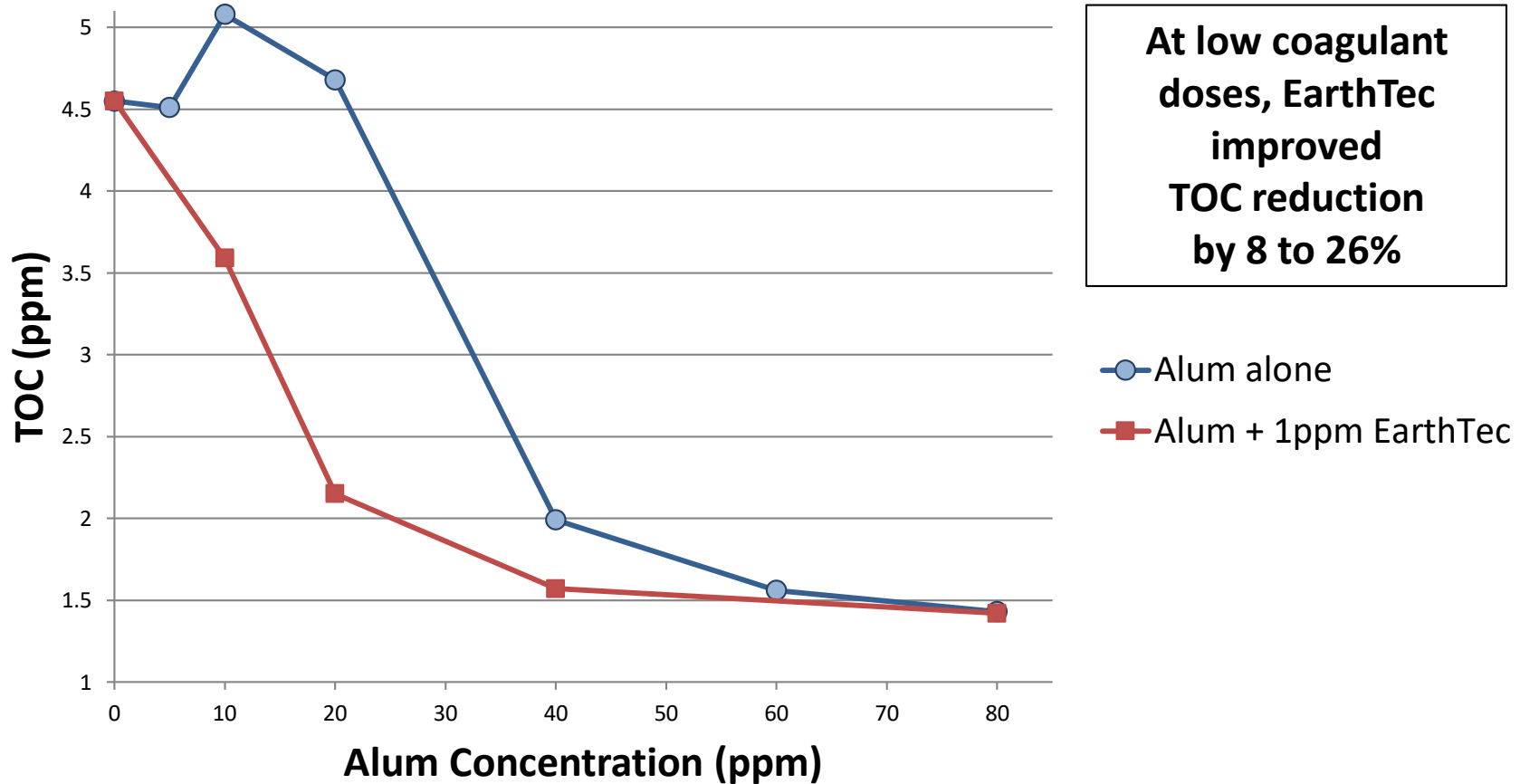
- PAC at <3ppm as needed,  $\$0.90/\text{lb} \times 1,250 \text{ lbs/d} = \$1,125/\text{d}$
- No copper sulfate
- EarthTec =  $\$750/\text{d}$
- Total for 50 MGD =  **$\$1,875/\text{d}$**

- **EarthTec saving them  $\$2,775/\text{d}$  during season**

**A 2-3 ppm reduction in consumption of PAC (Powdered Activated Carbon) offsets the cost of 1 ppm EarthTec**

# GE Water's Data on TOC and DOC Reduction using Alum alone vs Alum + EarthTec at 1 ppm:

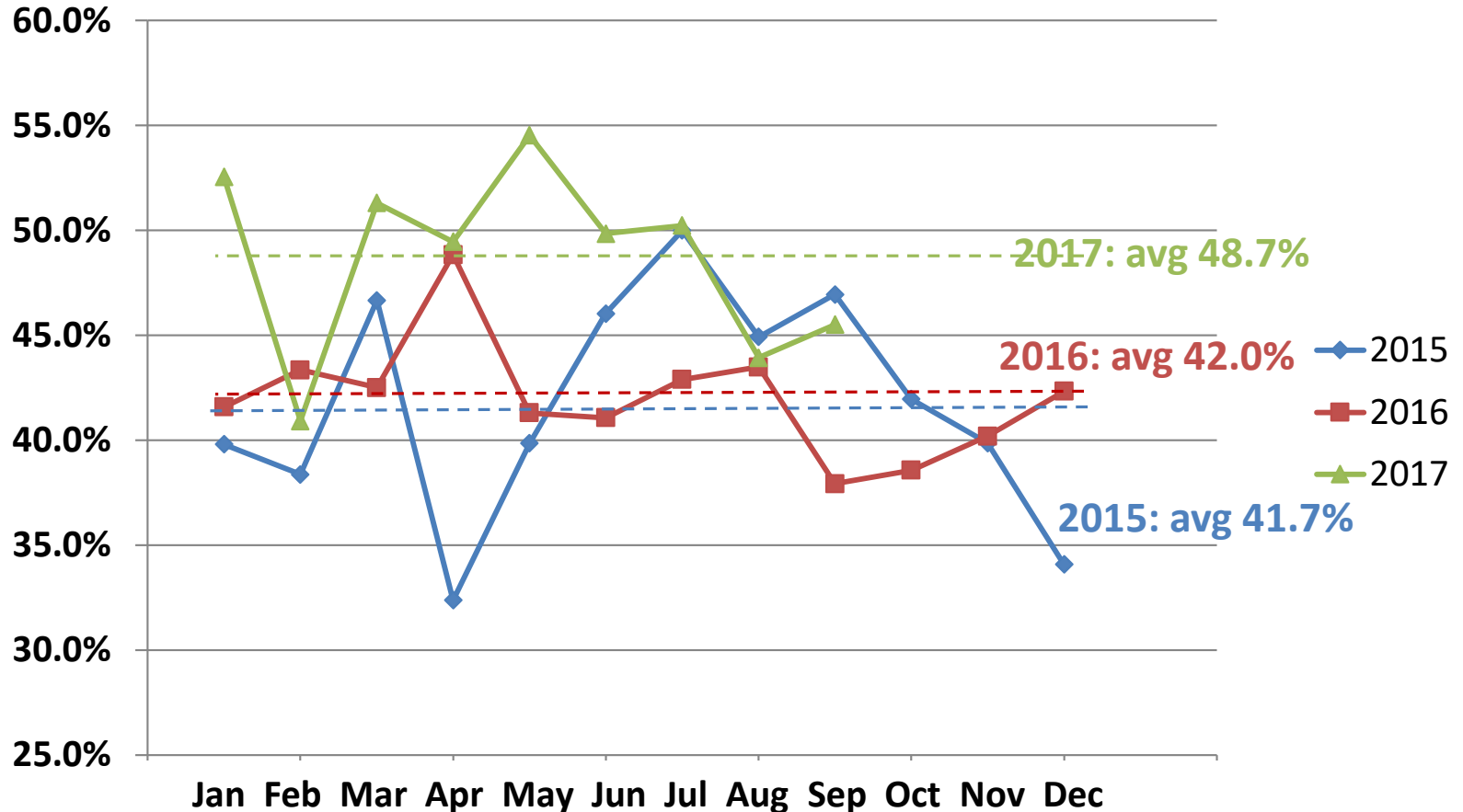
## TOC - Spavinaw, OK



# Treatment Example - Pennsylvania WTP

## TOC Reduction

without (2015 and 2016) vs with EarthTec (2017)



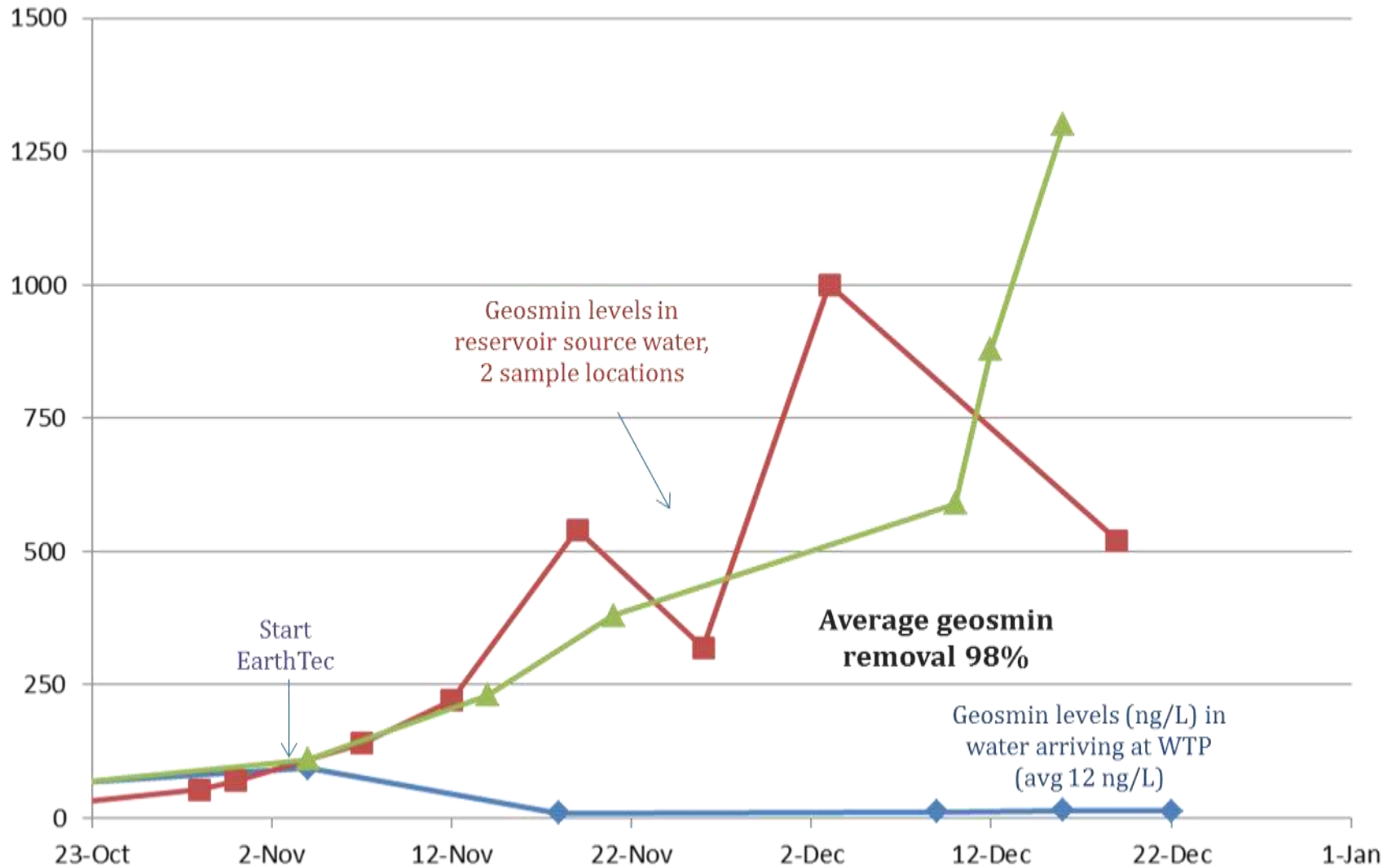
TOC reduction improved by 6-7% with the addition of 1 ppm EarthTec





# Geosmin Reduction

Geosmin removal from source water during fall of 2013.



Data from City of Tulsa, Oklahoma, Dec 2013



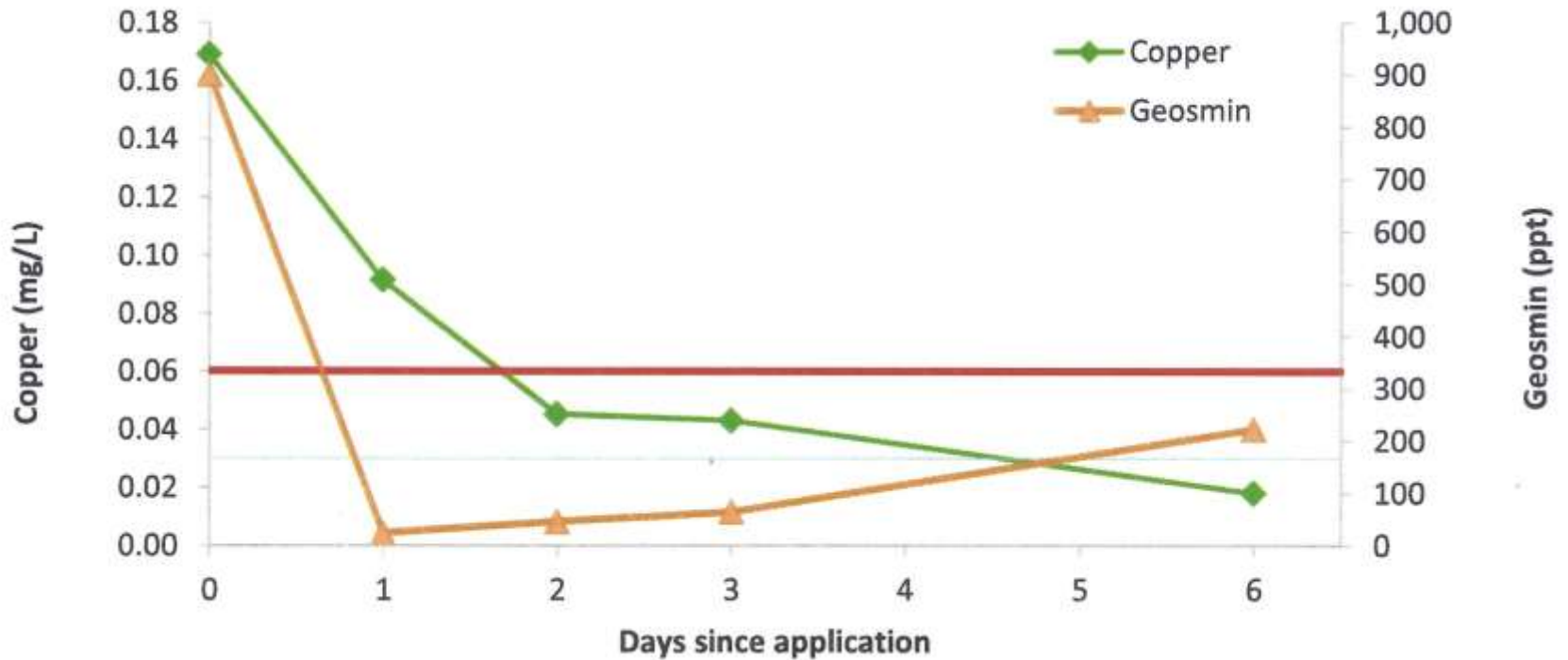
## Treatment Example Geosmin Reduction

# Tampa



- Source water: Slow-moving river
- Geosmin at time of dose 900 ng/L
- Applied 1 ppm EarthTec at water surface
- Geosmin at 24 h <30 ng/L

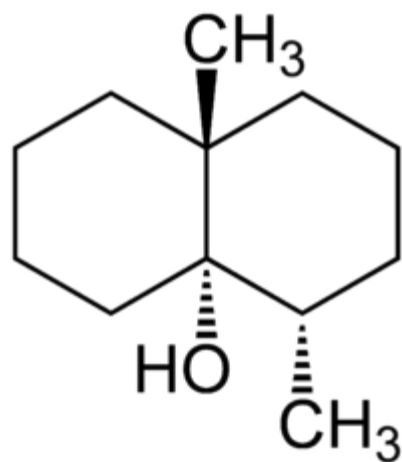
# Geosmin Reduction at Tampa using EarthTec



**EarthTec quickly reduced geosmin concentration in municipal source water by >95%**

Data from City of Tampa WTP, Florida, 2015

# Proposed Mechanism for Destruction of Geosmin



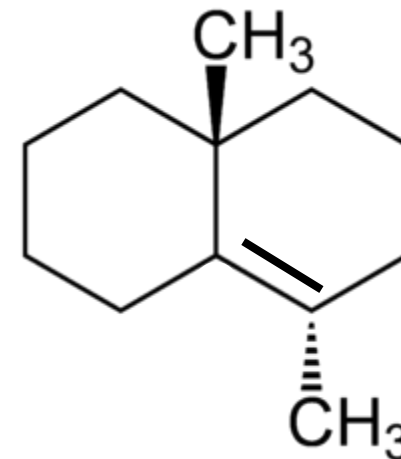
**Geosmin**

trans-1,10-dimethyl-trans-9-decalol

182 g/mol.

Boiling point: 270 °C

Acidic Dehydration



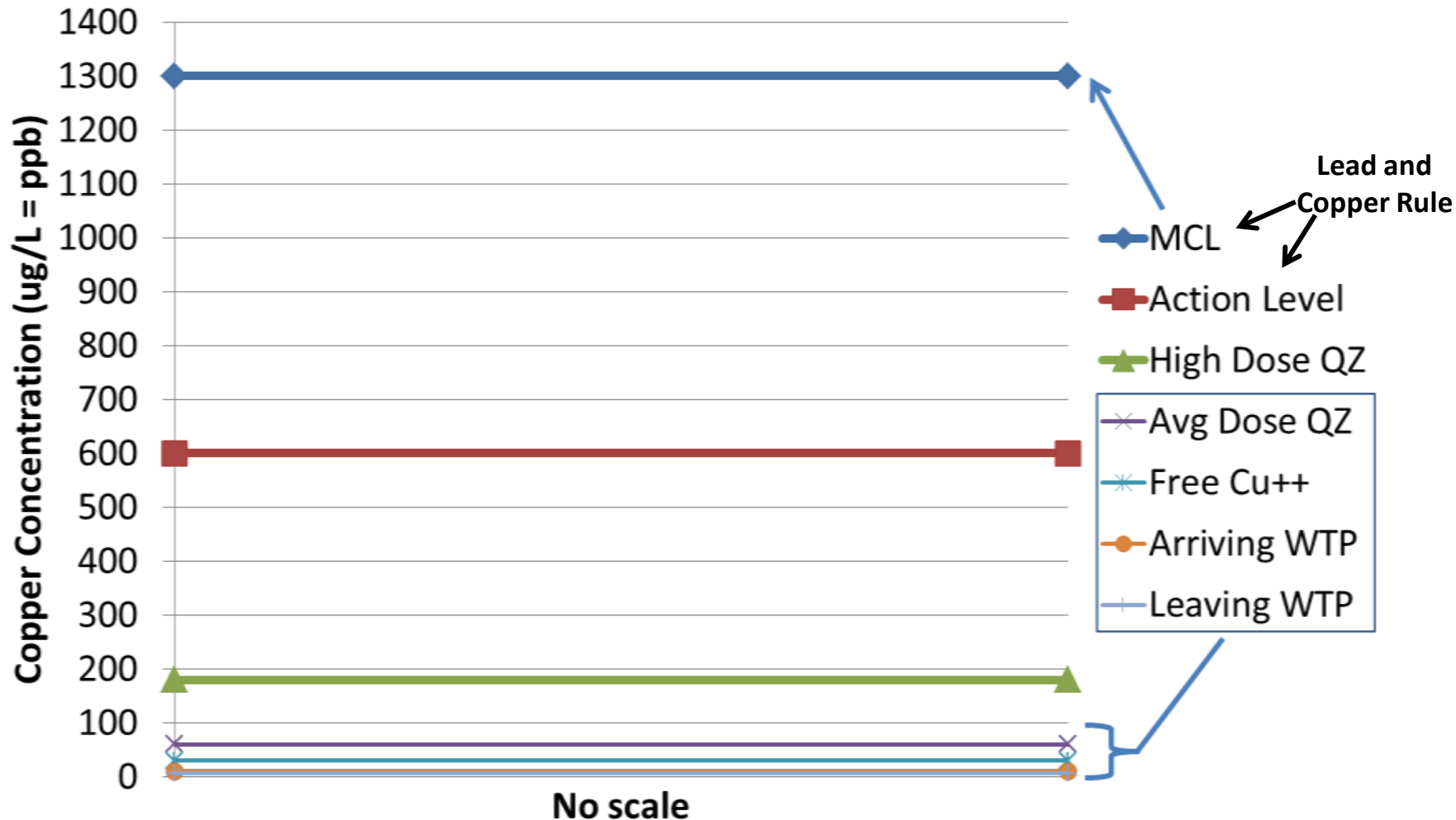
**Argosmin C**

1, 10-dimethyl-1(9)-octalin

182 g/mol.

Boiling point: 230 °C

# Copper Concentrations in Drinking Water



The copper residual concentration arriving at a WTP is approximately 1/100<sup>th</sup> of the Lead and Copper Rule standard

# Harmful Algal Blooms and common perception on cell lysis

## **The Lysed Cell (or Leaky Cell) Hypothesis:**

Cyanobacteria contain microcystin internally, and upon treatment with algaecides the cells are lysed and release microcystin into the water, consequently posing increased threats to organisms.

## **Implication:**

If you've got a cyanobacterial bloom, you better not treat (and especially not with copper sulfate) because you'll make a bad problem a lot worse!

**How accurate and relevant is this depiction?  
In what situations should this thinking carry the day?**

Source: Modified from West M. Bishop, Brenda M. Johnson, John H. Rodgers, Jr., Clemson University, Clemson SC  
"Microcystin concentrations following treatments of harmful algal blooms"

# Harmful Algal Blooms and cyanotoxins

## WHO's Provisional Guideline for Microcystin Risk in Drinking Water:

- Total microcystin-LR (free plus cell-bound) is 1 µg/L

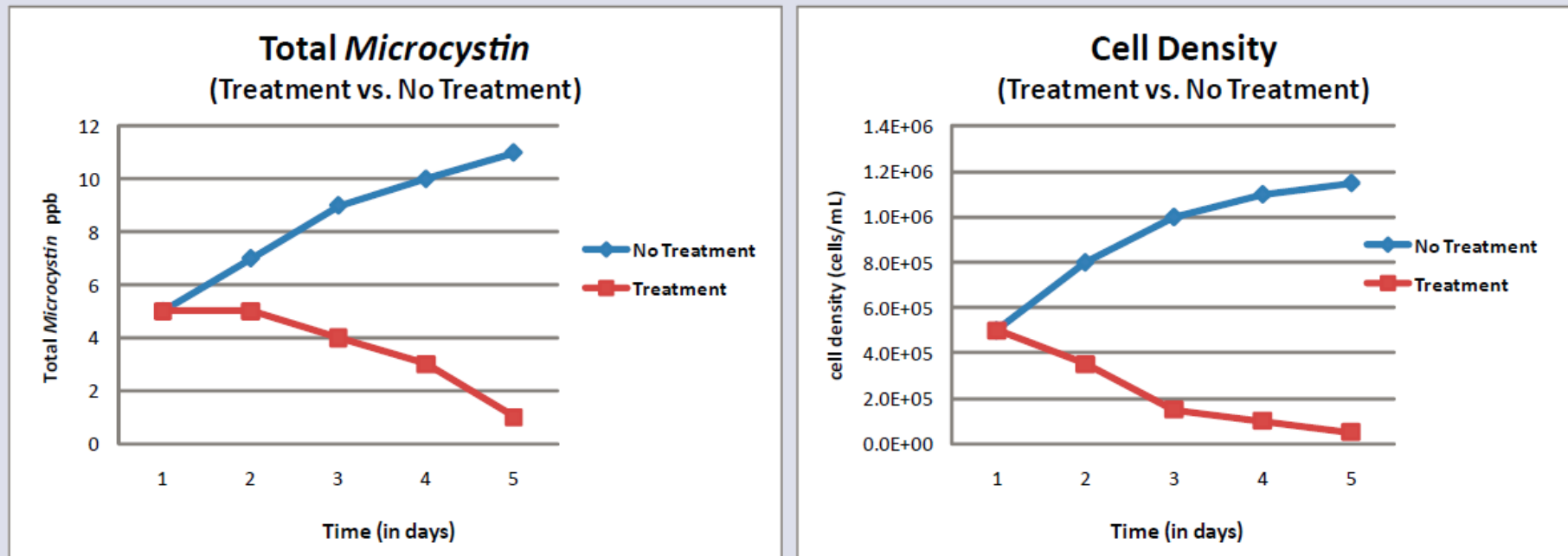
## EPA 10-Day Drinking Water Health Advisories:

- Microcystin – 0.3 ug/L in children, 1.6 ug/L in adults
- Cylindrospermopsin – 0.7 ug/L in children, 3.0 ug/L in adults

**There is no distinction made between the toxicity of intracellular and extracellular cyanotoxins in drinking water. They're equally toxic, whether inside the cell or outside the cell.**

**The question of intracellular vs extracellular is relevant primarily in the context of a WTP's capacity to remove those cyanotoxins.**

# Harmful Algal Blooms and Microcystin



The result of treatment with algaecide is a far lower concentration of total cyanotoxin as compared to taking no action

Source: West M. Bishop, Brenda M. Johnson, John H. Rodgers, Jr., Clemson University, Clemson SC  
"Microcystin concentrations following treatments of harmful algal blooms"



# Harmful Algal Blooms and microcystins

## **The Lysed (or Leaky) Cell Hypothesis:**

Cyanobacteria contain microcystin internally, and upon treatment with algaecides the cells are lysed and release microcystin into the water, consequently posing increased threats to organisms.

## **The Rebuttal:**

- If the source of the toxin is controlled (i.e. cyanobacteria) no more toxin can be produced.
- Any cyanotoxin present begins to degrade (bacteria help!)
- Treatments do not have to lyse the cell for cell death to occur.
- A decision to take “no action” often results in increased toxin.

# EarthTec study against a severe cyanobacterial bloom in Florida

Fred Singleton, Ph.D.



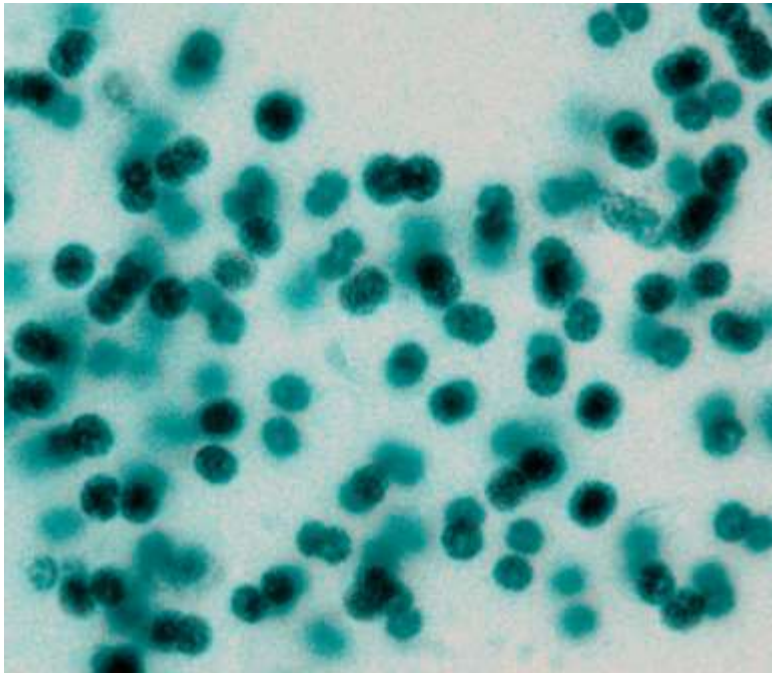
Location: Central Marine Stuart, Stuart, FL (July 2016)

Severity: Significant – Biomass mat was *ca.* 8" thick. Primarily *Microcystis*.

Understanding a model-of-action model begins with an understanding of the morphology of the target organisms

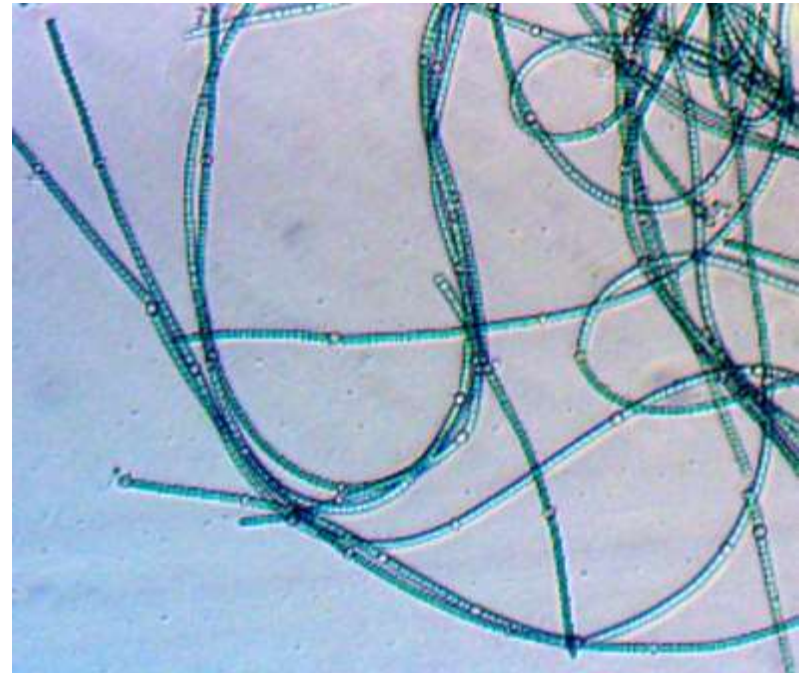
### Non-Filamentous

*Microcystis* sp. (400X Mag.)

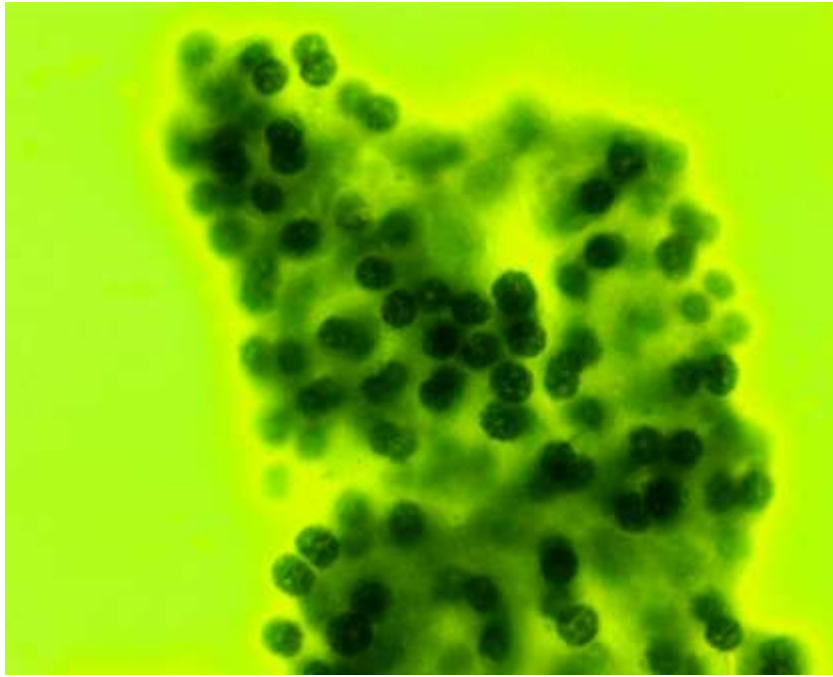


### Filamentous

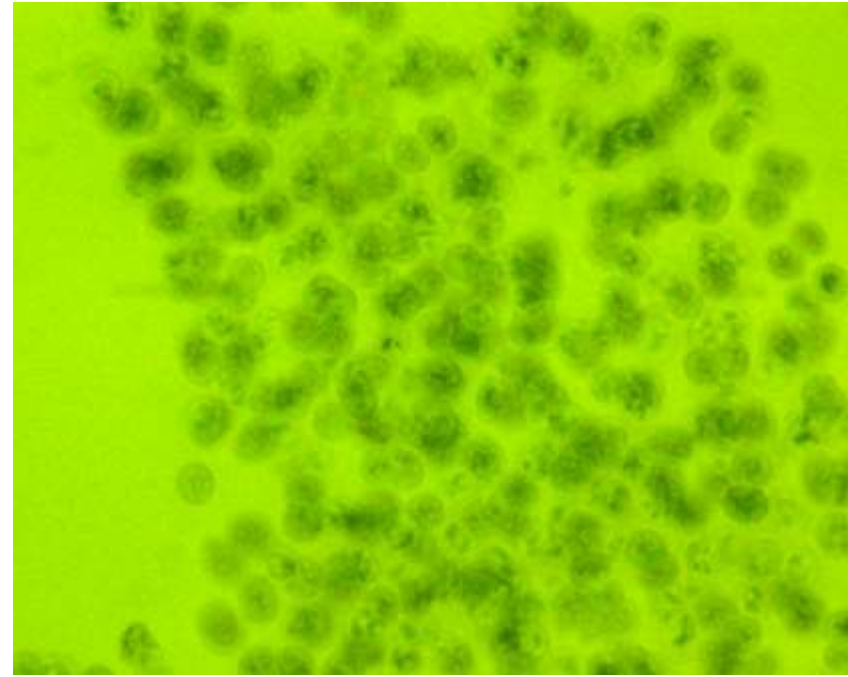
*Anabaena* sp. (125X Mag.)



*Microcystis* sp. + 120 ppb Cu (EarthTec), T = 0



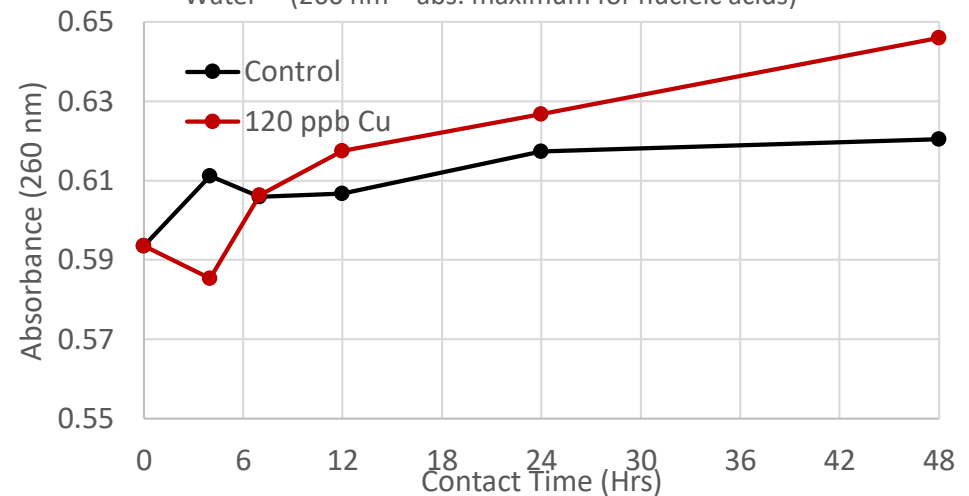
*Microcystis* sp. + 120 ppb Cu (EarthTec), T = 24 hr



### OBSERVATIONS

- Mass of cell clusters greatly reduced
- EarthTec does NOT cause immediate or extensive lysis of *Microcystis* cells
- EarthTec treatment results in cells slowly leaking their cytoplasmic materials into the surrounding water
- EarthTec does NOT inhibit non-target microorganisms that consume leaked cytoplasmic materials

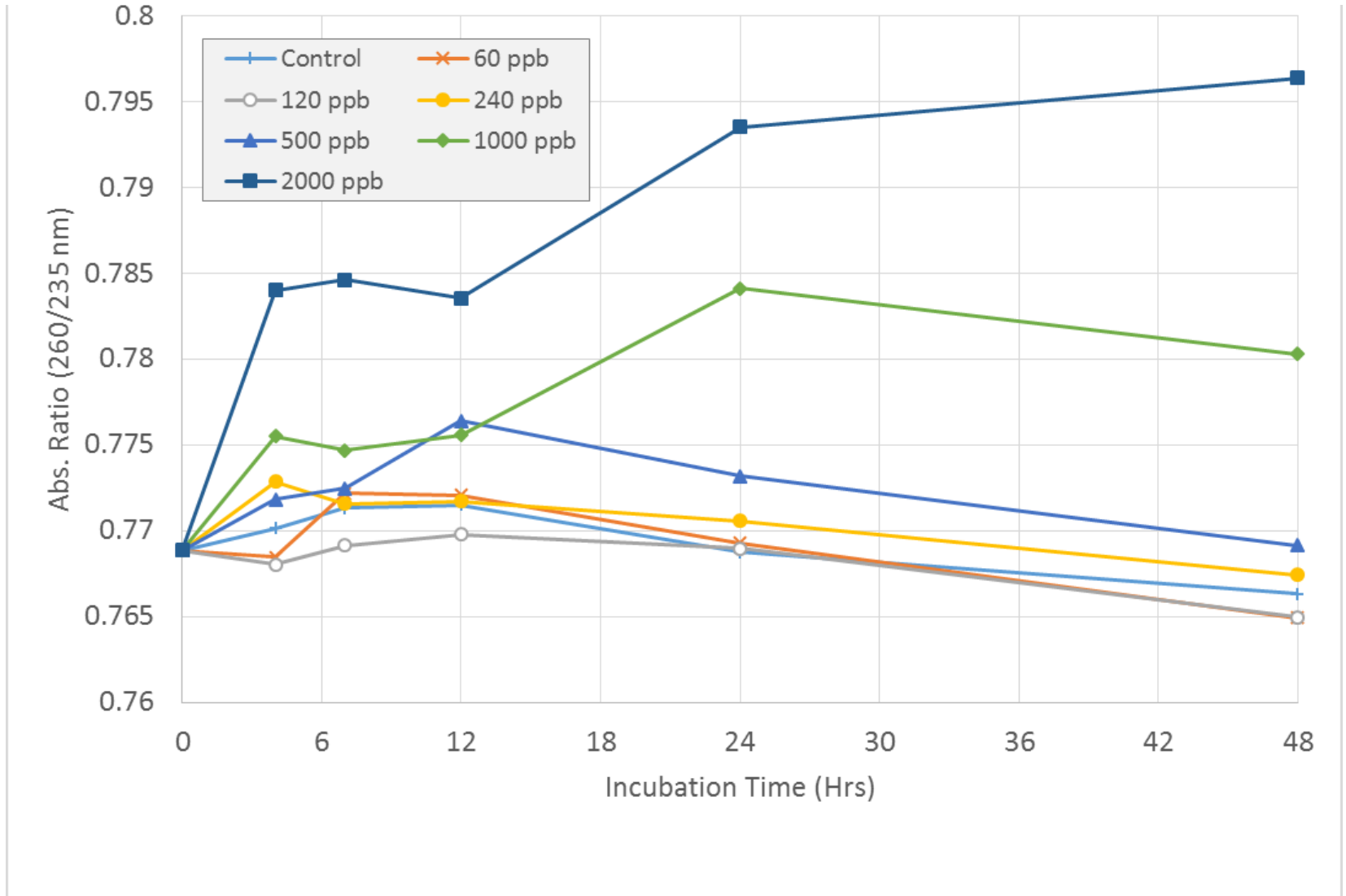
Membrane Leakage of Organics from *Microcystis* sp. in Marina Water -- (260 nm = abs. maximum for nucleic acids)



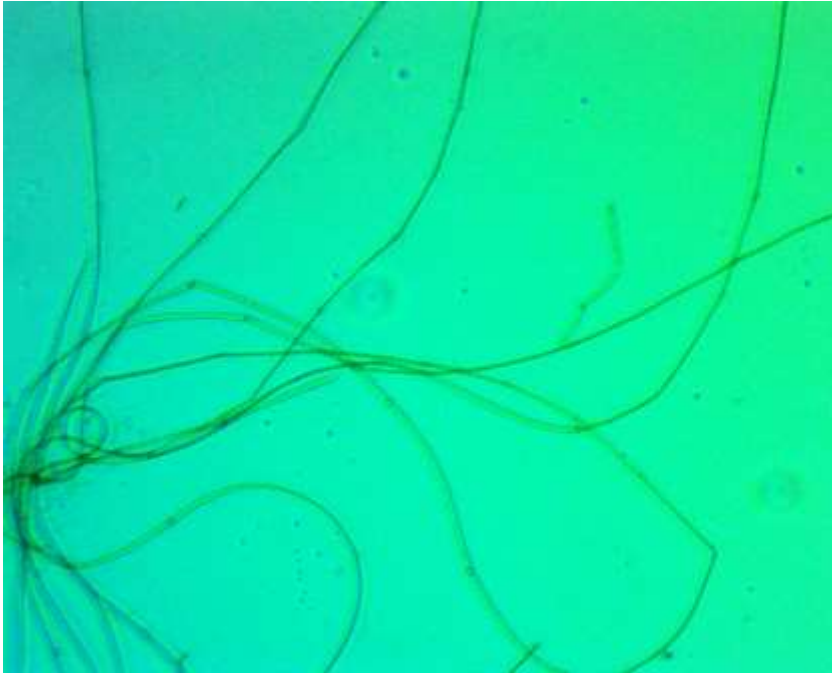
Change in relative concentrations of dissolved organics in marina water (collected during a heavy *Microcystis* bloom) treated with various concentrations of Cu (as EarthTec).

Wavelengths = 260 and 235 nm as indices of nucleic acids and carbohydrates, respectively.

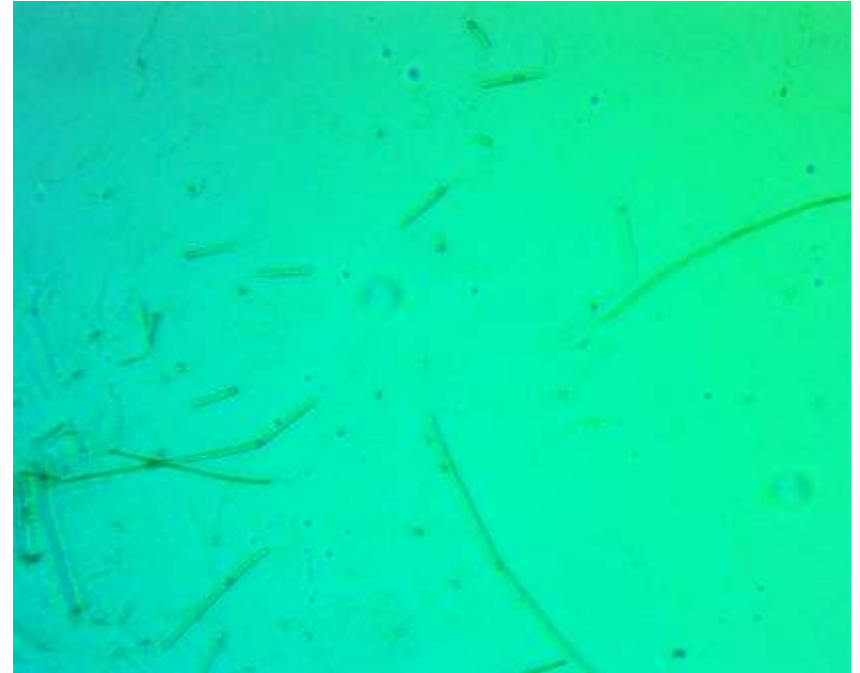
**Significant changes occur only at doses of 500 ppb and higher.**



***Anabaena*, 120 ppb Cu (EarthTec), T = 0**



***Anabaena*, 120 ppb Cu (EarthTec), T = 8 hr**



- **Release of cells from filaments during 8 hr contact**
- **Many of the photosynthetic cells remained structurally intact**
- **Heterocysts remained structurally intact**

# Filamentous *Anabaena* treated with 120 ppb Cu as EarthTec

Remnant of sheath/gelatinous layer

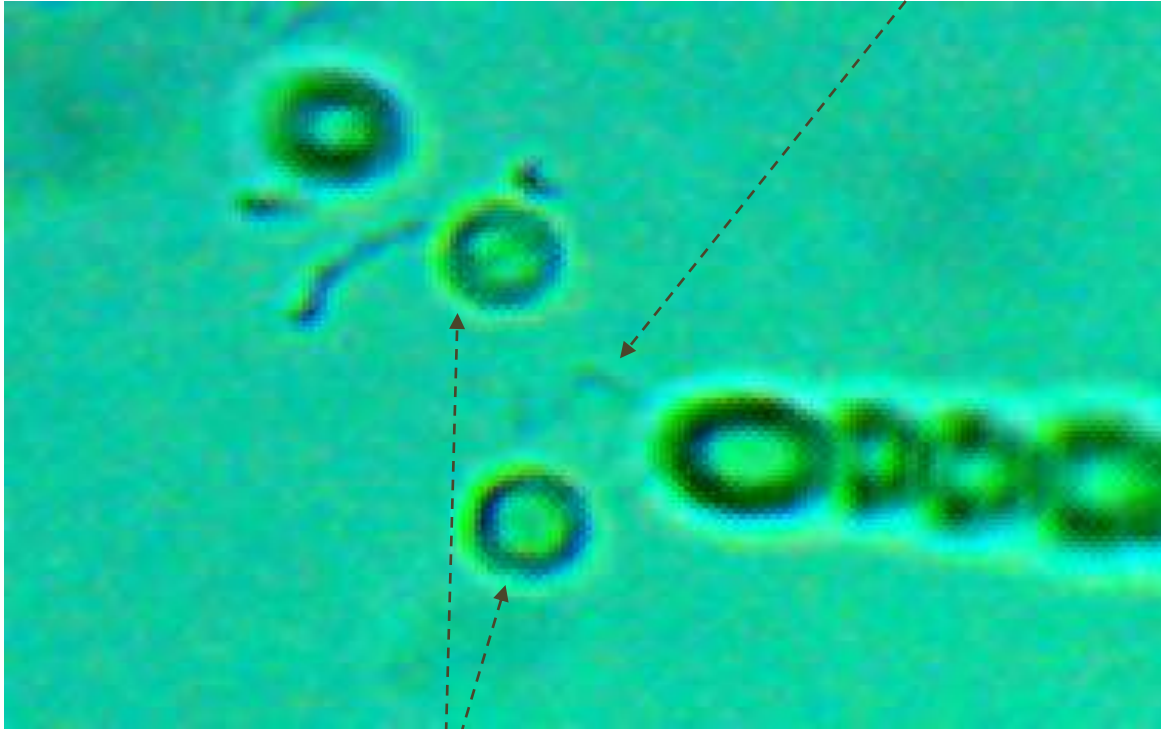


Cell being released from filament –

Cell is intact (no lysis)

*Anabaena*, 120 ppb Cu as EarthTec

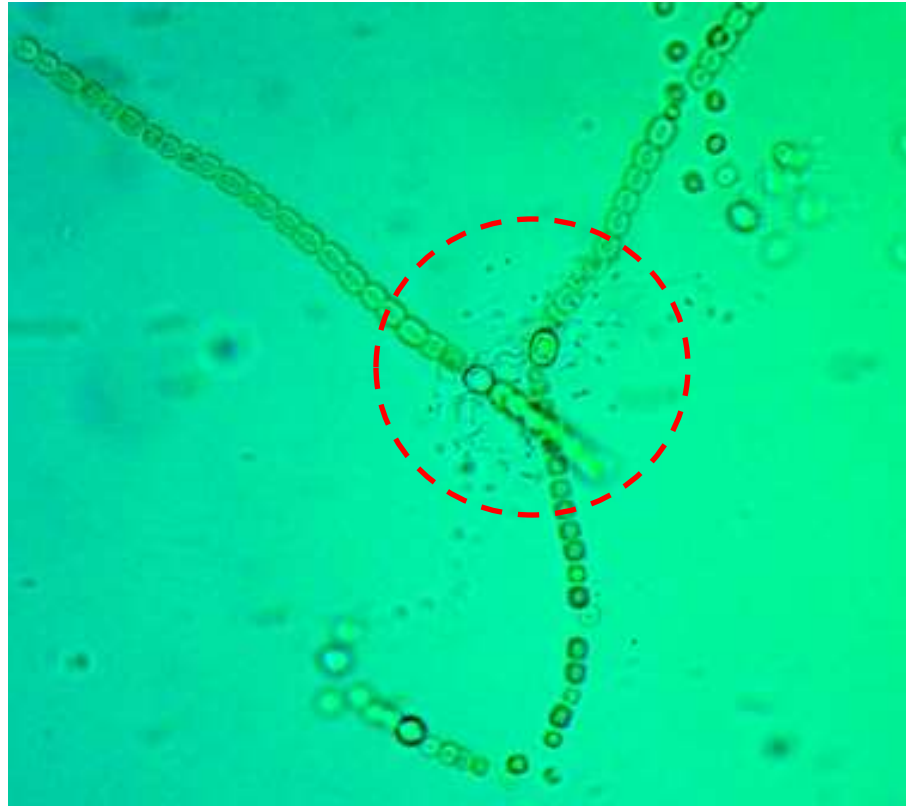
Remnant of sheath/gelatinous layer



Cells immediately after separation from filament



*Anabaena*, 120 ppb Cu as EarthTec, T = 14.5 hr



- **Heterotrophic bacteria feeding on materials released from cyanobacterial cells –**
- **Illustrates non-target organisms are not affected by EarthTec copper**
- **Most of the photosynthetic cells remained structurally intact**
- **Heterocysts remained structurally intact**

Percarbonate added to cyanobacterial culture, T = 0 to 30 mins

LW Algae Plus percarbonate

Percarbonate (strong oxidizer) is wide-spectrum, killing everything.

EarthTec added to cyanobacterial culture, T = 48 hrs

Mixed species after 48 hr contact with 60 ppb Cu (added as EarthTec)

Amoebas happily feeding on cytoplasm leaking through cyanobacterial cell wall

## **Effect of Chlorination on *Microcystis aeruginosa* Cell Integrity and Subsequent Microcystin Release and Degradation**

Robert I. Daly ,<sup>†</sup> Lionel Ho ,<sup>\*††</sup> and Justin D. Brookes <sup>††</sup>

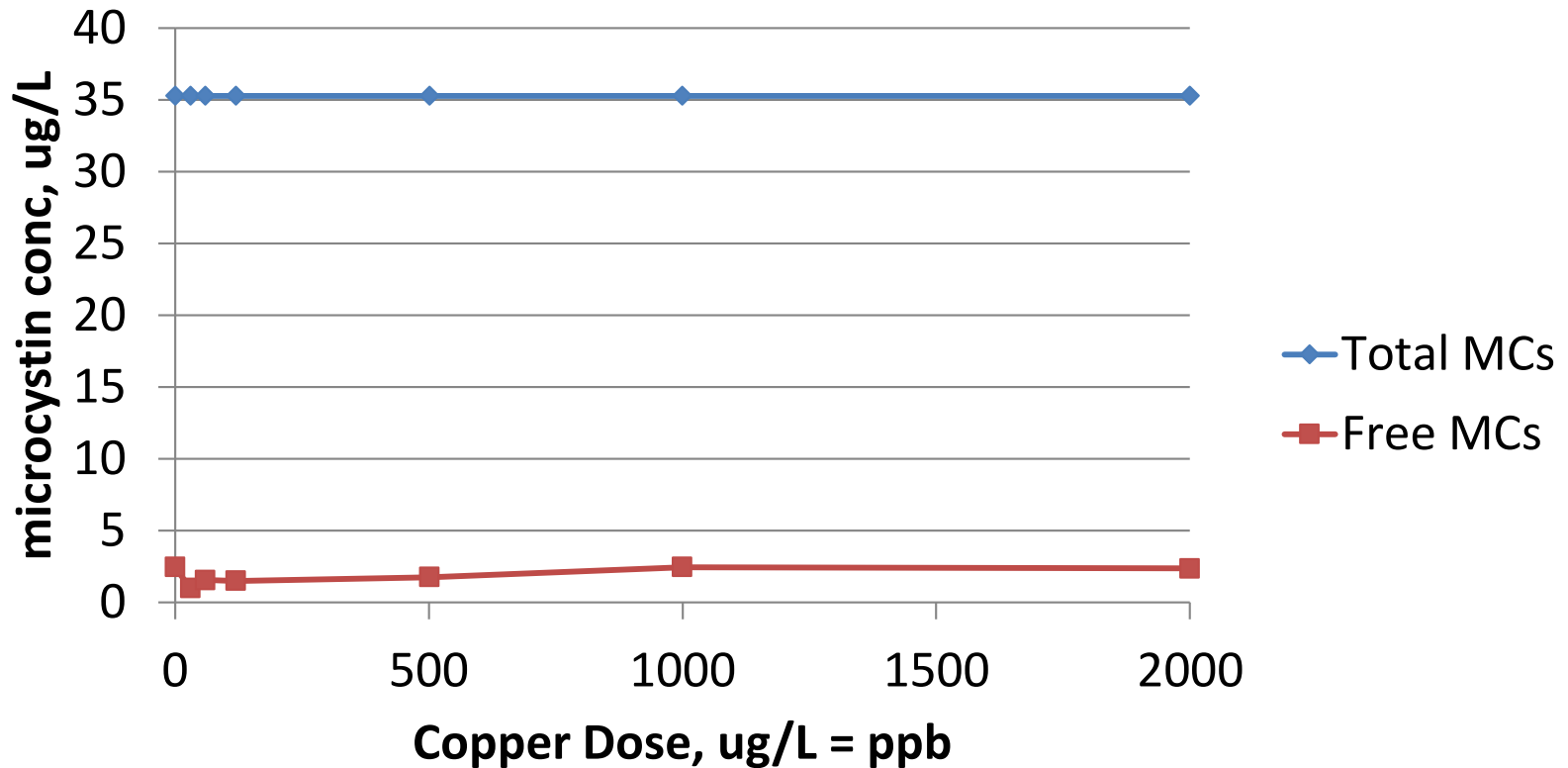
CRC for Water Quality and Treatment, Australian Water Quality Centre, SA Water Corporation, PMB 3, Salisbury, SA 5108, Australia, and School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

Chlorine lyses the cell – and does so very quickly, like  
<1 min.

**Toxins are released faster than they can be degraded.**

With a slower cell death, the degradation rate can more closely keep pace with the rate at which toxins are becoming extracellular

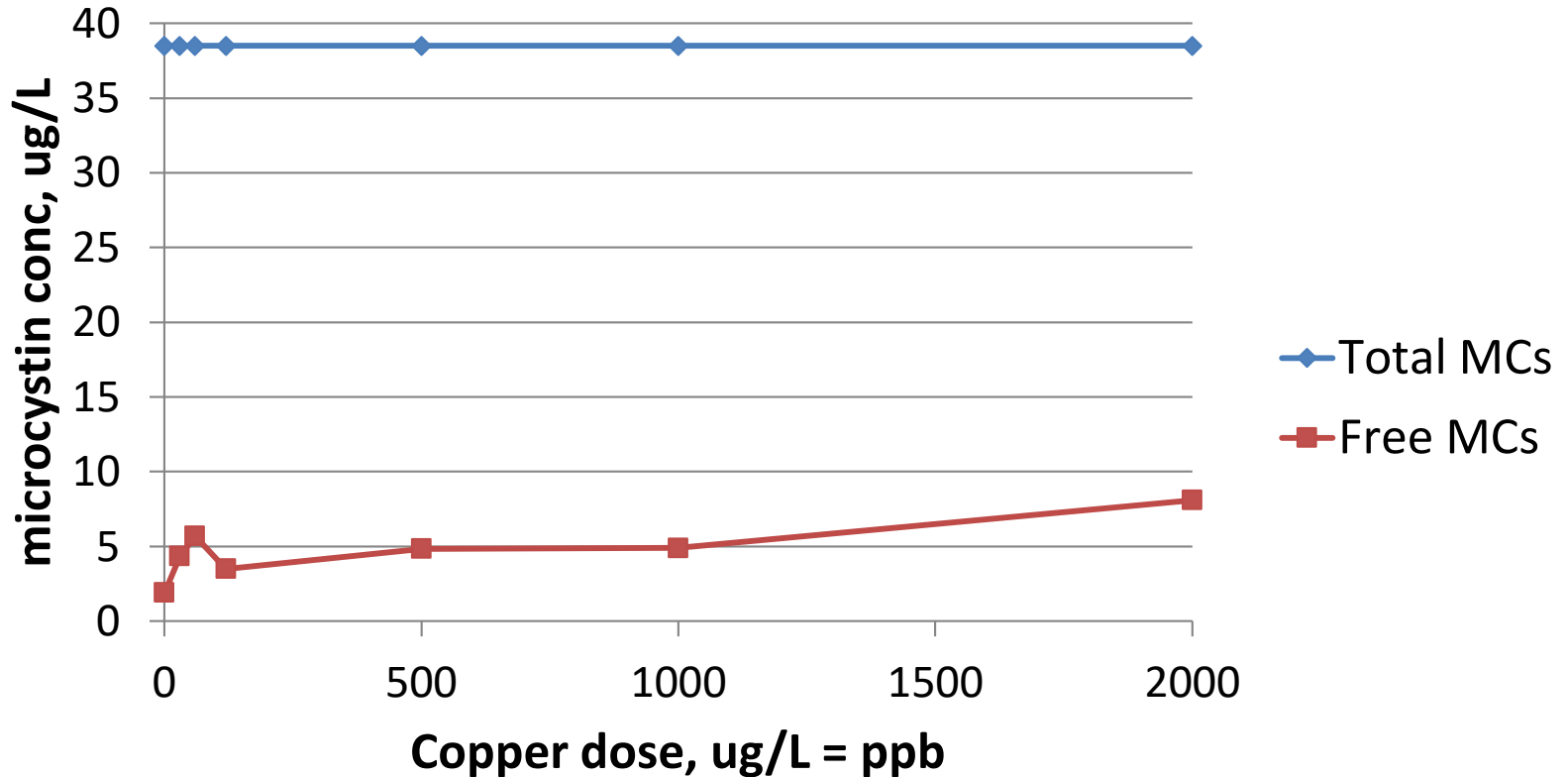
## Total vs Free microcystins (MC) following different doses of copper as EarthTec, T= 1 hr



Even at high doses, copper as EarthTec shows no catastrophic release of microcystins

# Total vs Free microcystins (MC)

following different doses of copper as EarthTec, T=24 hr



Even at high doses, copper as EarthTec shows no catastrophic release of microcystins

# **In Summary, Regarding the Cell Lysis Conversation**

**Copper is relatively slow-acting, on various metabolic functions**


**EarthTec copper is somewhat selective against cyanobacteria**

**EarthTec doses relevant to HAB management don't have to lyse the cell**

**There is slow leaking of cytoplasmic materials at a pace compatible with bacterial decomposition**

**If you're treating a location that is days away from the intake of a WTP, algaecidal treatment will stop production of more toxin and allow existing toxins to begin degrading**

**At or near the WTP, your protocol should be customized to the situation, but low doses of copper are a valuable part of the toolbox**



# Thank you!

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**Senior Scientists**  
**Earth Science Labs, Inc.**

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**Skype: David-Hammond**

