

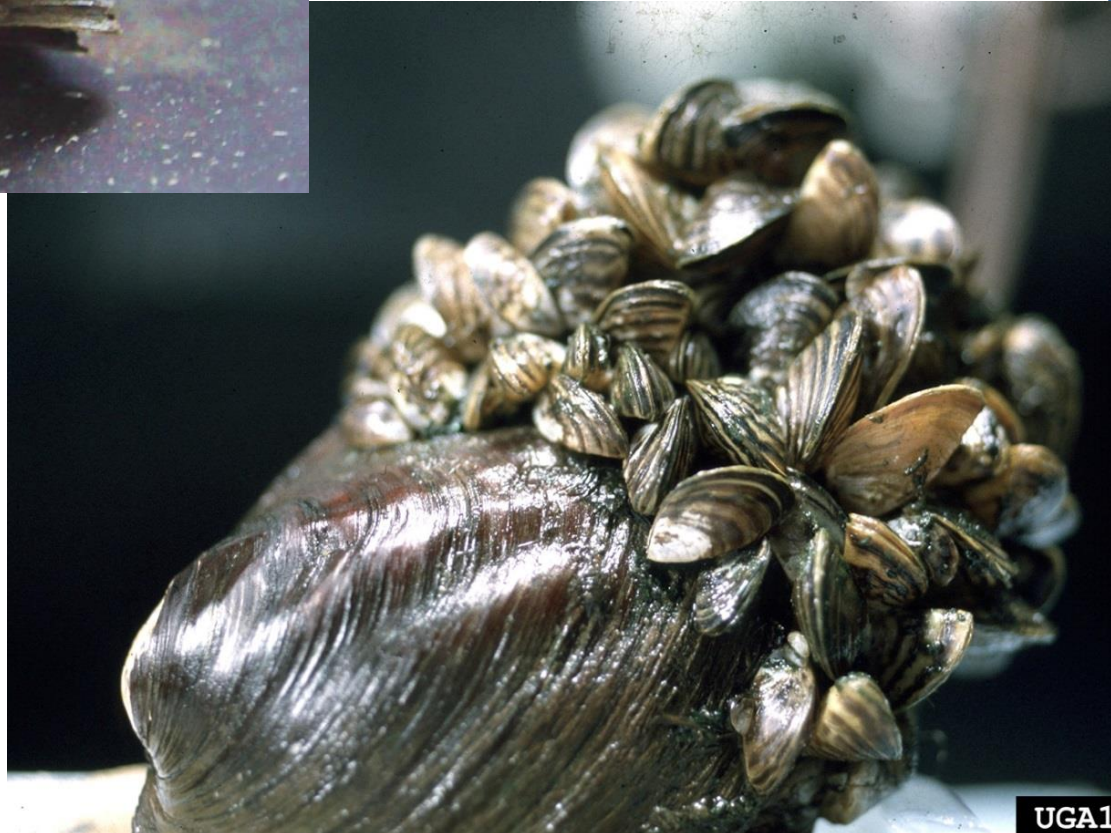


**EarthTec QZ:  
Control of Dreissenid Mussels with a More Rational  
Use of Copper**  
David Hammond, PhD



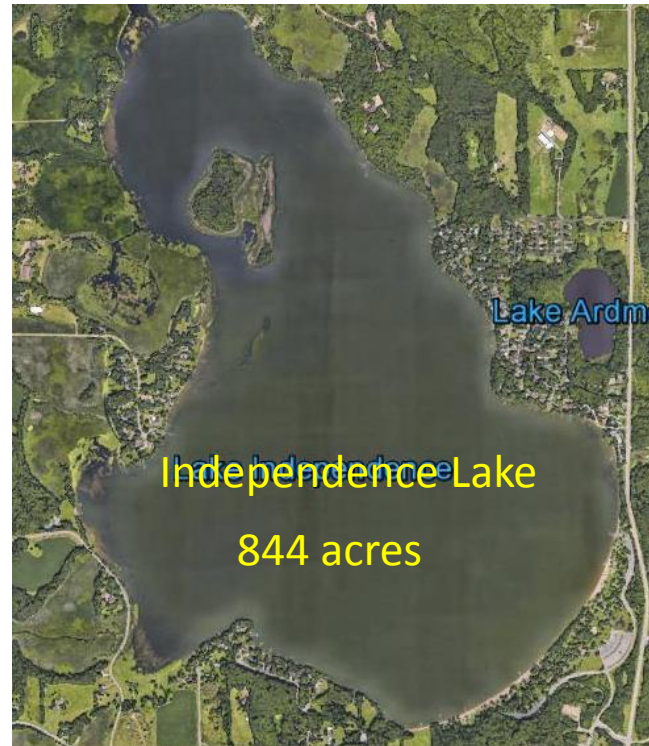
# Priority Sites for Mussel Control

- Flowing Waters (pipelines, aqueducts)
- **Open Waters (lakes)**
- Closed Systems (ballast, sprinkler)





# Recent Treatments to Control Mussels using EarthTec QZ in Open Waters of Lakes



*Work performed by PLM, Inc.,  
out of Brainerd MN*

# Control of Mussels with EarthTec QZ in the Open Waters of Lakes Ruth Lake, MN



# Control of Mussels with EarthTec QZ in the Open Waters of Lakes Ruth Lake, MN



# Control of Mussels with EarthTec QZ in the Open Waters of Lakes

## Rapid Response, Christmas Lake, MN





# Control of Mussels with EarthTec QZ in the Open Waters of Lakes

## Rapid Response, Independence Lake, MN



# Control of Mussels with EarthTec QZ in the Open Waters of Lakes Independence Lake, MN



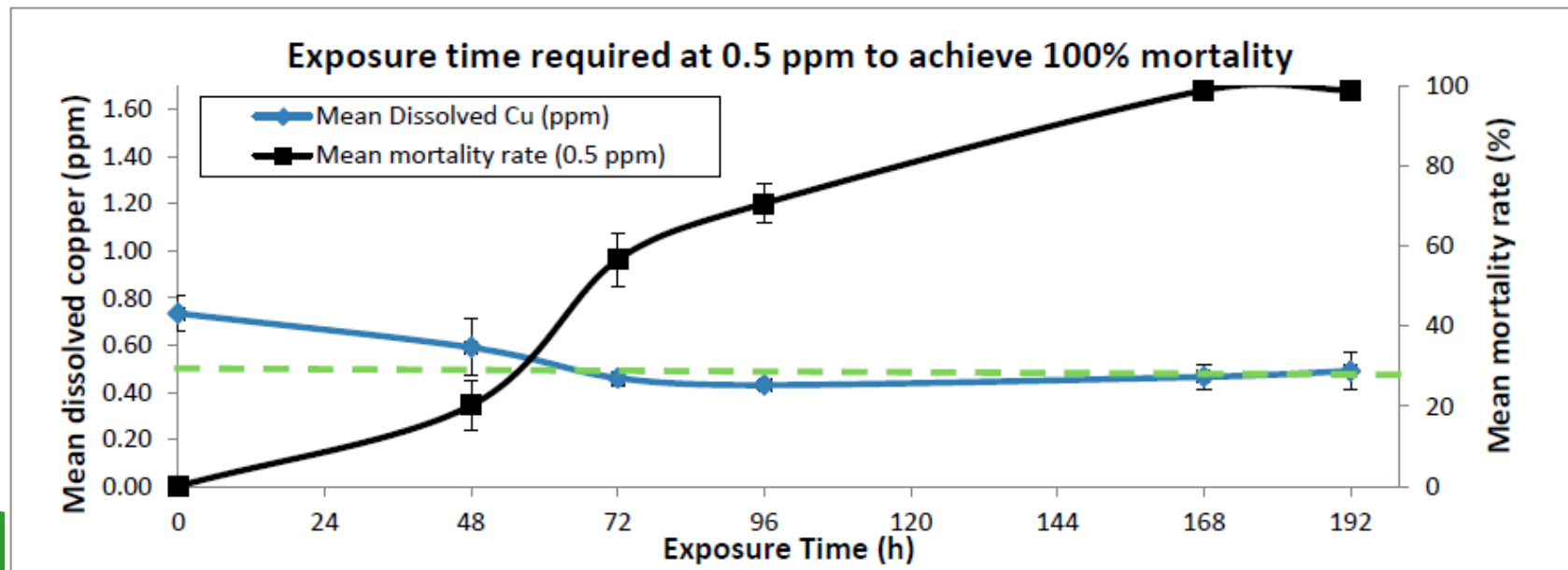
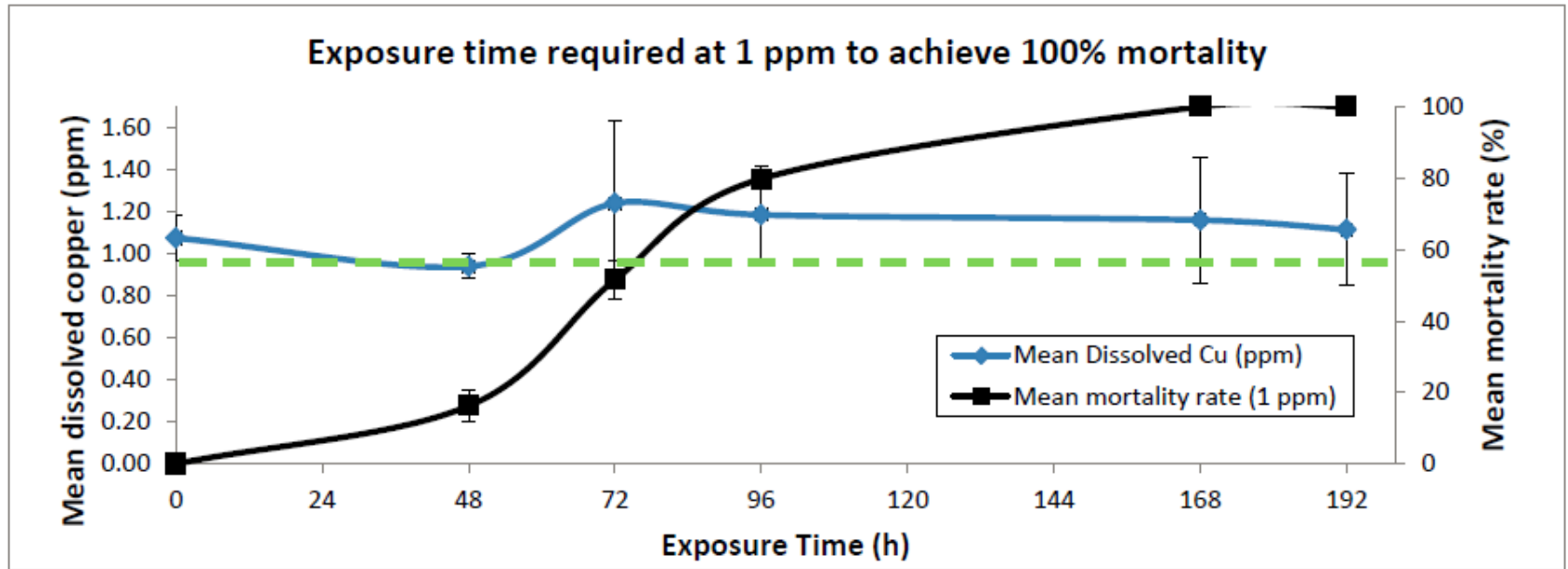
# Control of Mussels with EarthTec QZ in the Open Waters of Lakes Independence Lake, MN



# Control of Mussels with EarthTec QZ in the Open Waters of Lakes Independence Lake, MN



# Aquaria Bioassays by Minnehaha Creek Watershed District using EarthTec QZ against Zebra Mussels



# Recent Efforts to Control Mussels Using QZ in the Open Waters of Lakes



Lake Name	Christmas Lake	Independence Lake	Ruth Lake
State	Minnesota	Minnesota	Minnesota
Size (acres)	265	844	588
Treatment area (acres)	0.64	0.4	2.8
Treatment start date	2014/11/3	2014/11/3	2015/10/12
Water Temperature	39.8 F	41.9 F	56.4 F
Duration of Treatment (days)	8	8	6
Number of Doses	4	7	6
Avg Copper Conc during treat (ppb)	780	762	760
Target Organism	Zebra mussel	Zebra mussel	Zebra mussel
Outcome	Eradicated in Treatment Area	Eradicated in Treatment Area	Eradicated in Treatment Area
Cost	\$1,200	\$2,000	\$4,910

*Work performed by PLM, Inc., out of Brainerd MN*

*Lessons: Warmer=Better, Rapid Response must be Rapid!*

# Estimate of Relative Costs to Control Zebra and Quagga Mussels in Open Waters

	Zequanox	Potash	EarthTec QZ
<b>Cost per MG treated</b>	?	\$4,000	\$1,000

Based on data from Millbrook Quarry, VA, Deep Quarry Lake, IL,  
Christmas Lake, Independence Lake and Ruth Lake, MN




# 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



**What about the fish?**

## **What about the fish?**

- **EarthTec has 15-year history of use in fish farms.**
  - **Never had a fish kill.**
  - **Start at shoreline and move outward in bands, allowing fish to move to untreated areas.**
  - **Apply at dose that fish tolerate, but mussels don't**
  - **Salmonids are about 10x more sensitive.**
- 



# Priority Sites for Mussel Control

- **Flowing Waters (pipelines, aqueducts)**
- **Open Waters (lakes)**
- **Closed Systems (ballast, sprinkler)**

3.5" = 9 cm



**Quagga Mussels from Lake Mead  
display by Arizona Game and Fish Dept**



**new**

**2 months**

**4 months**

**6 months**

NEW

2 MONTHS

4 MONTHS

6 MONTHS

ABS PIPE WITH QUAGGA MUSSELS FROM LAKE MEAD





# Evaluation of Copper Based Aquatic Algaecides as Potential Control of Adult Dreissenid Mussels

Renata Claudi MSc, RNT Consulting Inc.

Carolina Taraborelli MSc, RNT Consulting Inc.

Jeff Janik PhD, California Dep. Of Water Resources

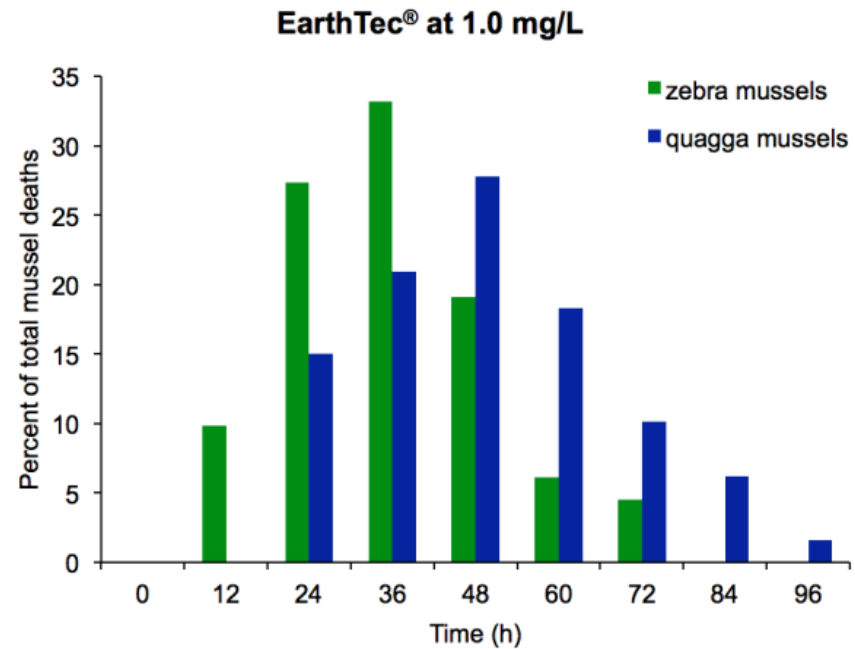
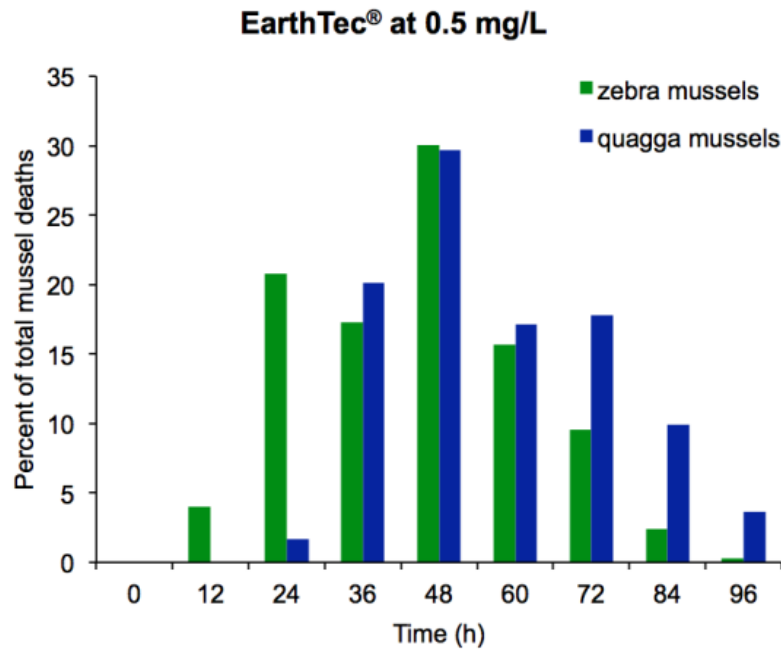
Tanya Veldhuizen MSc. California Dep. Of Water Resources



R N T C O N S U L T I N G I N C

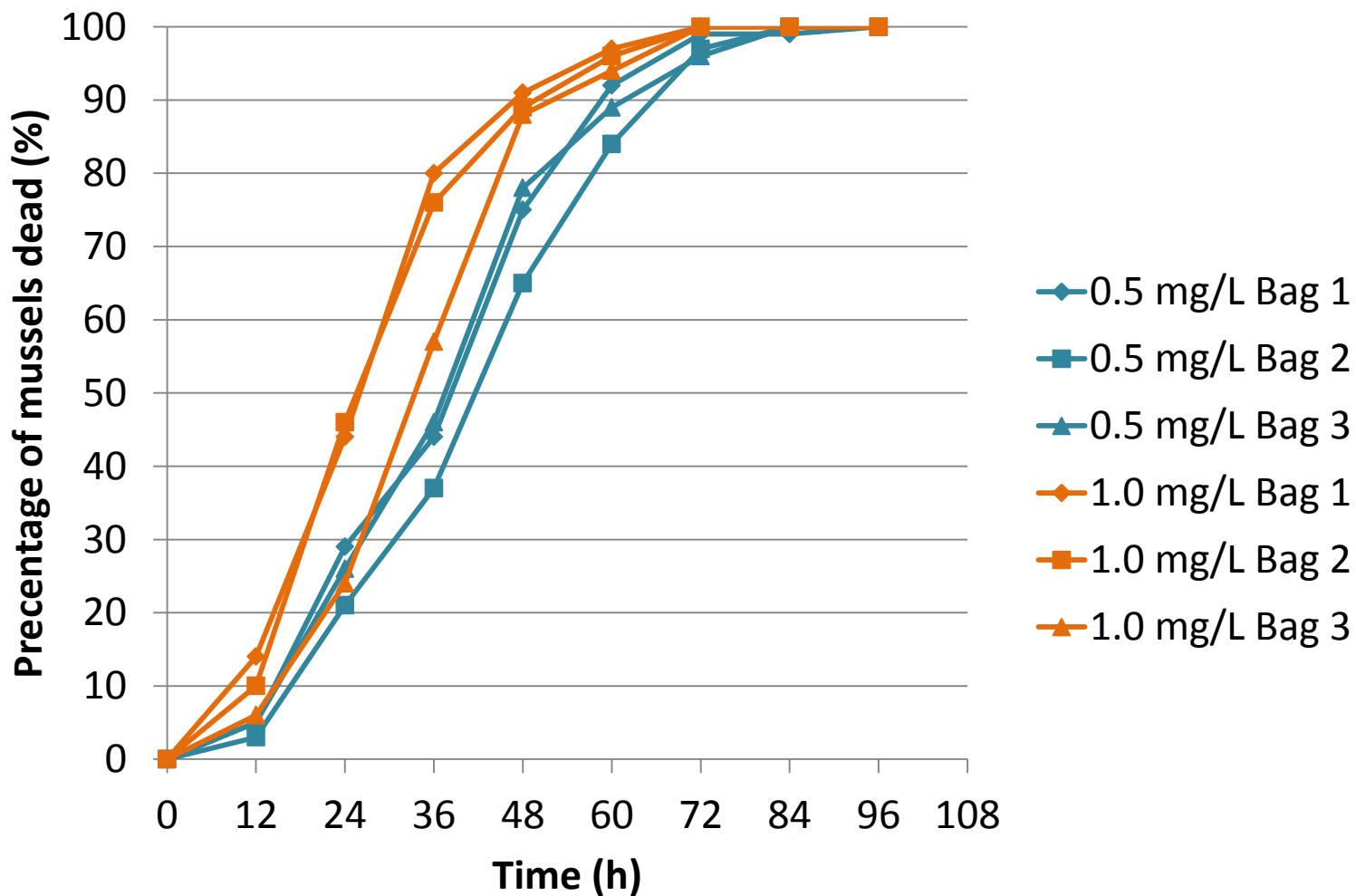


# Time-Course Mortality During Exposure to EarthTec QZ<sup>®</sup>



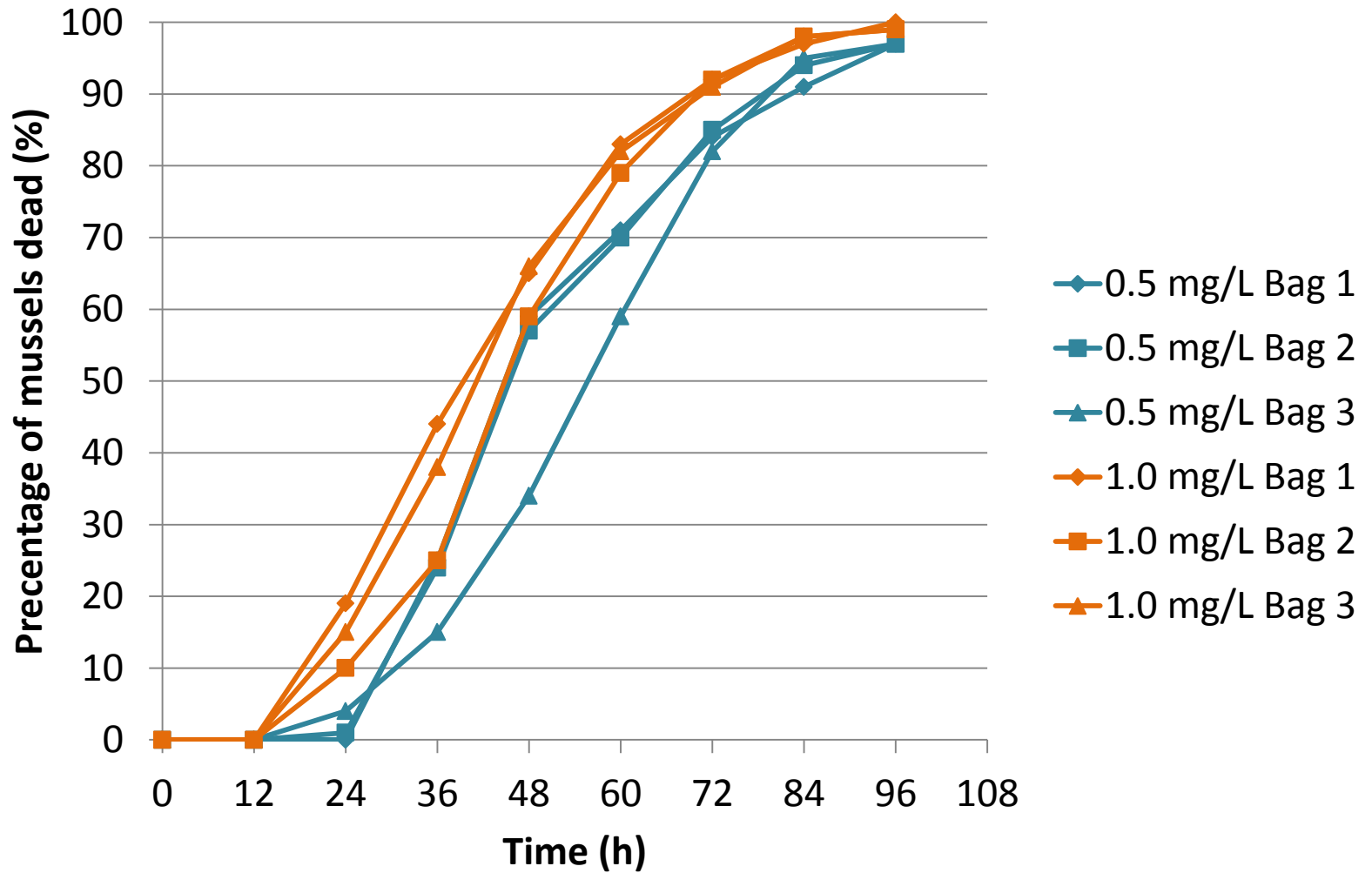


**Figure 34. Zebra mussel mortality when exposed to EarthTec® for 96 hours**



Average Temperature 17.2 C = 63 F

**Figure 35. Quagga mussel mortality when exposed to EarthTec® for 96 hours**

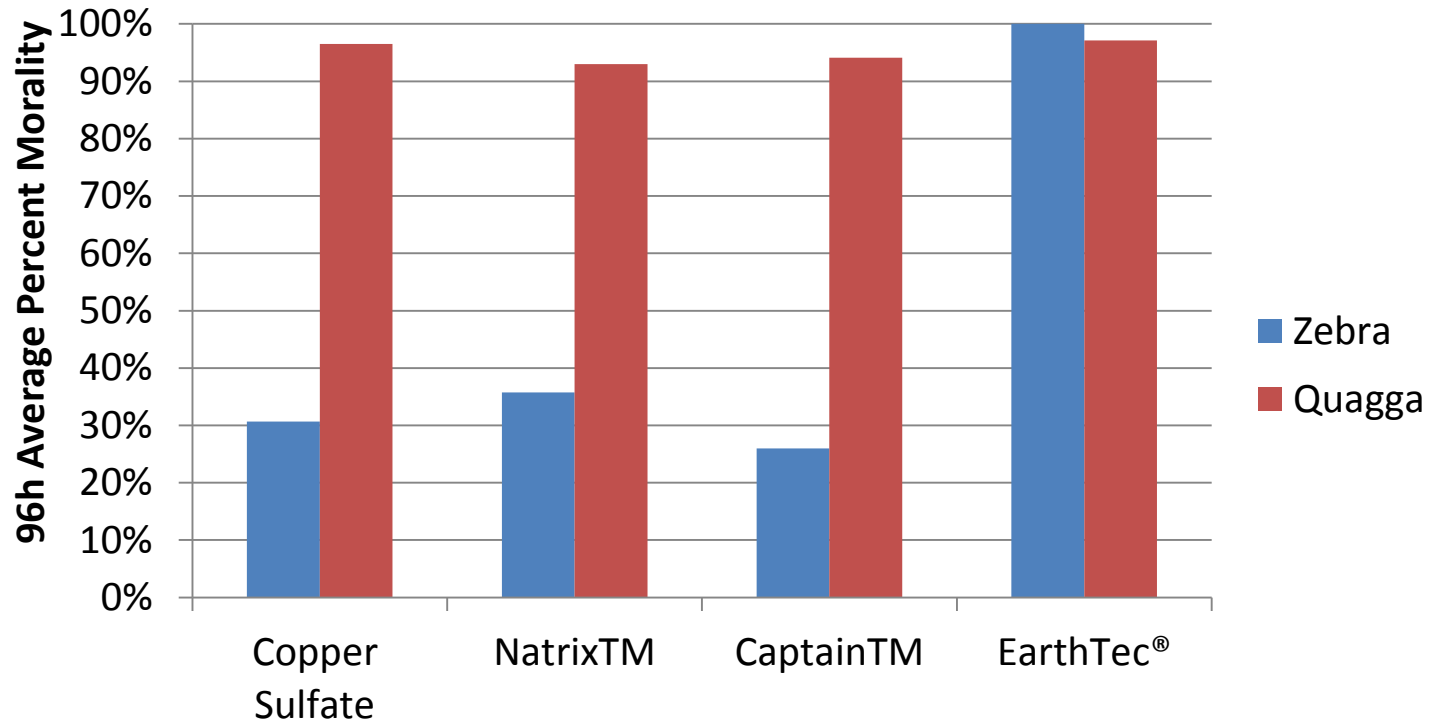


Average Temperature 17.2 C = 63 F

# Evidence that EarthTec Facilitates Biological Uptake of Copper

Figure 44. Average percent mortality after 96h of exposure to algaecides at 0.5 mg/L copper equivalent

0.5 mg/L copper equivalent



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.



# EarthTec QZ for Mussel Control



**Watters, Gerstenberger and Wong (2012)**

**Biofouling, : 29:1, 21-28**

**Effectiveness of EarthTec<sup>®</sup> for killing invasive quagga mussels (*Dreissena rostriformis bugensis*) and preventing their colonization in the Western United States**

Ashlie Watters<sup>a</sup>, Shawn L. Gerstenberger<sup>a</sup> and Wai Hing Wong<sup>a,b\*</sup>

<sup>a</sup>*Department of Environmental and Occupational Health, University of Nevada Las Vegas, 4505 Maryland Parkway, Las Vegas, NV 89154-3064, USA;* <sup>b</sup>*Department of Biology, State University of New York at Oneonta, 108 Ravine Parkway, Oneonta, NY 13820, USA*

*(Received 16 May 2012; final version received 25 October 2012)*



Table 1. Time for quagga mussel veligers to reach 100% mortality at different doses of EarthTec<sup>®</sup>.

EarthTec <sup>®</sup>	Minutes (Mean $\pm$ SD)	Replicates
0 ppm	Mortality was 0	8
1 ppm	Mortality was 0	6
3 ppm	27.5 $\pm$ 7.5	4
5 ppm	20.3 $\pm$ 8.1	3
10 ppm	6.0 $\pm$ 2.0	3
17 ppm	6.0 $\pm$ 1.0	3
83 ppm	5.7 $\pm$ 4.5	3

Ashlie Watters , Shawn L. Gerstenberger & Wai Hing Wong (2013): Effectiveness of EarthTec<sup>®</sup> for killing invasive quagga mussels (*Dreissena rostriformis bugensis*) and preventing their colonization in the Western United States, *Biofouling: The Journal of Bioadhesion and Biofilm Research*, 29:1, 21-28

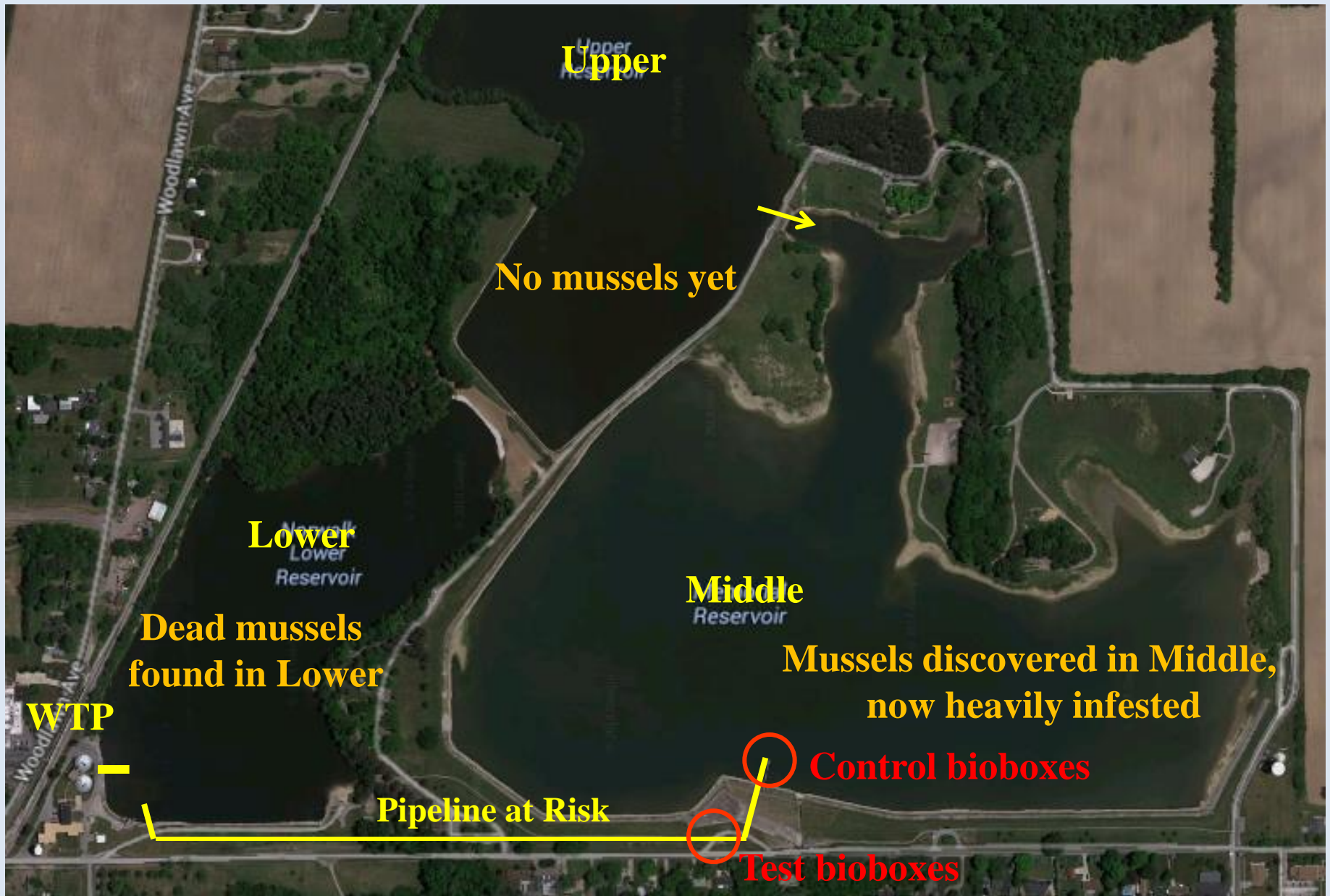


# Control Mussels Using QZ in the Flowing Waters

## 2014 Case Study Norwalk, Ohio

Objective: Keep a supply pipeline at a drinking water treatment plant free of infestation by zebra mussel adults, using low doses of copper ions.

Acknowledgement: Rick Schaffer, Chief Operator, WTP



**Upper**

**No mussels yet**



**Lower**

**Dead mussels found in Lower**

**Middle**

**Mussels discovered in Middle, now heavily infested**

**WTP**



**Pipeline at Risk**



**Control bioboxes**



**Test bioboxes**



We collected adult mussels from the reservoir

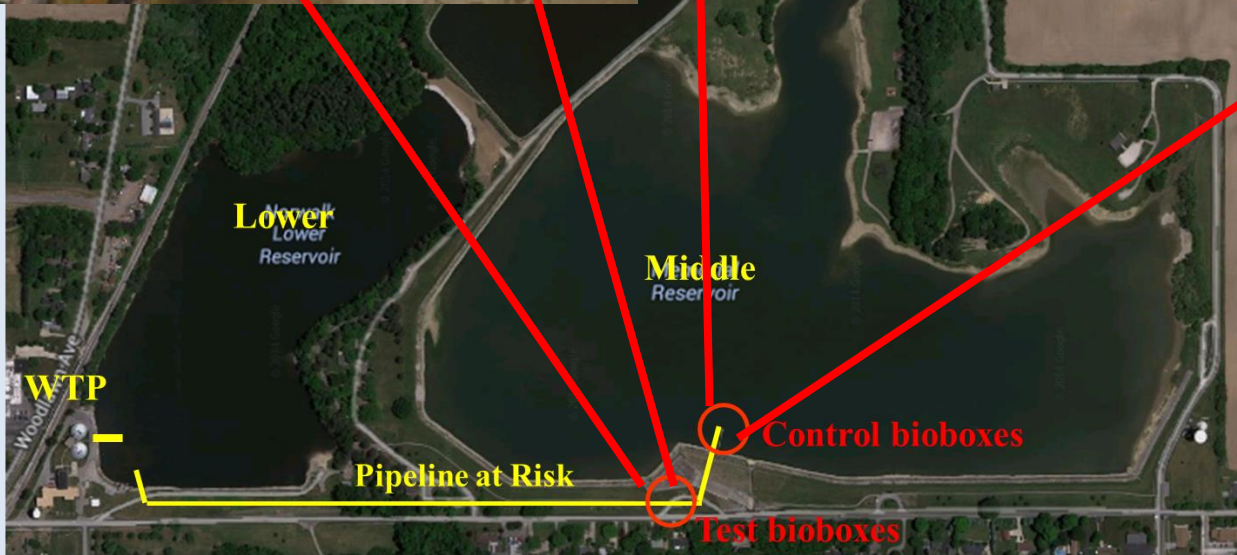




Adult mussels were placed in mesh bags.  
Mixture of some loose, some still attached to rocks

# Test bioboxes

# Control bioboxes





Intake structure for transfer from Middle reservoir to  
Lower Reservoir



EarthTec QZ delivered to pipeline intake structure by metering pump



No new or different equipment needed for switch  
from other chemicals to EarthTec QZ



## Mortality of zebra mussels exposed to EarthTec QZ (copper ions)

Dose as EarthTec	Dose as elemental copper	Mortality after:			
		6 days	11 days	13 days	19 days
Control	0 ppb	<5%	<5%	<5%	<5%
3 ppm	180 ppb	100%			
2 ppm	120 ppb	100%			
1 ppm	60 ppb	50%	100%		
0.5 ppm	30 ppb	15%	55%	70%	80%

Average alkalinity 120 mg/L, Temp: 20-22°C (68-72°F)

Copper limit for drinking water is 1.3 mg/L (= 1,300 ppb)



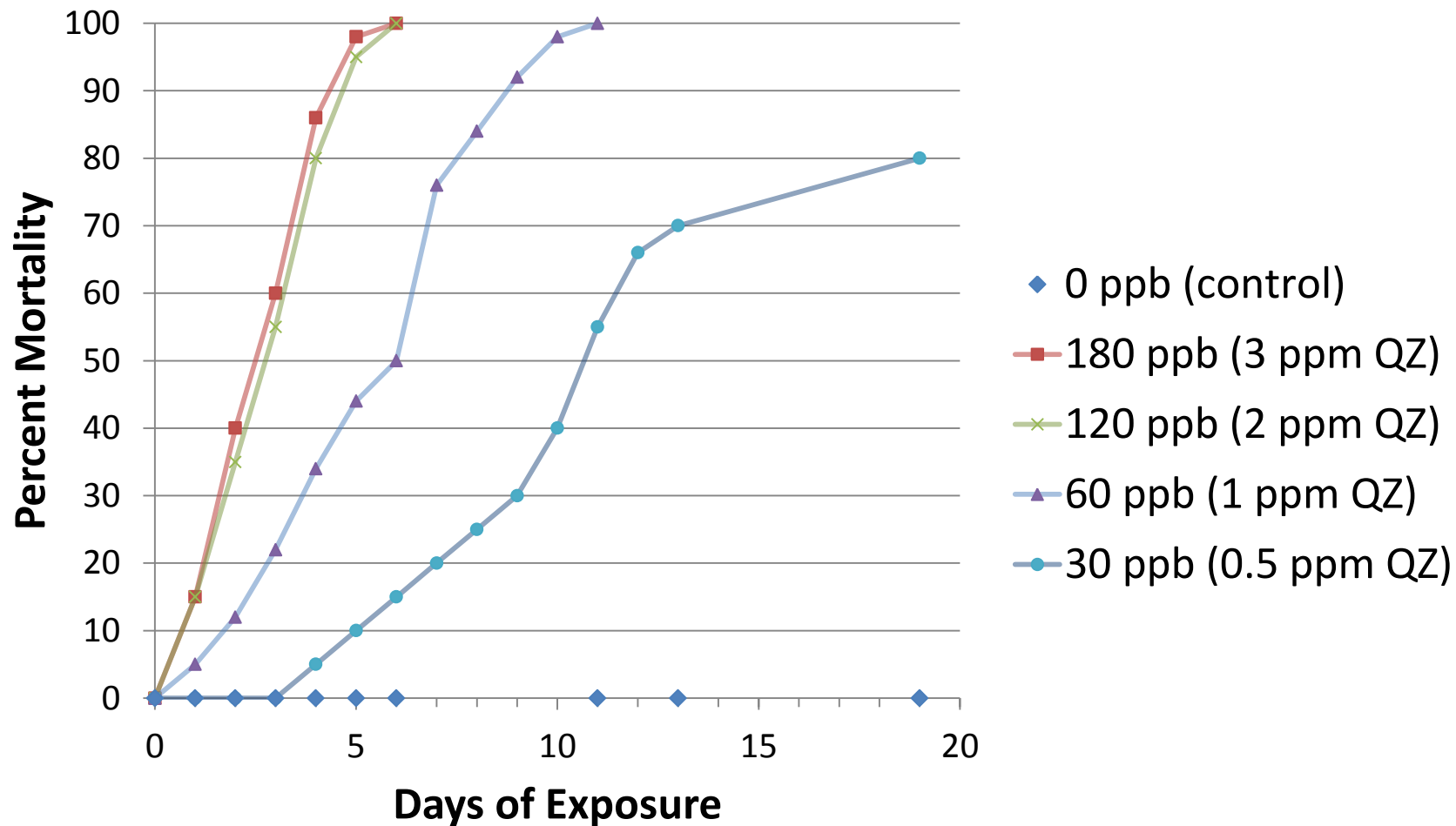
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Average alkalinity 120 mg/L, Temp: 20-22°C (68-72°F)

Copper limit for drinking water is 1.3 mg/L (= 1,300 ppb)

## Mortality of zebra mussels exposed to EarthTec QZ (copper ions)



Average alkalinity 120 mg/L, Temp: 20-22°C (68-72°F)

Copper limit for drinking water is 1.3 mg/L (= 1,300 ppb)







Dead mussels exposed to 2 ppm of EarthTec QZ  
(about 114 ppb as copper)



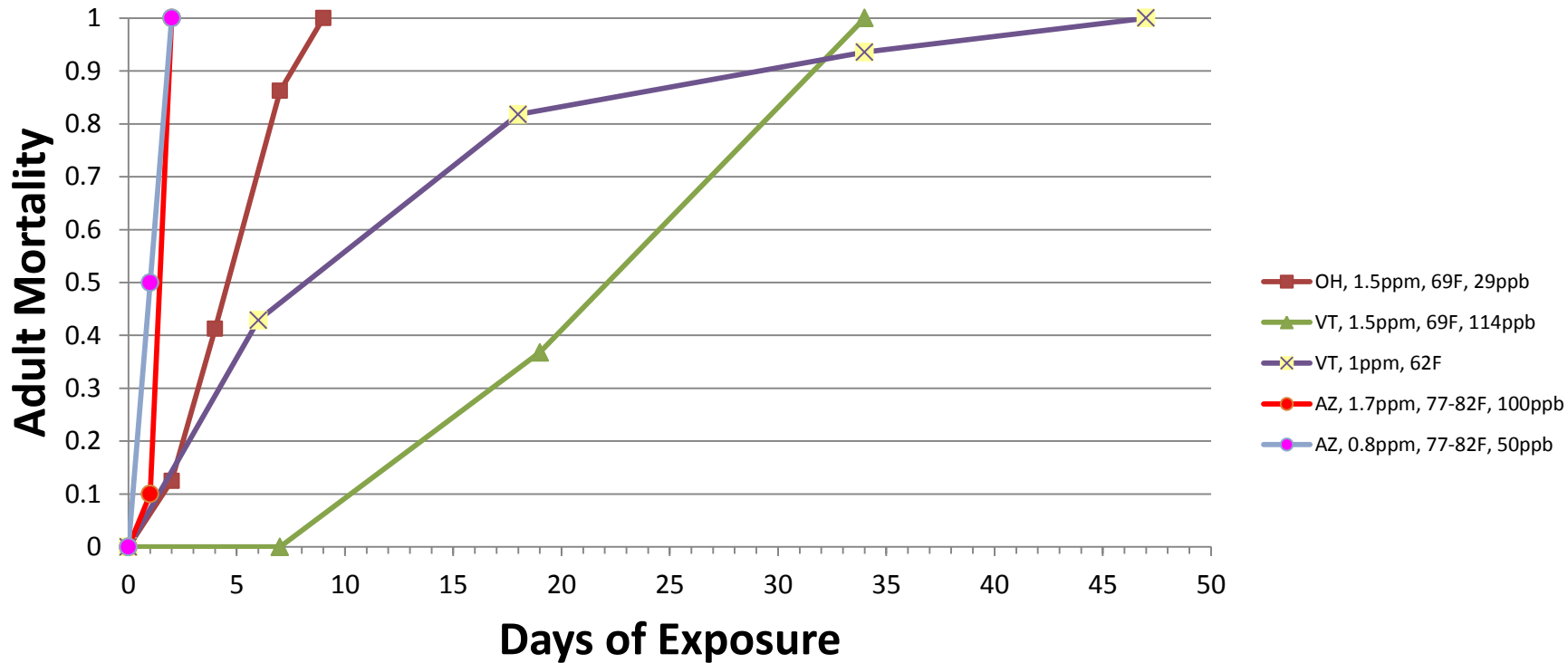
We continued the testing even under ice



**Table 2: Mortality of zebra mussels exposed to EarthTec QZ in cold flowing water, 12.5 - 1.8°C (55-35°F)**

Dose as EarthTec QZ	Dose as elemental copper	100% Mortality after:	Start Temp	End Temp
2 ppm	120 ppb	28 days	12.5	1.8

## Time for Mussel Mortality at Various EarthTec Doses, Water Temperatures, and Measured Copper Present



# Cost Comparison



Sodium hypochlorite			
Low	Med	High	Description
1.00	1.50	2.20	mg/L, dose of chlorine from NaOCl
12.0%	12.0%	12.0%	NaOCl stock concentration
8.33	12.50	18.33	mg/L, (and L/ML) dose of NaOCl solution
\$0.25	\$0.25	\$0.25	cost per liter of NaOCl
\$2.08	\$3.13	\$4.58	cost per ML treated
<b>\$7.89</b>	<b>\$11.83</b>	<b>\$17.35</b>	<b>cost per MG treated with sodium hypochlorite</b>

Potassium permanganate			
Low	Med	High	Description
1.50	2.25	3.00	mg/L dose of potassium permanganate
12.49	18.74	24.98	lbs of potassium permanganate to treat 1 MG
\$1.30	\$1.30	\$1.30	cost per lb of potassium permanganate
<b>\$16.24</b>	<b>\$24.36</b>	<b>\$32.48</b>	<b>cost per MG with potassium permanganate</b>

EarthTec QZ			
Low	Med	High	Description
0.60	1.00	1.75	mg/L, EarthTec QZ
34	57	100	ppb, copper concentration
\$20	\$20	\$20	cost per gallon of EarthTec QZ
<b>\$12.00</b>	<b>\$20.00</b>	<b>\$35.00</b>	<b>cost per MG treated with EarthTec QZ</b>

Cost of control using EarthTec QZ is comparable with the cheapest existing alternatives



# QZ Customer Concerns: Copper Residual

**Copper is removed by conventional WTP processes**

Data from Benbrook, TX

		<u>Calculated ET dose (Cu)</u>	<u>Measured Cu In (ppb)</u>	<u>Measured Cu Out (ppb)</u>	<u>% removal</u>	<u>MGD</u>
<b>At 2 ppm:</b>	n = 17	120	150	80	47%	3.0
<b>At 4 ppm:</b>	n = 10	240	300	80	69%	3.0

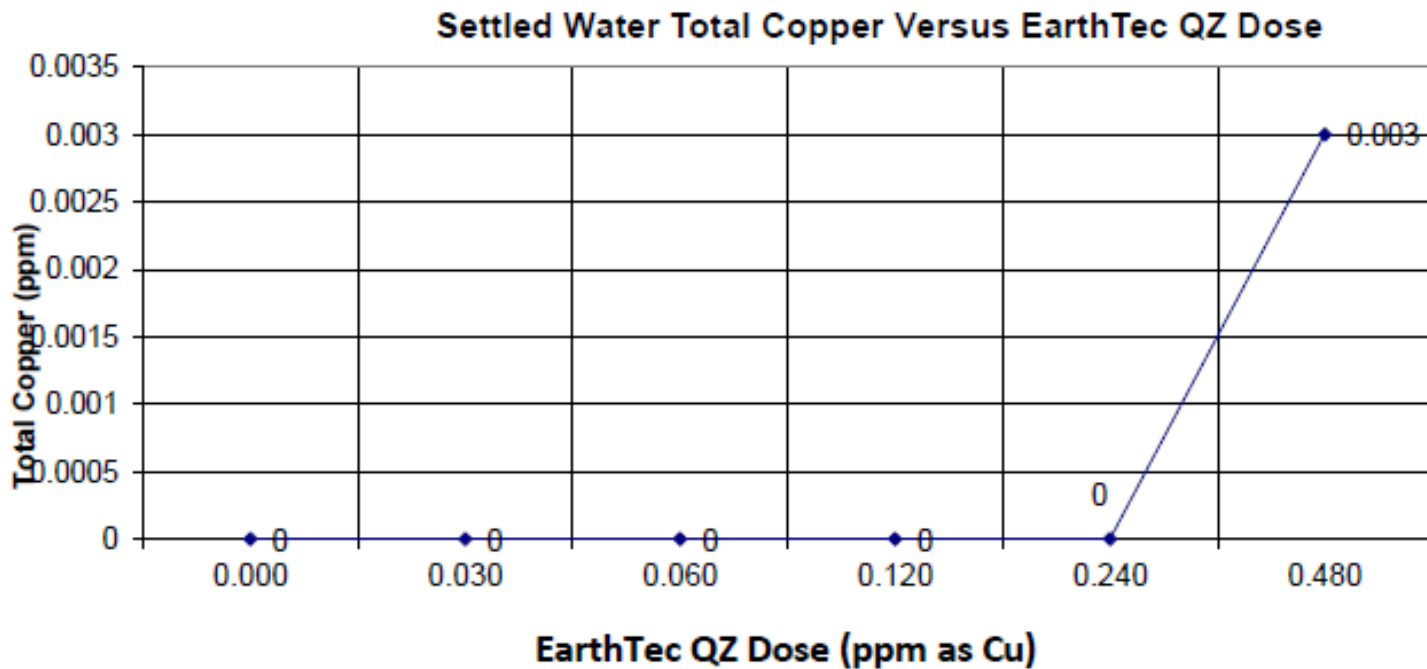
**(copper standard for drinking water is 1.3 mg/L = 1,300 ppb)**



## QZ Customer Concerns: Copper Residual

**Copper is removed by conventional WTP processes**

Data from St Paul, MN: **Total copper in settled water**



**(copper standard for drinking water is 1.3 mg/L = 1,300 ppb)**



## **APPENDIX**

# **Ancillary Benefits of EarthTec QZ**

- **Algae control**
- **Geosmin reduction**
- **Anti-microbial activity**
- **Better than copper sulfate**
- **No disinfection by-products**



# EarthTec use in WTPs



**Before**

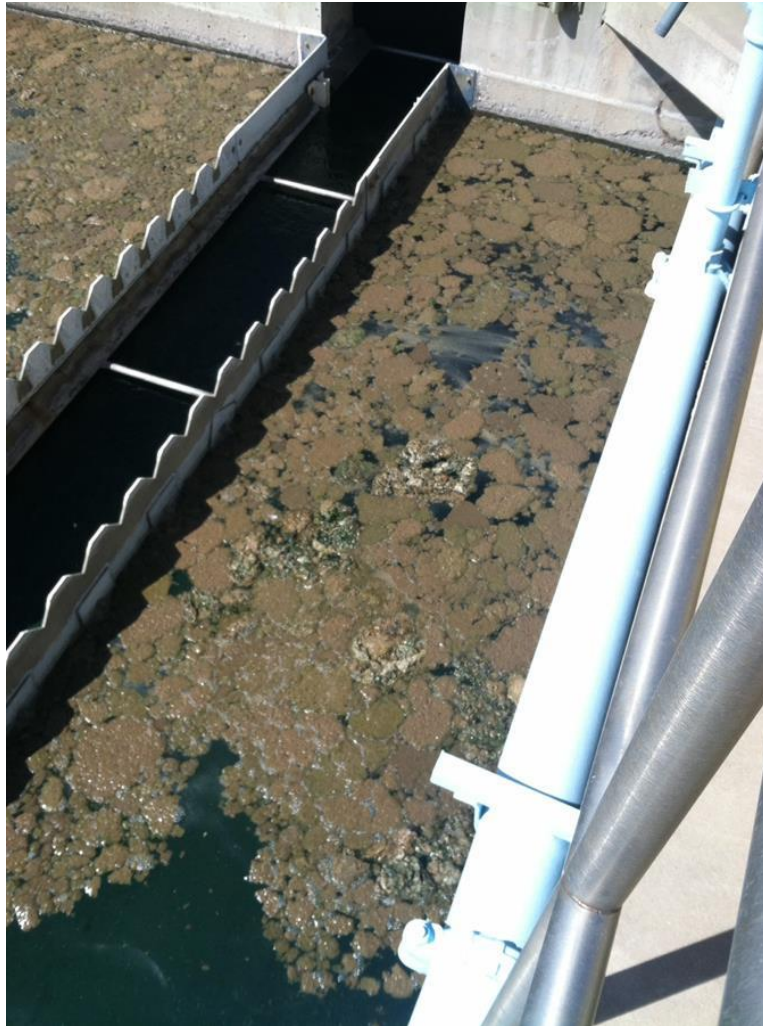
# EarthTec use in WTPs



After



# EarthTec use in WTPs



**Before**

# EarthTec use in WTPs

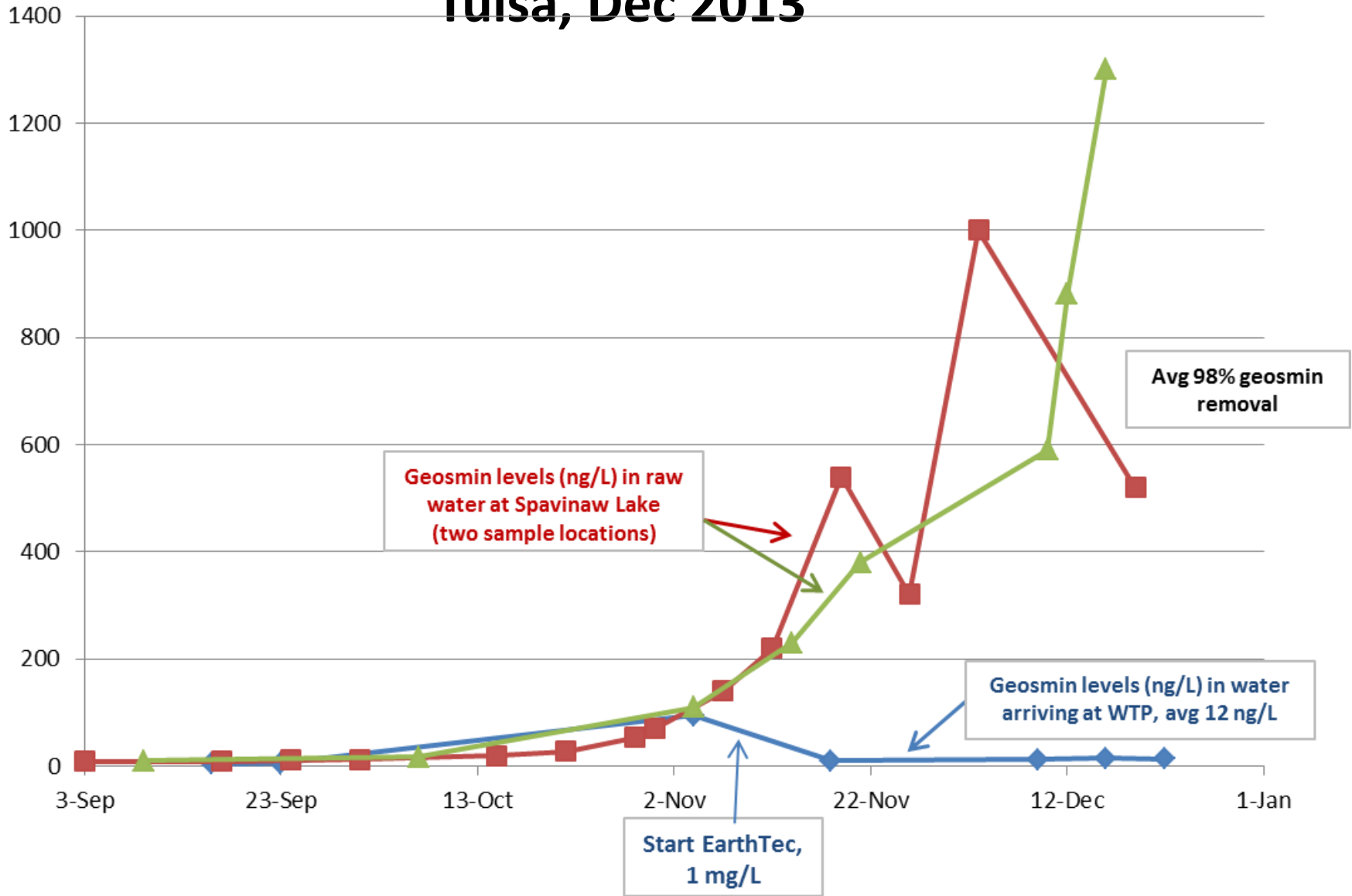


After

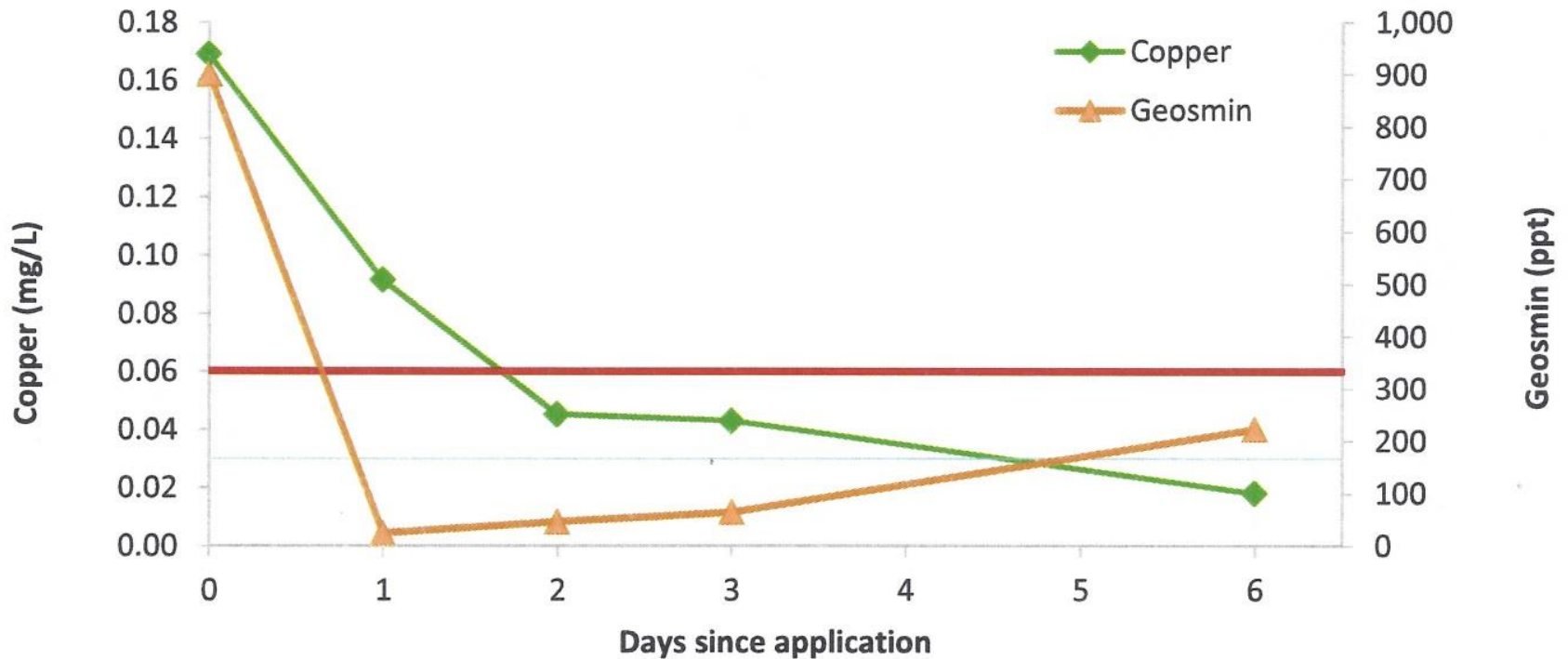


# Geosmin Reduction

## Tulsa, Dec 2013



# Florida, Open Water, Feb 2015



Geosmin of 900 ng/L  
was reduced to about 30 ng/L at 24 hours  
following surface application of 1 ppm EarthTec



# Product Comparison

## Copper Sulfate vs EarthTec

Algaecide	Copper sulfate	EarthTec
application rate	10.00 lbs/acre	1 gal/acre
application rate	3.07 lbs/acre-ft	1 ppm
application rate	9.41 lbs/MG	1 gal/MG
cost (bulk)	\$1.50 per lb	\$15 per gallon
<b>cost per volume treated</b>	<b>\$14.11 per MG treated</b>	<b>\$15 per MG treated</b>
% copper in product	25%	5%
metallic copper added	0.28 mg/L	0.06 mg/L
<b>metallic copper added</b>	<b>2.35 lbs per MG</b>	<b>0.49 lbs per MG</b>
% copper as Cu <sup>++</sup> ion	10%	99.99%
metallic copper, useful	0.24 lbs per MG	0.49 lbs per MG
metallic copper, wasted	2.12 lbs per MG	0.00 lbs per MG



# Product Comparison

Copper Sulfate vs EarthTec

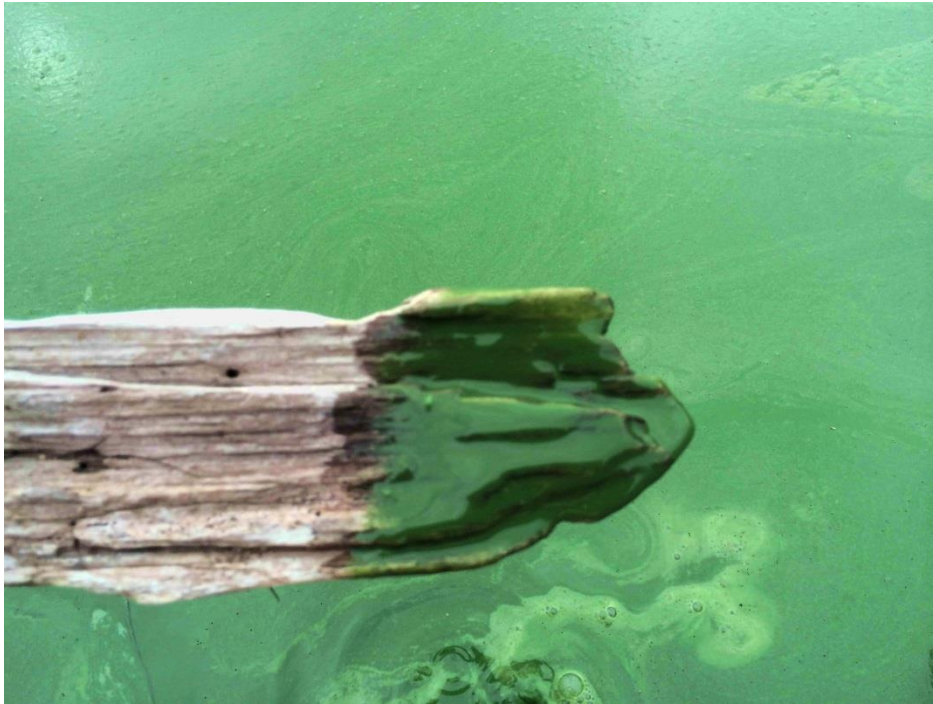
## Norwalk, OH (2012 vs 2013)

Copper sulfate	EarthTec	
10	8	treatments per year
500	60	lbs or gallons per treatment
	10	lbs per gallon
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, %



# Harmful Algal Blooms and microcystins

## HAB in Norwalk, OH 2014



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



**Wednesday morning**  
**36 h post-treatment.**  
**Microcystin <1 ug/L by Friday**



# 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**
  - **Rapidly 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**



# EarthTec Chemistry

- **EPA Registered** as an Algaecide/Bactericide
- Registered in **All 50 States** as Algaecide/Bactericide, in 26+ States as Molluscicide
- Certified to **NSF** Standard 60
- Reduces **Labor** Costs
- EarthTec Is the **Easiest, Safest and Most Efficient** Method to Deliver Copper





# Thank you!

David Hammond, PhD

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