



**EarthTec QZ:
Control of Dreissenid Mussels with a More Rational
Use of Copper**

David Hammond, PhD, Senior Scientist, Earth Science Labs, Inc.



EarthTec Chemistry

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



Public Perception:

“In 25 years, in hundreds of lakes and rivers across North America, it has been proven again and again that eradication does not exist...”

“Zebra and quagga mussels, once in a lake or river, cannot be stopped.”

Okanagan filmmaker Brynne Morrice.

Quoted October 21, 2015, in *The Osoyoos Times*, “Failure to eradicate mussels on Lake Winnipeg should be lesson for B.C., filmmaker tells Polak”

True or False? Should we just give up?

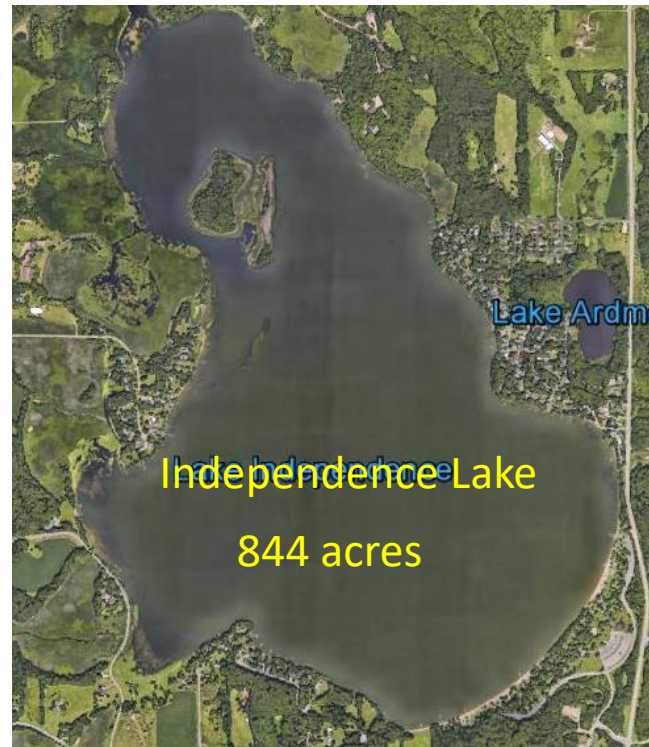




Priority Sites for Mussel Control

- **Open Waters (lakes)**
- **Flowing Waters (pipelines, aqueducts)**
- **Closed or Semi-Closed Systems (ballast water, 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 Independence Lake, MN



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





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

Lake Name	Christmas	Independence	Ruth Lake
	Lake	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	70% mortality in Treatment Area	Eradicated in Treatment Area
Chemical Cost	\$1,200	\$2,000	\$4,910

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

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

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

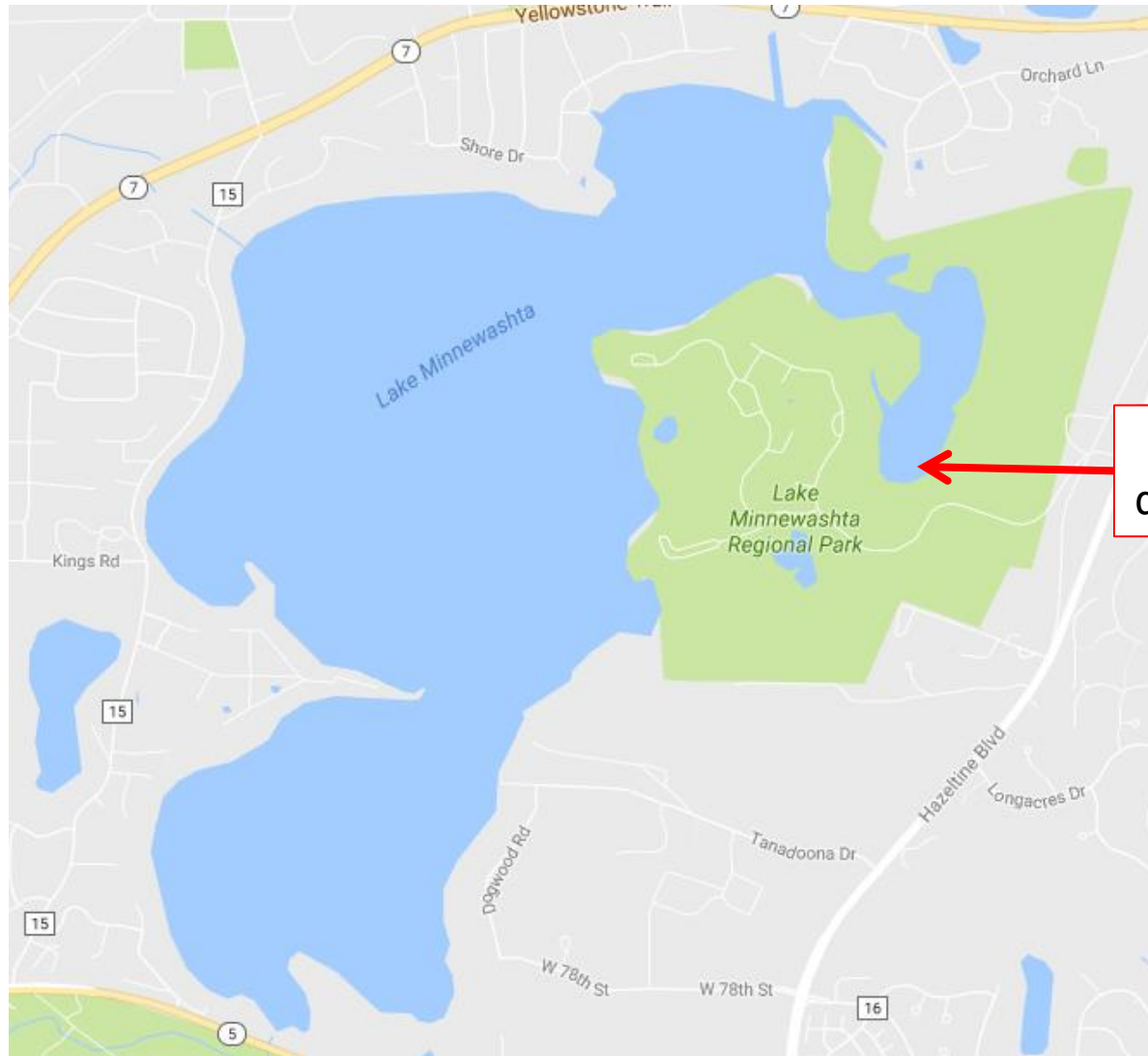


Last day of treatment at Independence Lake

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

Zebra Mussels discovered in Lake Minnewashta, Minnesota

August 18, 2016



Mussels
discovered here

Zebra Mussels discovered in Lake Minnewashta, Minnesota

August 18, 2016



Mussels
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Zebra Mussels discovered in Lake Minnewashta, Minnesota

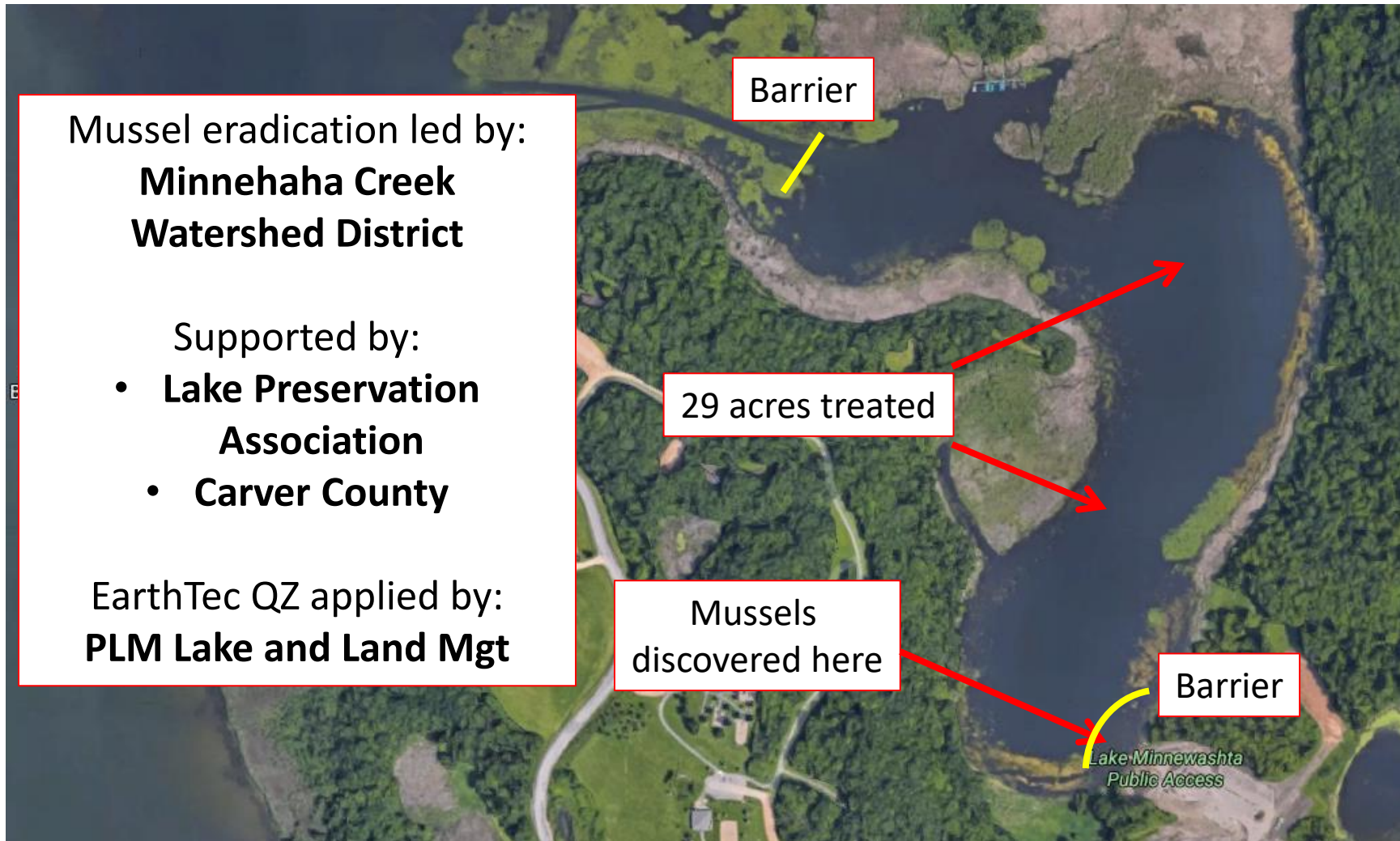
August 18, 2016

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



Eradication of Zebra Mussels from Lake Minnewashta, Minnesota

Sept 13-23, 2016



Work performed by PLM Lake and Land Management, Inc.

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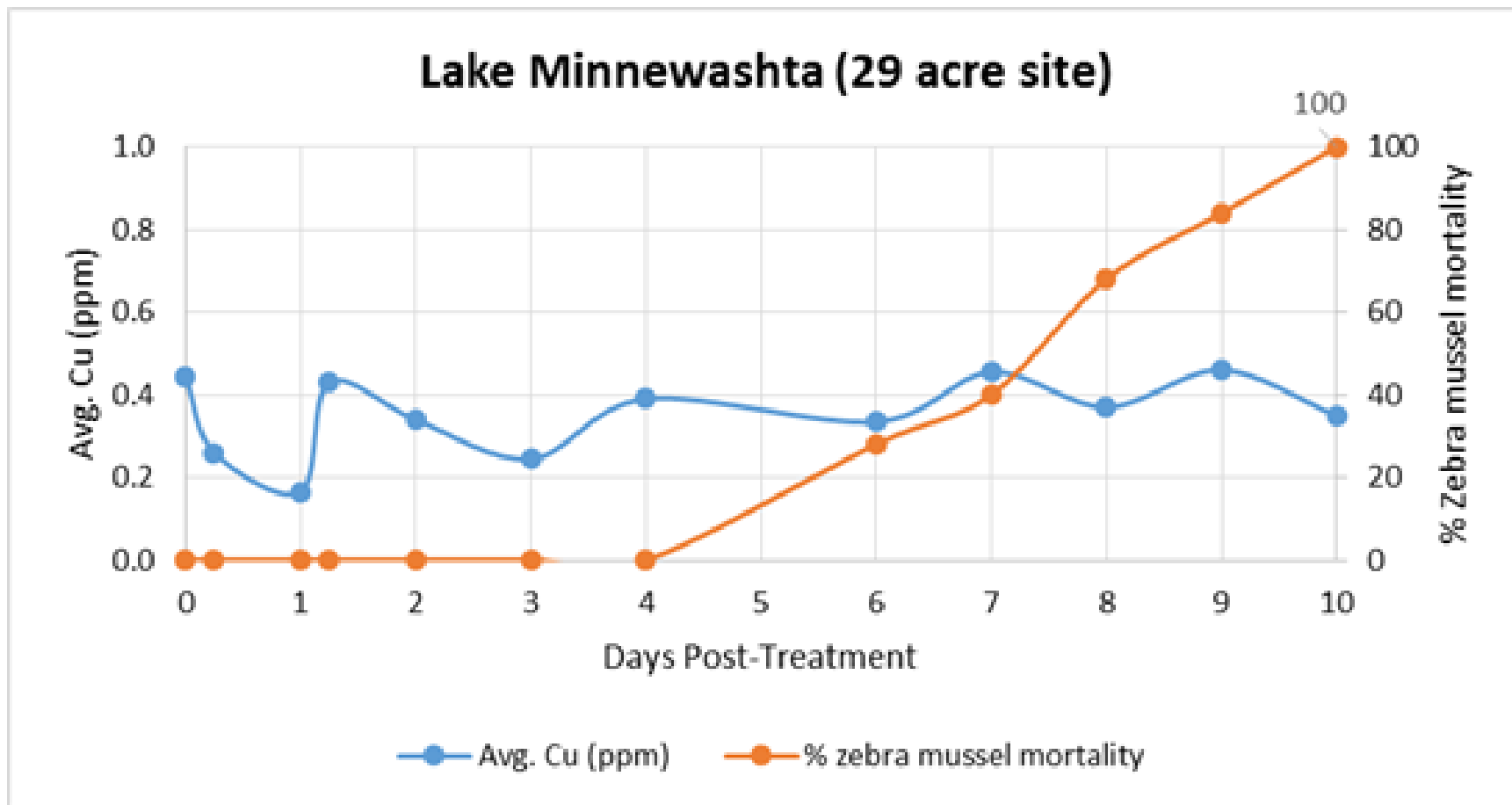
A “gaping” mussel, unresponsive to gentle prodding,
is considered dead



Eradication of Zebra Mussels from Lake Minnewashta, Minnesota

Sept 13-23, 2016

Water Temperature 19°C = 66°F



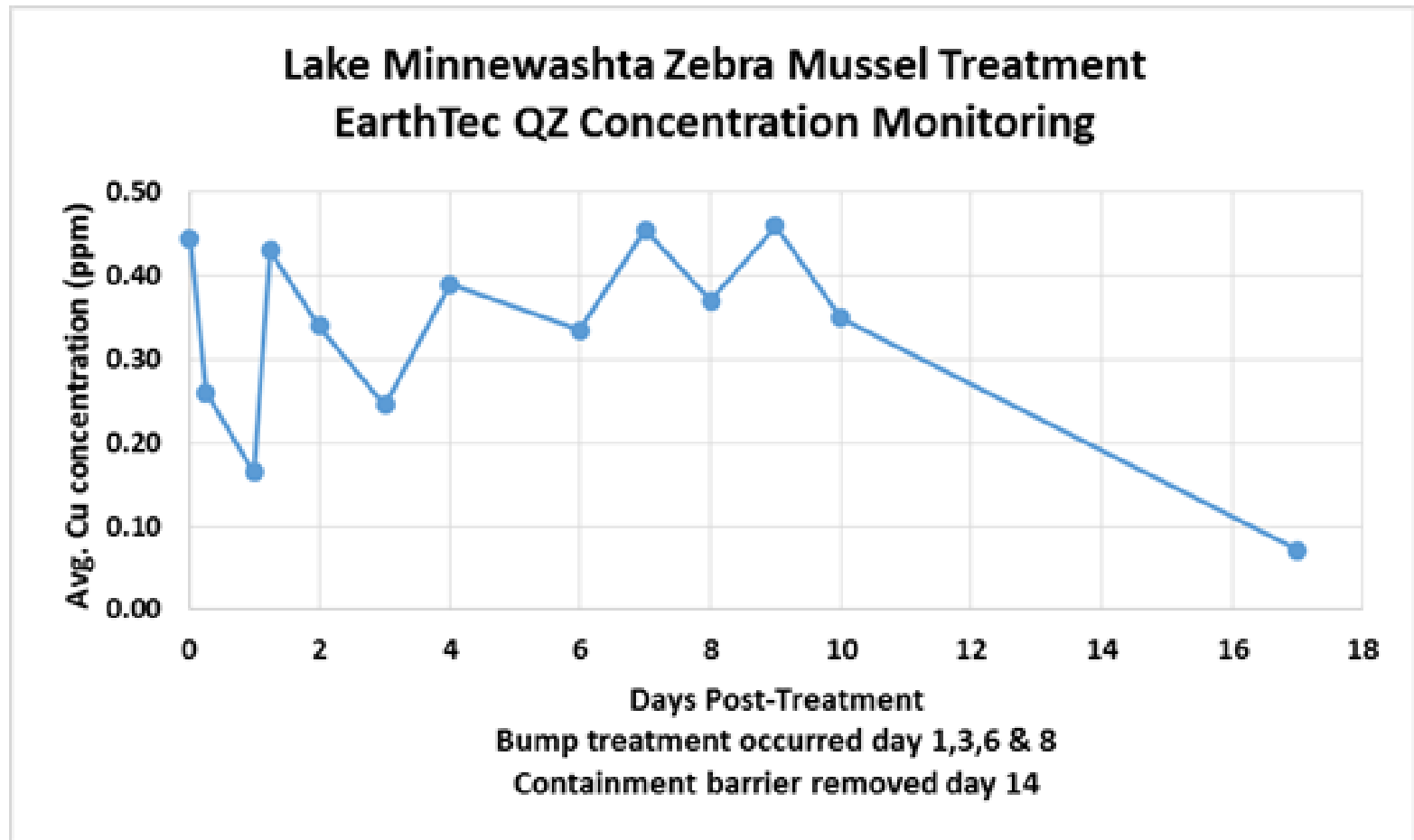
Source: Eric Fieldseth and Jill Sweet, Minnehaha Creek Watershed District



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

Main message of this talk:

There is a new generation of liquid copper products that

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

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:

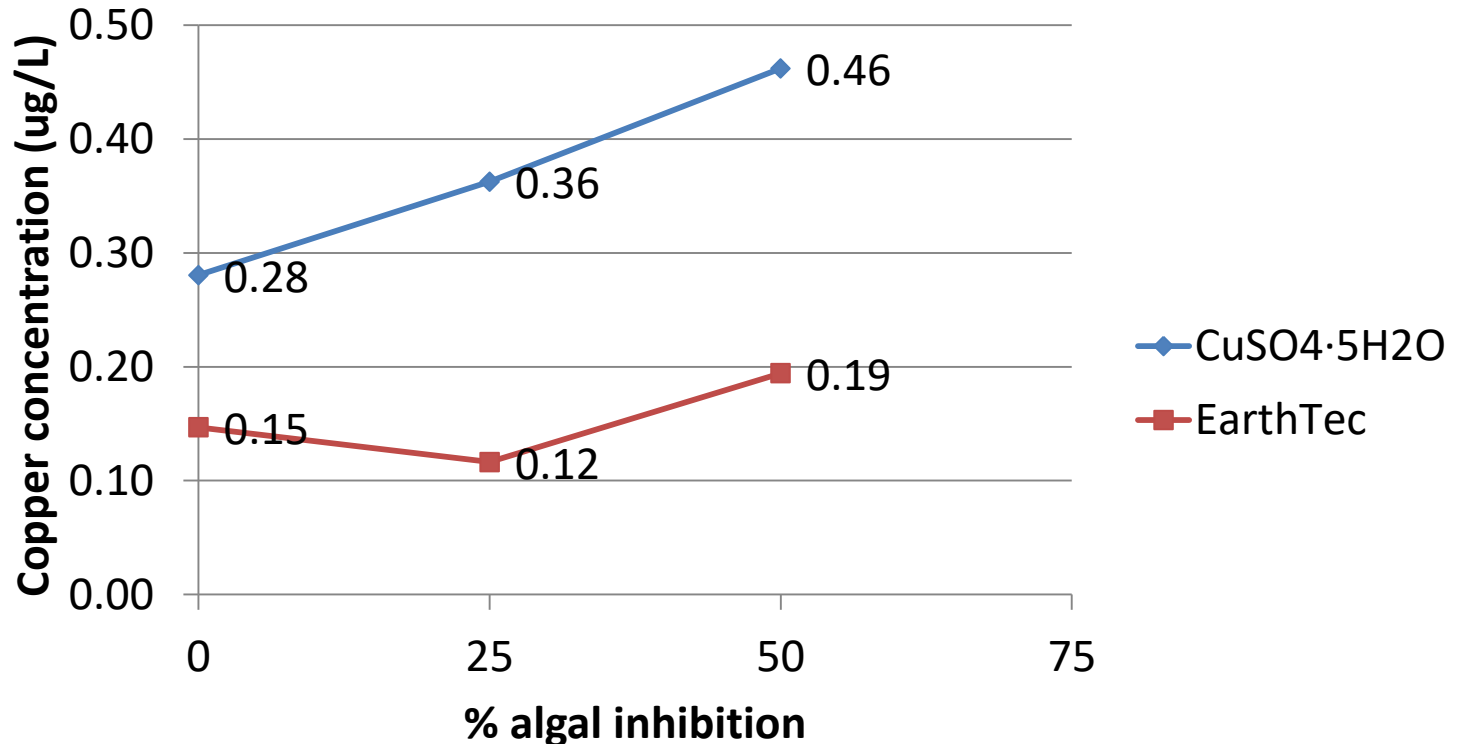
a safer and more efficient formulation that

achieves the desired benefits at lower doses, with less waste



Copper Sulfate vs EarthTec

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



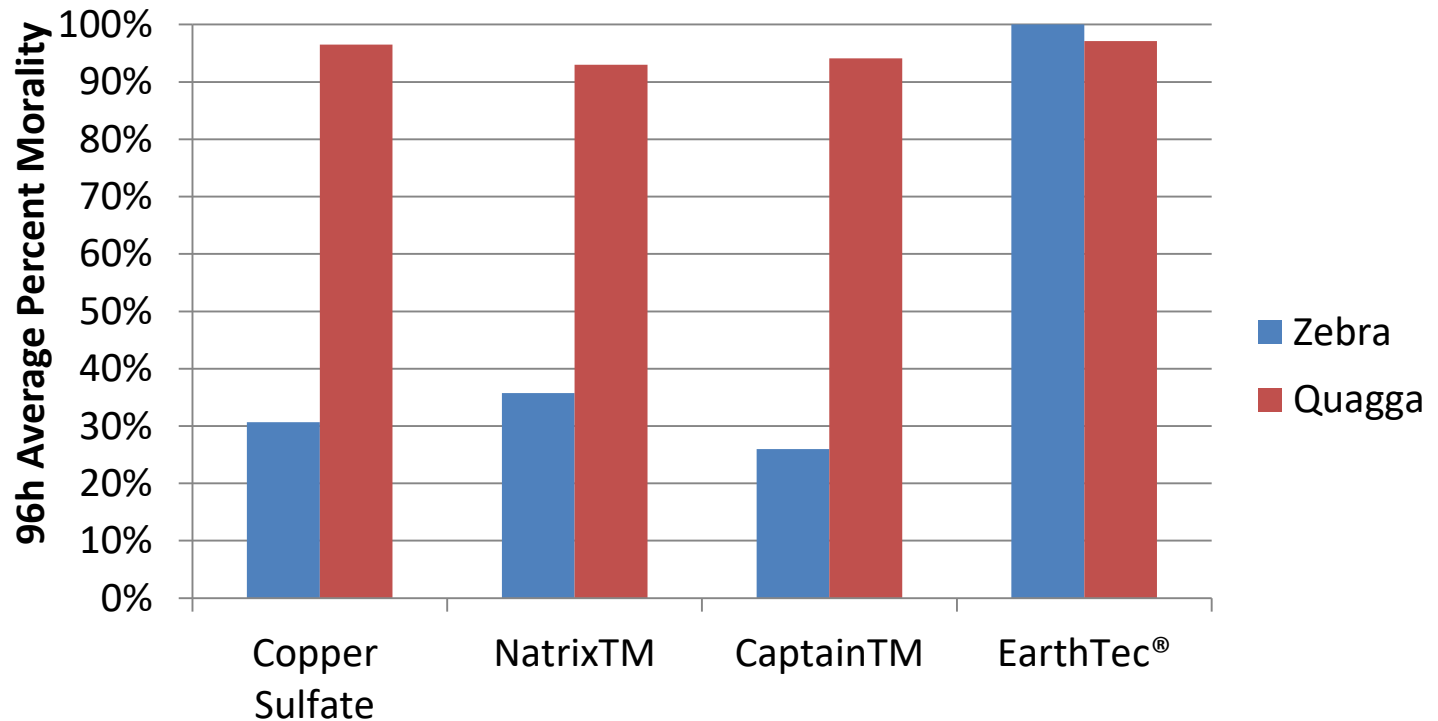
The copper dose required to achieve a given % inhibition of algae is much lower if applied as EarthTec than if applied as copper sulfate

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.



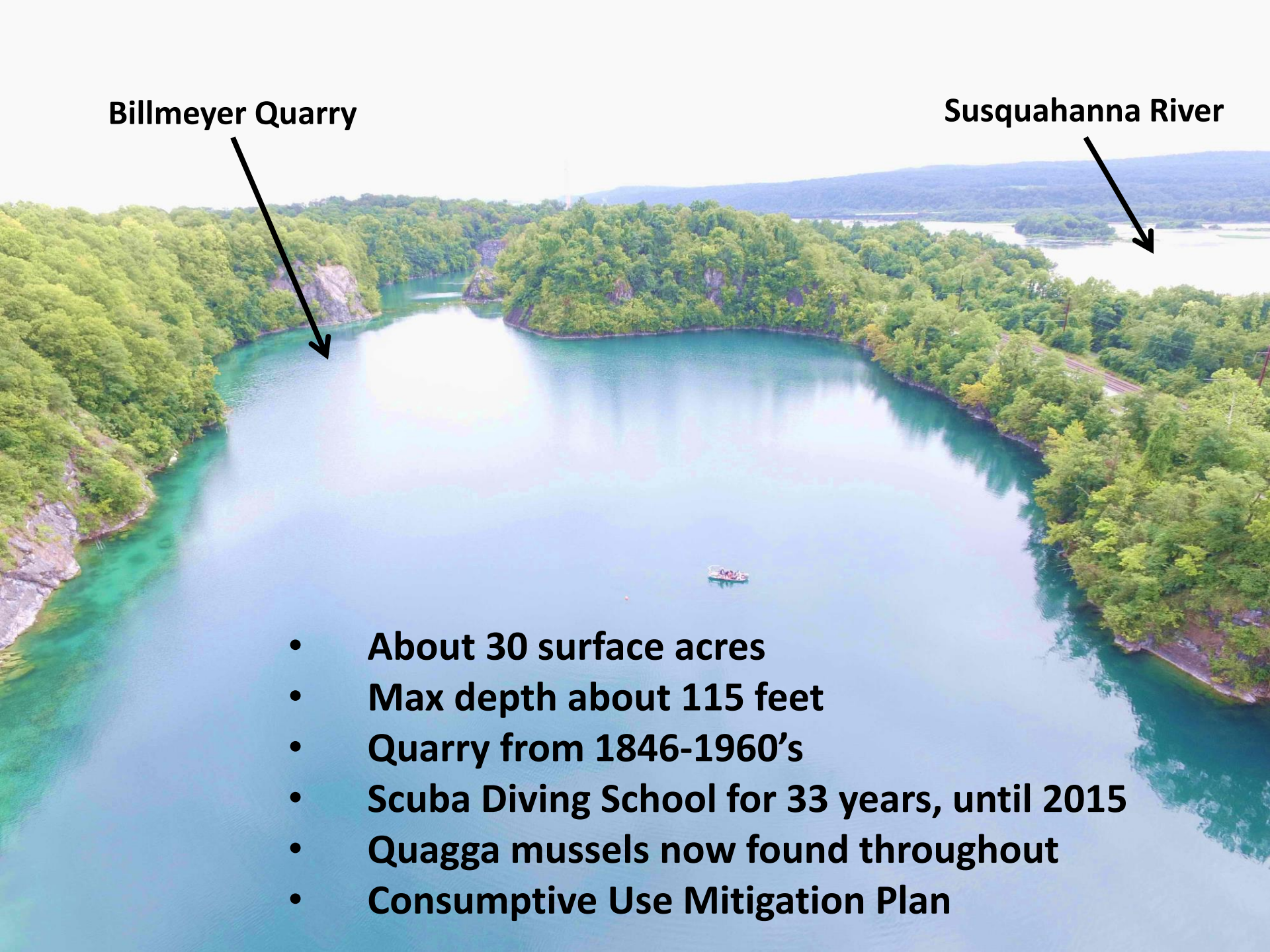
Eradication of Quagga Mussels from Billmeyer Quarry Lake, Pennsylvania

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

Staging Area





EARTHTEC

Billmeyer Quarry Lake, Pennsylvania

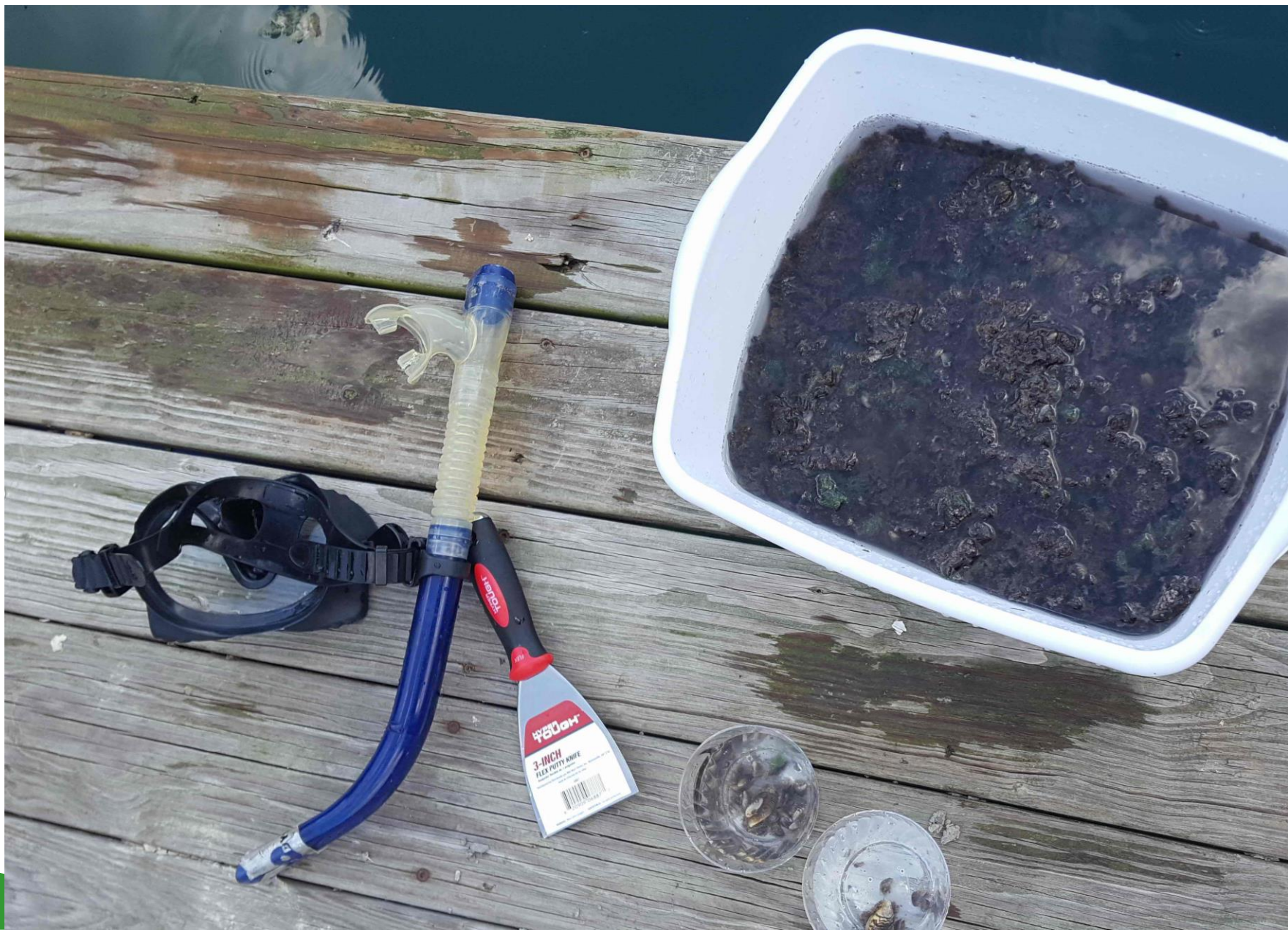
Full of Fish: Bluegill, Largemouth Bass, Catfish, Gizzard Shad



Collected quagga mussels for placement into cages



Collected quagga mussels for placement into cages



Collected quagga mussels for placement into cages



Cages



Work performed SOLitude Lake Management, Inc.

Cages for surrogate or proxy quagga mussels



Work performed SOLitude Lake Management, Inc.

Proxy mussels ready for deployment



Work performed SOLitude Lake Management, Inc.



Placing cages

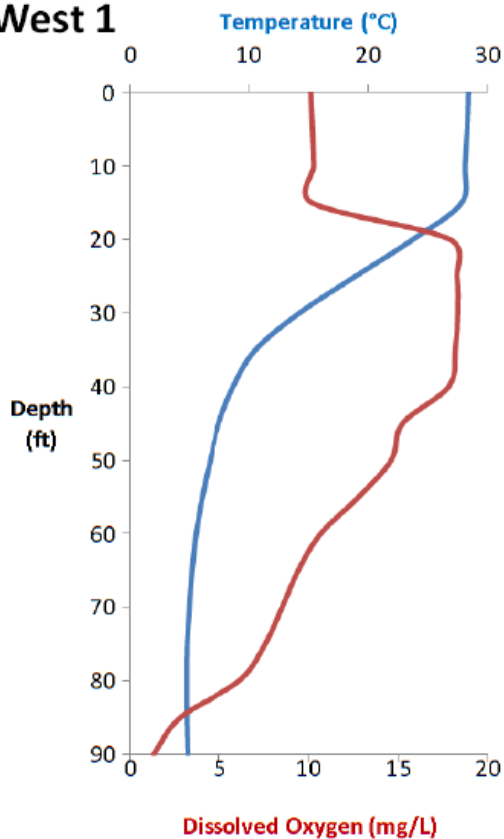


Work performed SOLitude Lake Management, Inc.

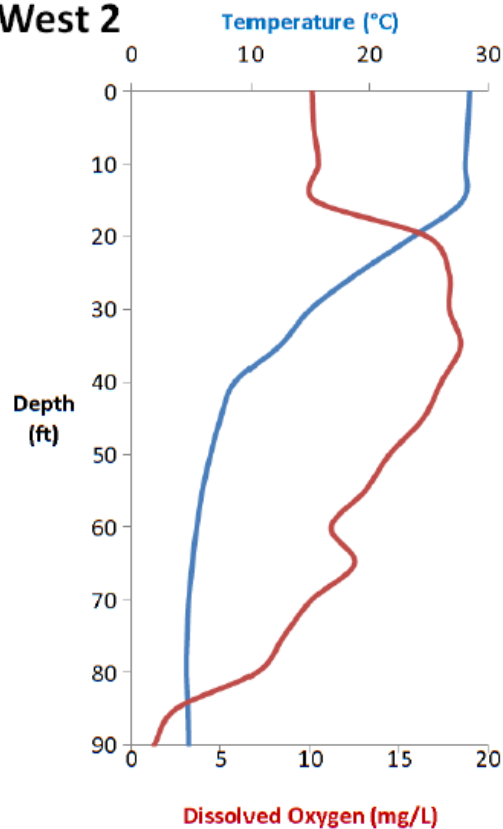
Temperature and Dissolved Oxygen vs Depth

Billmeyer Quarry

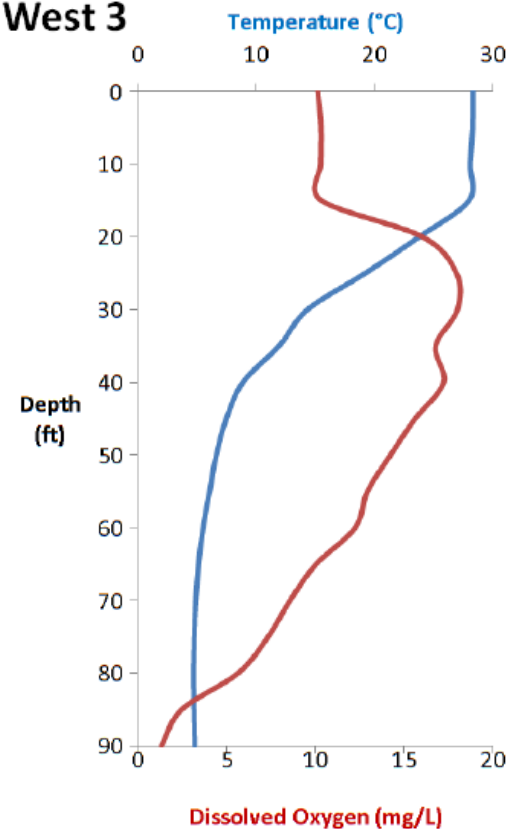
West 1



West 2



West 3



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

Eradication of Zebra Mussels from Private Lake, Indiana

November, 2016

Mortality at 16 days post-treatment

Location	Dead	Alive	Total	Mortality Rate
1 - Slides	425	0	425	100%
2 - Zip line	350	0	350	100%
3 - bank	270	0	270	100%
4 - bank	200	0	200	100%
5 - small dock	200	0	200	100%
6 - near beach	150	0	150	100%
All other locations around pond	400	0	400	100%



Examples of Mussel Eradication or Control with 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: Idaho



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.**
- 
- A thick, green, wavy line that spans the width of the slide at the bottom, resembling a stylized horizon or a wave.

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

Algal bloom conditions	$\mu\text{L/L}$, as EarthTec	ppm, as copper	ppb, as copper
Preventative dose	0.5	0.030	30
Mild bloom	1	0.060	60
Full bloom	2	0.120	120
Severe bloom	3	0.180	180

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

<u>Measured Effect</u>	<u>$\mu\text{L/L}$, as EarthTec</u>	<u>ppm, as copper</u>	<u>ppb, as copper</u>
NOEC	4.0	0.240	240
LC25	4.4	0.263	263
LC50	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.



Eradication of Zebra Mussels from Fawn River Fish Hatchery, Indiana

July, 2016



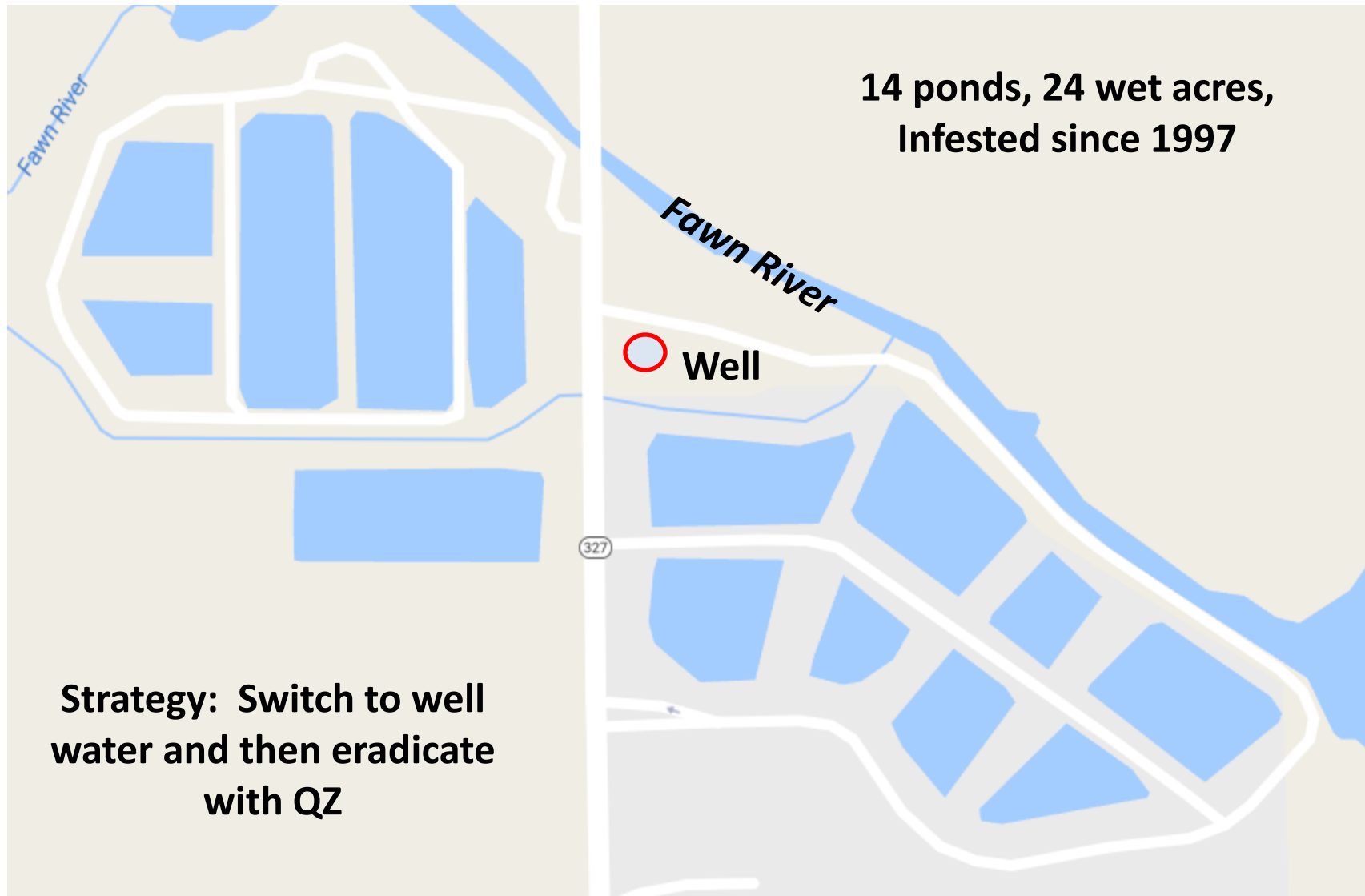
Eradication of Zebra Mussels from Fawn River Fish Hatchery, Indiana

July, 2016



Eradication of Zebra Mussels from Fawn River Fish Hatchery, Indiana

July, 2016



Eradication of Zebra Mussels from Fawn River Fish Hatchery, Indiana

July, 2016

**Switched to well water,
used QZ to treat the
static water in sealed
pipes, then treated the
ponds themselves**



Eradication of Zebra Mussels from Fawn River Fish Hatchery, Indiana

July, 2016

Results:

- Now monitoring for presence of veligers
- Hope to be removed from the “mussel positive” list in 2018.



Decontamination of Zebra Mussels from Oklahoma state fish hatchery



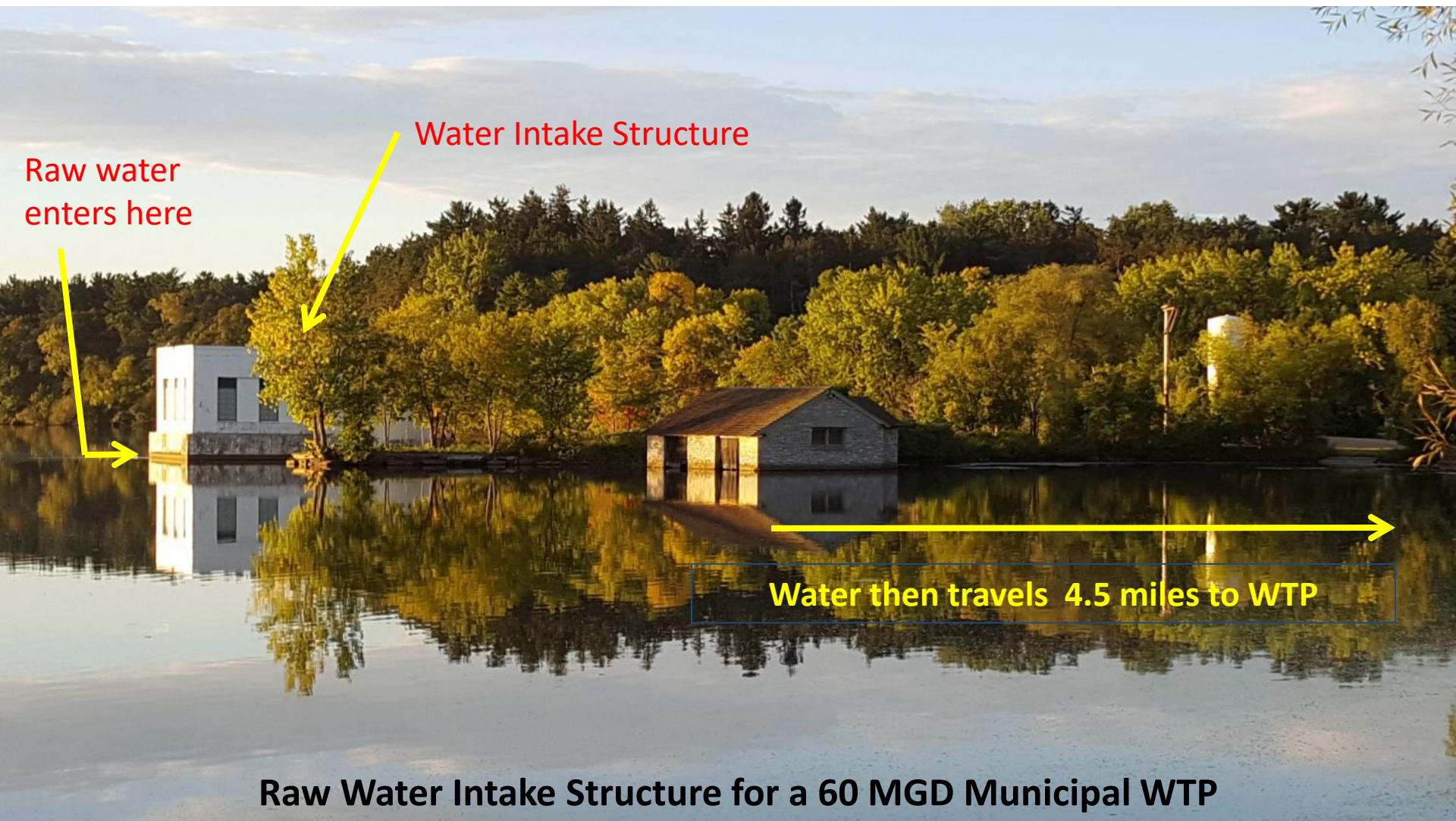
Side benefits: Improved yields, healthier fish



Priority Sites for Mussel Control

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

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





This is what the clean screens should look like

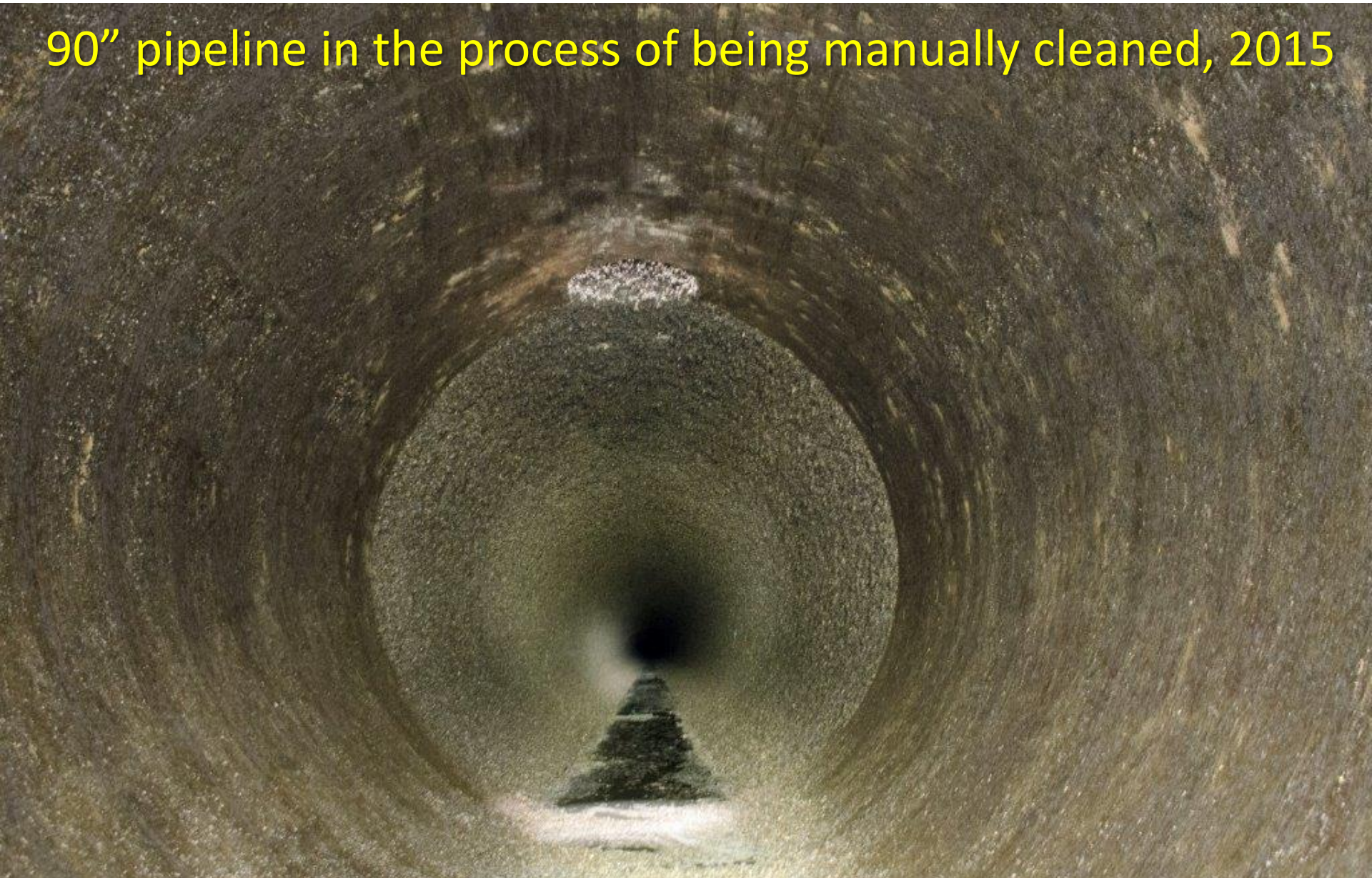


Screens and intake fouled
with zebra mussels, 2015

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

Zebra Mussel Control using EarthTec QZ

Summer, 2016



Bulk storage tank for EarthTec QZ next to intake -- 5,500 gallons

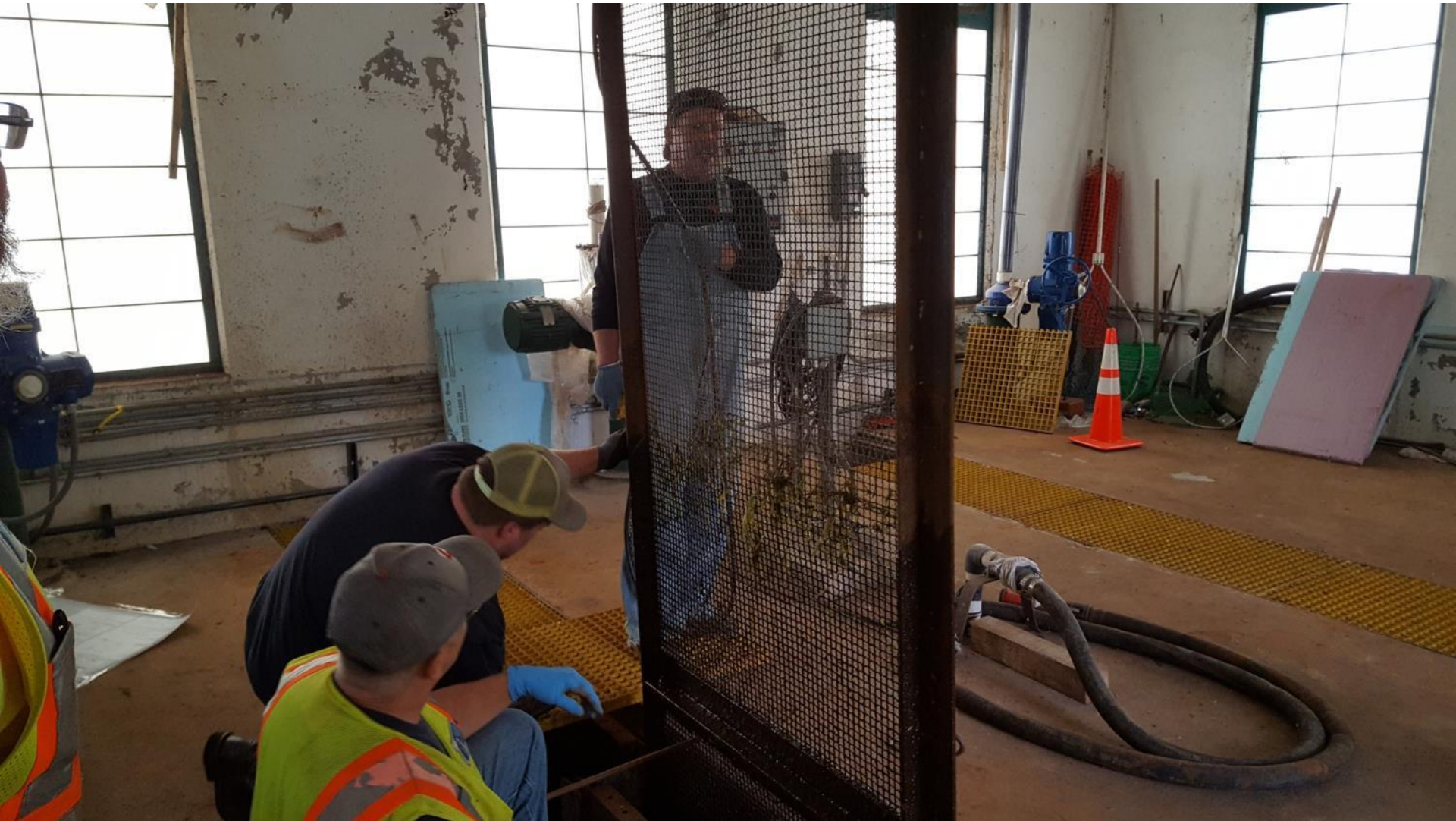
Metering pump and wall skid

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

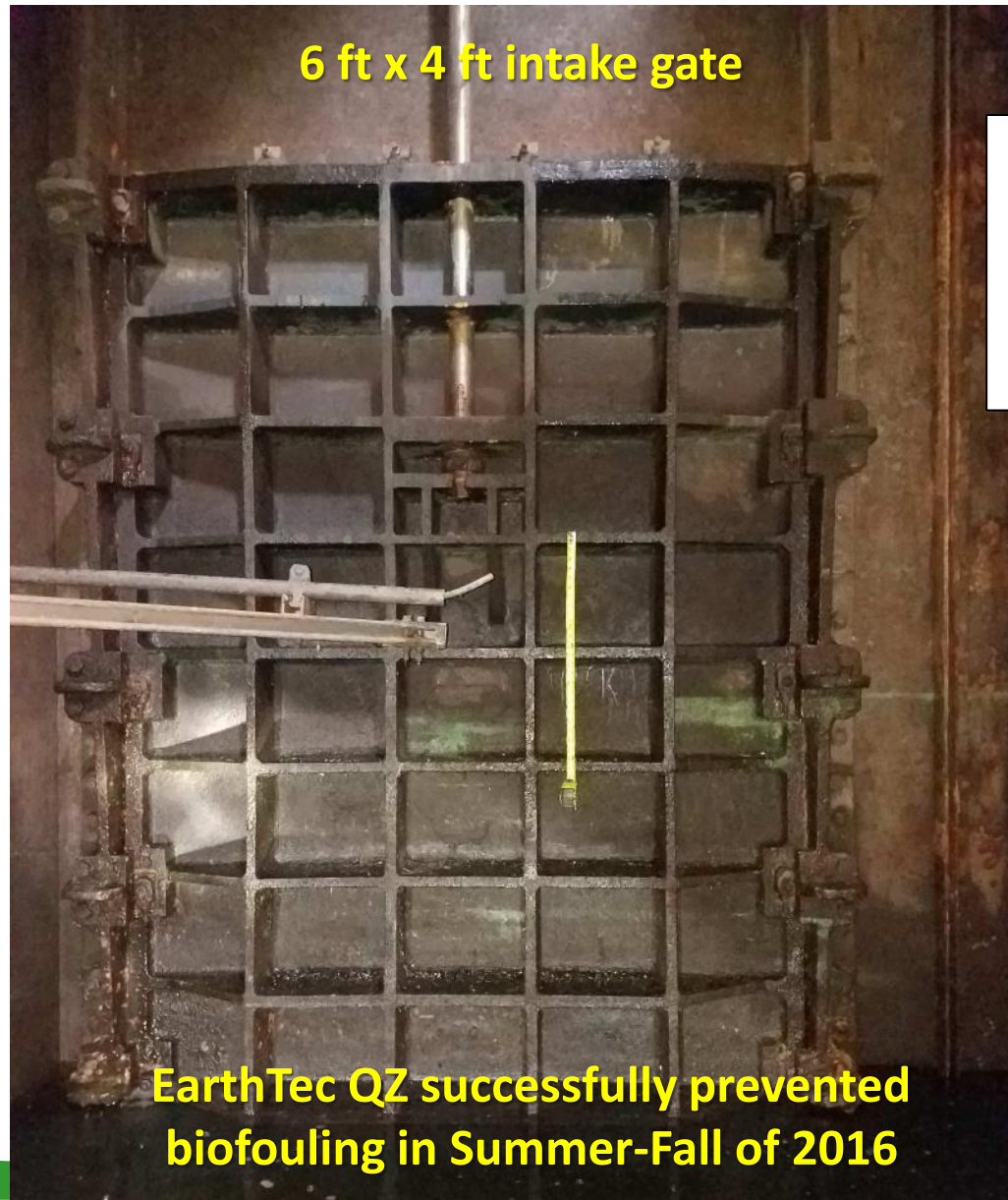


**1 ppm dose as QZ
= 60 ug/L as copper
sufficient to achieve
complete control**

**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**

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

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

September, 2016



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 on the feed
line itself.

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**

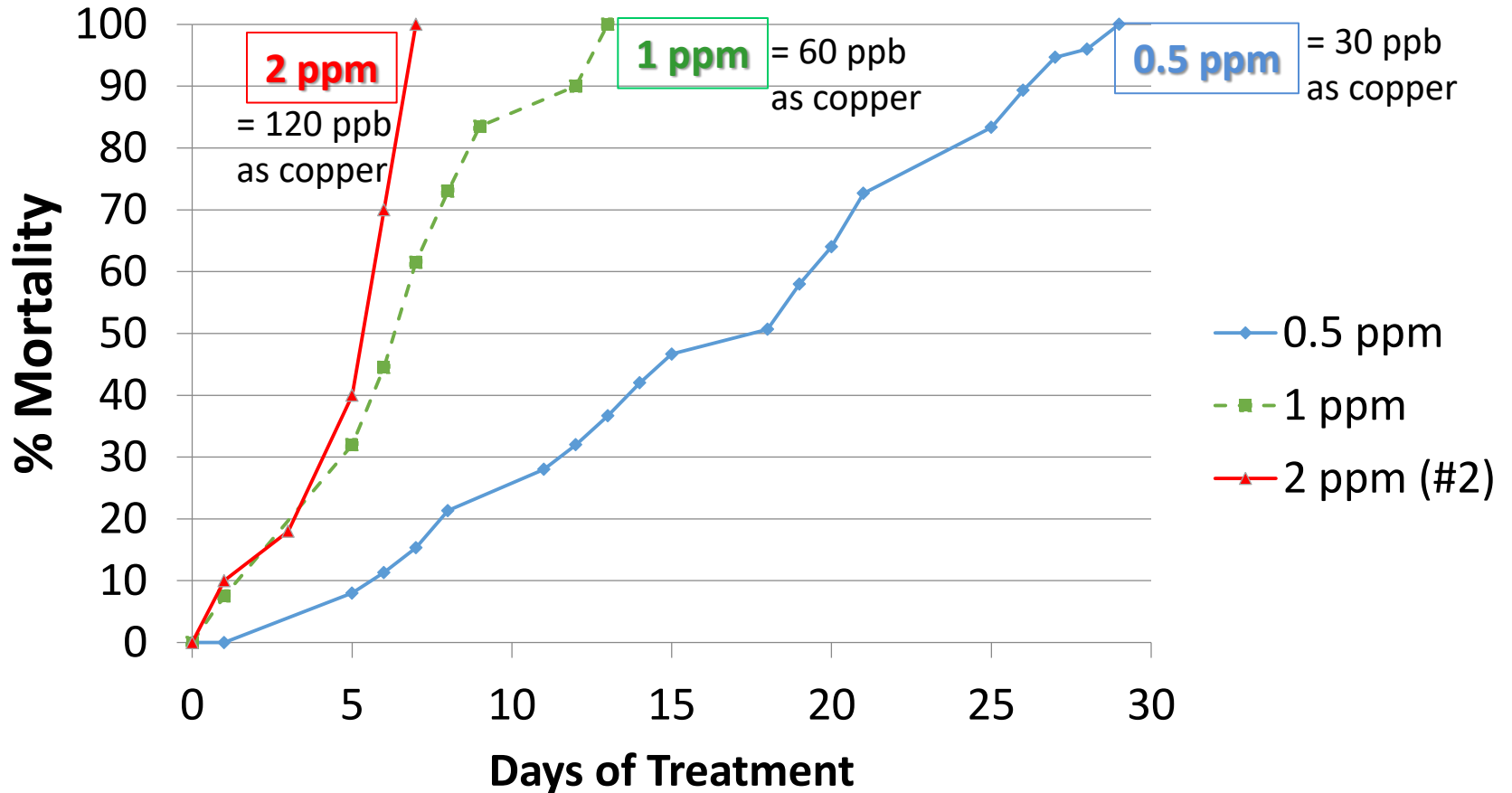
**Dose applied at
pipeline intake
1 ppm as QZ
= 60 ug/L as copper**

Date	WTP
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
Average:	0.92

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

Ohio WTP

Avg Mussel Mortality to QZ Concentration Applied in Pipeline



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

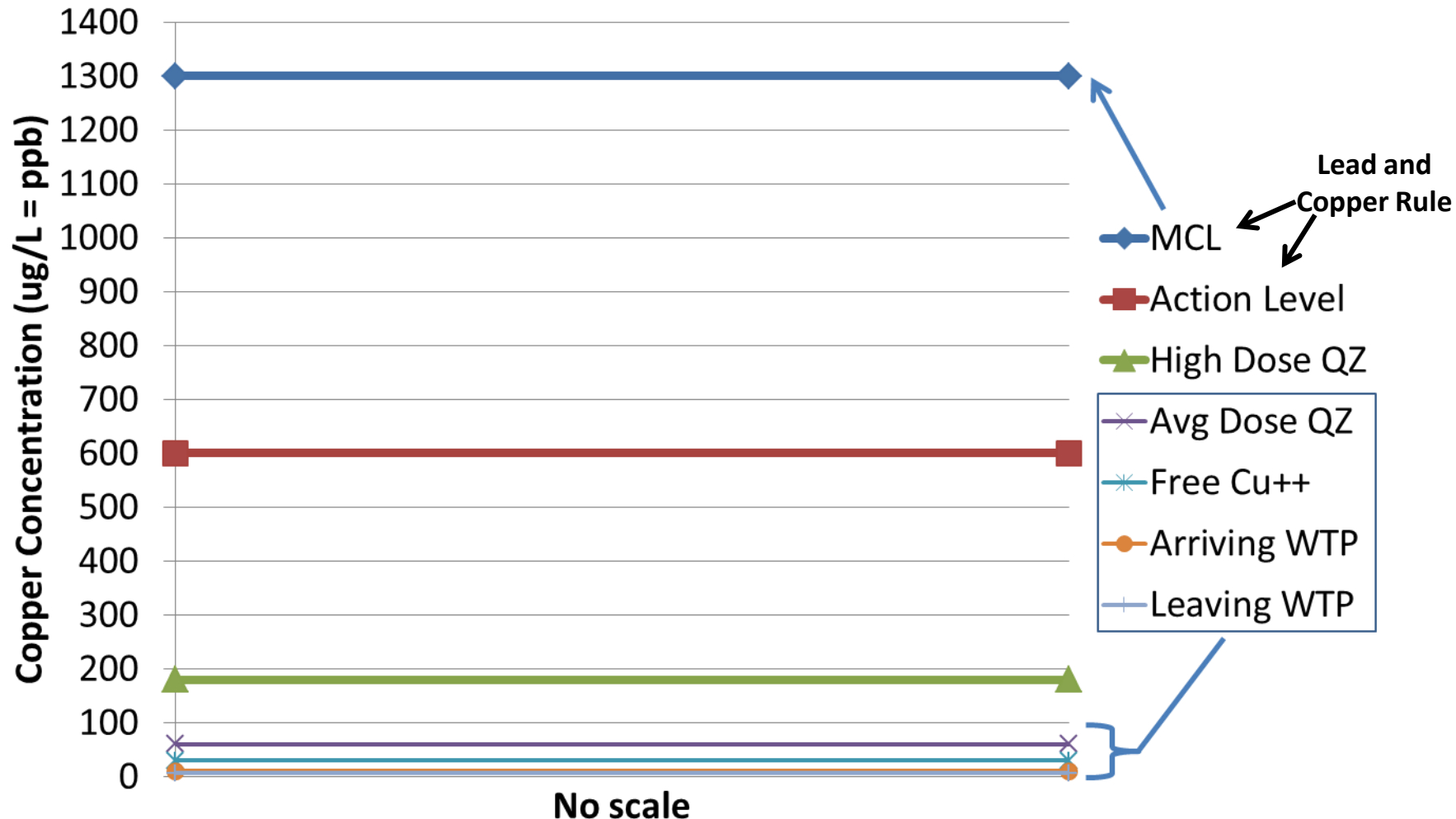


We continued the testing even under ice

**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

Copper Concentrations in Drinking Water



The copper residual concentration arriving at a WTP is in the range of 1/1000th to 1/100th of the Lead and Copper Rule standard



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^{++})** 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**



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





Thank you!

**EarthTec and EarthTec QZ:
A more rationale use of copper**

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