

**EarthTec QZ Case Study:
Control of colonial hydroids
(*Cordylophora caspia*) occurring in
association with quagga mussels**

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A thick, solid green line with a wavy, undulating shape that spans the width of the slide at the bottom.

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: South Dakota

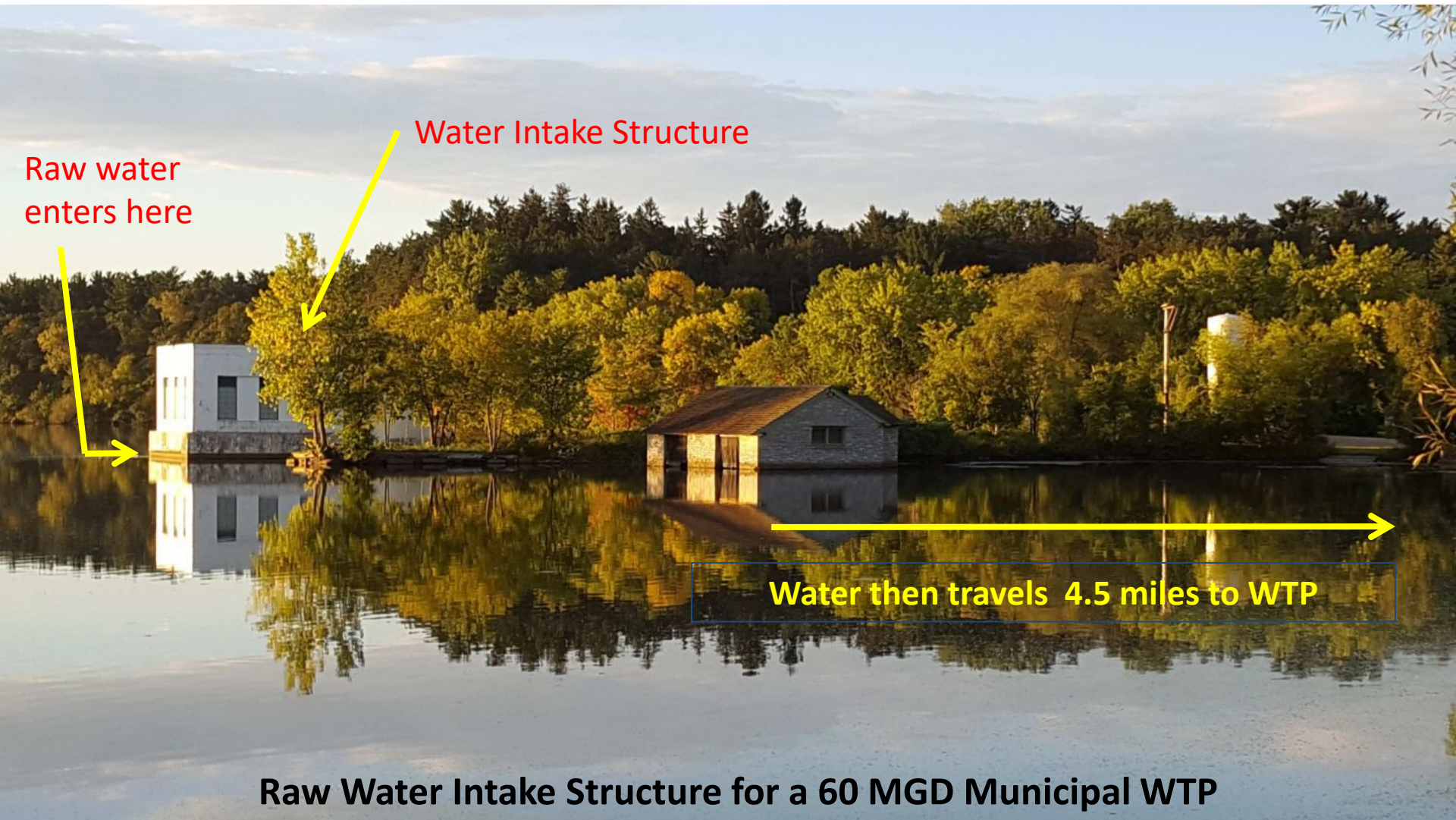




Priority Sites for Mussel Control

- **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

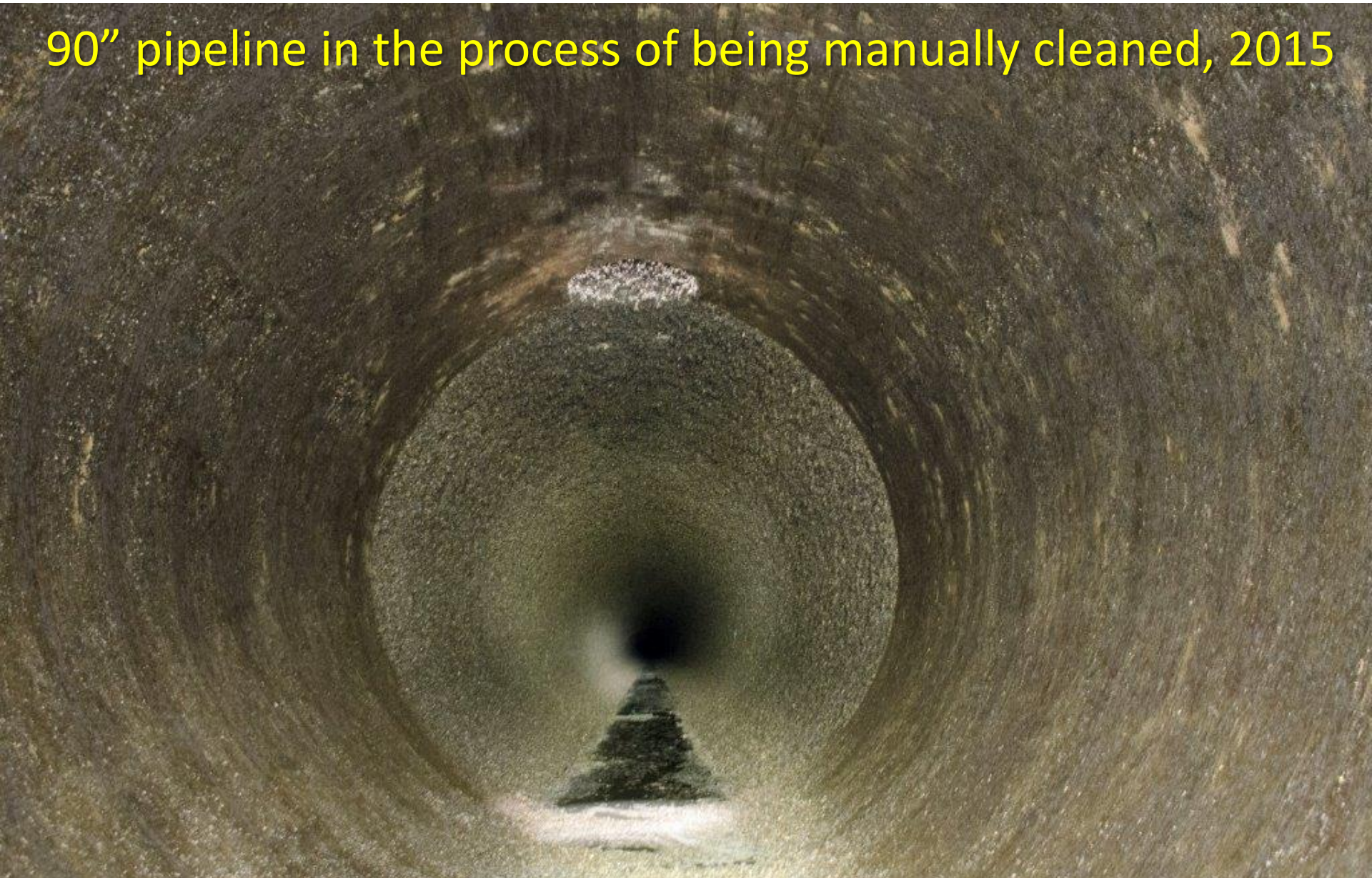


Screens and intake fouled
with zebra mussels, 2015

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

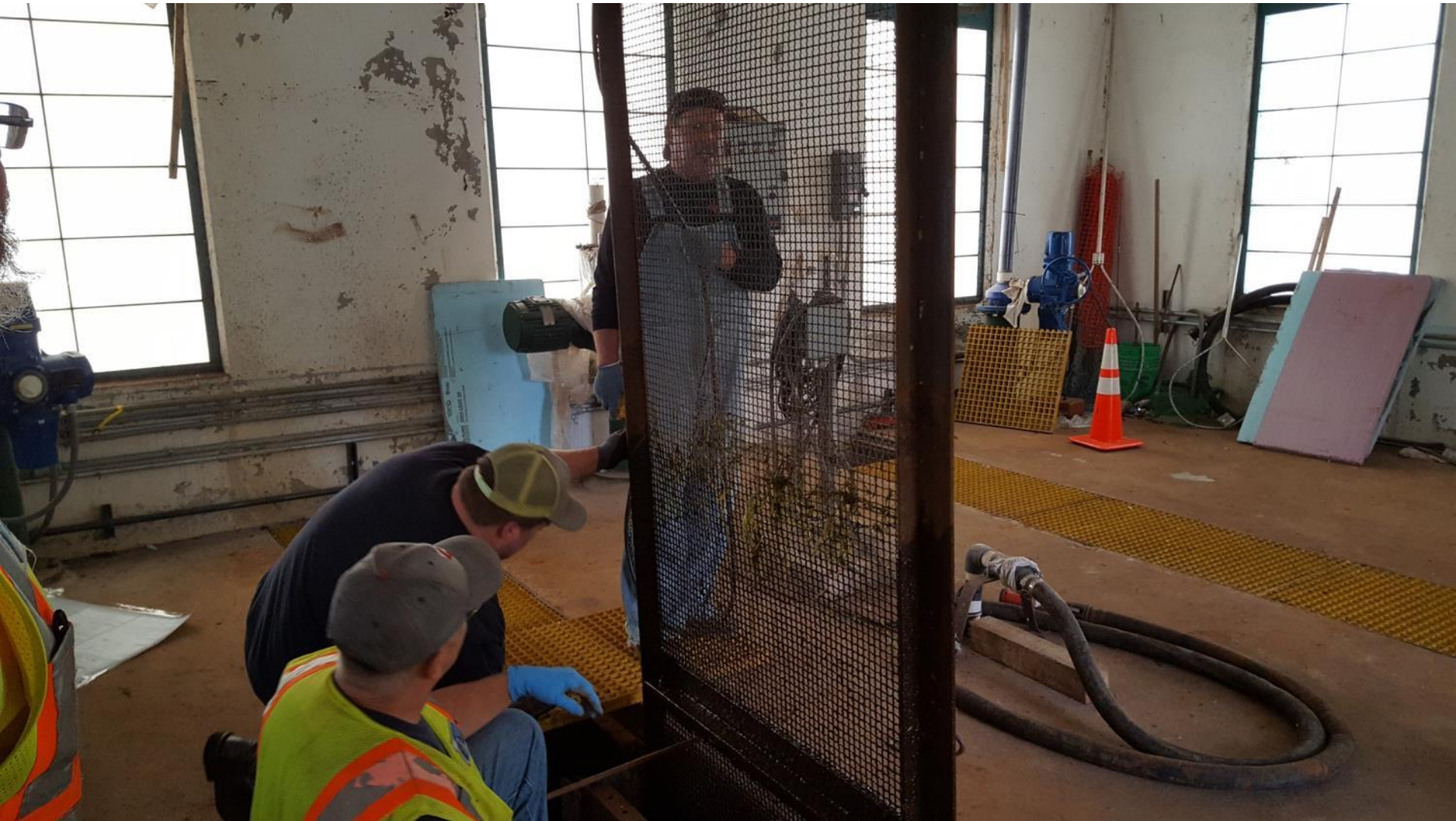
Metering pump and wall skid

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

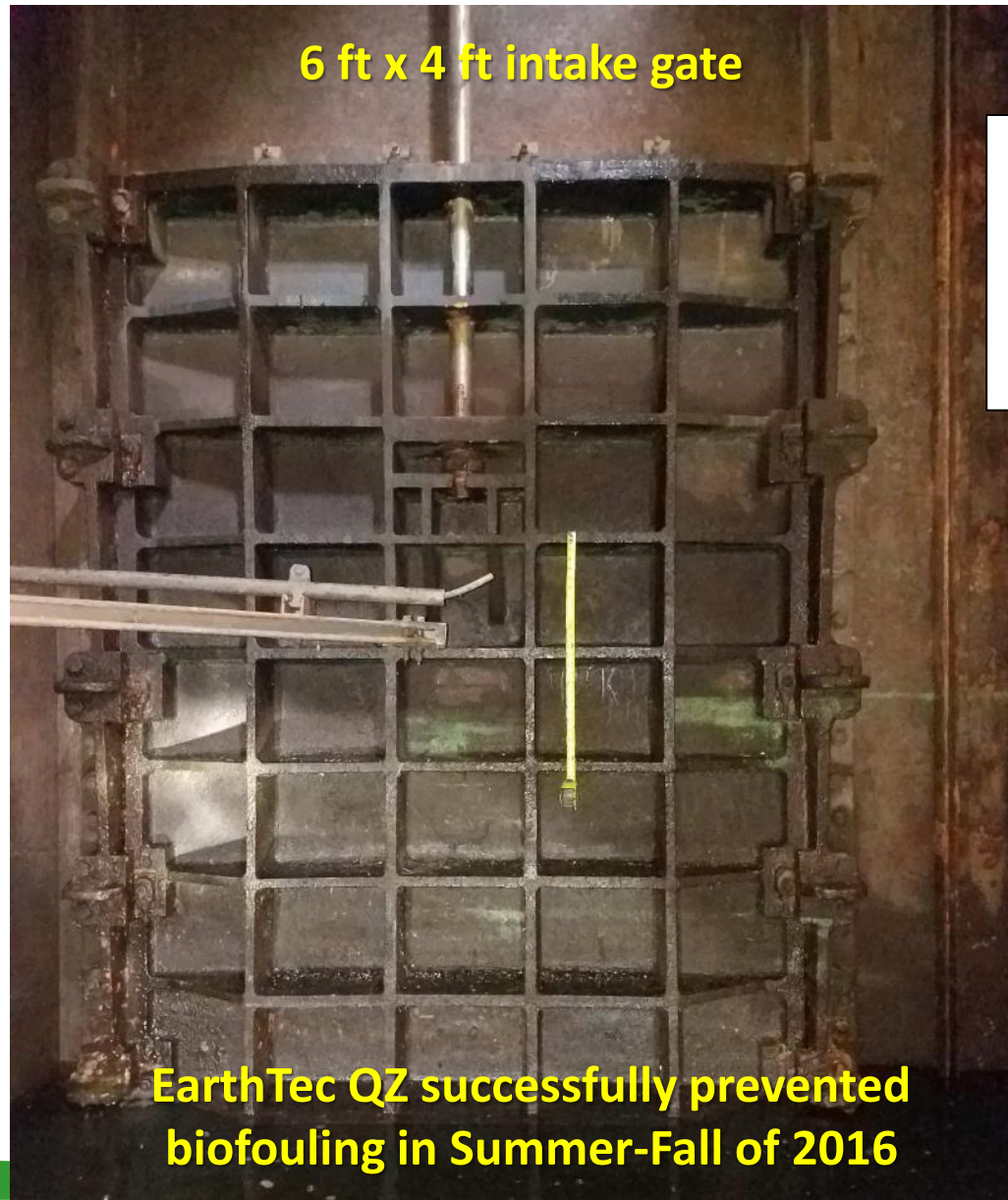


**1 ppm dose as QZ
= 60 ug/L as copper
sufficient to achieve
complete control**

**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**

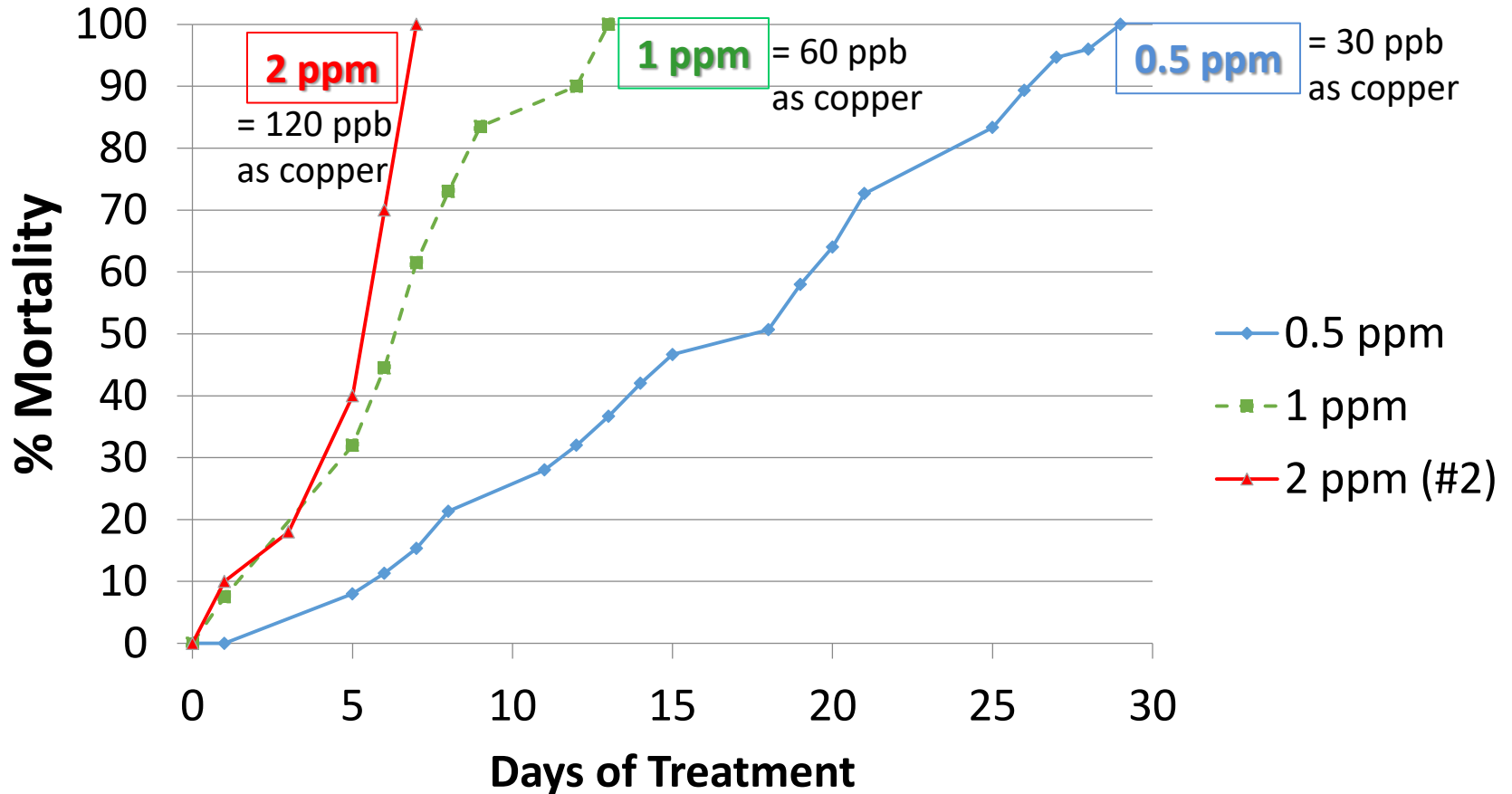
**Dose applied at
pipeline intake
1 ppm as QZ
= 60 ug/L as copper**

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

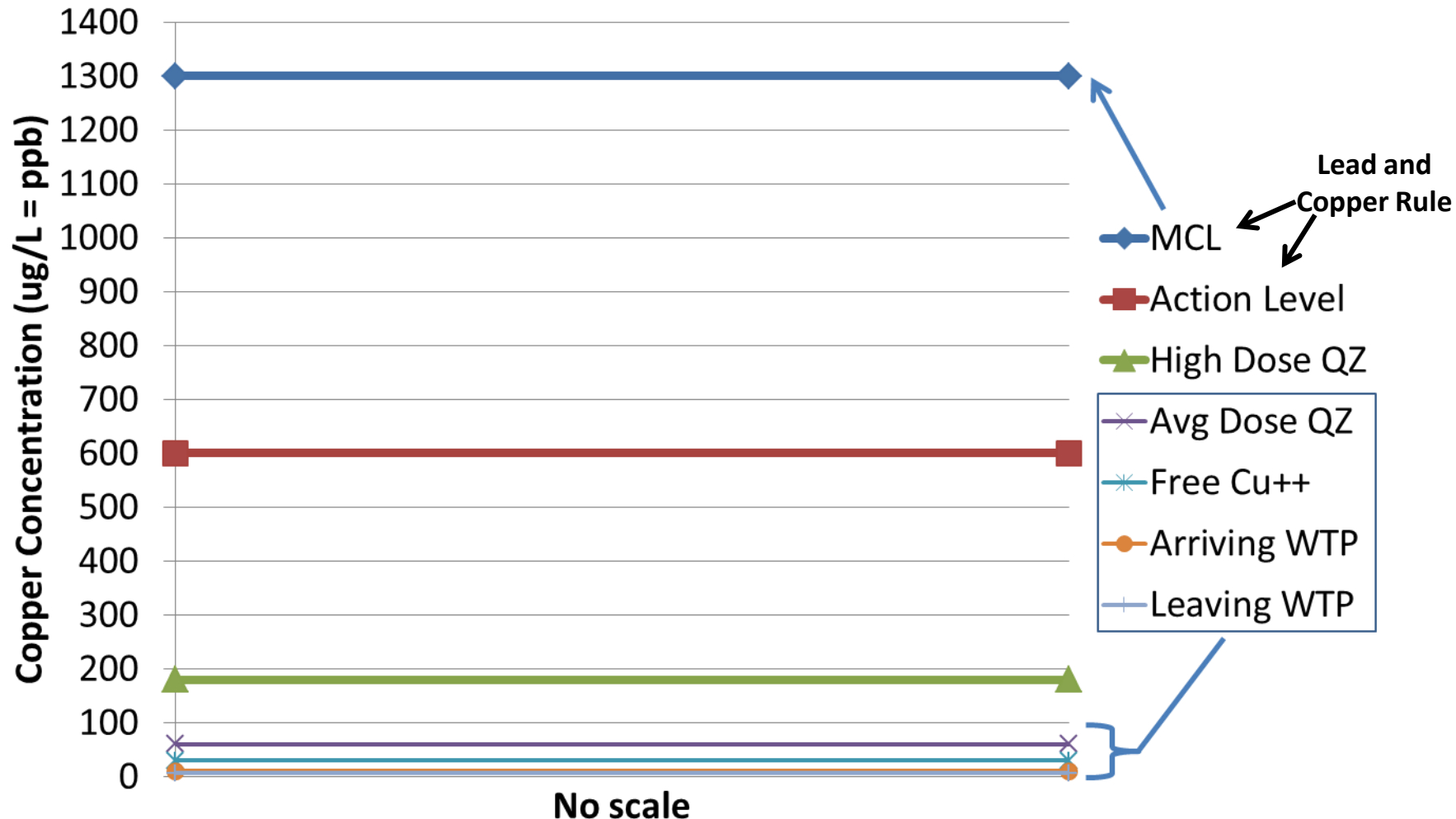


100% mortality in 6 days at 2 ppm, in 12 days at 1 ppm, in 28 days at 0.5 ppm



We continued the testing even under ice

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



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:

- More efficient formulation
 - Desired benefits at lower doses
 - Safer
 - Less waste
- 
- A green decorative wave graphic at the bottom of the slide.

Quagga Mussel and Colonial Hydroid Control in Colorado River Water

Sept, 2016



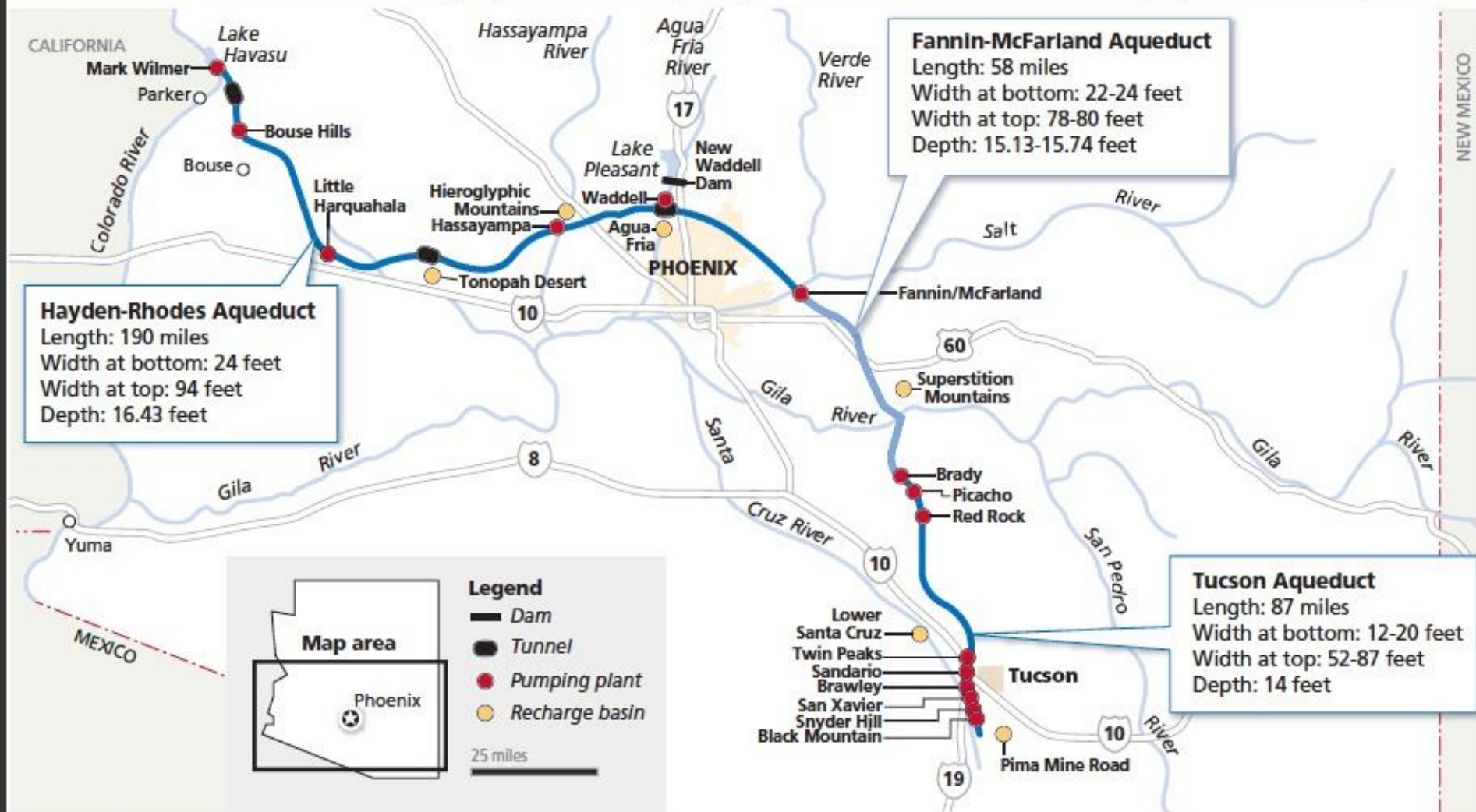
Central Arizona Project

- About 550 trillion gallons per year (1.6 million acre-ft)
- 336 miles of canals
- 15 Pumping stations
- Tunnels, siphons
- Lifts the water >3,000 ft vertically from the Colorado River to Phoenix and Tucson
- Delivers to 57 water providers



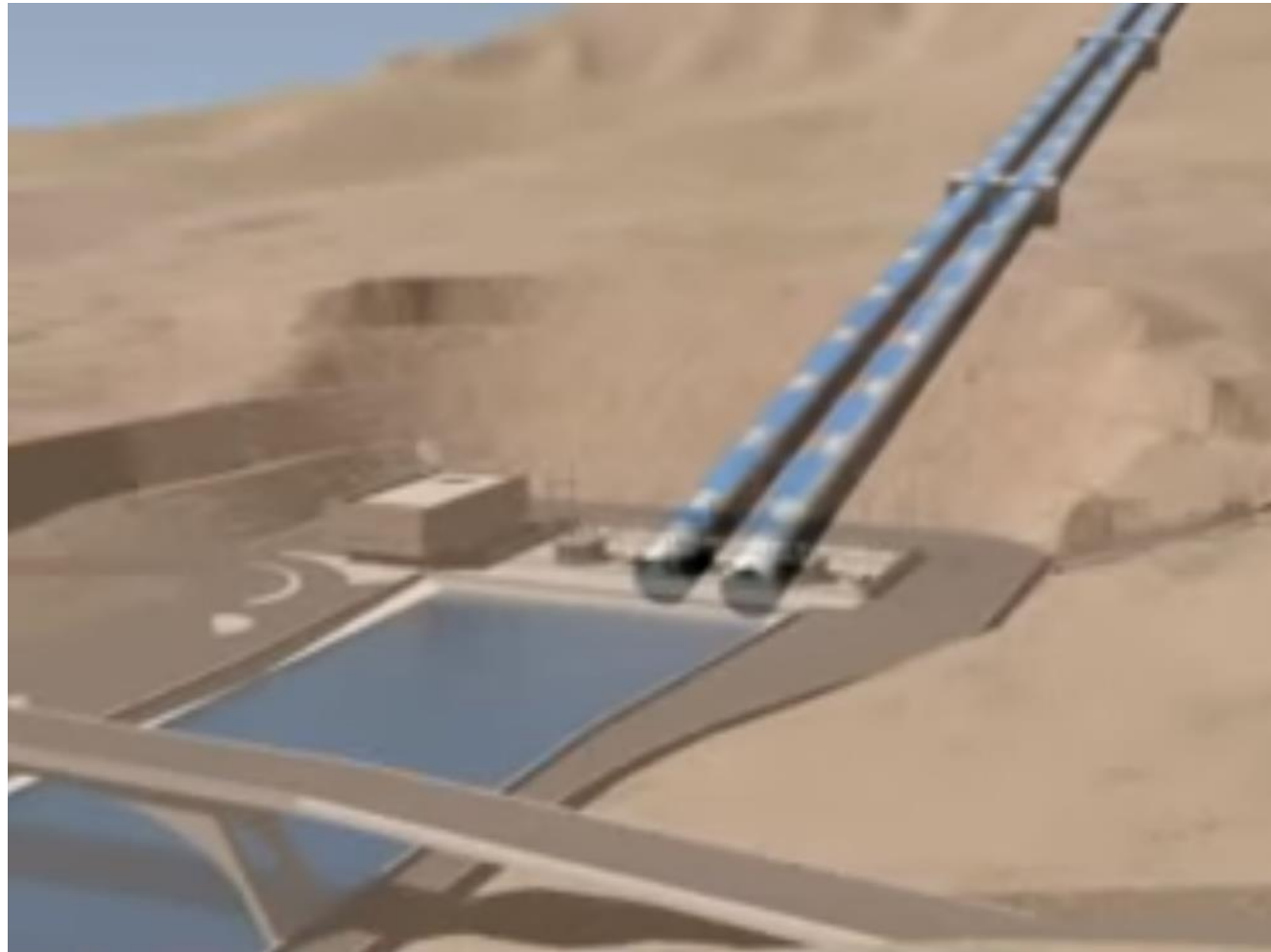
CENTRAL ARIZONA PROJECT CANAL

The CAP Canal has allowed the cities it serves to grow, even in arid country. It begins at the Colorado River and moves water uphill, from Lake Havasu (elevation 447

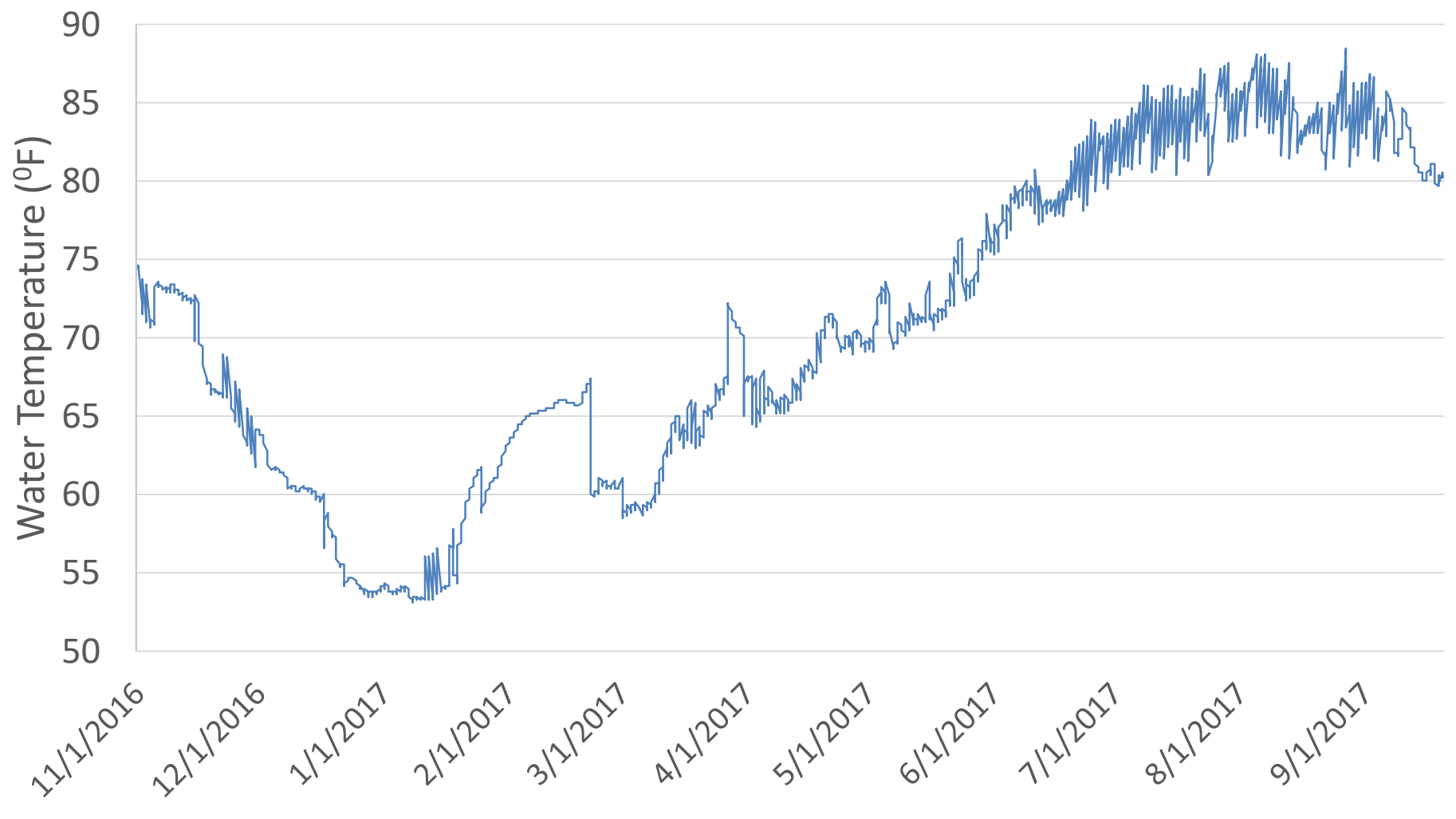


Central Arizona Project

- 6 pumps
- 60,000 hp each
- 824 ft vertical rise in first section
- >50% of all energy budget for CAP used in first rise



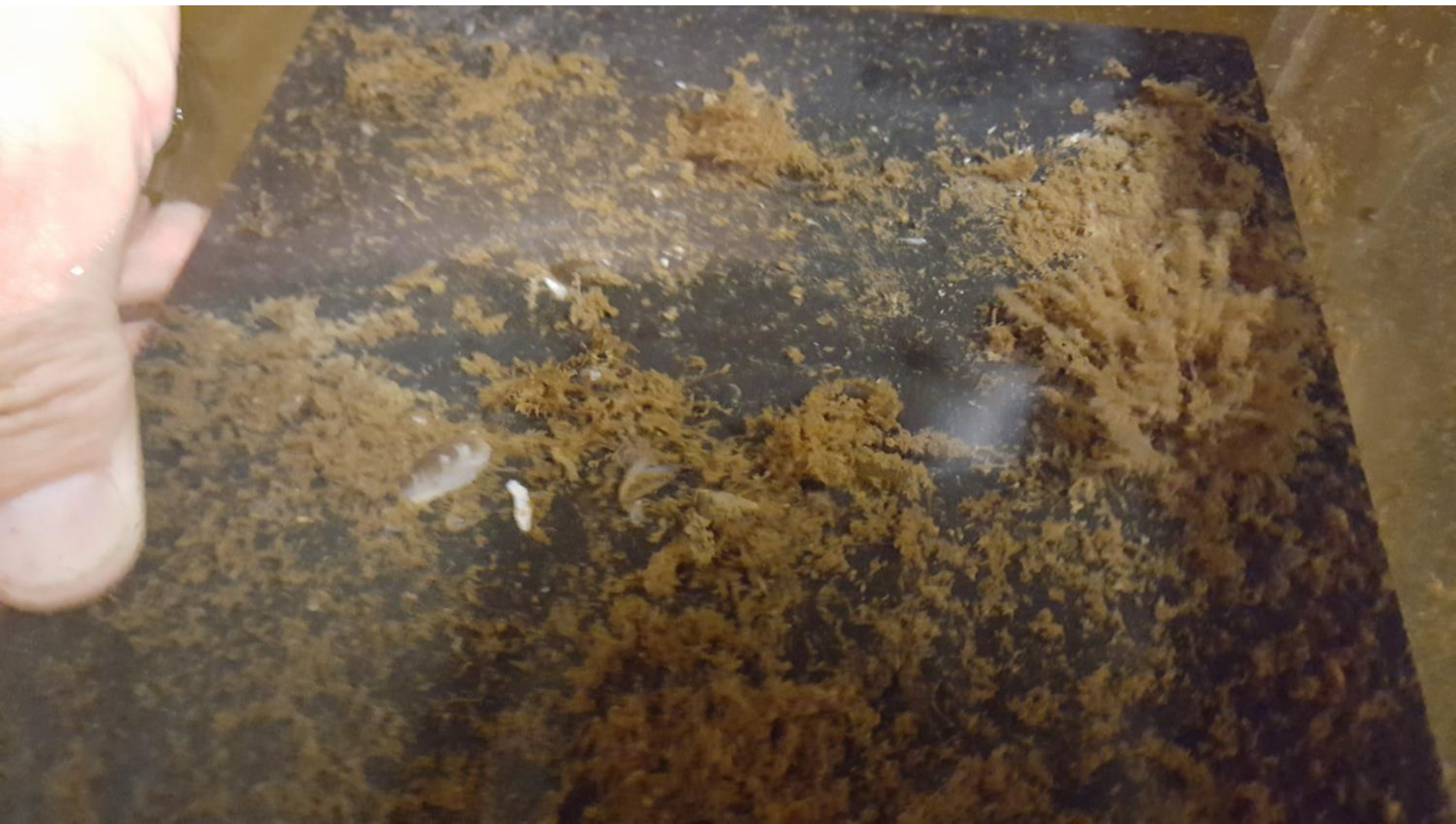
Water Temperatures in the Cooling System





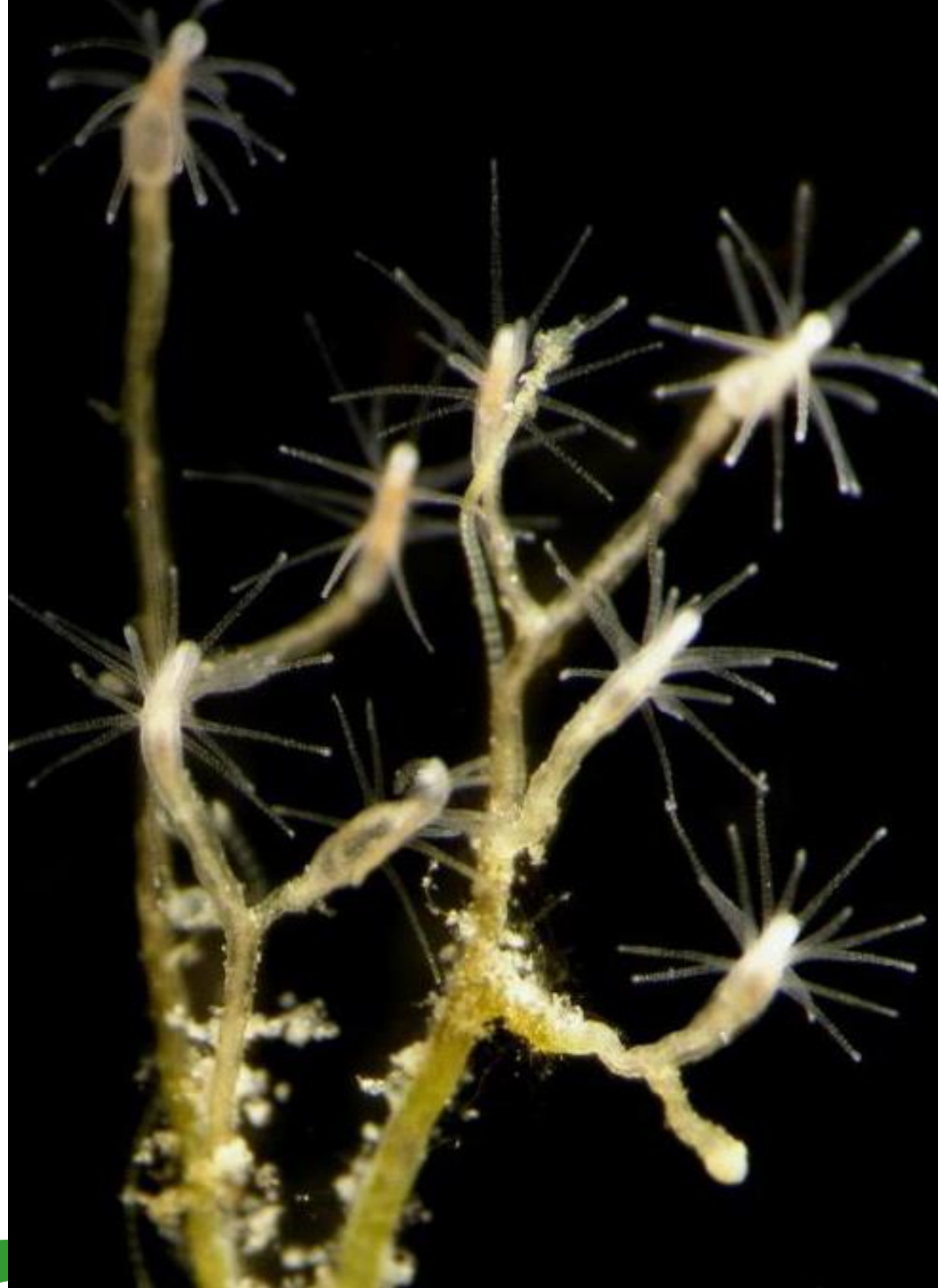
Quagga Mussel and Colonial Hydroid Control in Colorado River Water

Sept, 2016



Colonial Hydroid

- Native to Caspian Sea
- Stinging tentacles to capture zooplankton
- Species: *Cordylophora caspia*
- Order: Hydroida
- Class: Hydrozoa





0.25 mm

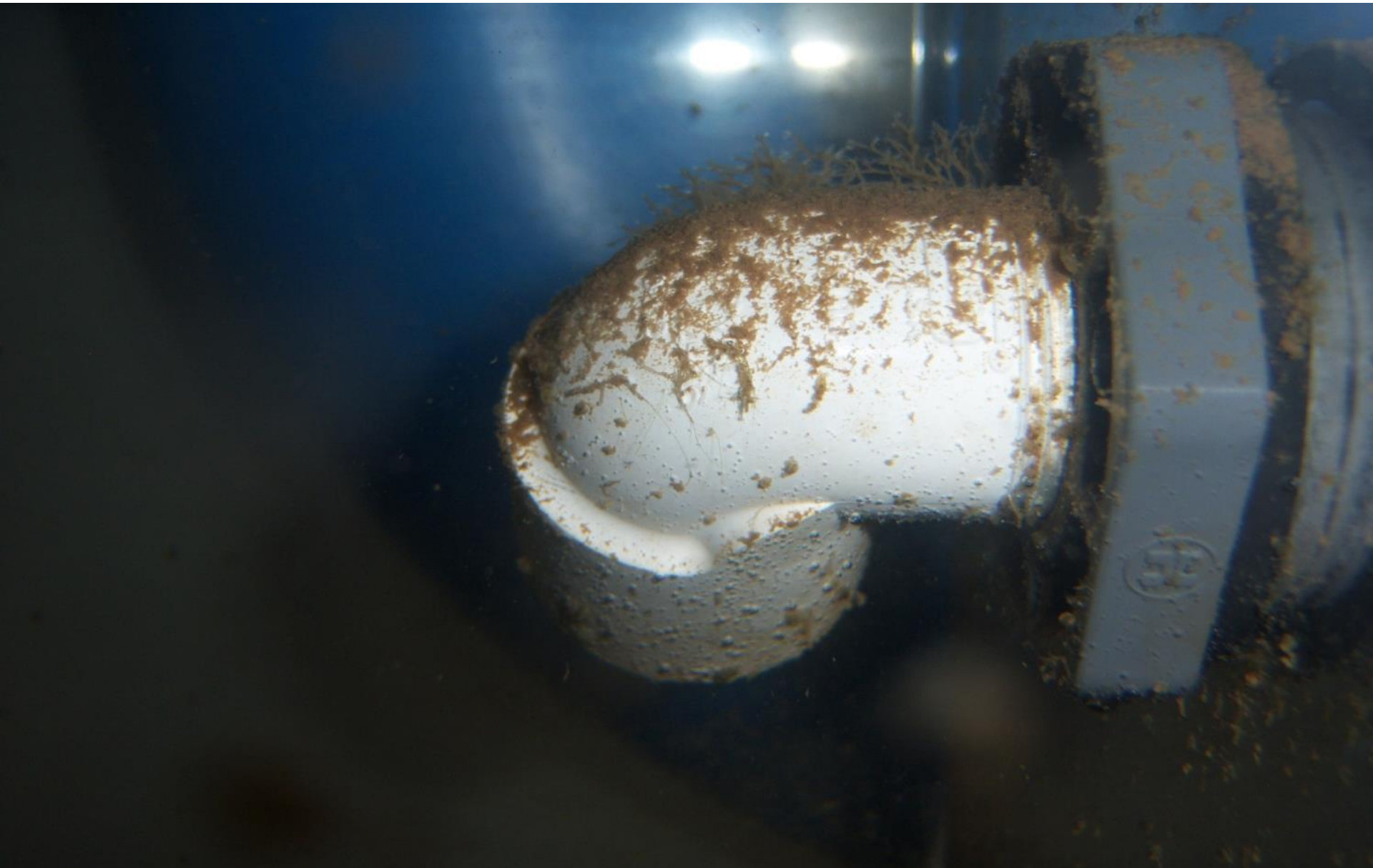


Quagga Mussel and Colonial Hydroid Control in Colorado River Water



Quagga Mussel and Colonial Hydroid Control in Colorado River Water

Sept, 2016



Quagga Mussel and Colonial Hydroid Control in Colorado River Water

Sept, 2016



Study Objective:

To compare two strategies for protection
against biofouling of the cooling system

Sher-Release

Foul-Release Coating
Silicone-based
by Sherwin Williams

VS

EarthTec QZ

Liquid Ionic Copper, Cu^{++}
by Earth Science Labs

and no chemical treatment

and no coating



Applied to Units 4 and 5 in July, 2016

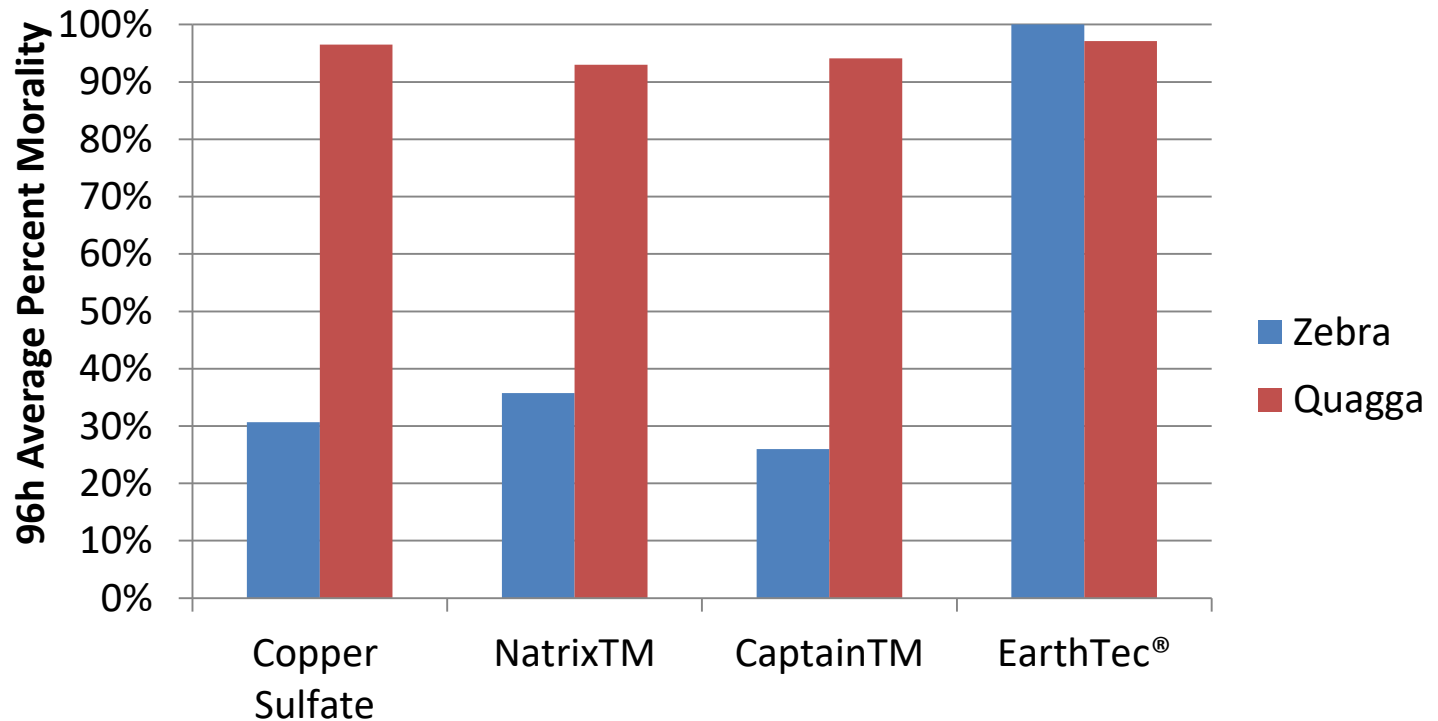


Continuous dose into Unit 6

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.

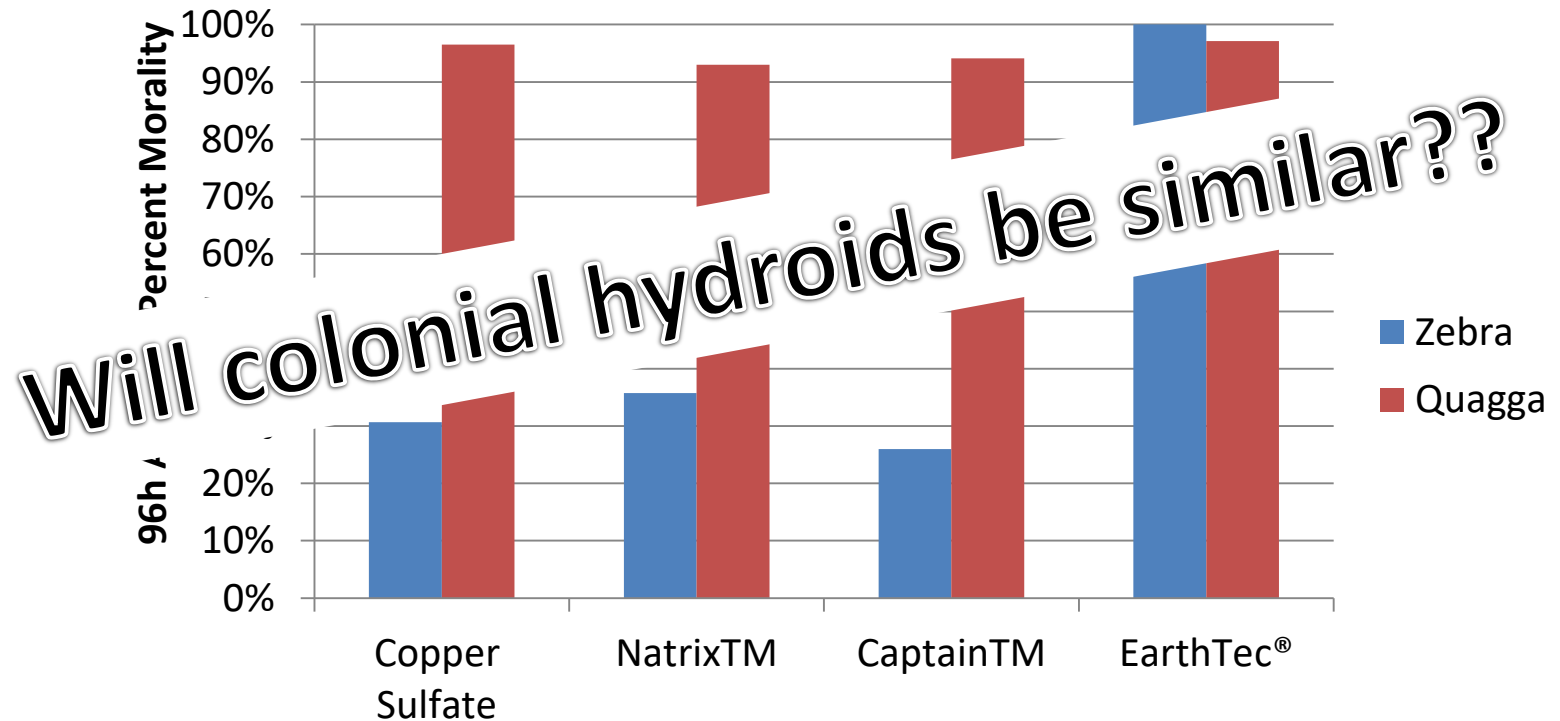
And we now know much lower doses of EarthTec are still effective against mussels.

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.

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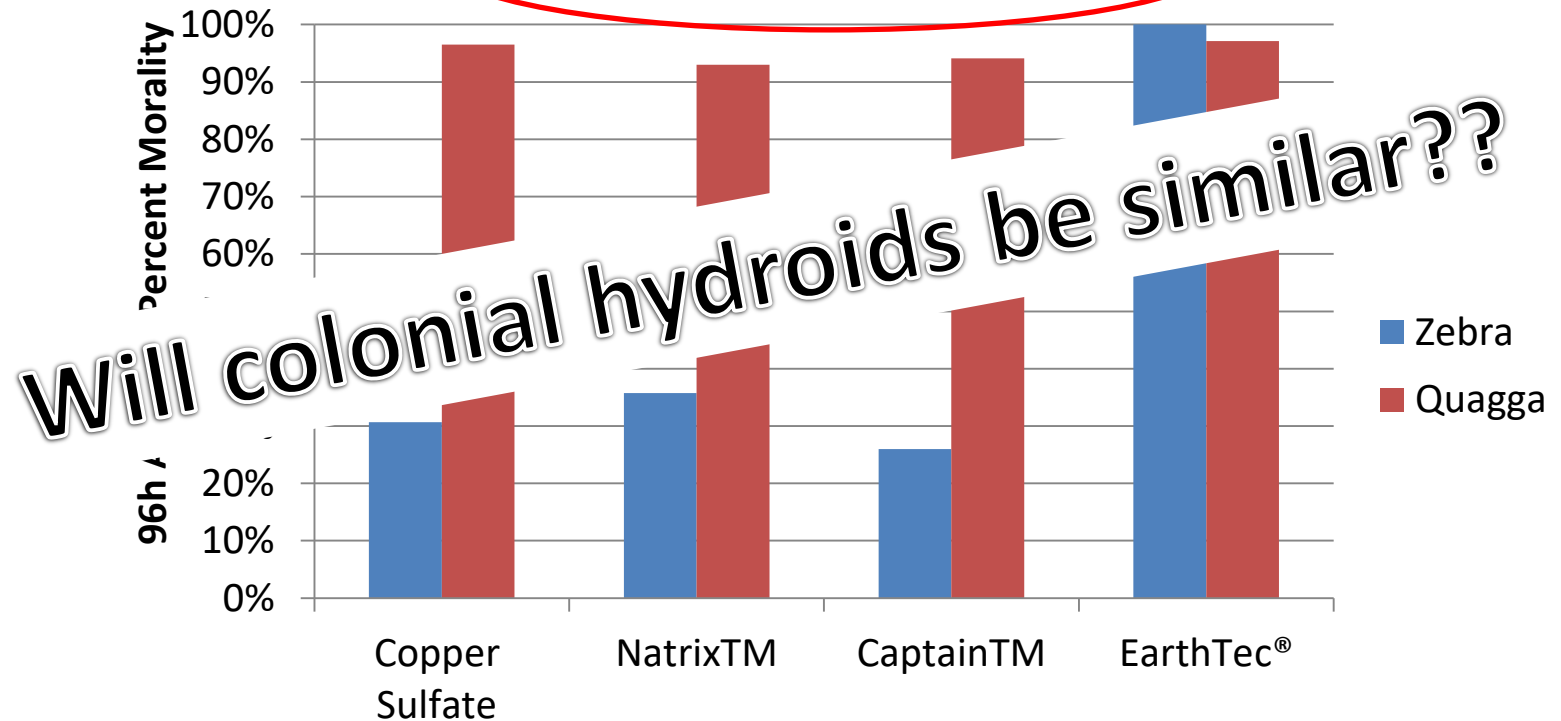
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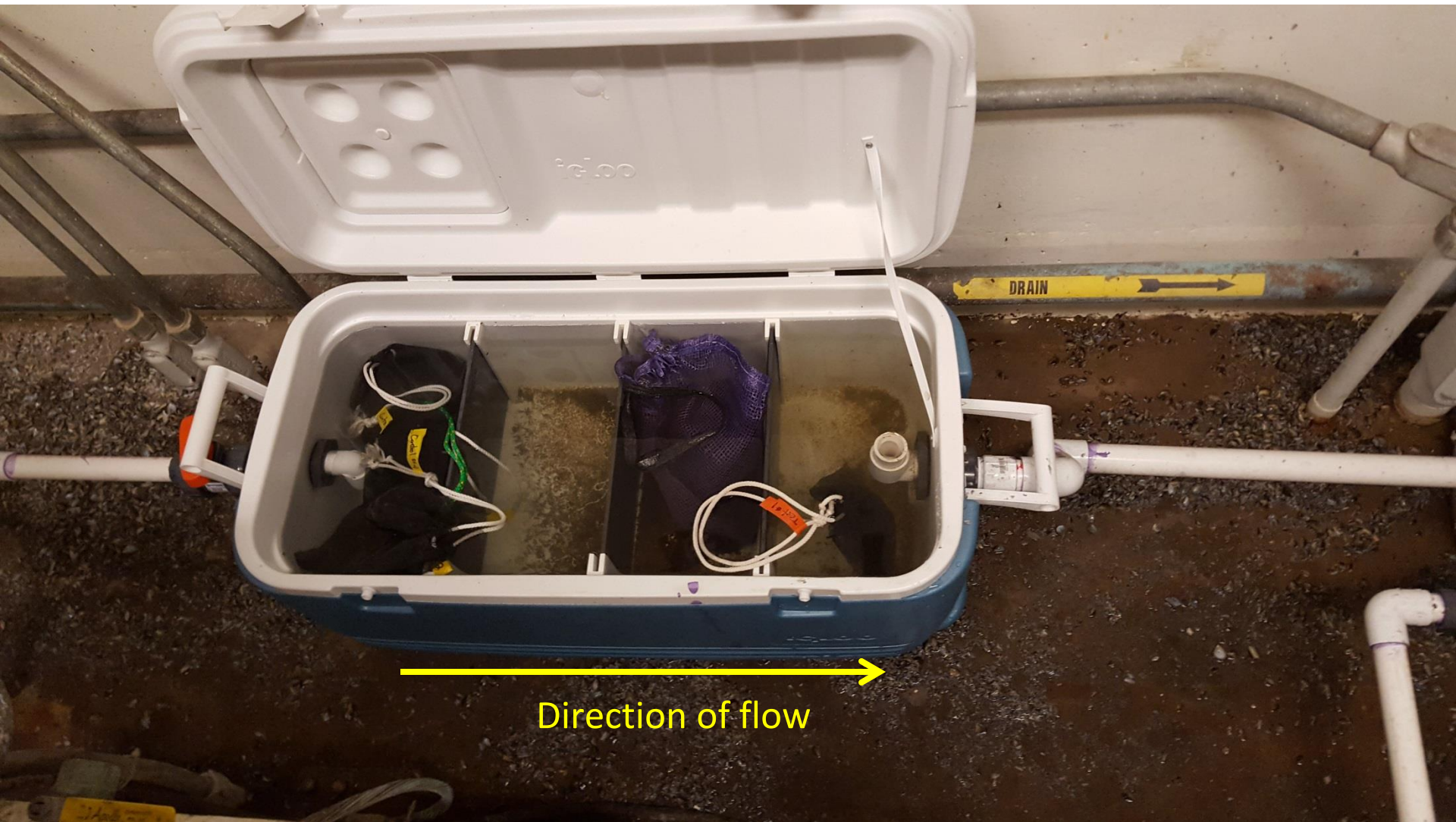
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Metering pump
mounted to
wall skid

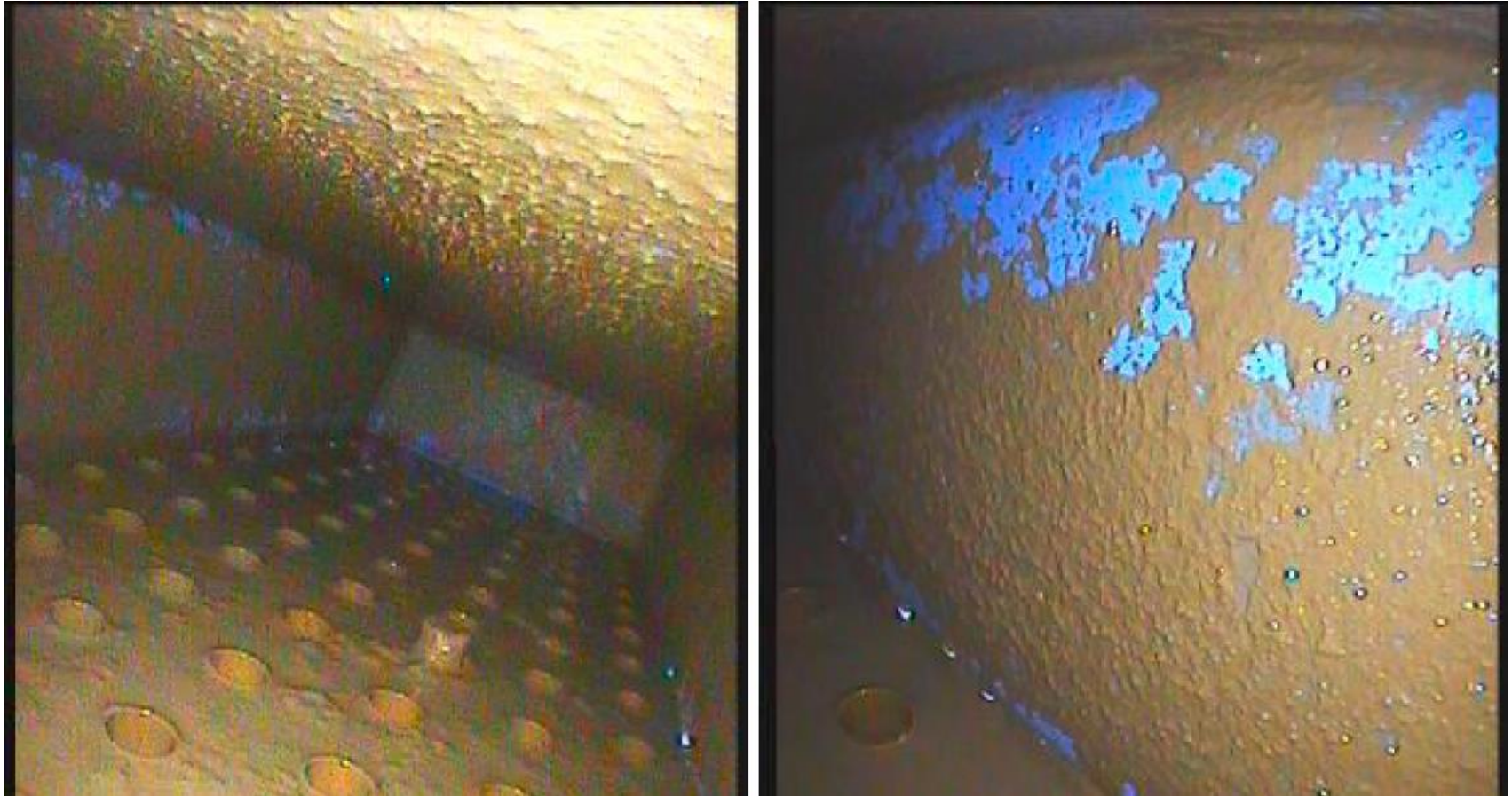
Injection port

Supply tanks



Borescope Observation of Unit 4, mid-Dec, 2017

Foul-Release Coating (Sherwin Williams Sher-Release) and no chemical treatment



Borescope Observation of Unit 4 (Cooler A on left and Cooler B on right)

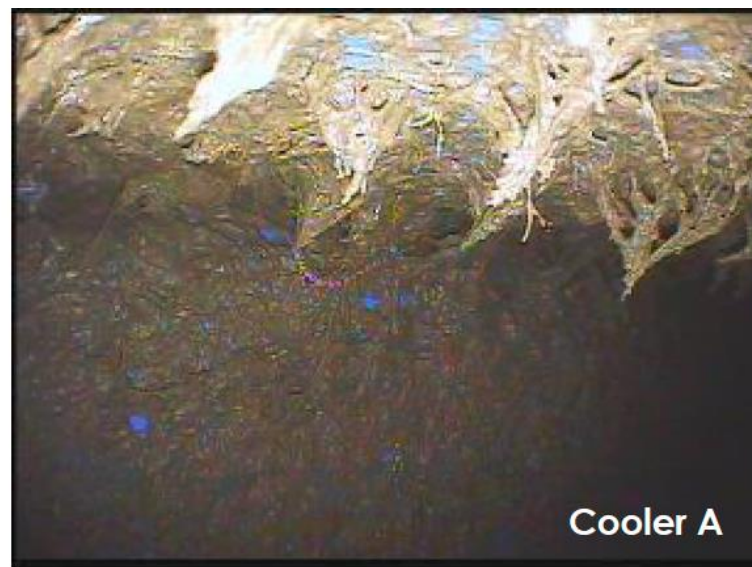
Borescope Observation of Unit 6, mid-Dec, 2017

Treatment with EarthTec QZ at 0.75 ppm (= 45 ppb as copper)



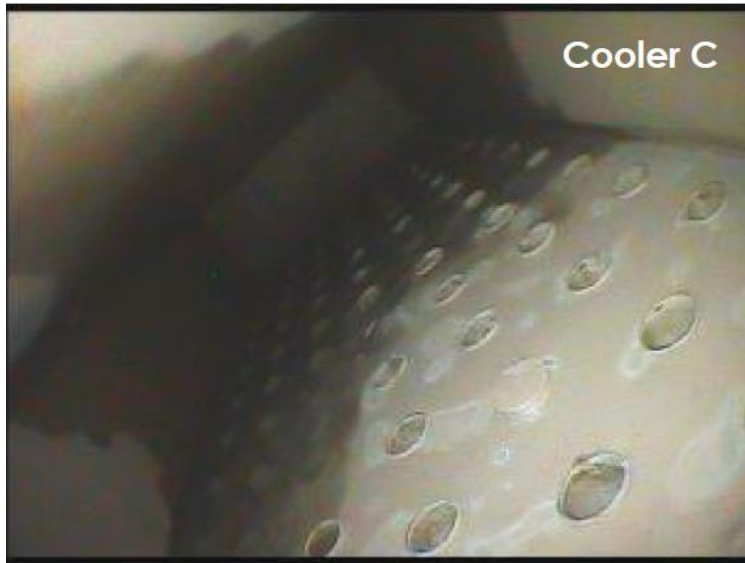
Borescope Observation of Unit 6 (Cooler A on left and Cooler C on right),
after treatment with EarthTec QZ at 0.75 ppm (= 45 ppb as copper)
and no foul-release coating

Foul-Release Coating (Sherwin Williams Sher-Release) and no chemical treatment

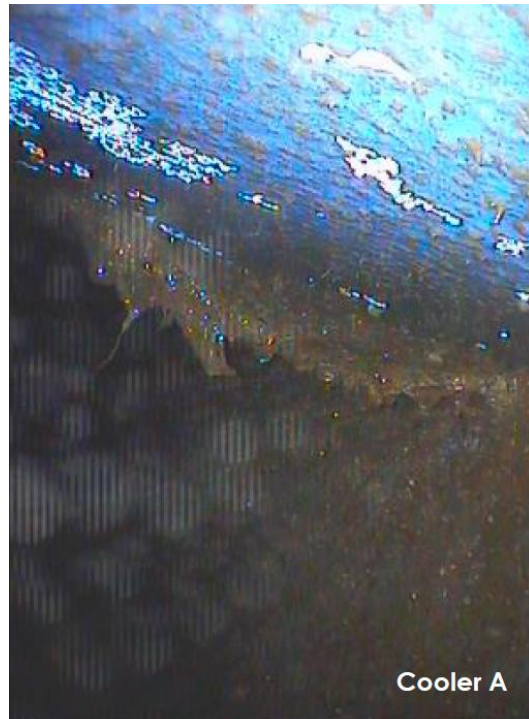


Borescope Observation of Unit 6, Jan-Feb, 2017

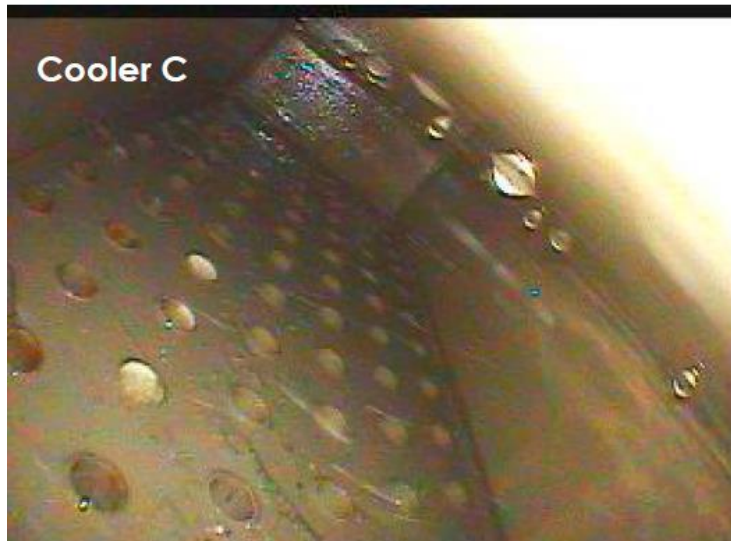
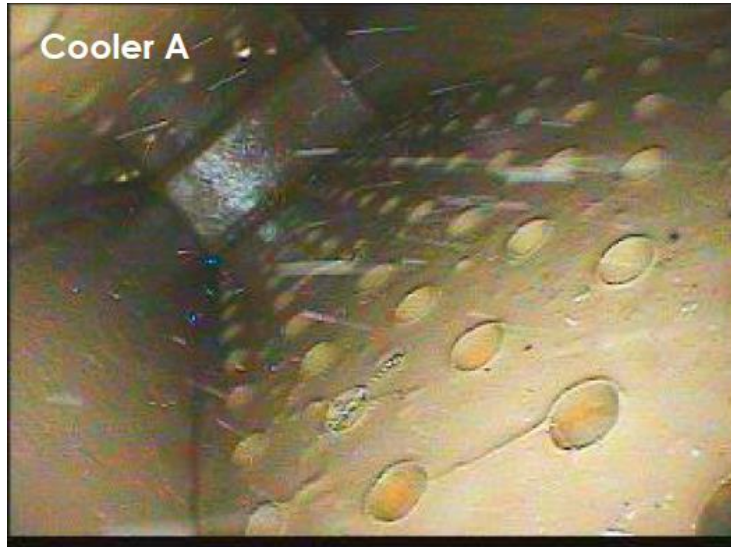
Treatment with EarthTec QZ at 0.75 ppm (= 45 ppb as copper)



Foul-Release Coating (Sherwin Williams Sher-Release) and no chemical treatment



Treatment with EarthTec QZ at 0.75 ppm (= 45 ppb as copper)



Condition of plates prior to placement in EarthTec QZ at 1.0 ppm (= 60 ppb as copper)



Heavily infested settlement plates were taken from Lake Havasu on 5/15/2017 and placed into bioboxes representing a control vs treatment at 1.0 ppm as EarthTec QZ.

Plates after 2 weeks in untreated (Control) biobox



Settlement plates in the untreated Control biobox as of 5/31/2017. Quagga mussels are healthy and dense. Hydroids are present.

Plates after 2 weeks in biobox fed with EarthTec QZ at 1.0 ppm (= 60 ppb as copper)



Heavily infested settlement plates 5/31/2017, after 15 days in the treatment biobox.
Note that the mussel shells are open and empty, the flesh having washed away.
Hydroid tissues are still present, but readily slough off.

Infested Plates being placed in biobox

7/12/2017



Before 2 weeks of treatment at 0.75 ppm (= 45 ppb Cu++)

Quagga shells mostly healthy and closed.

Infested Plates after 2 weeks in Treated bioboxes

7/24/2017



After 2 weeks of treatment at 0.75 ppm (= 45 ppb Cu++)
Quagga shells open and empty. 95+% dead vs 30% dead on Control plate

Infested Plates in Control vs Treated Bioboxes after 2 weeks exposure at 0.75 ppm (= 45 ppb as copper)



Treated bioboxes, 0.75 ppm (= 45 ppb Cu⁺⁺). Quagga shells open and empty. Many sloughed off when plate was examined. Many empty shells found in bottom of biobox.

Control biobox. Quagga mussels are mostly healthy and dense, about 30% mortality

Foul-Release Coating and no chemical treatment



Significant growth of colonial hydroid, but no quagga mussels

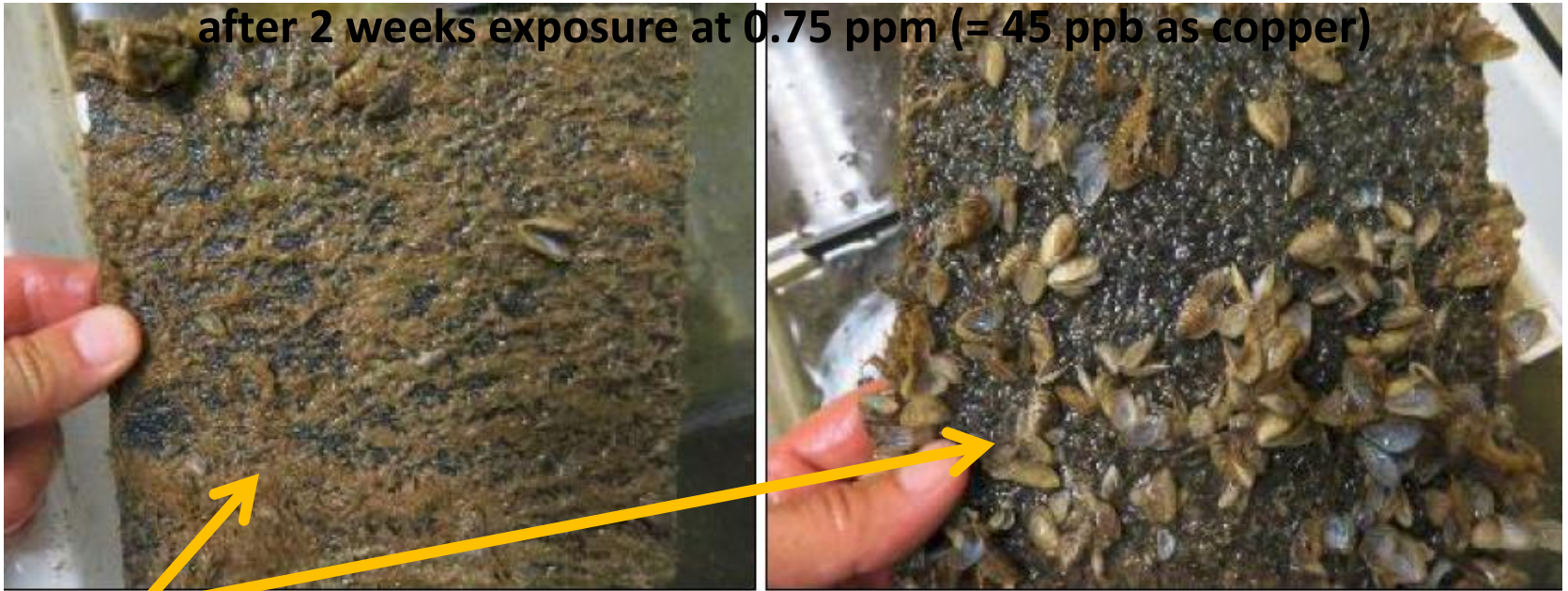
Borescope Observation of Unit 6, July 26, 2017

Treatment with EarthTec QZ at 0.75 ppm (= 45 ppb as copper)



No growth of colonial hydroid or quagga mussels, just a few strands of aquatic weeds that managed to get through the strainers

**Infested Plates in Control vs Treated Bioboxes, 8/9/2017,
after 2 weeks exposure at 0.75 ppm (= 45 ppb as copper)**



Treated bioboxes, 0.75
ppm (= 45 ppb Cu⁺⁺).
Hydroids present but
not expanding.
Quagga shells open
and empty.



Control biobox.
Some hydroids.
Quagga mussels are
healthy and dense.

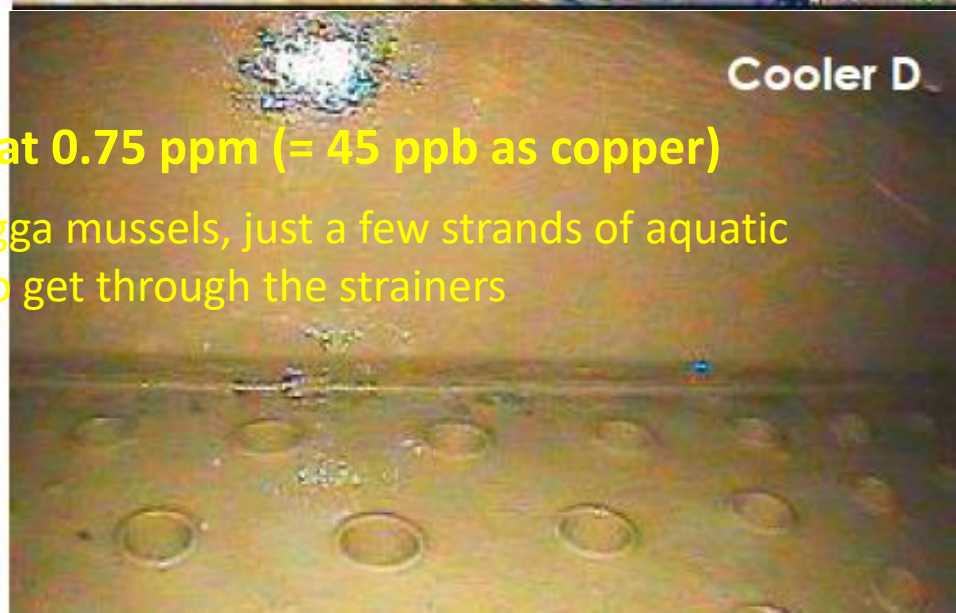
Borescope Observation of Unit 5 (top) and Unit 6 (bottom), Aug 23 2017



Foul-Release Coating and no chemical treatment
Significant growth of colonial hydroid, but no quagga mussels

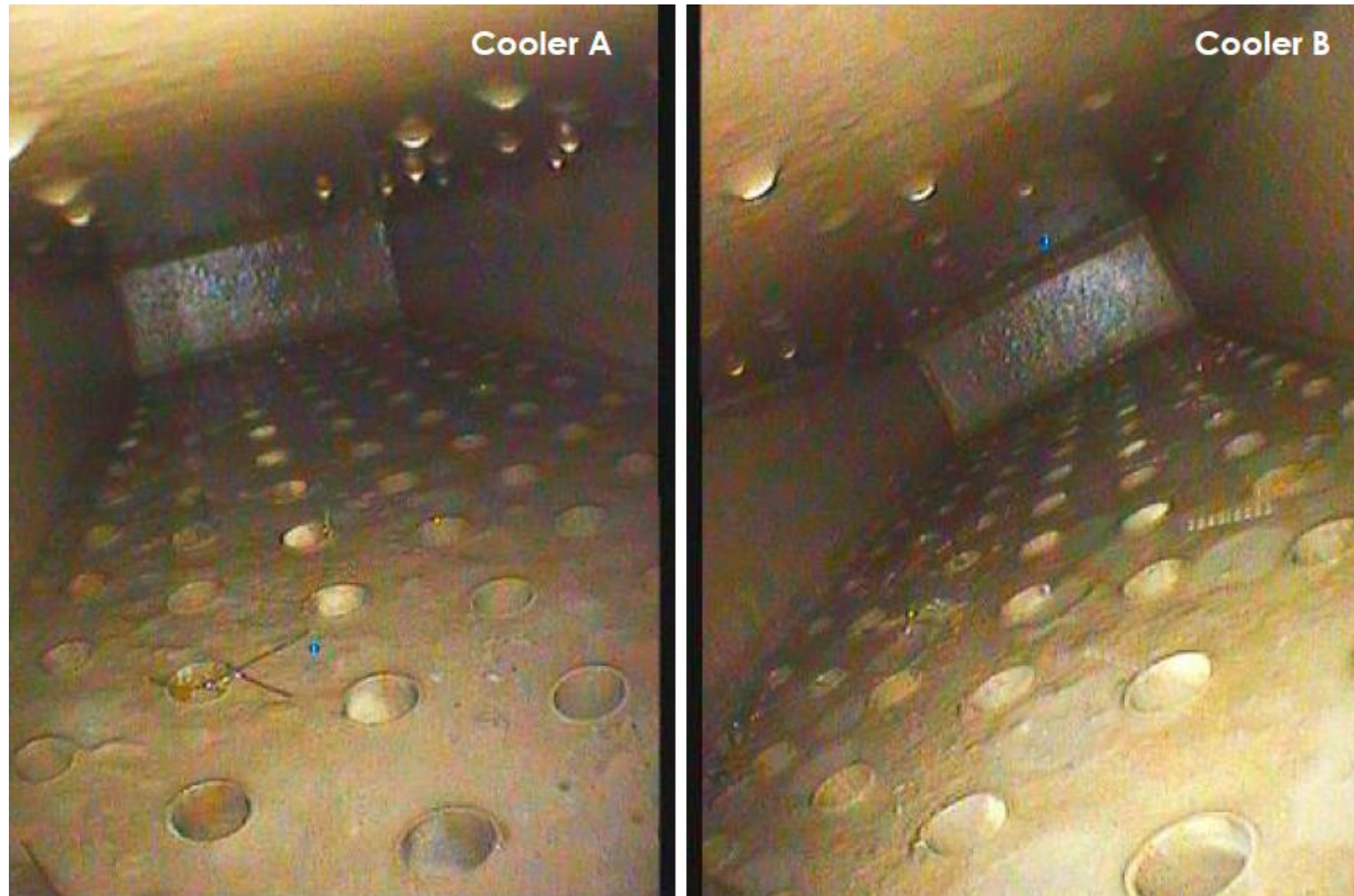


Treatment with EarthTec QZ at 0.75 ppm (= 45 ppb as copper)
No growth of colonial hydroid or quagga mussels, just a few strands of aquatic weeds that managed to get through the strainers



Borescope Observation of Unit 6, Aug 23, 2017

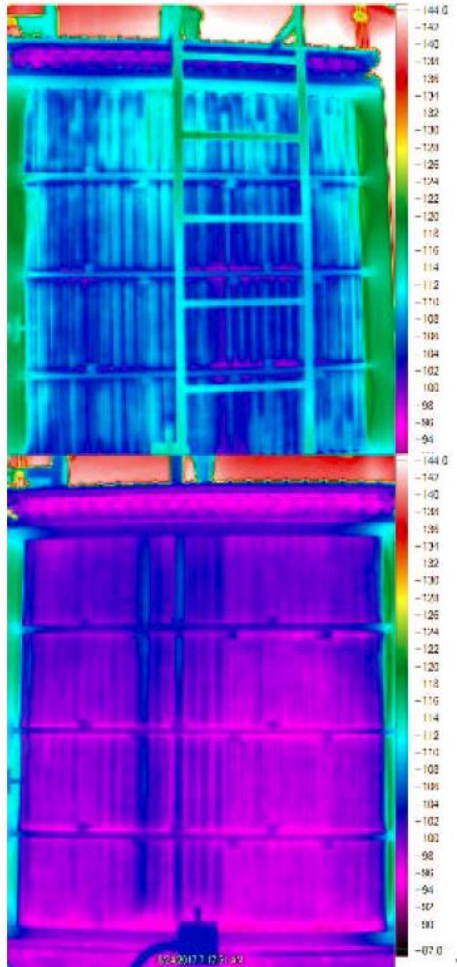
Treatment with EarthTec QZ at 0.75 ppm (= 45 ppb as copper)



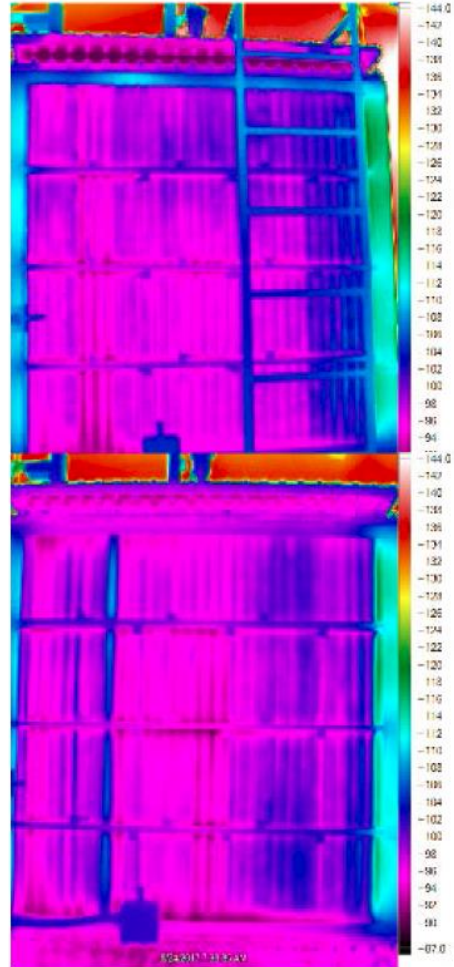
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Infrared-Based Measure of Operating Temperature of Cooling Systems

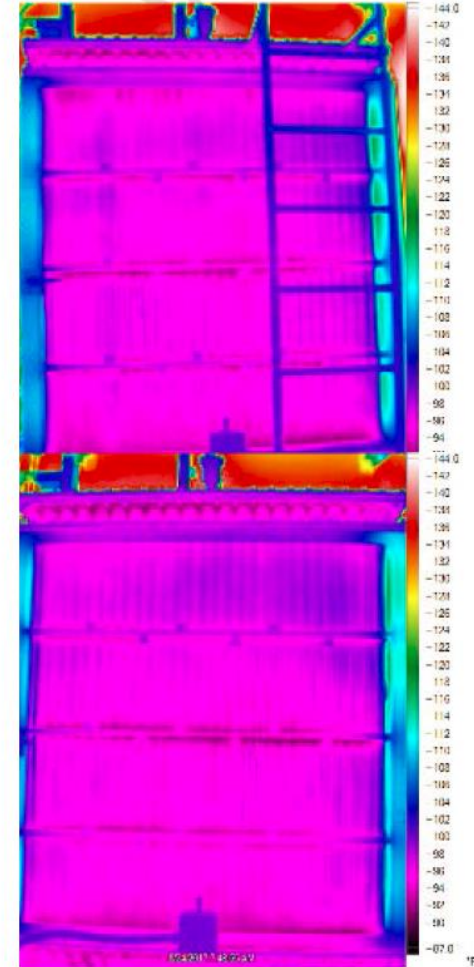
8/23/2017



Cooler 4
(Foul-release coating)



Cooler 5
(Foul-release coating)



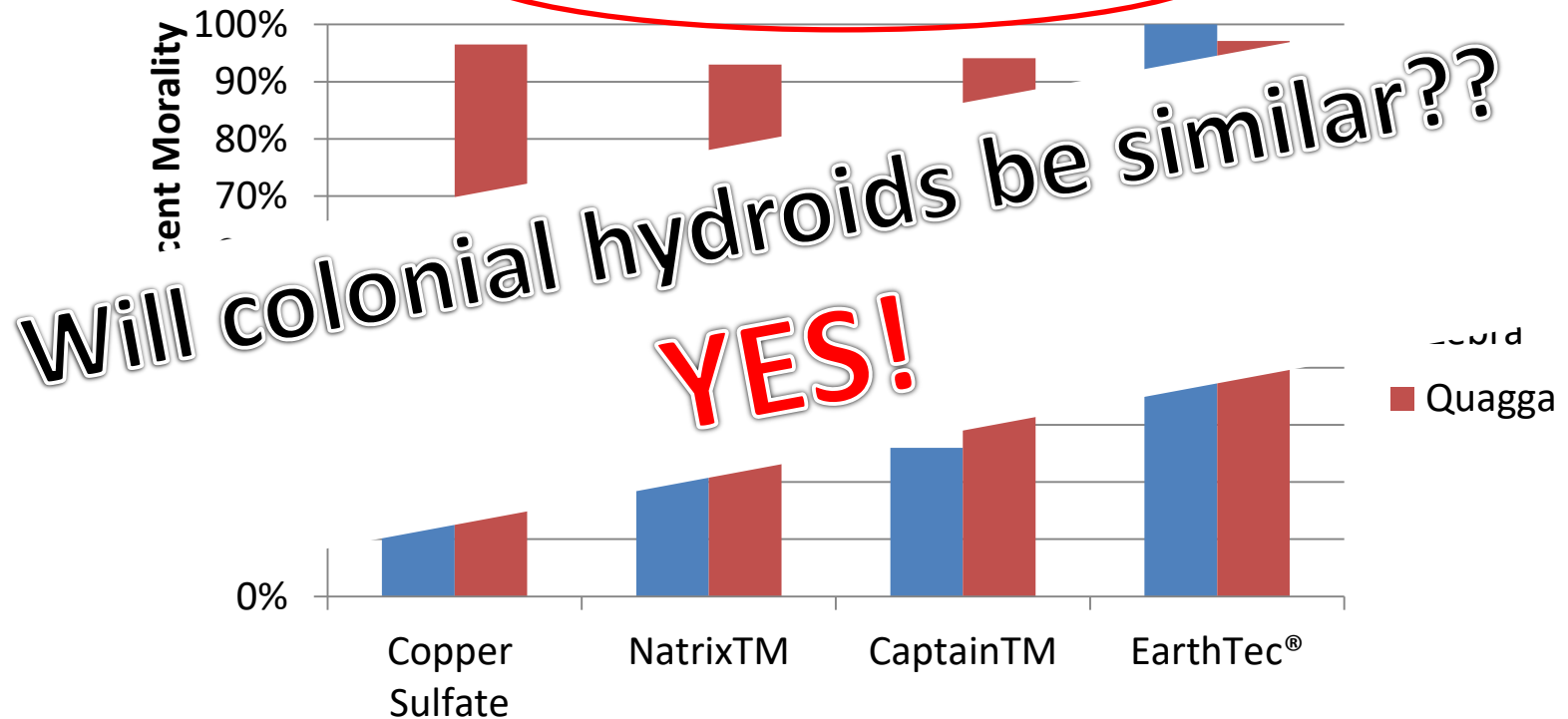
Cooler 6
(EarthTec QZ)

All three units are running in the desirable range, but Cooler 6 is the coolest

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.

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Conclusions

1. **The Foul-Release Coating** worked as advertised:
 - a. Biofouling does occur, but is readily removed with mechanical cleaning of the fouled surface
 - b. Lifespan of the coating material is still unknown
2. **EarthTec QZ** worked as hoped:
 - a. Quagga mussels did not colonize
 - b. Adult mussels introduced to the system were killed
 - c. Effective at unprecedentedly low concentrations, in the range of 0.75 ppm as product, equivalent to 45 ppb as copper
3. EarthTec QZ treated units operated at the **greatest efficiency**, although thus far all units are within acceptable range
4. **Preventing biofouling altogether is preferable** vs a coating of surface that gets biofouled but is easily cleaned

Pennsylvania WTP in Sept, 2016

Bryozoan or sponge infesting intake, prior to treatment at 0.5 ppm (= 30 ppb as copper)



Acknowledgements

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Renata Claudi
Kelly Stockton-Fiti

Thank you!

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