Low doses of EarthTec QZ ionic copper used in effort to eradicate quagga mussels from an entire Pennsylvania lake

David Hammond, PhD
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Gavin Ferris
Ecologist, SOLitude Lake Management

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SUSQUEHANNA RIVER BASIN COMMISSION
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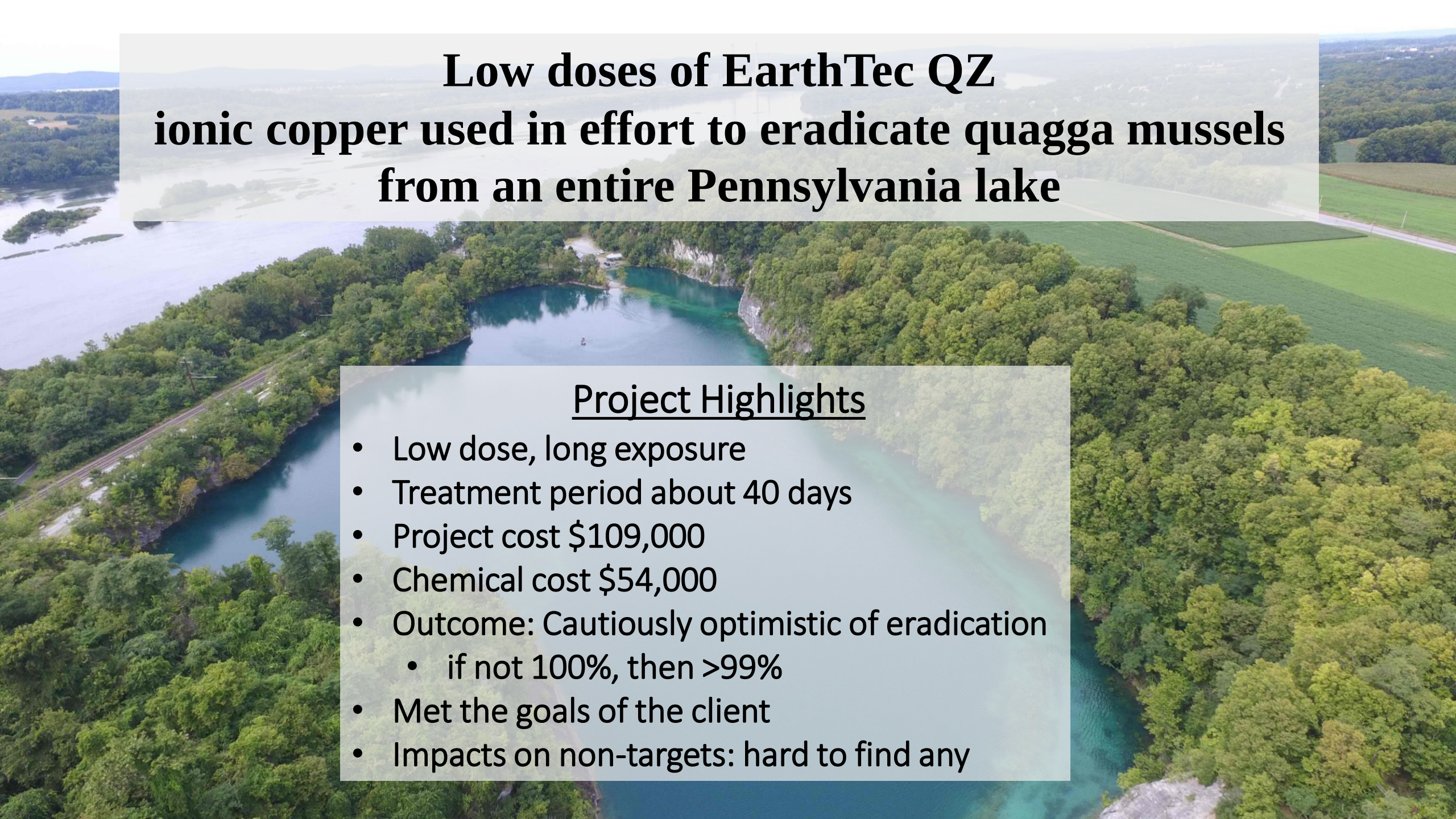
EARTHTEC QZ

SOLITUDE LAKE MANAGEMENT

Low doses of EarthTec QZ ionic copper used in effort to eradicate quagga mussels from an entire Pennsylvania lake



Project Highlights

- Low dose, long exposure
- Treatment period about 40 days
- Project cost $109,000
- Chemical cost $54,000
- Outcome: Cautiously optimistic of eradication
  - if not 100%, then >99%
- Met the goals of the client
- Impacts on non-targets: hard to find any


Erie
Allegheny
National Forest
Scranton
PENNSYLVANIA
Billmeyer Quarry
Pittsburgh
Hershey
Harrisburg
Lancaster
York
Allentown
New York
Philadelphia
Morgantown
MARYLAND
NEW JERSEY
86
88
81
79
84
80
476
380
99
76
95
195
68

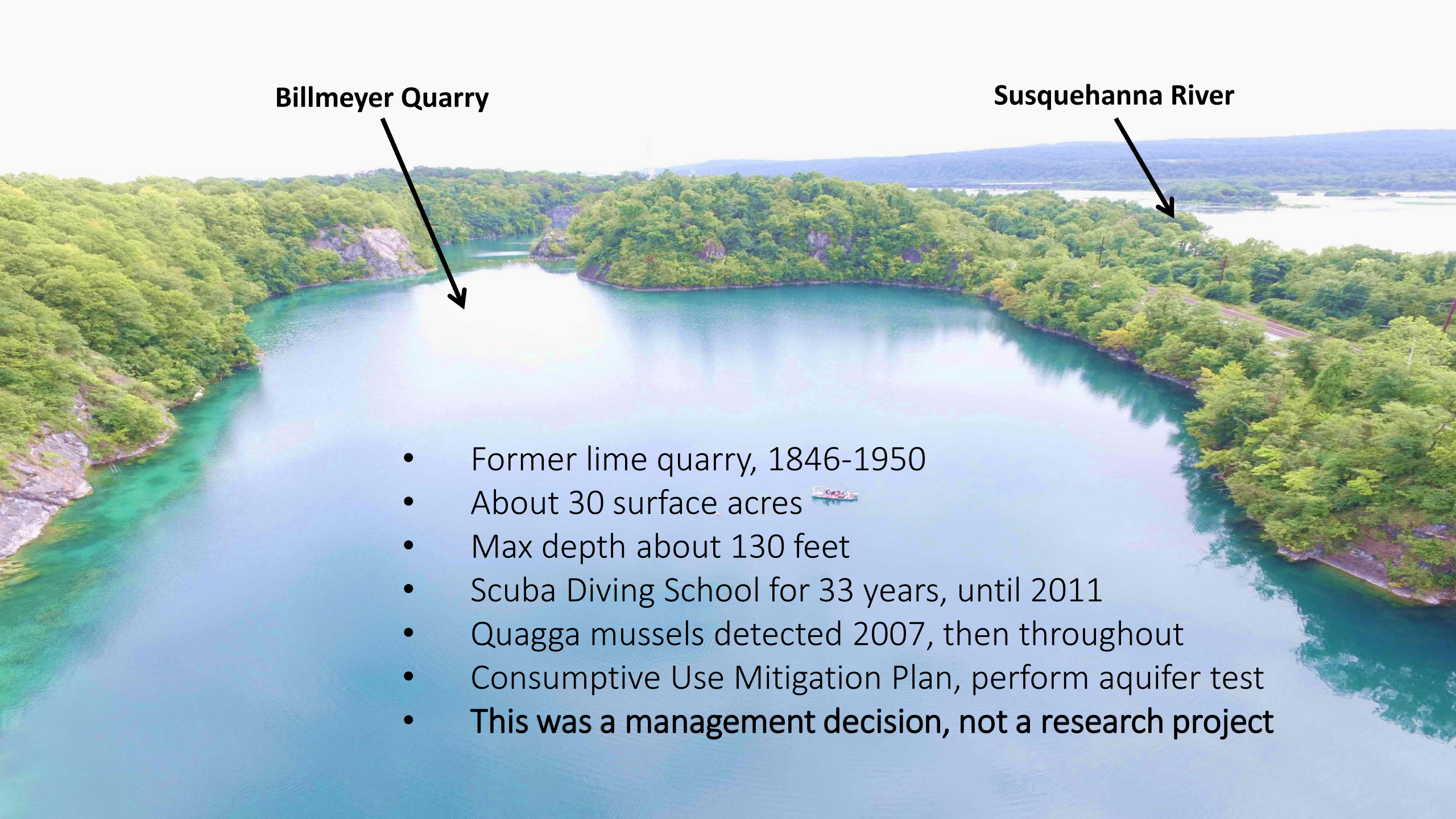
SRBC
SUSQUEHANNA RIVER BASIN COMMISSION
NY ▪ PA ▪ MD ▪ USA

RFP issued by Susquehanna River Basin Commission in April 2017

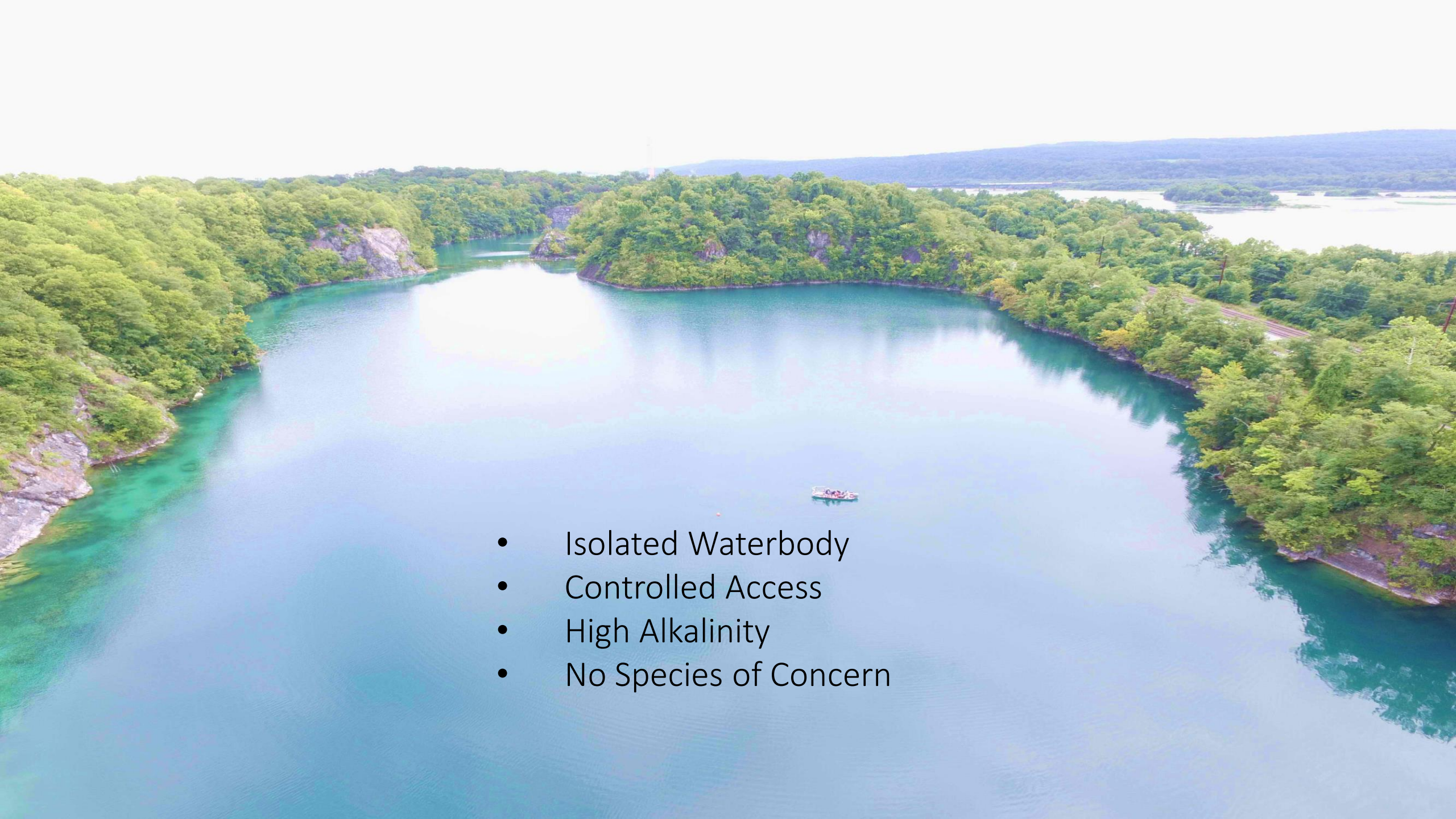
EarthTec QZ was awarded the contract June 2017
Treatment scheduled for Sept 2017

EARTHTEC and EARTHTEC QZ

- Acid-stabilized ionic copper
- 5% copper by weight
- EPA-labeled as molluscicide for Open Waters
- Approved in all states with dreissenids
- No special permits required for this Pennsylvania project



- Former lime quarry, 1846-1950
- About 30 surface acres
- Max depth about 130 feet
- Scuba Diving School for 33 years, until 2011
- Quagga mussels detected 2007, then throughout
- Consumptive Use Mitigation Plan, perform aquifer test
- **This was a management decision, not a research project**

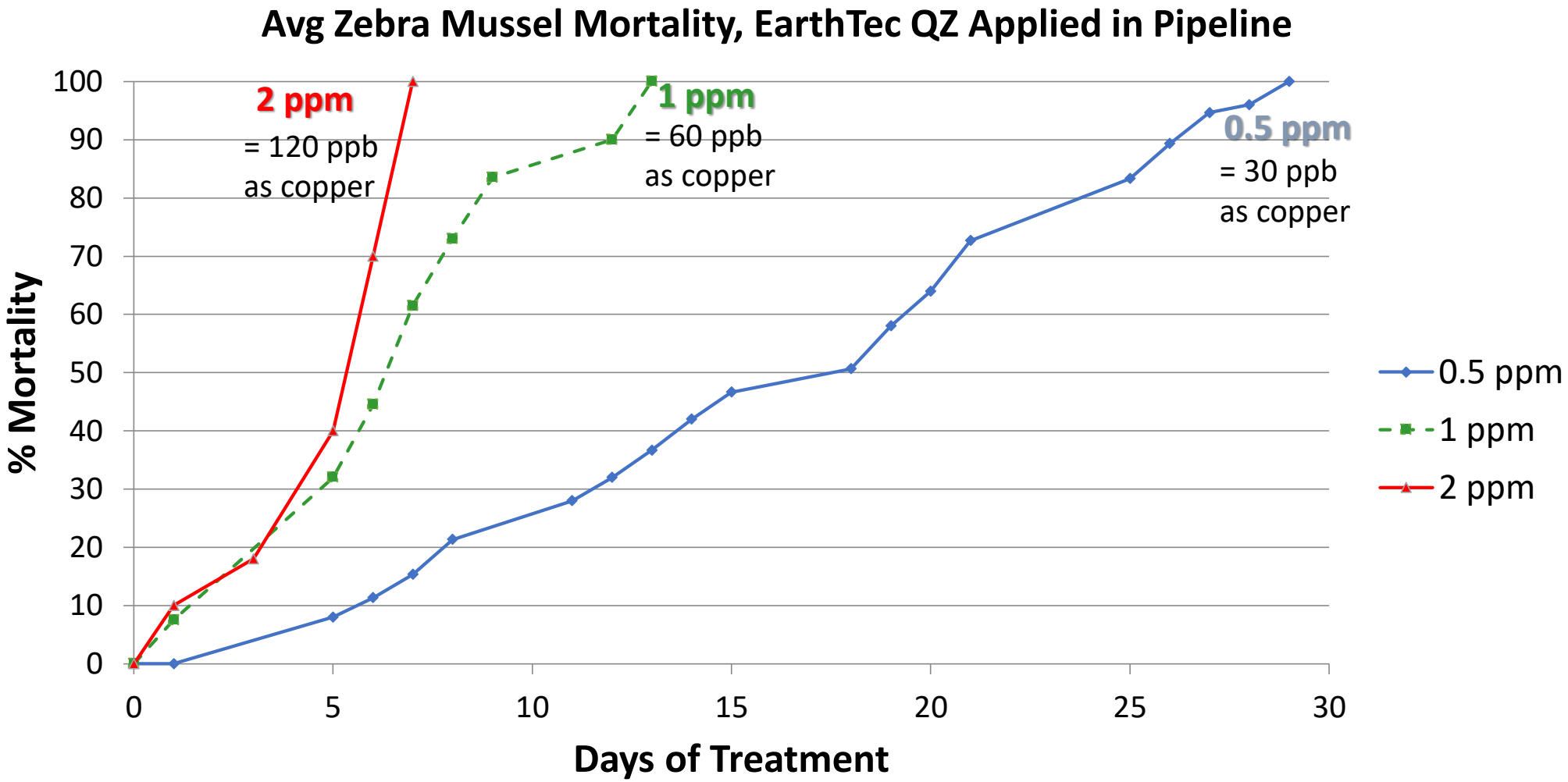


- Isolated Waterbody
- Controlled Access
- High Alkalinity
- No Species of Concern

Billmeyer Quarry Lake, Pennsylvania

Lots of Fish: bluegill, largemouth and smallmouth bass, channel catfish, gizzard shad, bullhead

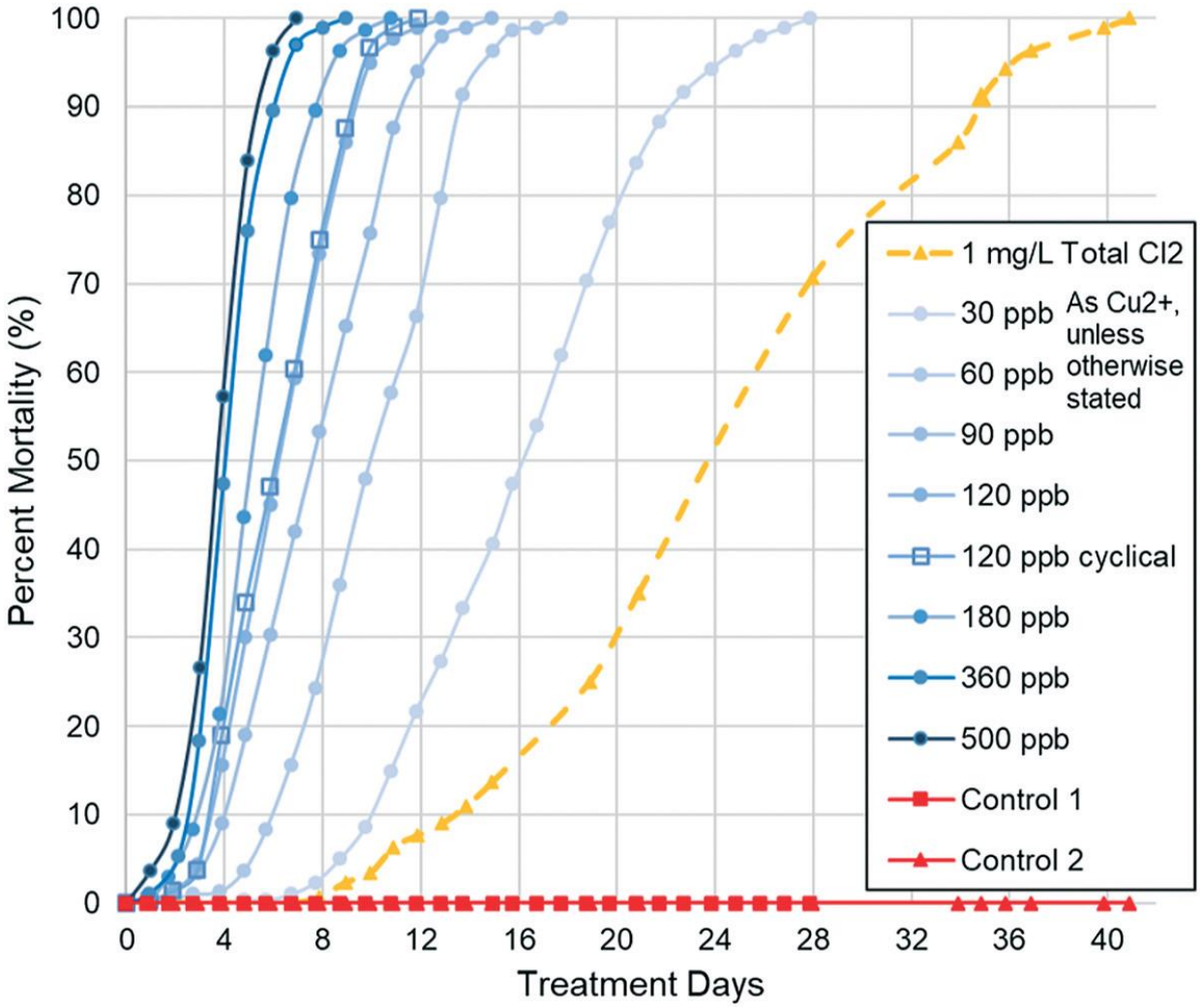
What dose? Strategy at Billmeyer Quarry: Low dose for a long exposure



100% mortality in 6 days at 120 ug/L, in 12 days at 60 ug/L, in 28 days at 30 ug/L
(EPA max = 1 mg/L = 1,000 ug/L)

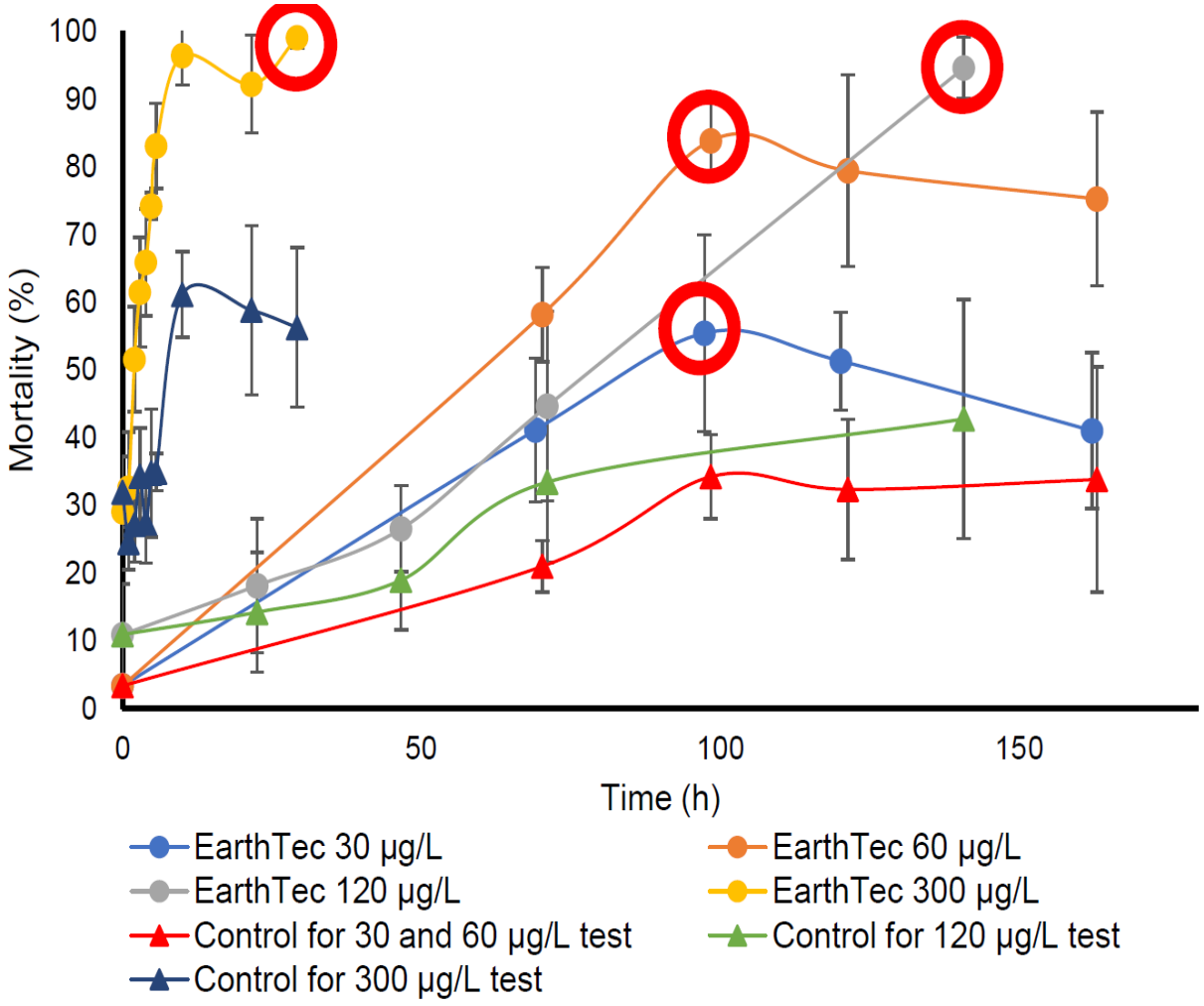
Dose-Mortality using EarthTec QZ

Adult mussels



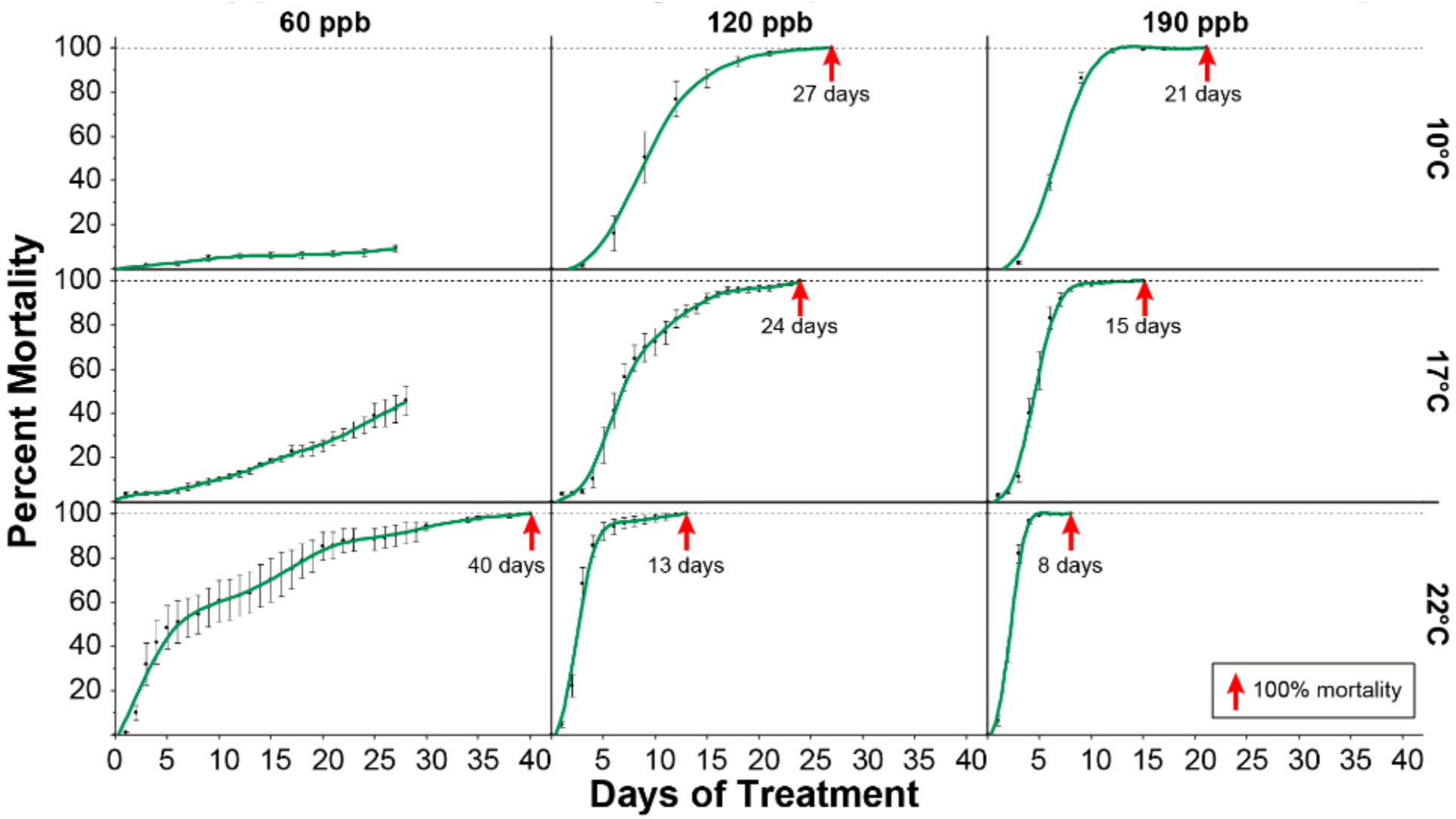
"Effectiveness of a copper based molluscicide for controlling: Dreissena adults", Ian Lake-Thompson and Ron Hofmann, February 2019, Environmental Science: Water Research & Technology 5(4). DOI: 10.1039/C8EW00890F

Veligers



"Zebra and Quagga Mussel Veliger Mortality After Continuous Exposure to EarthTec® QZ", Carlos Alonzo Moya and Ron Hofmann, April 2019, University of Toronto, in press.

Ionic Copper (EarthTec QZ formulation) in Lake Piru, CA water



Katherine Ayres, Renata Claudi, Tom Prescott, Michael Booth. "Temperature and Dose Response of Invasive Quagga Mussels to Various Molluscicides in High Conductivity Water", 2017.

Dose required for 100% mortality
Luoma et al, 2018

Temperature (°C)	EarthTec QZ, niclosamide, and KCl				Zequanox	
	Exposure duration (h)	EarthTec QZ (mg/L)	Niclosamide (mg/L)	KCl (mg/L)	Exposure duration (h)	Zequanox (mg/L)
7	24	NE	> 0.552	NE	8	NE
	96	> 58.8	> 0.189	NE	12	NE
	336	11.3	0.054	> 586	24	NE
12	24	> 150.4	0.182	NE	8	NE
	96	25.5	0.066	NE	12	NE
	336	4.5	0.053	165	24	NE
17	24	> 47.6	> 0.200[a]	> 2,071	8	NE
	96	9.5	0.100[a]	422	12	NE
	336	2.0	0.075[a]	147	24	> 323
22	24	> 49.6	0.181	> 3,066	8	NE
	96	21.5	0.137	220	12	> 315
	336	5.8	> 0.092	125	24	> 310

"Effects of temperature and exposure duration on four potential rapid-response tools for zebra mussel (Dreissena polymorpha) eradication"
James A. Luoma*, Todd J. Severson, Matthew T. Barbour and Jeremy K. Wise, 2018

Examples of Invasive Mussel Eradication or Control in Open Waters 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
6. 2018: Richland Chambers, TX

B. Full-lake eradications:

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

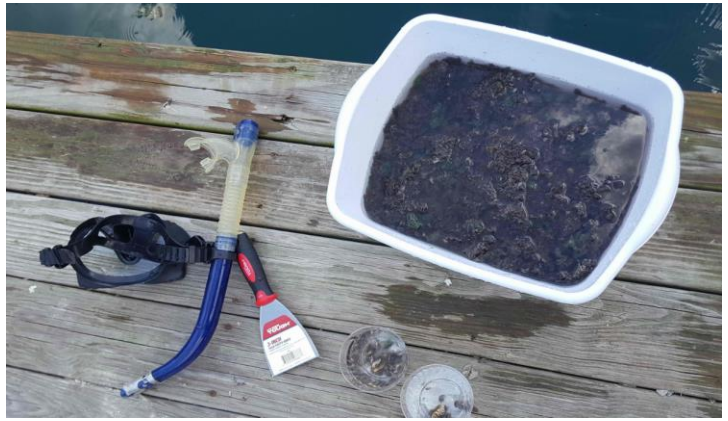
C. Fish Hatchery eradications and decontaminations:

9. 2016: Indiana
10. 2017: Oklahoma
11. 2017: South Dakota
12. 2019: Sedona, AZ

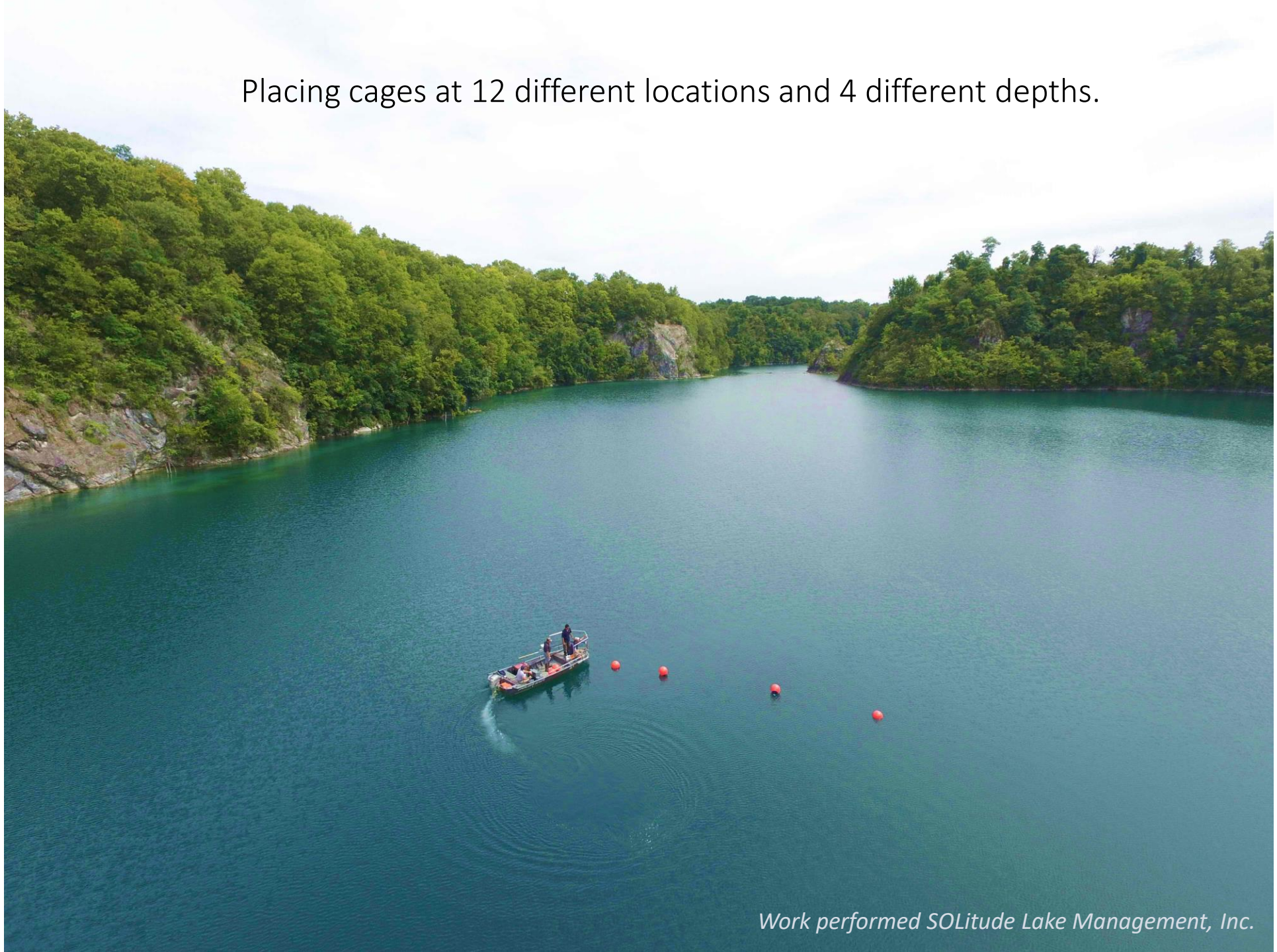
EARTHTEC QZ


Billmeyer Quarry
Susquehanna River
Google earth


Target dose 0.4 mg/L in the treatment area,
and 0.2 mg/L n the basis of the entire volume

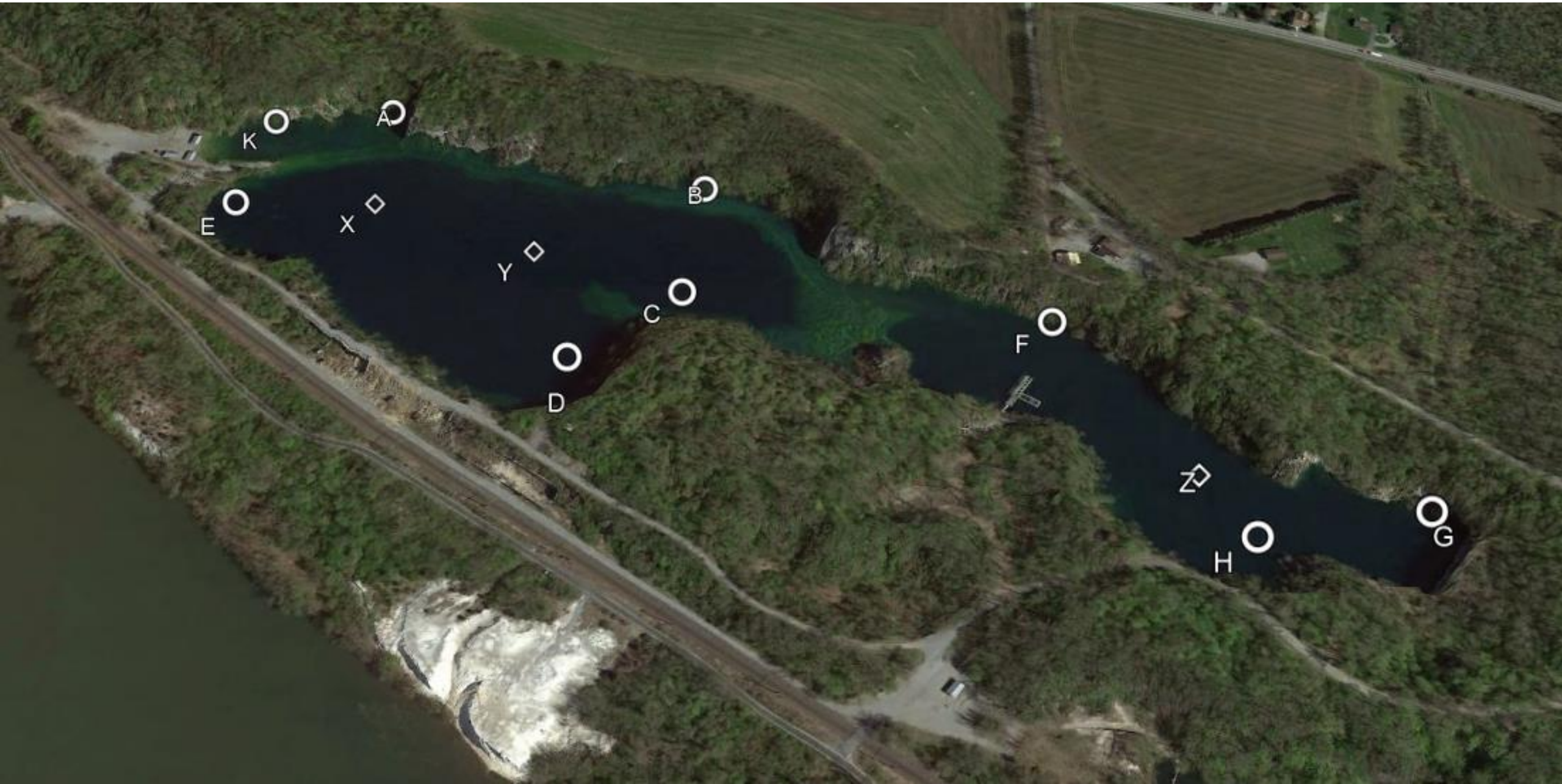


Placing cages at 12 different locations and 4 different depths.

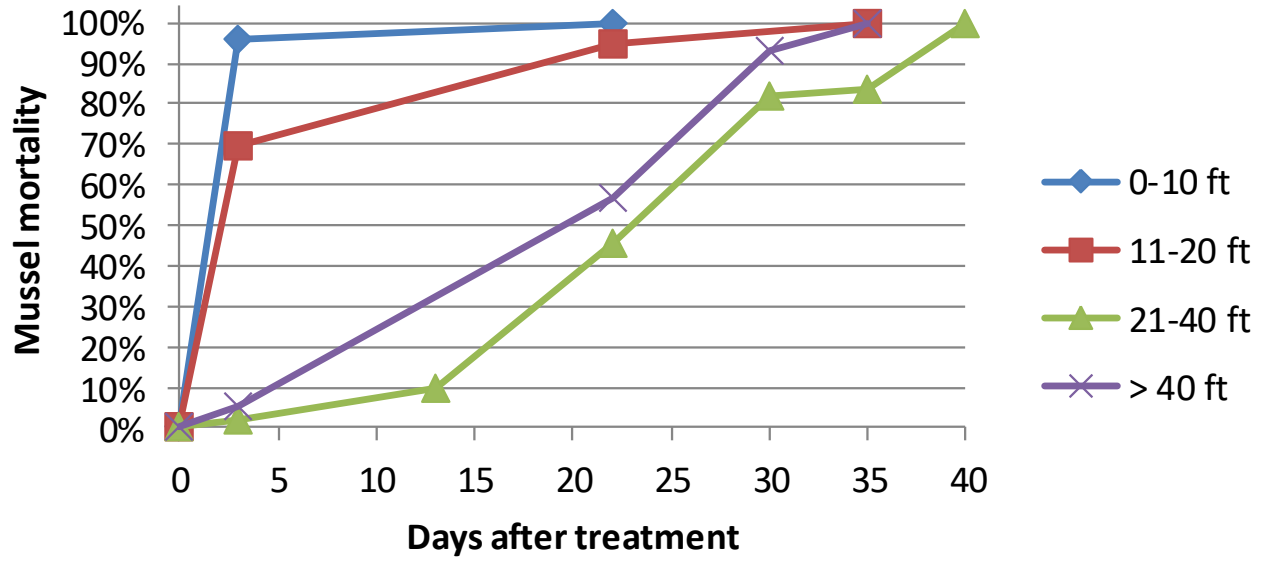


Work performed SOLitude Lake Management, Inc.

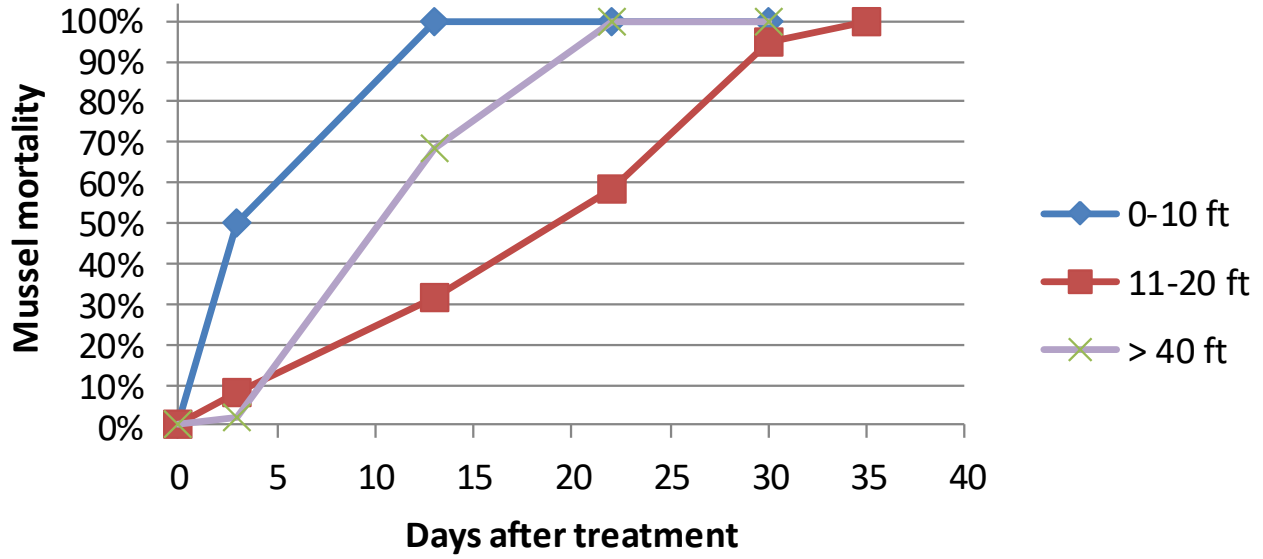
Cages were placed at 12 different locations and 4 different depths.

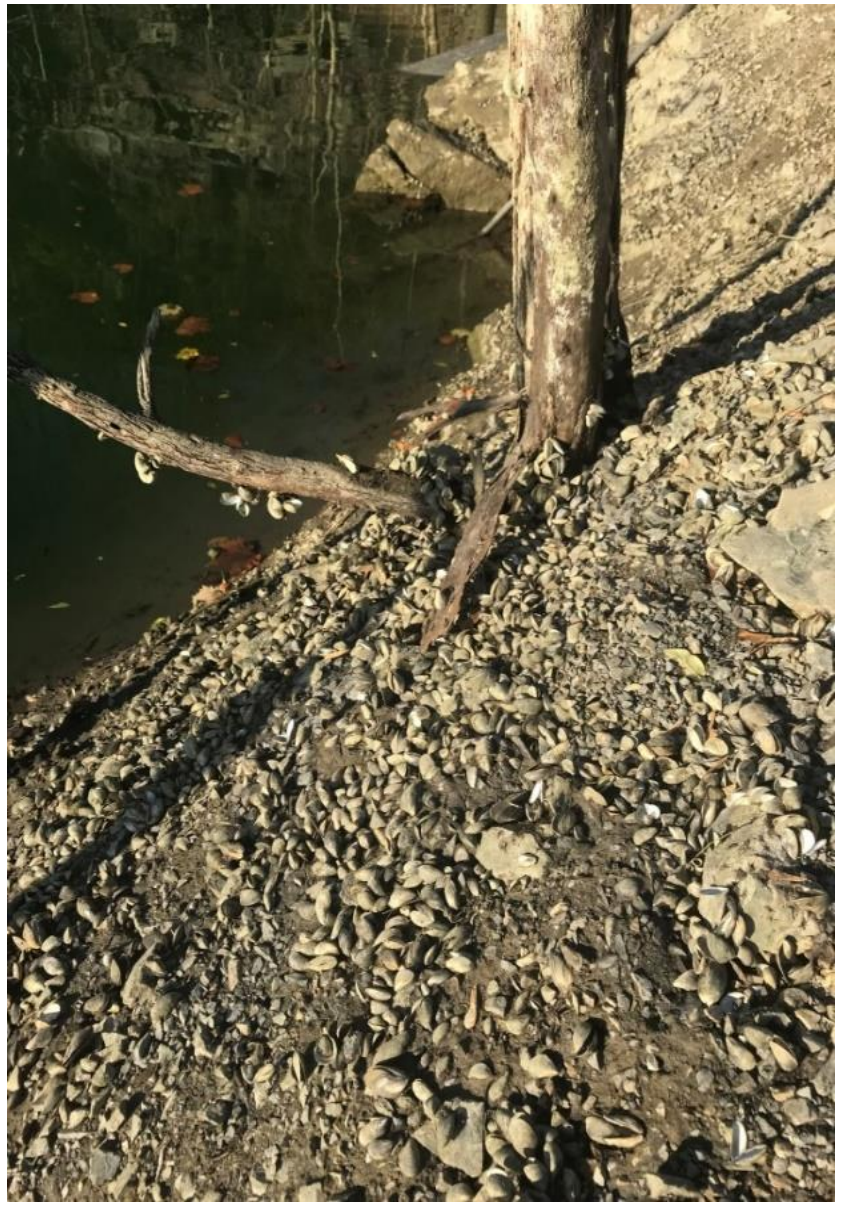


Mussel Mortality vs Depth (at periphery)



Mussel Mortality vs Depth (lake center)





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	30
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	$1,788
Cost per million gallons	$110

Work performed SOLitude Lake Management, Inc.

Monitoring Results 2017-2019

eDNA by qPCR:

- Early Dec, 2017: Trace eDNA detected, but not enough to qualify as a positive
- July 2018: No dreissenid eDNA detected
- Aug 27, 2019: Four eDNA samples, all negative for dreissenid mussel DNA

Plankton Tows and microscopy:

- July 2018: possible veliger shells detected in preserved sample collected by SRBC – dead or alive? Washed in by rain on rocks?
- Aug and Sept 2018: 2 further rounds of veliger tows found no dreissenids
- Aug 27, 2019: Four vertical plankton tows contained nothing resembling a mussel.

Monitoring will continue in 2019-2020.

Aug, 2019: Non-target Organisms in Plankton Tows at 2 years post-treatment:

Cladocerans >> Copepods >> Ostracods > Phantom midge larvae

Other Diptera, rotifers, chironomids, mayfly, caddisfly, coleoptera Ditistid diving beetle larvae.

Base of Food Web Still Intact

Work performed Normandeau and Associates, Inc.

Abundance of non-target zooplankton at 1 year post-treatment

Individuals per field of view:

Work performed Normandeau and Associates, Inc.

Abundance of non-target zooplankton at 1 year post-treatment

Individuals per liter:

	Site 1	Site 2	Site 3	Site 4
Cladocerans	25	17	16	15
Copepods	3	2	2	2
Ostracods	3	3	3	3

Individuals per 5-10 meter tow:

	Site 1	Site 2	Site 3	Site 4
Cladocerans	72,491	69,287	64,080	66,964
Copepods	9,612	9,212	9,612	11,214
Ostracods	8,330	10,894	12,816	15,059
Nauplei	6,408			

Work performed Normandeau and Associates, Inc.

Non-Target Impacts

- Negligible impact on fish population
  - Abundant fish observed before, during, and post treatment.
- 4 clam veligers observed in 2018 samples
- Abundant macroinvertebrate life observed in 2018 and 2019 samples

Management in Practice

Low doses of EarthTec QZ ionic copper used in effort to eradicate quagga mussels from an entire Pennsylvania lake

David Hammond[1,*] and Gavin Ferris[2]

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[2]*SOLitude Lake Management, Inc., PO Box 969, Virginia Beach, Virginia 23451, USA*

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**Corresponding author*

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Published: xx xxxxx 2019

Abstract

A liquid formulation of acid-stabilized ionic copper called EarthTec QZ was used in an effort to eradicate invasive quagga mussels (*Dreissena rostriformis bugensis*) from an entire 12-hectare lake in Pennsylvania in fall of 2017. The treatment consisted of three separate applications of ionic copper delivered over a period of 37 days with the intent to minimize likelihood of spreading invasive mussels during a one-time water transfer event planned for later that year, from the treated lake to an adjacent

EarthTec QZ used to successfully eradicate invasive Chinese Pond Mussel from sole known U.S. infestation.

San Francisco Chronicle

US & WORLD // NATION

Giant invasive mussel species eradicated from New Jersey ponds

By Wayne Parry | Nov. 29, 2019

EarthTec QZ also used to eradicate New Zealand mud snail from a brown trout hatchery in Arizona and parasitic fluke in Mississippi catfish farms

EarthTec QZ being used in 2019 to eradicate New Zealand mud snail from a brown trout hatchery in Arizona

EarthTec QZ scenario for Eradicating Quaggas from San Justo Reservoir

EarthTec QZ estimate	Existing Water	Mid Water	Low Water
ac-ft in San Justo	7,445	5,059	1,055
mg/L as copper	1.2	1.2	1.2
gals QZ required	48,541	32,985	6,879
Truckloads	**10.8**	**7.3**	**1.5**
Est. chem cost using QZ	**$583,000**	**$396,000**	**$82,000**
Est. applied cost, EarthTec QZ	**$783,000**	**$516,000**	**$156,000**

Conservative estimate, allowing for almost 3x the concentration applied to Billmeyer Quarry

40% smaller than Billmeyer Quarry

Comparison of Options for Eradicating Quaggas from San Justo Reservoir: ionic copper vs potash

RECLAMATION
Managing Water in the West

Draft FINDING OF NO SIGNIFICANT IMPACT

Zebra Mussel Eradication Project for San Justo Reservoir, Hollister Conduit, and San Benito County Water Distribution System

EarthTec QZ estimate	Existing Water	Mid Water	Low Water
ac-ft in San Justo	7,445	5,059	1,055
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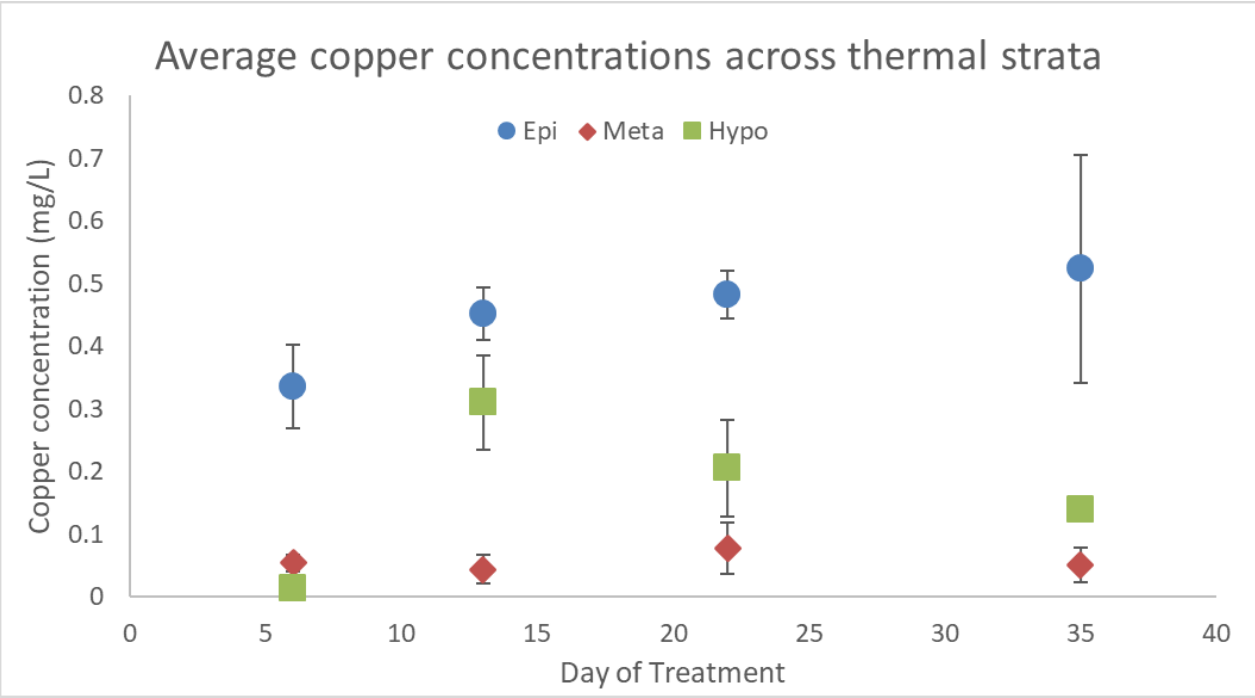
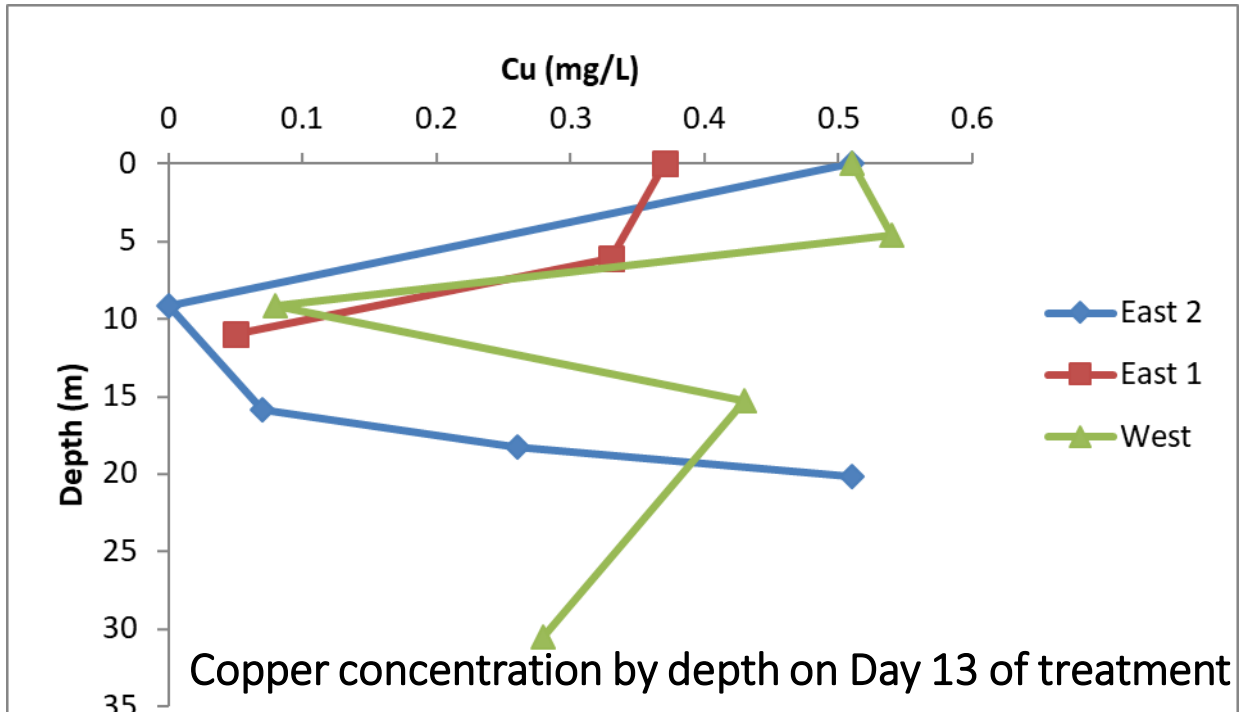
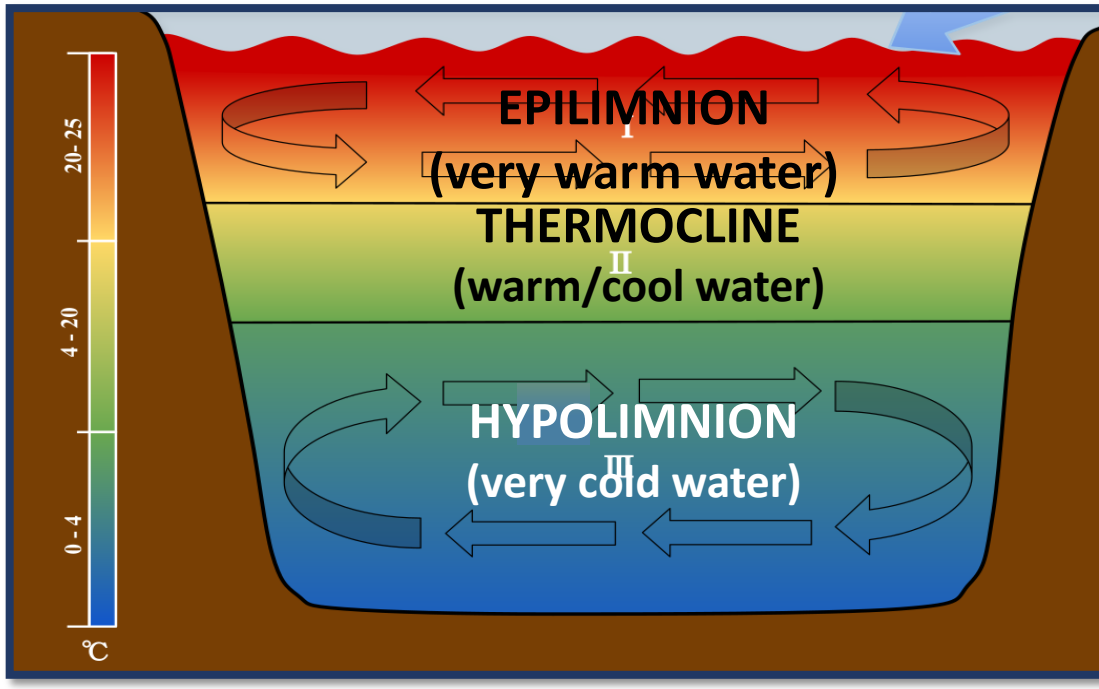
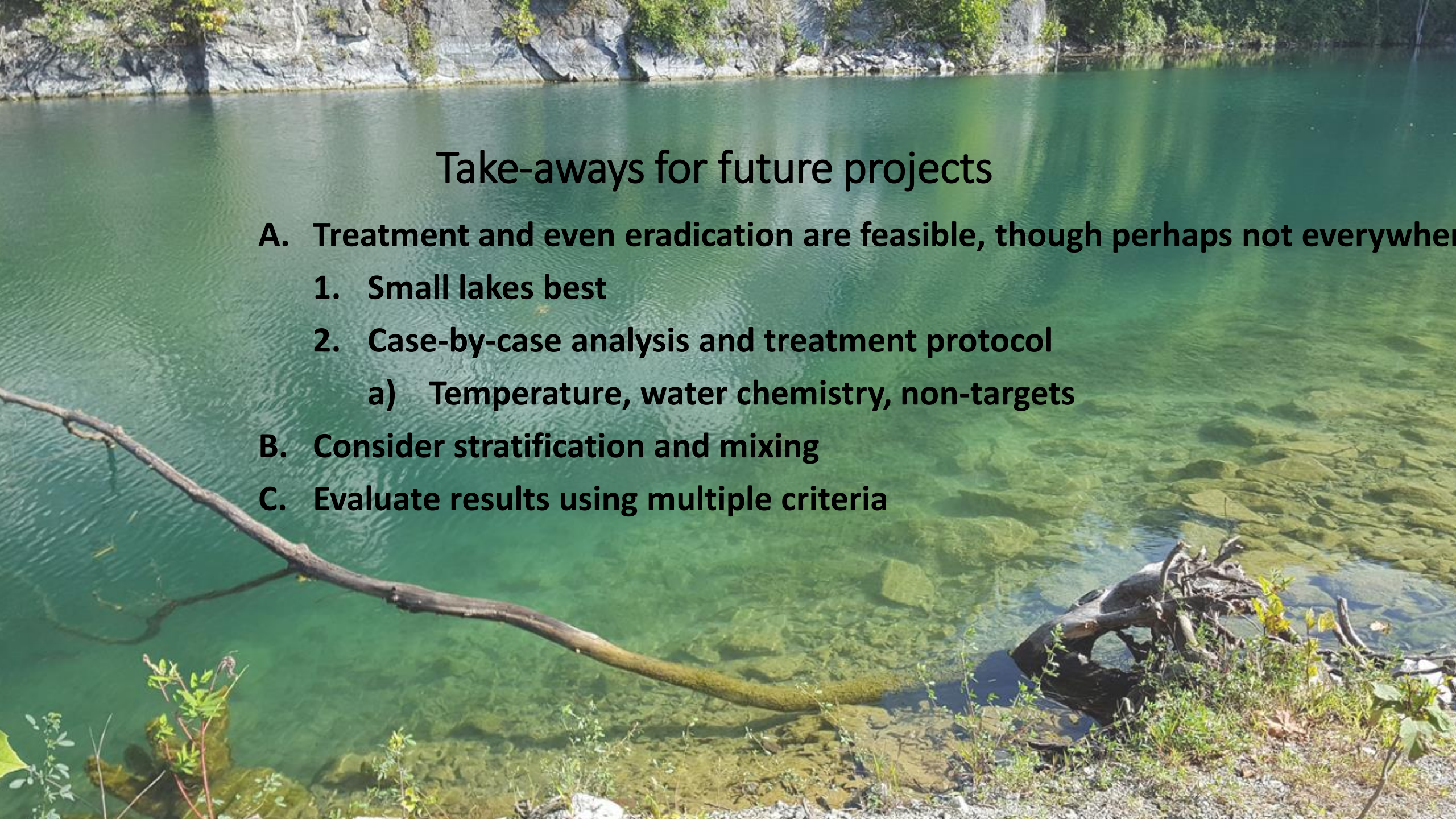
Potash per Bureau of Rec	Existing Water	Mid Water	Low Water
ac-ft in San Justo	7,443	2,638	525
mg/L, dose as potassium	100	100	100
gals potash slurry	1,866,000	661,361	131,620
Truckloads	**374**	**133**	**27**
Est. chem cost using potash	**$2,220,000**	**$787,000**	**$157,000**
Est. applied cost, potash	**$5,611,000**	**$1,989,000**	**$396,000**
Cost of QZ vs Potash	14%	26%	39%





Copper concentration by depth on Day 13 of treatment





Take-aways for future projects

A. **Treatment and even eradication are feasible, though perhaps not everywher**
   1. **Small lakes best**
   2. **Case-by-case analysis and treatment protocol**
      a) **Temperature, water chemistry, non-targets**
B. **Consider stratification and mixing**
C. **Evaluate results using multiple criteria**

Thank you!

David Hammond, PhD
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Appendix

Decontamination of Zebra Mussels from Oklahoma state fish hatchery

Decontamination of Zebra Mussels from Oklahoma state fish hatchery

Side benefits: Improved yields, healthier fish

Decontamination of Zebra Mussels from Oklahoma state fish hatchery

Side benefits: Improved yields, healthier fish

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

4-Day Toxicity of EarthTec to Rainbow Trout (*Oncorhynchus mykiss*)

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

21-Day Toxicity of EarthTec to Rainbow Trout (*Oncorhynchus mykiss*)

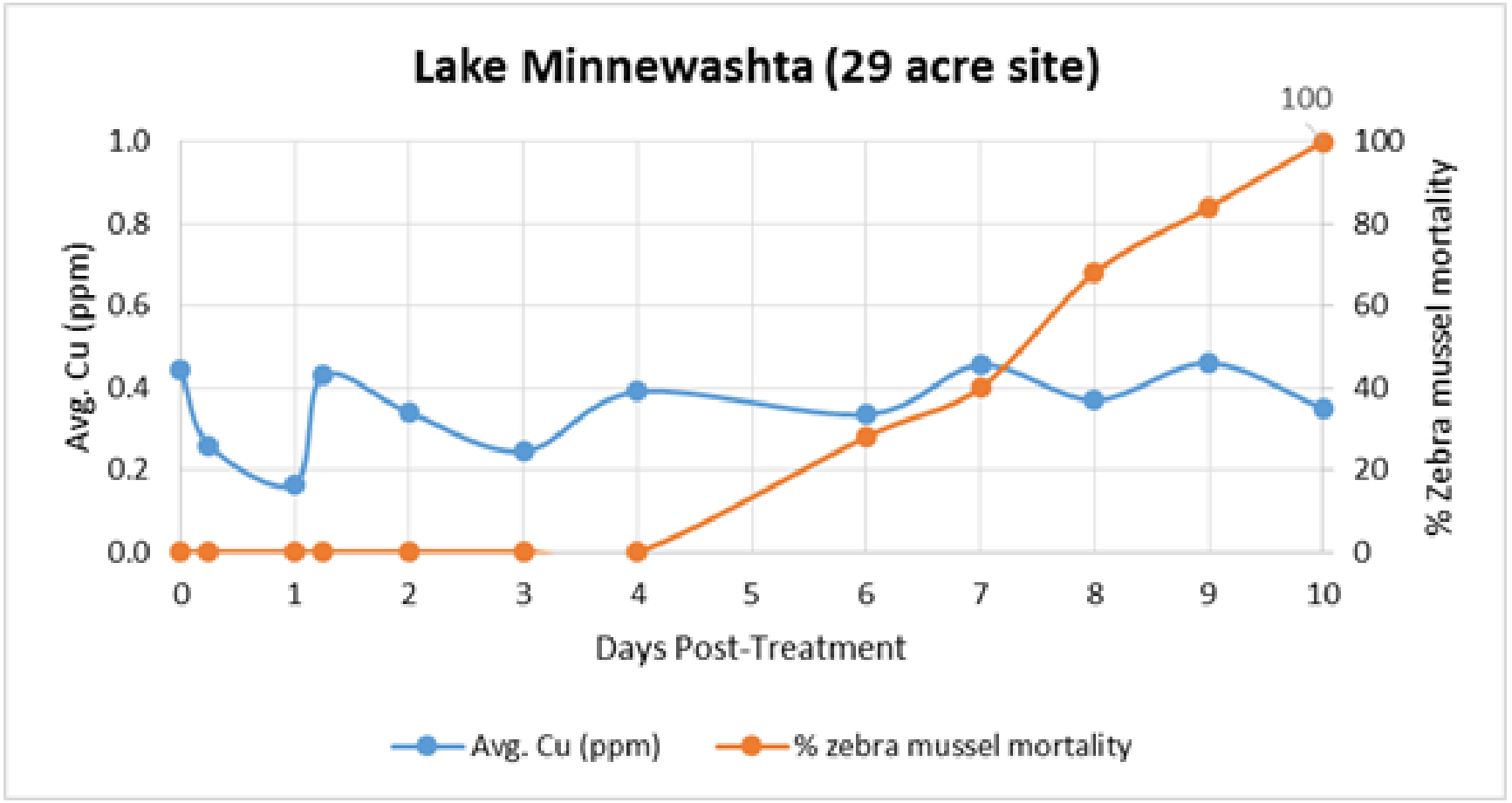
Measured Effect	µL/L, as EarthTec	ppm, as copper	ppb, as copper
NOEC	4.000	0.240	240
LC25	4.530	0.272	272
LC50	4.840	0.290	290

Both tests performed by Aquatic Bioassay & Consulting, Inc., Ventura, CA
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 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

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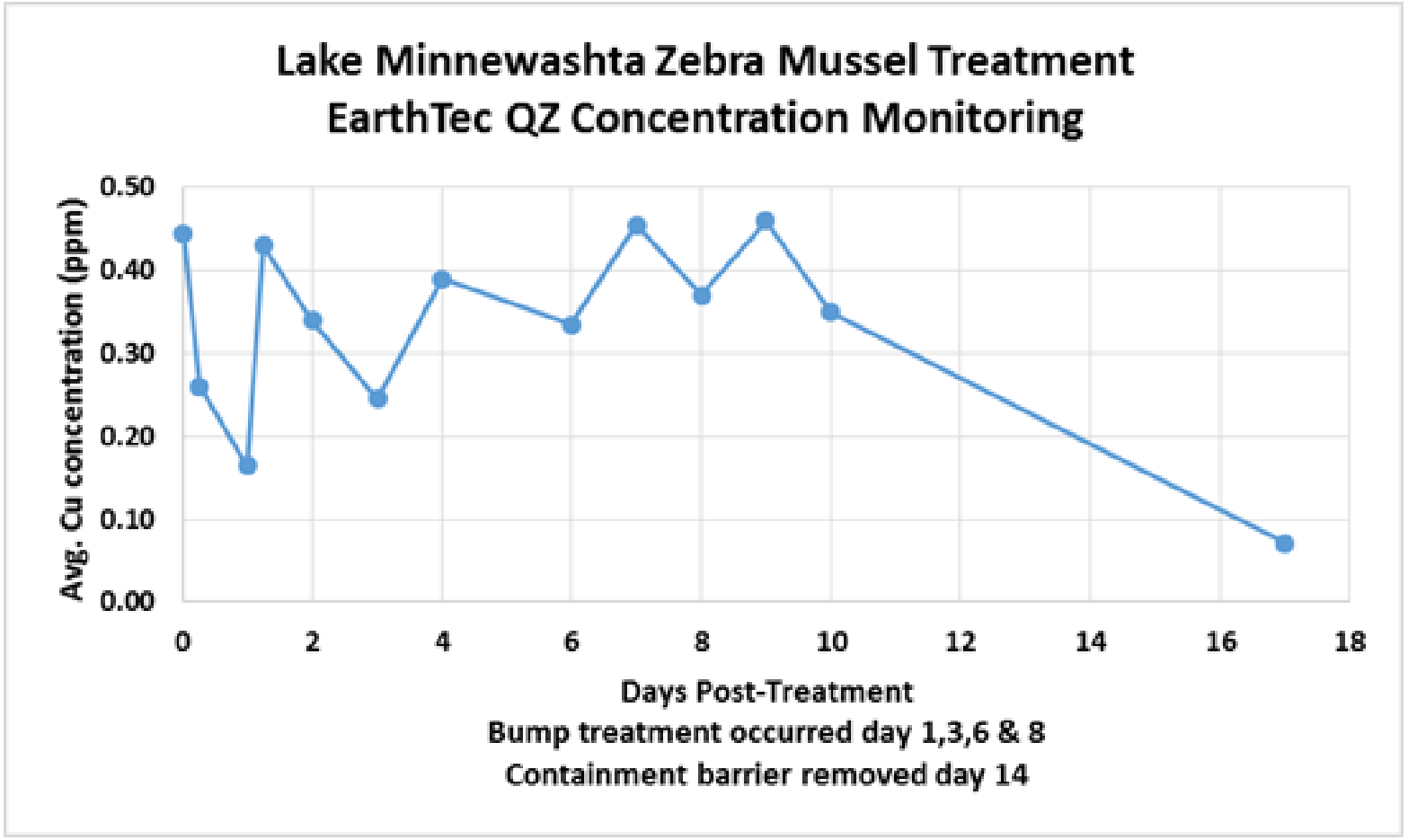

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Current Biology

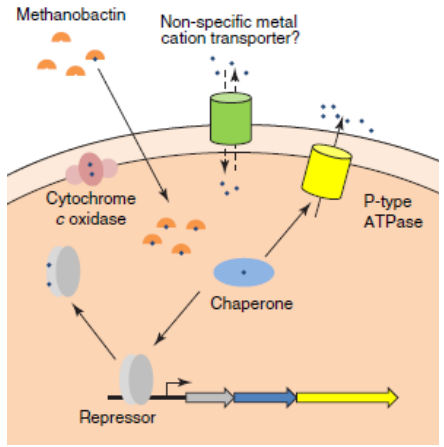
2011, Vol 21, Issue 21
Department of Pharmacology and Cancer Biology, Duke University School of Medicine,

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



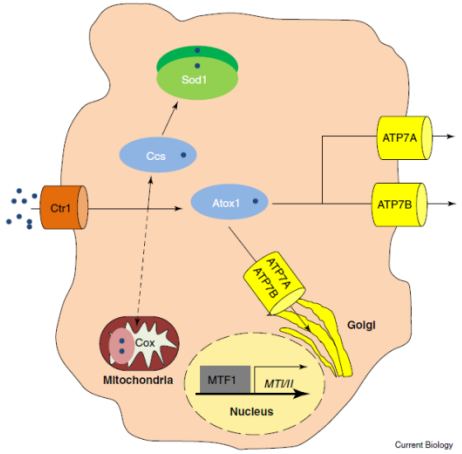


Table 1. Examples of Cu-dependent proteins and Cu homeostasis proteins.

Protein	Function	Bacteria	Fungi	Animals	Plants
Transcriptional regulators					
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
Chaperones/storage					
Atox1	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
Cell surface/secretory compartment transporters and receptors					
P1B-type ATPases	Cu^{+}-exporting proteins	X	X	X	X
Ctr	Cu^{+}-importing proteins		X	X	X
Ethylene receptor	Uses Cu as a cofactor for ethylene signaling				X
Oxidoreductases					
Ascorbate oxidase	Reduction of L-ascorbate			X	
Dopamine-monooxygenase	Tyrosine metabolism			X	
Galactose oxidase	Reduction of galactose		X		
Amine oxidase	Oxidation of diamines	X	X	X	X
Electron transfer/energy production/blue Cu proteins					
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			
Free radical scavenging					
Cu/Zn SOD	Free radical scavenging	X	X	X	X
Oxidase					
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
Monooxygenase					
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

Current Biology

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

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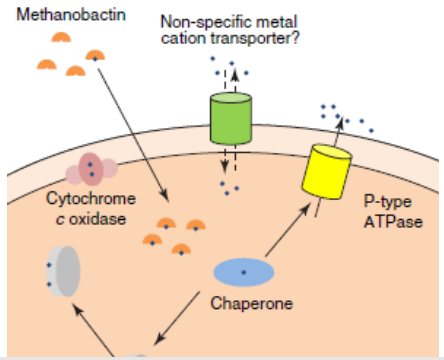
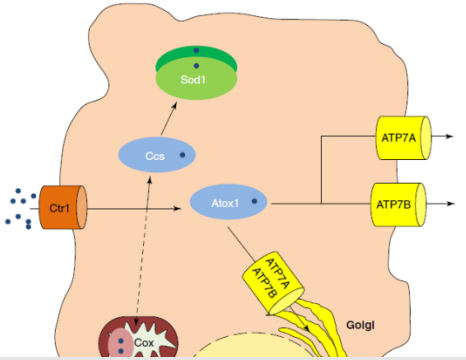




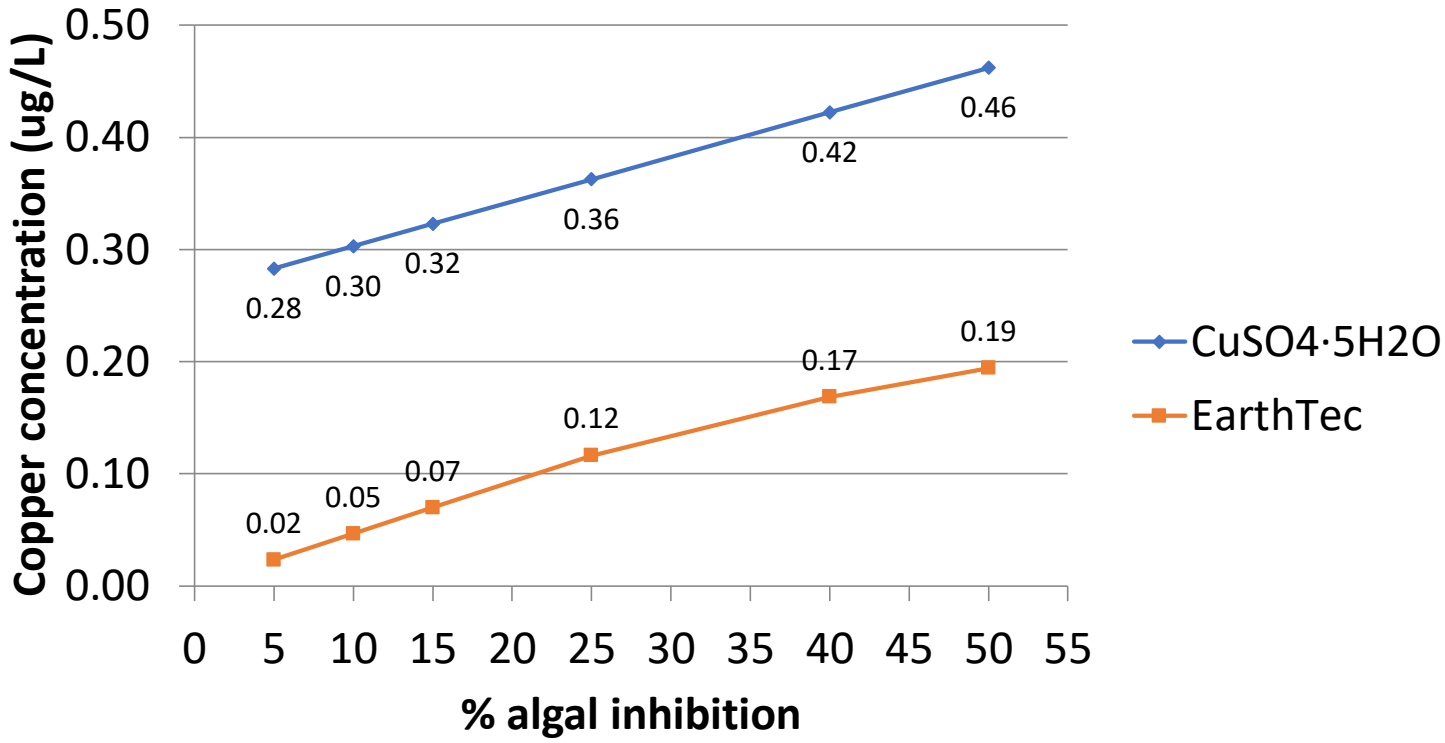
Copper is an essential micronutrient across all kingdoms and phyla, and participates in:

- 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
Monooxygenase					
Methane monooxygenase	Oxidizes C–H bond in methane	X			
Phenylalanine hydrolase	Hydroxylation of the aromatic side chain of phenyl-alanine to generate tyrosine			X	
Tyrosinase	Monophenol monooxygenase, catalyzes the oxidation of phenols, melanin synthesis	X	X	X	X

Copper Sulfate vs EarthTec

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

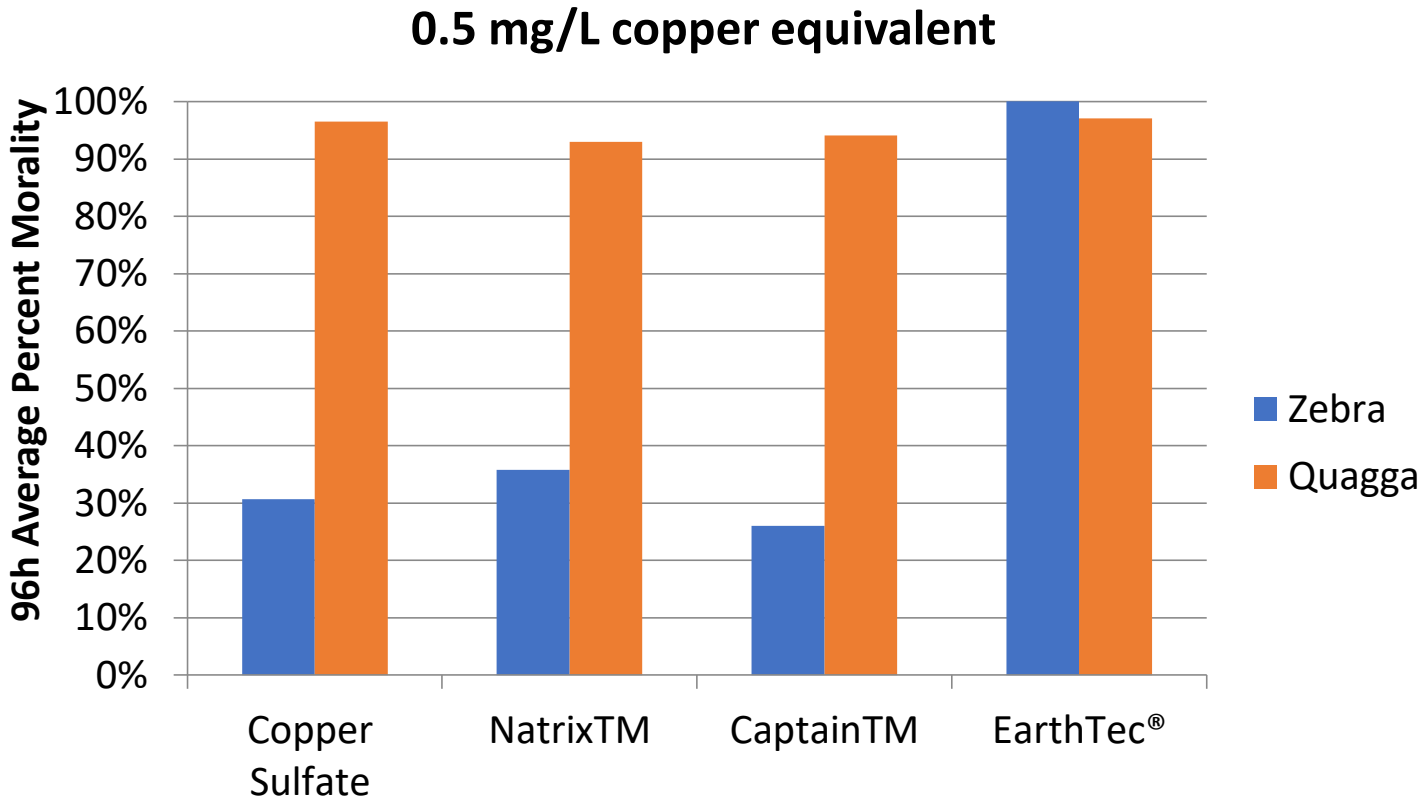


The copper dose required to achieve a given % inhibition of algae is much lower if applied as EarthTec than if applied as copper sulfate

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



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.

Comparison of Scenarios for Millbrook Quarry, VA: potash vs ionic copper

	Millbrook (potash)	Billmeyer (ionic copper)	unit	factor
Area:	12	30	acres	2.5
Volume:	180	485	million gallons	2.7
Cost:	$365,069	$109,400	contract total	30%
Cost/vol:	$2,028	$226	project cost per million gallons	11%
Chemical:	174,000	3,545	gallons of product	49.1

Several tanker trucks per day for 3 weeks