Combatting toxic cyanobacteria

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Great Lakes Moment: Harmful algal blooms negatively impact the Lake Erie economy

Many people are aware of the environmental and health impacts of toxic algae, but harmful algal blooms have an impact on the economy as well.

The cyanobacterial bloom on Lake Erie has grown 20 miles in the past week. It now covers 620 square miles of Lake Erie, taking up about 6 percent of the entire lake and covering more area than Detroit and its suburbs.

Hugh McDiarmid is with the Michigan Department of Environment, Great Lakes, and Energy. He says summer is the peak time for these blooms.

"The warm water in the heat of summer has a lot to do with it. The amount of nutrients the algae has to feed off of is greater in the summer when there's more activity in the lake. And calm conditions also tend to make the conditions right for the blooms."

The open water swim across the Ohio River was canceled due to a blue-green algae bloom, which can produce harmful levels of toxins.
Harmful algal blooms showing up in northern Michigan lakes

Algae bloom raises concern for Hillsdale Co. lake

The Lake Leann Homeowners Association in Hillsdale County recently raised concerns about a white foam and a blueish green sheen on the lake.
Anthropogenic Acceleration

• Environmental Changes
  – Atmospheric CO₂ passed 400ppm (NOAA)
  – UV light increases
  – Salinity increases
  – Global temperature increasing (Miller 2002)
  – Stratification
  – Water use dynamics

• Ecosystem degradation
  – Invasive species proliferation
  – Rough fish dominance
  – Eutrophication accelerated by 100’s to 1000’s of years (Anderson et al. 2002)
Water Supply

- Liver cancer
  - 0.19 pg mcyn per day during 4 summer months
  - Ueno et al. 1996

“A study that analyzed data from Florida determined that there is a significantly higher risk of liver cancer in residents serviced by surface water treatment plants that experience cyanobacterial blooms than those in areas serviced by groundwater.”

Doctors warn of potential airborne toxins from algae & red tide

Lee Health just released brand new numbers regarding how many patients they are seeing for algae-related health concerns.

Even in areas where blue-green algae isn’t easy to see, signs are still posted warning to stay out of the water due to cyanobacteria.

Now, some doctors are saying you should stay away from the air as well.

Microsystins and cyanobacteria could be causing major health problems for those exposed.

Air Supply

- Banack et al. 2015
- Backer et al. 2010
- Wood and Dietrich 2011
- Cheng et al. 2007
- Stommel et al. 2013

Algae crisis: Airborne particles of toxic cyanobacteria can travel more than a mile inland, new FGCU study shows
Cyanobacterial Blooms and the Occurrence of the neurotoxin beta-N-methylamino-L-alanine (BMAA) in South Florida Aquatic Food Webs

Larry E. Brand¹,*, John Pablo², Angela Compton¹, Neil Hammerschlag¹, and Deborah C. Mash²

With toxic blue-green algae bloom, don't eat Lake Okeechobee fish, Audubon biologist says
Potential exposure routes to CHAB toxins

- Terrestrial transfer
- Irrigated crop accumulation
- Recreation
- Drinking water contamination
- Fish accumulation
- Aerosolization
- Seafood accumulation
- Freshwater Lakes and Reservoirs
- Estuary
- Ocean

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Who is impacted?

• Dogs

• Cows
  – Kerr 1987; Mez et al. 1997; Loda et al. 1999

• Pigs, ducks
  – Cook et al. 1989

• Sheep
  – Carbis et al. 1995
Toxic algae kills 4 dogs in North Carolina, Georgia lakes. How to keep your pets safe

BY CHARLES DUNCAN

AUGUST 12, 2019 11:07 AM, UPDATED AUGUST 12, 2019 10:13 PM
Alzheimer's 'cause' discovered: Poisonous algae found in UK freshwater lakes and reservoirs could be fuelling dementia epidemic afflicting one million people

- It is the first direct evidence that a chemical, produced by algae, might be linked to devastating brain conditions
- Scientists have discovered the toxin in seafood and plants, through which it is feared it is entering the food chain
- Researchers highlighted a growing body of evidence that the toxin, named BMAA, could trigger brain diseases
- If confirmed, the chemical would be the first major environmental factor linked to increasing rates of Alzheimer’s
Toxins

• Cyanobacteria Toxins
  • Hepatotoxins “liver”
  • Neurotoxins “brain”
  • LPS “stomach”
  • Aplysiatoxins “skin”

• EPA CCL (USEPA 2012)
  – microcystin-LR, anatoxin-a, and cylindrospermopsin

• EPA Health Advisory Drinking Water
  – < 6 years old; 10 day exposure
    • 0.3 ug/L microcystins and
    • 0.7 ug/L cylindrospermopsin (USEPA 2015a,b)
    • Recreational guidelines 8ppb; 15ppb
Are we safe if no toxin detected?

• Toxin production is intermittent

• Shown to be toxic but no toxin has been isolated and characterized
  • Coelosphaerium, Cylindrospermopsis, Fischerella, Gloeotrichia, Gomphosphaeria, Hapalosiphon, Microcoleus, Schizothrix, Scytonema, Spirulina, Symploca, Tolypothrix, Trichodesmium (Scott 1991; Skulberg et al. 1992b)

• New toxin classes
EPA Summary Guidelines

- **Measurement parameters**
  - Cell densities, proportion of toxigenic cyanobacteria, chlorophyll concentration, and Secchi disk depth measurement
  - State guidelines address up to four cyanotoxins, Mcyn most prevalent (n=20)

**Routes of exposure.** Exposure to cyanotoxins from recreational water sources can occur via oral exposure (incidental ingestion while recreating); dermal exposure (contact of exposed parts of the body with water containing cyanotoxins during recreational activities such as swimming, wading, surfing); and inhalation exposure to contaminated aerosols (**while recreating**).
Recommended Action

• Recreation
  – Close system, issue advisory, post warning signs, contact health department

  – Utah
    • Consider closure

  – Nebraska
    • Close beach, allow recreation
      – But public advised to use caution and avoid prolonged exposure to the water

  – Maine
    • Do not drink lake water during a bloom. Well maintained domestic water treatment systems may make lake water safe to drink in many instances, but they are not guaranteed to remove algal toxins.
One State

• Kansas
  – Extreme bloom
  – Picnic, camping and other public land activities adjacent to affected waters be closed

<table>
<thead>
<tr>
<th>Kansas</th>
<th>cyanobacteria: ≥ 10,000,000 cells/mL</th>
<th>recommended that all in-lake recreation cease and that picnic, camping and other public land activities adjacent to affected waters be closed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cyanobacteria: ≥ 250,000 cells/mL</td>
<td>issue public health warning</td>
</tr>
<tr>
<td></td>
<td>cyanobacteria: ≥ 80,000 and &lt; 250,000 cells/mL</td>
<td>issue public health watch</td>
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<tr>
<td></td>
<td>microcystin: ≥ 2,000 μg/L</td>
<td>recommended that all in-lake recreation cease and that picnic, camping and other public land activities adjacent to affected waters be closed</td>
</tr>
<tr>
<td></td>
<td>microcystin: ≥ 20 μg/L</td>
<td>issue public health warning</td>
</tr>
<tr>
<td></td>
<td>microcystin: ≥ 4 and &lt; 20 μg/L</td>
<td>issue public health watch</td>
</tr>
</tbody>
</table>
Close the lake

Close the system, **Hope** there is no exposure to the toxins

USEPA 2016
*Human Health Recreational Ambient Water Quality Criteria* or *Swimming Advisories* for *Microcystins* and *Cylindrospermopsin*
Ecological impacts cyanos?

Microcystin LR exposure:

- **Damaged gonad tissue in fish**
  - Lesions, cell apoptosis, and testicular ultrastructure
    - Trinchet et al. 2011; Zhao et al., 2012; Qiao et al. 2013
- **Endocrine disruption**
  - Rogers et al. 2011
- **Decrease growth/ immune function of juveniles**
  - Developmental defects and physiological stress
  - Fish embryo lethality
    - Oberemm et al. 1997; Wang et al. 2005
- **Daphnia**
  - Avoidance, toxins, clog feeding structures
    - Webster and Peters, 1978; DeMott et al. 2001 Lampert 1987
- **Habitat destruction**
Potential solutions
Proactive management

AN OUNCE OF PREVENTION IS WORTH A POUND OF CURE
Watershed nutrients?

• BMP’s may not be efficient or sufficient
  – If all retrofits conducted, New Hope Creek watershed show 6% decrease of P
    • Debusk et al. 2010

• Continued inputs
  – Soil accumulations (Reddy et al. 2011)
  – Groundwater (Martin et al. 2007; Lapointe et al. 2015)
  – Wildlife (Nürnberg and LaZerte 2016)
  – Atmospheric deposition (Wetzel 2001; Paerl et al. 2016)

• Internal load difficult and expensive to address

• The cyanobacteria may not directly relate to nutrients
In Situ Management Options

• P mitigation
  – Aluminum sulfate (Alum, non-specific, pH/other impacts)
  – Lanthanum modified bentonite (Phoslock®, specific, no buffer, permanent)
  – Algaecide combined with phosphorus remover (SeClear)
  – Polymers (Floc Log, Chitosan)
  – Iron (non-specific, release)/ Calcium (high pH only, release)

• Other
  – Aeration/oxygenation/mixing (oxygenate benthic layers)
  – Dredging (remove/re-suspension possible)
  – Bacteria
Phosphorus Mitigation Efficacy

- 8.2 surface acres; Lake Lorene, WA
- Avg. depth 5 feet, max. depth 12 feet
- Multi-purpose lake, community focal point
- Cyanobacteria blooms, toxins (mcy >2,000 ppb; atx >100ppt)
Lake Lorene, WA Summary

Phosphorus Summary

Lanthanum/Bentonite (Phoslock®) Application

1 year after
Nutrient mitigation

- Phosphorus amount and stoichiometric ratios with other nutrients are key factors in water resource management.
- Phosphorus is tied to intensity of management and promotes nuisance algae.
- *In situ* mitigation is critical to address cause of negative water quality.
  - Legacy P
- Phosphorus mitigation integration can have significant impacts.
Nutrients

• Yes and no
Cylindrospermopsis and nutrients

- Grows under both low and high N:P ratios
  - Many forms of nutrients (e.g. organic)
  - (Chislock et al. 2014)
- Grows with no dissolved nitrogen (O’neil et al. 2013)
  - Fixation from atmosphere (Sinha et al. 2012)
- Dominates in low phosphate
  - High uptake, affinity/ storage, scavenge episodic inputs (Wu et al. 2012)
- Likes static or mixed conditions, especially to dark zones
  - Kehoe 2010; Antenucci et al. 2005; Burford and O’Donohue 2006
- Meteorological and chemical factors were not related to the dominance of C. raciborskii (Figueroedo and Giani 2009)
- “Can tolerate a wider range of P concentrations” and “proliferate in a wide range of N conditions” (Sinha et. al 2012)
- “In summary, the ecological flexibility of this organism means that controlling blooms of C. raciborskii is a difficult undertaking” (Buford and Davis 2011)
Microcystis and Phosphorus

- Massive benthic populations of *Microcystis*
  - Preston et al. 1980; Fallon & Brock 1981; Takamura et al. 1984
- Migrate to/from sediments to form blooms
  - Perakis et al. 1996
- *Microcystis* blooms resulted in high pH (9.0–10.0)
  - Induce release of dissolved P from the sediments (iron hydroxides)
    - Xie et al. 2003; Chang and Jackson, 1957
- Mutualism with heterotrophic bacteria for nutrients
- *Microcystis* strongly upregulates (by 50- to 400-fold) two high-affinity, phosphate-binding proteins (*pstS* and *sphX*) and alkaline phosphatase gene (*phoX*)
  - Harke et al. 2012
Nutrient mitigation v Climate

• “in a future warmer climate, nutrient concentrations may have to be reduced substantially from present values in many lakes if cyanobacterial dominance is to be controlled”


• 60% more decrease in nutrients needed with 6°C temperature increase
Direct control
Control Techniques

- **Action Options**
  - **Mechanical**
    - harvesters, sonication, cavitation, aeration
  - **Physical**
    - dyes, raking, flushing
  - **Biological**
    - bacteria, grass carp, tilapia
  - **Chemical**
    - Nutrient binding, algaecides

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Mechanical

• Pros
  – Remove biomass and nutrients
  – Can open channels rapidly
  – Cost, O&M

• Cons
  – Selective efficiency
    • Algal type and location in water
  – Fragment and spread
  – Increase turbidity and suspend legacy nutrients
  – Operational feasibility
Physical: Aeration

• Pros
  – Organisms breath oxygen
  – Take the cyanobacteria buoyancy (scum) advantage out of play
  – Keep circulated to select for better types of algae... usually
  – Oxygenated benthic zone to decrease internal phosphorus cycling, other sediment gas release

• Cons?
  – Temperature increase throughout water column
  – Carbon addition
  – Circulate nutrients from benthic zones
  – Some planktonic cyanos prefer
Turbulent mixing

- Huisman et al. 2005
Pretty good mixing: still toxic cyanos
Physical: Light

• Absorb light at different wavelengths
  – Reflect different colors
• Different functions
• Diagnostic of different groups
• Carotenoids
  – Carotenes v. xanthophylls
• Chlorophylls
• Phycobilins

<table>
<thead>
<tr>
<th>Algal Pigment</th>
<th>Chlorophyta (Green algae)</th>
<th>Cyanophyta (Cyanobacteria)</th>
<th>Bacillariophyta (Diatoms)</th>
<th>Pyrrophyta (Dinoflagellates)</th>
<th>Haptophyta (Golden algae)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorophyll a</td>
<td>X</td>
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<tr>
<td>Chlorophyll b</td>
<td>X</td>
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<tr>
<td>Fucoxanthin</td>
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<td>Peridinin</td>
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<tr>
<td>Phycocyanin</td>
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</table>
Shade balls
Biological

• Preferences
  – Grass carp prefer to eat *Hydrilla* 55x > *Lyngbya* (Dyck 1994)

• Increase turbidity

• Viability of algae

• Suspend legacy nutrients
Chemical: USEPA registered pesticides

- Diquat Dibromide
  - PSI inhibition
- Endothall
  - Proteins and lipid disruption
- Peroxides
- Copper
  - Chelated v. free ion
- Adjuvants
USEPA Registration

• Numerous studies required
• EPA review and set label instructions
  – Negligible risks to humans and environment
    • Follow label
  – Approved use sites
  – Widely used
  – Copper, peroxide, diquat, endothall
Non-target Species?

• Present?
• Toxins impacts?

• Management objectives
  – Irrigation canals
  – Drinking water
• Accurate risk assessment
Field algaecide application

**Scenedesmus** surface area (1 million cells) = 1,320mm²

**Daphnia** average gill surface area = 7.57mm²
Copper exposure
Copper sulfate shift

Percent Mortality

Total Copper Concentration (µg Cu/L)

75 µg Cu/L
318 µg Cu/L
518 µg Cu/L
Captain shift

![Graph showing percent mortality vs. total copper concentration (µg Cu/L)].

- 354 µg Cu/L
- 414 µg Cu/L
- 589 µg Cu/L

Legend:
- Captain No Algae
- Captain 5 x 10^5 Algae
- Captain 5 x 10^6 Algae

Equations:
- y = 87.76/(1+exp(-(x-346.93)/25.96))
- y = 105.35/(1+exp(-(x-421.62)/71.48))
- y = 129.66/(1+exp(-(x-642.33)/114.88))
Formulation

• Chelating agents
  – Stability, corrosivity, water chemistry
  – Degree of interaction

• Toxicity to targets
  – Lipid soluble can diffuse through membrane
    • Stauber and Florence 1987
  – Membranes impermeable to charged/polar species
    • Sunda 1989

  – TEA
    • Decrease surface tension
    • Emulsifier: water-soluble and oil-soluble ingredients can be blended

  – EDA is a solvent
    • Miscible with polar solvents
    • Solubilize proteins
    • Bidentate chelating ligand
Chelation safety

• Komeen
  – Delta smelt
  – LC$_{50}$ 1.4 mg Cu/L
• Komeen/Nautique
  – Bluegill/bass/shiner/perch
  – LC$_{50}$ 5.4-496 ppm Cu
• Nautique
  – 96 hr LC$_{50}$ > 20 mg Cu/L
  – Trout, fathead minnow
  – Wagner et al. 2017

ACUTE TOXICITIES OF HERBICIDES USED TO CONTROL WATER HYACINTH AND BRAZILIAN ELODEA ON LARVAL DELTA SMELT AND SACRAMENTO SPLITTAIL by Frank Riley and Sandra Finlayson. California Department of Fish and Game. Aquatic Toxicology Laboratory

WA DOE Supplemental Environmental Impact Statement Assessments of Aquatic Herbicides volume 6: copper
**Frequency**

- **Standard Tox Tests copper**
  - Constant concentration
  - Flow through or static renewal

- **Field**
  - 14 days between treatments
  - Fraction of max label rate
  - 1/3 - 1/2 of the system
Control 8 miles downstream
CET *Lyngbya wollei*

- Factor
  - Concentration
  - Duration
- Formulation efficiency
- Critical infused Copper threshold

Bishop et al. 2017
Infusion = control: *Lyngbya wolleii*

R² = 0.920, P < 0.0001

internal threshold = same for all treatments

R² = 0.920, P < 0.0001
Lyngbya control

May 2017 biomass

Nov 2018 biomass
Toxin Release?
Leaky Cell Hypothesis

• Internal toxin can be released with some chemical treatments/concentrations
  – Kenefick et al. 1993; Jones and Orr 1994; Peterson et al. 1995; Daly et al. 2007; Touchette et al. 2008; Greenfield et al. 2014; Lurling et al. 2014; Tsai 2015

• If treat:
  – Dilutes through water/ biodegrades
    • Even leaky cell papers < 1 d half-life open water
    • Dermal absorbed dose of microcystins is likely to be negligible (EPA 2016)
  – No hot spot accumulation potential
  – Total toxin decreases
  – Possible to treat without releasing
    • Formulation/ concentration
    • Tsai 2015; Iwinski et al. 2016

• If fear free toxin, need to fear total toxin
• Only way to not have an exposure is not have produced
Total *or* free toxin?

- In latter bloom stages, more cells lyse, extracellular Mcyn becomes more abundant
  - White et al. 2005

- Mcyn release cultured *M. aeruginosa* began to occur late in exponential growth phase and increased significantly in stationary phase
  - Chorus and Bartram 1999

- Increase in population numbers could produce a more intense toxin level (described or unknown) and impending natural release
  - White et al. 2005; Lehman et al. 2013

- Dried Ma scums may contain high concentrations of mcyn for several months
  - Released back into the water when re-immersed

- “Under bloom conditions, a substantial proportion of toxin would also be expected to be released to the water column, making removal of soluble toxin an unavoidable concern.”
  - Chorus and Bartram 1999 (and references therein)
Cylindrospermopsin

- CYN is hydrophilic and commonly found in extracellular toxin fractions
  - Sivonen & Jones 1999; Shaw et al. 2000; Griffiths & Saker 2003

- Cyn production can correlate with cell division in exponential growth phase
  - Though 2x toxin produced in stationary phase verses cell division; Hawkins et al. 2001

- Extracellular CYN accounted for 50% in day 20 of culture of one C. raciborskii strain
  - Saker and Griffiths 2000

- Extracellular CYN varied between 19% and 98% of total in C. raciborskii, based on bloom stage
  - Chiswell et al. 1999

- 85% of the CYN produced by Aphanizomenon ovalisporum was extracellular
  - Shaw et al. 1999
<table>
<thead>
<tr>
<th>Cyano toxins</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>• No good level to have</td>
<td>• Essential nutrient</td>
</tr>
<tr>
<td>• EPA candidate contaminate list drinking water; HA listings</td>
<td>– Hemocyanin</td>
</tr>
<tr>
<td>• 0.3µg/L MCYN in drinking water-EPA guideline children</td>
<td>– Suggested Daily Intake (2mg)</td>
</tr>
<tr>
<td>• WHO/ EPA guidelines in recreational water</td>
<td>• 1,300 µg/L is MCL in drinking water</td>
</tr>
<tr>
<td>• WHO possible carcinogen list</td>
<td>• 26th most abundant element in Earths Crust</td>
</tr>
<tr>
<td>• Accumulates through time</td>
<td>• Does not bio-accumulate</td>
</tr>
<tr>
<td>• Multiple exposure routes</td>
<td>• Transfers to less available sediment forms through time</td>
</tr>
<tr>
<td>• ALS, PDS, Alzheimer's link</td>
<td>• No swimming/drinking/irrigation restrictions on USEPA approved label</td>
</tr>
<tr>
<td>• Caused deaths of cows, elk, dogs, birds, people etc.</td>
<td></td>
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</tbody>
</table>
Peroxide based algaecides

• NSF approval is for use in drinking water
• OMRI certified
• All ingredients in PAK 27 have either Generally Recognized as Safe (GRAS) food additive status from the U.S. Food and Drug Administration (FDA)
• Peroxide gone within hours, decomposition leads to the formation of water and oxygen (Bauza et al. 2014)
  – Cyanobacteria more sensitive than green algae and diatoms (Drabkova et al. 2007b)

• Long-term impacts
  – Cyanobacterial population and microcystin concentration collapsed by 99%; remained very low until 7 weeks after treatment (Matthijs et al. 2012)
  – ‘prolonged suppression of cyanobacteria’ and “new state with a diverse phytoplankton community” (Weenink et al. 2015)
Silverwood Lake, CA

• 935 acres (73,000 AF)
• Supplies 3 Million people in Los Angeles area
• Severe taste/odor issues
• *Anabaena* sp. culprit
Implementation
Cyanobacteria significantly decreased at most sites 1 and 7 DAT.
Summary

• Copper widely use, less risk than the disease
• Copper formulation matters
  – Non-target safety
  – Target specificity
• Other non-copper options can be effective in some scenarios
  – Peroxide
• Site character and management objectives need to be considered
Summary

• Nutrient mitigation tricky, but important

• Not directly managing is not without risk

• Released toxin mindset flawed
  – Total risk, accumulation risks, external toxin, wildlife, other exposures

• Source control of bacterial infections critical
Suggested Approach

• ‘guilty until proven innocent approach’
  – Otten and Paerl 2015
    – *Data support more toxins being identified, more exposure routes, more knowledge on impacts (acute and chronic)*
    – *Acknowledge both known and unknown risks*

• Approach to ensure safety of the water resource
  – Low tolerance for toxic cyanobacteria
  – Try to prevent
  – Not allow toxin to be produced in sufficient amounts to harm humans/wildlife
  – Mitigate source and/or toxin if found
    • Nutrient mitigation may not correlate
Questions

Solutions to Preserve our most Precious Natural Resource...Water

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Host
References


