Cyanotoxins in Freshwaters of the United States: Occurrence and Emerging Technologies

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U.S. Geological Survey

EPA Region 10 HAB Workshop

May 25, 2017

Laboratory Measurement of Cyanotoxins

Each Step Effects the Final Result and What it Means!

Study Design and Sample Collection





The Laboratory

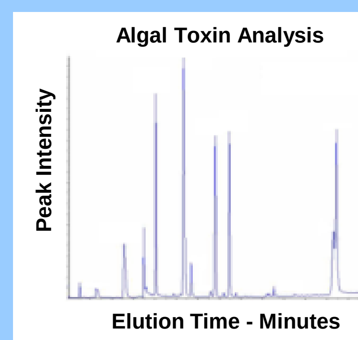
Laboratory Processing



Analysis

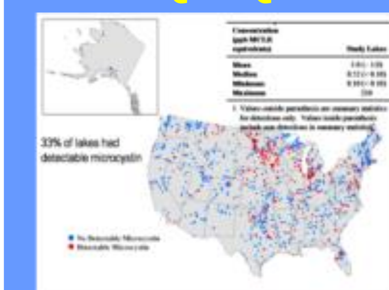


Data Reduction And Laboratory QA/QC



Study Results

Data Release, Interpretation And Project QA/QC



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So Many Methods… Which One Should We Use?

	Freshwater Cyanotoxins				
	Anatoxins	Cylindrospermopsins	Microcystins	Nodularins	Saxitoxins
Bioloigcal Assays (Class Specific Methods at Best):					
Mouse	Yes	Yes	Yes	Yes	Yes
PPIA	No	No	Yes	Yes	No
Neurochemical	Yes	No	No	No	Yes
ELISA	Yes	Yes	Yes	Yes	Yes
Chromatographic Methods (Compound Specific Methods):					
Gas Chromatography:					
GC/FID	Yes	No	No	No	No
GC/MS	Yes	No	No [1]	No	No
Liquid Chromatography:					
LC/UV (or HPLC)	Yes	Yes	Yes	Yes	Yes
LC/FL	Yes	No	No	No	Yes
Liquid chromatography combined with mass spectrometry can analyze cyanotoxins very specifically.					
LC/IT MS	Yes	Yes	Yes	Yes	Yes
LC/TOF MS	Yes	Yes	Yes	Yes	Yes
LC/MS	Yes	Yes	Yes	Yes	Yes
LC/MS/MS	Yes	Yes	Yes	Yes	Yes

1 MMPB method is used for total microcystins in some cases, especially for tissues.

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What Does Each Method Really Do For Me?

	Specificity
Biological Assays (Class Specific Methods at Best):	
Mouse	Non-specific, test must be rapid therefore endpoint usually death.
PPIA	Of the freshwater cyantoxins, only microcystins are known to inhibit protein phosphatase.
Neurochemical	Of the freshwater cyanotoxins, only anatoxins and saxitoxins are known to inhibit neurochemical processes.
ELISA	Compound and toxin class specificity dependent on antibody or mix of antibodies used.
Chromatographic Methods (Compound Specific Methods):	
Gas Chromatography:	
GC/FID	Only the anatoxins have been routinely measured. Derivitization is typically required.
GC/MS	Only the anatoxins have been routinely measured. Derivitization is typically required.
Liquid Chromatography:	
LC/UV (or HPLC)	Variable. Subject to interference with co-eluting matrix.
LC/FL	Variable. Subject to interference with co-eluting matrix.
Liquid chromatography combined with mass spectrometry can analyze cyanotoxins very specifically.	
LC/IT MS	Second in compound specificity only to LC/TOF MS.
LC/TOF MS	Accurate mass capability makes this technique the most specific.
LC/MS	Weaker cousin of LC/MS/MS. Fourth most specific.
LC/MS/MS	Third most specific technique routinely employed

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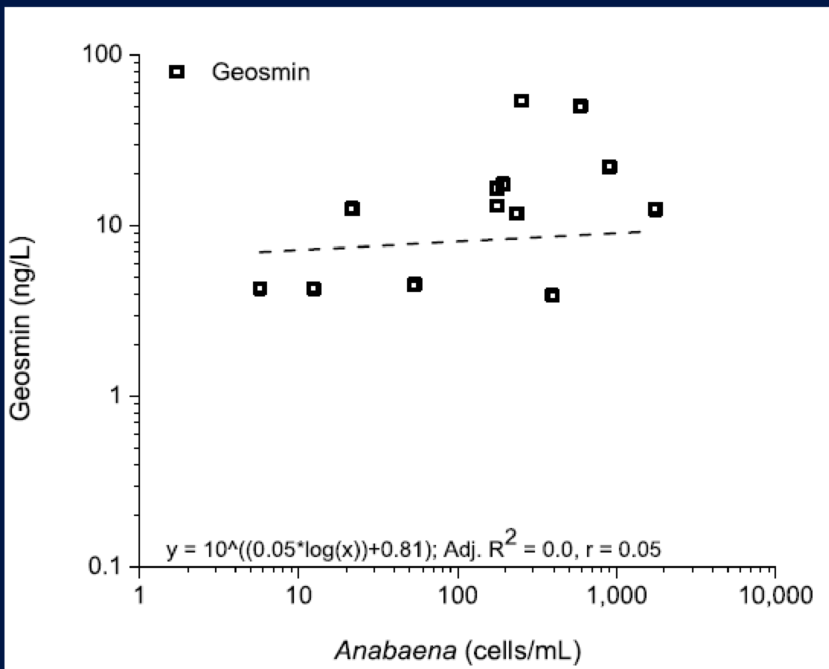
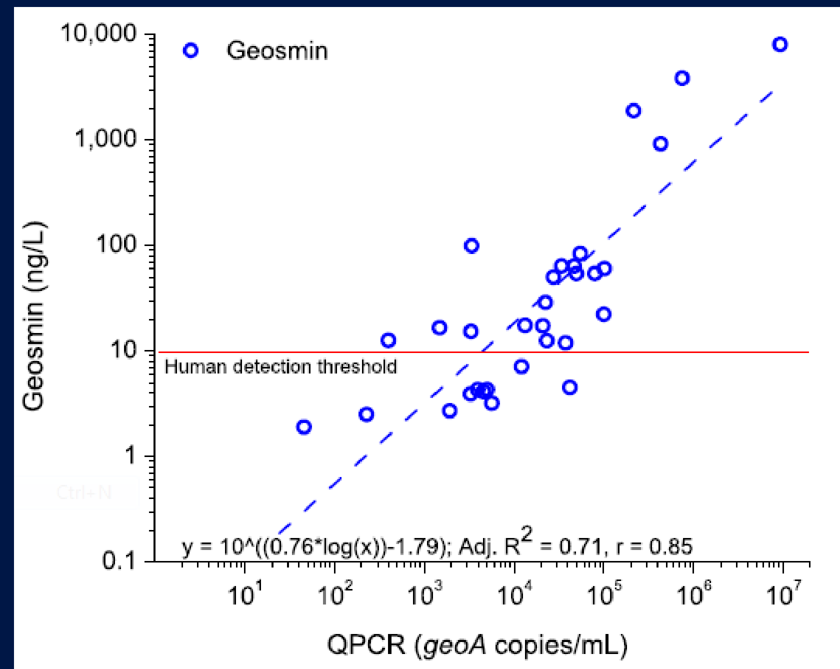
Genetic Data Improve Understanding of the Occurrence of Cyanobacteria and Associated Compounds





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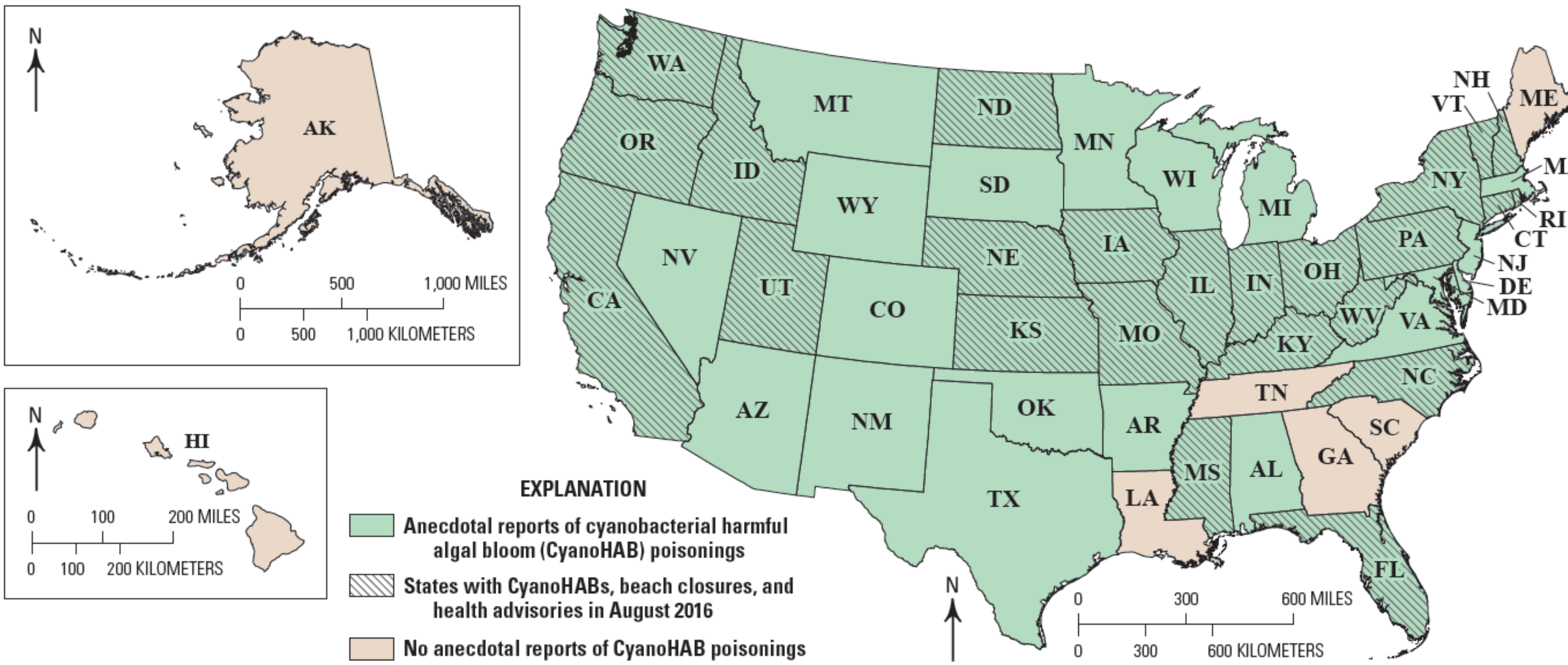
Otten et al., 2016, Applied and Environmental Microbiology

In August 2016, At Least 19 States Had Beach Closures or Health Advisories



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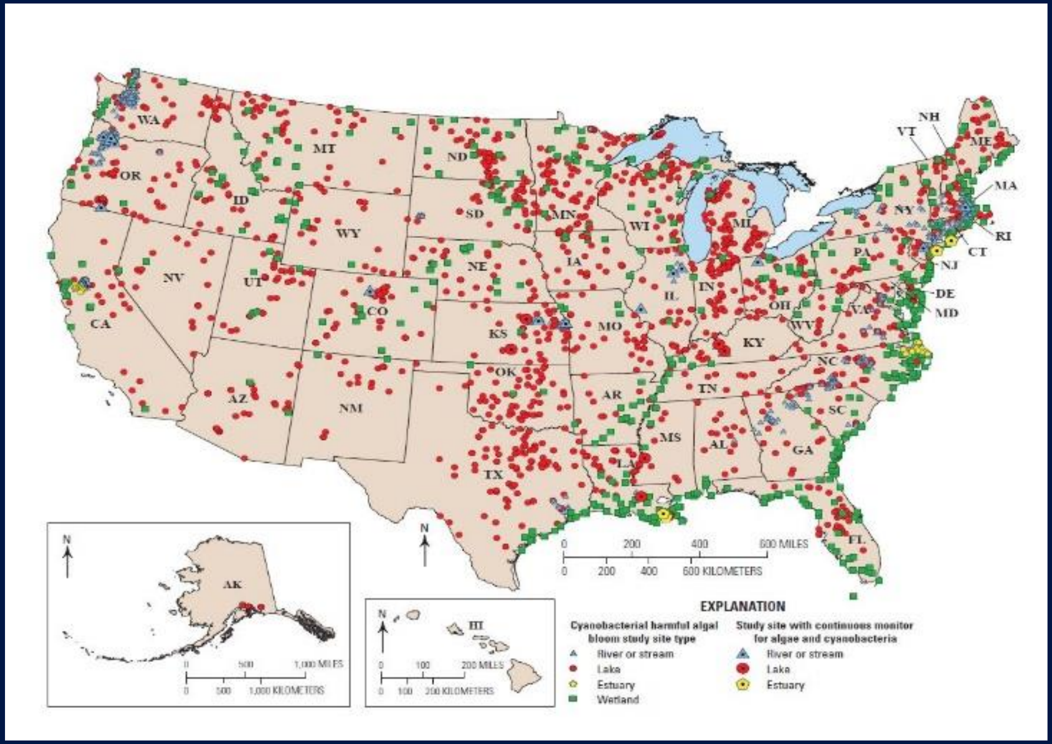
Graham and others, 2016, USGS OFR 2016-1174
http://dx.doi.org/10.3133/ofr20161174

Cyanotoxins Are Detected in All Types of Waterbodies Throughout the Nation

- Small Streams
- Lakes and Reservoirs
- Great Lakes
- Rivers
- Inland and Coastal Wetlands
- Estuaries



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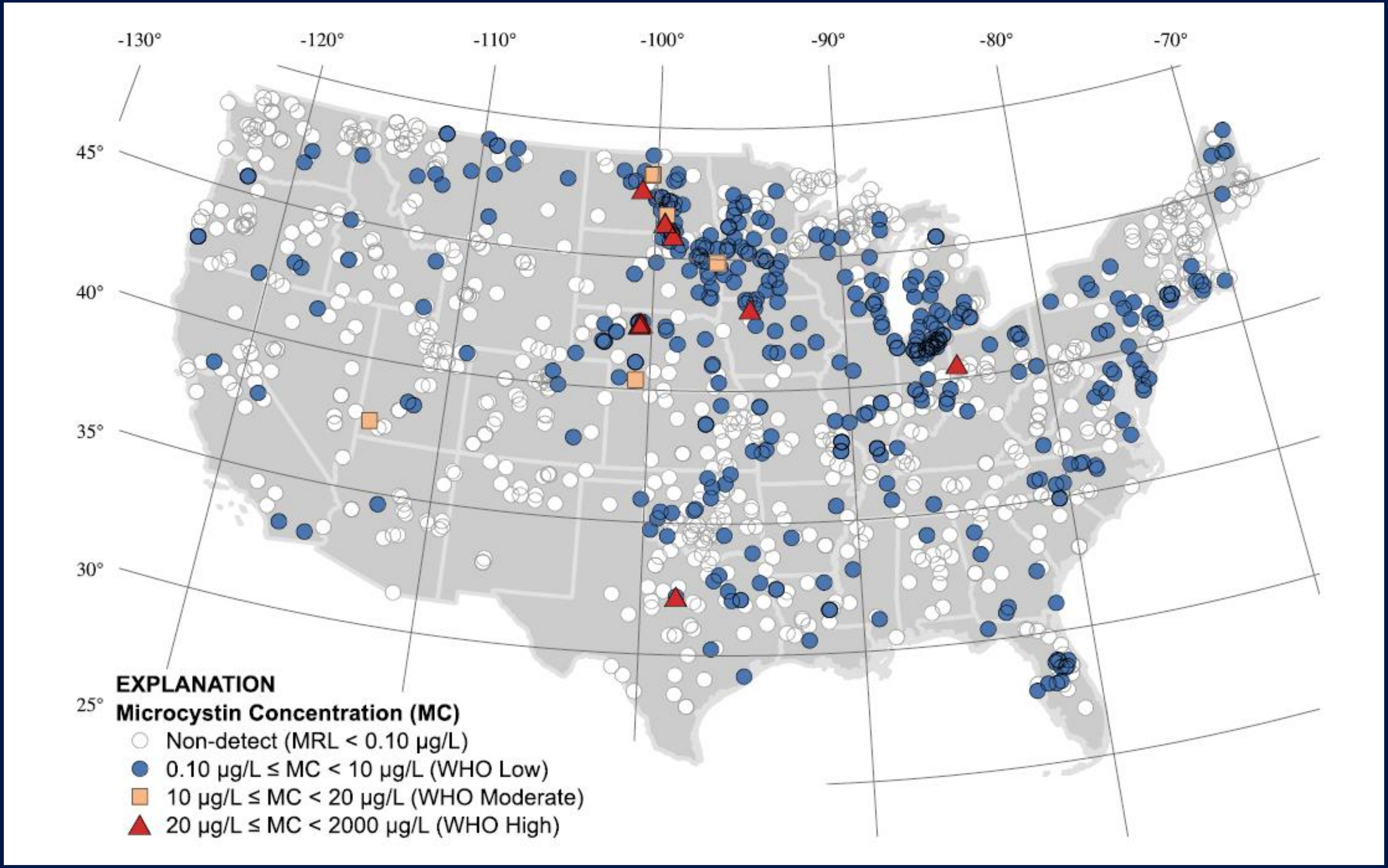
Graham and others, 2016, USGS OFR 2016-1174
http://dx.doi.org/10.3133/ofr20161174

In the 2007 National Lakes Assessment, Microcystins Were Detected by ELISA in About 32% (n=1252) of Analyzed Samples



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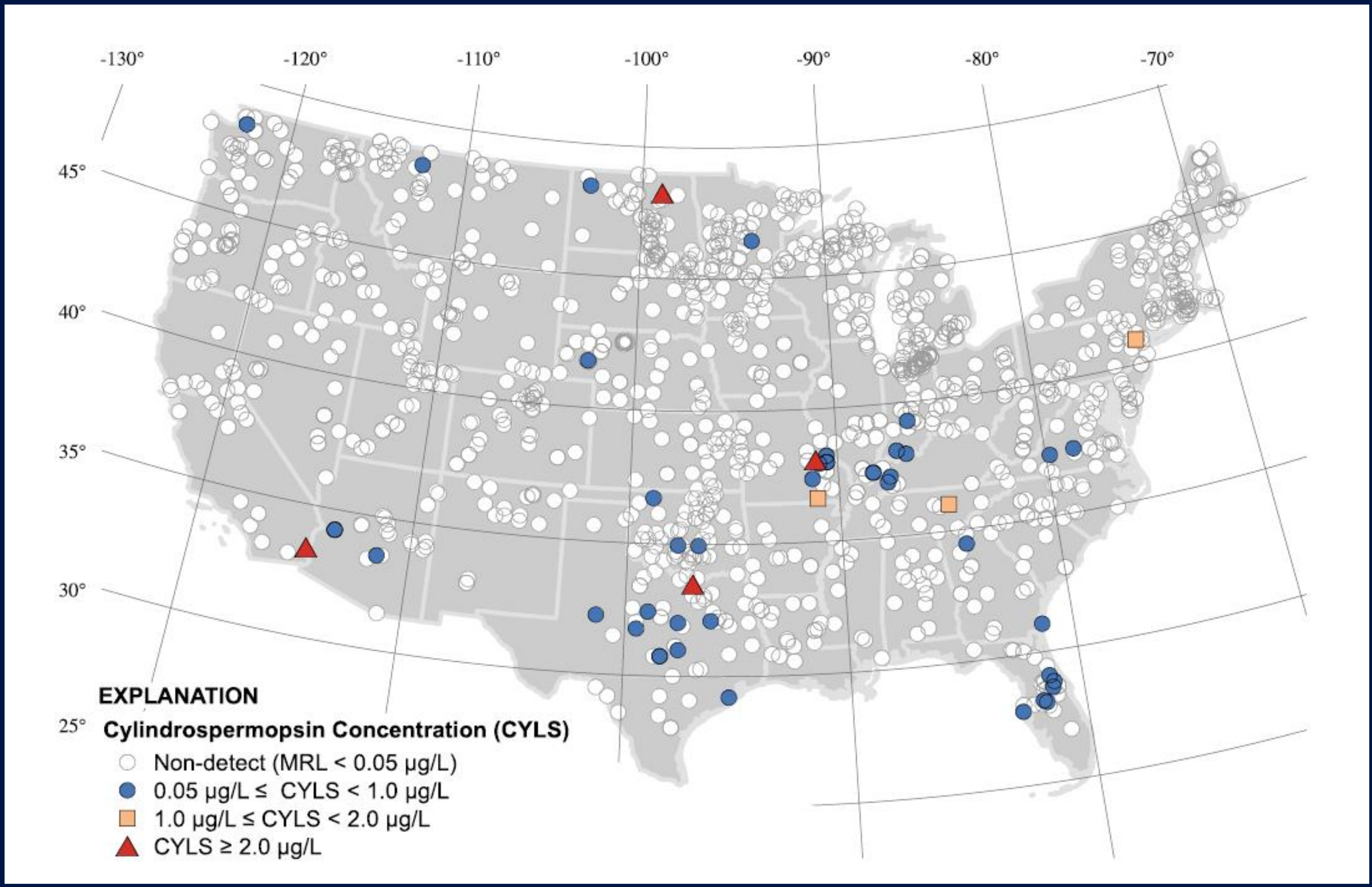
Loftin and others, 2016, Harmful Algae
https://toxics.usgs.gov/highlights/2016-05-31-cyanotoxins_in_lakes.html

In the 2007 National Lakes Assessment, Cylindrospermopsins Were Detected by ELISA in About 4% (n=1252) of Analyzed Samples



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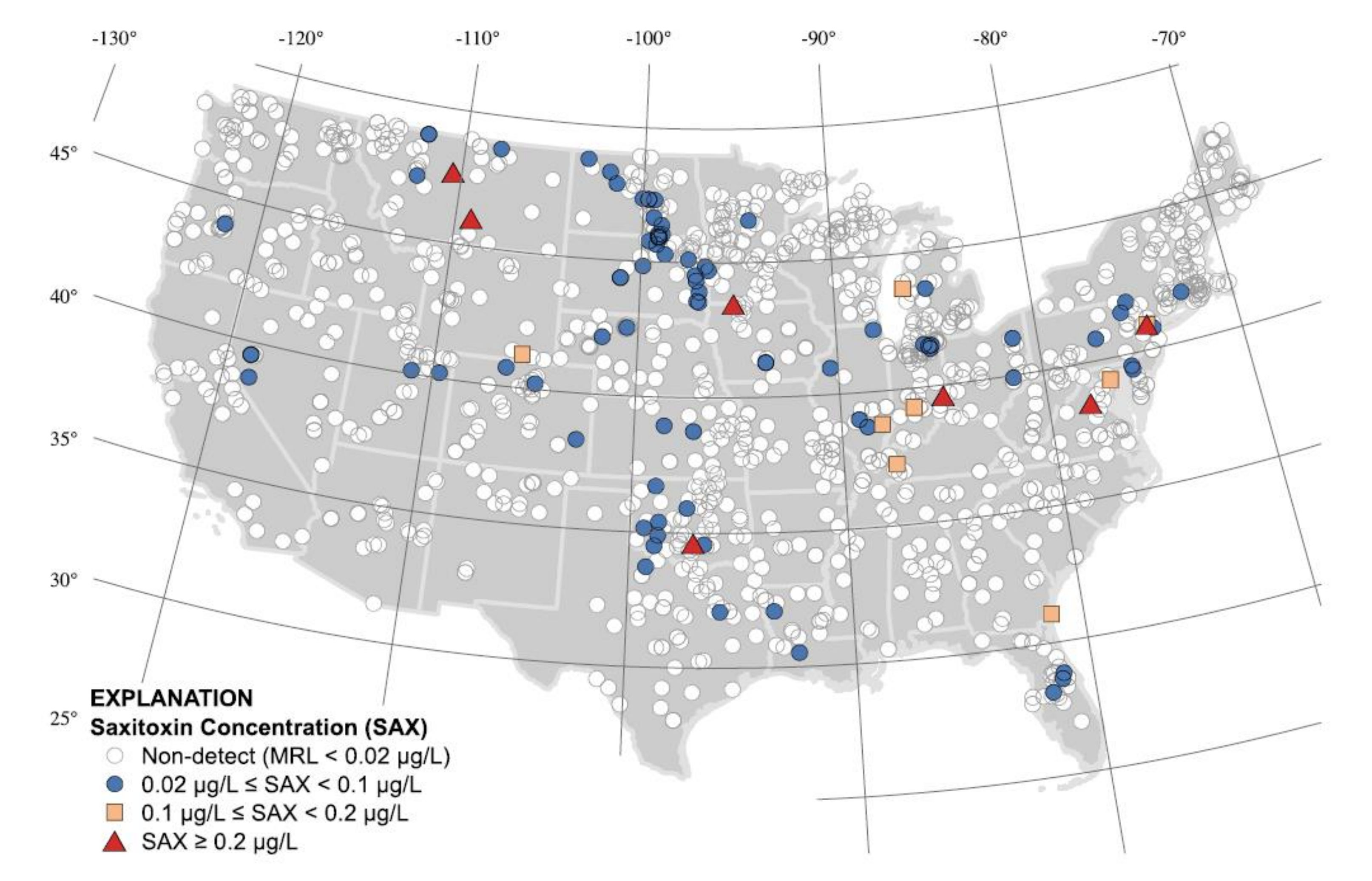
Loftin and others, 2016, Harmful Algae
https://toxics.usgs.gov/highlights/2016-05-31-cyanotoxins_in_lakes.html

In the 2007 National Lakes Assessment, Saxitoxins Were Detected by ELISA in About 8% (n=678) of Analyzed Samples



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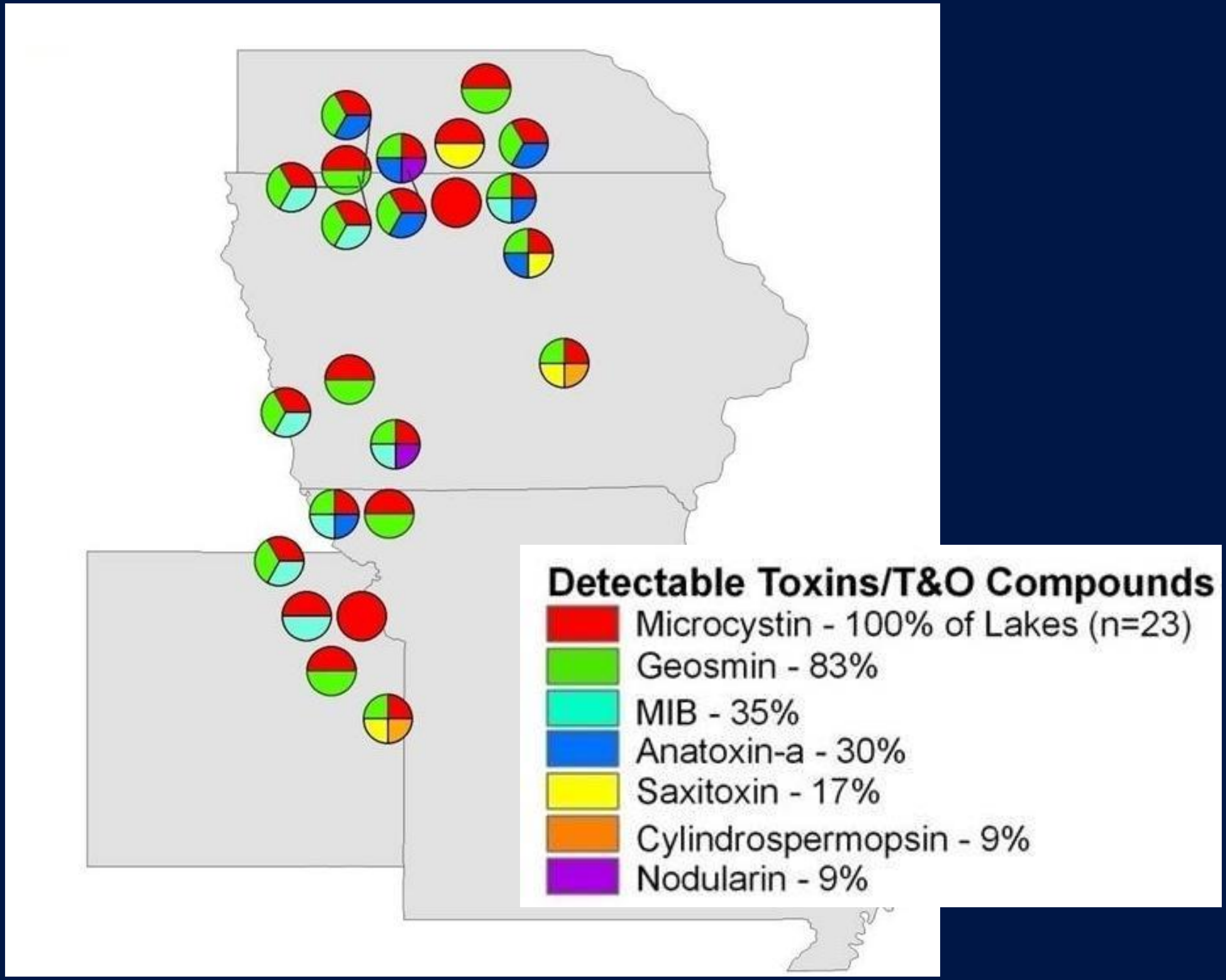
Loftin and others, 2016, Harmful Algae
https://toxics.usgs.gov/highlights/2016-05-31-cyanotoxins_in_lakes.html

Multiple Toxins and Taste-and-Odor Compounds Frequently Co-Occur in Cyanobacterial Blooms



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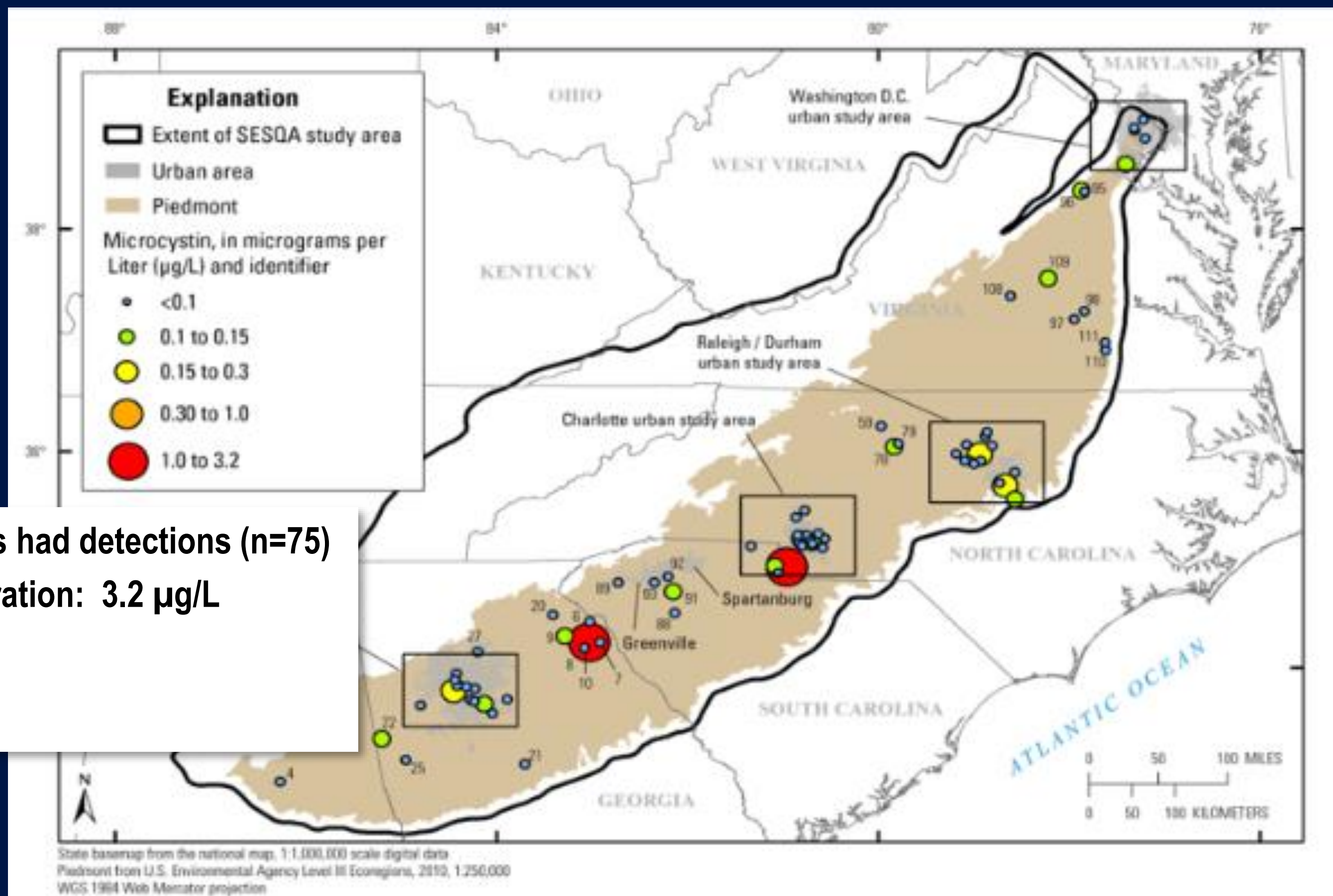
Graham and others, 2010, ES&T

Microcystins Occurred in 39% of Small Stream Sites Sampled in the Southeastern United States



39% of stream sites had detections (n=75)

Maximum concentration: 3.2 µg/L

Median: 0.11 µg/L

Mean: 0.29 µg/L

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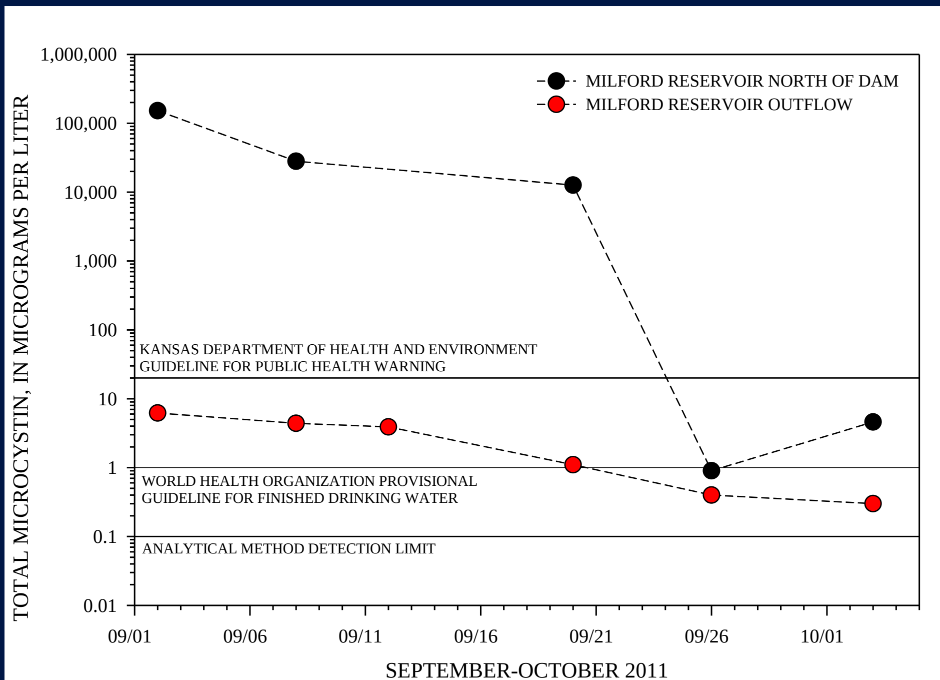
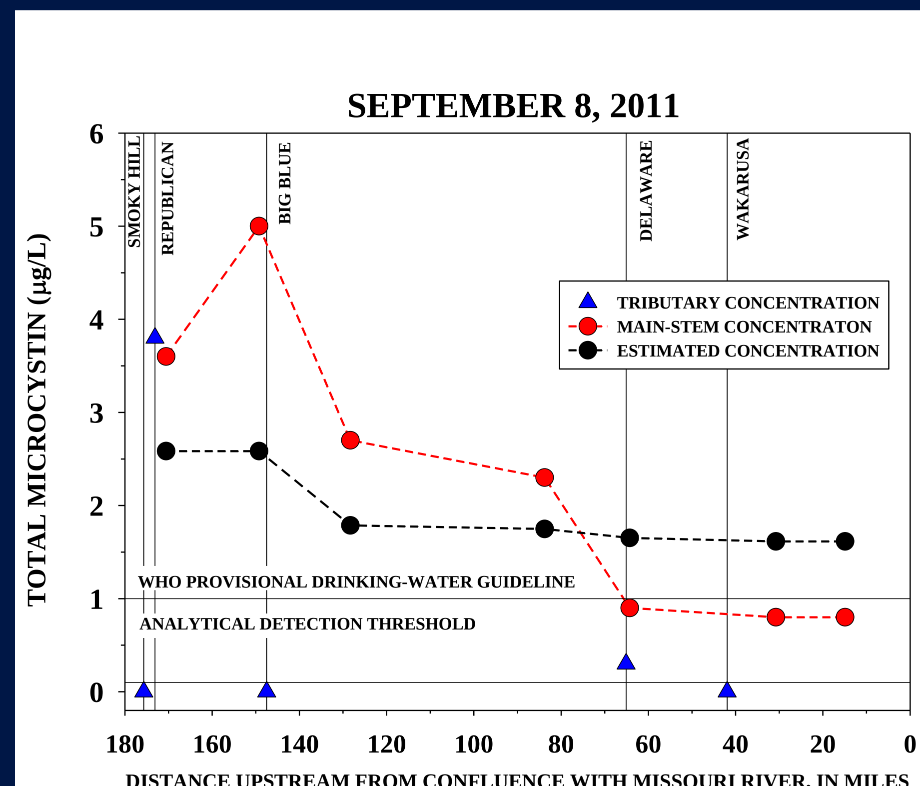
Loftin and others, 2016, Environmental Toxicology and Chemistry
https://toxics.usgs.gov/highlights/2016-02-17-algal_toxins_in_streams.html

Cyanobacteria and Associated Compounds May Be Transported for Relatively Long Distances Downstream from Lakes and Reservoirs





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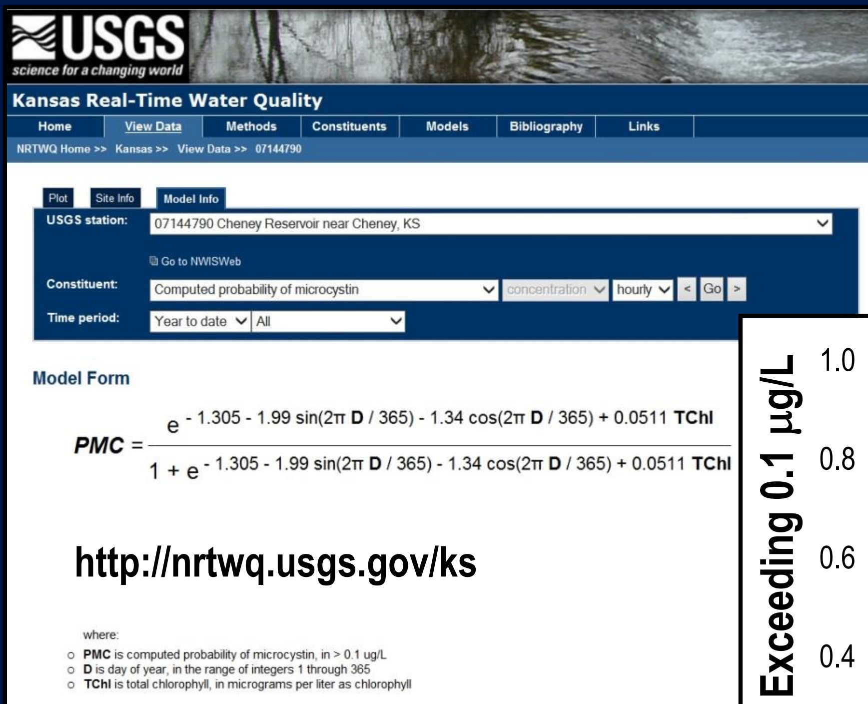
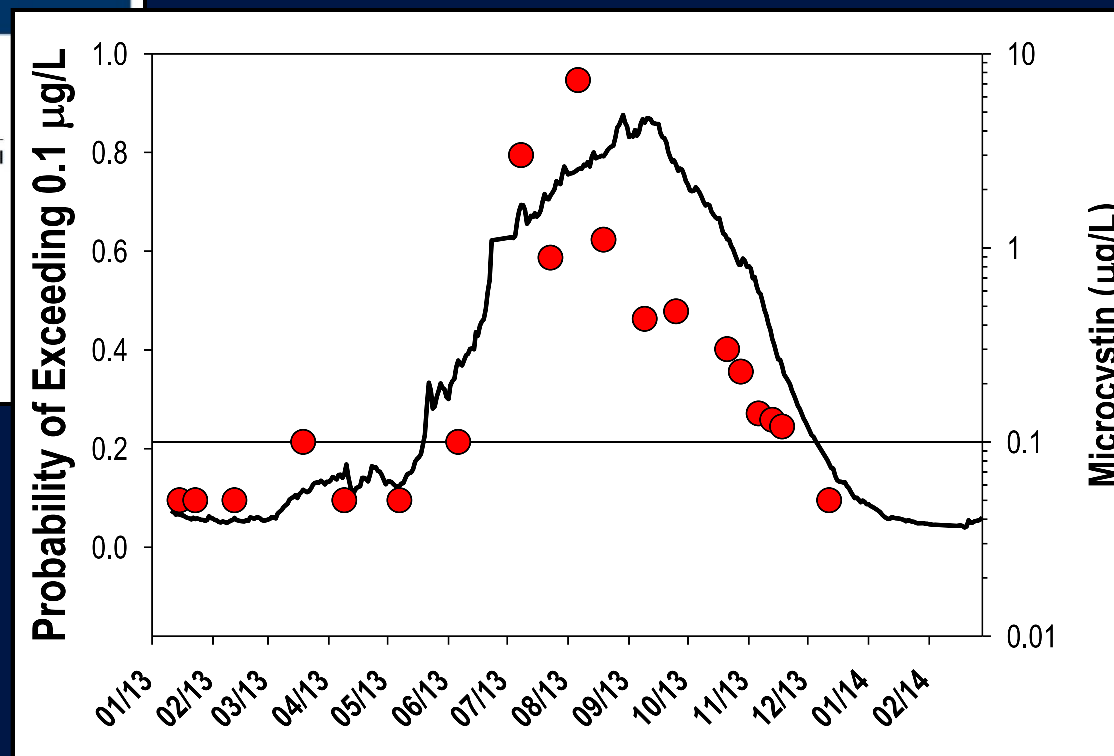
Graham and others, 2012, USGS SIR 2012-5129

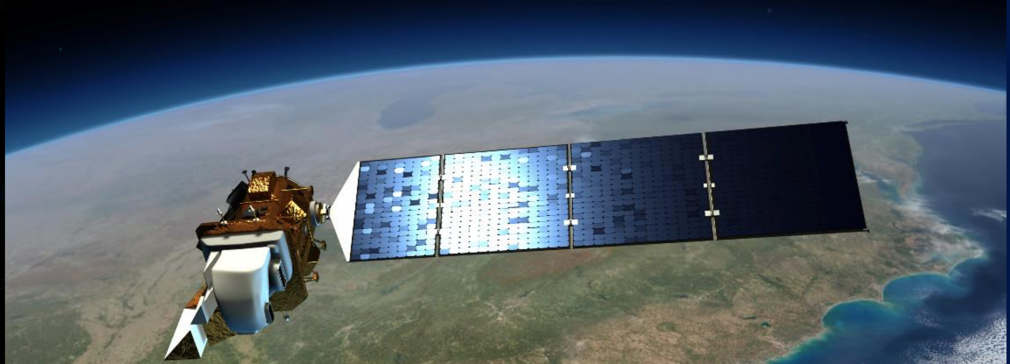
Continuous Water-Quality Monitors Can Be Used to Develop Models to Compute Probability of Cyanotoxin Occurrence in Real Time

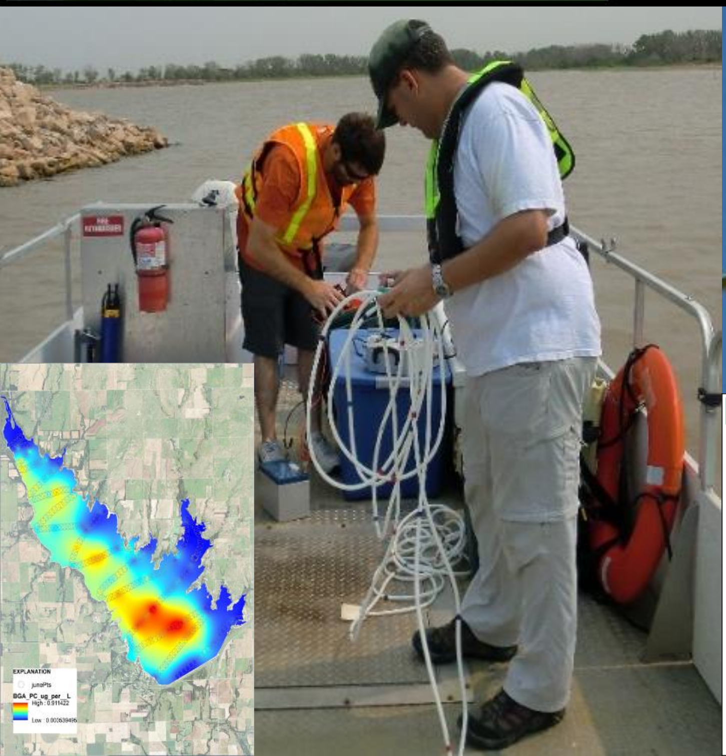


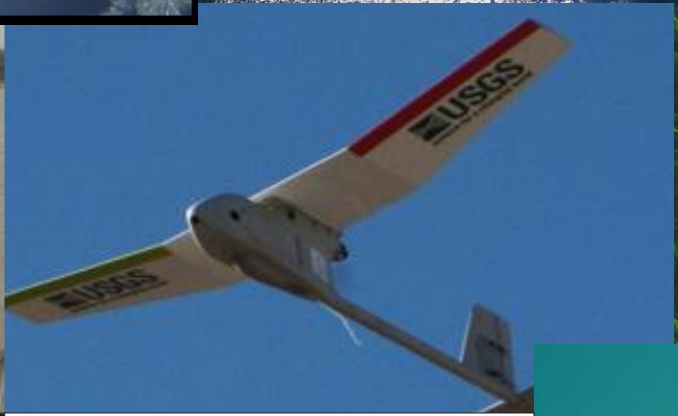


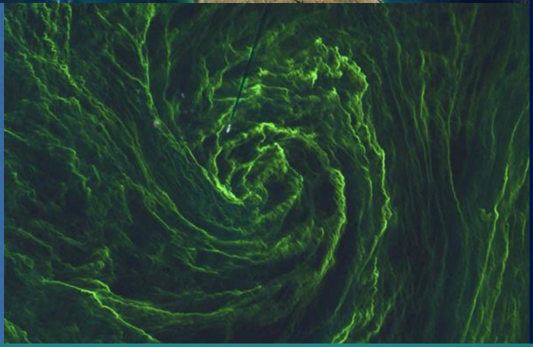
Stone and others, 2013, USGS OFR 2013-1123

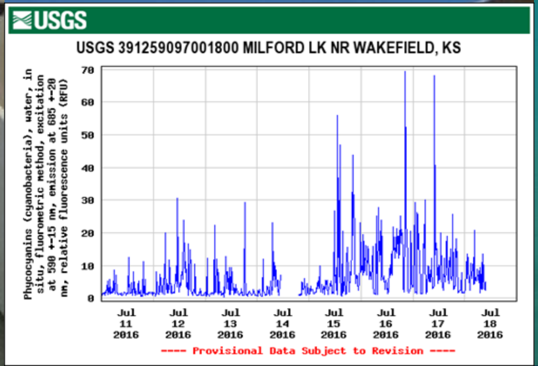
Applied technologies on HAB's- multiple approaches are needed to understand the issue

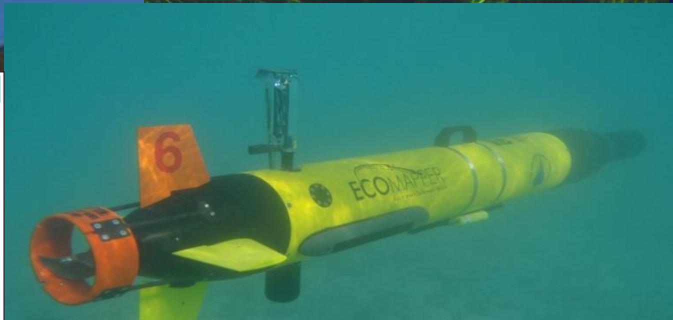












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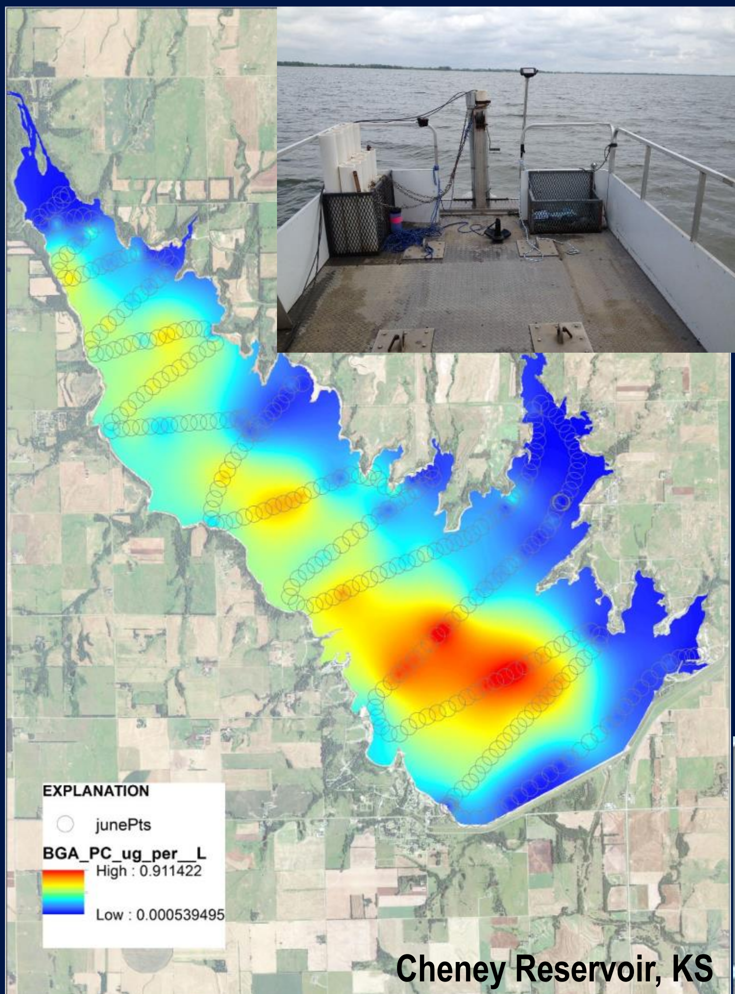
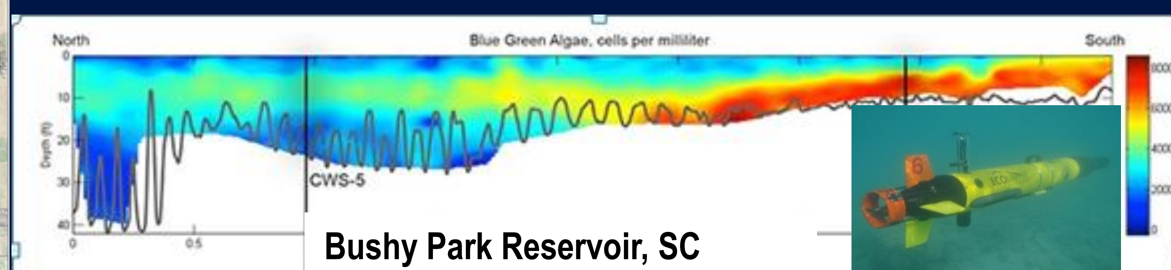
New Sensor Technologies Allow New Applications, Such as High Resolution Spatial Data Collection





Foster, KSWSC
Bergamaschi, CAWSC
Journey, SAWSC

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Aerial- and Ground-Based Cameras Show Potential as Early Warning Indicators

Courtesy of E. Emory

Courtesy of C. Smith

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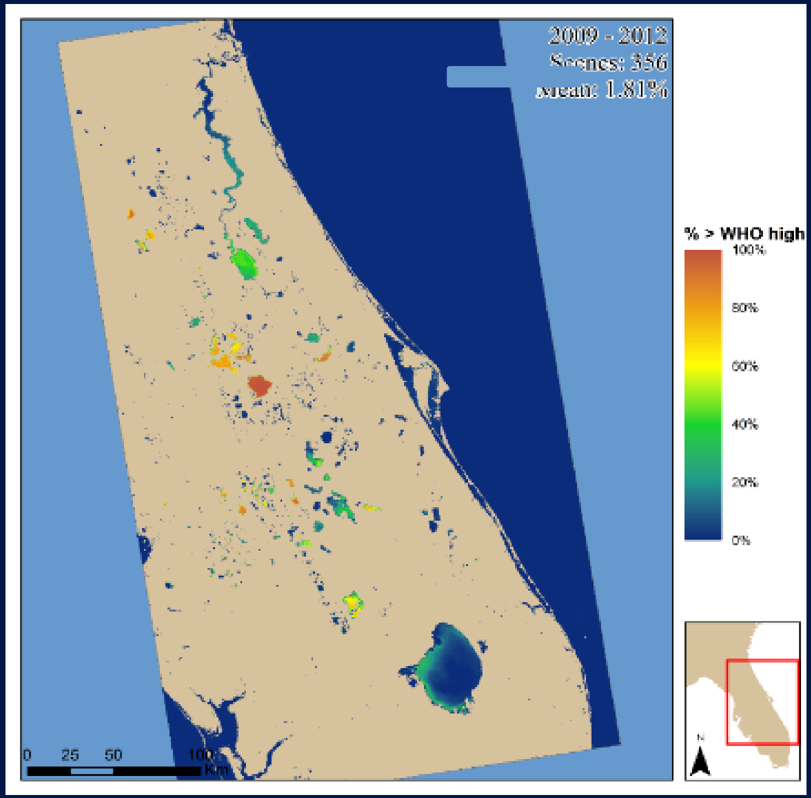
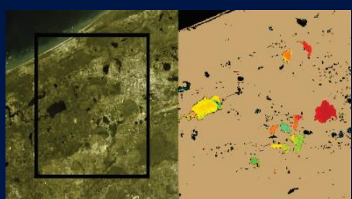
Satellite (and Other Aerial) Imagery Captures Spatial Variability Across an Entire Lake Surface and on a Regional Scale



https://www.epa.gov/water-research/cyanobacteria-assessment-network-cyan-project
https://toxics.usgs.gov/highlights/2015-12-21-cyanobacteria_sensing.html

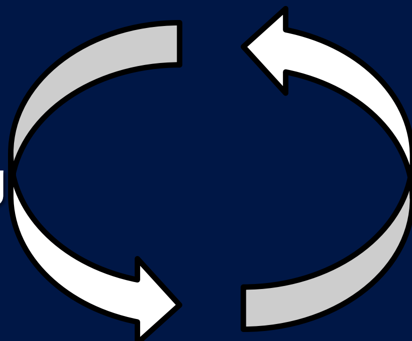
Tools that Utilize Satellites for Inland HAB Monitoring are Being Developed

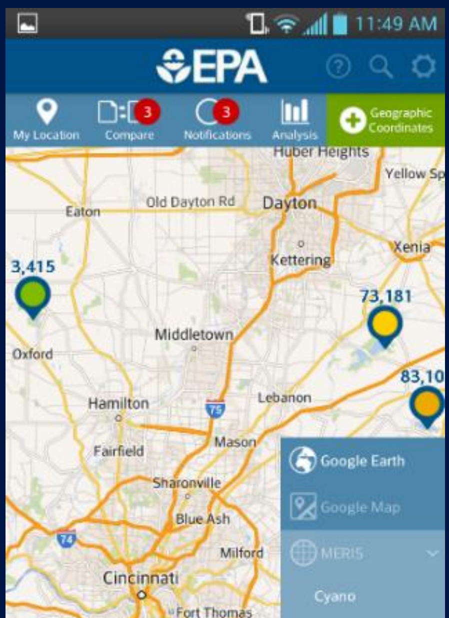
Cyanobacteria Assessment Network (CyAN) Project

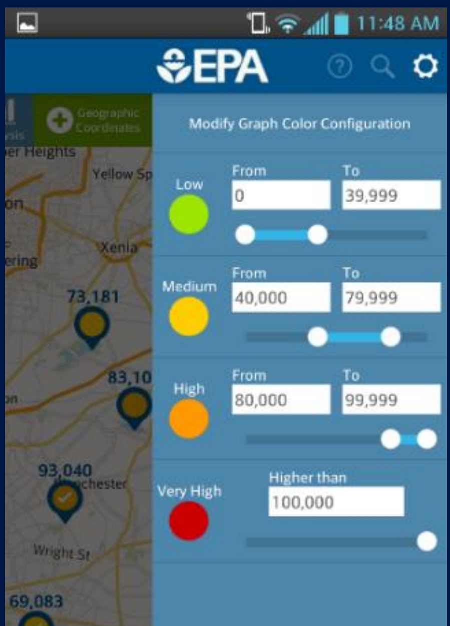


Remote Sensing

Field Data

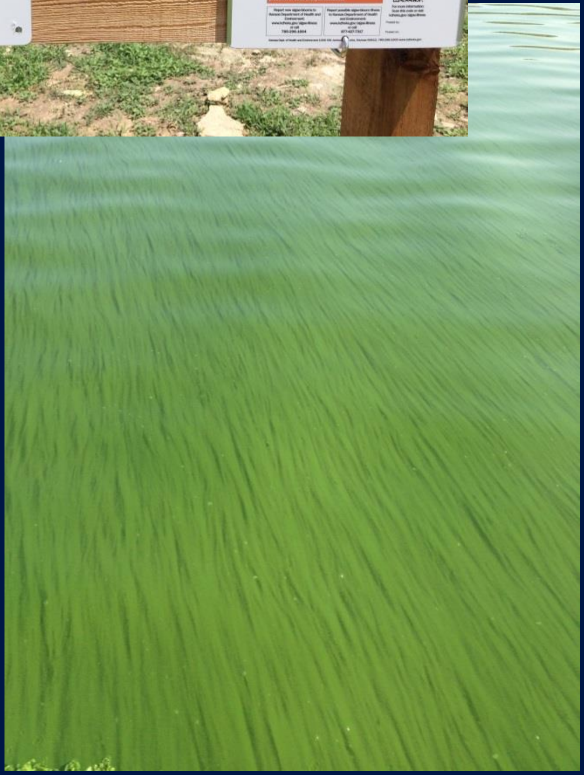






Unifying Themes in Harmful Algal Bloom Research

- Individual systems are unique.
- Spatial and temporal variability present challenges to data collection, analysis, and interpretation.
- Sensor technology including odor detection and genetic approaches provide important information on spatiotemporal variability and environmental influences.
- A variety of tools for early warning and prediction are being developed and used.



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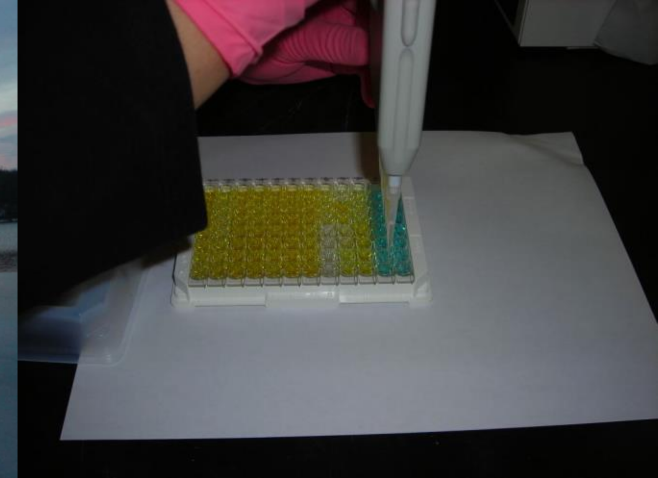


Additional Information:

http://ks.water.usgs.gov/cyanobacteria/

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