Cyanobacterial Blooms: Toxins, Tastes, and Odors

USGS Kansas Water Science Center Algal Toxin Team

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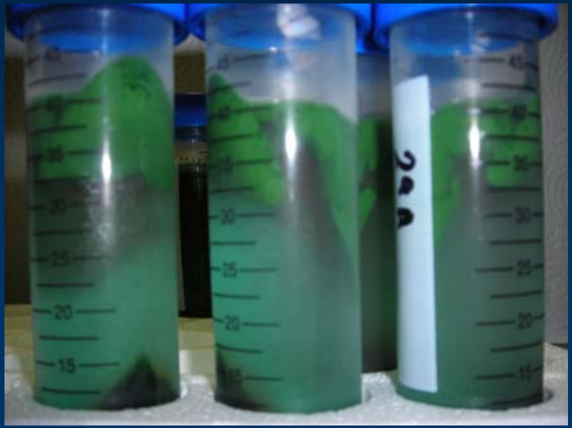
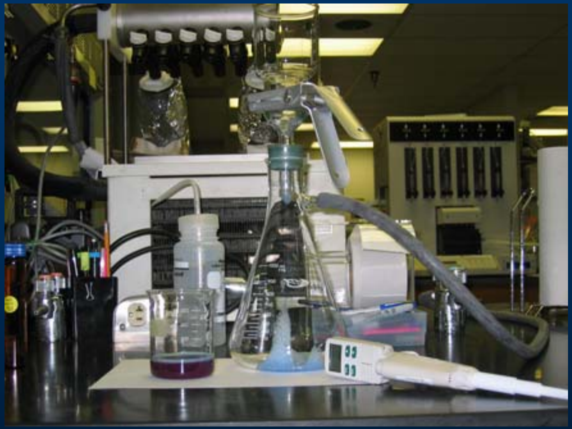
February 4, 2008

Overview

- Cyanobacterial (Blue-Green Algal) Toxins and Taste-and-Odor Compounds
- Microcystin in the Midwest
- Research Needs
- USGS Studies





Cyanobacterial toxins are "…anthropogenically amplified, but basically a natural phenomenon…"

I. Chorus, 1993

Binder Lake, IA Aug 2006

Thomas Lake, NE May 2006

USGS

- **Ecologic Concerns**
  - Zooplankton avoidance or death
  - Accumulation by mussels
  - Fish kills
  - Losses to bird and mammal populations
- **Economic Concerns**
  - Added drinking water treatment costs
  - Loss of recreational revenue
  - Death of livestock and domestic animals
  - Medical expenses
- **Health Concerns**
  - Tastes-and-Odors
    - Olfactory sensitivity at low concentrations (< 0.01 µg/L)
    - Chronic effects?
  - Toxins
    - Human and animal illness and death
    - EPA contaminant candidate list
    - Drinking water - microcystin
      - WHO guideline – 1.0 µg/L
      - Drinking-water treatment processes effectively remove most toxins
    - Recreational water – WHO guidelines for microcystin
      - Low Risk - < 10 µg/L
      - Moderate Risk - 10-20 µg/L
      - High Risk - > 20 µg/L
    - Known chronic effects

Toxins and Taste-and-Odor Compounds Produced by Cyanobacteria

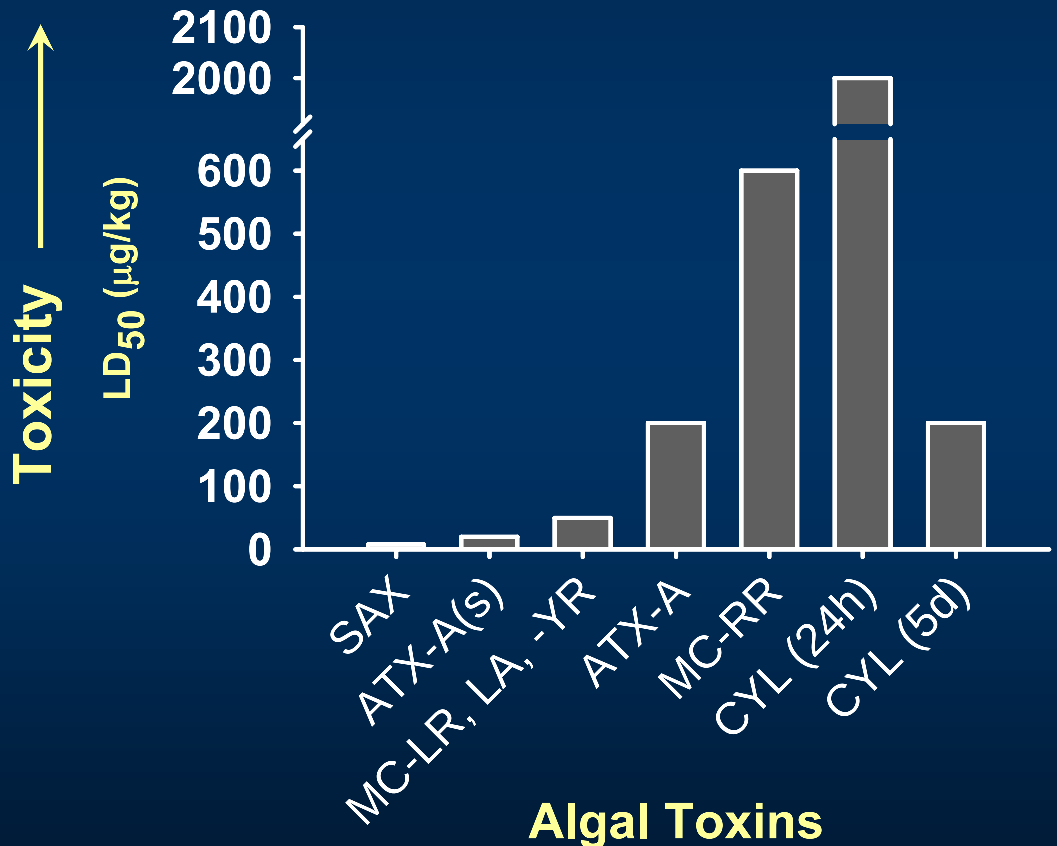
	Dermatoxins	Hepatotoxins		Neurotoxins		Taste/Odor	
		CYL	MC	ANA	BMAA	GEOS	MIB
Colonial/Filamentous							
Aphanizomenon	X	X	X	X	X	X	
Anabaena	X	X	X	X	X	X	?
Cylindrospermopsis	X	X			X		
Microcystis	X		X		X		
Oscillatoria/Planktothrix	X		X	X	X	X	X
Unicellular							
Synechococcus	X		X		X	X	X
Synechocystis	X		X		X		

Cyanobacterial Toxins and Taste-and-Odor Compounds Are Not Produced By The Same Biochemical Pathway But Patterns in Distribution Are Similar

- Extreme spatiotemporal variability
- Lack of relation with cyanobacterial community composition or chlorophyll concentration
- Coupling with lake/river processes as influenced by physiochemical, biological, hydrological, and meteorological factors

Upper Gar, IA Aug 2006

Cyanotoxins Exhibit a Wide Range of Toxicities and Toxic Effects and Are Currently Listed on the U.S. EPA Contaminant Candidate List

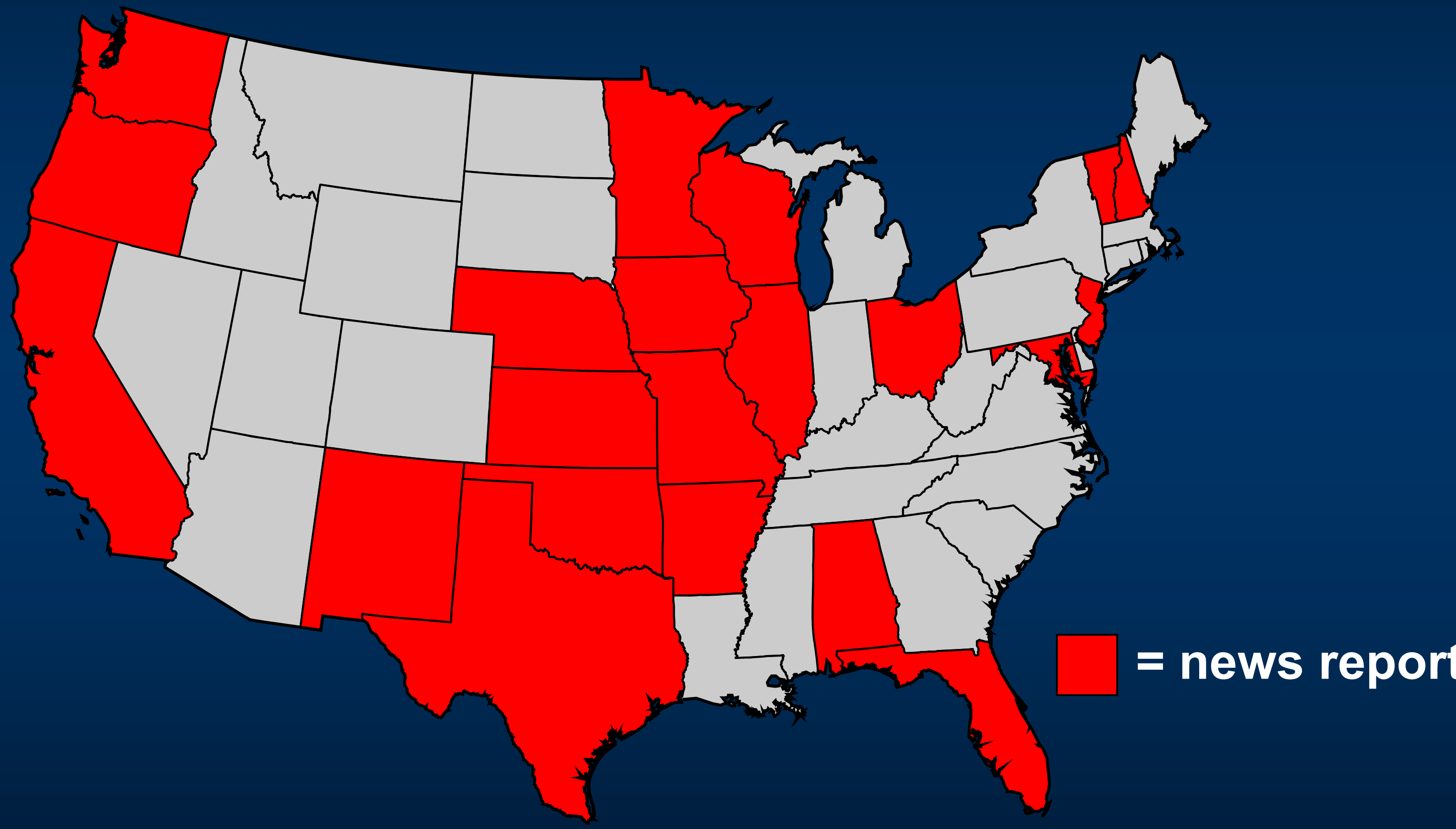


- **Acute Toxicity**
  - Neurotoxic
  - Hepatotoxic
  - Dermatoxic
- **Chronic Toxicity**
  - Carcinogen
  - Tumor Promotion
  - Mutagen
  - Teratogen
  - Embryolethality

USGS

After Chorus and Bartram, 1999

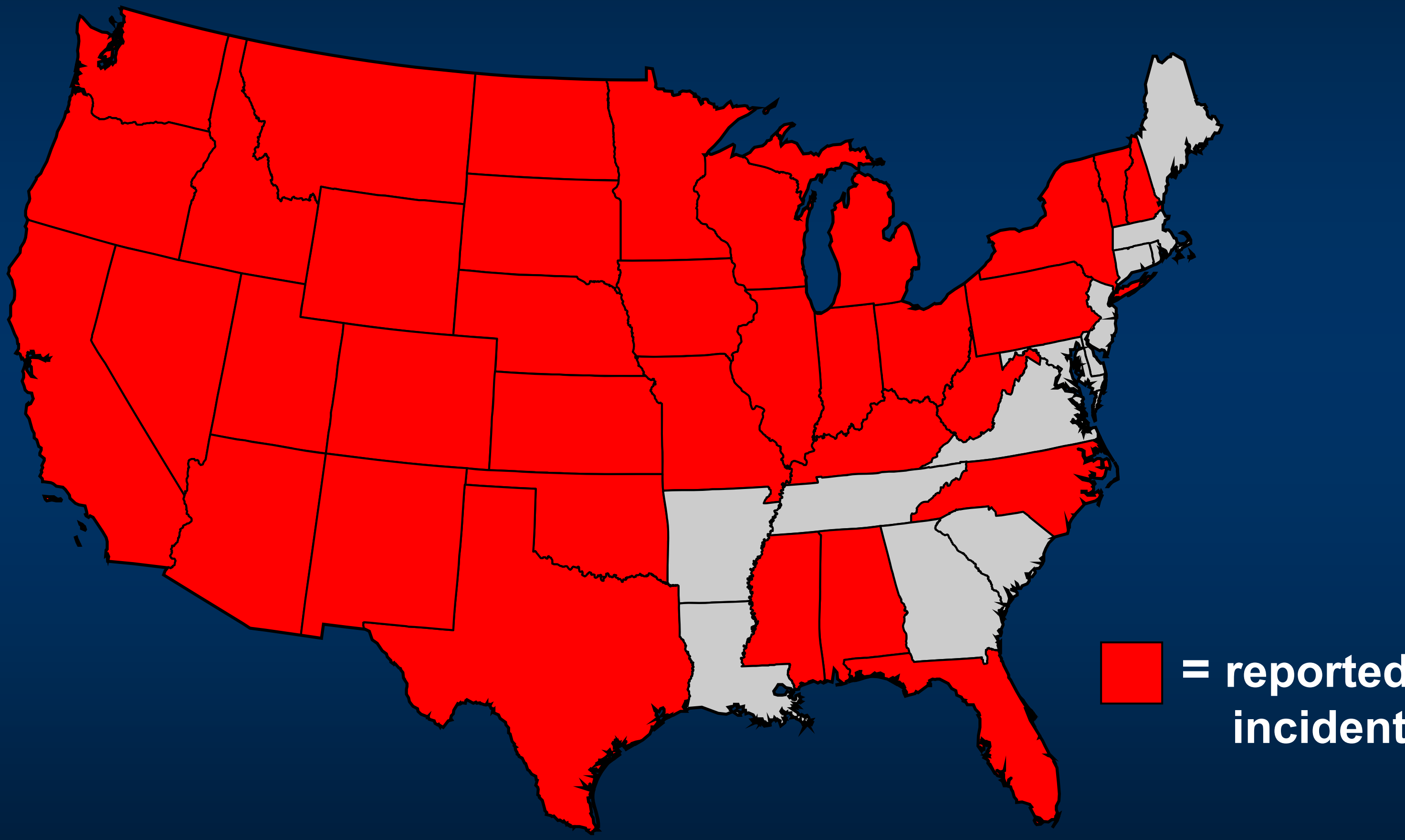
Cyanobacteria Made the News in at Least 21 U.S. States During 2006



USGS

After Graham, 2006 USGS FS-2006-3147

At Least 35 U.S. States have Anecdotal Reports of Human or Animal Poisonings Associated with Cyanotoxins



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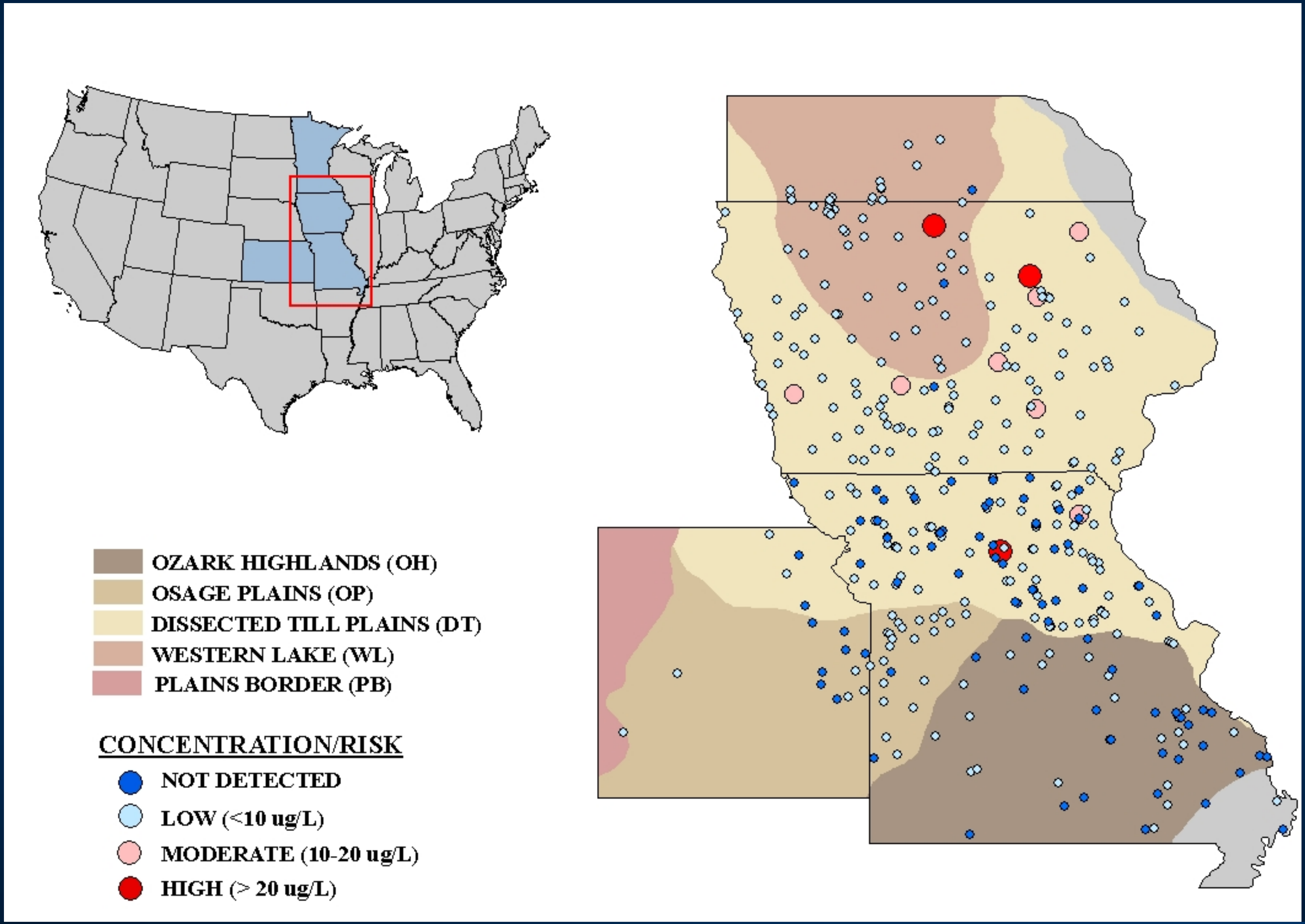
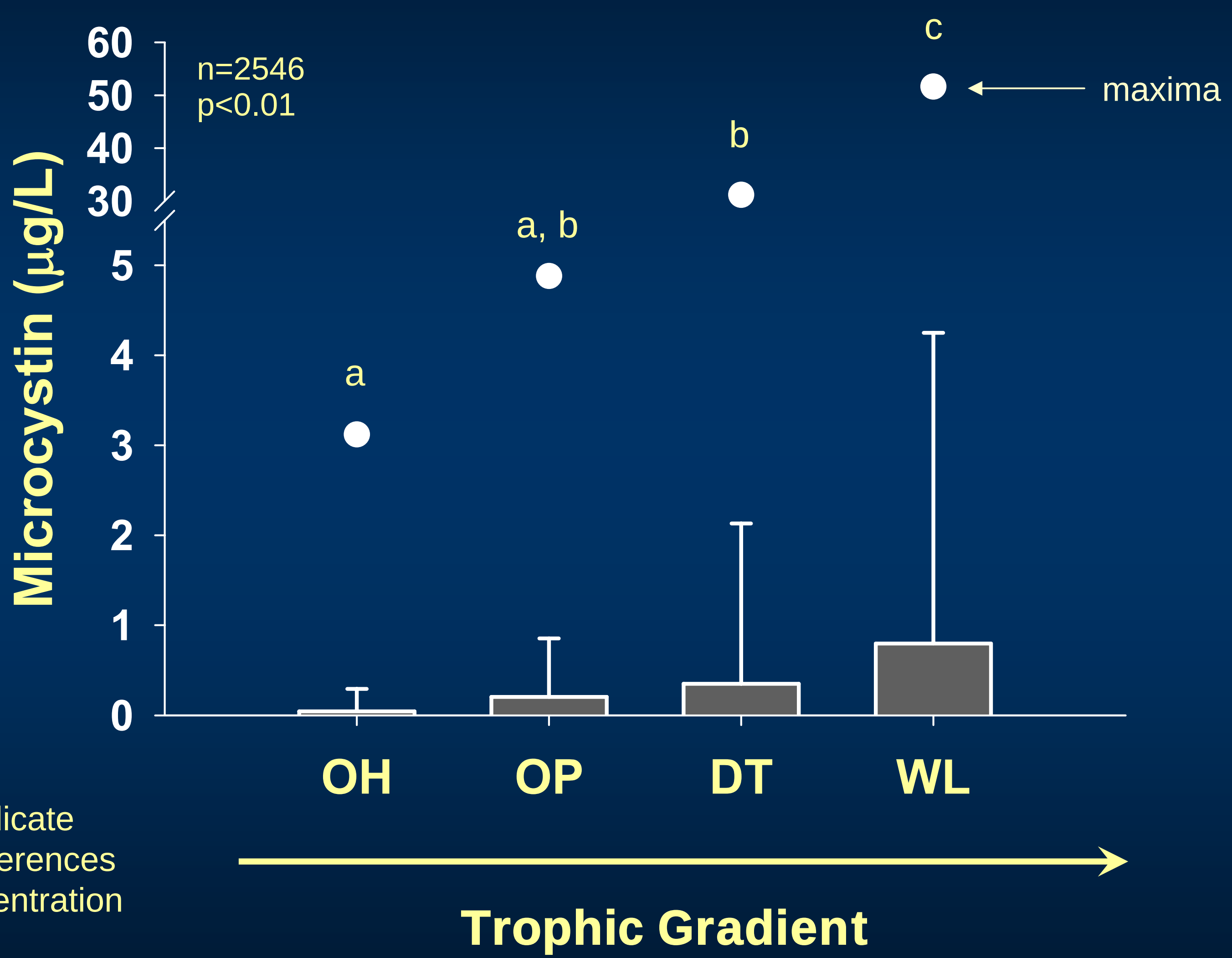
During 1999-2006 Microcystin was Detected in INTEGRATED PHOTIC ZONE Samples from 78% of Lakes (n=359) and TOTAL Concentrations Ranged from <0.1 to 52 µg/L



USGS

After Graham and others 2004 and 2006

Mean and Maximum TOTAL Microcystin Concentrations Significantly Increased Along the Natural Trophic Gradient in the Study Region

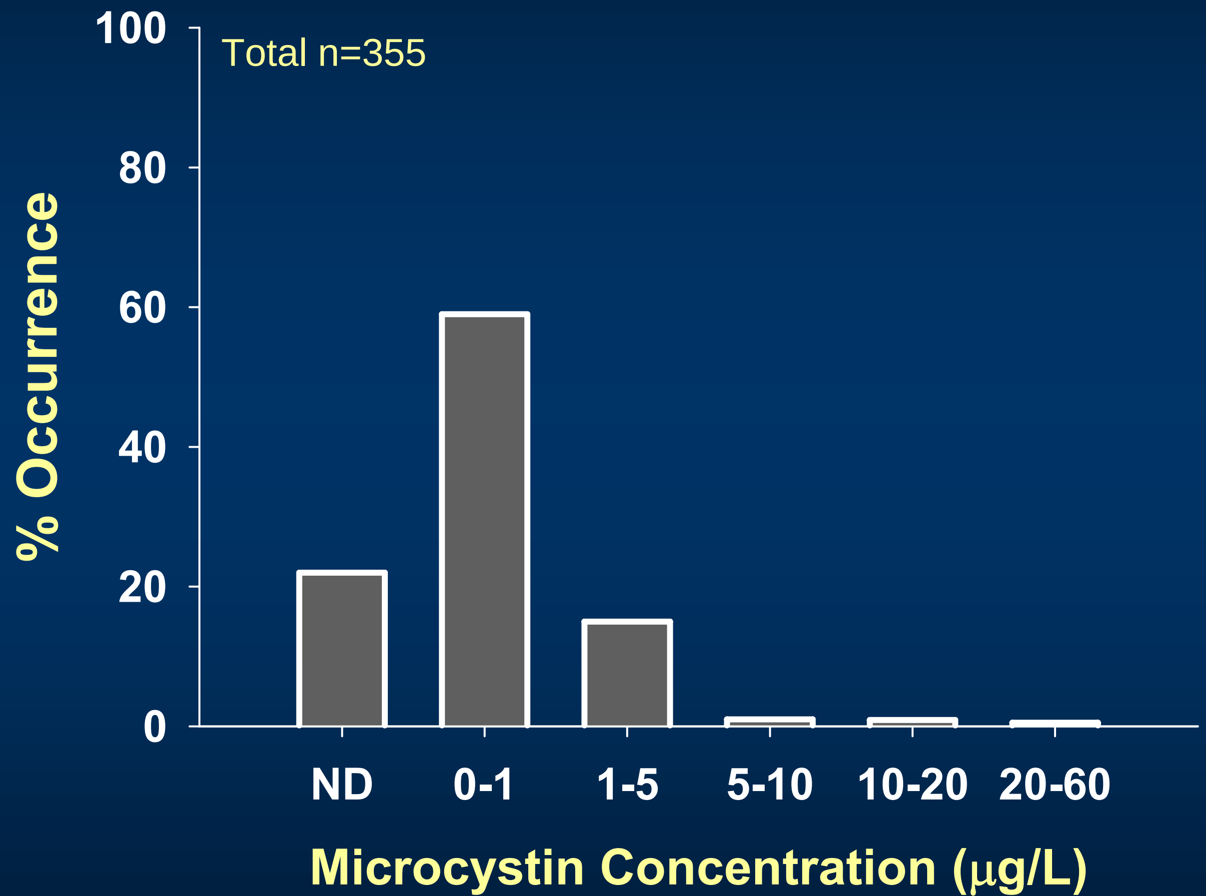


a, b, and c indicate significant differences in mean concentration

USGS

After Graham and others 2004 and 2006

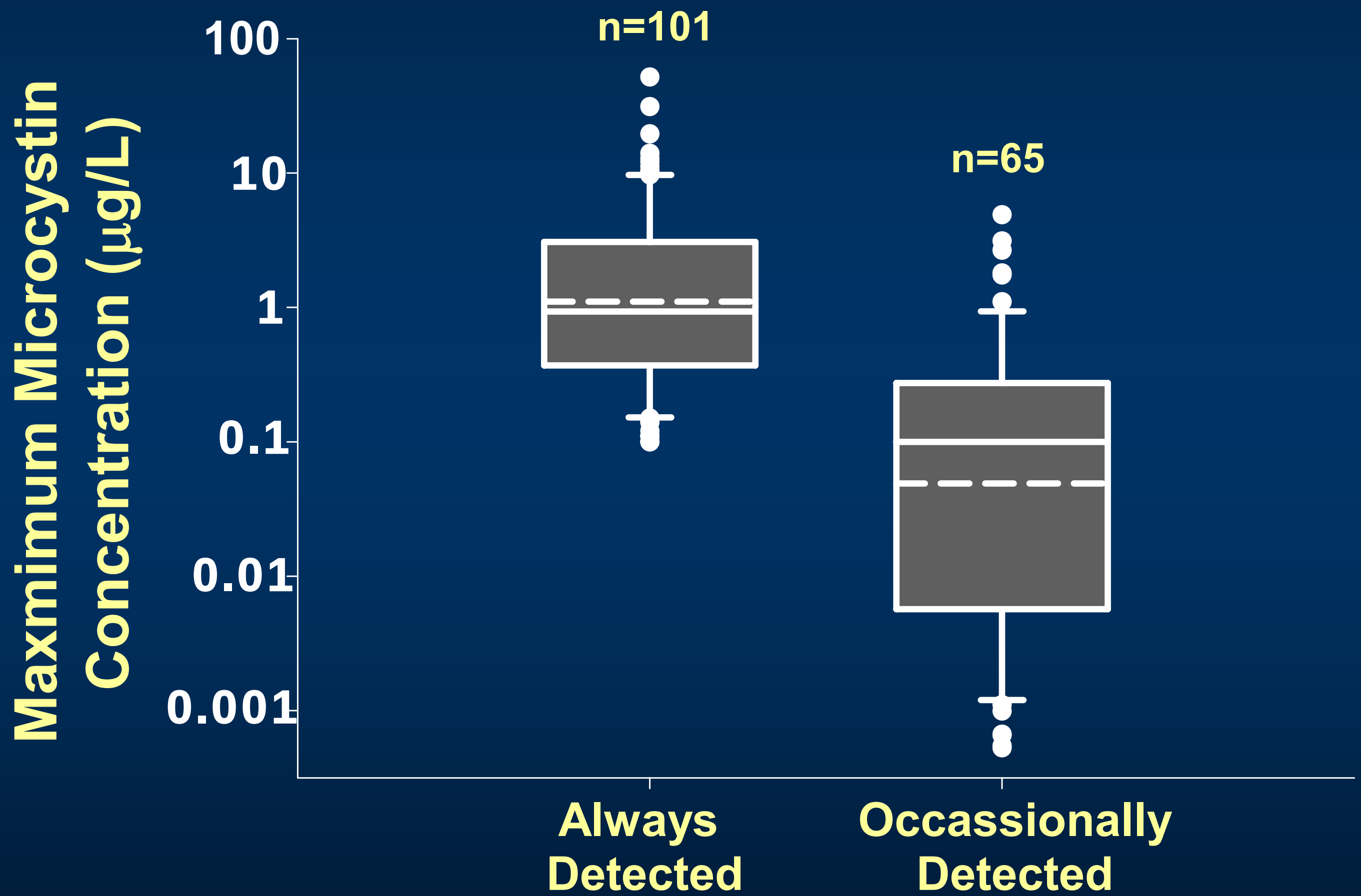
80% of All Lakes Sampled During 1999-2006 Had Maximum TOTAL Microcystin Concentrations ≤ 1 μg/L in Open Water Samples



USGS

After Graham and others 2004 and 2006

61% of Lakes Sampled During 3-6 Years Always Had Detectable Microcystin During Summer, and Microcystin Maxima Were Greatest in These Lakes



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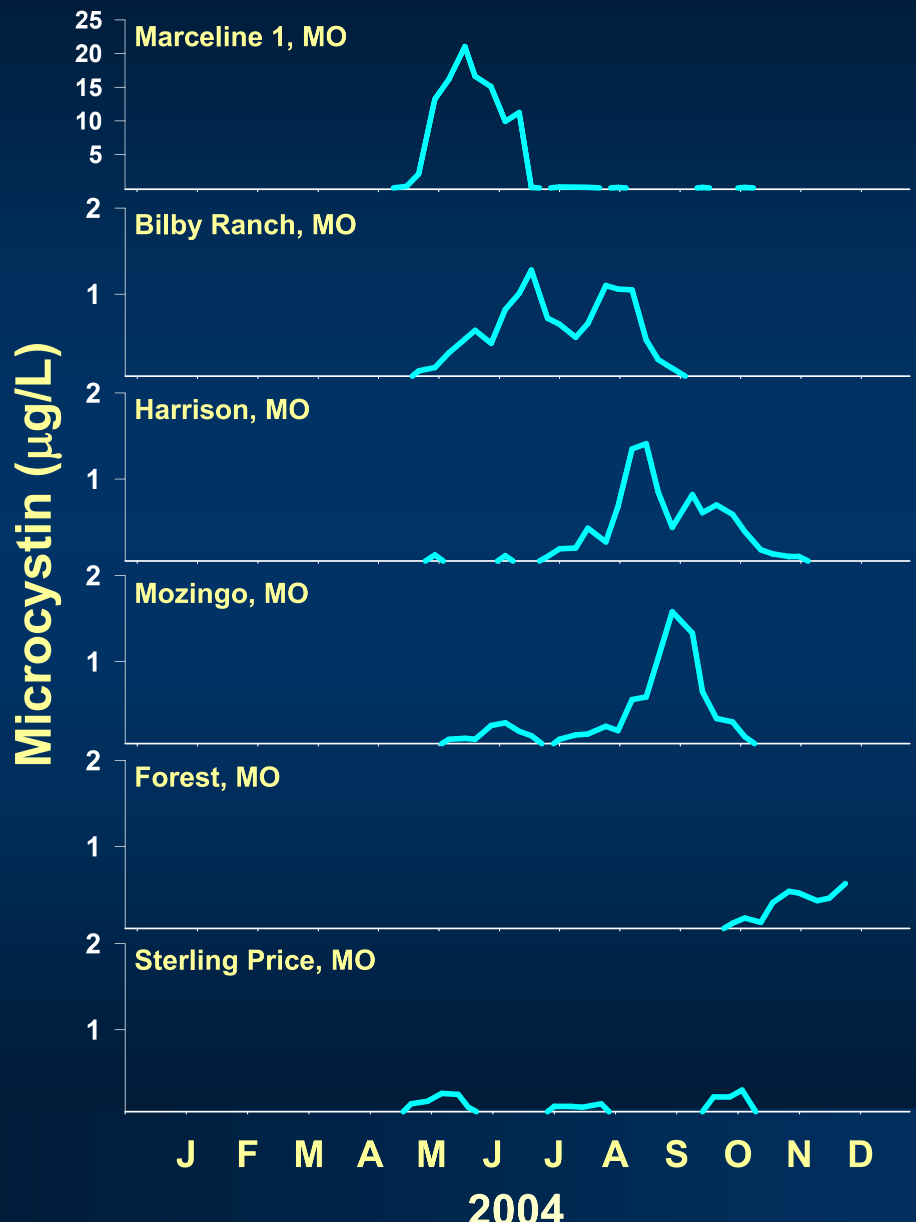
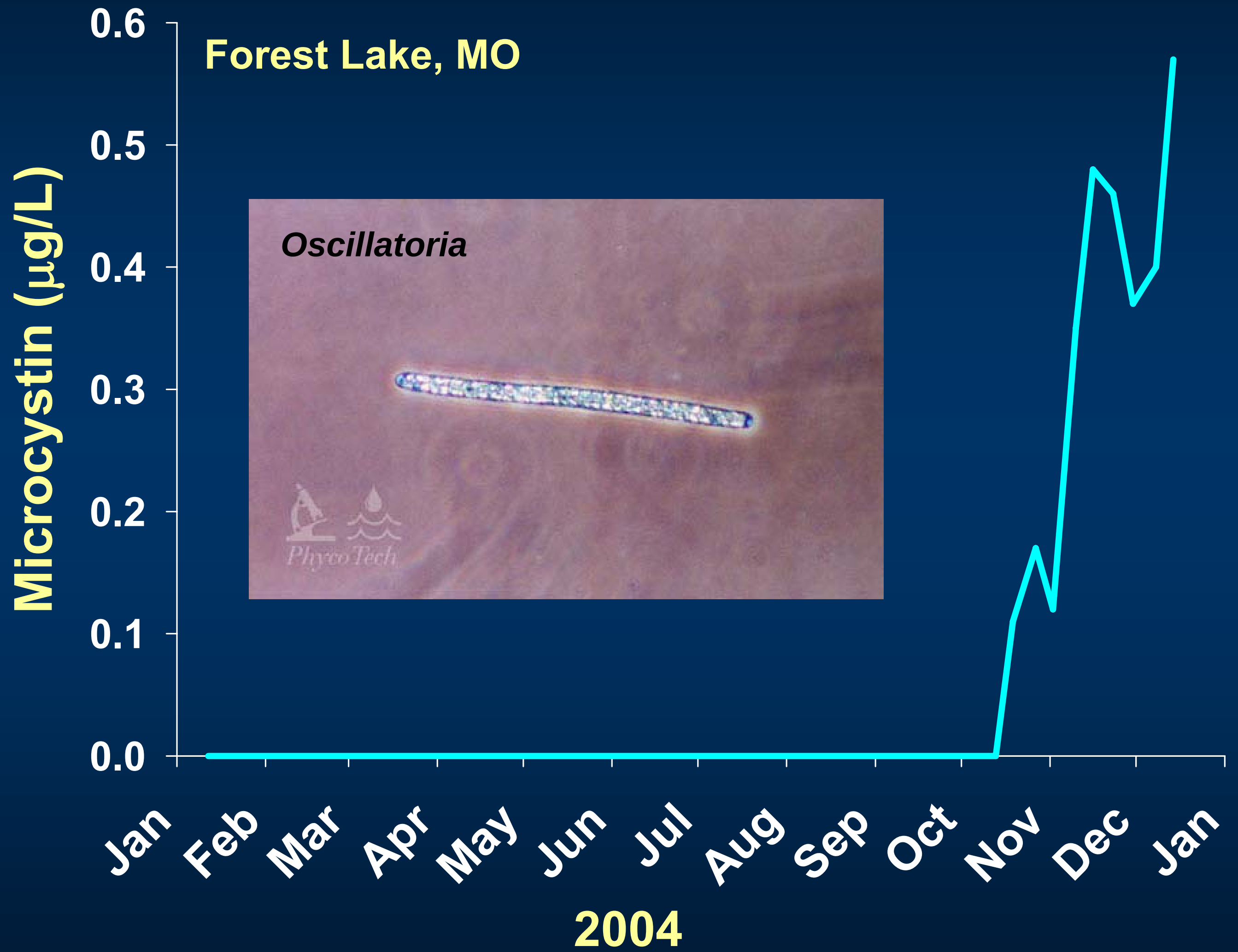
After Graham and others 2004 and 2006

Seasonal Patterns in Microcystin Concentration are Unique to Individual Lakes and Peaks May Occur Anytime Throughout the Year



Peak Microcystin Values May Occur in the Winter



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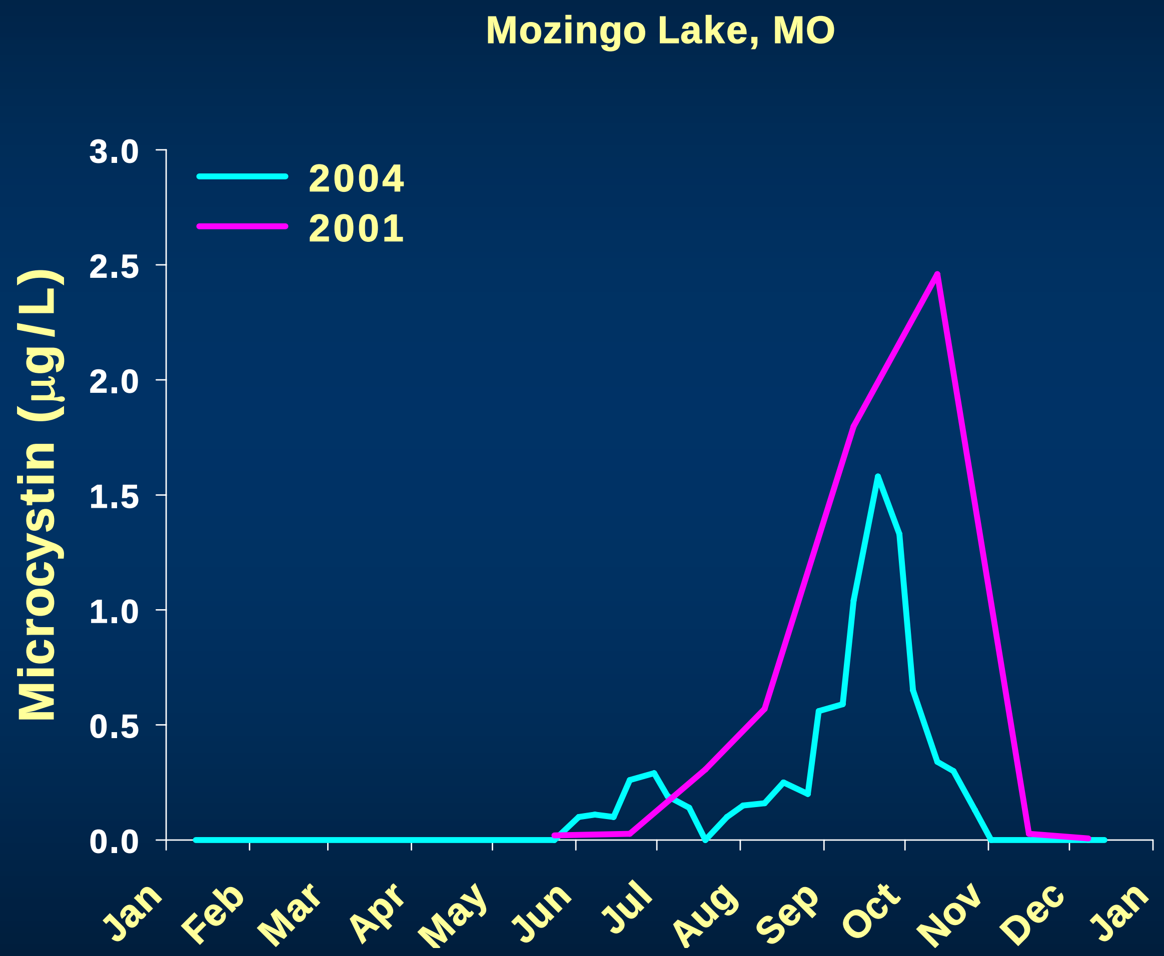
Seasonal Patterns Were Relatively Consistent Between Years in Some Lakes



USGS

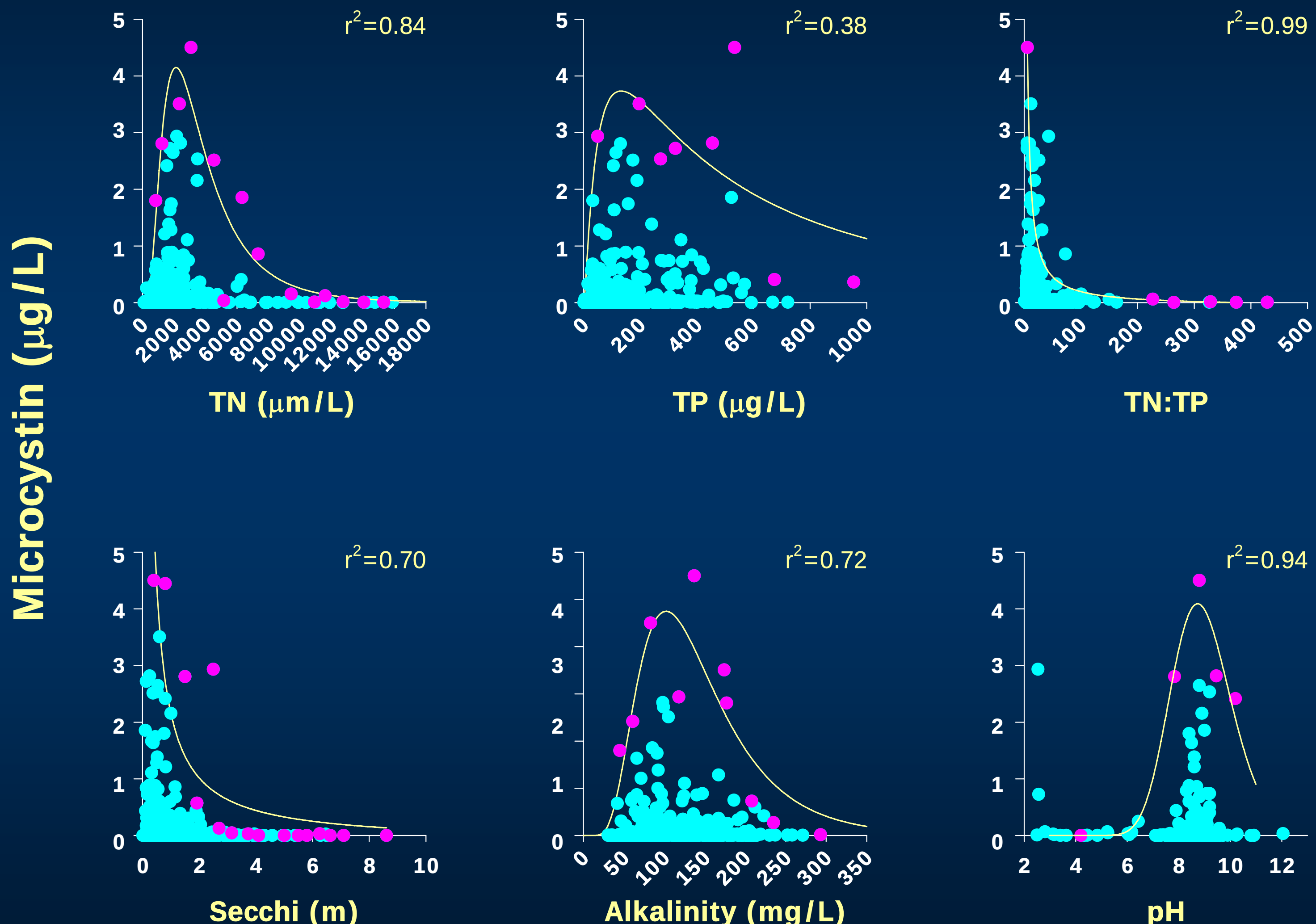
After Graham and Jones, 2006

Regionally, Microcystin Was Significantly Correlated With Factors That Affect Cyanobacterial Growth

Variable	r_s	p-value	n
Latitude	0.66	<0.01	800
Total Nitrogen (TN)	0.58	<0.01	795
Total Phosphorus (TP)	0.46	<0.01	795
Secchi	-0.27	<0.01	796
pH	0.17	<0.01	507
Alkalinity	0.15	<0.01	432
TN:TP	-0.15	<0.01	791

After Graham and others 2004

Regional Associations Between Microcystin and Environmental Variables Were Complex



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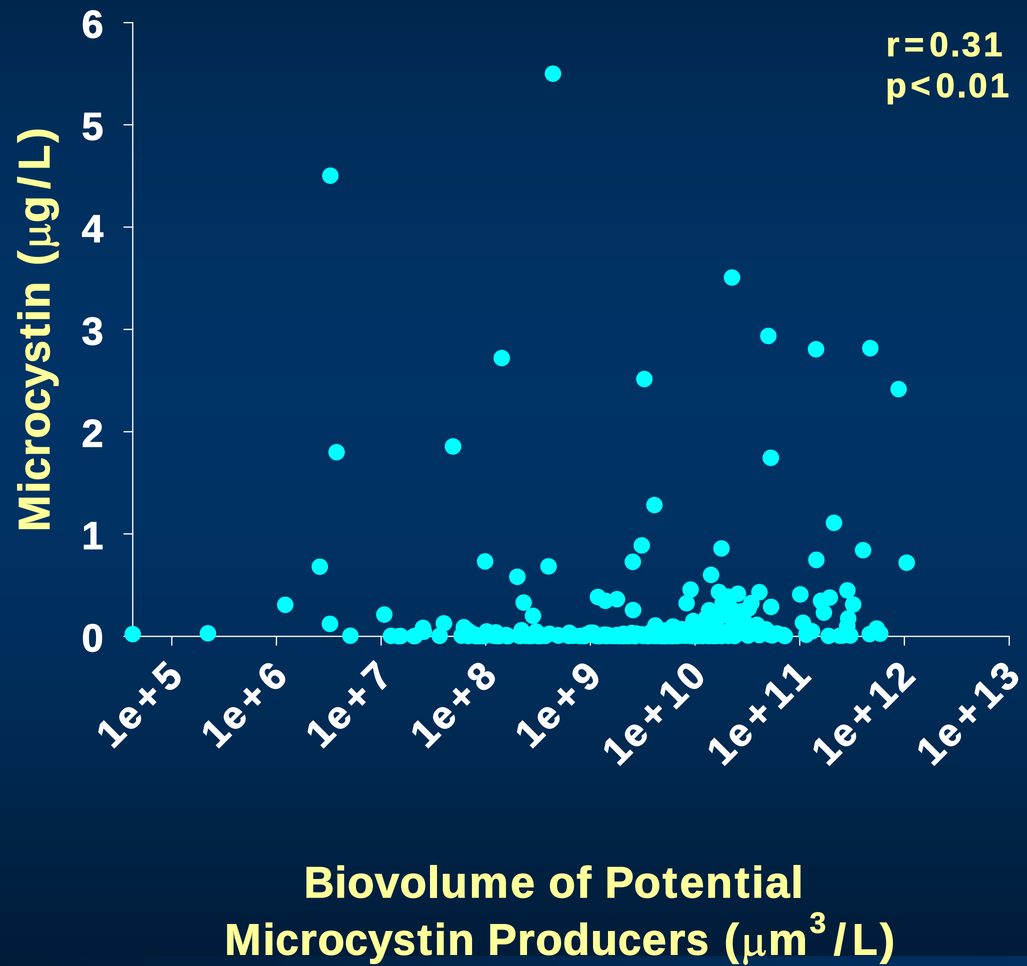
After Graham and others, 2004

Microcystin Was Not Strongly Correlated With Measures of the Cyanobacterial Community



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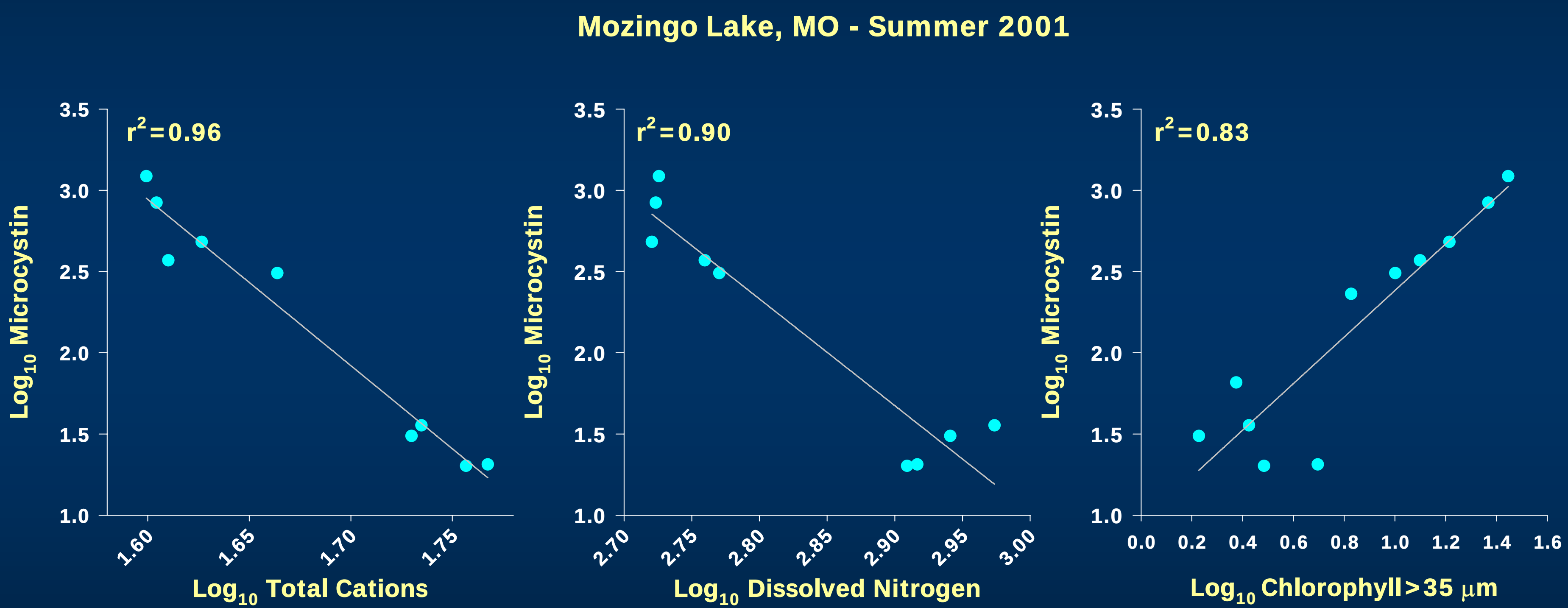
After Graham and others, 2004

Individual Lake Correlations Between Microcystin and Environmental Variables Were Linear



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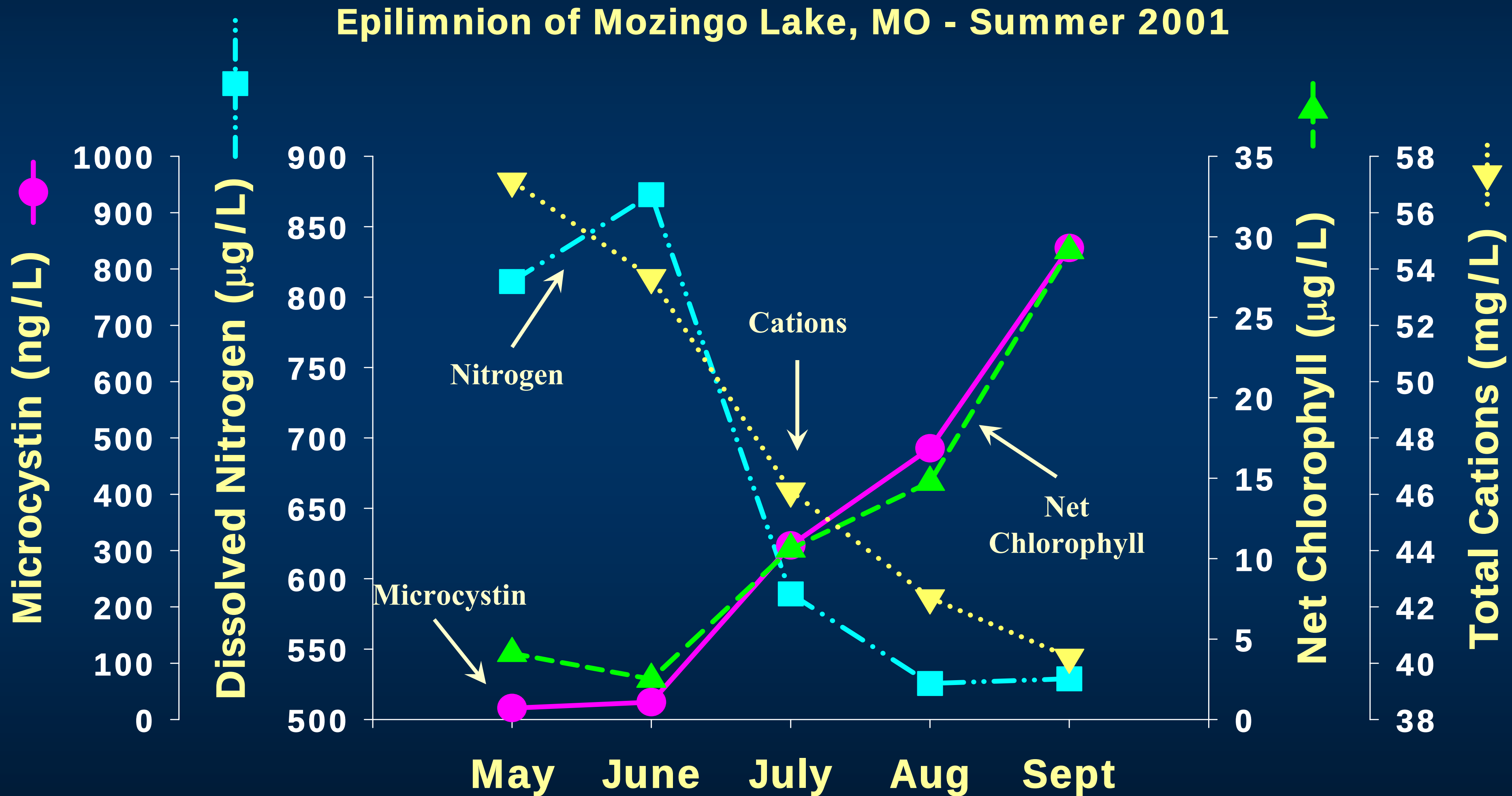
After Graham and others, 2006

Seasonal Patterns in Individual Lakes are Coupled with Seasonal Lake Processes, Including Stratification and Nutrient Loss from the Epilimnion



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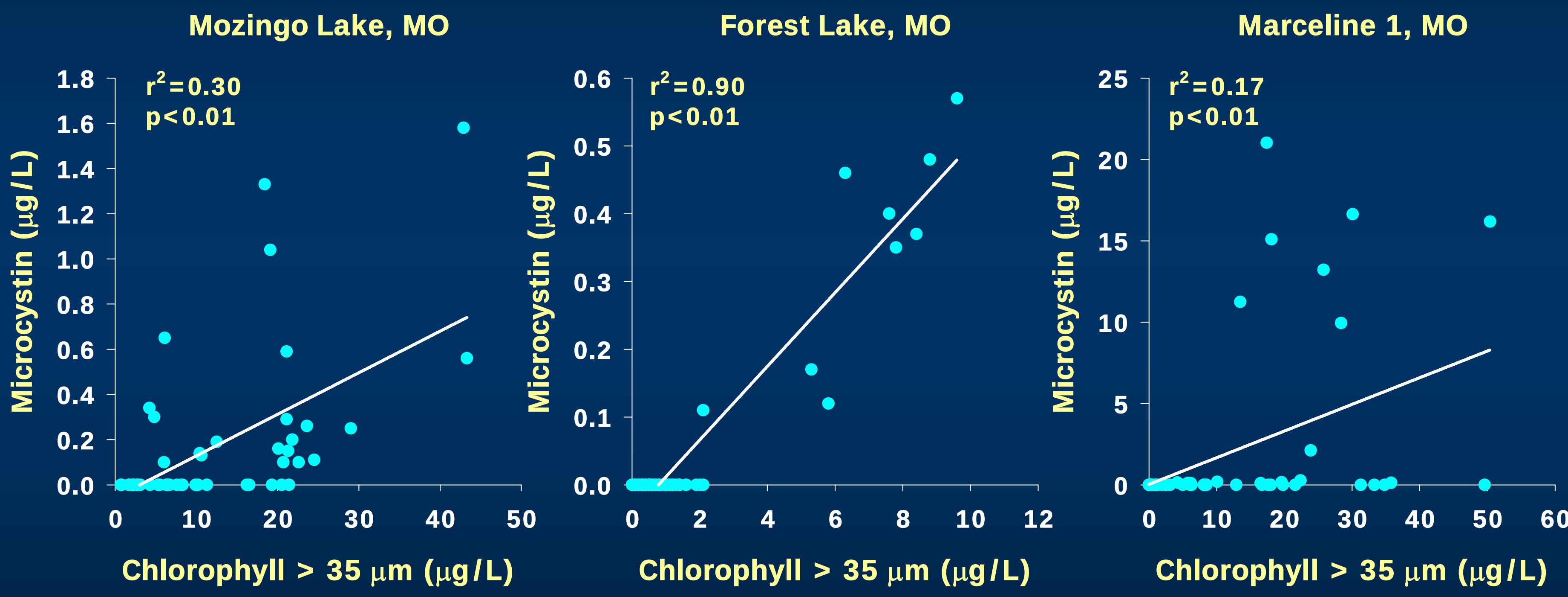
After Graham and others, 2006

Factors Most Strongly Correlated With Microcystin Vary Among Lakes and Years



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Microcystin in Midwestern Lakes - Conclusions

- Microcystin is common in the Midwest and may reach levels that can cause health concerns
- Seasonal patterns in microcystin are unique to individual lakes and maxima may occur in any season
- Regional relations between microcystin and environmental variables are complex
- Microcystin and environmental variables may be tightly coupled in individual lakes, but relations vary among lakes and years

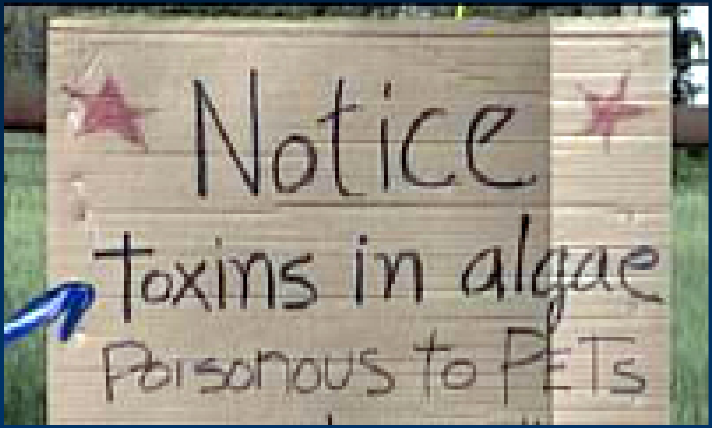
Elysian Lake, MN Aug 2006

Binder Lake, IA Aug 2006

USGS

Research Needs

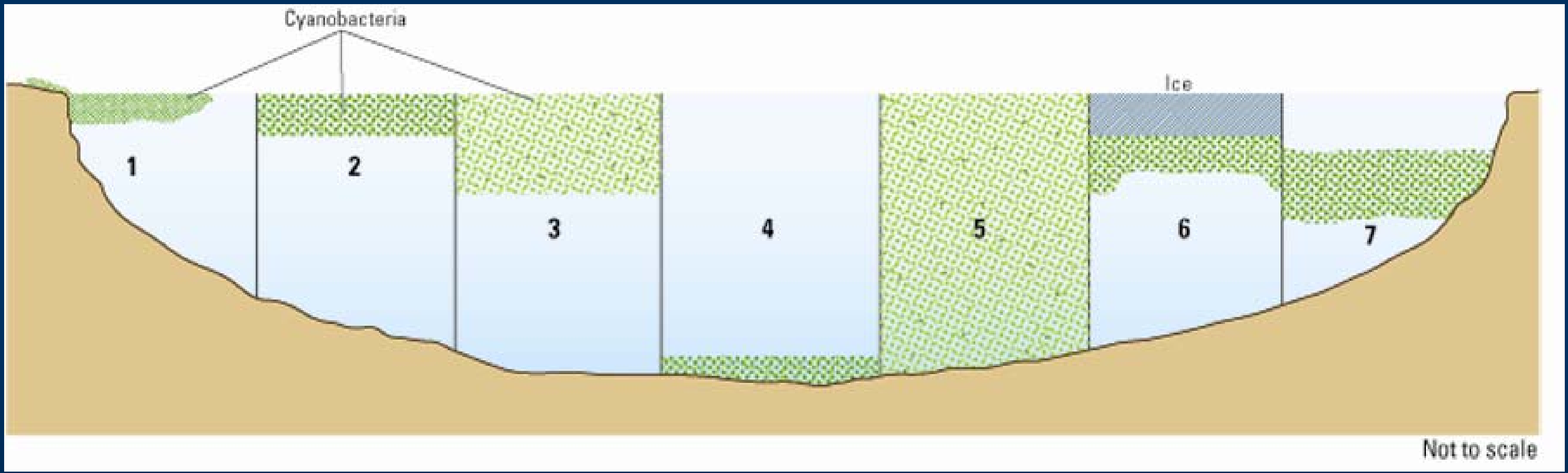
- Certified Standards
- Consistent Sampling Protocols
- Robust and Quantitative Analytical Methods for a Variety of Toxins
- Distribution of Microcystin Variants and Other Cyanobacterial Toxins
- Long Term Studies to Identify the Key Environmental Factors Leading to Toxic/Taste-and-Odor Producing Blooms
- Methods for Early Detection
- Predictive Models



Thomas Lake, NE May 2006
Photo from Omaha NBC News


Cheney Reservoir, KS June 2003
Photo Courtesy of KDHE

Consistent Sampling Protocols – Sample Location is Important



After Chorus and Bartram, 1999

Concentrations of Toxins and Taste-and-Odor Compounds May Vary by Orders of Magnitude at Different Sample Locations Within a Lake

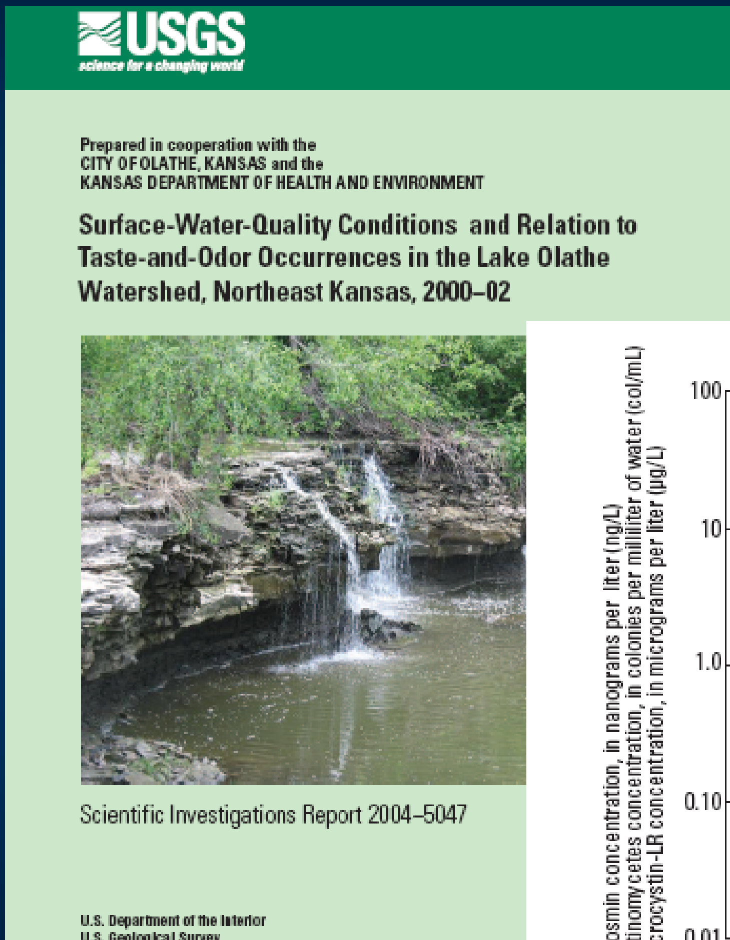
Microcystin: 13 µg/L
Geosmin: 0.25 µg/L

Microcystin: 4 µg/L
Geosmin: Not Detected

Cheney Reservoir, KS September 2006

USGS

Actinomycetes Bacteria Also Produce Geosmin and MIB and May Contribute to Taste-and-Odor Problems in Drinking Water Supplies



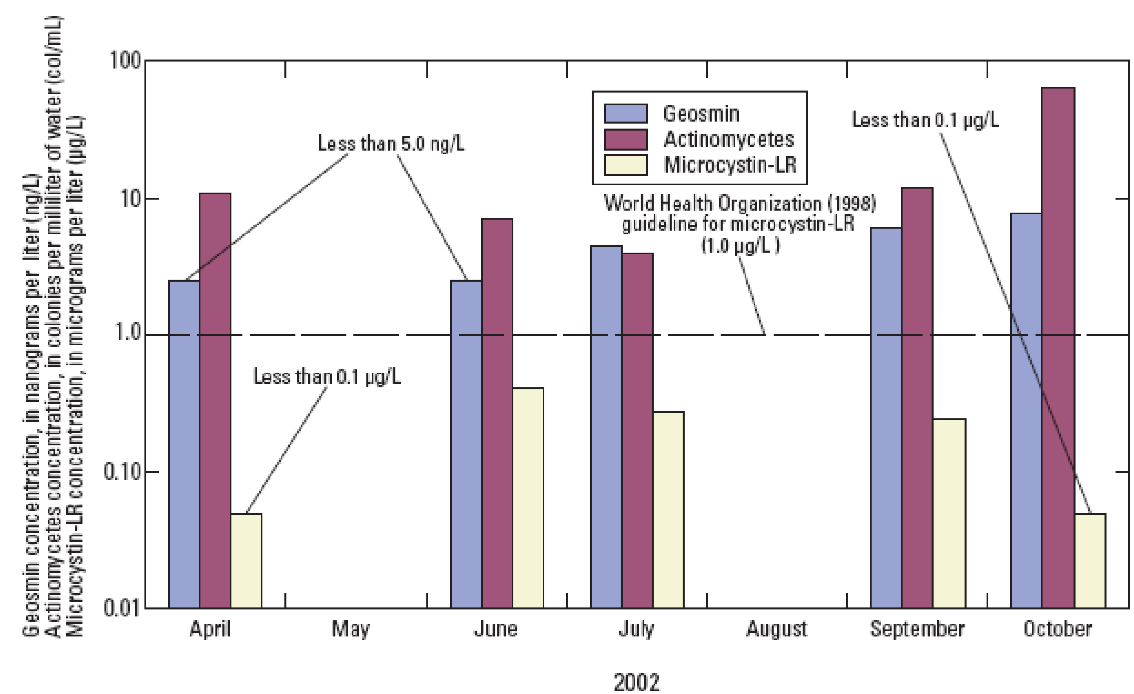


Figure 14. Concentrations of geosmin, actinomycetes, and microcystin in Lake Olathe near dam (site 2), April–October 2002.

Consistent Sampling Protocols – Collection Technique is Important

Plankton Net Sampling

Whole Water Sampling

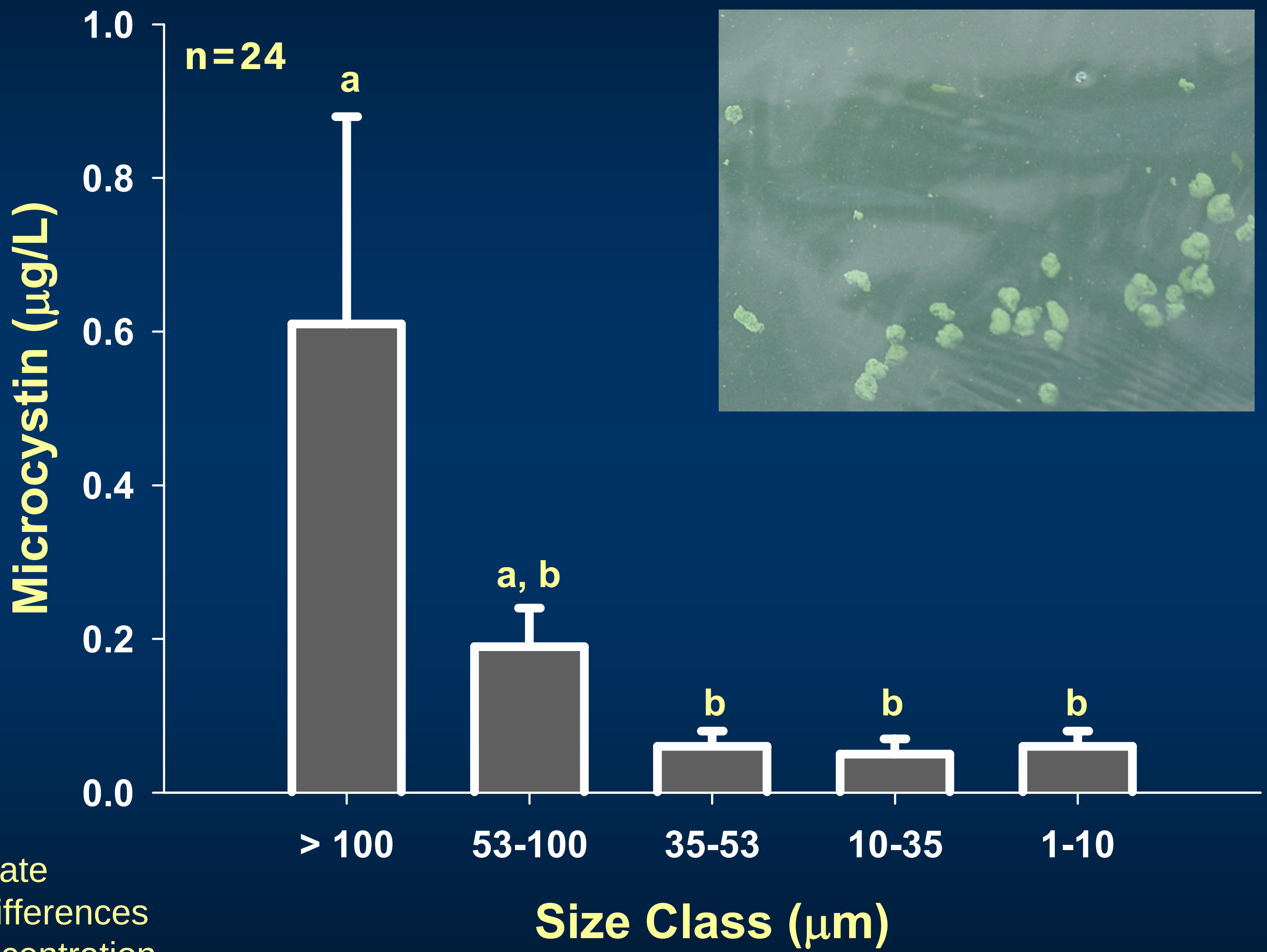
Filter/Filtrate Sampling

Total Toxin

Dissolved Phase Toxin

Particulate Toxin

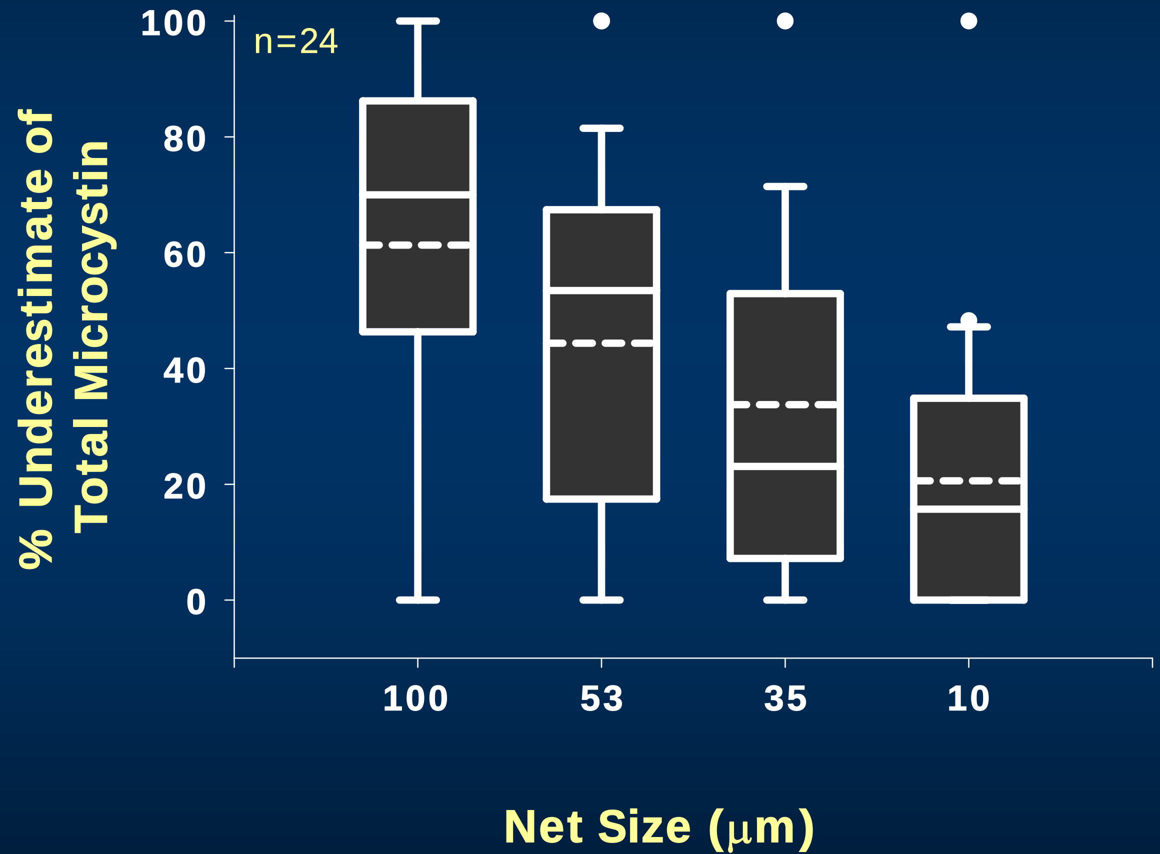
Microcystin Concentrations Decreased with Decreases in Cyanobacterial Size Class



Letters indicate significant differences in mean concentration

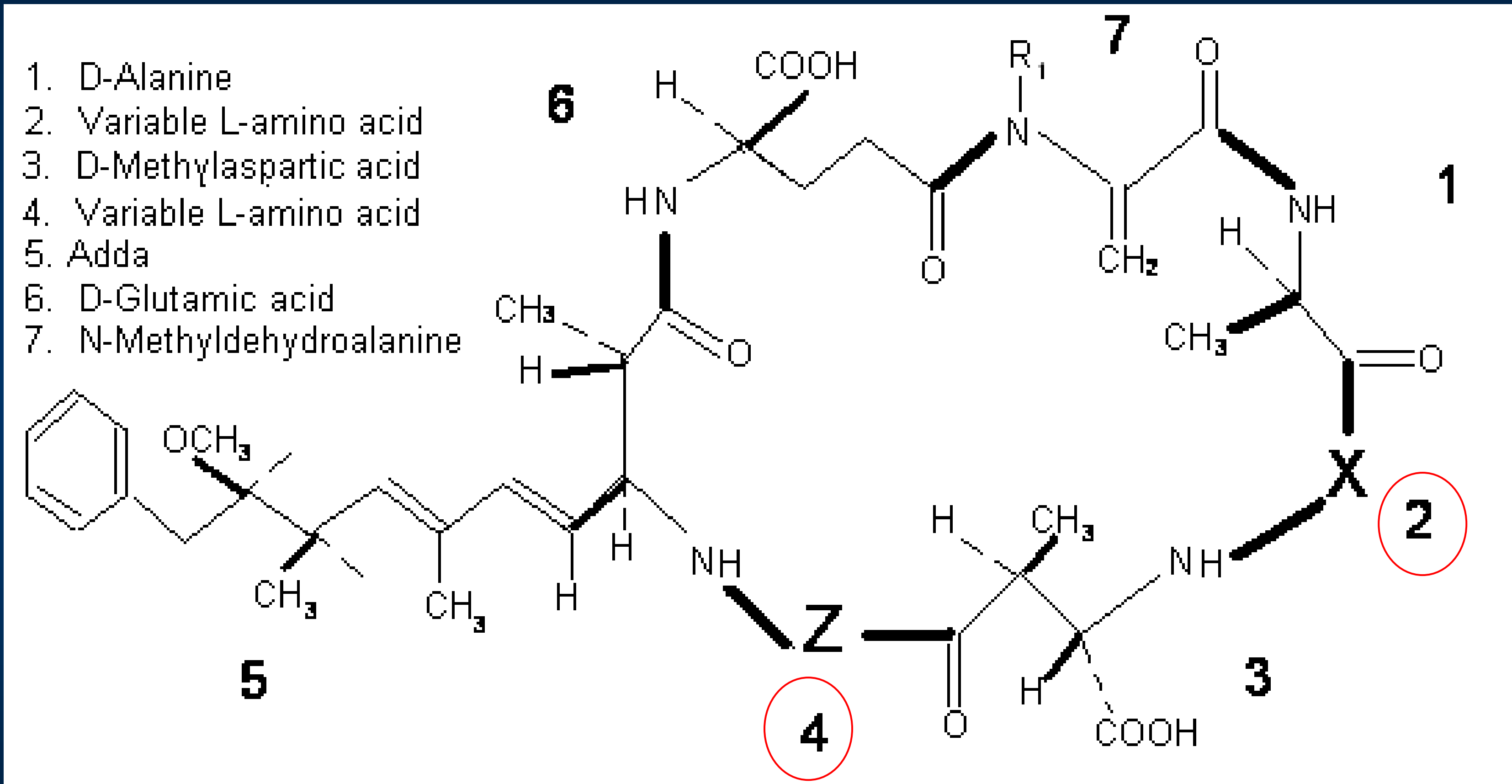
Graham and Jones, 2007

Use of Plankton Nets Consistently Underestimated Microcystin Concentrations Relative to Whole Water Samples



Graham and Jones, 2007

There are Currently Over 80 Known Microcystin Variants



From McKinnon, 2003

Analytical Methods for Cyanotoxins - Bioassays

Bioassays

Enzyme-linked immunosorbent assays (ELISA)
- Microcystins/Nodularin
- Cylindrospermopsins
- Saxitoxins

Inhibition Assays
- Protein Phosphatase Inhibition (Microcystins/Nodularin)

Radioassays
- Neurotoxicity (Anatoxins/ Saxitoxins)

Advantages

Easy to Use

Rapid

Inexpensive

Useful screening tools

May indicate toxicity

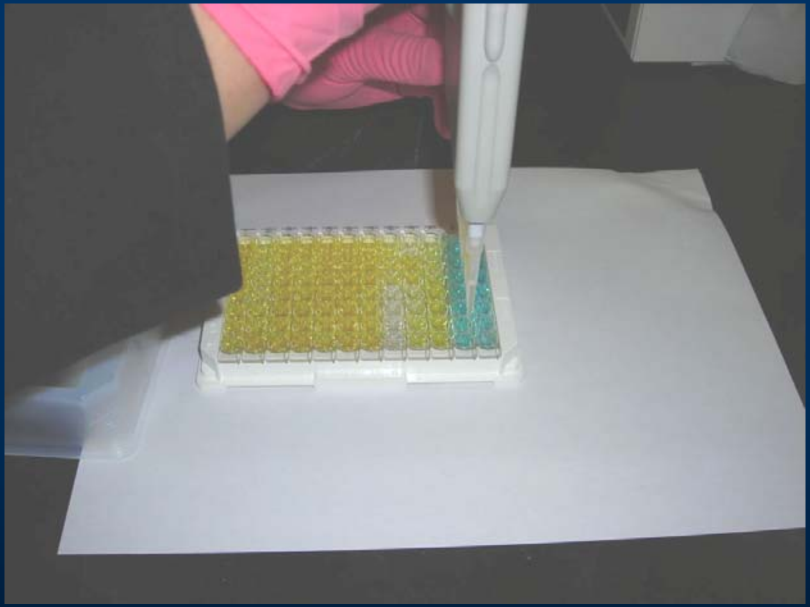
Disadvantages

Cross-reactivity

Matrix effects

Semi-quantitative

Radioassays use radio-labeled isotopes



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Analytical Methods for Cyanotoxins – Gas Chromatography

Gas Chromotography (GC)

Flame ionization detector (FID)

Mass spectrometry (MS)

Advantages

Specificity

Intermediate cost

Quantitative

Disadvantages

Availability of analytical standards

Derivitization likely required

Not all compounds are amenable to derivitization

GC-FID requires further confirmation

Sample concentrating may be necessary

USGS

Analytical Methods for Cyanotoxins – Liquid Chromatography

Liquid Chromotography (LC)

UV-Visible (UV-Vis)
Fluorescence
Mass spectrometry (MS)
Tandem MS (MS/MS)
Ion trap MS (ITMS)
Time of flight MS(TOFMS)

Advantages

Specificity

Derivitization not typically necessary

Many toxins amenable to LC techniques

Multi-analyte methods are cost-effective

TOFMS good for determining unknowns (not quantitative)

Disadvantages

Availability of analytical standards

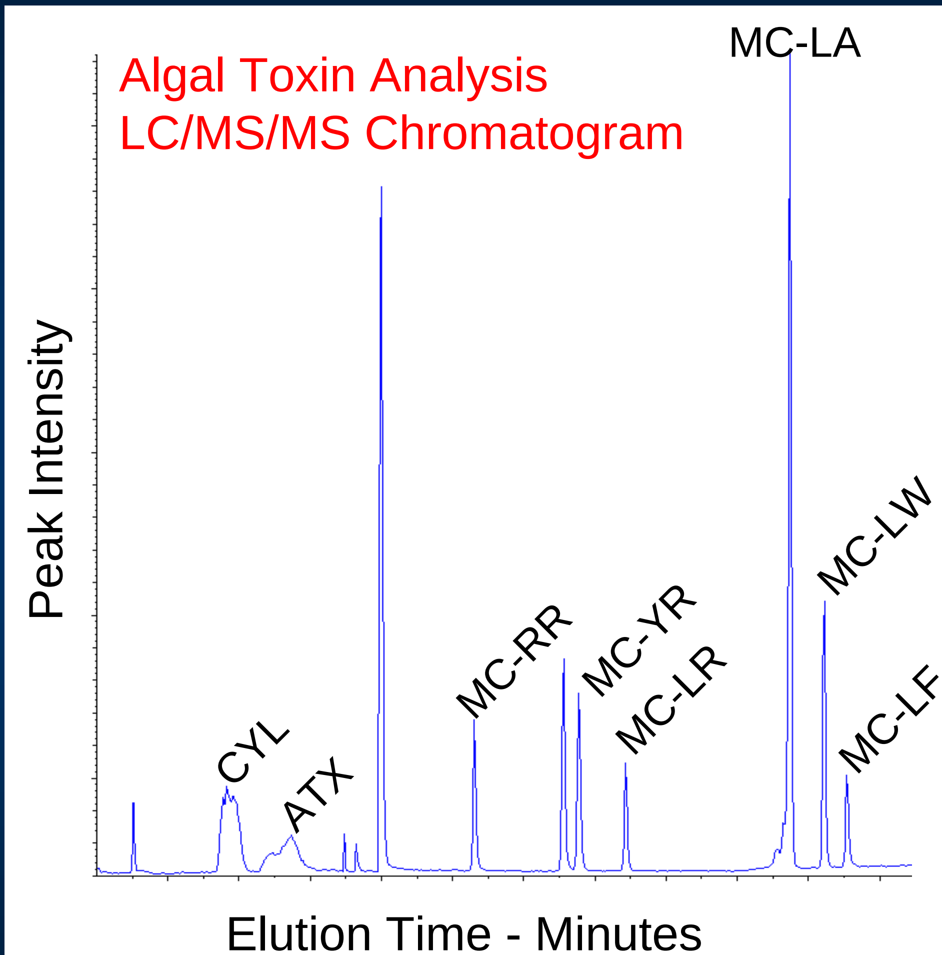
Matrix effects

Expensive

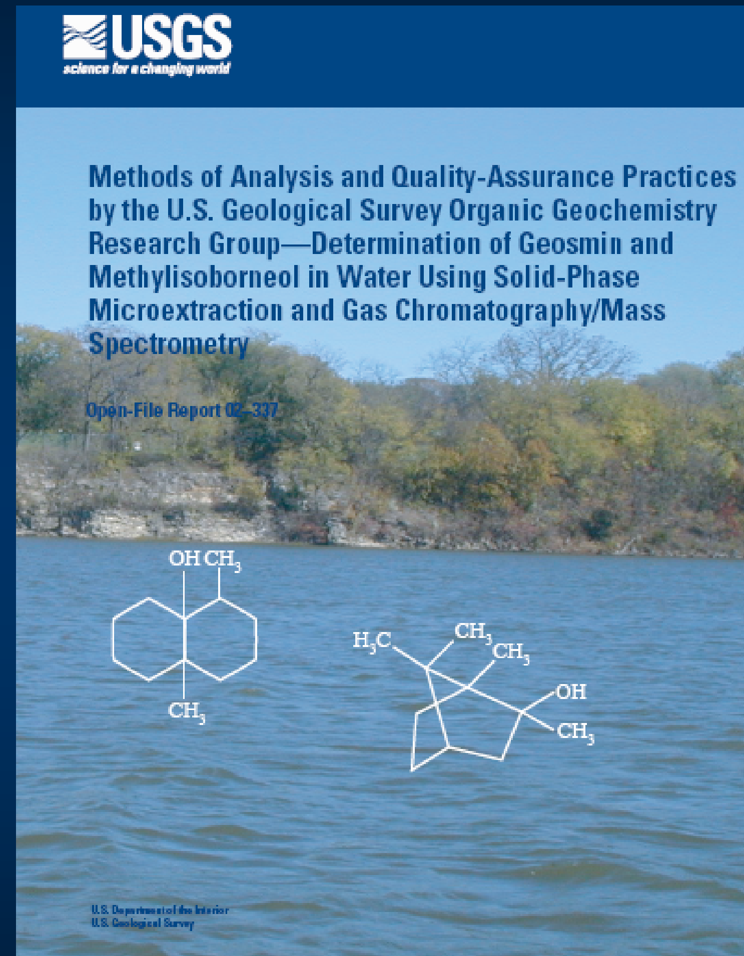
Sample concentrating may be necessary

Spectroscopic techniques may require further confirmation

Robust and Quantitative Analytical Methods - Capabilities of the USGS Organic Geochemistry Research Laboratory



Toxin MRL's: ~25 ppt

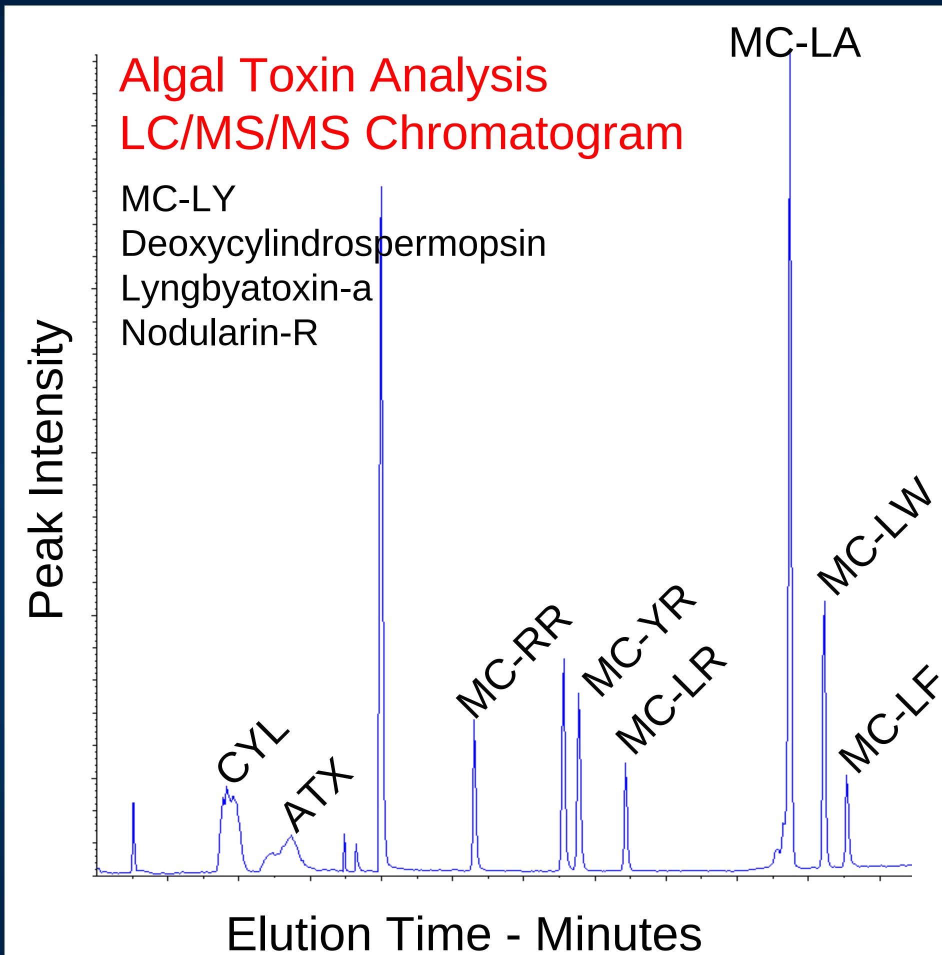


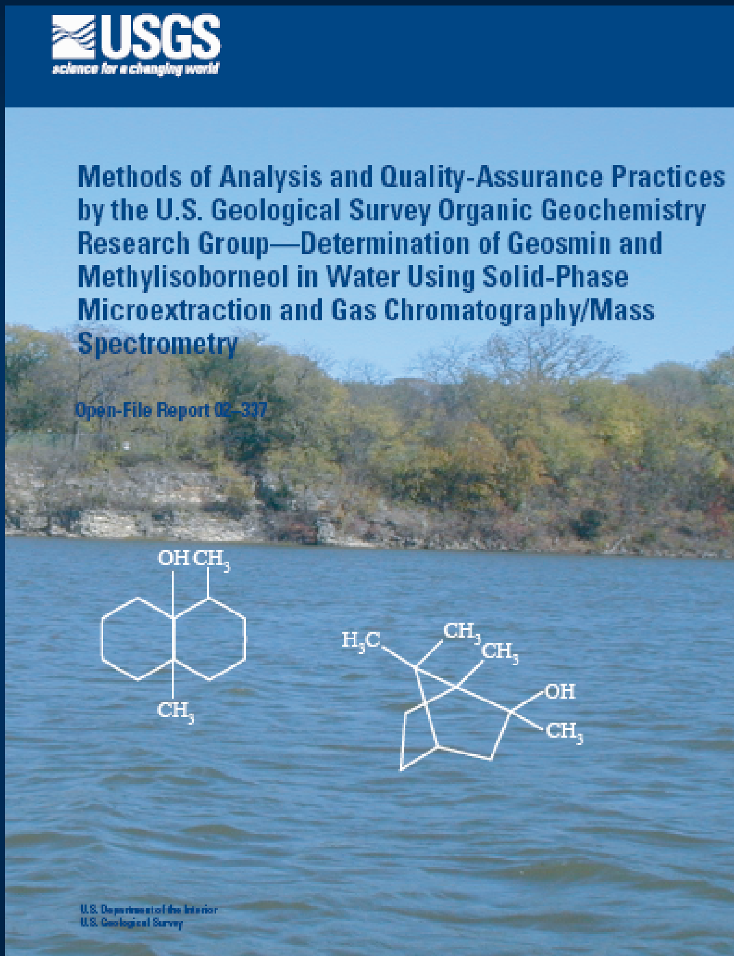
Geosmin and MIB MRL: 5 ppt

USGS

http://ks.water.usgs.gov/Kansas/researchlab.html

Robust and Quantitative Analytical Methods - Capabilities of the USGS Organic Geochemistry Research Laboratory





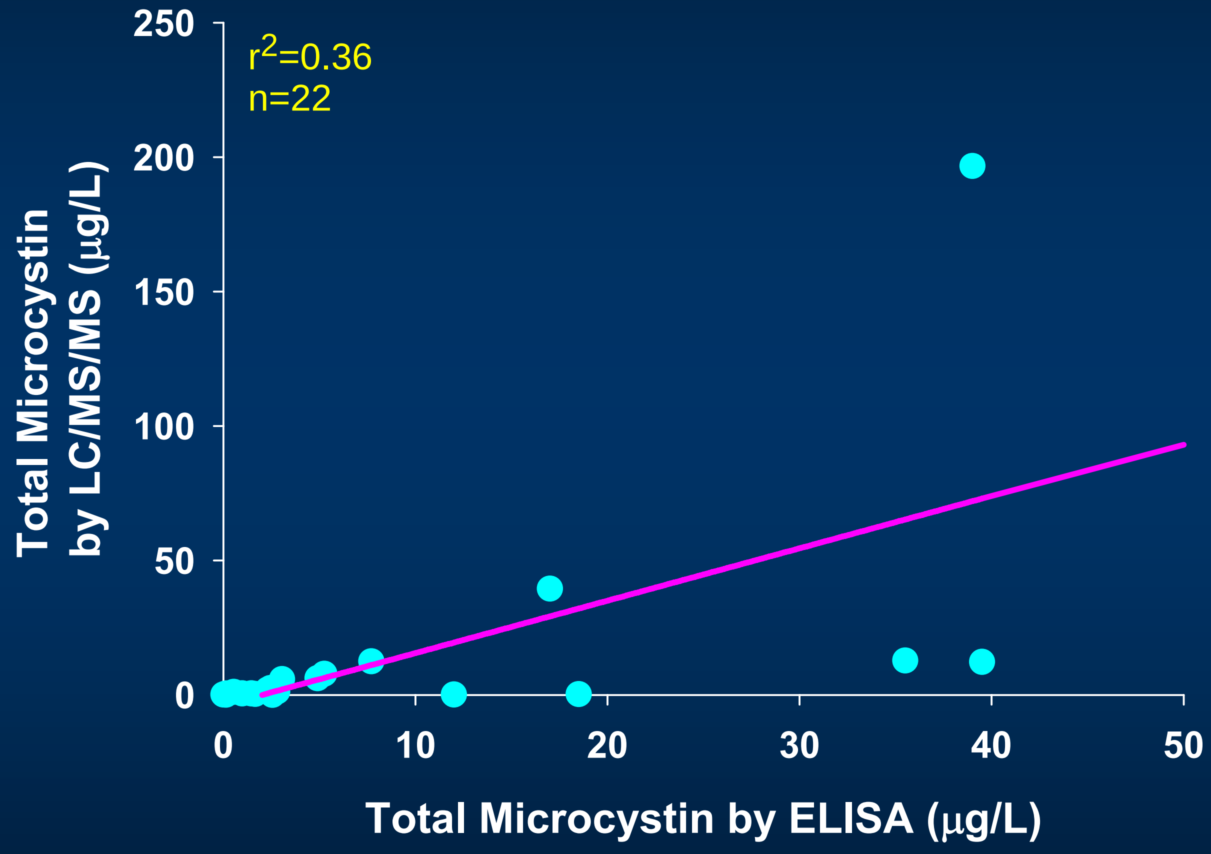
Toxin MRL’s: ~25 ppt

Geosmin and MIB MRL: 5 ppt

USGS

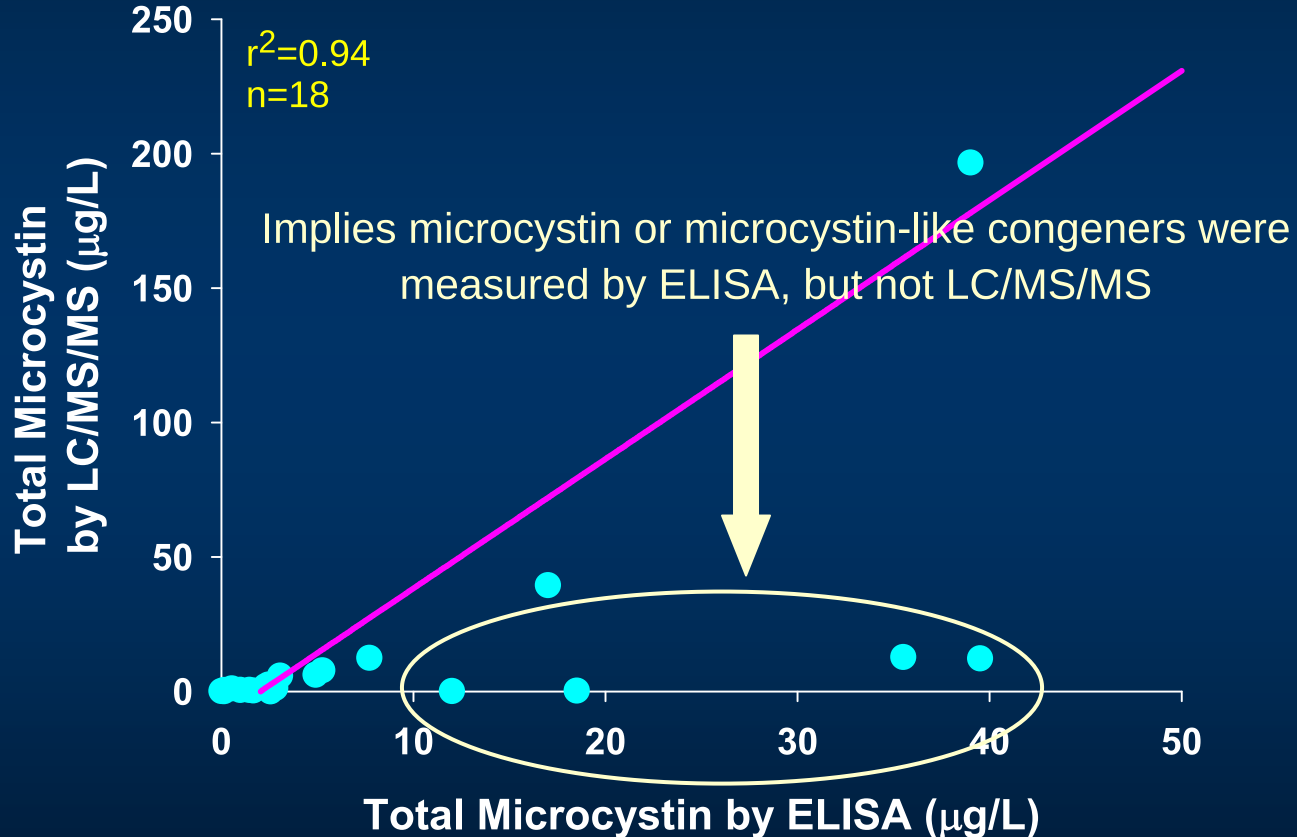
http://ks.water.usgs.gov/Kansas/researchlab.html

Total Microcystin Comparison – ADDA Specific ELISA vs LC/MS/MS for –LR, -RR, -LY, -YR, -LA, -LW, and –LF variants



USGS

ELISA (ADDA) can be a useful tool in conjunction with LC/MS/MS

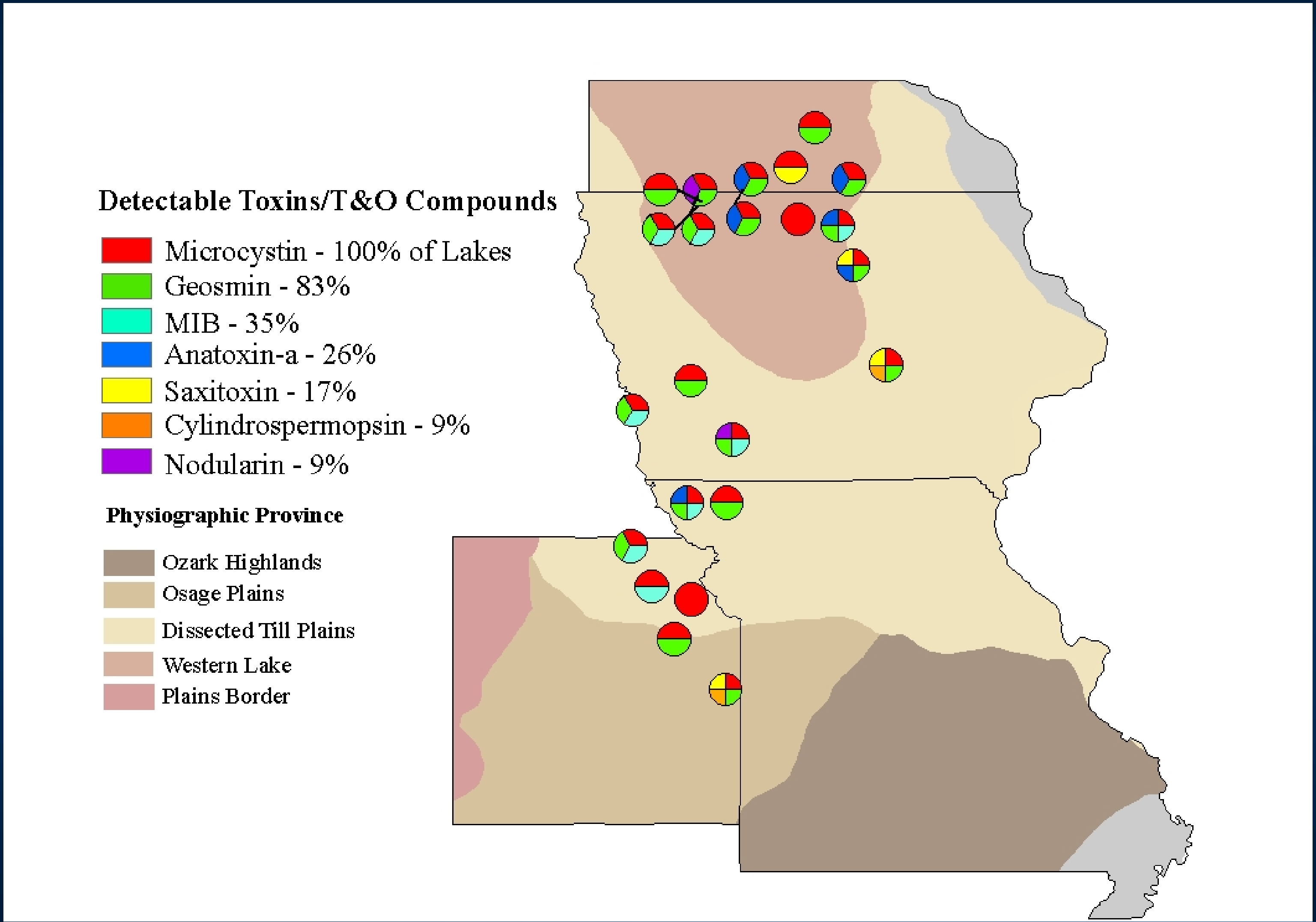


USGS

Distribution of Microcystin Variants and Other Cyanobacterial Toxins – August 2006 Midwestern Cyanotoxin Lake and Reservoir Reconnaissance

- Objectives:
  - Characterize occurrence and co-occurrence of taste and odor compounds and cyanotoxins
  - Determine the specific toxins by LC/MS/MS
- Design:
  - States: IA, KS, MN, MO (23 Lakes and Reservoirs)
  - **Targeted Sampling: Blooms and Scums**
  - Analyses:
    - Taste and Odor – SPME GC/MS
    - Toxins – TOTAL and Dissolved Concentrations
      - ELISA – Microcystins (ADDA), Microcystin LR, Cylindrospermopsins, Saxitoxins
      - LC/MS/MS – 7 microcystins (LR, RR, YR, LW, LA, LF, LY), Nodularin, Anatoxin-a, Cylindrospermopsin, Deoxycylindrospermopsin, Lyngbyatoxin a
    - Water Chemistry
    - Chlorophyll
    - Phytoplankton

During August 2006 100% of BLOOMS Sampled (n=23) Had Detectable Microcystin, 83% Had Detectable Geosmin, and 26% Had Detectable Anatoxin



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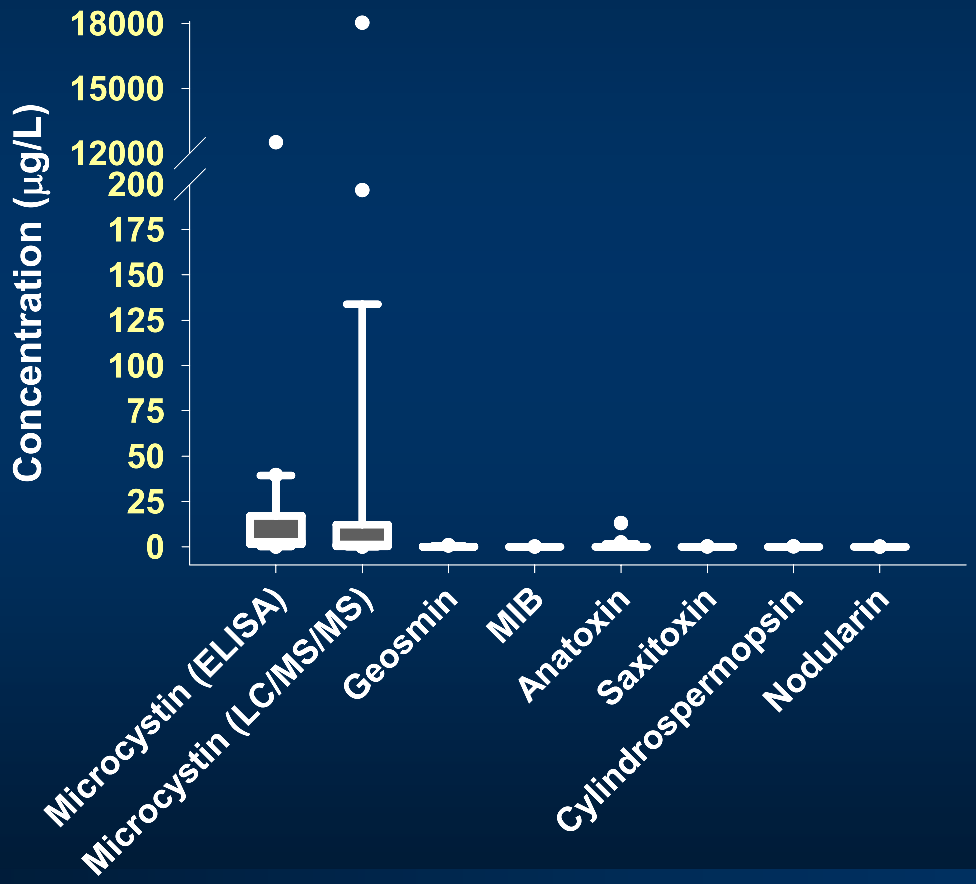
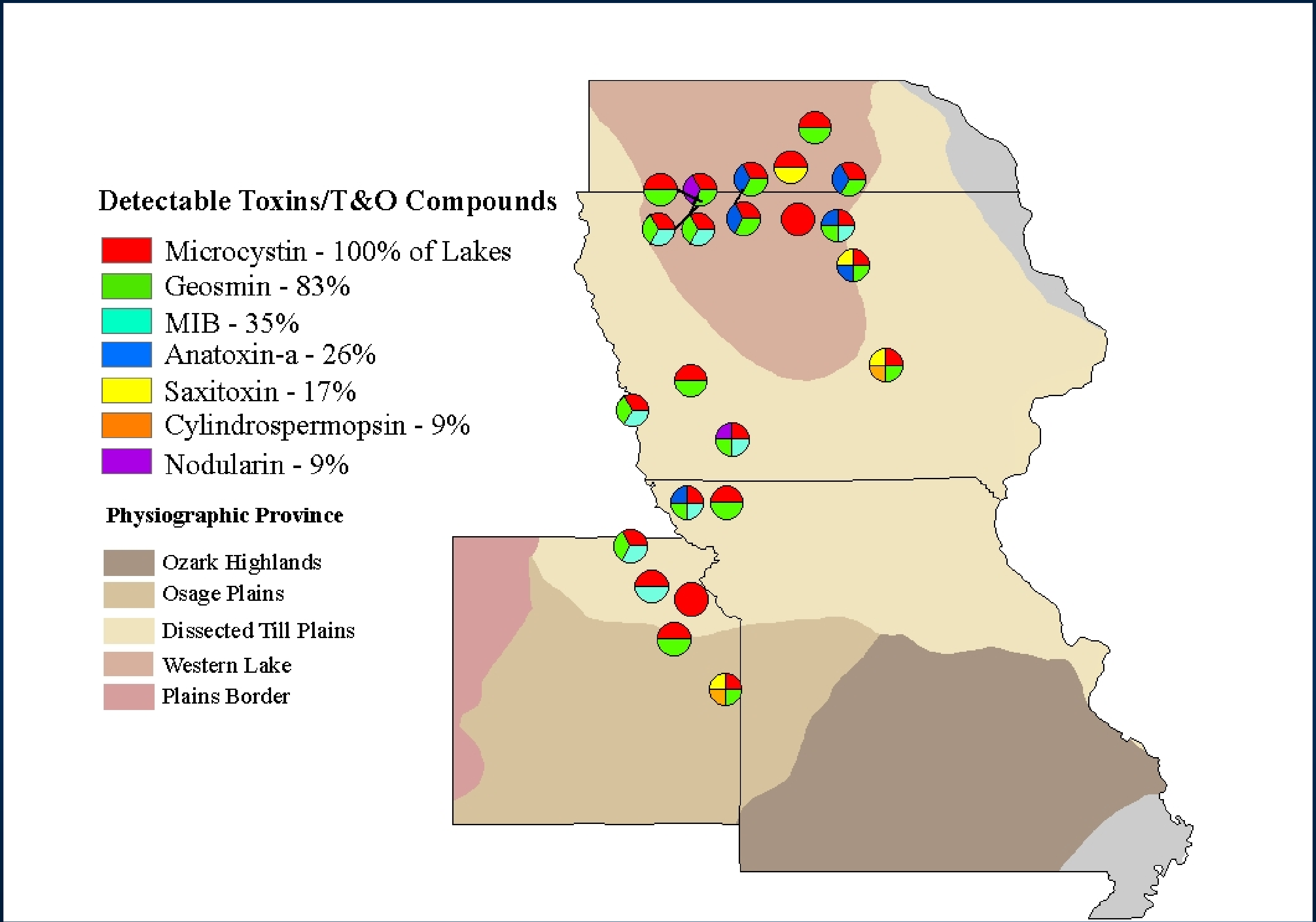
TOTAL Microcystin Maxima (12,500 – 18,030 µg/L) in BLOOM Samples Were Orders of Magnitude Greater Than Maxima for Other Compounds (Anatoxin Maxima = 13 µg/L, All Other Maxmima < 1 µg/L)



USGS

During August 2006 Toxins and Taste-and-Odor Compounds Co-Occurred in 87% of BLOOMS Sampled (n=23) and Anatoxin-a Always Co-Occurred with Geosmin



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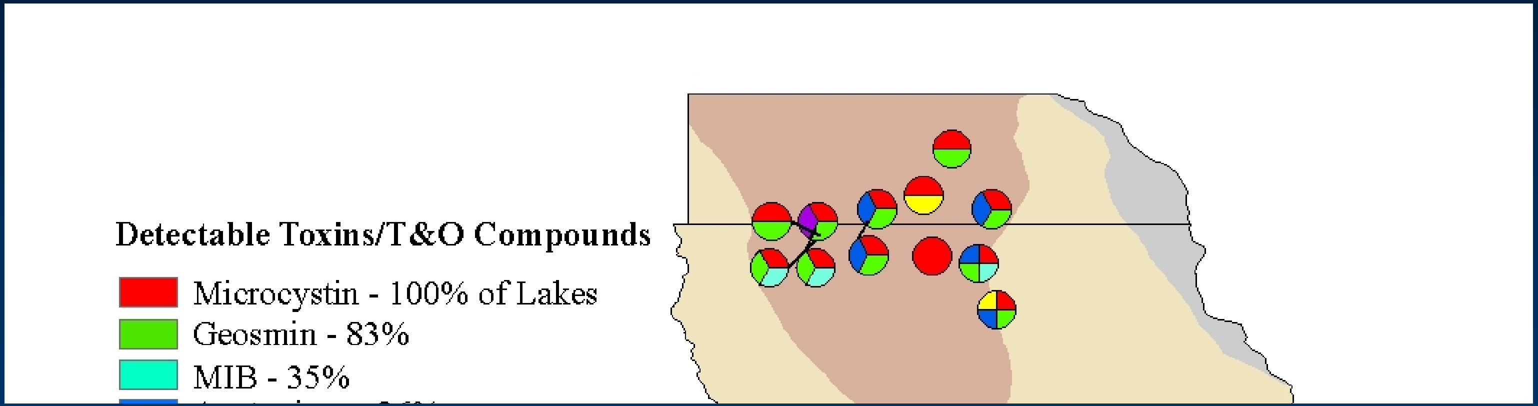
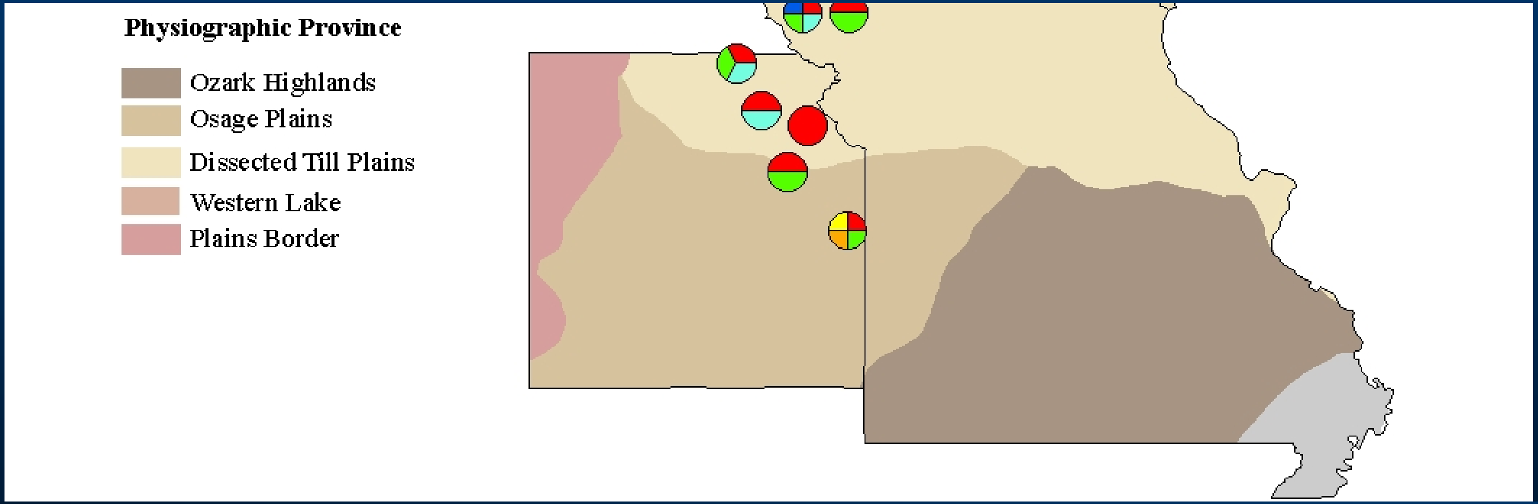


“Algae may make for stinky water, but it poses no health risks”

-Concord Monitor, Concord, NH July 7, 2006



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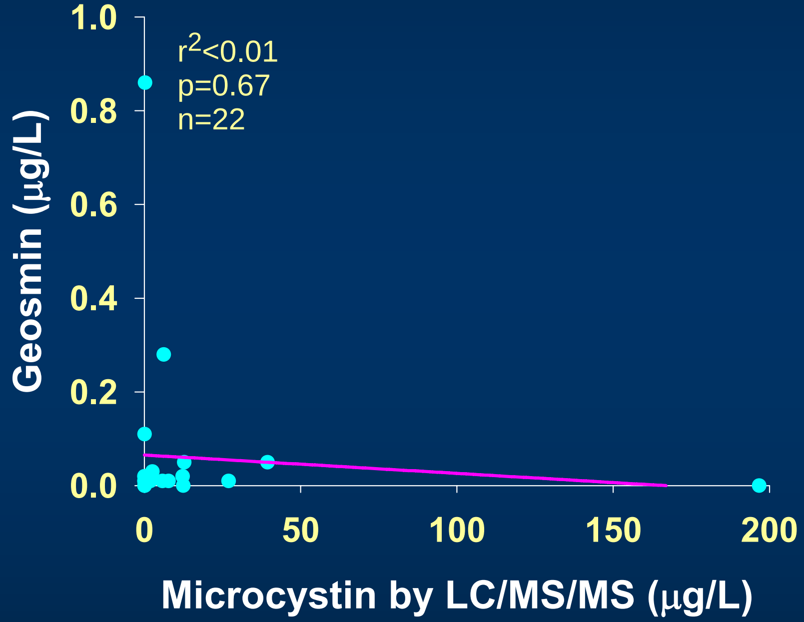
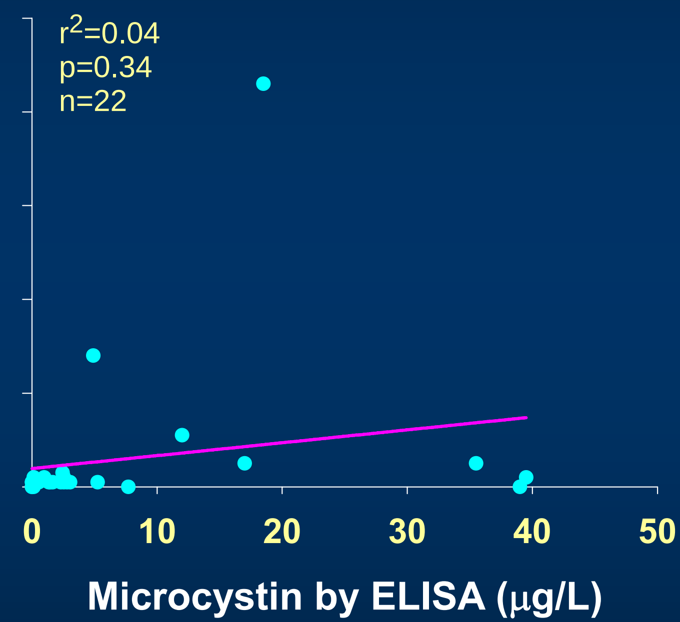
Although Toxins and Taste-and-Odor Compounds Frequently Co-Occurred Concentrations Were Not Linearly Related





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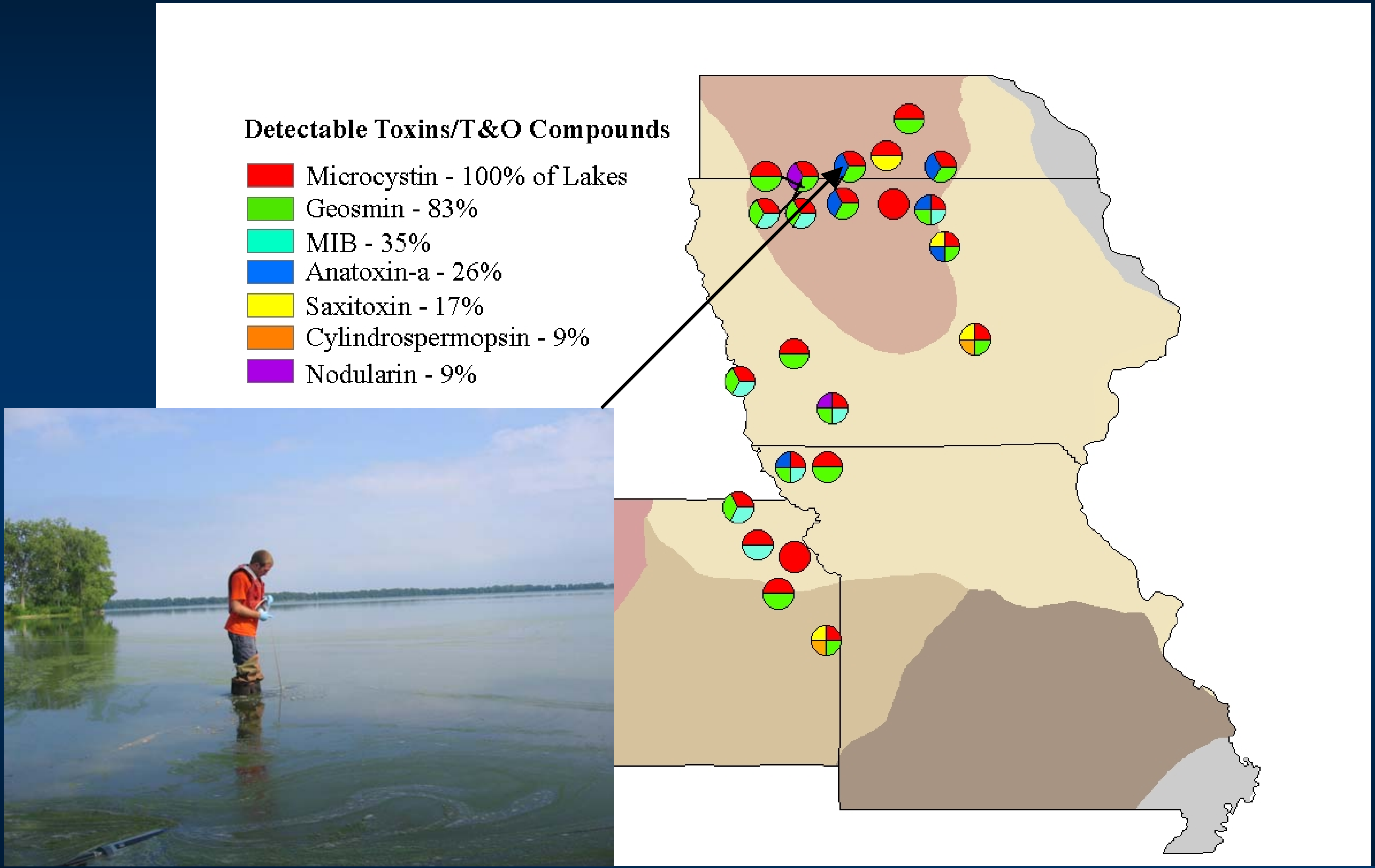
Cyanobacterial BLOOM with TOTAL Microcystin = 0.6 µg/L, Anatoxin = 0.1 µg/L , and Geosmin = 0.02 µg/L



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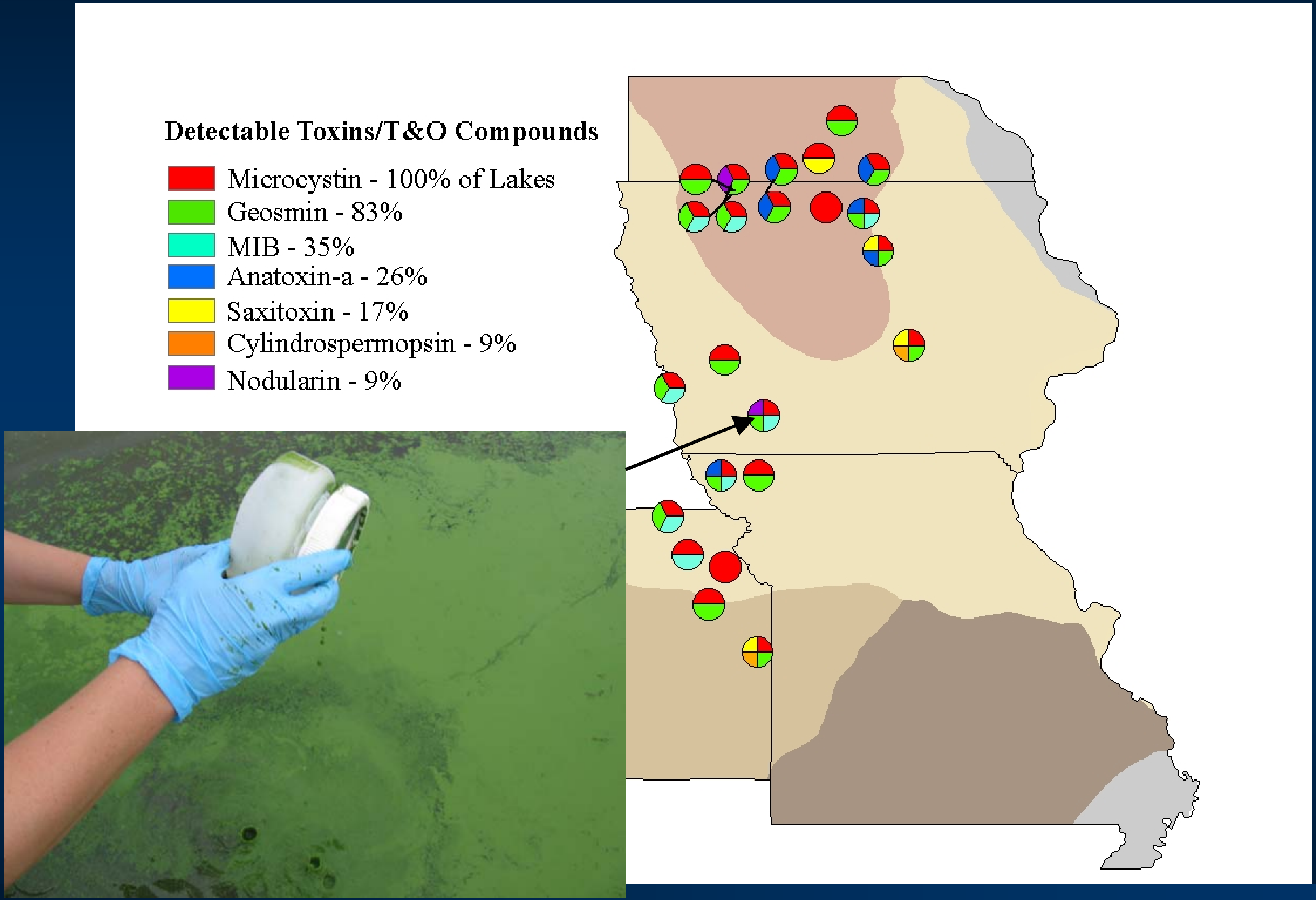
Cyanobacterial BLOOM with TOTAL Microcystin = 12.3 µg/L, Nodularin = 0.1 µg/L, Geosmin = 0.02 µg/L, and MIB = 0.06 µg/L



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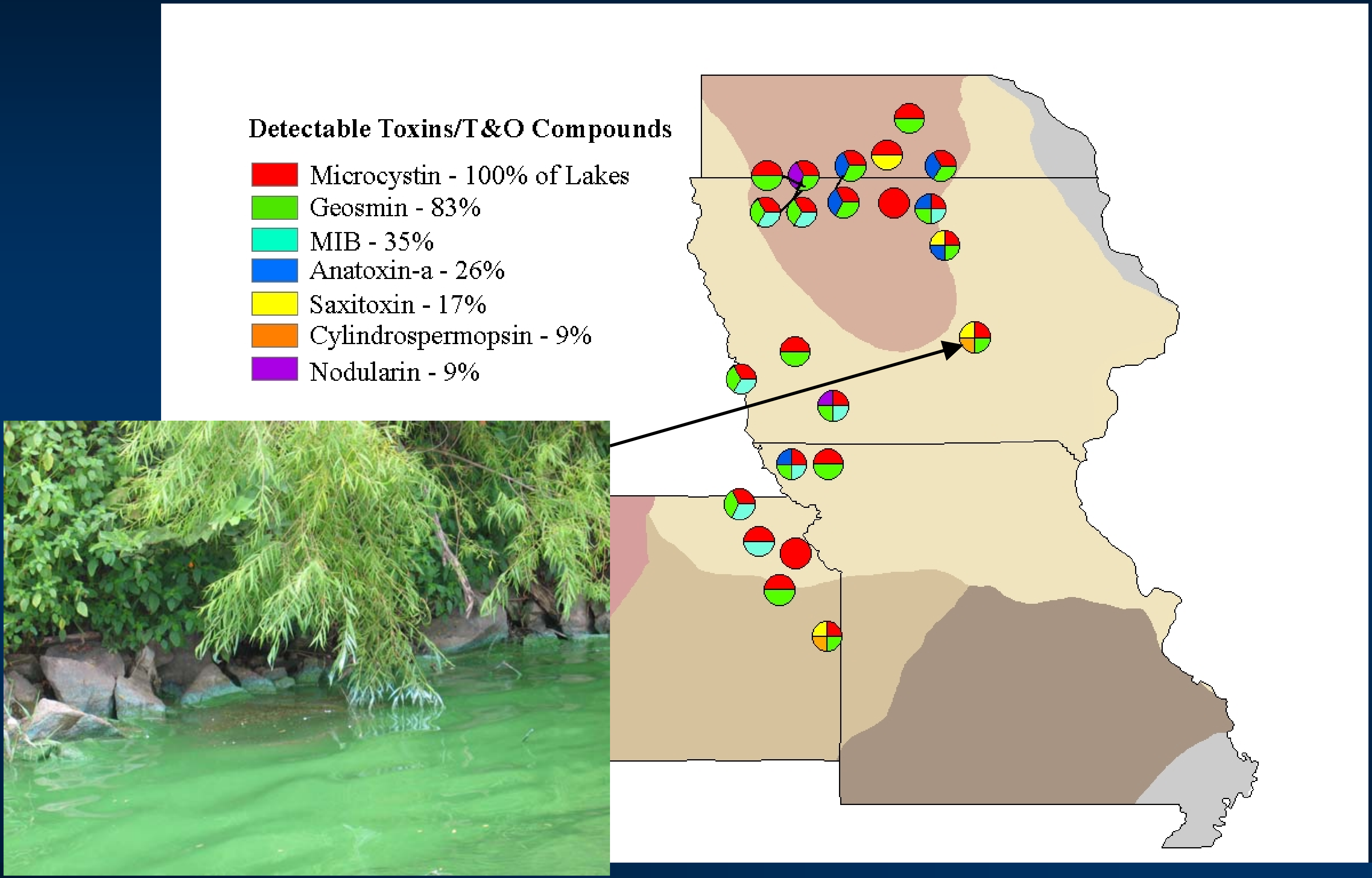
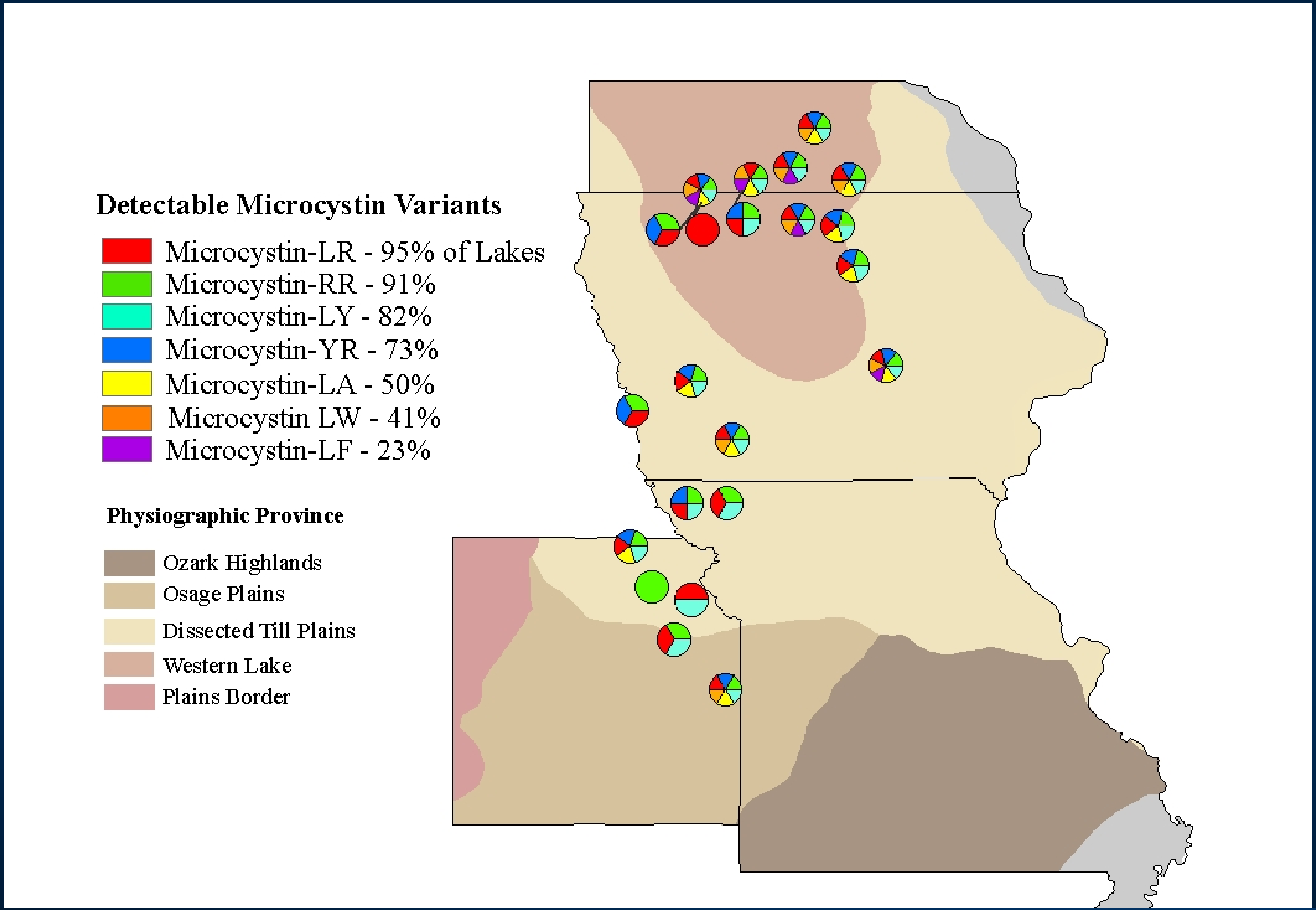
Cyanobacterial BLOOM with TOTAL Microcystin = 18,000 µg/L, Cylindrospermopsin = 0.12 µg/L Saxitoxin = 0.04 µg/L, and Geosmin = 0.69 µg/L



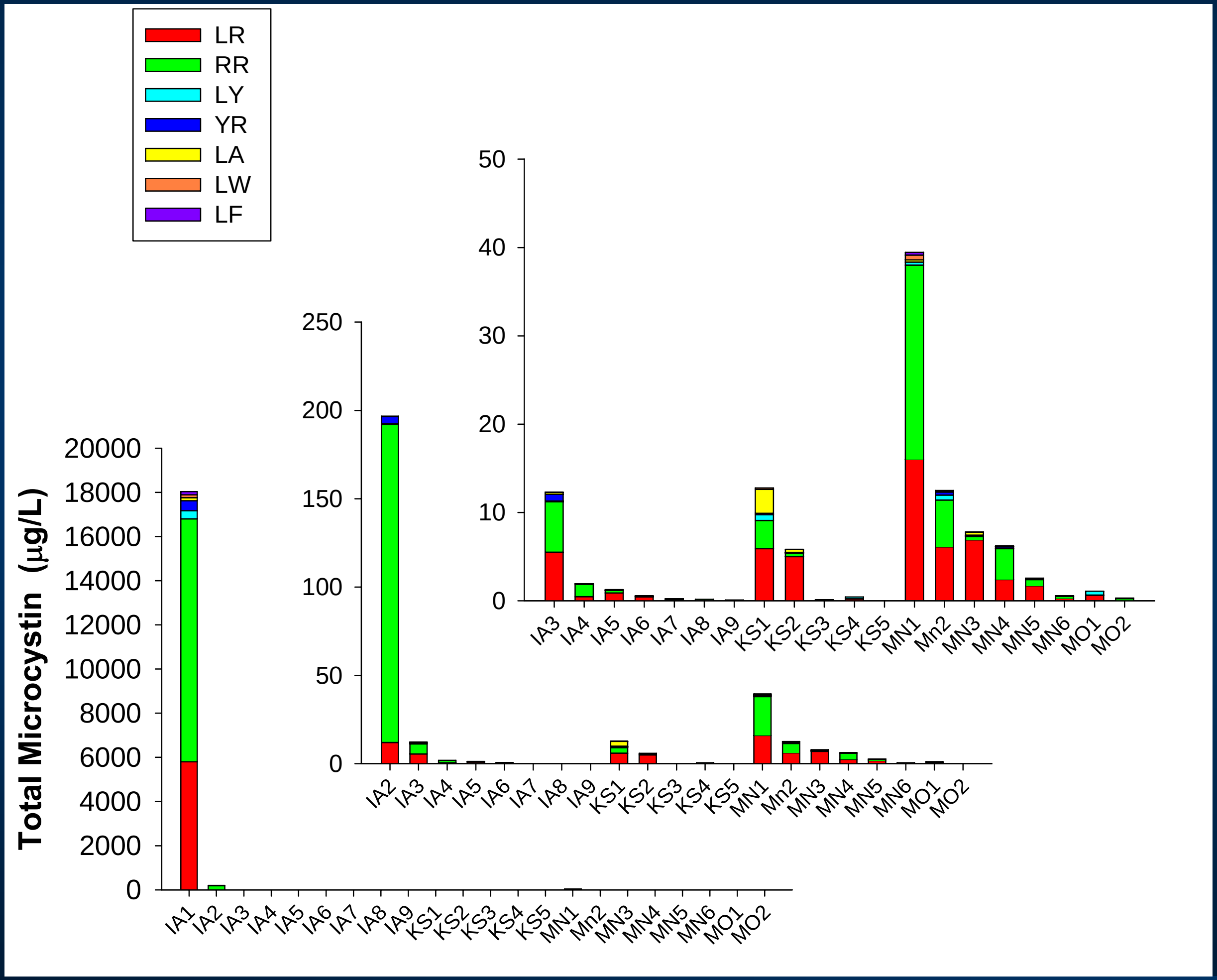
USGS

Microcystin-LR and –RR Were the Most Common Microcystin Variants, and 41% of Lakes Had All 7 Measured Variants Present



USGS

Microcystin-LR and –RR Comprised the Majority of TOTAL Microcystin Concentrations



2006 Texas Reservoir Survey for DISSOLVED Microcystin in Surface Samples at OPEN WATER Locations

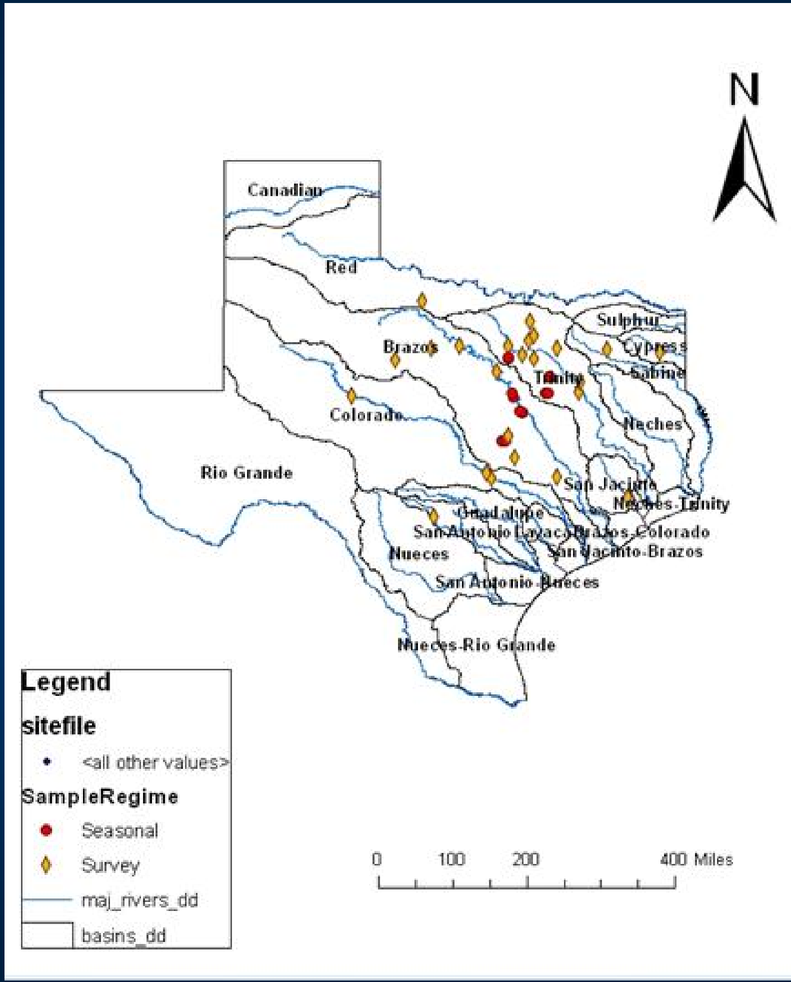
Results:

28% of reservoirs (n=36) had detectable microcystin by ELISA

Maximum DISSOLVED Microcystin concentrations: < 1 µg/L

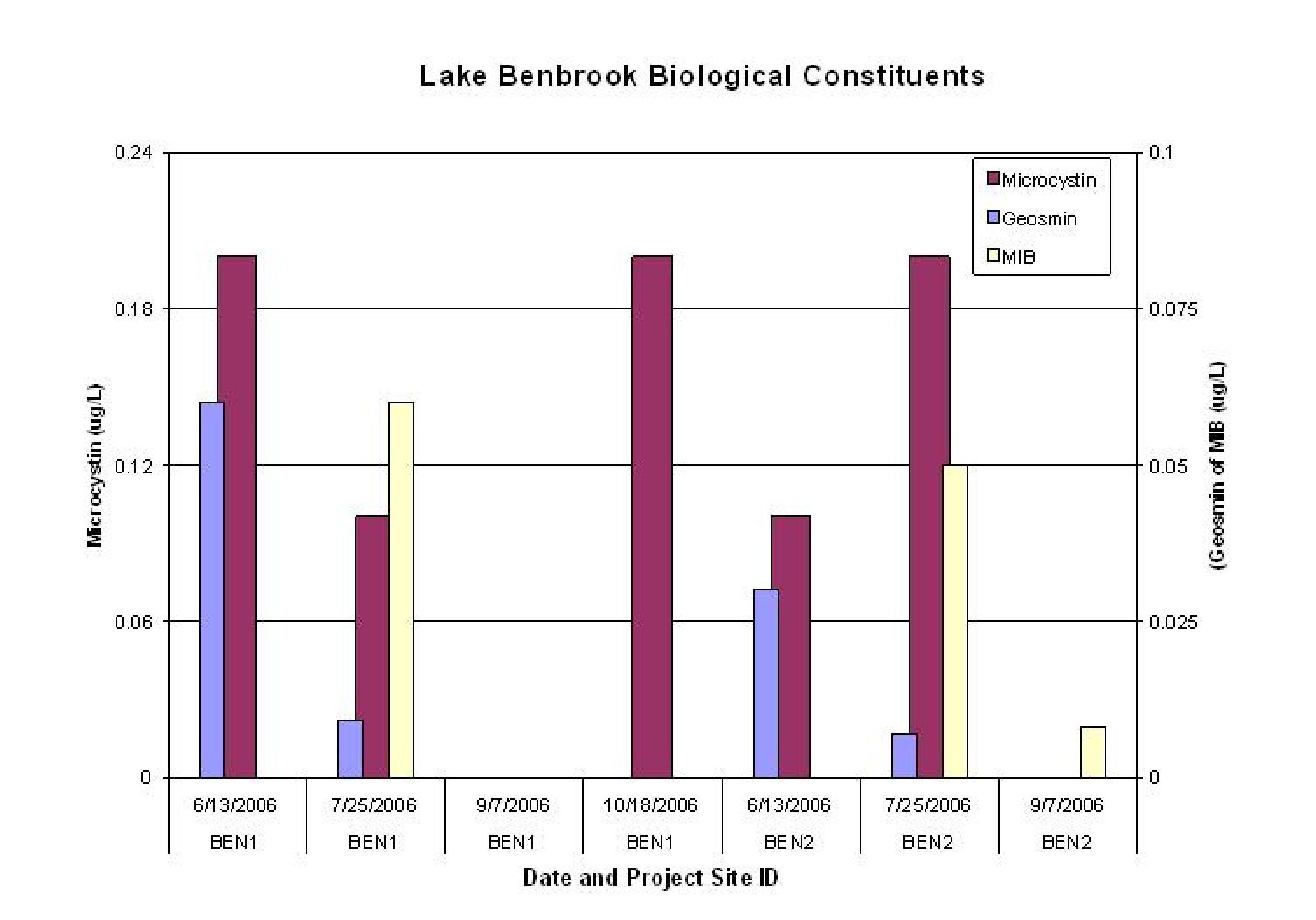
69% of reservoirs had detectable MIB

30% of reservoirs had detectable Geosmin



After Kiesling and others, in prep

Microcystins and Taste-and-Odor Compounds Frequently Co-Occurred in Texas Reservoirs



USGS

After Kiesling and others, in prep

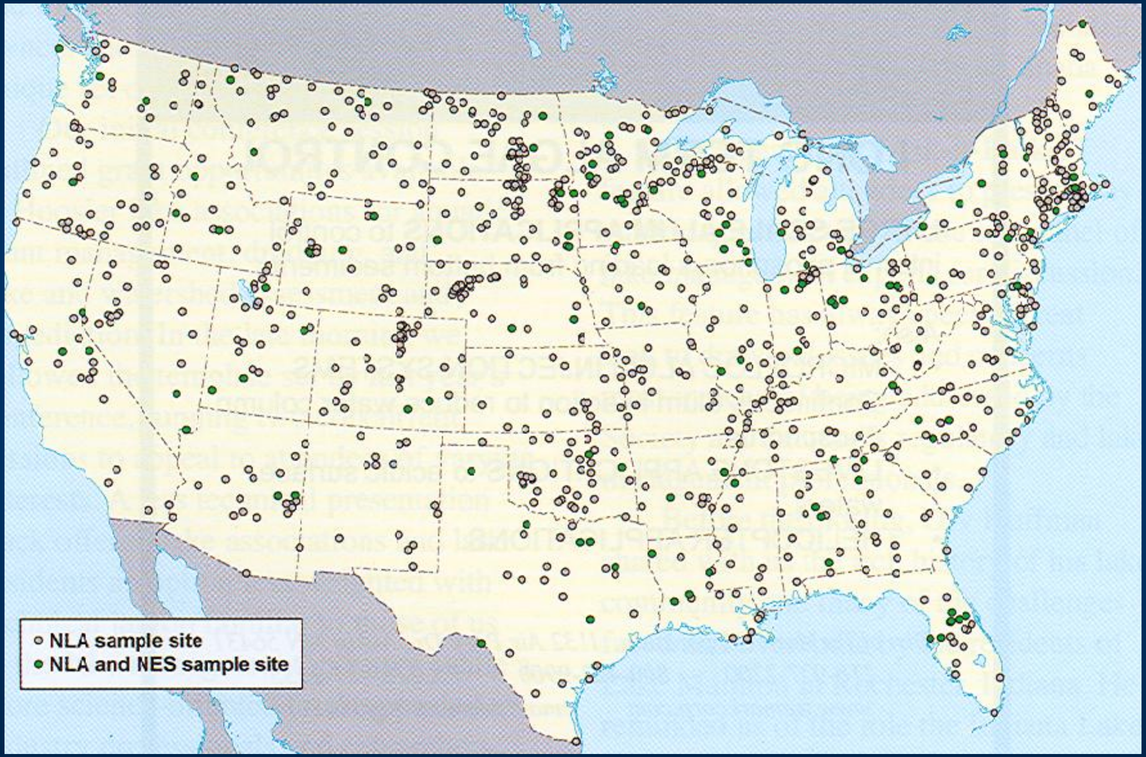
2007 US EPA National Lake Assessment: ~1200 Lakes and Reservoirs TOTAL Microcystin in Integrated Photic Zone Samples

Preliminary Results:

33% of samples (n=711) had detectable microcystin by ELISA

Mean TOTAL microcystin concentration: 0.97 μg/L

Maximum TOTAL microcystin concentration: 74 μg/L



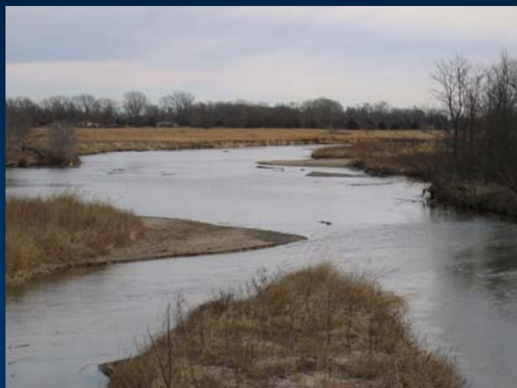
USGS

Sample Location and Type are Important

Study	Sample Location	Sample Type	n	% Samples with MC	Maximum MC (µg/L)
Graham and others 1999-2006	Open Water, Integrated Photic	Total	2546	39	52
Midwest Recon 2006	Targeted Blooms, Bloom Grab	Total	23	96	12,500
Texas Recon 2006	Open Water, Surface Grab	Dissolved	67	22	0.2
EPA NLA 2007	Open Water, Integrated Photic	Total	711	33	74

Microcystin was measured by ELISA in all studies

<u>Long Term Studies</u> – Assessment of Water Quality in the North Fork Ninnescah River and Cheney Reservoir, 1997-Present



North Fork Ninnescah River
March 2006

Cheney Reservoir, KS June 2003
Photo Courtesy of KDHE

- **Concerns**
  - Taste-and-odor occurrences related to algal blooms
  - Relation between watershed inputs and taste-and-odor causing algae
- **Approach**
  - Describe current and historical loading inflow
    - Sediment Cores
    - Continuous Water-Quality Monitoring
  - Describe physical, chemical, and biological processes associated with cyanobacteria and cyanobacterial by-products
    - Discrete Samples
    - Real-Time Monitors

USGS science for a changing world

http://ks.water.usgs.gov/Kansas/studies/qw/cheney/

CITY OF WICHITA

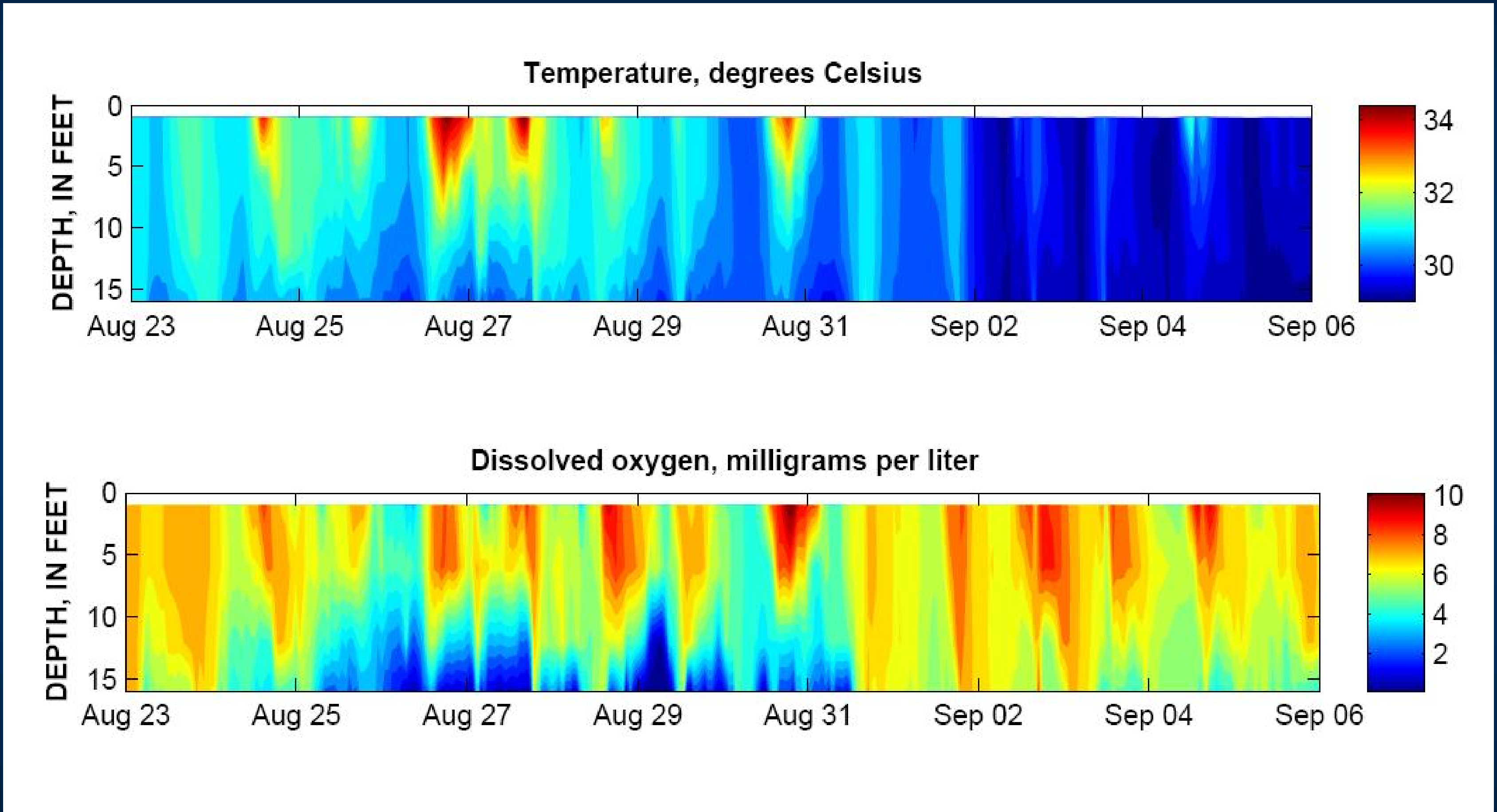
Early Detection and Predictive Models – Continuous Real-Time Water-Quality Monitors

- **Real-Time Variables**
  - Specific conductance, pH, temperature, turbidity, dissolved oxygen
  - Chlorophyll
  - Light
  - Blue-green algae
  - Nitrate

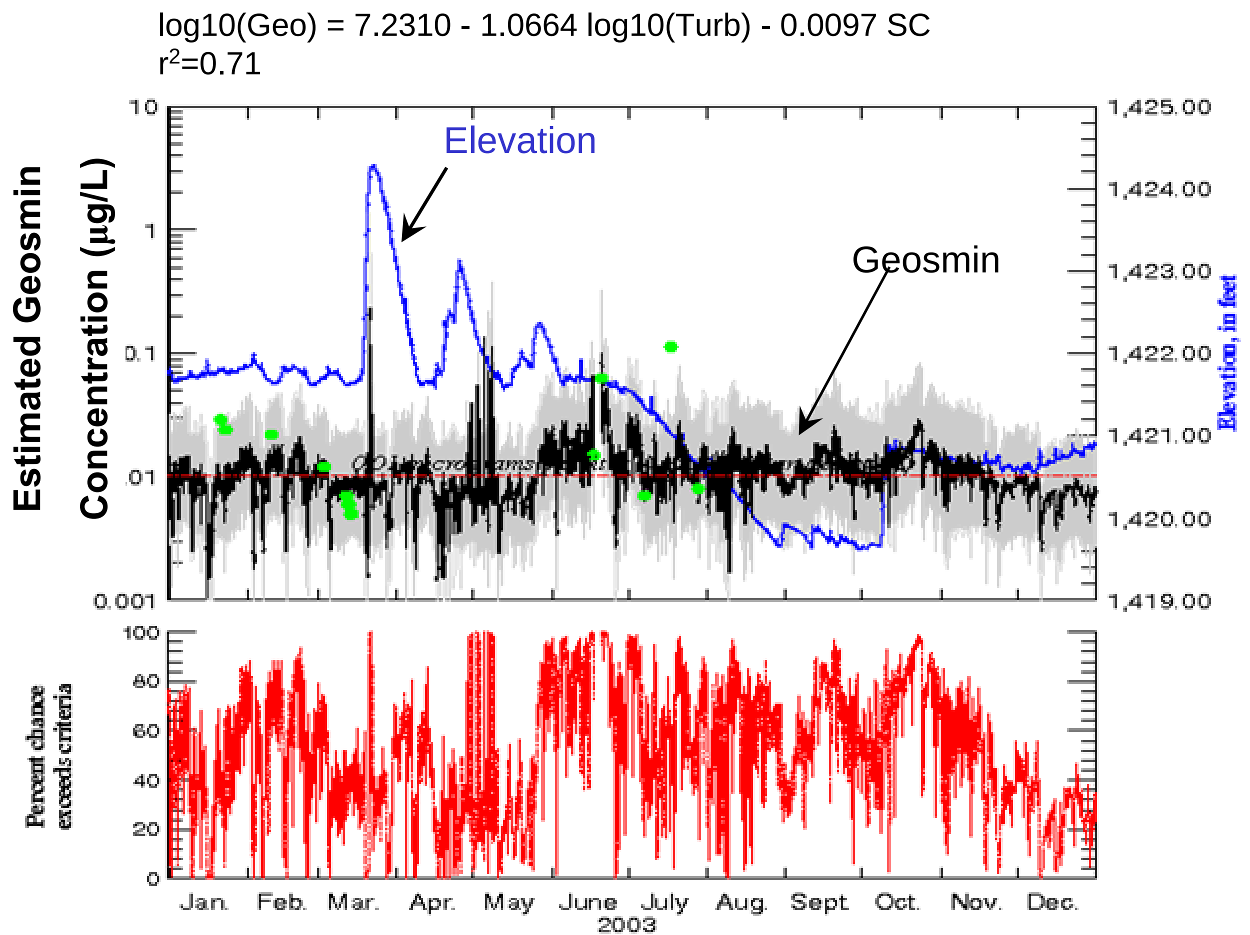
The J. W. Powell
USGS Monitoring Station on Lake Houston, Texas

Station Developed by Michael J. Turco, Timothy D. Oden, William H. Asquith, Jeffery W. East, and Michael R. Burnich

Continuous Monitoring Allows the Identification and Description of Events that Occur Within Relatively Short Periods of Time



Early Detection - Geosmin Concentrations in Cheney Reservoir Frequently Exceed the Human Detection Limit of 10 ng/L



Estimated Geosmin Concentration 2003

USGS

http://ks.water.usgs.gov/Kansas/rtqw/index.shtml

After Christensen and others, 2006 USGS SIR 2006-5095

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Additional Information Available on the Web:

Cyanobacteria - http://ks.water.usgs.gov/Kansas/studies/qw/cyanobacteria
Cheney - http://ks.water.usgs.gov/Kansas/studies/qw/cheney
Olathe - http://ks.water.usgs.gov/Kansas/studies/qw/olathe
RTQW - http://ks.water.usgs.gov/Kansas/rtqw/index.shtml

USGS