Cyanobacterial Blooms: Toxins, Tastes, and Odors

USGS Kansas Water Science Center Algal Toxin Team
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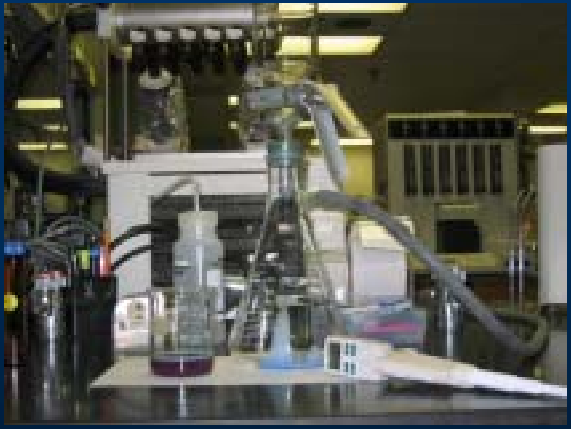
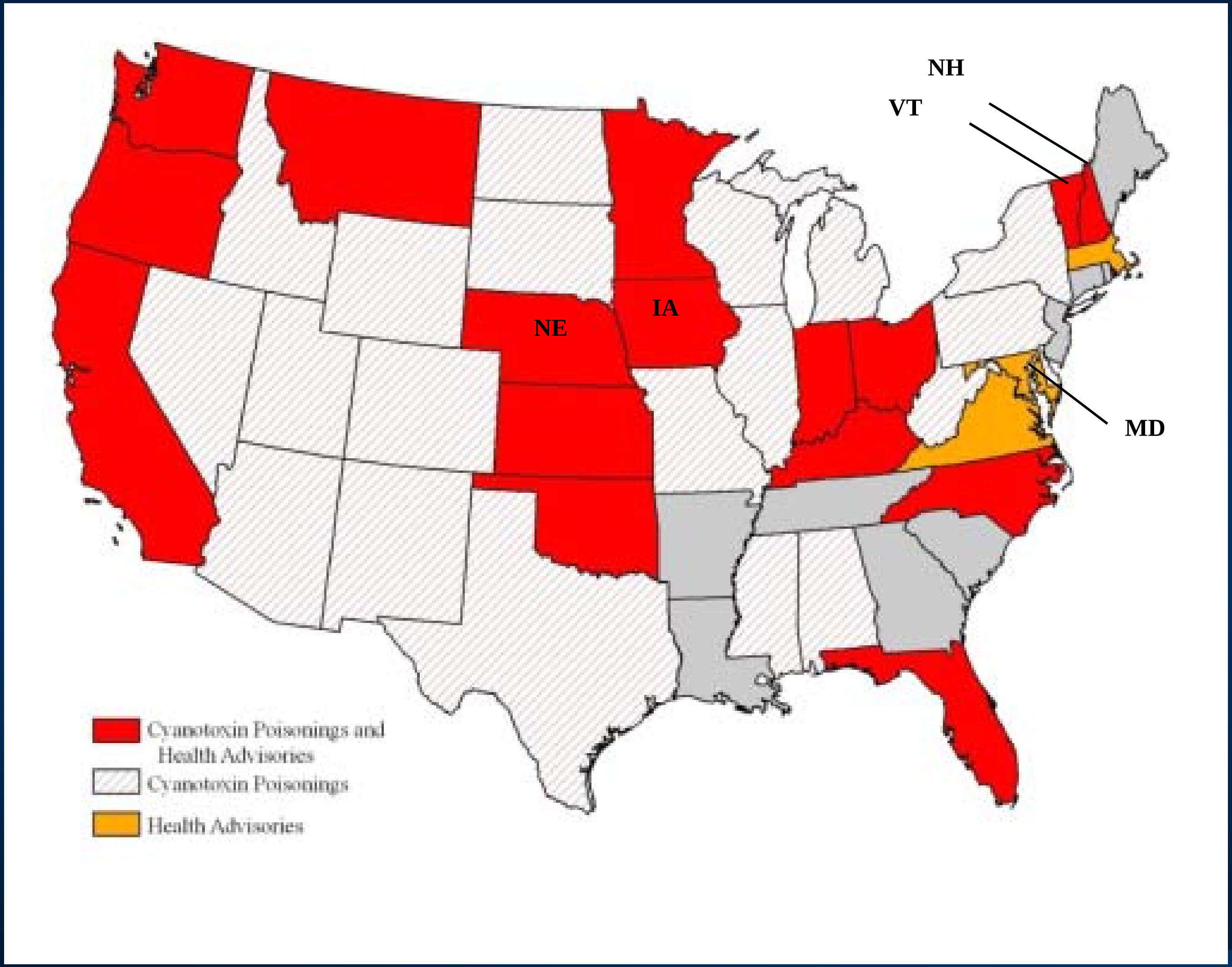
Information Sharing on Algal Issues
November 10, 2009

Overview

- Cyanobacterial Toxins and Taste-and-Odor Compounds
- Microcystin in the Midwest
- Research Needs
  - Methods
  - Studies
- USGS Studies



At Least 36 U.S. States Have Anecdotal Reports of Human or Animal Poisonings Associated with Cyanotoxins



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After Graham and others, 2009

Cyanobacterial Harmful Algal Blooms

- Health Concerns – Toxins
  - Human and animal illness and death
  - Included on EPA Drinking Water Contaminant Candidate List
  - Drinking water
    - Microcystin and Cylindrospermopsin Provisional Guidelines – 1 µg/L
    - Drinking-water treatment processes effectively remove most toxins
  - Recreational water
    - WHO Provisional Microcystin Guideline – 20 µg/L
  - Known chronic effects

USGS

Cyanobacterial Harmful Algal Blooms

- Ecologic Concerns
  - Low dissolved oxygen
  - Fish kills
  - Losses to bird and mammal populations
  - Zooplankton avoidance or death
  - Accumulation of toxins by mussels

- Economic Concerns
  - Added drinking water treatment costs
    - Olfactory sensitivity to taste-and-odors at low concentrations (5-10 ng/L)
  - Loss of recreational revenue
  - Death of livestock and domestic animals
  - Medical/veterinary expenses

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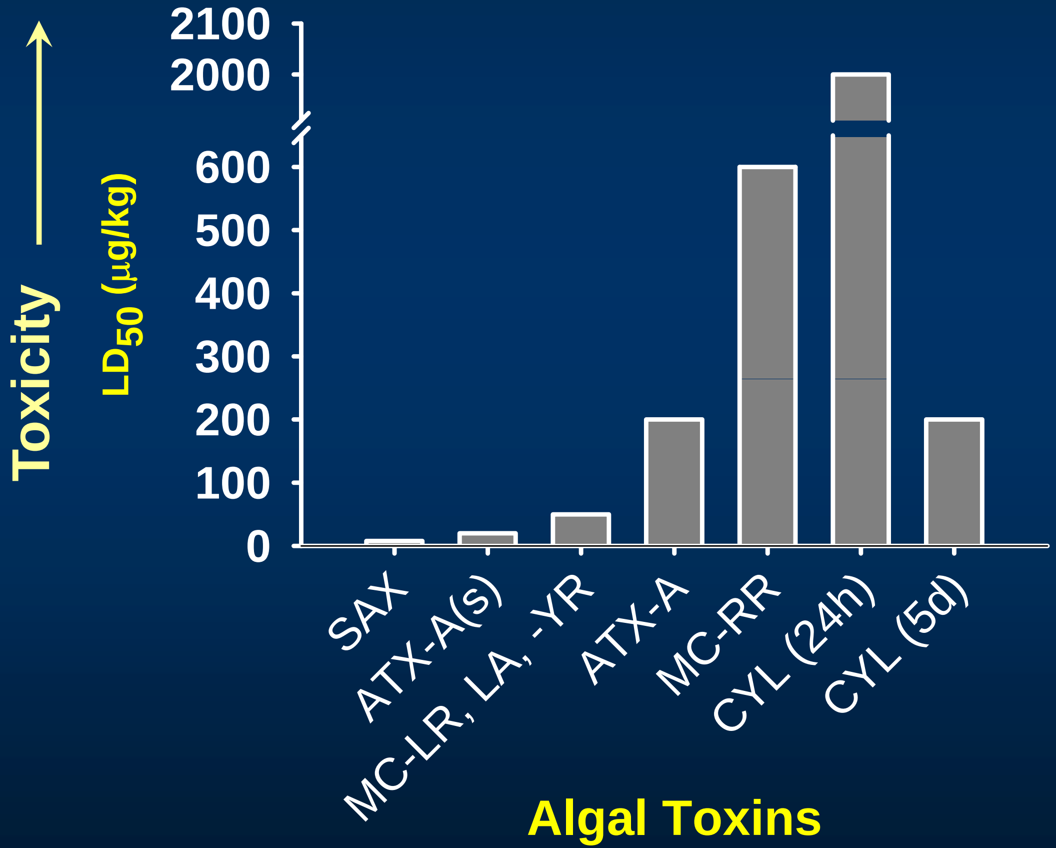
Toxins and Taste-and-Odor Compounds Produced by Cyanobacteria

	Dermatoxins	Hepatotoxins		Neurotoxins		Taste/Odor	
		CYL	MC	ANA	BMAA	GEOS	MIB
Colonial/Filamentous							
Aphanizomenon	X	X	?	X	X	X	
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		

USGS

After USGS SIR 2008-5038

Cyanotoxins Exhibit a Wide Range of Toxicities and Toxic Effects

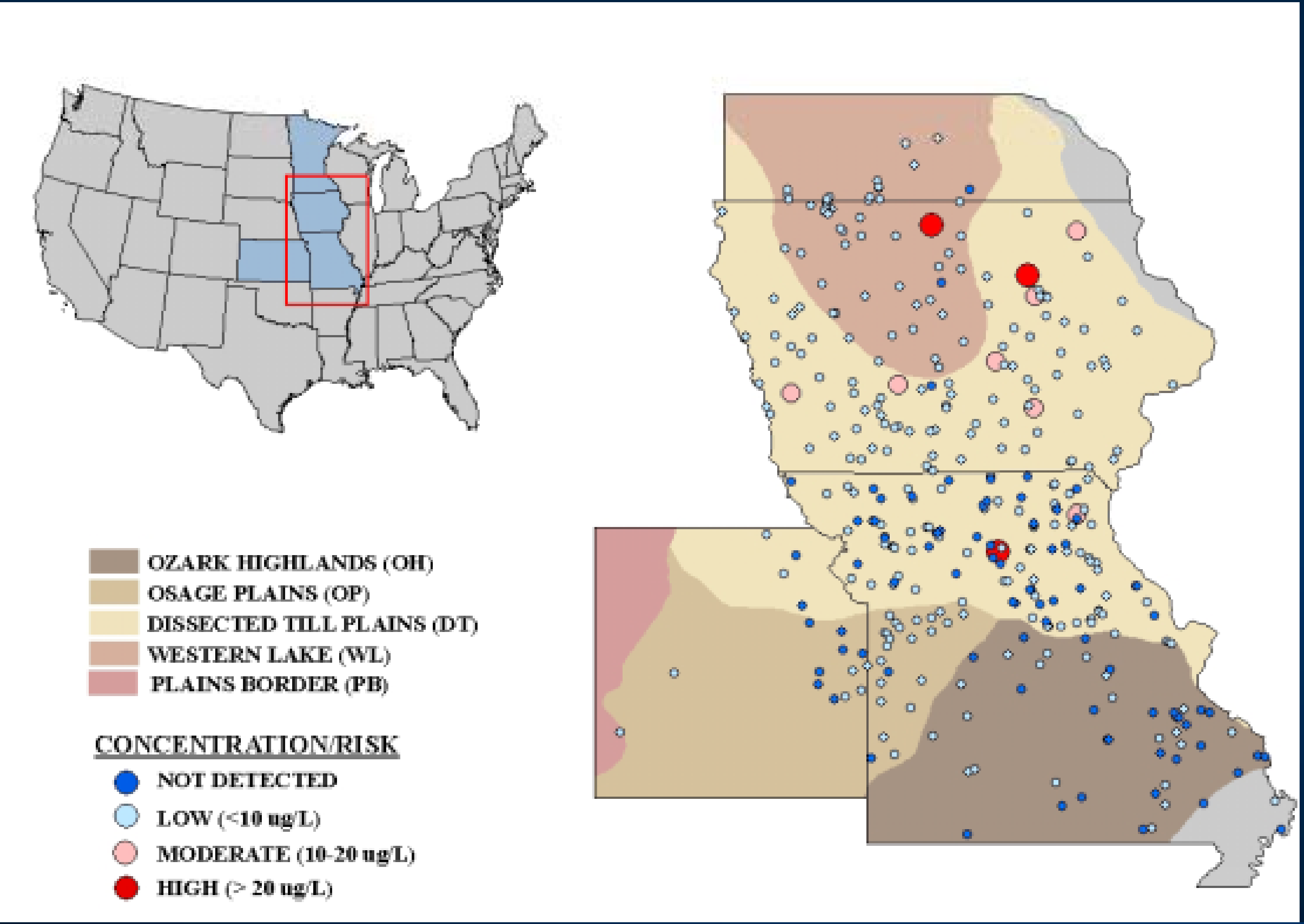


- **Acute Toxicity**
  - Neurotoxic
  - Hepatotoxic
  - Dermatoxic
- **Chronic Toxicity**
  - Carcinogen
  - Tumor Promotion
  - Mutagen
  - Teratogen
  - Embryolethality
  - Neurodegenerative Diseases?

USGS

After Chorus and Bartram, 1999

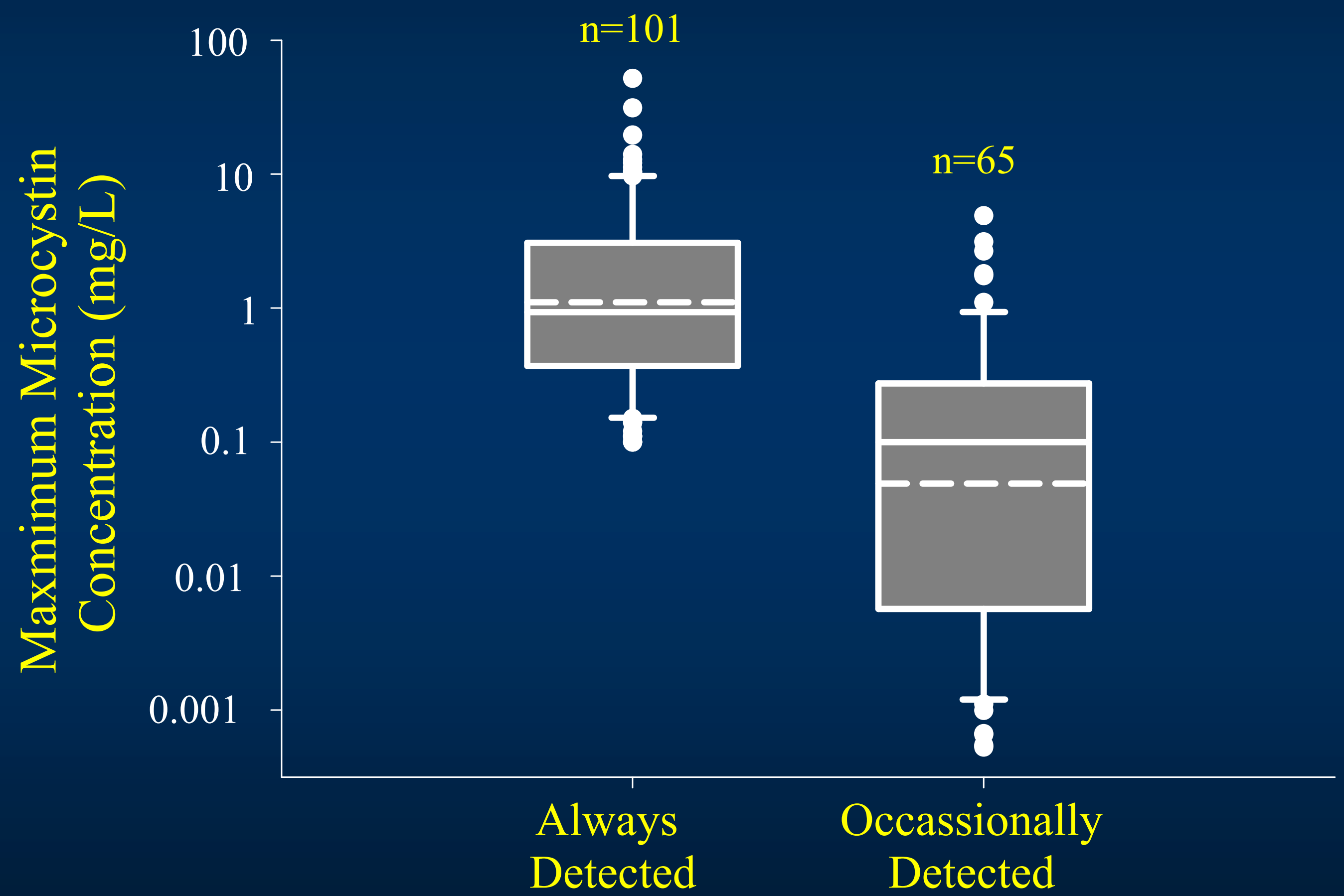
During 1999-2006 Microcystin was Detected in INTEGRATED PHOTIC ZONE Samples from 78% of Lakes (n=359) and TOTAL Concentrations Ranged from <0.1 to 52 µg/L



USGS

After Graham and others 2004, 2006, and 2009

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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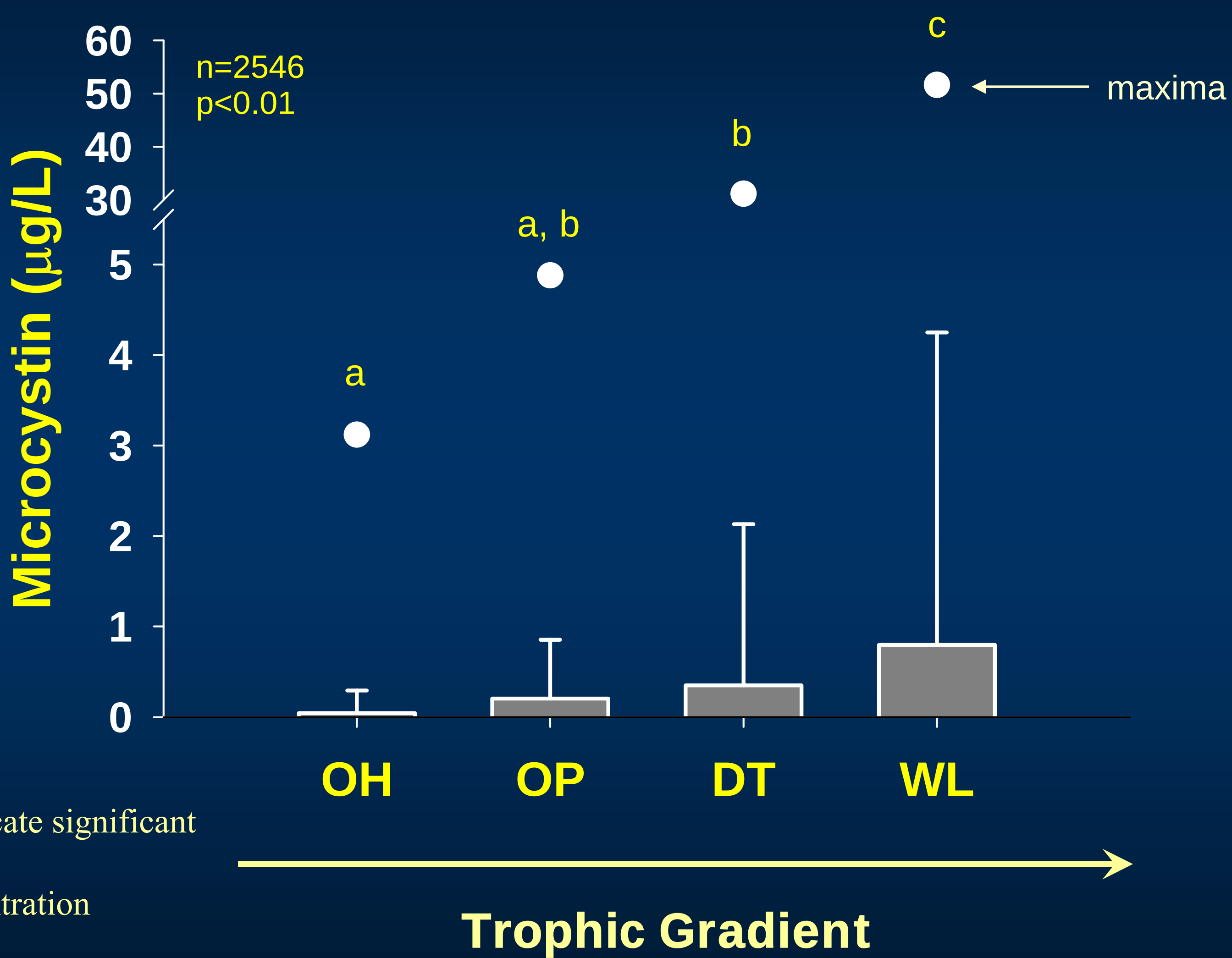
After Graham and others 2004, 2006, and 2009

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

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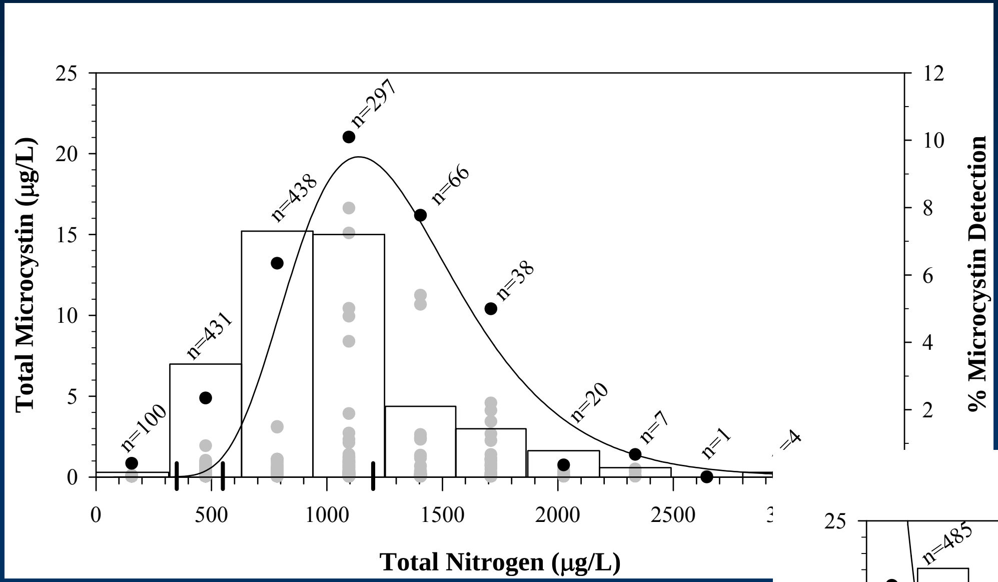
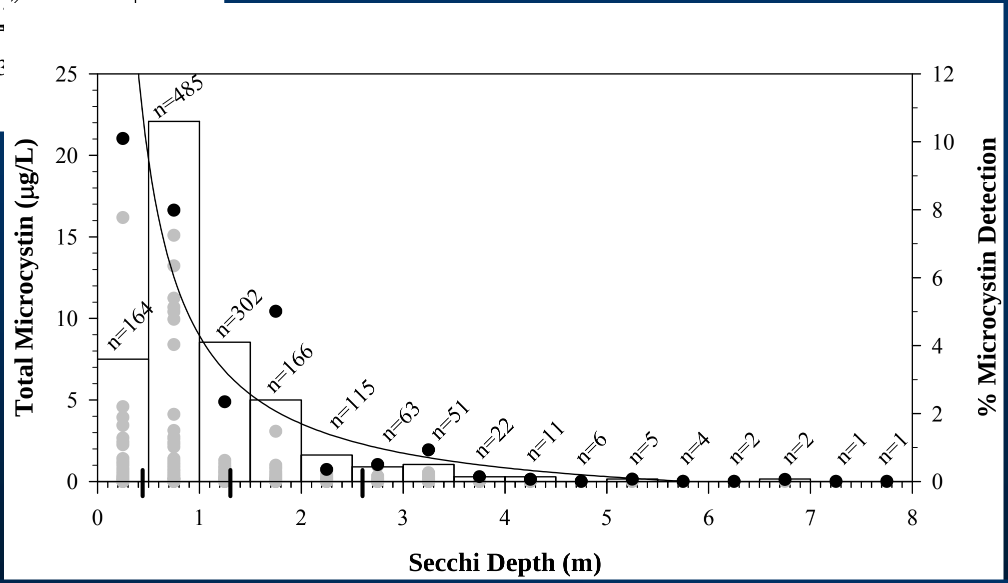
After Graham and others 2004 and 2006

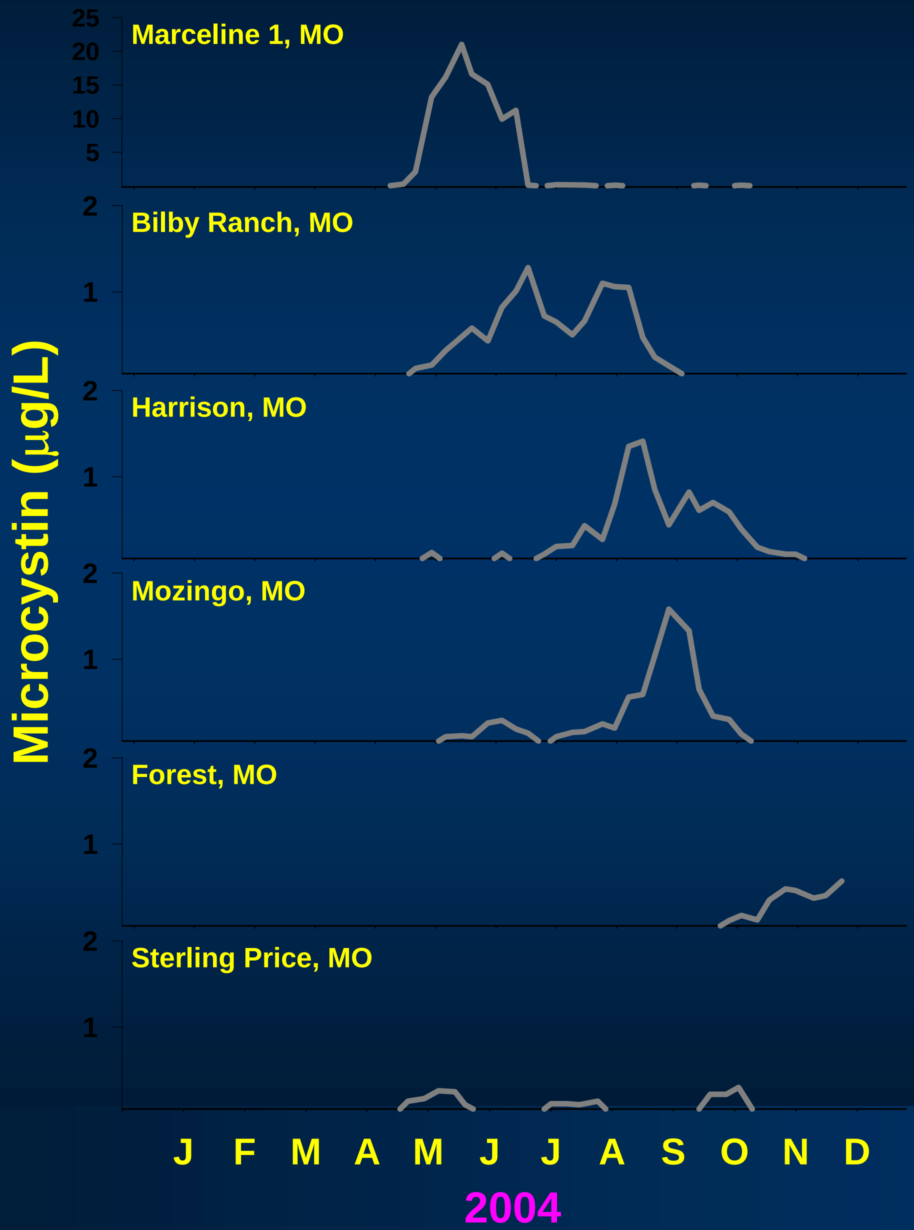
Regional Associations Between Microcystin and Environmental Variables Were Complex





After Graham and Jones, 2009

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



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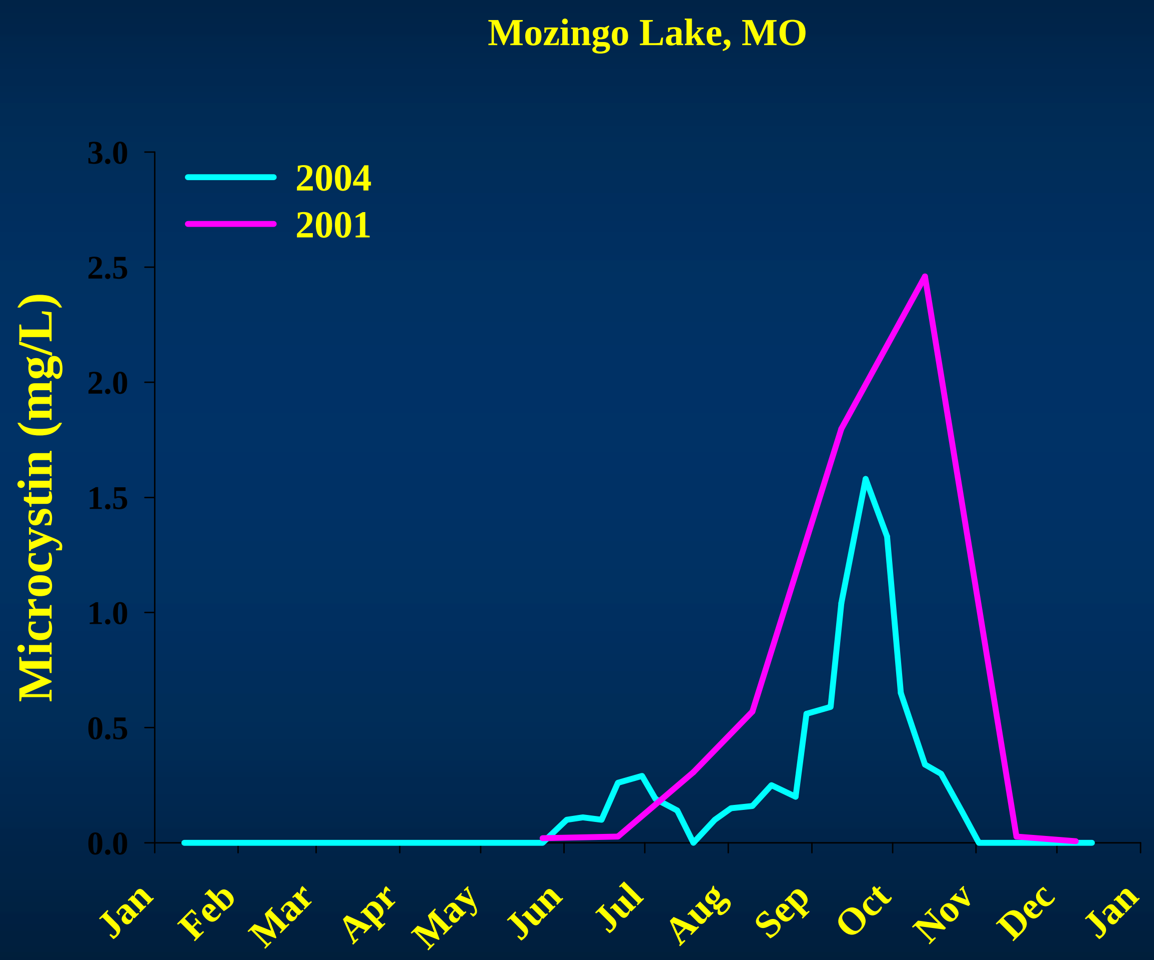
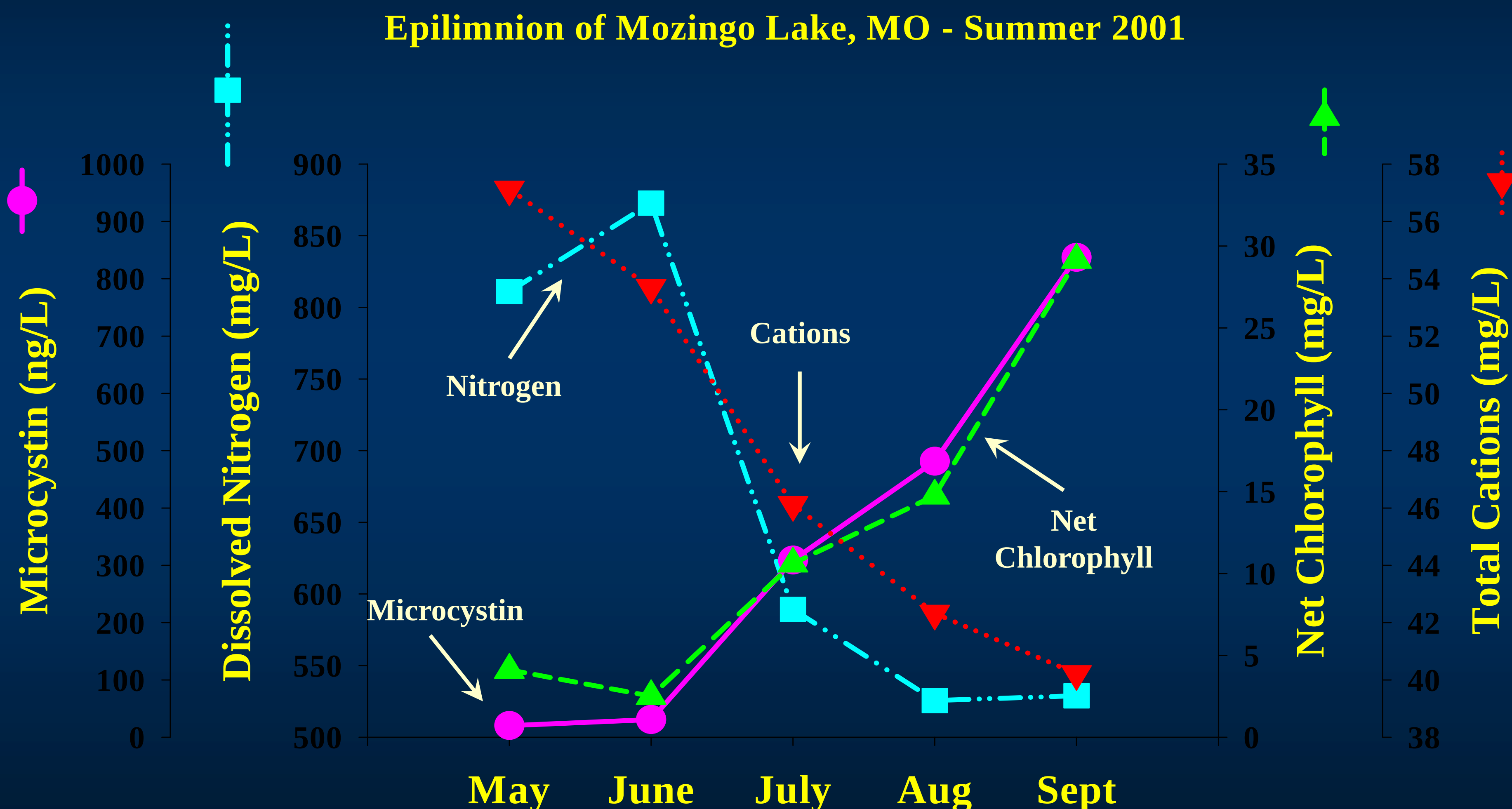
Seasonal Patterns Were Relatively Consistent Between Years in Some Lakes



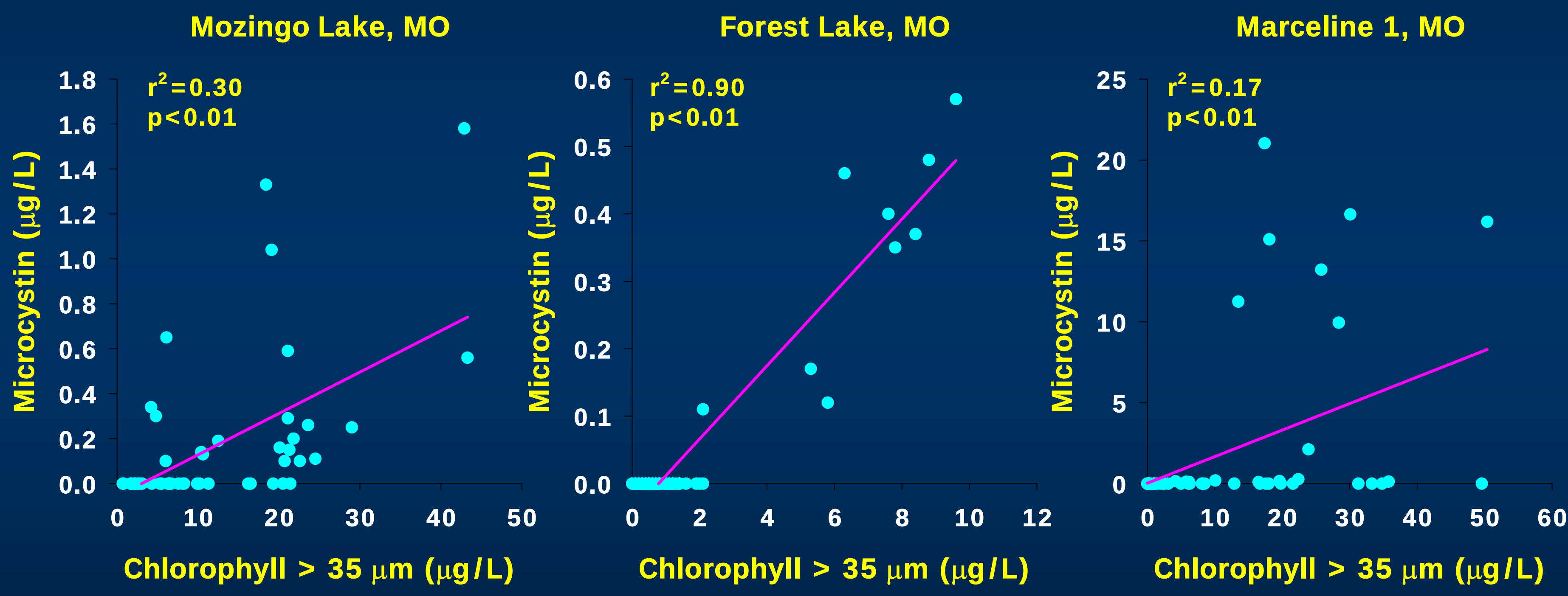
After Graham and Jones, 2006

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



After Graham and others, 2006

Factors Most Strongly Correlated With Microcystin Vary Among Lakes and Years



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

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Research Needs

- Methods
  - Certified Standards
  - Consistent Sampling Protocols
  - Robust and Quantitative Analytical Methods for a Variety of Toxins
- Studies
  - Cyanotoxin Occurrence
  - Long Term Studies
  - Methods for Early Detection
  - Predictive Models

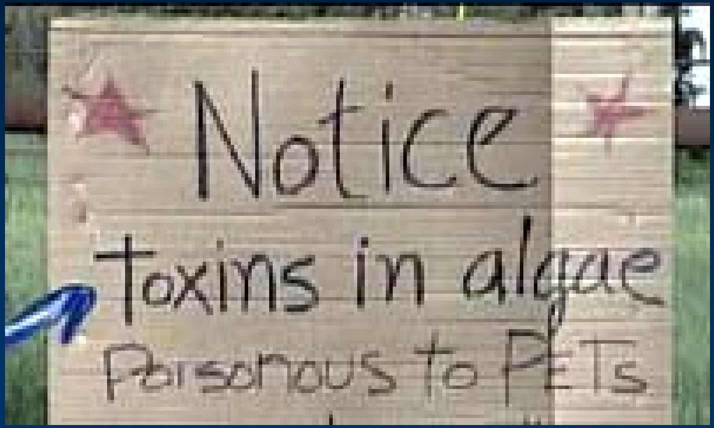

Photo from Omaha NBC News

Photo Courtesy of KDHE

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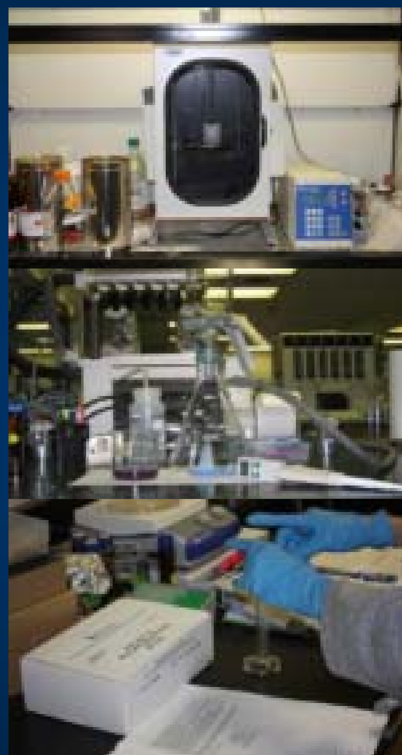
The Cyanotoxin Data Acquisition Process

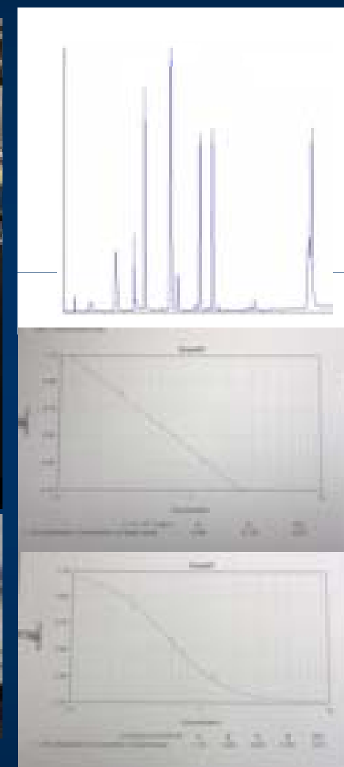
Sample Collection

Laboratory Processing

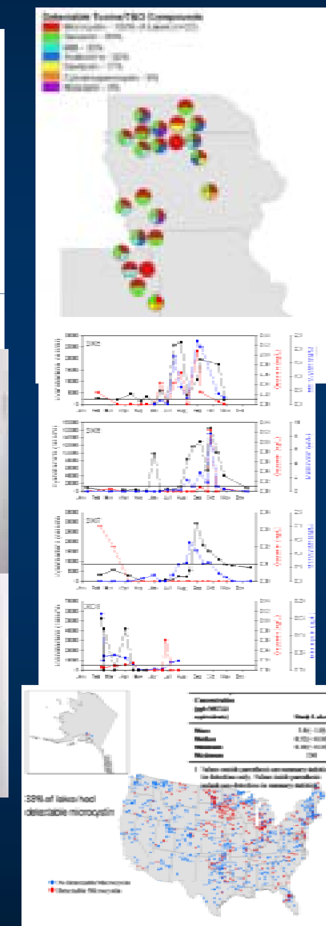


Analysis

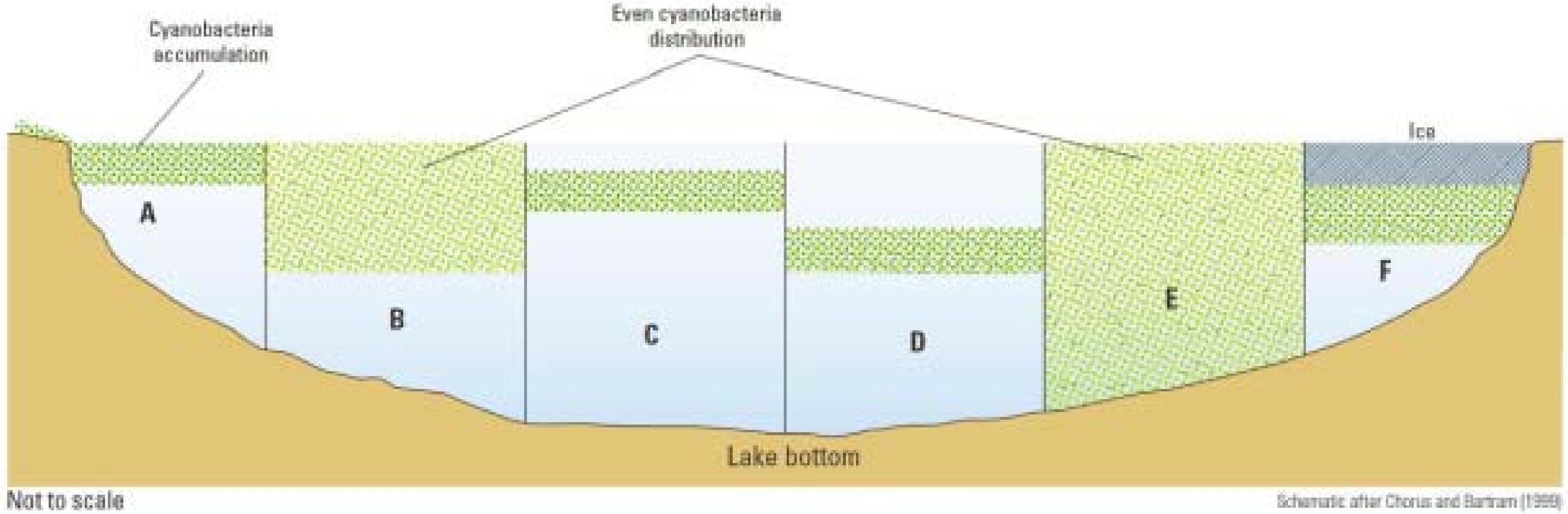
Data Reduction



Interpretation



<u>Consistent Sampling Protocols</u> – Sample Location is Important



EXPLANATION

Potential water column distributions of cyanobacteria

A Shoreline, near-shore, and open water accumulations and scums
B Even distribution throughout the photic zone or epilimnion
C Specific depth in the photic zone
D Metalimnetic bloom (special case of **C**)
E Even distribution throughout the water column
F Under ice bloom

From USGS SIR 2008-5038

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

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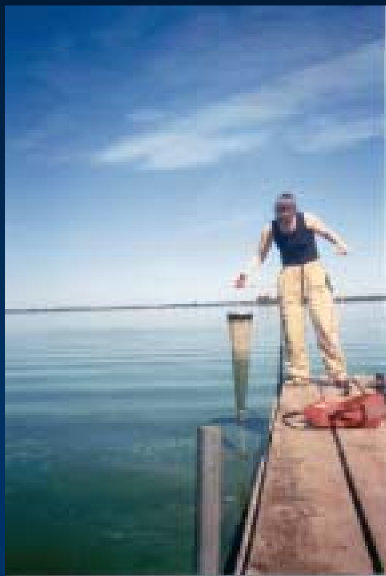
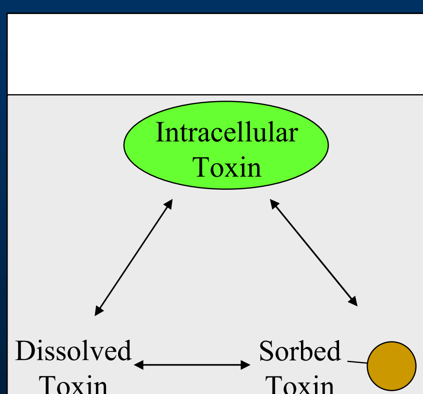
Consistent Sampling Protocols – Collection Technique is Important



Plankton Net Sampling

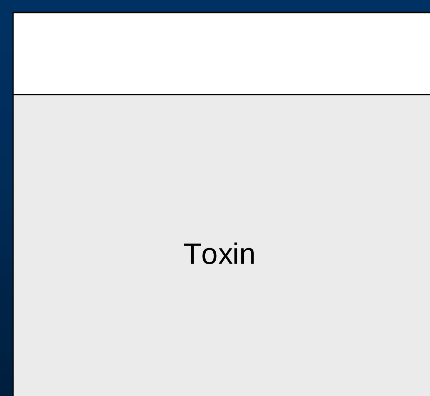
Whole Water Sampling

Filter/Filtrate Sampling



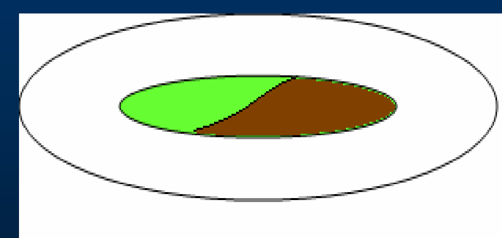
Total Toxin

=



Dissolved Phase Toxin

+



Particulate Toxin

Standardized Sample Collection Techniques

<u>SIR 2008-5038</u> *Guidelines for Design and Sampling for Cyanobacterial Toxin and Taste-and-Odor Studies in Lakes and Reservoirs*

http://pubs.usgs.gov/sir/2008/5038

<u>USGS National Field Manual Chapter 7.5</u>

Cyanobacteria in Lakes and Reservoirs: Toxin and Taste-and-Odor Sampling Guidelines

http://water.usgs.gov/owq/FieldManual/Chapter7/7.5.html

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Consistent Sampling Protocols – Sample Replication and Splitting Techniques Are Important

- Spatial variability may influence field replicates

- Cyanobacteria may influence split replicates
  - Physiology
  - Community Composition

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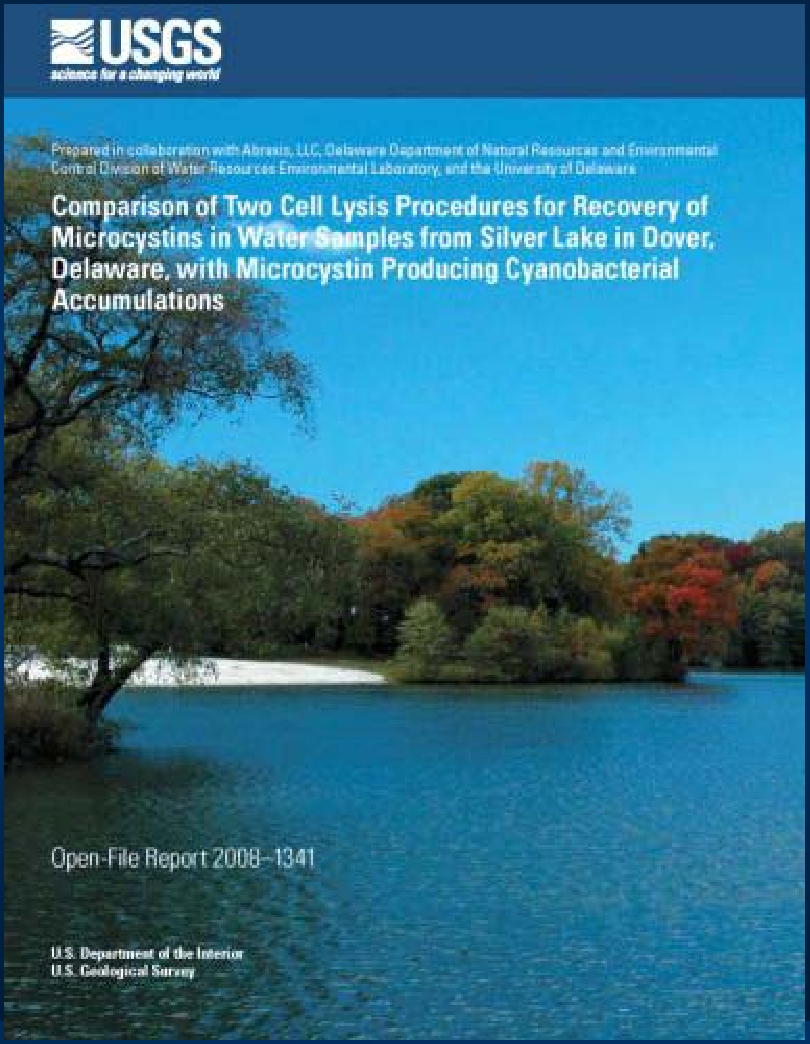
Consistent Processing Protocols – Sample Preparation Techniques Are Important

- Autoclaving
- Boiling
- Freeze-Thaw
- Sonication
- QuikLyse



http://pubs.usgs.gov/of/2008/1341/

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Analytical Methods for Cyanotoxins - Bioassays

Bioassays

Enzyme-linked immunosorbent assay
- 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

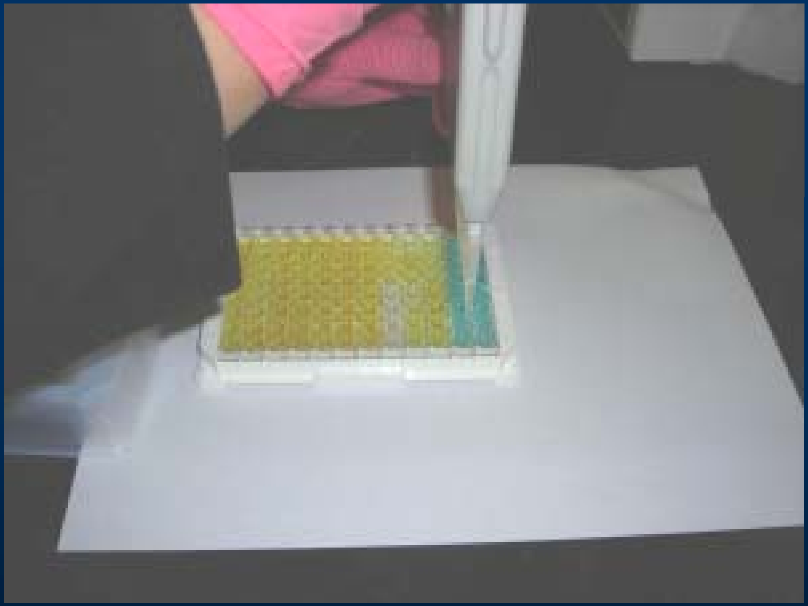
Disadvantages

Cross-reactivity

Matrix effects

Semi-quantitative

Radioassays use radio-labeled isotopes



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

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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

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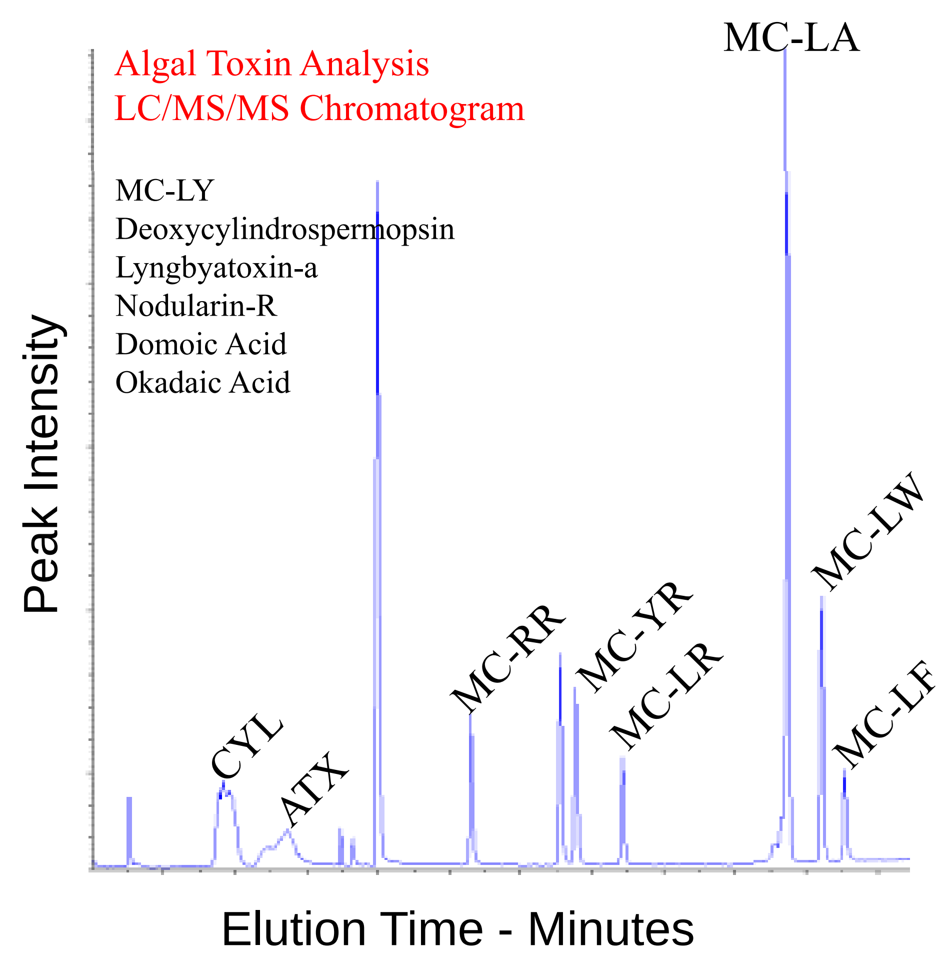
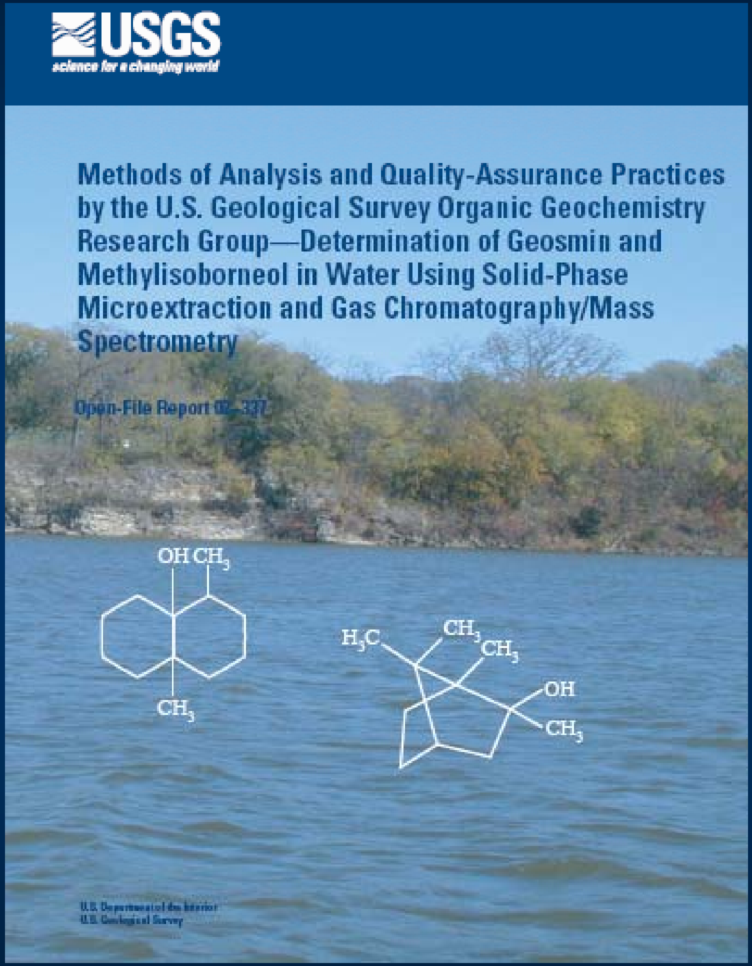
Robust and Quantitative Analytical Methods - Capabilities of the USGS Organic Geochemistry Research Laboratory





Toxin MRL's: ~10 ppt

Geosmin and MIB MRL: 5 ppt

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

Microcystin ELISA Cross-Reactivity

- With over 80+ microcystin and 10+ nodularins, most cross-reactivities are unknown
- None of these assays are MCLR specific

	Percent							
Microcystin Assays	**MCLA**	**MCLF**	**MCLR**	**MCRR**	**MCLW**	**MCLY**	**MCYR**	**NODR**
Monoclonal Assays								
Abraxis-DM	48	72	100	53	102	NA	64	76
Polyclonal Assays								
Abraxis-ADDA	125	108	100	91	114	NA	81	169
Beacon	5	NA	100	87	NA	NA	48	31
Envirologix	62	NA	100	54	NA	NA	35	69
Strategic Diagnostics	23	NA	100	97	NA	NA	82	66

ELISA Response = Σ (Cross-Reactivity x Actual Congener Concentration) $_i$

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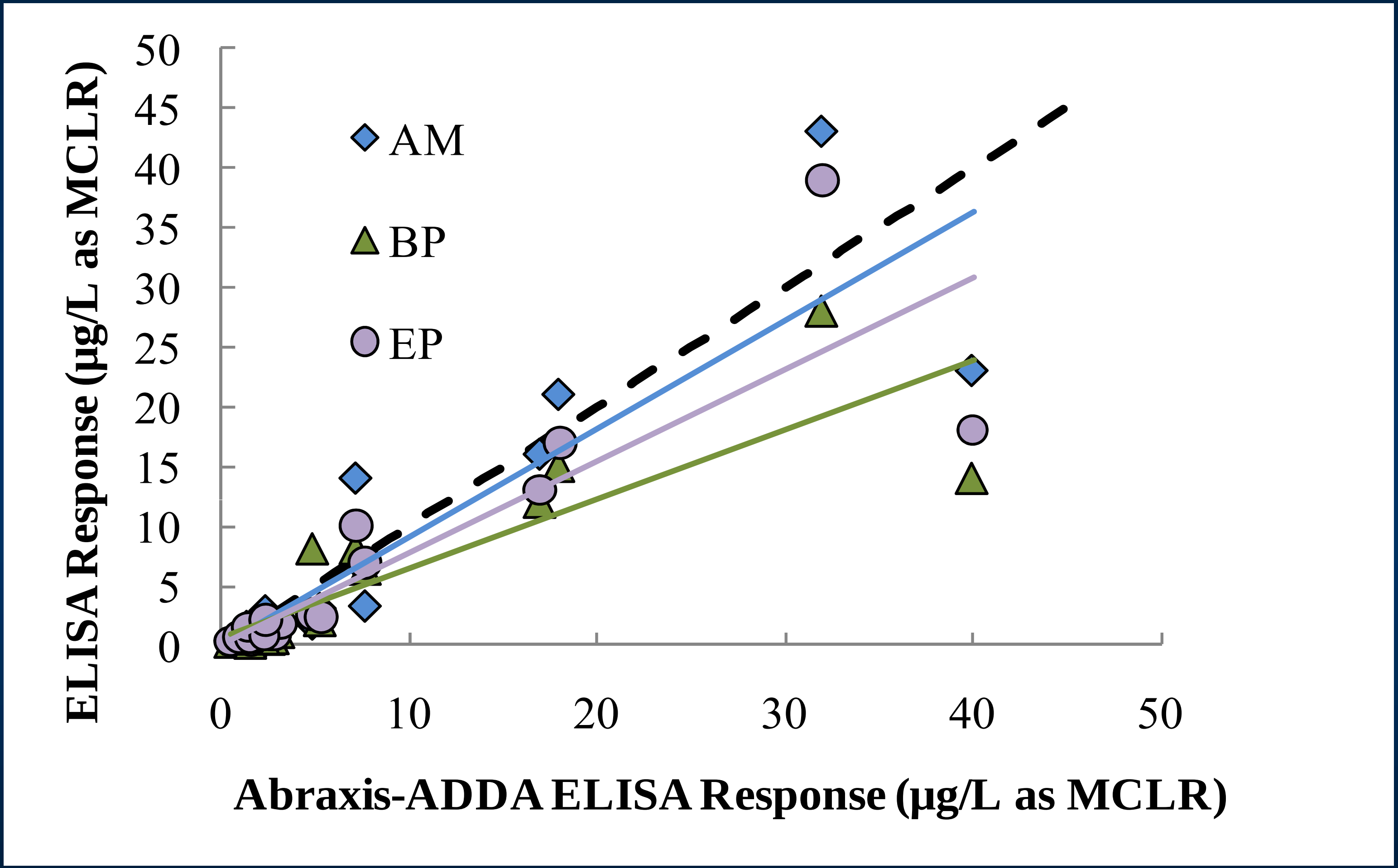
Microcystin Results May Vary Depending on the ELISA Used for Analysis



Abraxis-DM (AM), Beacon (BP), Envirologix (EP)

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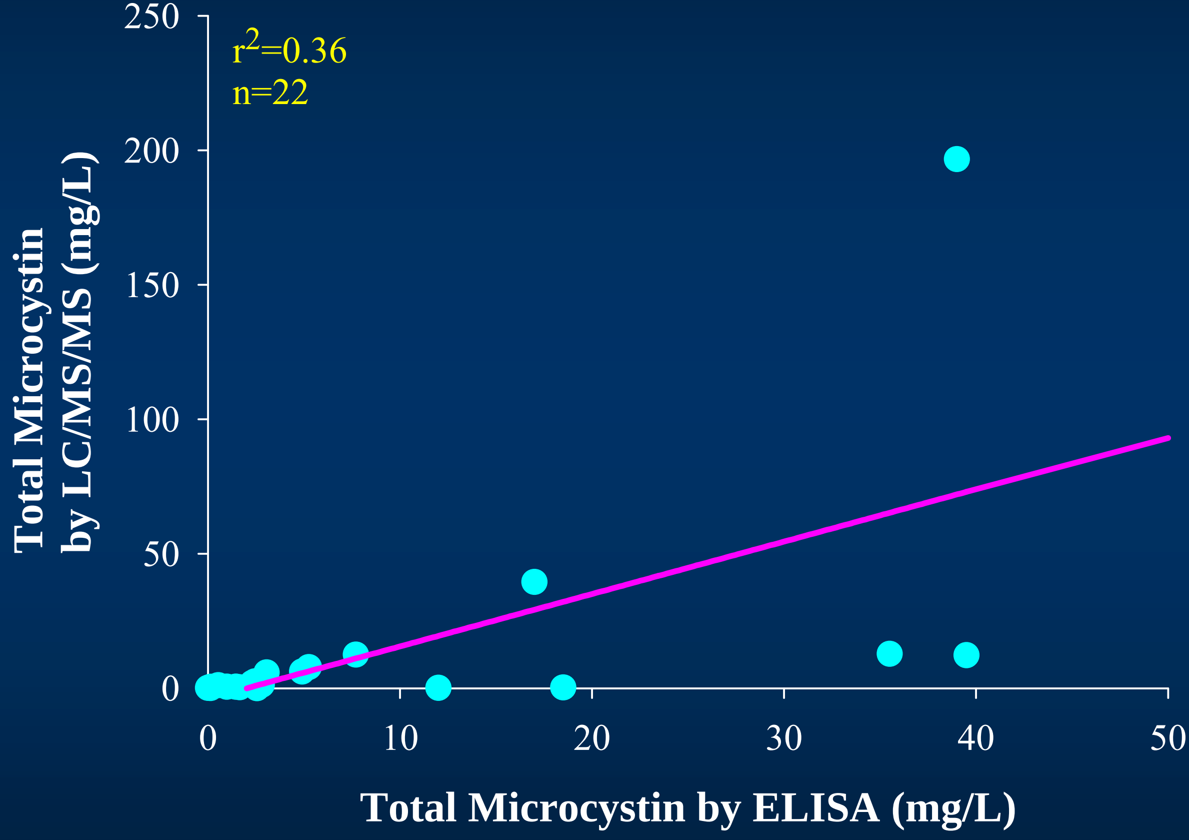
Total Microcystin Comparison – ADDA Specific ELISA vs LC/MS/MS for –LR, -RR, -LY, -YR, -LA, -LW, and –LF variants



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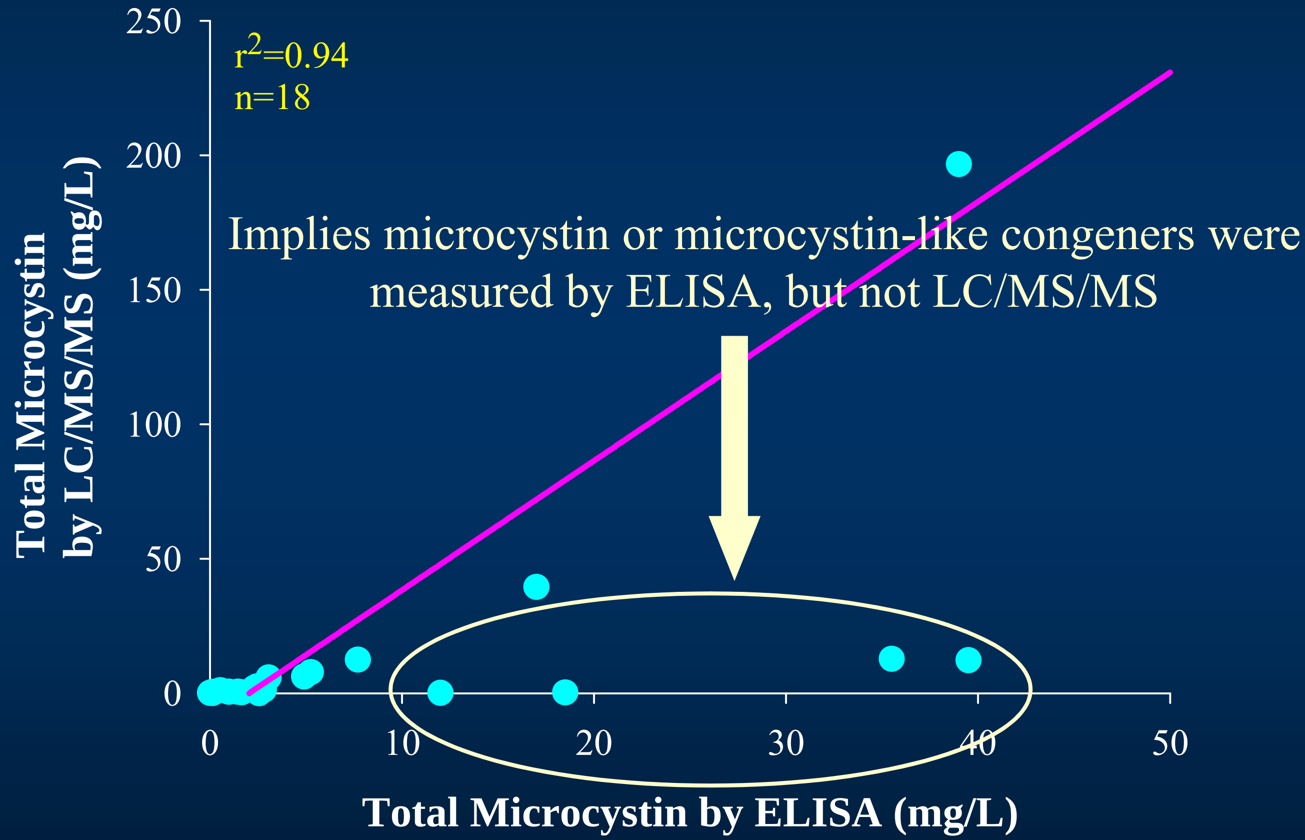
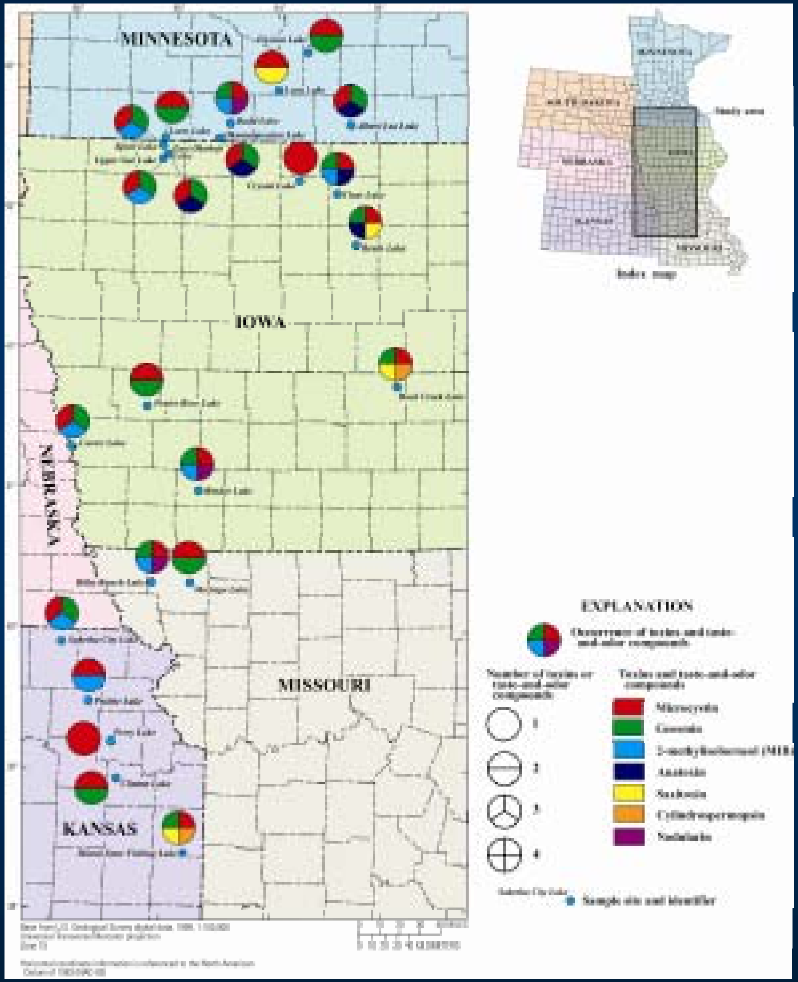
Congener Composition, Matrix Effects, and Detection Limits May Cause Differences When Comparing Results Measured by ELISA and LC/MS/MS



Cyanotoxin Occurrence - August 2006 Midwestern Reconnaissance TOTAL Concentrations of Multiple Toxins and Taste-and-Odor Compounds in 23 BLOOM Samples

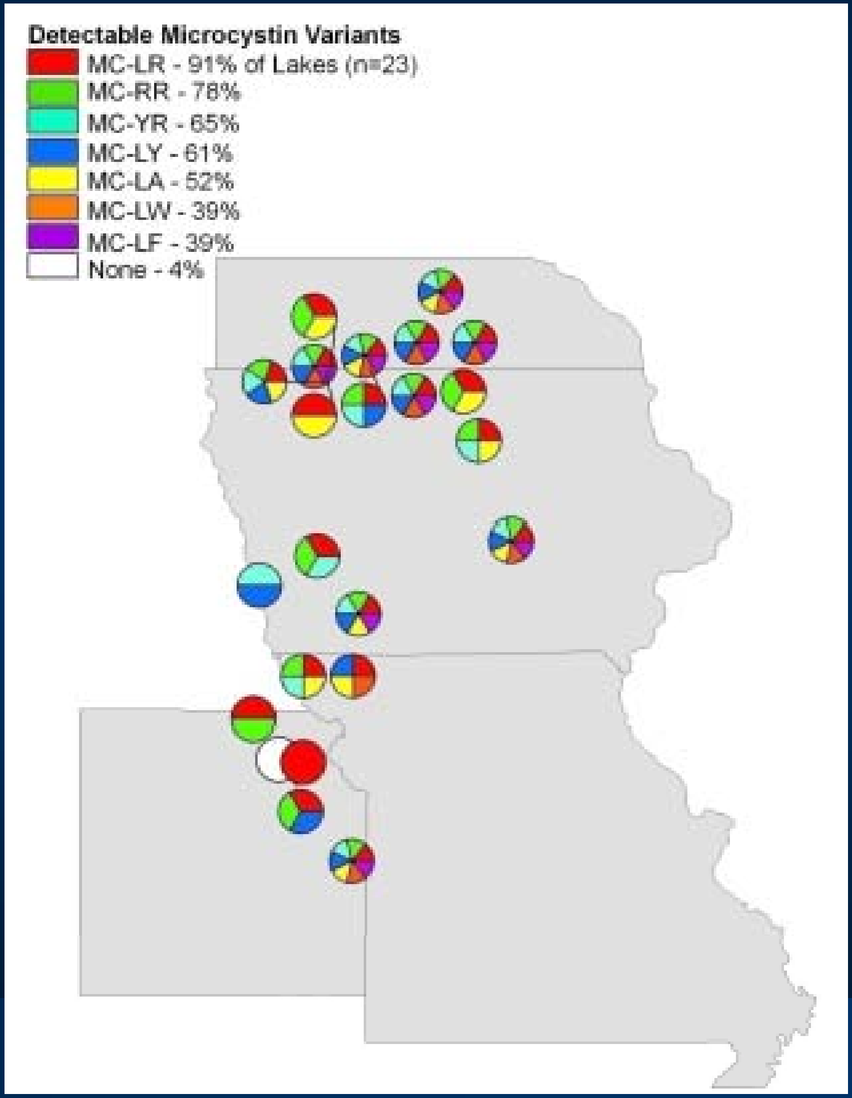
Results:

- 100% of BLOOMS sampled had detectable microcystin, 87% had detectable geosmin, and 30% had detectable anatoxin
- Maximum TOTAL microcystin concentration: 19,000 µg/L
- 17% of blooms had microcystin concentrations exceeding the WHO recreational guideline of 20 µg/L



Cyanotoxin Occurrence - Microcystin-LR Was the Most Common Variant, But It Was Not Detected in ALL Blooms With Detectable Microcystin

- Microcystin-RR, -YR, and –LY also were relatively common.
- 91% of blooms had two or more microcystin variants present.
- 17% of blooms had all seven measured microcystin variants present.



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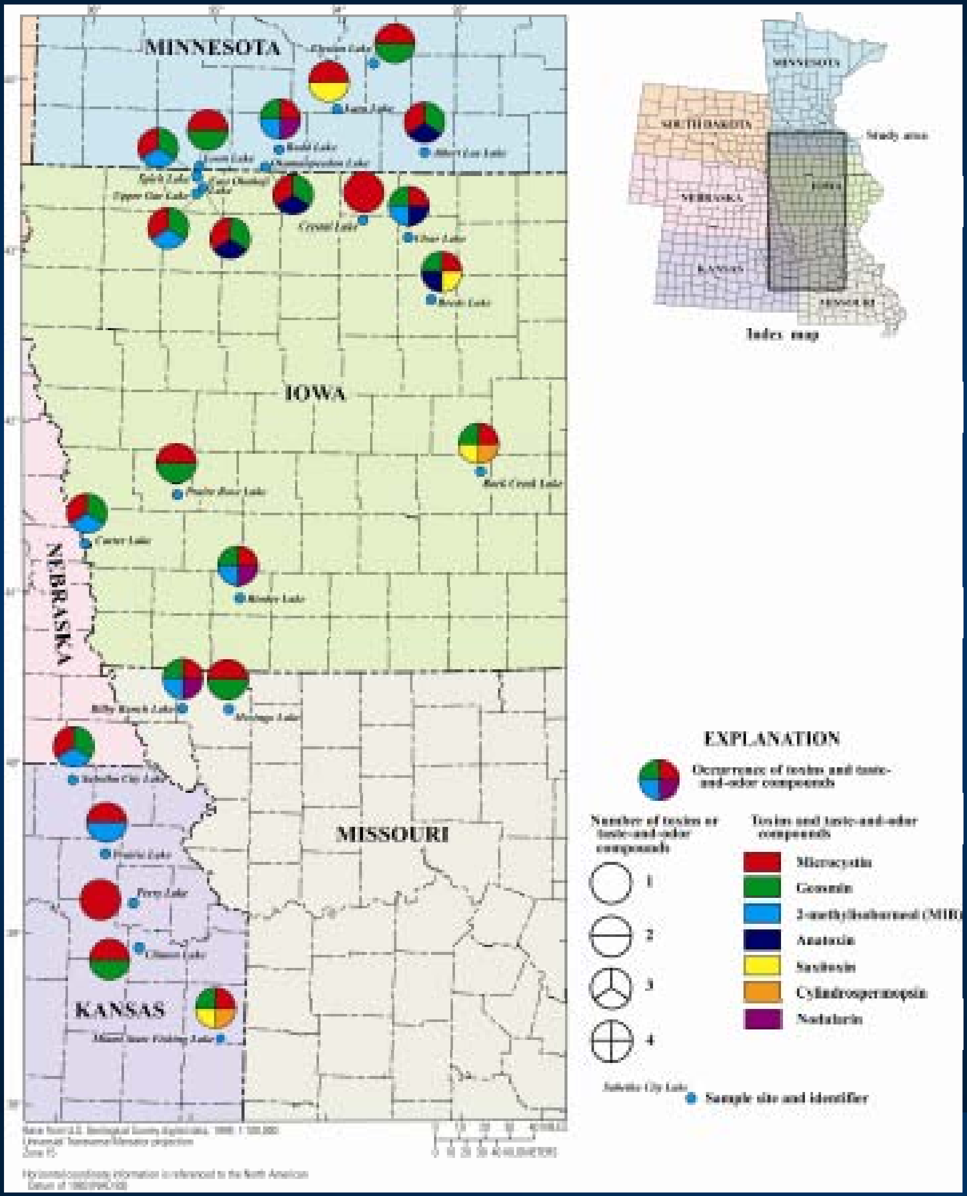
During August 2006 Toxins and Taste-and-Odor Compounds Co-Occurred in 91% of BLOOMS Sampled (n=23) and Anatoxin-a Always Co-Occurred with Geosmin



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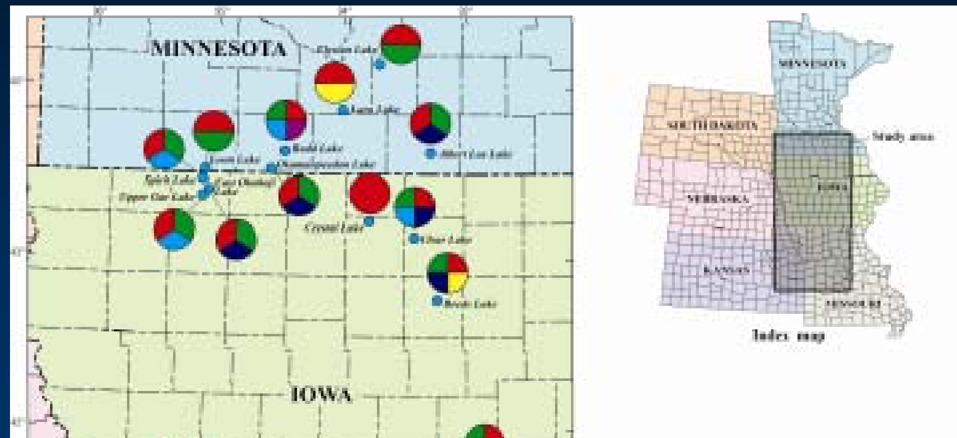
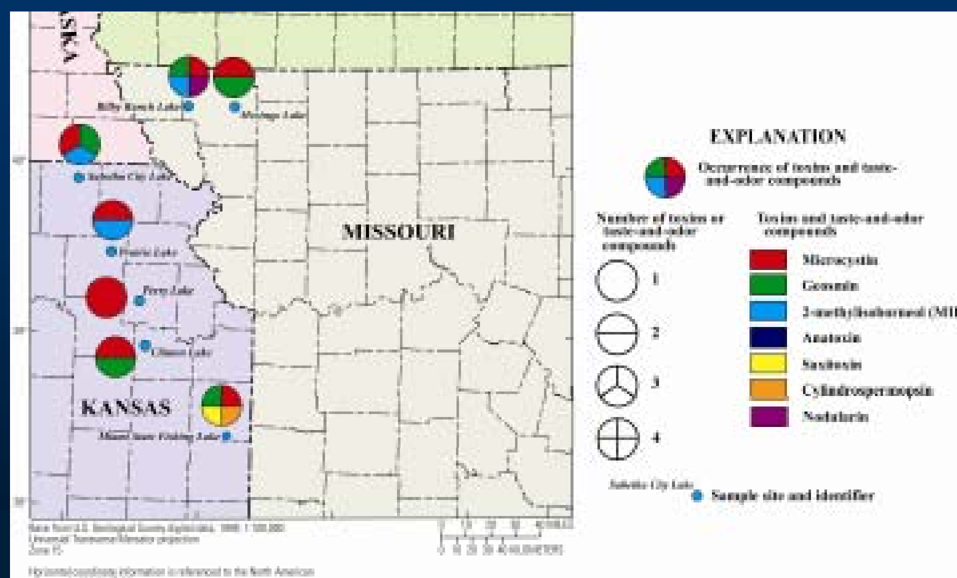


“Algae may make for stinky water, but it poses no health risks”

-Concord Monitor, Concord, NH July 7, 2006



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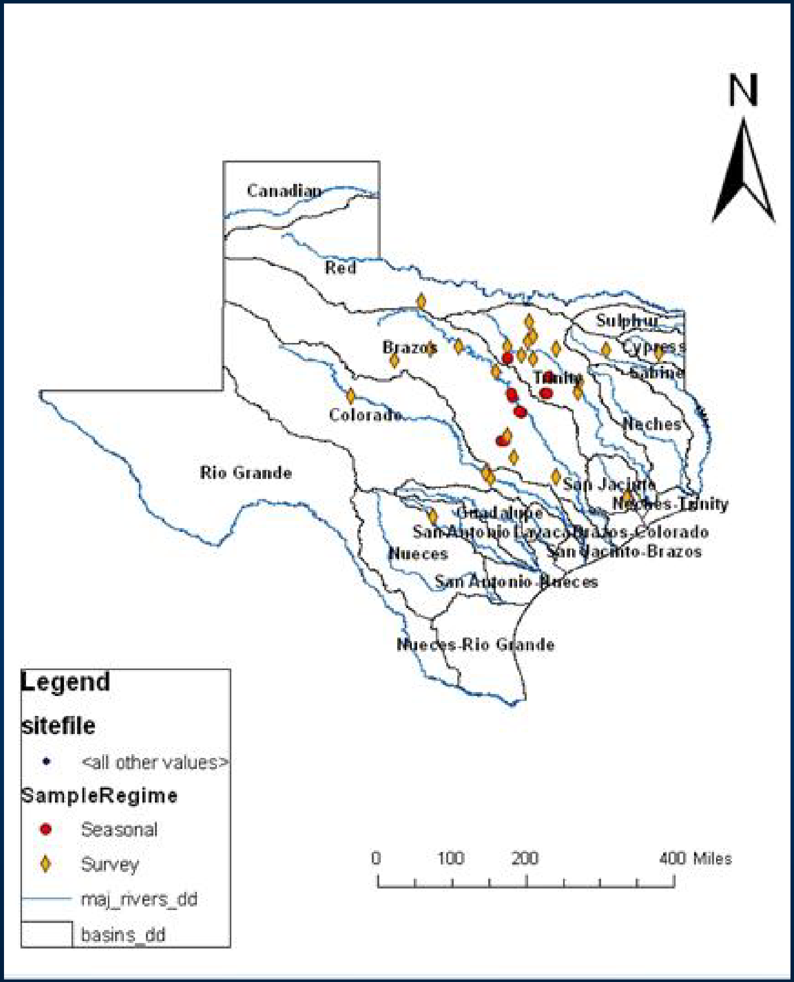
Cyanotoxin Occurrence - 2006 Texas Reservoir Survey for DISSOLVED Microcystin in Surface Samples at OPEN WATER Locations

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

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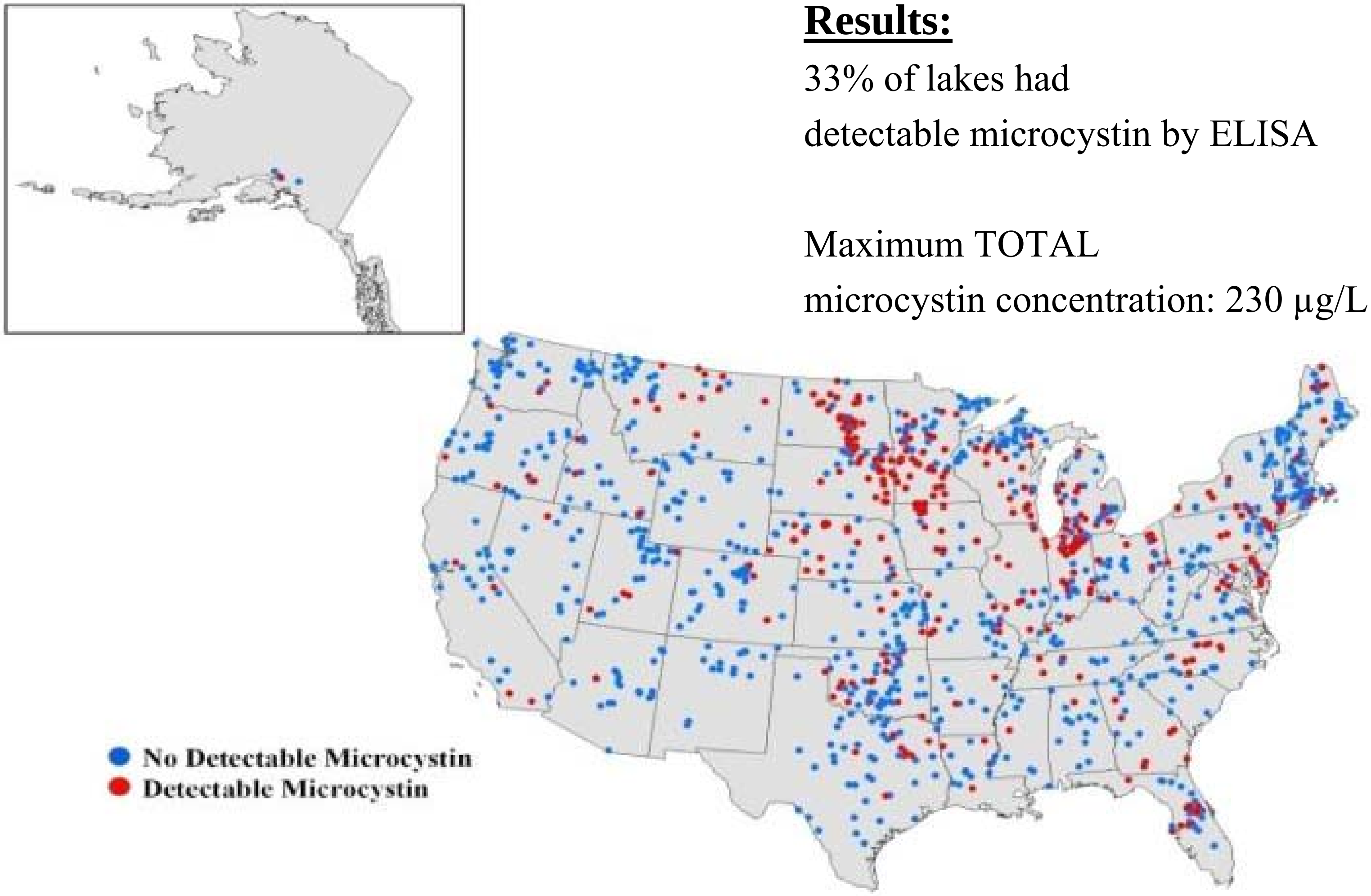
Cyanotoxin Occurrence - 2007 US EPA National Lake Assessment TOTAL Microcystin in INTEGRATED PHOTIC ZONE Samples



Results:

33% of lakes had detectable microcystin by ELISA

Maximum TOTAL microcystin concentration: 230 µg/L

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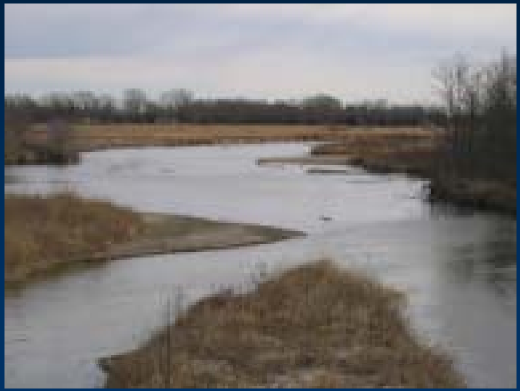
Sample Location and Type are Important

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	13,000
Texas Recon 2006	Open Water, Surface Grab	Dissolved	67	22	0.2
EPA NLA 2007	Open Water, Integrated Photic	Total	1332	33	230

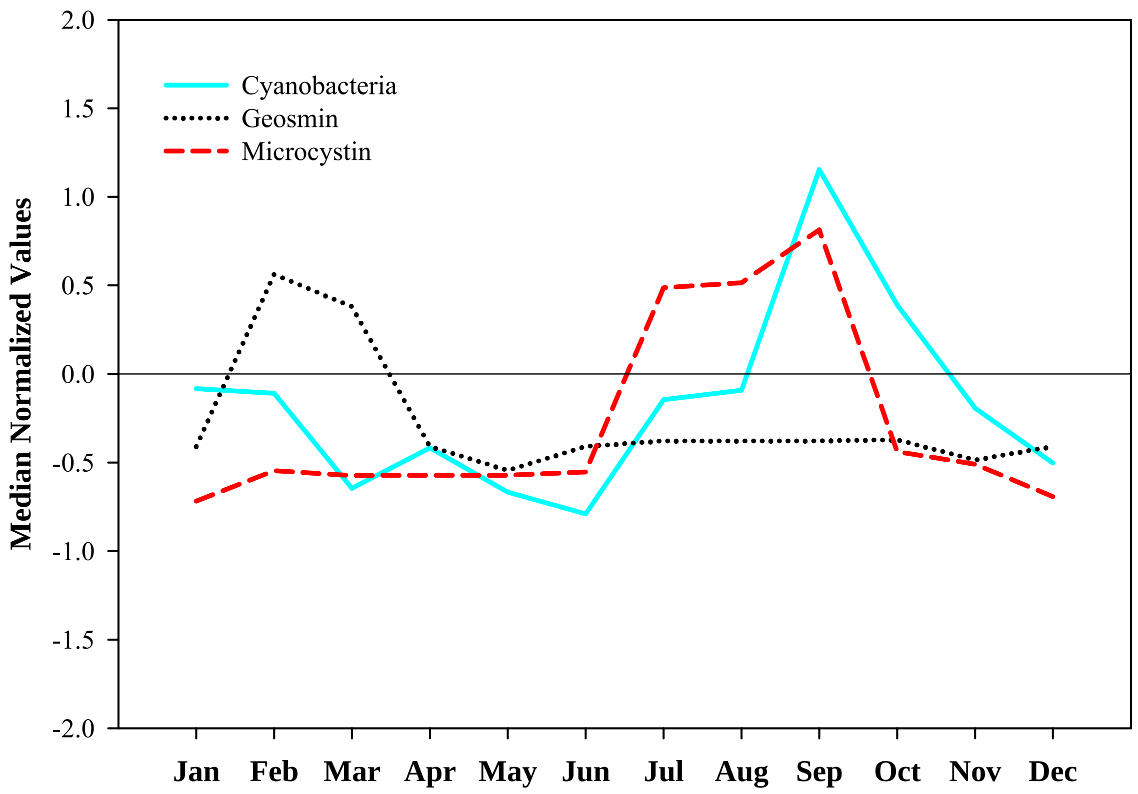
Microcystin was measured by ELISA in all studies

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

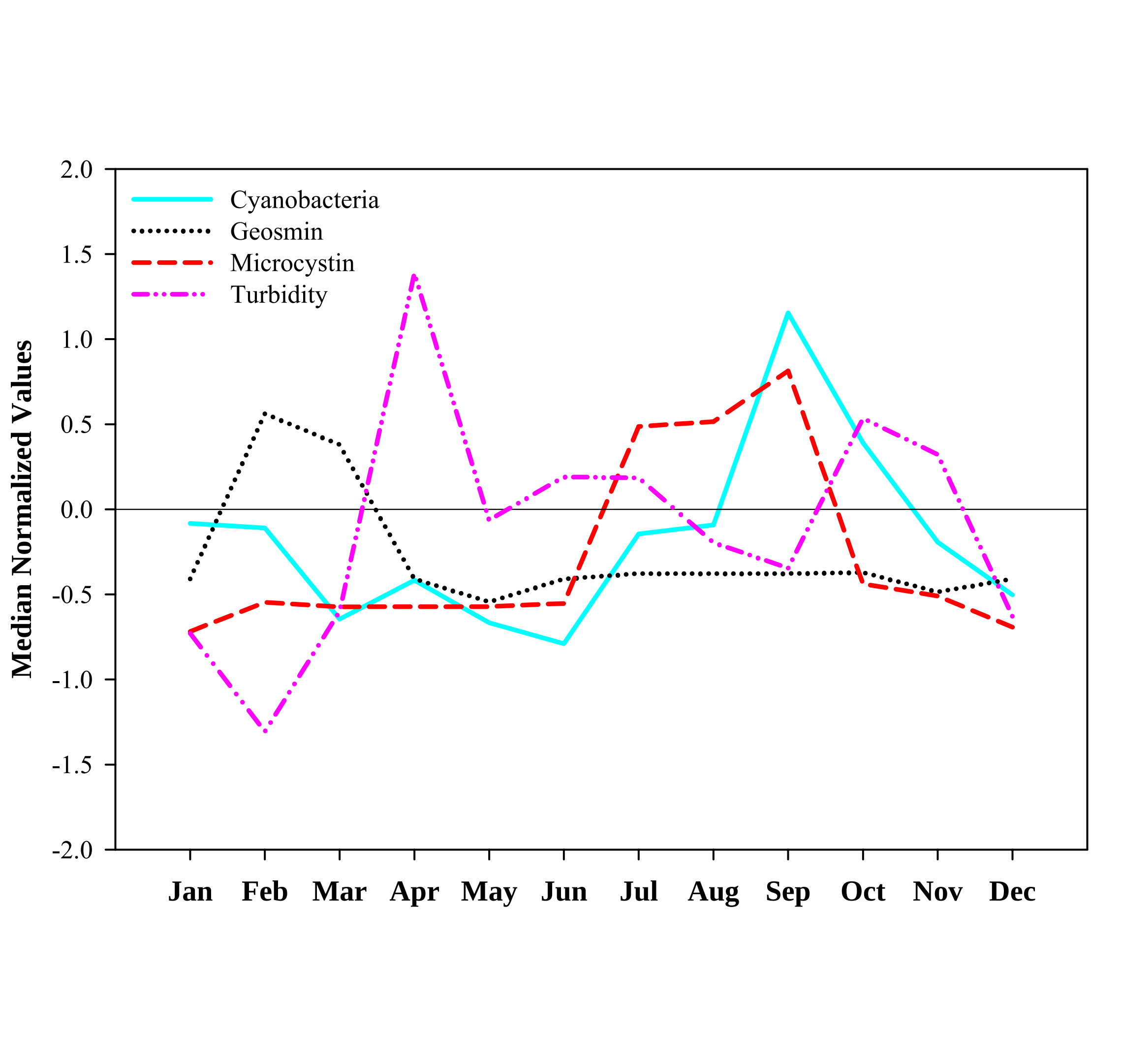


- **Concerns**
  - Taste-and-odor occurrences related to algal blooms
  - Relation between watershed inputs and taste-and-odor causing algae
- **Approach**
  - Describe current and historical loading inflow
    - Sediment Cores
    - Continuous Water-Quality Monitoring
  - Describe physical, chemical,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

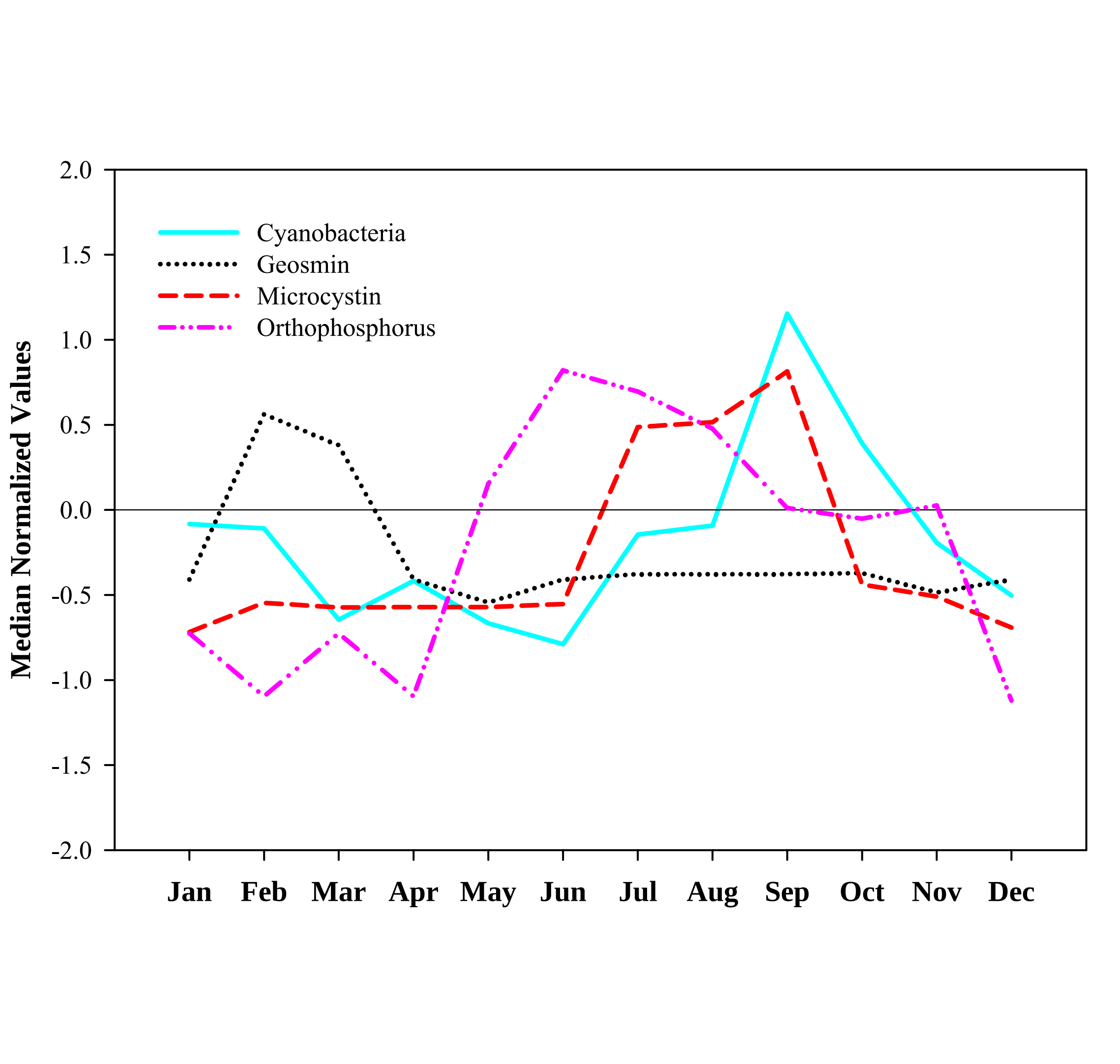
Despite Variability, Seasonal Trends in Cyanobacterial Abundance, Geosmin, and Microcystin are Fairly Consistent, with Peak Cyanobacterial Abundance and Microcystin in Summer and Peak Geosmin in Winter



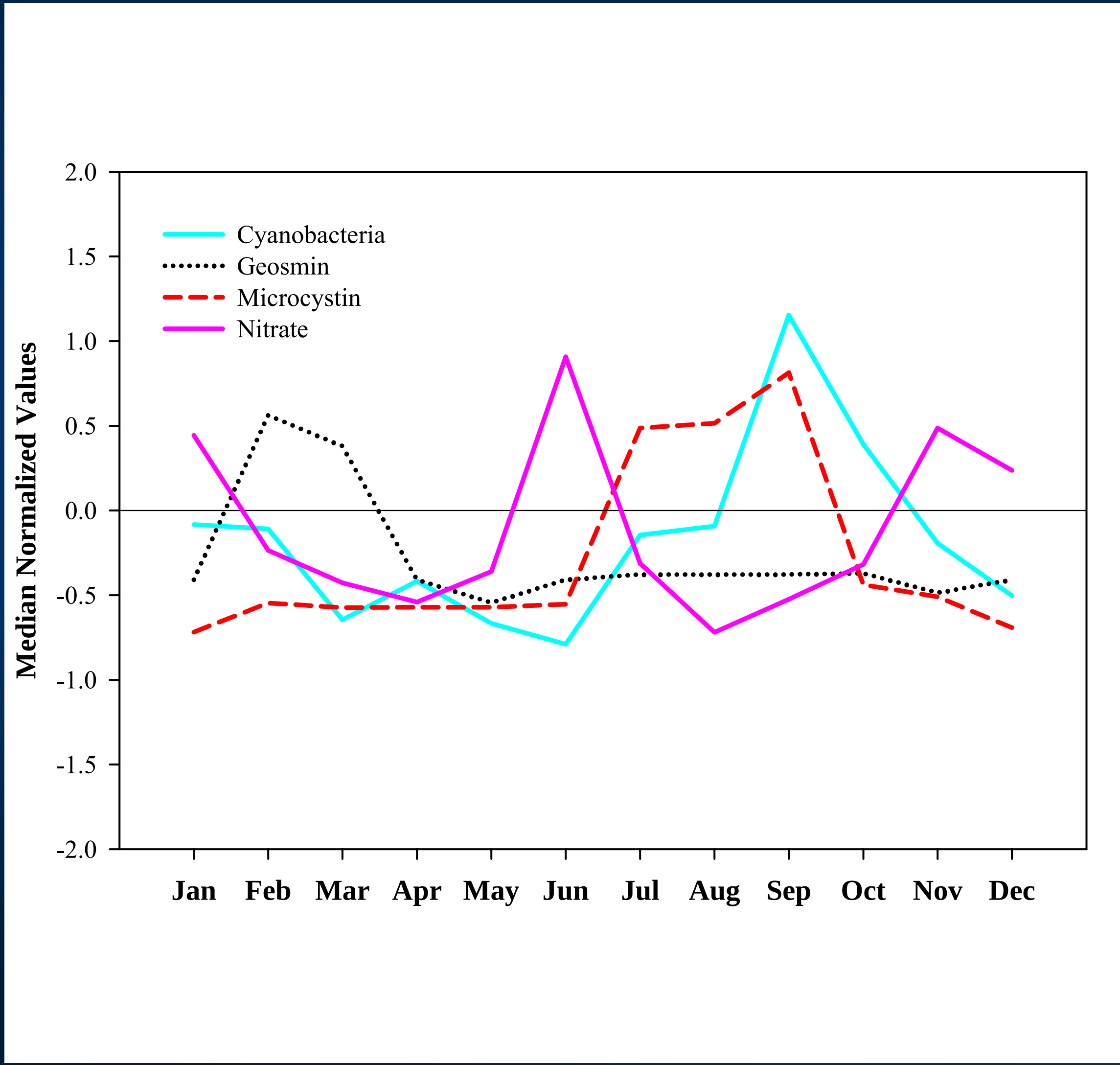
Winter Geosmin Peaks Coincide with Seasonal Minima in Turbidity



Winter Geosmin Peaks Coincide with Seasonal Minima in Orthophosphorus



Summer Peaks in Cyanobacteria and Microcystin Coincide with Seasonal Minima in Nitrate



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

- Recorded hourly, transmitted every 4 hours
- Data available online - http://nrtwq.usgs.gov/ks/
- Develop relations to estimate concentrations of variables that can not be measured in real time
- Real-time variables
  - 2001 – Specific conductance, pH, water temperature, turbidity, dissolved oxygen, chlorophyll
  - 2005 – light penetration
  - 2006 – second monitor near bottom, cyanobacteria, nitrate
  - 2007 – wind speed and direction

Multiple Regression Using Data Collected During 2001-2003 Resulted in a Real-Time Model for Geosmin Based on Turbidity and Specific Conductance

USGS
science for a changing world

Real-Time Water Quality for Kansas

Home | View Data | Methods | Constituents | Models | Bibliography | Links

NRTWQ Home >> Kansas >> View Data >> 07144790

Plot | Data Table | Statistics | Duration Curve | Site info | Model info

USGS station: 07144790 Cheney Reservoir near Cheney, KS — Go to NWISWeb

Constituent: Computed geosmin — concentration — hourly — < Go >

Time period: Last 31 days

Model Form

$$\log_{10}(\mathbf{Geo}) = 7.231 - 1.0664 \log_{10}(\mathbf{TURB}) - 0.0097\ \mathbf{SC}$$

where:

- **Geo** is computed geosmin, in micrograms per liter
- **TURB** is turbidity, YSI model 6026, in formazin nephelometric units
- SC is specific conductance at 25 degrees Celsius, in microsiemens per centimeter

Model Calibration

Basic Data

Number of measurements:	18
Mean squared error:	0.04730625
Multiple R^2:	0.71
Bias correction (smearing) factor:	1.159

Explanatory Variables

Variable	Value	Standard error
Intercept	7.231	1.6752
$\log_{10}$(TURB)	-1.0664	0.1903
SC	-0.0097	0.0018

http://nrtwq.usgs.gov/ks/

USGS
science for a changing world

Prepared in cooperation with the
City of Wichita, Kansas

Water Quality and Relation to Taste-and-Odor Compounds in the North Fork Ninnescah River and Cheney Reservoir, South-Central Kansas, 1997–2003

Scientific Investigations Report 2006–5095

U.S. Department of the Interior
U.S. Geological Survey

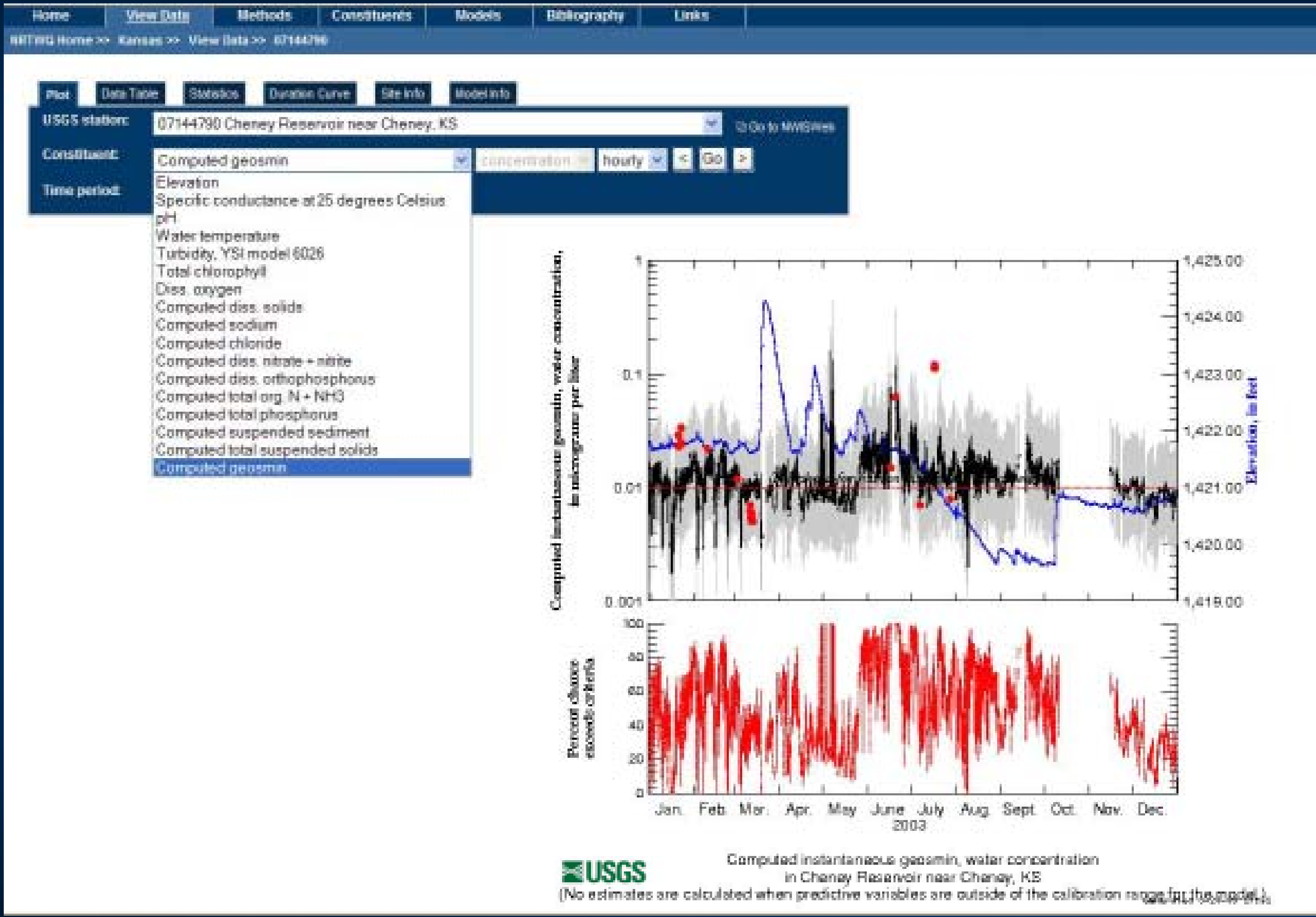
USGS

http://pubs.usgs.gov/sir/2006/5095/

CITY OF WICHITA

Continuous Estimates are Available in Real Time on the Web

http://nrtwq.usgs.gov/ks/



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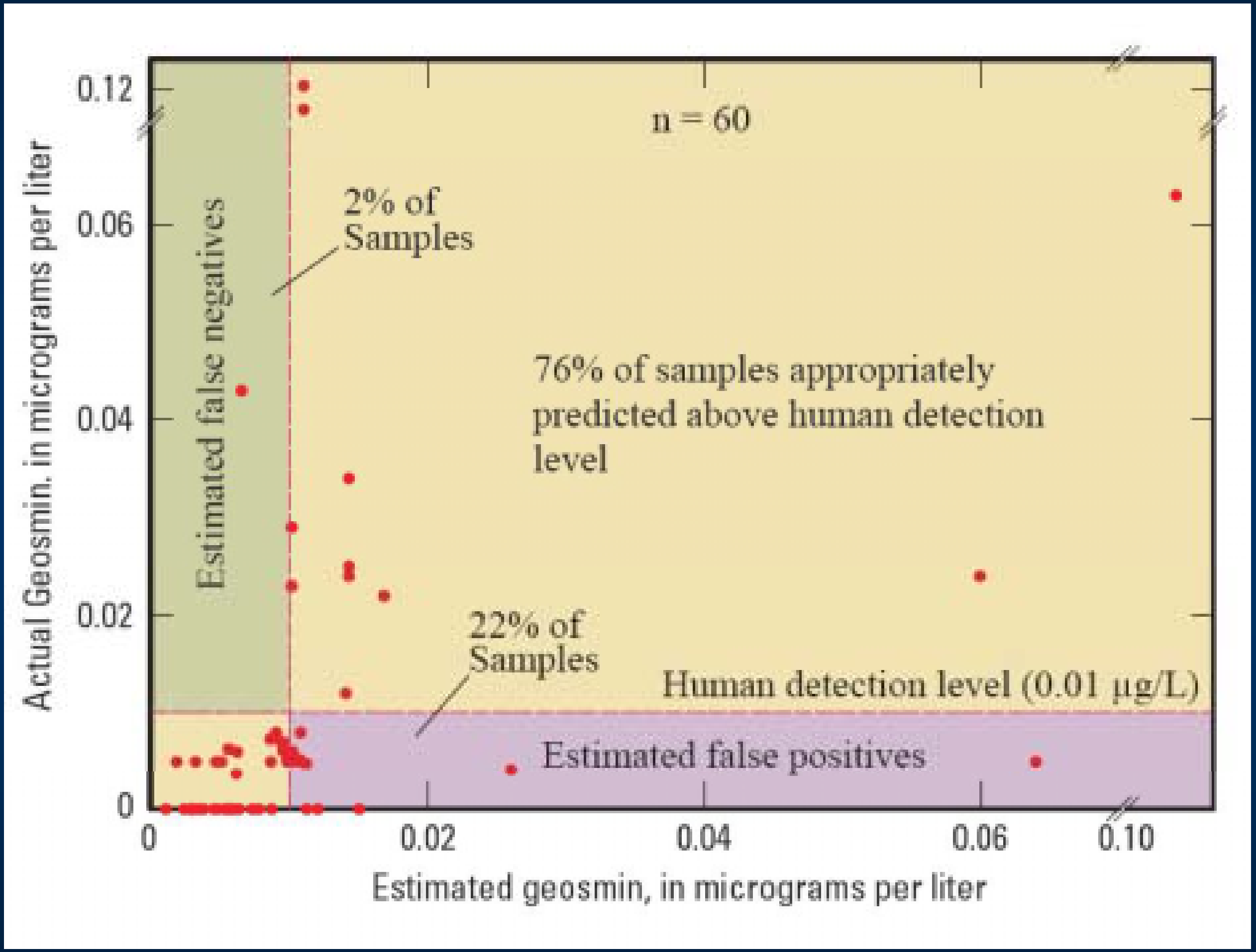
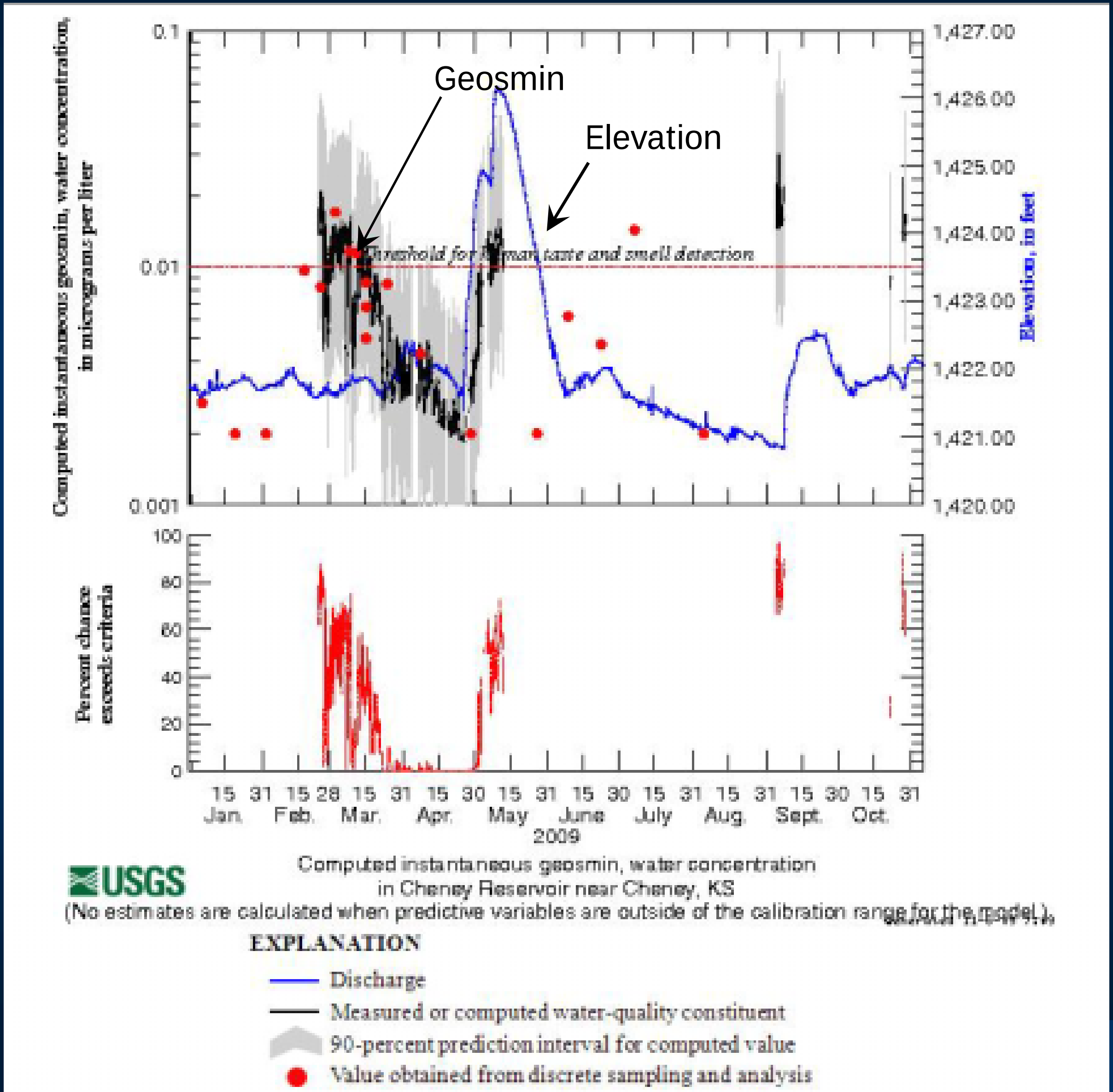
Within Existing Model Limits Geosmin Concentrations Were More Likely to Be Overestimated than Underestimated During 2001-2008



The Model Does Not Perform Well When Predictive Variables Are Outside of the Calibration Range

Model Limits:
FNU: < 36
µS/cm: 790-915



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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

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