EMERGING CONTAMINANTS SUMMIT

DETECTION // TREATMENT // REGULATION

Harmful Algal Blooms: Nature, Occurrence and Regulatory Outlook

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Refinery Specialties, Inc.

Scope

- Harmful Algal Blooms (HABs) defined
- Algal species of concern and associated toxins
- Factors contributing to HAB development
- Current Recommended Exposure Guidelines
- Recommendations

Four Main Questions

- What are HABs?
- What toxins are associated with HABs?
- Under what conditions do HABs form?
- How can they be controlled?

Harmful Algal Blooms - defined

- An algal bloom is a rapid increase or accumulation in the population of algae in a water system.
  - Often due to human influences, e.g. cultural eutrophication
  - May be due to natural fluctuations
- A Harmful Algal Bloom (HAB) is an algal bloom which results in (or has the potential to result in) adverse impacts to human health and the environment.
- May occur in marine, freshwater, and brackish water environments.

Harmful Algal Blooms - Impacts

Adverse environmental impacts of HABs include:

1. Dramatic alterations of water chemistry (pH and DO)
   - Raise pH by removing CO_2 and increasing OH^- concentration
   - Supersaturate DO levels in upper water column (near-surface)
   - Reduce DO through cellular respiration and biological degradation
2. Reducing light transmission – habitat alteration
3. Contributing to taste and odor problems (drinking water sources)
   - Geosmin and 2-methylisoborneol (MIB) often associated with HABs
4. Other aesthetic effects
   - Water discoloration, interference with recreational activities
5. Releasing toxins into water bodies (source and receiving)
   - Cause illness and death via food chain or biomass accumulation (neurotoxins)
   - Cause mechanical damage to freshwater and marine organisms
   - Human health risk through exposure and consumption of contaminated seafood and drinking water

Harmful Algal Blooms – Impacts (cont.)

The adverse impacts of HABs fall into three main categories:

- Ecological Impacts
  - Zooplankton avoidance or death
  - Bioaccumulation
  - Fish kills
  - Losses to bird and mammal populations
- Economic Impacts
  - Increased drinking water treatment costs
  - Loss of recreational revenue
  - Decimation of recreational and commercial fisheries
  - Death of livestock and domestic animals
  - Increased medical expenses
- Human Health and Aesthetic Impacts

HAB-related illnesses

- Examples of documented human illnesses and / or syndromes associated with HABs include:
  - Paralytic Shellfish Poisoning (PSP)
  - Diarrheal Shellfish Poisoning (DSP)
  - Neurotoxic Shellfish Poisoning (NSP)
  - Ciguatera Fishfood Poisoning (CFP)
  - Estuary Associated Syndrome (EAS)
  - Amnesic Shellfish Poisoning (ASP)
  - Cyanobacterial Toxin Poisoning (CTP)

HAB-related illnesses – causal organisms

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PSP, DSP, NSP, CFP, EAS: **Dinoflagellate (marine)**

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Dinoflagellate (marine) (PSP, DSP, NSP, CFP, EAS)

Diatom (marine) (ASP)

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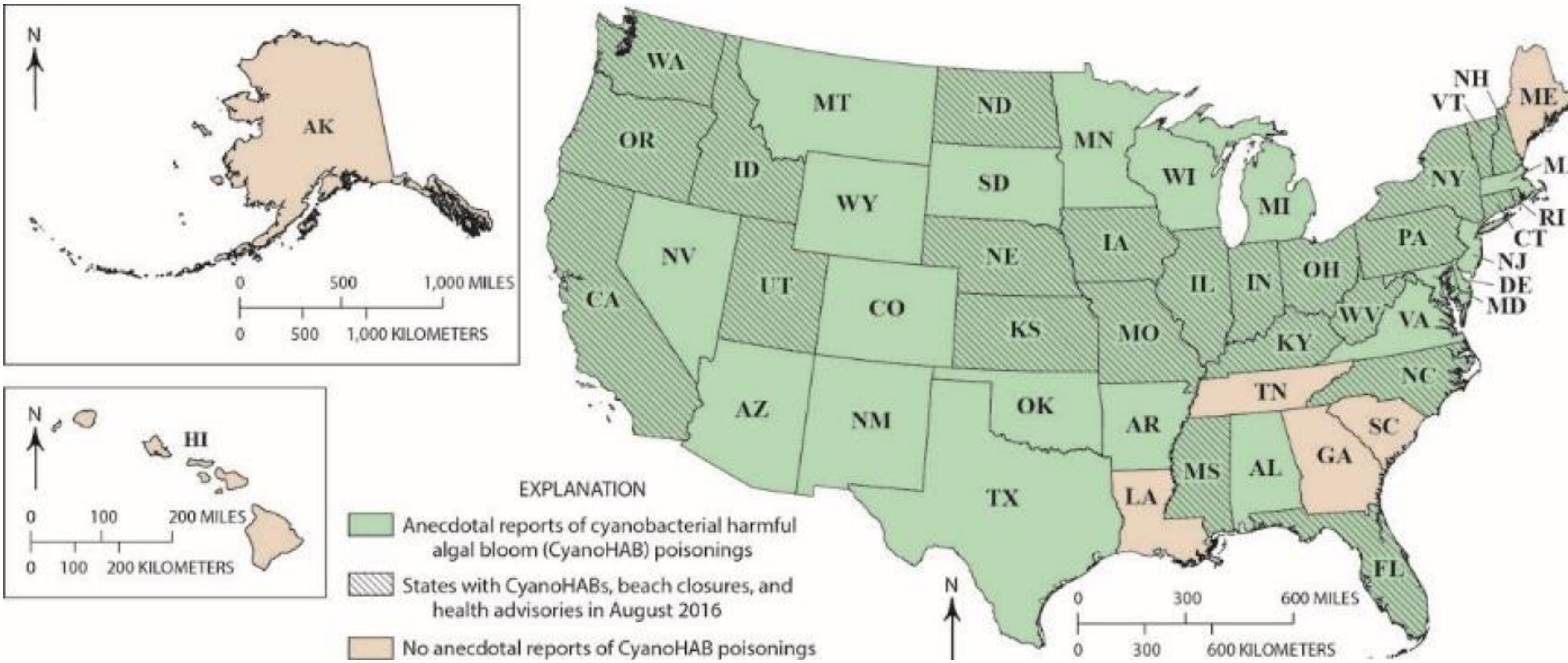
→ **Dinoflagellate (marine)**

- Amnesic Shellfish Poisoning (ASP) → **Diatom (marine)**
- Cyanobacterial Toxin Poisoning (CTP) → **Cyanobacteria (freshwater)**
  - Usually the result of drinking contaminated water
  - A sub-acute condition characterized by liver damage (jaundice)
  - May be accompanied by other, often reversible, symptoms
  - Acute cases can result in neurotoxic effects

Source: Mosby's Medical Dictionary, 9th edition. © 2009, Elsevier)

Cyanobacteria – Impacts Distribution (U.S.)

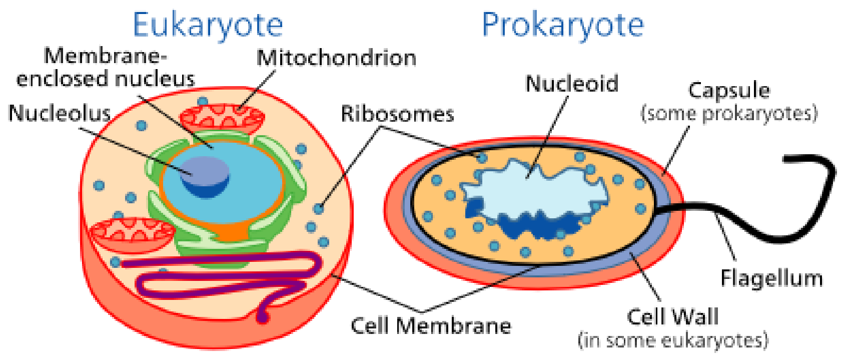


Cyanobacteria - Overview

General features:

- Single-celled organism
  - Unicellular and filamentous species
  - May form colonies or aggregations – phototrophic biofilms or microbial mats
  - Can exist as free-living individuals or in symbiotic relationships, e.g. lichen
  - Found in a variety of ecosystems
- Autotrophic
  - Reduce atmospheric CO_2 to produce carbohydrate (under aerobic conditions)
  - Fix both N_2 and C; produce O_2

Cell type comparison



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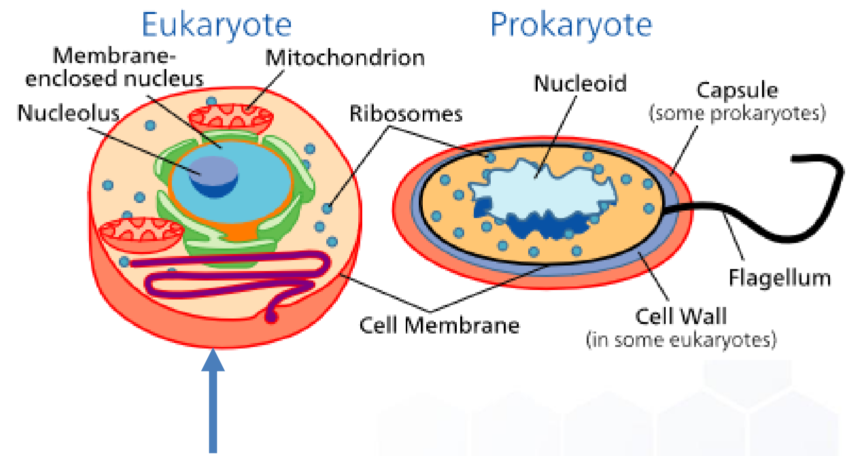

- **Complex internal structure (organelles)**
- **Membrane-bound "true" nucleus**
- **Common metabolic pathways**
- **Chlorophyll within chloroplasts**

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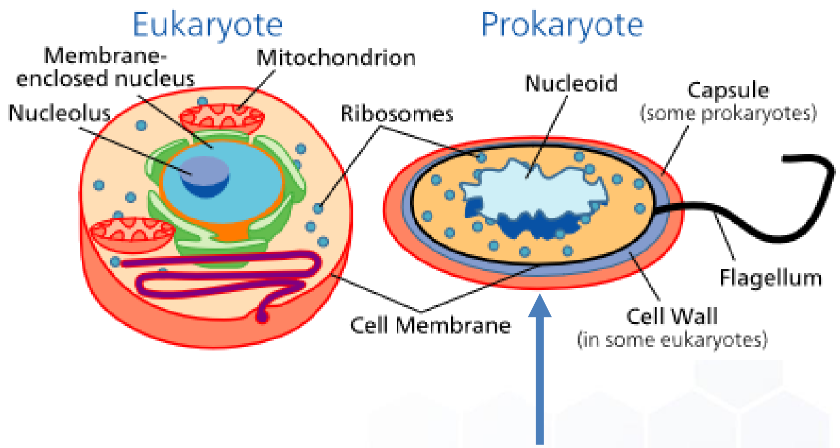
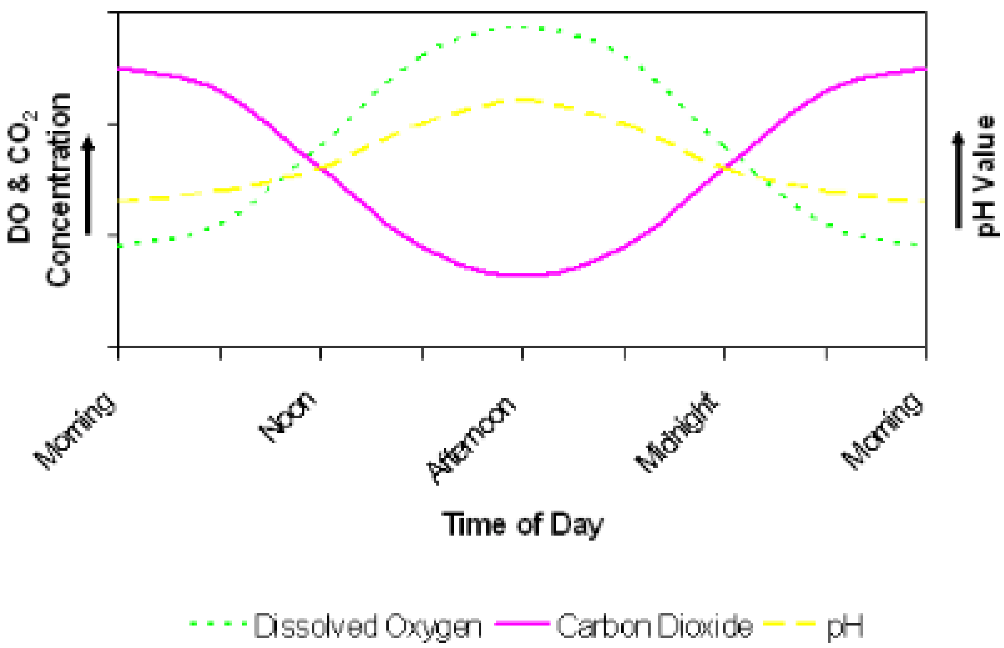


- **Simple internal structure (few organelles)**
- **No true nucleus; not membrane-bound**
- **Variety of metabolic pathways**
- **Chlorophyll throughout cytoplasm**

Algal Activity in Aquatic Environments

- Algae exhibit strong diurnal patterns of activity (photosynthetic activity)
- During day, algae migrate upward in water column, DO and pH levels increase
  - Photosynthesis results in O_2 production
  - CO_2 removal from atmosphere and water (results in increased OH^- concentration and increased alkalinity)
- During day, pattern is reversed – DO consumed through respiration, CO_2 given off



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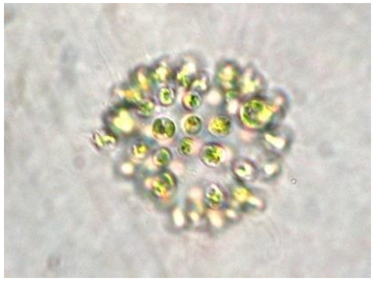
Algal Species and Cyanotoxins Associated with HABs

Genera	Cyanotoxins	Target Organ
Microcystis, *Anabaena*, *Planktothrix* (Oscillatoria), *Nostoc*, *Hapalosiphon*, *Anabaenopsis*, *Woronichinia*	Microcystins	Liver
Nodularia	Nodularins	Liver
Anabaena, *Planktothrix* (Oscillatoria), *Aphanizomenon*, *Woronichinia*	Anatoxin-a	Synapse
Anabaena	Anatoxin-a(S)	Synapse
Cylindrospermopsis, *Aphanizomenon*, *Umezakia*	Cylindrospermopsins	Liver
Lyngbya	Lyngbyatoxin-a	Skin, GI tract
Anabaena, *Aphanizomenon*, *Cylindrospermopsis*, *Lyngbya*	Saxitoxin	Synapse
All	Lipopolysaccharides	Exposed Tissue (irritant)
Lyngbya, *Planktothrix* (Oscillatoria), *Schizothrix*	Aplysiatoxins	Skin
All	BMAA	CNS

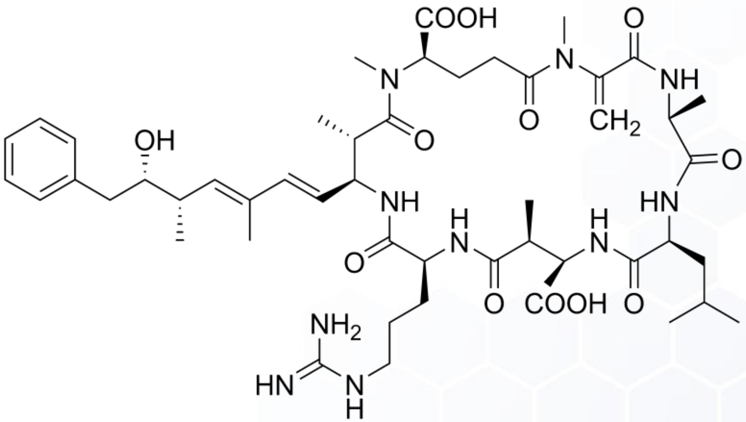
Microcystin/Microcystin-LR



(M. aeruginosa)

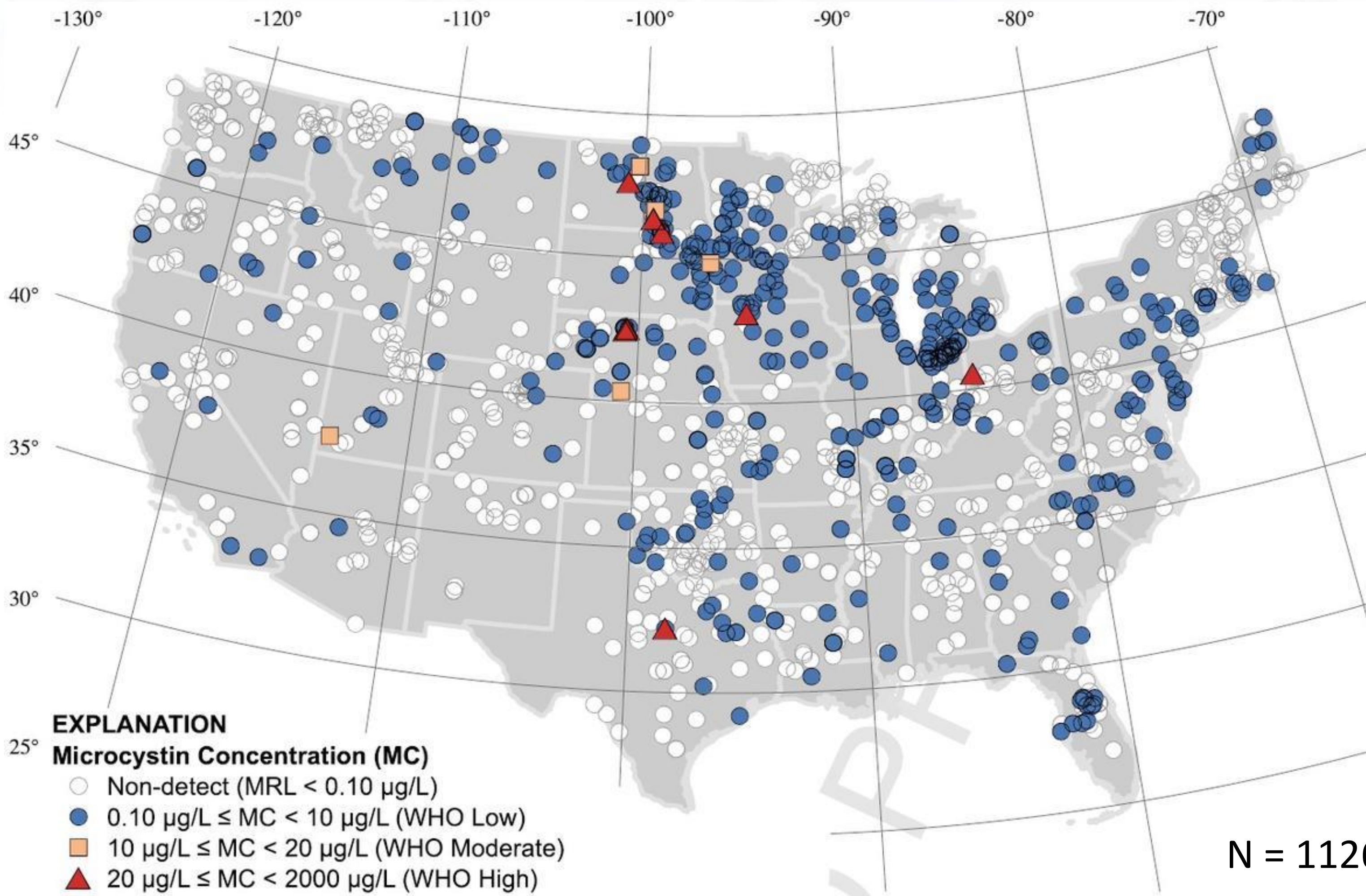
- Named after Microcystis aeruginosa
- Most prevalent and well-known algal toxin – has been intensively studied
- 60 known variants (congeners); Microcystin-LR most commonly reported (standard lab method)
- Cyclic peptides as a class represent greatest human health concern
- Hepatotoxin; may be tumor promoter at low doses
- Stable over wide range of temperature and pH, not easily removed by traditional water treatment methods

Structure – cyclic peptide



Microcystin-LR

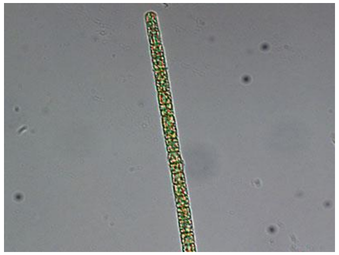
Microcystin Concentrations in U.S. Inland Lakes and Reservoirs (2016)



N = 1126

Source: https://www.usgs.gov/news/new-science-challenges-old-assumptions-about-harmful-algal-blooms. Downloaded 4/19/2017

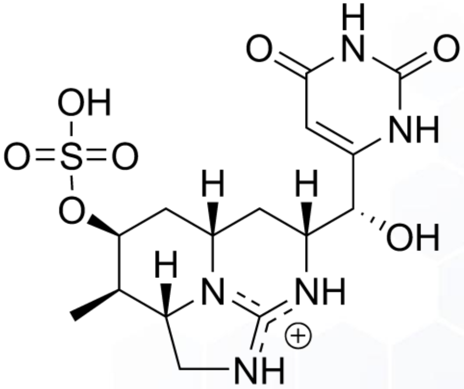
Cylindrospermopsins (CYN or CYL)



(C. raciborskii)

- Named for Cylindrospermopsis raciborskii – a filamentous algae
- Certain Cylindrospermopsis strains also capable of producing anatoxins and saxitoxin
- Implicated in hepatoenteritis outbreak in Palm Island, Australia in 1979
- Typically found in tropical regions but now present in temperate zones, e.g. Great Lakes (South American strain)
- A hepatotoxin and nephrotoxin
- Bioaccumulation potential
- After microcystins, the algal toxins of greatest concern in US

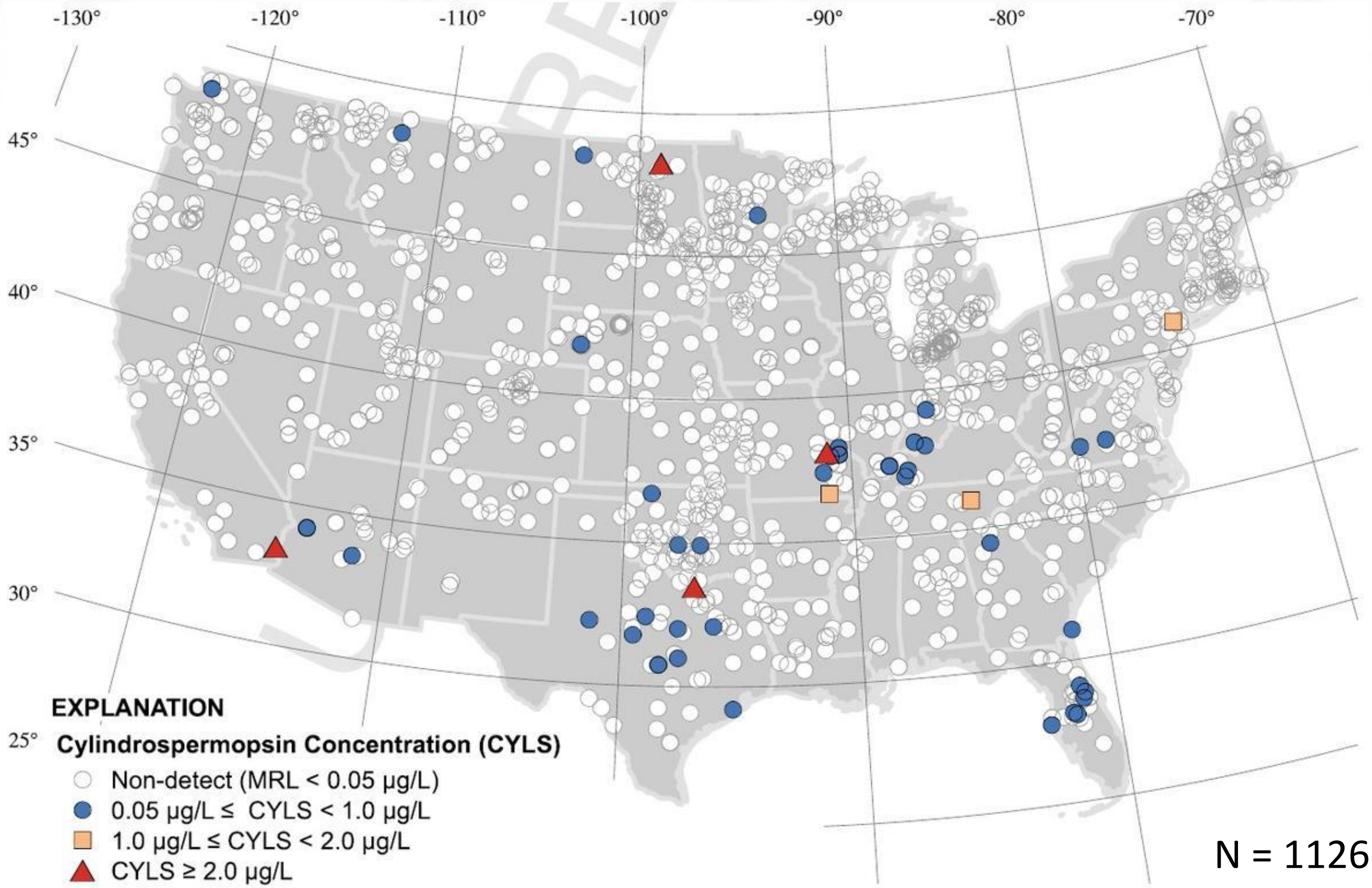
Structure – alkaloid



Cylindrospermopsin

Photo courtesy http://oceandatacenter.ucsc.edu/PhytoGallery/Freshwater/Cylindrospermopsins.html

Cylindrospermopsin Concentrations in U.S. Inland Lakes and Reservoirs (2016)



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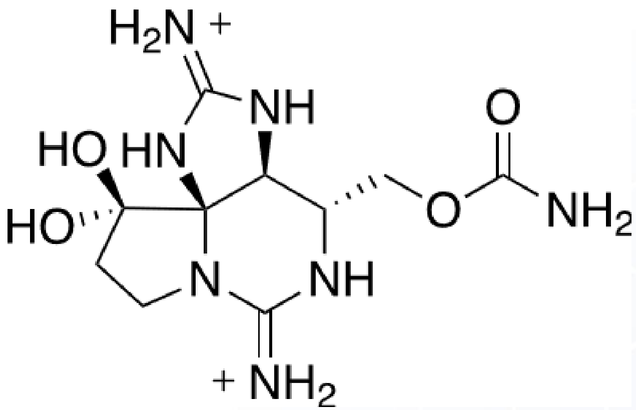
Saxitoxin (STX)

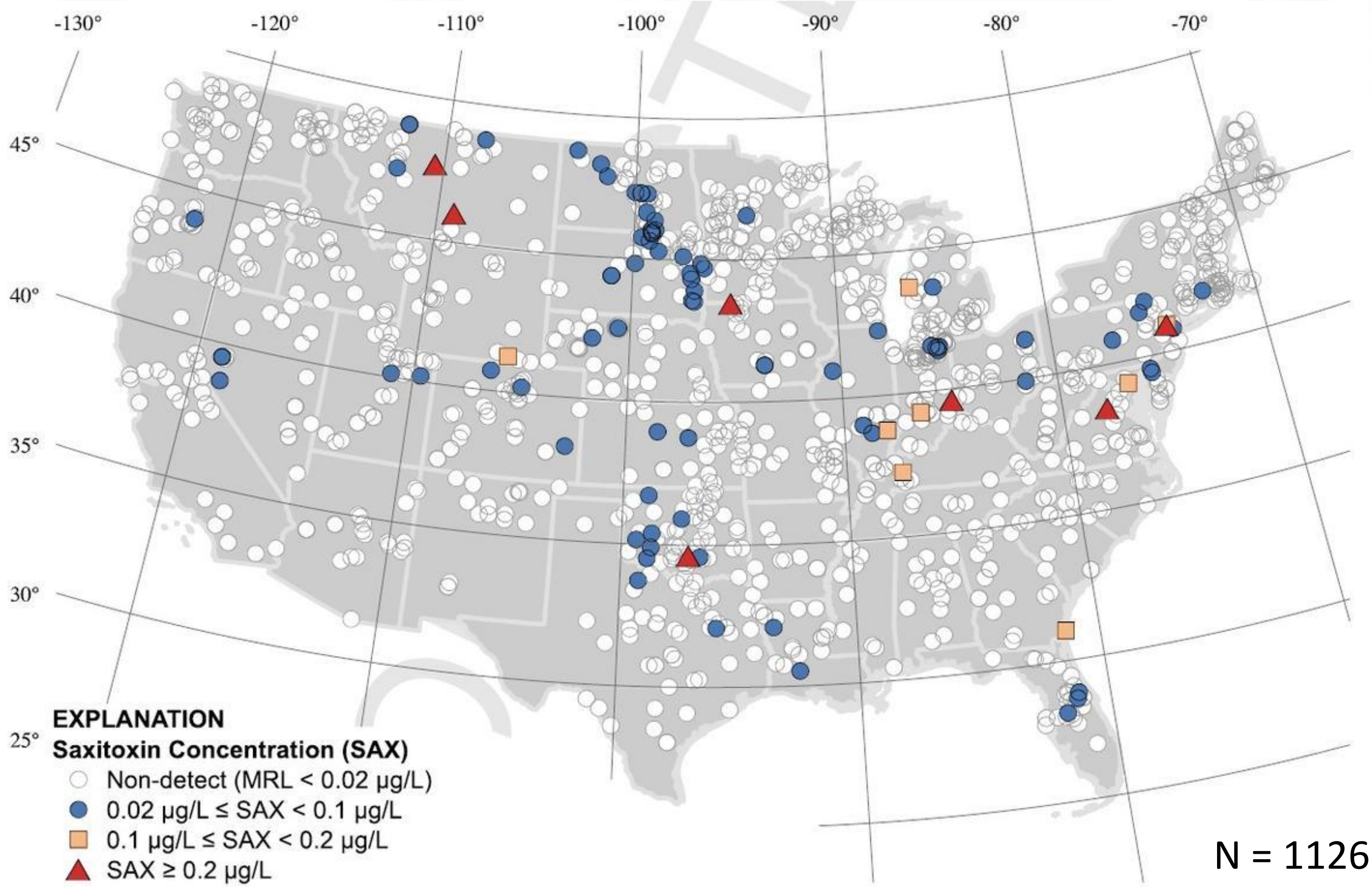
- First identified in butter clam (Saxidomus giganteus)
- Produced by some marine dinoflagellates and puffer fish; several strains of algae
- One of most potent natural neurotoxins known
- Cause of Paralytic Shellfish Poisoning (PSP)
- Na-channel blocker – disrupts neural response and prevents normal cell function
- Results in flaccid paralysis and can lead to death from respiratory failure
- Originally isolated and described by US military; chemical weapon designation TZ

Structure – alkaloid



Saxitoxin

Saxitoxin Concentrations in U.S. Inland Lakes and Reservoirs (2016)



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Role of Nutrients in HAB Formation

- In natural systems nitrogen, carbon, and phosphorus are three principal nutrients:
  - N present as metabolic waste products (NH_3, urea)
  - N also present as nitrates and nitrites from agricultural runoff (fertilizers, CAFOs, etc.)
  - Cyanobacteria have ability to fix atmospheric N_2
  - P is in shortest supply – a limiting nutrient
- Algae will incorporate bioavailable N and P in water column; synthesize C through photosynthesis

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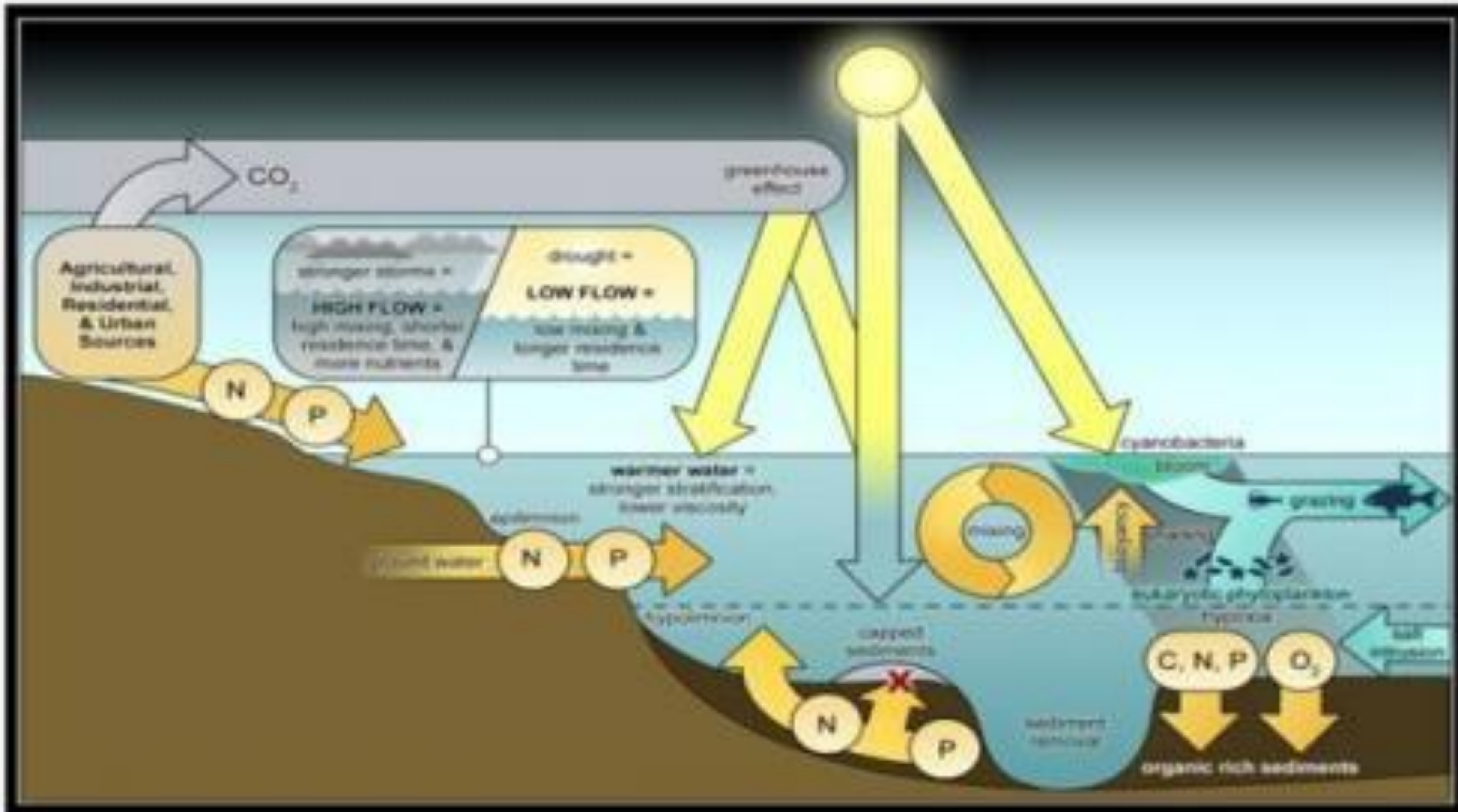
  - P is in shortest supply – a limiting nutrient
- Algae will incorporate bioavailable N and P in water column; synthesize C through photosynthesis
- Suggests control of N and P critical!

Role of Nutrients in HAB Formation (cont'd)

- However….
  - The picture with respect to HAB formation (and the species implicated) is considerably more complex
- While nutrients play a crucial role, other environmental variables are also important, such as

1. Temperature (optima vary by species)
2. Water Chemistry (pH, salinity, etc.)
3. Light (photoperiod and transmissivity)
   - Abiotic sources of turbidity
4. Weather
   - Wind (promotes mixing and overturn)
   - Rainfall events (flushing/nutrient transport)
5. Biotic factors

Factors Influencing HAB Formation



Source: Pearl, H., Hall, N., and Calandrino, E. (2011). "Controlling harmful cyanobacterial blooms in a world experiencing anthropogenic and climatic-induced change." Science of the Total Environment, Vol. 409, Issue 10, April, 2011, Pages 1739-1745.

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Role of Nutrients in HAB Formation (cont'd)

- Trophic State Index (TSI) – relates presence/absence of nutrients to estimate of biological condition
  - Trophic state = the total weight of biomass in a given water body at the time of measurement
- Carlson Index – relates three independent, correlated variables to classify water bodies in terms of algal biomass:
  1. Chlorophyll pigments (μg/l)
  2. Phosphorus concentration (μg/l)
  3. Secchi depth (m)

Role of Nutrients in HAB Formation (cont'd)

Trophic Index (TI)	Chlorophyll (µg/l)	P (µg/l)	Secchi Depth (m)	Trophic Class
< 30 – 40	0 – 2.6	0 – 12	> 8 – 4	Oligotrophic
40 – 50	2.6 – 20	12 – 24	4 – 2	Mesotrophic
50 – 70	20 – 56	24 – 96	2 – 0.5	Eutrophic
70 – 100+	56 – 155+	96 – 384	0.5 – < 0.25	Hypereutrophic

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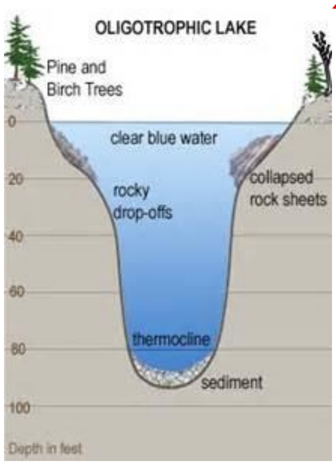

- Nutrient poor/low algal biomass
- Low primary productivity
- Relatively little sediment loading
- Almost no turbidity
- DO levels high; support oxygen-sensitive species

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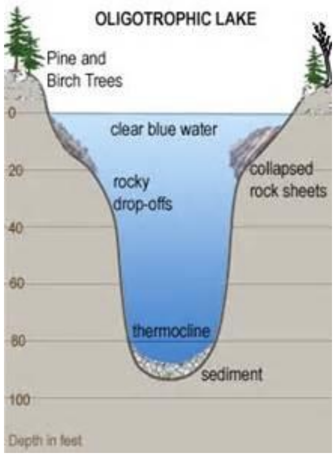

- Nutrient poor/low algal biomass
- Low primary productivity
- Relatively little sediment loading
- Almost no turbidity
- DO levels high; support oxygen-sensitive species
- **Low HAB formation potential**

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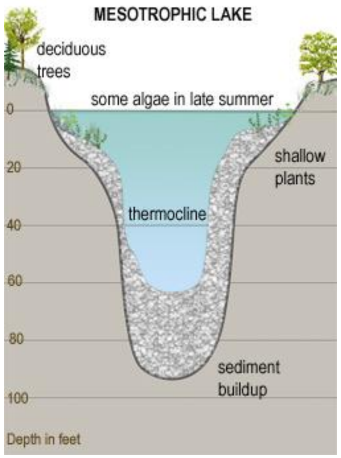

- Moderate nutrient/sediment loads
- Good primary productivity; seasonal algae increase
- Higher turbidity
- DO levels high; vary seasonally

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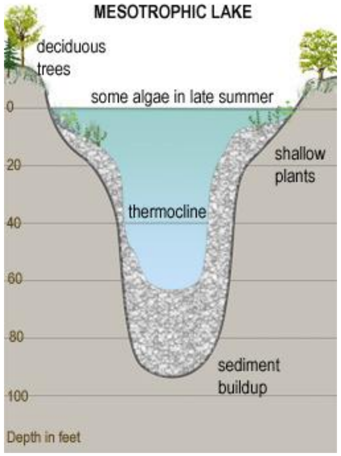

- Moderate nutrient/sediment loads
- Good primary productivity; seasonal algae increase
- Higher turbidity
- DO levels high; vary seasonally
- **Moderate HAB formation potential**

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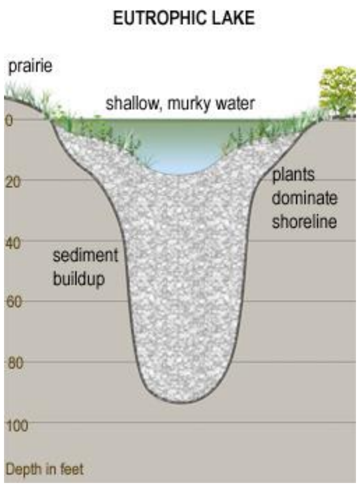

- High nutrient/sediment loads
- High primary productivity; algal populations year-round
- Much higher turbidity
- DO levels high but may be seasonally low, esp. at depth

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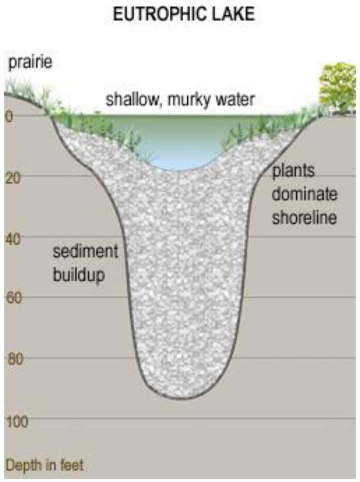

- High nutrient/sediment loads
- High primary productivity; algal populations year-round
- Much higher turbidity
- DO levels high but may be seasonally low, esp. at depth
- **Significant HAB formation potential**

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- Primary producers abundant – other species significantly impacted or absent altogether
- Extremely high turbidity
- DO levels low, pH high

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- Extremely high nutrient/sediment loads
- Primary producers abundant – other species significantly impacted or absent altogether
- Extremely high turbidity
- DO levels low, pH high
- **HAB formation likely!**

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HAB Events – Three Scenarios

Lake Erie Algal Blooms of 2011 and 2014

- Maumee and Cuyahoga River watersheds feed into Western Basin of Lake Erie
  - Maumee – largely agricultural, non-point source runoff
  - Cuyahoga – predominantly urban/suburban land use; point and non-point sources
  - Phosphorus is key nutrient
- Heavy rainfall events in Maumee watershed in Summer 2011 and 2014 resulted in high phosphorus levels – peaks coincided with HAB events
- High rainfalls event in urban watershed tend to dilute P; not a major HAB contributor

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- HABs an ongoing/recurring problem!

HAB Events – Three Scenarios (cont.)

Field Remediation Site – Central Texas

- NWIRP McGregor (active 1945 – 1995)
  - Manufactured munitions and solid rocket motors
  - Perchlorate > 4 ppb identified in surface runoff in 1998 – threat to drinking water source (Lake Belton)
  - Remedial strategy involved passive and active treatment and removal of perchlorate
- Anaerobic WWT system brought on-line in 2002 – fluidized bed reactor (FBR)
- Treated effluent stored in holding ponds prior to batch or continuous discharge
- pH increase (> 9) noted in summer months – correlated to low flows and longer residence times
- Potential discharge permit implications

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- Potential discharge permit implications
- No HAB formation – but potential existed!

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HAB Events – Three Scenarios (cont.)

Industrial WWTP – Texas Gulf Coast

- Industrial WWTP – Regional Wastewater Treatment Authority
  - Facility constructed in 1972 to meet new CWA standards
  - Serves industrial customers exclusively (two petrochemical facilities; one terminal facility)
  - Activated sludge system – formerly relied on combination of anaerobic, aerobic and facultative ponds
  - System upgraded in 2007 with construction of oxygen aeration basin (OAB) at front-end – 95% of treatment occurs here
- Seasonally adjust pH during summer months using sulfuric acid
- Presence of algae noted in storage basins
- Periodic biomonitoring included in permit
- Failure of biomonitoring test led to identification of Microcystin and triggered Toxicity Reduction Evaluation (TRE)

HAB Events – Three Scenarios

Industrial WWTP – Texas Gulf Coast

- Industrial WWTP – Regional Wastewater Treatment Authority
  - Facility constructed in 1972 to meet new CWA standards
  - Serves industrial customers exclusively (two petrochemical facilities; one terminal facility)
  - Activated sludge system – formerly relied on combination of anaerobic, aerobic and facultative ponds
  - System upgraded in 2007 with construction of oxygen aeration basin (OAB) at front-end – 95% of treatment occurs here
- Seasonally adjust pH during summer months using sulfuric acid
- Presence of algae noted in storage basins
- Periodic biomonitoring included in permit
- Failure of biomonitoring test led to identification of Microcystin and triggered Toxicity Reduction Evaluation (TRE)
- HAB <u>and</u> cyanotoxins identified!

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Exposure Guidelines for and Regulation of Cyanotoxins

- In 1998 , the World Health Organization (WHO) proposed provisional drinking water guideline of 1 µg/l for Microcystin-LR
- WHO subsequently issued recreational contact guidelines for Microcystin-LR:
  - Low Risk (< 10 µg/l)
  - Moderate Risk (10 – 20 µg/l)
  - High Risk (> 20 µg/l)
- No current federally enforceable limits; Health Advisories (HAs) have been issued with recommended exposure limits (state approaches similar)
- Cyanotoxins and cyanobacteria listed on Contaminant Candidate List (CCL) – CCL 1 of 1998, CCL 2 of 2005 and CCL 3 of 2009
- Anatoxin-a, cylindrospermopsin, and microcystin-LR listed on draft CCL 4 (April 2015)

International Guideline Values for Microcystin-LR

Country	Guideline Value	Source
Brazil, China, Czech Republic, Denmark, Finland, France, Germany, Italy, Japan, Korea, Netherlands, Norway, New Zealand, Poland, South Africa, and Spain	1.0 µg/l Microcystin-LR	Based on the WHO Provisional Guideline Value of 1.0 µg/l for drinking water (WHO, 1999; 2003)
Australia	1.3 µg/l Microcystin-LR (toxicity equivalents)	Australian Drinking Water Guidelines 6 (NHMRC, NRMMC, 2011)
Canada	1.5 µg/l Microcystin-LR	Guidelines for Canadian Drinking Water Quality: Supporting Documentation Cyanobacterial Toxins – Microcystin-LR (Health Canada, 2002)

State Guideline Values for Cyanotoxins (Drinking Water)

State	Guideline Value	Source
Minnesota	0.04 µg/l Microcystin-LR	Minnesota Department of Health (MDH, 2012)
Oregon	1.0 µg/l Microcystin-LR; 3.0 µg/l Anatoxin-A; 1.0 µg/l Cylindrospermopsin; 3.0 µg/l Saxitoxin	Public Health Advisory Guidelines, Harmful Algae Blooms in Freshwater Bodies (OHA, 2015)
Ohio	1.0 µg/l Microcystin	Public Water System Harmful Algal Bloom Response Strategy (Ohio EPA, 2014)

Ohio Guideline Values for Cyanotoxins (Drinking Water and Recreational Contact)

Cyanotoxin	Do Not Drink (children < 6 and sensitive groups)	Do Not Drink (children > 6 and adults)	Do Not Use (Recreational Contact)
Microcystin	0.3 µg/l	1.6 µg/l	20 µg/l
Anatoxin-a	20 µg/l	20 µg/l	300 µg/l
Cylindrospermopsin	0.7 µg/l	3.0 µg/l	20.0 µg/l
Saxitoxin	0.2 µg/l	0.2 µg/l	3.0 µg/l

Summary and Conclusions

- A host of factors influence and control HAB development
- Role of key nutrients is paramount
  - N:P, N:S, N:Si ratios play role
- Understanding overall context also crucial
  - Relevant biotic and abiotic factors
  - Role of biological communities in controlling/mediating HABs
- HAB formation in industrial/remedial site settings
  - Potential to form anywhere water is held or stored prior to discharge
  - Establishing and maintaining good site controls essential
  - Monitoring of nutrient inputs (baseline) and periodically during warm and wet weather months
- Prevention of HAB formation is key!

- Questions?

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