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Harmful Algal Blooms: Nature, Occurrence and Regulatory Outlook

Karl Mueller
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Refinery Specialties, Inc.

Scope

- Harmful Algal Blooms (HABs) defined
- History
- Algal Species of Concern
- Algal Toxins
- Factors Contributing to HAB development
- Current Recommended Exposure Levels
- Regulatory Outlook

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Scope (continued)

- Implications for Regulated Community
- Algal Control Methods
- Recommendations
- Conclusion

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Four Main Questions

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

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Harmful Algal Blooms - defined

- An algal bloom is a rapid increase or accumulation in the population of algae in a water system.
- 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.

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Harmful Algal Blooms - Impacts

HABs can have a variety of adverse impacts, including:

1. Dramatically altering 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)
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

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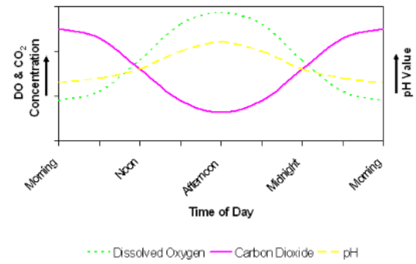
Algal Activity in Aquatic Environments

- 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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HAB-related illnesses

- Examples of documented human illnesses / 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)

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HAB-related illnesses – causal organisms

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

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- Estuary Associated Syndrome (EAS)

→ **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)

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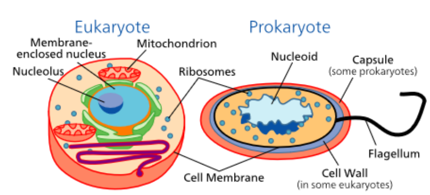
Cyanobacteria - Overview

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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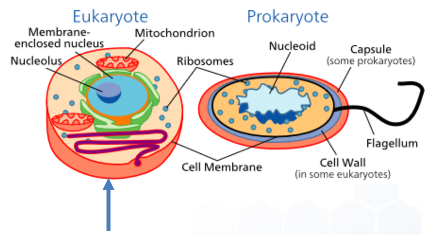

- **Complex internal structure (organelles)**
- **Membrane-bound "true" nucleus**
- **Common metabolic pathways**
- **Chlorophyll within chloroplasts**

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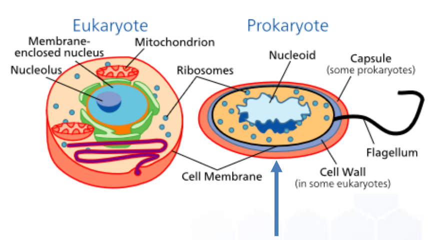

- **Simple internal structure (few organelles)**
- **No true nucleus; not membrane-bound**
- **Variety of metabolic pathways**
- **Chlorophyll throughout cytoplasm**

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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

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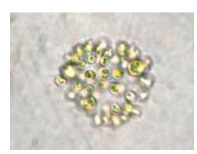
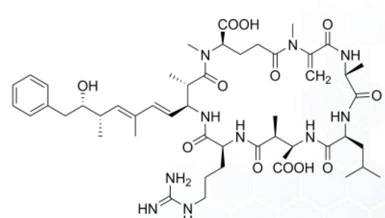
Microcystin/Microcystin-LR



(M. aeruginosa)

- Named after Microcystis aeruginosa
- Most prevalent and well-known algal toxin – has been intensively studied
- 60 known variants; 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

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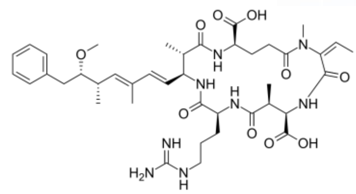
Nodularins

- Named after Nodularia spumigena (type species) – filamentous algae
- HABs associated with nodularin formation occur in saline inland waters and brackish systems, e.g. estuaries
- Similar chemical structure to microcystin
- Very stable and resistant to breakdown within natural environment
- Most common toxin associated with HABs globally

(N. spumigena)

Structure – cyclic peptide



Nodularin

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

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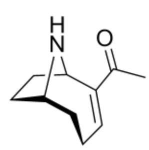
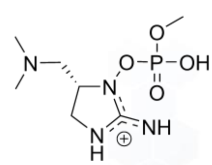
Anatoxins

- Alkaloids as a class known to exhibit both toxic and psychotropic effects on mammals – biologically active
- Associated with at least four algal genera
- Anatoxin-a first identified in 1961 ("Very Fast Death Factor") following cattle poisoning event in Canada
- Potent, fast-acting neurotoxins
- Stimulates nicotinic acetylcholine receptors, but not degraded by cholinesterase
- Used for investigating acetylcholine receptors in the nervous system
- Potential use as bioweapon

Structure – alkaloid



Anatoxin-a



Anatoxin-a-S

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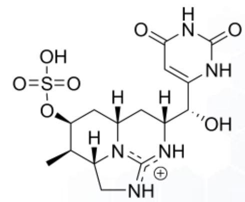
Cylindrospermopsins (CYN or CYL)

- 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

(C. raciborskii)

Structure – alkaloid



Cylindrospermopsin

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

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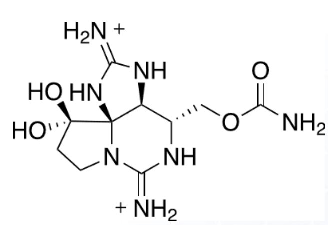
Saxitoxin (STX)

- 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

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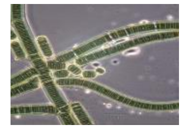
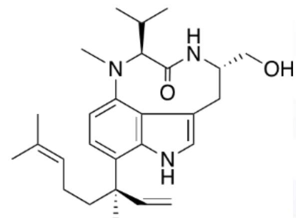
Lyngbyatoxin-a

- Cyanotoxin produced by Moorea producens (formerly Lyngbya majuscule)
- Lyngbya sp. also responsible for producing aplysiatoxins
- A defensive toxin produced to deter predators
- Low concentrations can cause dermatitis
- A blister agent (vesicant) and carcinogen (tumorigenic properties)
- Inflammatory agent



(Lyngbya sp.)

Structure – alkaloid



Lyngbyatoxin-a

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Photo courtesy http://oceandatacenter.ucsc.edu/PhytoGallery/Freshwater/Lyngbya

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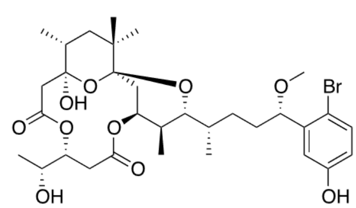
Aplysiatoxins

- Produced by marine algal species (Lyngbya sp.)
- Also associated with filamentous species such as Schizothrix calcicola and Oscillatoria nigroviridis
- Dibromoaplysiatoxin (hydroxyl group on six-member ring replaced with 2nd Br atom)
- Dermatotoxic – an irritant most commonly associated with skin inflammation through direct contact
- Potent tumor promotors – activate Protein kinase C – mechanism in common with Lyngbyatoxins

(Lyngbya sp.)

Structure – alkaloid



Aplysiatoxin

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

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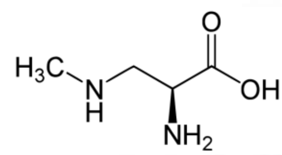
B-Methylamino-L-alanine (BMAA)

- Produced by cyanobacteria in marine, freshwater, brackish and terrestrial settings
- Also found in aquatic organisms, lichens, fern species, cycads and in humans and animals that consume cycad seeds
- Multiple mechanisms of action; not completely understood
- BMAA present in brains of patients suffering from progressive non-genetic neurological diseases; causally implicated in so-called "tangle diseases" of brain
- Research underway to confirm and understand disease-causing mechanisms

Structure – amino acid



BMAA

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Role of Nutrients in HAB Formation

- In natural systems nitrogen, carbon, and phosphorus are key nutrients:
  - N present as metabolic waste products from aquatic organisms (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 own C through photosynthesis

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Role of Nutrients in HAB Formation (cont'd)

- 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 own C through photosynthesis
- Suggests control of N and P critical!

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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. Light (photoperiod and transmissivity)
     - Abiotic sources of turbidity
  3. Weather
     - Wind (promotes mixing and overturn)
     - Rainfall events (flushing/nutrient transport)
  4. Biotic factors

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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)

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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 – < 2.5	Hypereutrophic

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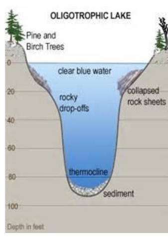

- Nutrient poor/low algal biomass
- Low primary productivity
- Relatively little sediment loading
- Almost no turbidity
- DO levels high; support oxygen-sensitive species
- Low HAB formation potential

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Role of Nutrients in HAB Formation (cont'd)

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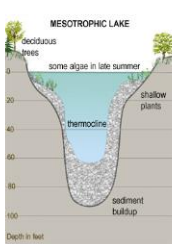

- Moderate nutrient/sediment loads
- Good primary productivity; seasonal algae increase
- Higher turbidity
- DO levels high; vary seasonally
- Moderate HAB formation potential

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Role of Nutrients in HAB Formation (cont'd)

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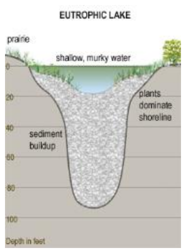

- High nutrient/sediment loads
- High primary productivity; algal populations year-round
- Much higher turbidity
- DO levels high but may be seasonally low, esp. at depth
- Significant HAB formation potential

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Role of Nutrients in HAB Formation (cont'd)

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- Extremely high nutrient/sediment loads
- Primary producers abundant – other species significantly impacted or absent
- Extremely high turbidity
- DO levels low, pH high

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Role of Nutrients in HAB Formation (cont'd)

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- Extremely high nutrient/sediment loads
- Primary producers abundant – other species impacted
- 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 sources 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
- HABs an ongoing/recurring problem

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HAB Events – Three Scenarios

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
- No HAB formation – but potential existed!

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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 and 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
- No similar guideline proposed for recreational contact
- No current federally enforceable limits; Health Advisories (HAs) have been issued with recommended exposure limits
- 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)
- State approaches:
  - Minnesota - Microcystin-LR: 0.1 µg/l
  - Oregon
    - Microcystin-LR: 1 µg/l
    - Anatoxin-A: 3 µg/l
    - Cylindrospermopsin: 1 µg/l
    - Saxitoxin: 3 µg/l

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- Ohio – following slide

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- Ohio

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

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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!

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- Questions?

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