Harmful Algal Blooms: Nature, Occurrence and Regulatory Outlook

Karl Mueller
Environmental Manager
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
Scope (continued)

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

• 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

HABs can have a variety of adverse impacts, including:

1. Dramatically altering water chemistry (pH and DO)
   - Raise pH by removing CO₂ 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
**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
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)
HAB-related illnesses – causal organisms

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- Diatom (marine)
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- 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

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 CO₂ to produce carbohydrate (under aerobic conditions)
  – Fix both N₂ and C; produce O₂

Cell type comparison
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Cell type comparison

• Complex internal structure (organelles)
• Membrane-bound “true” nucleus
• Common metabolic pathways
• Chlorophyll within chloroplasts
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• Autotrophic
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Cell type comparison

- Simple internal structure (few organelles)
- No true nucleus; not membrane-bound
- Variety of metabolic pathways
- Chlorophyll throughout cytoplasm
# Algal Species and Cyanotoxins Associated with HABs

<table>
<thead>
<tr>
<th>Genera</th>
<th>Cyanotoxins</th>
<th>Target Organ</th>
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<tr>
<td><em>Microcystis, Anabaena, Planktothrix (Oscillatoria), Nostoc, Hapalosiphon, Anabaenopsis, Woronichinia</em></td>
<td>Microcystins</td>
<td>Liver</td>
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<td>Skin, GI tract</td>
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<td>Saxitoxin</td>
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<td><em>All</em></td>
<td>Lipopolysaccharides</td>
<td>Exposed Tissue (irritant)</td>
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<td><em>Lyngbya, Planktothrix (Oscillatoria), Schizothrix</em></td>
<td>Aplysia toxins</td>
<td>Skin</td>
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<td><em>All</em></td>
<td>BMAA</td>
<td>CNS</td>
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Microcystin/Microcystin-LR

- 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


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

Structure – cyclic peptide

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

By Cacycle (Own work) [GFDL (http://www.gnu.org/copyleft/fdl.html), CC-BY-SA-3.0 (http://creativecommons.org/licenses/by-sa/3.0/) or Public domain], via Wikimedia Commons
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

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

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

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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 2\textsuperscript{nd} Br atom)
- Dermatotoxic – an irritant most commonly associated with skin inflammation through direct contact
- Potent tumor promoters – activate Protein kinase C – mechanism in common with Lyngbyatoxins

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

Structure – alkaloid
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
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 (NH₃, urea)
  – N also present as nitrates and nitrites from agricultural runoff (fertilizers, CAFOs, etc.)
  – Cyanobacteria have ability to fix atmospheric N₂
  – P is in shortest supply – a limiting nutrient

• Algae will incorporate bioavailable N and P in water column; synthesize own C through photosynthesis
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!
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
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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- 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
- 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
- Significant HAB formation potential
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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

![Images of HAB and water quality issues](images)
### Trophic Index (TI) and Chlorophyll (µg/l)

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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
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
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!
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!
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
- 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
Exposure Guidelines for and Regulation of Cyanotoxins

- State approaches:
- Ohio

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<th>Cyanotoxin</th>
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<th>Do Not Drink (children &gt; 6 and adults)</th>
<th>Do Not Use (Recreational Contact)</th>
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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!
• Questions?