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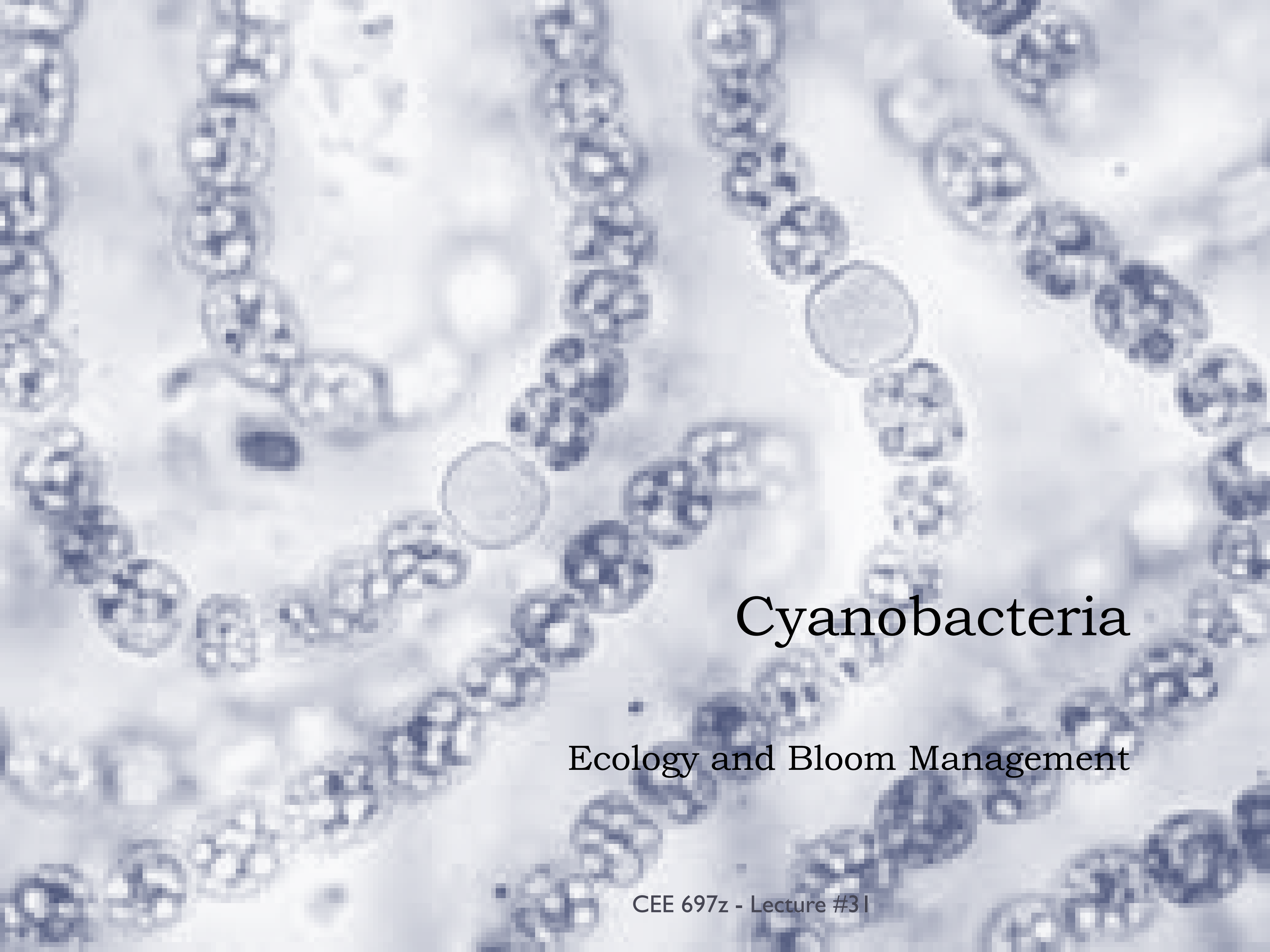
CEE 697z
Organic Compounds in Water and Wastewater

Cyanotoxins

Aquatic Ecology and In-situ Control

Lecture #31

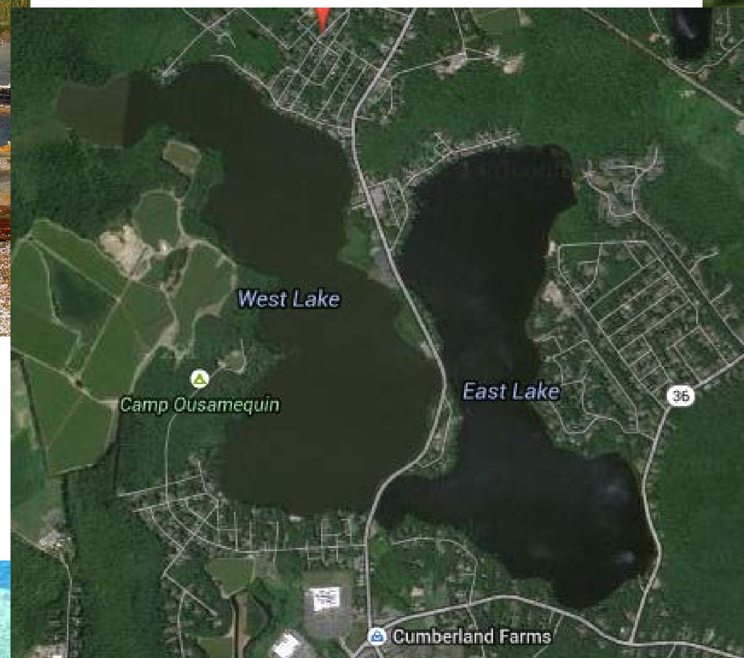


Cyanobacteria

Ecology and Bloom Management

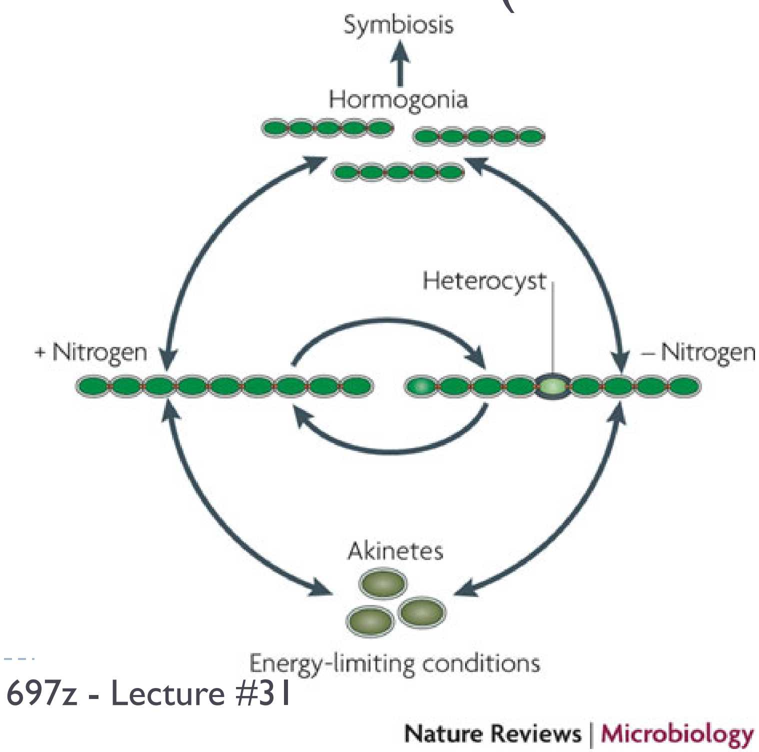
CEE 697z - Lecture #31

Cyanobacteria are Ubiquitous



Ecology: Adaptations

- Gas-filled cavities allow cyanobacteria to float to the surface or within the water column based on light conditions and nutrient levels
  - E.g. *Anabaena flos-aquae*
  - Leads to concentration of cyanobacteria on surface (creation of ”scum”)
- Nitrogen fixation
- Ability to resume photosynthesis after periods of light exclusion and dehydration



Flores & Herrero, 2010

What is a "bloom"?

- "a significant production of biomass over a short period of time correlated with a diminution of phytoplankton diversity"
- Often appears as a dense layer of cells at the surface of the water
- May also be
  - dispersed through the water column with no surface "scum"
  - located in the sediments (benthic)
- Diversity of genera often low
- Primarily occur in lentic surface waters

Ecology: Bloom Impacts

- Toxic effects
  - Humans, dogs, livestock, fish, birds…
- Oxygen levels
  - Elevated during the day due to photosynthesis
  - Drop due to
    - Nightly respiration
    - Bloom decay
  - Hypoxic conditions may result in plant and animal die-off
- Water temperature elevation
- Food web disruption

Monitoring for CyanoHABs in Massachusetts

- Health risk rises with cell counts
  - With some uncertainties
- Measures on which action can be taken:
  - Observation of visible scum or mat layer
  - Total cell count of cyanobacteria (total cells/mL of water)
    - Threshold = 70,000 cells/mL water
  - Concentration of cyanotoxin
    - Threshold = 14 ug microcystin/L water

MDPH Guidelines for Cyanobacteria in Freshwater Recreational Water Bodies in Massachusetts

Actions taken in Massachusetts

- State actions
  - Post advisories against contact with water
  - Advisories may be lifted after two consecutive and representative sampling rounds one week apart demonstrate cell counts *and* toxin levels below those at which an advisory would be posted.
- City/Town
  - Rope off water body and/or close bathhouses
  - Bloom treatment

Algae Information

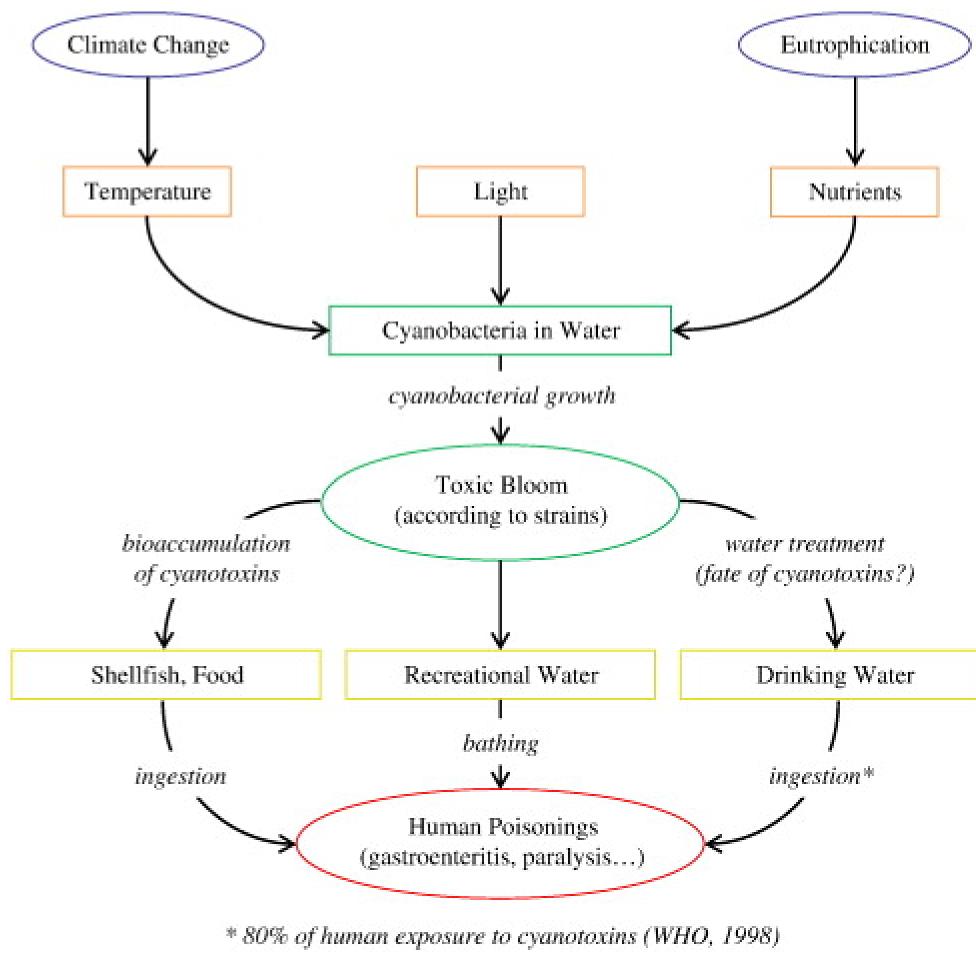
Cyanobacteria Advisories in Massachusetts Current as of October 30, 2014

- Congamond Lake - Southwick
- Lake Wampatuck - Hanson
- West Monponsett Pond - Halifax, Hanson

http://www.mass.gov/eohhs/gov/departments/dph/programs/environmental-health/exposure-topics/beaches-algae/algae-information.html

Factors Affecting Bloom Formation

- Light intensity
- Total sunlight duration
- Nutrient availability
  - P & N
- Water temperature
- pH
- Precipitation events
- Water flow
- Water column stability



Eutrophication

- CyanoHABs are stimulated by excess nutrient loading
- P is often the limiting nutrient for in freshwater
- N is limiting in estuaries and marine systems
- Evidence exists for co-limitation by N & P

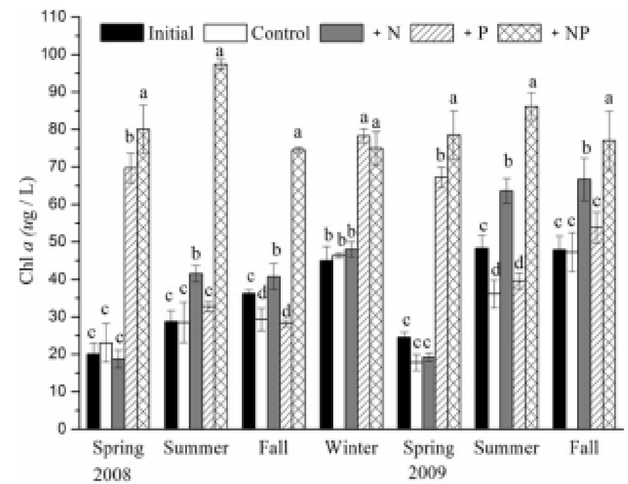


Fig. 6 – Phytoplankton biomass (chlorophyll *a*) responses in bioassays conducted in May, July, October, and December 2008 and May, July and October 2009. Water samples for bioassays were collected from the surface at the Inner Bay location in Meiliang Bay. Initial chlorophyll *a* content is shown. Responses were for 3-day incubations in spring, summer, and fall, 6-day incubations in winter 2008, and 2-day incubations in spring, summer, and fall 2009. Mean values are shown. Error bars represent ±1SD of triplicate samples. Differences between treatments are shown based on ANOVA post hoc tests ($a > b > c$; $p < 0.05$).

Lake Taihu, China

Paerl et al., 2011

Atmospheric CO_2 Concentrations

- CyanoHABS exhibit high demand for CO_2 → limitation
- Buoyant CyanoHABs can directly intercept CO_2 diffusing into the water from the atmosphere
- Photosynthetic potential is largely determined by atmospheric CO_2 concentration

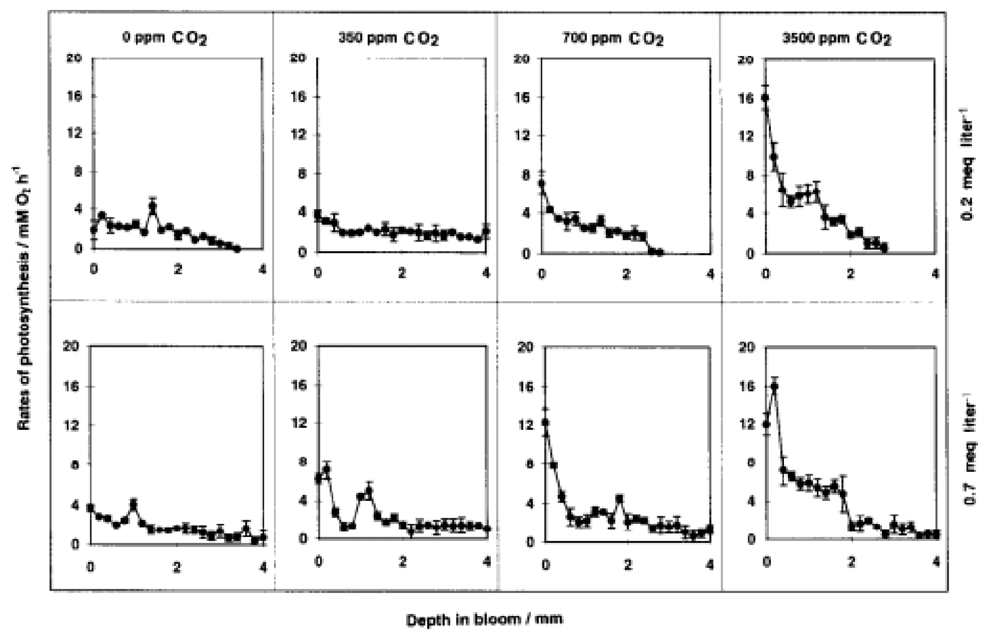


Fig. 3. Gross rates of photosynthetic O_2 production, corresponding to the oxygen profiles shown in Fig. 2 at an alkalinity of 0.2 meq liter^{-1} (top) and 0.7 meq liter^{-1} (bottom) under variable CO_2 concentrations in the headspace of the bloom—0 ppm; air (350 ppm); twice the amount of CO_2 in air (700 ppm); and 10× the amount of CO_2 in air (3,500 ppm). The error bars denote the standard error of the mean.

Ibelings and Maberly, 1998

Climate Change

- Increased temperatures
- Extreme patterns in precipitation
  - Increasing severity and length of droughts
  - Large precipitation events

Increased Temperatures

- Faster growth
- Longer ice-free growing season
- Decreased viscosity
  - Decreased resistance to migration
- Increased stability of stratification
- Exacerbate bottom water hypoxia
  - May stimulate internal nutrient loading

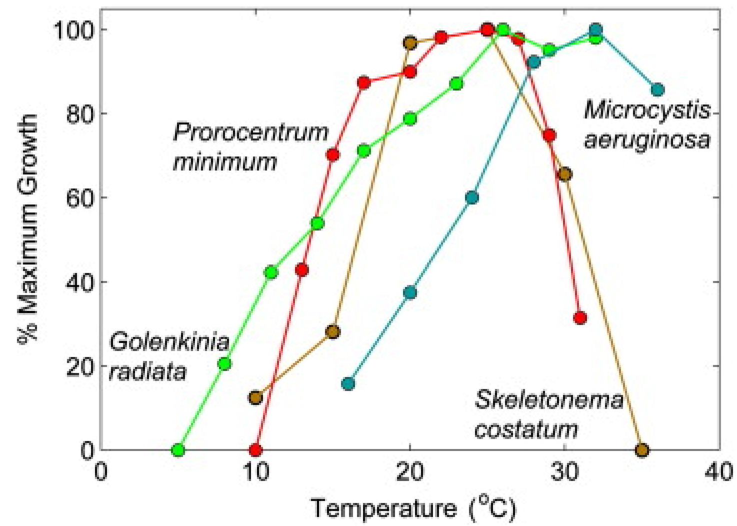


Fig. 4 – Effects of temperature on species-specific growth rates of a representative CyanoHAB species (*Microcystis aeruginosa*) vs. commonly encountered eukaryotic algal bloom species, including the chlorophyte *Golenkinia radiata*, the diatom *Skeletonema costatum*, and the dinoflagellate *Prorocentrum minimum*. Growth rate data are from Reynolds (2006), Grzebyk and Berland (1995), and Yamamoto and Nakahara (2005).

Implications: cyanoHABs, once thought to be a tropical phenomenon may become more common in temperate as well as tropical environments

Paerl & Paul, 2012

Changes in Precipitation

- Low-flow droughts promote CyanoHABs
  - Less mixing
  - Longer residence time
- Salination
  - Stronger stratification
  - Some freshwater genera tolerate high salinity
- Intense precipitation events
  - Enrichment of nutrients through erosion, surface runoff, and groundwater dischrage
  - Flushing & mixing of water column
    - May simply pass cyanobacteria downstream

Summary

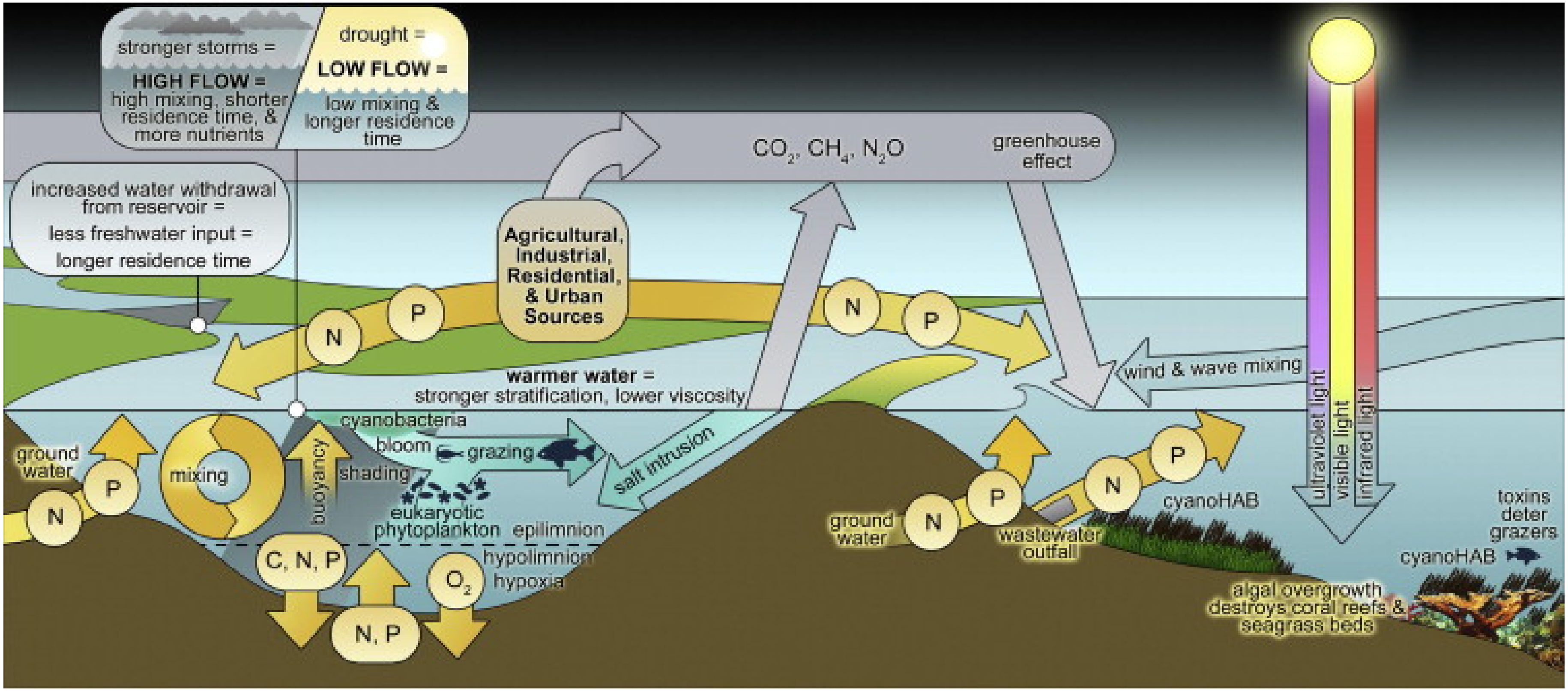


Fig. 3. Conceptual figure, illustrating the environmental processes that control cyanobacterial blooms, including man-made management actions and impacts of climate change.

Paerl & Paul, 2012

Summary

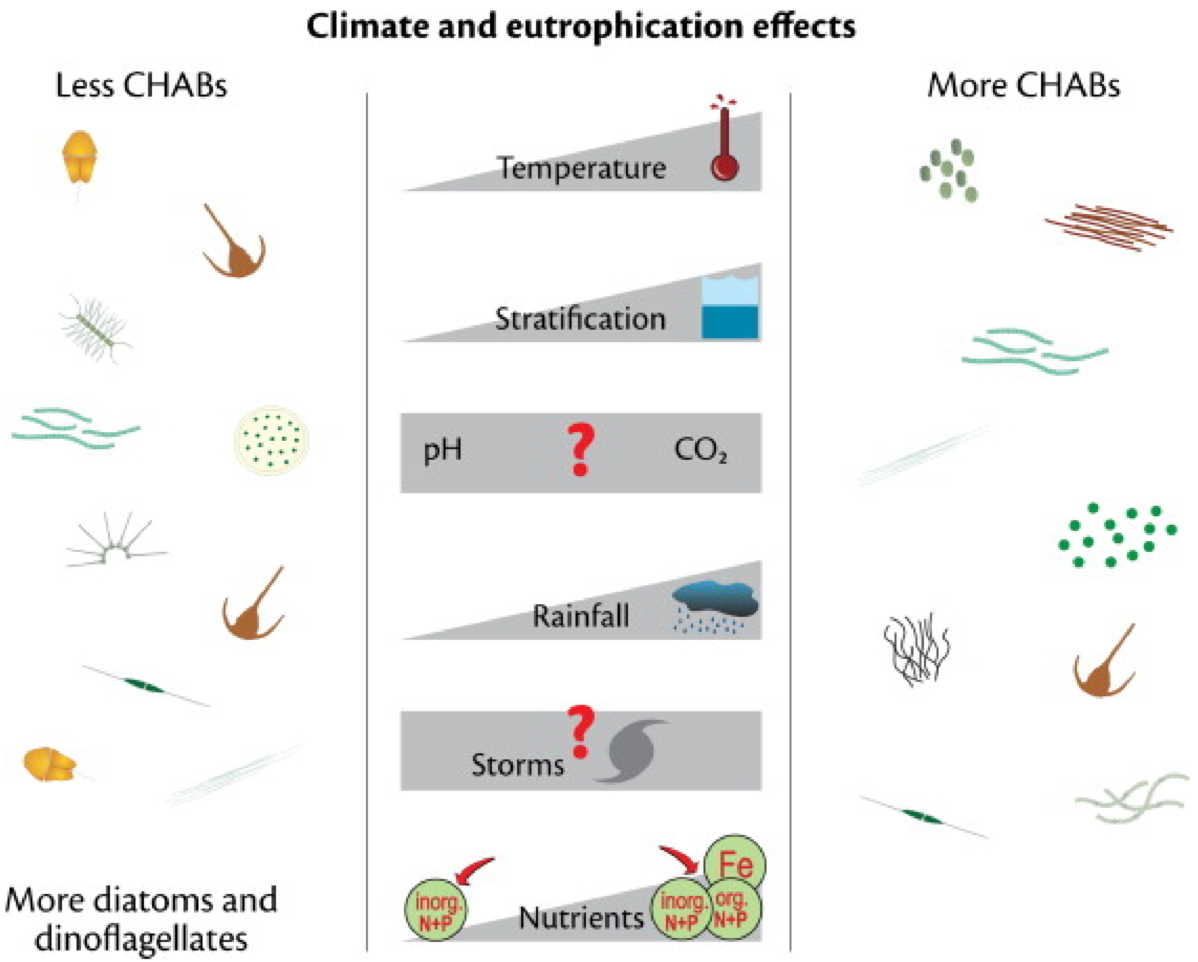


Fig. 2.

Eutrophication and potenital effects of climate change on Cyanobacterial Harmful Algal bloom (CHAB) abundance.

O'Neil et al. 2012

Eradication of Blooms

- Options:
  - Chemical treatment of blooms
  - Aeration and mixing
  - Sediment dredging
  - Sediment inactivation (us. Using aluminum sulfate)

Chemical Treatment

- **Algaecides:** Copper sulfide, hydrogen peroxide, …
  - Reduce cyanobacteria biomass by interfering with cell processes
  - Negative impacts
    - Short term solution: bloom may recur within weeks
    - Toxicity to non-target organisms
- **Flocculants**
  - Cause coagulation and sedimentation the cyanobacteria layer
  - Reduce lysis and resulting cyanotoxin release
  - Prevent regrowth and resuspension of the cyanoHAB

Algaecides

- Algaecides induce cell lysis, leading to release of intracellular toxins

Table 1. Recommended dosages for lake water and dosages of the six chemicals used in the three Batches (mg l^{-1}). The dosages used in the batch experiments were higher than recommended, as the phytoplankton biomass (as dry wt) was 80-fold more concentrated than in the lake water. NA indicates the chemical was not used in that batch experiment

		Dosages used		
Chemical	Recommended dosages	Batch 1	Batch 2	Batch 3
Reglone	2–3.9	20	20	20
NaOCl	0.5–1.5	NA	44	44
$KMnO_4$	1–3	10	10	10
Simazine	0.5	5	15	NA
Alum	132	200	200	300
Lime	25–200	100	100	200

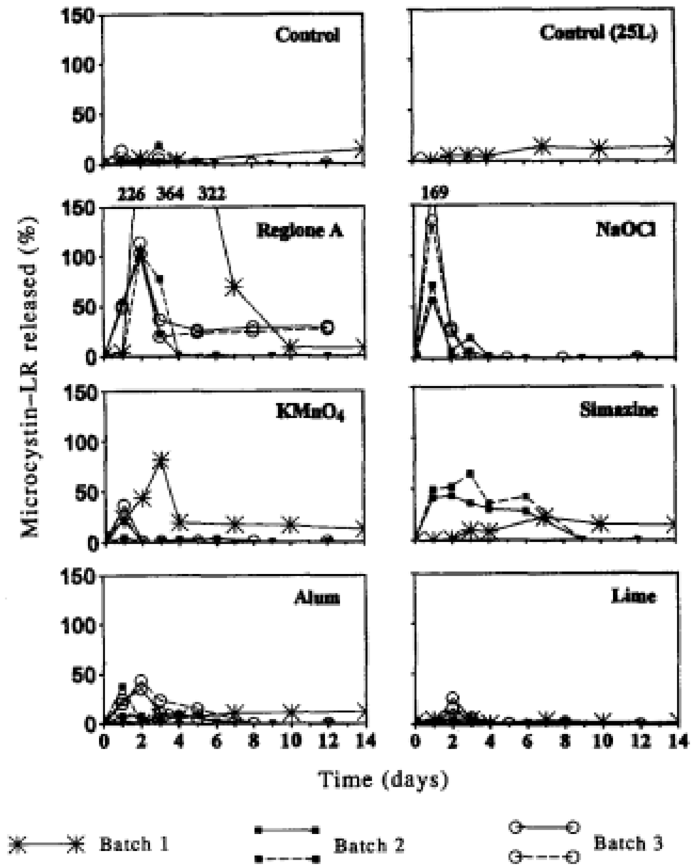


Fig. 1. Release of MCLR into the surrounding water after chemical treatments. The amount released is expressed as a percent of detectable MCLR within the cyanobacterial cells at day 0. Note that one lime treatment and one control in Batch 1 were carried out in 25-liter jars. Replicates for Batches 2 and 3 are shown.

- *Lam et al., 1995*

Table 1
Summary of advantages and disadvantages of chemical measures for management of cyanobacterial blooms.

Method or technique	Advantages	Disadvantages
Metals with the mode of action based on cell toxicity (copper, silver)	– Extremely low price	– Toxicity against non-target species – Accumulation in the environment – Release of toxins after treatment
Metals as coagulation agents (aluminum, iron, calcium)	– Extremely low price – Low toxicity against non-target species if used correctly – Suitable for phosphorus removal as well – Long-term effects if used in water bodies with high residence time	– Can influence pH values in water body – Short-term effect if used in water bodies with low residence time
Hydrogen peroxide	– Low price – Low toxicity for non-target species – Fast degradability – Selective towards cyanobacteria	– Risky manipulation with concentrated hydrogen peroxide – Fast degradability (short time of action)
Phthalocyanines	- High toxicity towards photoautotrophs – Biodegradable	– Insufficient knowledge about toxicity towards fish and macrophytes – Blue/green coloration
Titanium dioxide and other insoluble photosensitizers	– Toxicity towards photoautotrophs via ROS production	– Insoluble in water
Herbicides (diuron, endothal, atrazine, simazine and others)	– Low price – Toxicity towards photoautotrophs	– Toxicity against non-target species – Accumulation in the environment – Toxic residues – Release of toxins after the treatment
Chemicals derived from natural compounds	– Effective in low concentrations – Biodegradable – Natural products	– Preparation of extracts or isolation of alkaloids in high amounts – Unknown toxicity towards other non-target species – Price for extraction/synthesis

Jancula & Marsalek, 2011

Artificial Mixing

- Counter formation of surface blooms
- Oxegenate the hypolymnion
  - Reduce internal nutrient loading from sediments

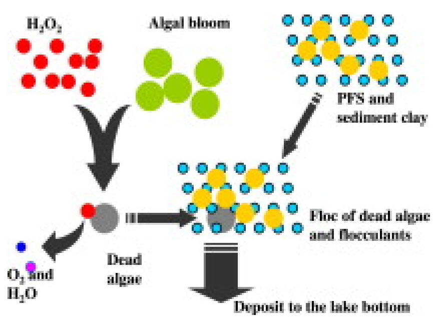
Bloom Prevention

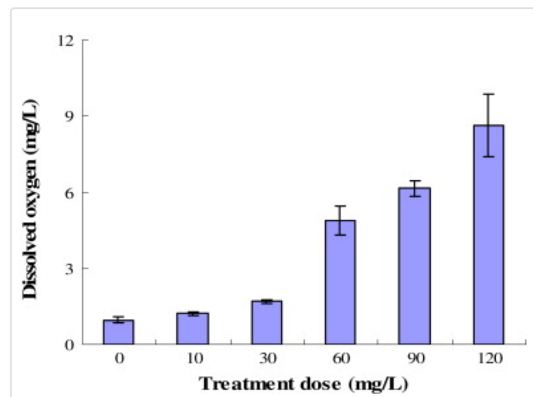
- Controlling nutrient concentrations
  - C, N, P
  - Long-term treatment strategy
- TMDLs
  - Program to control non-point sources of pollution
  - Run on a state-by-state basis
  - Require some level of watershed assessment
  - Limitations
    - Difficulty controlling autocthonous nutrient recycling
    - No "one size fits all" solution
- Monitoring

Additional Slides

Less Common Methods of HAB Treatment

- Sediment
  - Dredging
  - Capping
  - Chemical treatment to "lock in" nutrients and cyanobacteria
- Integrated approaches (e.g. *Wang et al., 2012*)
  - Combined use of:
    - hydrogen peroxide as an algaecide
    - Lake sediment clay and polymeric ferric sulfate as flocculants





Effects of the algaecide-flocculants on the dissolved oxygen in lake sediment.

Toxin Production

- Some cyanobacteria produce multiple types of toxins
- Some produce no toxins
- Some produce toxins that are held within the cell (e.g. Microcystis), while others release a portion of the toxins produced into the environment immediately (e.g. Cylindrospermopsis)

Why Produce Toxins?

There are many speculated reasons…

- These tend to fall into two categories:
  - Theory 1: Direct Competitive Advantage
  - Theory 2: Internal Chemical used in Cell Physiology

- Known abiotic factors
  - Nutrient concentration
  - Light intensity
  - Temperature

Holland & Kinnear, 2013

Theory 1: Direct Competitive Advantage

- Grazing defense
  - Toxins are toxic to zooplankton (e.g. rotifers, daphnia,
- Allelopathy
  - The production of chemicals to prohibit the function &/or growth of other organisms
- Assistance in Nutrient Uptake
  - e.g. Iron Scavenging

Theory 2: Internal Role in Cell Physiology

- Assistance in nutrient uptake
- Iron scavenging
- Adaptation to oxidative stress &/or carbon-nitrogen metabolism
- Maintenance of homeostasis
- Infochemicals
  - Chemical cues in the environment which act as a source of information about both the biotic and abiotic environment
  - May act as "signaling molecules" between cyanobacteria

Final thoughts:

- Triggers for cyanotoxin production are not well understood!
- Cyanobacteria have been around a long time
  - The original ecological roles of cyanotoxins may have been lost or replaced over time.

- To next lecture