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OXIDATION OF ALGAL METABOLITES AND TOOLS FOR OPERATORS

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AGENDA

Background

Oxidation

- Summary, Effectiveness, Considerations

Tools for Operators

Conclusions

BACKGROUND

INTRACELLULAR VS EXTRACELLULAR

- **What is inside versus outside the algal cells**
- **Concentrations inside and outside vary**
  - Number of algal cells
  - Type of algae
  - Growth cycle
  - Dilution/volume
- **Oxidation can cause cell lysing**
  - What was inside is now outside

WHY IS THIS A CONCERN IN WTP?

- **Many utilities practice some form of preoxidation**
  - Taste and odor control
  - Biological control in raw water pipeline
  - Iron and manganese
  - Enhance coagulation/sedimentation
  - Reduce chlorinated disinfection byproducts (TTHM)
- **Preoxidation could make removal more difficult**

REMOVAL OF CELLS VS TOXINS

- **First goal – remove cells**
  - Sedimentation/Softening
  - Floatation
  - Filtration
- **Second goal – remove toxins**
  - Adsorption
  - Oxidation

THIS CREATES CHALLENGES TO WTPS WITH THE POTENTIAL FOR ALGAL TOXINS

- **Can I discontinue preoxidation?**
  - Can I still meet my disinfection requirements?
  - What about other biological growth?
  - Do I have adequate time or a place downstream?
- **Alternative oxidant locations**
  - May have less reaction time
  - May be at “high” pH
  - Barrier is close to my finished water
  - Will lose my preoxidation benefits

OXIDATION

WHICH OXIDANTS ARE EFFECTIVE?

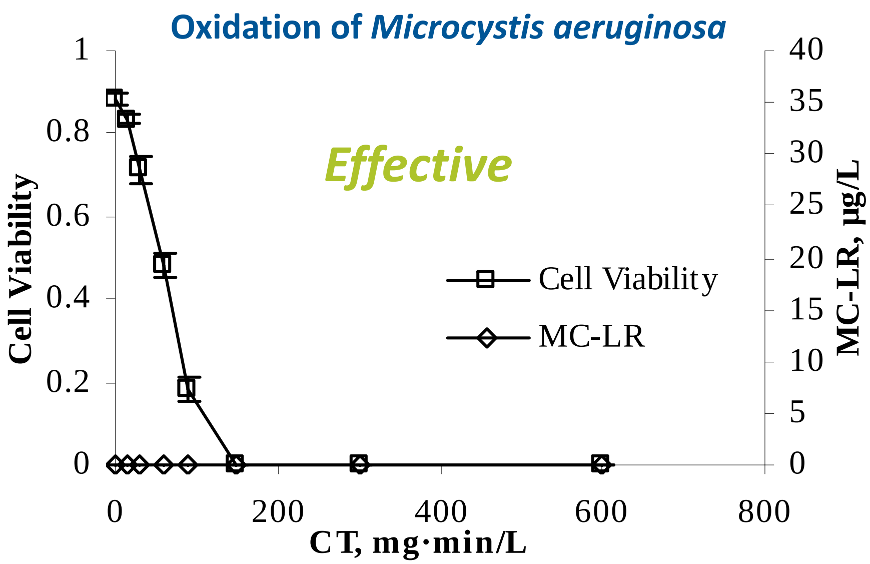
	Microcystin	Anatoxin-a	Cylindrospermopsin	Saxitoxin
Chlorine	Yes	No	Yes	Yes
Ozone	Yes	Yes	Yes	No
Chloramine	No	No	No	Need data
Chlorine Dioxide	No	No	No	Need data
Advanced oxidation	Yes	Yes	Yes	Need data
Permanganate	Yes	Yes	No	No
Chlorine & Permanganate	Yes	Yes	Yes	Yes
Chlorine & Ozone	Yes	Yes	Yes	Yes

Adapted from Westerick et al. 2010

CHLORINE - SUMMARY

- **Effective**
  - Microcystin, Cylindrospermopsin, Saxitoxin
- **Not Effective**
  - Anatoxin
- **Impact of pH??**
  - Microcystin – lower pH better
    - Rate at pH 9 is ~10% of pH 7
  - Cylindrospermopsin – low or high pH?
  - Saxitoxin – high pH better
- **Lower overall toxicity**

CHLORINE EFFECTIVENESS



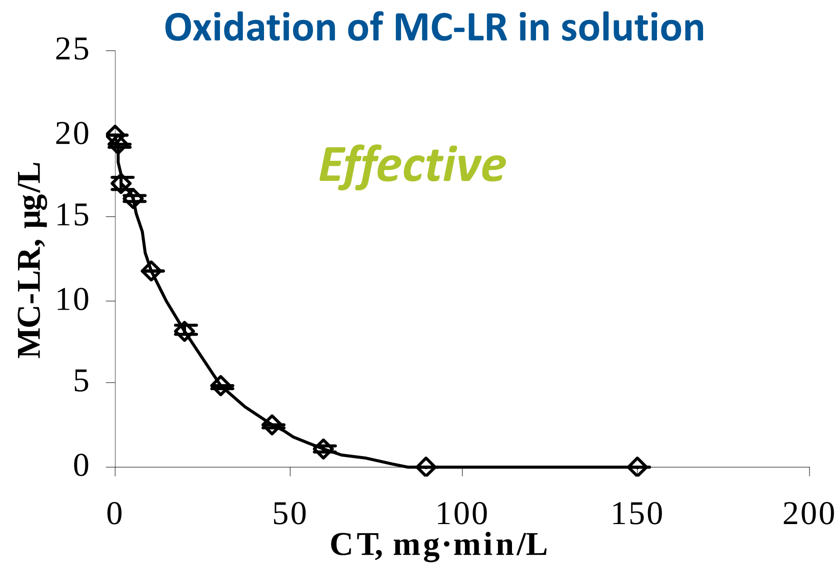


Fig. 9 *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during free chlorine (HOCl/OCl^{-}) treatment

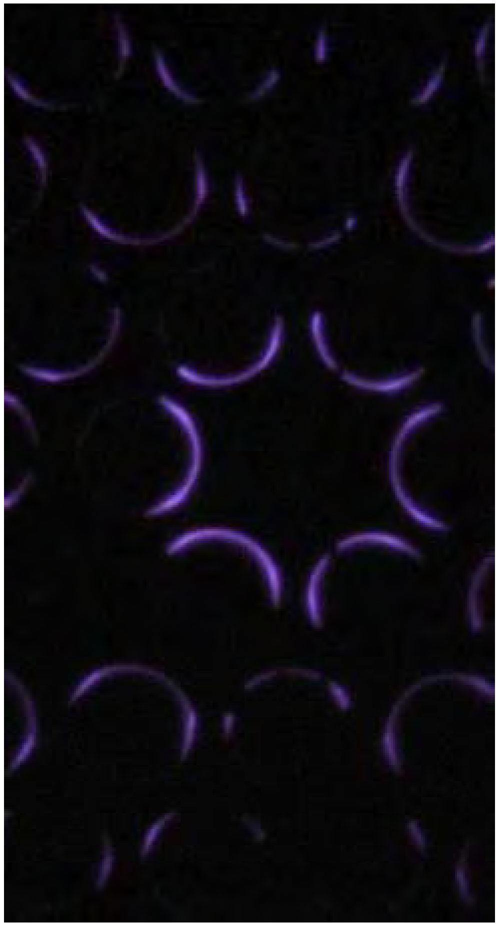
Source: Ding et al. 2010

CHLORINE - CONSIDERATIONS

- **Impact of high pH**
  - Especially lime softening plants
  - Preoxidation – more effective but before cell removal
  - After sedimentation
    - Less effective?
    - Less reaction time
- **Impact on algal cells**
- **Disinfection byproduct formation**

OZONE - SUMMARY

- **Effective**
  - Microcystin, Cylindrospermopsin, Anatoxin
- **Not Effective**
  - Saxitoxin
- **Very effective for taste and odor control**
- **Preozone or intermediate ozonation**
- **High initial cost**
- **Low operating cost**



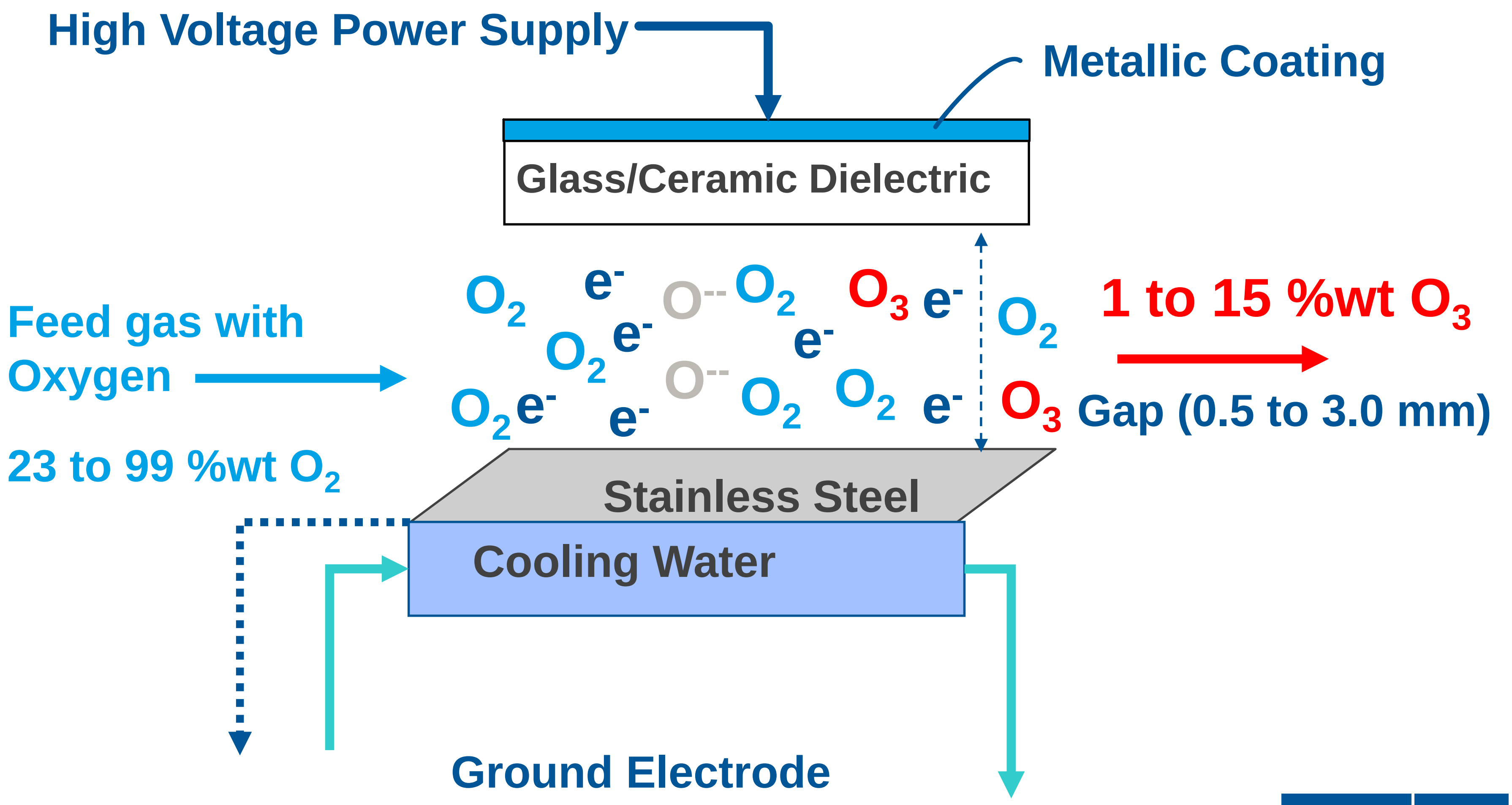
Ozone corona discharge

WHAT IS OZONE?

- **Unstable form of oxygen**
- **Produced on-site (electricity and oxygen)**
- **Reversible reaction ($2O_3 \Leftrightarrow 3O_2$)**
- **Temperature sensitive (lower is better)**
- **Dust and moisture sensitive**
  - fouling impacts electrical efficiency
  - acid production from nitrogen and water

OZONE BACKGROUND

OZONE GENERATION PRINCIPLES




Ozone contactor gallery

WHAT IS IT USED FOR?

- Disinfection
- DBP control
- Microflocculation
- Taste and odor control
- Iron and manganese oxidation
- Organics oxidation
- Hydrogen sulfide oxidation

WHAT OTHER IMPACTS ARE THERE?

LOX tank and ambient vaporizers

- **Inorganic byproduct - bromate**
  - High pH, raw bromide concentrations
  - Counteract by optimized dose, ammonia, lower pH
- **Organic byproducts**
  - Oxygenated byproducts
  - Assimilable organic carbon (AOC)
- **Dissolved oxygen**

OZONE EFFECTIVENESS

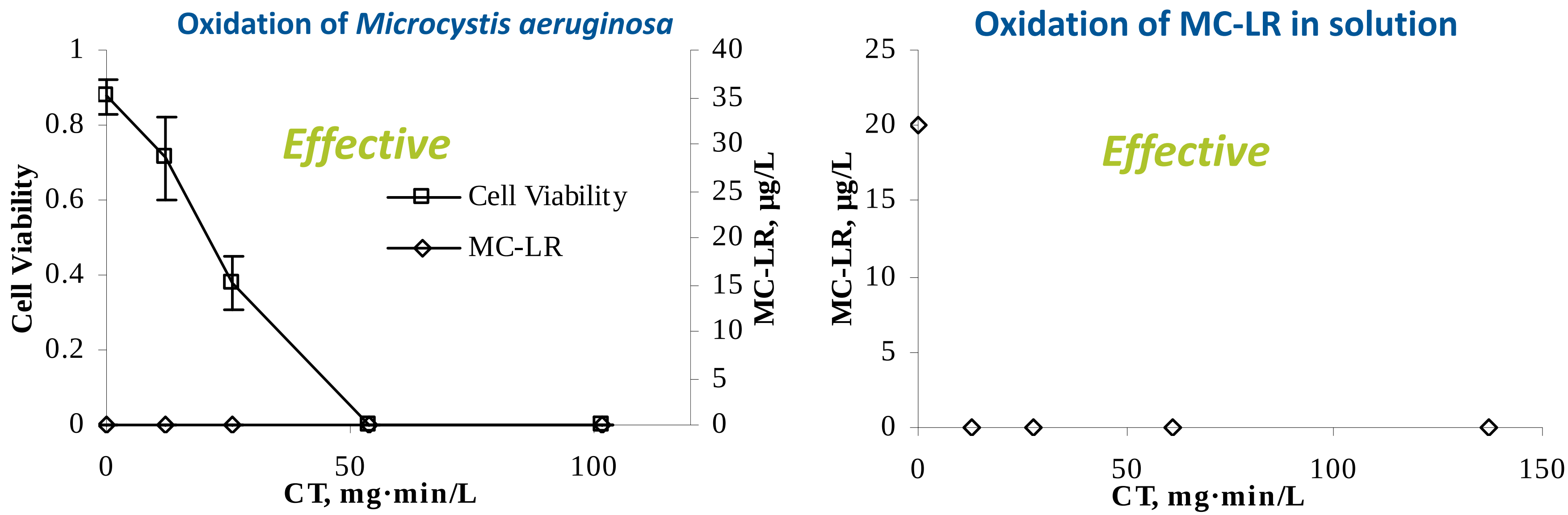


Fig. 12 *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during ozone treatment

Source: Ding et al. 2010

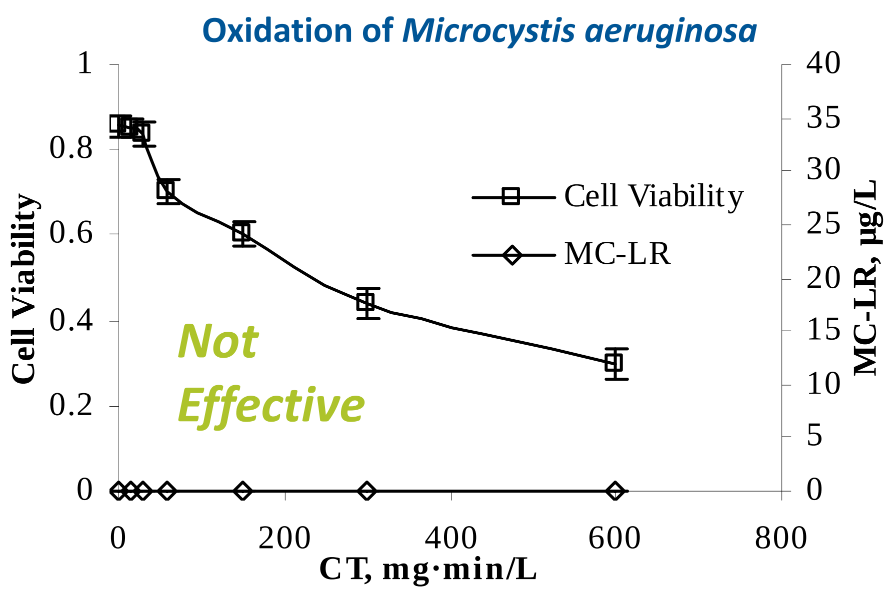
OZONE - CONSIDERATIONS

- **Cost effectiveness**
  - Also address T&O or DBPs
- **Meet disinfection requirements**
- **May need biological filtration**
- **Bromate formation**

CHLORAMINE - SUMMARY

- **Not Effective**
  - Microcystin, Cylindrospermopsin, Anatoxin
  - Saxitoxin?
- **Not a powerful primary disinfectant**
- **Used by many as a secondary disinfectant**
  - Long reaction times
  - A barrier to protection?

CHLORAMINE EFFECTIVENESS



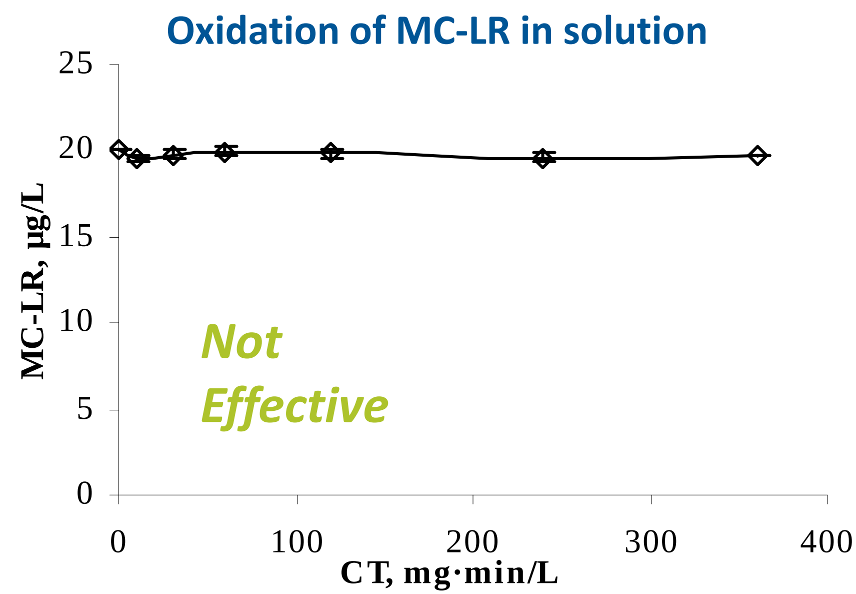


Fig. 16 *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during monochloramine treatment

Source: Ding et al. 2010

CHLORAMINE - CONSIDERATIONS

- Would not be considered as a primary barrier
- Would still be part of overall treatment as secondary disinfectant

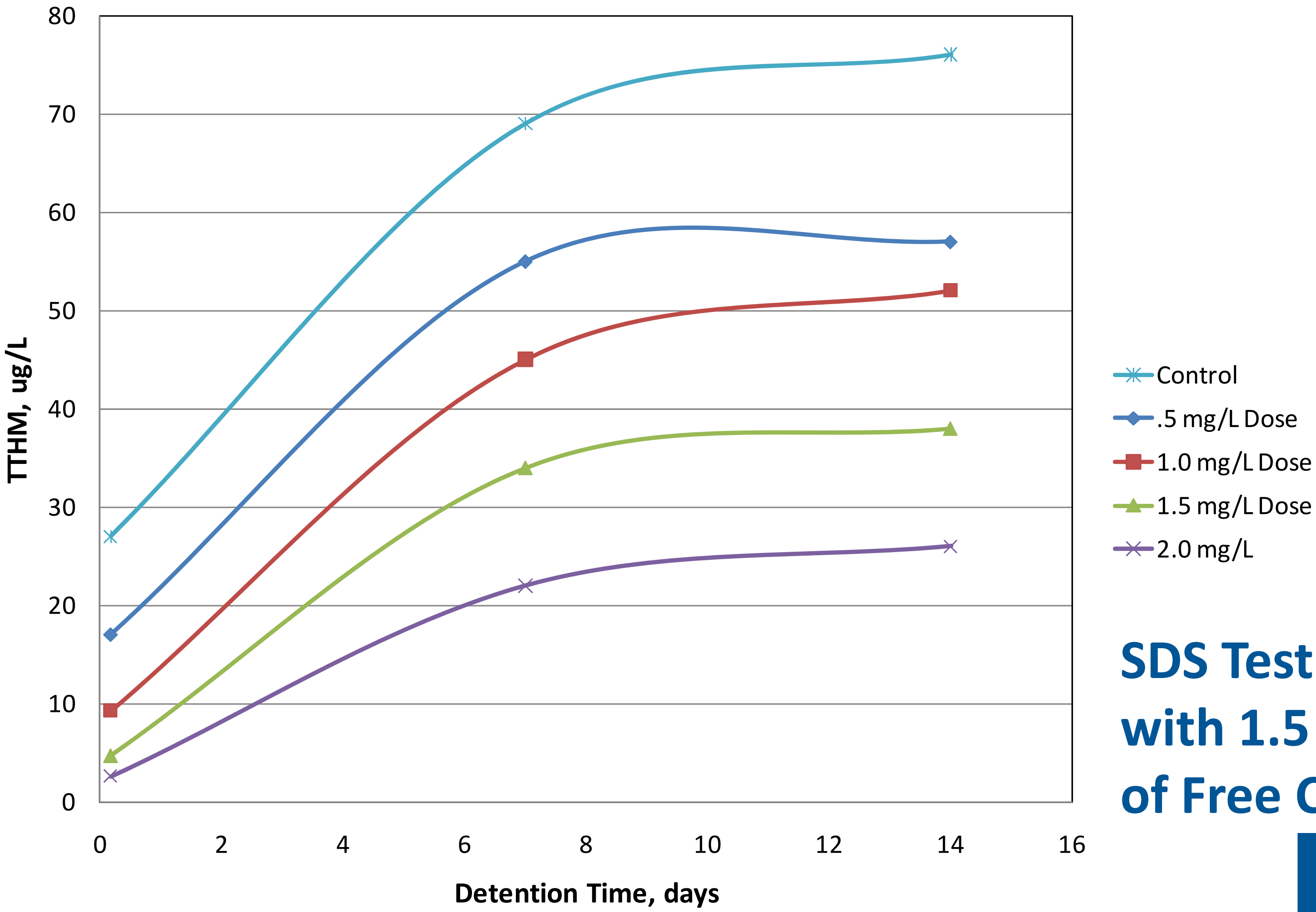
CHLORINE DIOXIDE - SUMMARY

- **Not Effective**
  - Microcystin, Cylindrospermopsin, Anatoxin
  - Saxitoxin?
- **Lower toxicity reported**
- **Primarily used as a preoxidant**
  - Potential lysing of algal cells
- **Impact at “high” pH?**

WHY USE CHLORINE DIOXIDE?

- Powerful oxidant for Mn
- Some phenolic T&O, minimal MIB & geosmin
- Effective algicide and mollusk control
- Doesn’t react with NOM to form halogenated DBPs
- Reduces oxidant demand for subsequent disinfectant(s)
- Effective against viruses, bacteria and *Giardia*
- Control nitrification is the distribution system

PREOXIDATION WITH CHLORINE DIOXIDE IS EFFECTIVE AT REDUCING TTHM FORMATION



SDS Testing with 1.5 mg/L of Free Chlorine

CHLORITE BASED GENERATION

2 Chemical

Sodium Chlorite Solution
Chlorine Gas

"Rio Linda" "pH Control"

Solid Chlorite

Sodium Chlorite Solid
Chlorine Gas

3 Chemical

Sodium Chlorite Solution
Sodium Hypochlorite
Hydrochloric Acid

2 Chemical - Acid

Sodium Chlorite Solution
Hydrochloric Acid

Electrochemical

Sodium Chlorite Solution
Energy

CHLORATE BASED GENERATION

Three Chemical

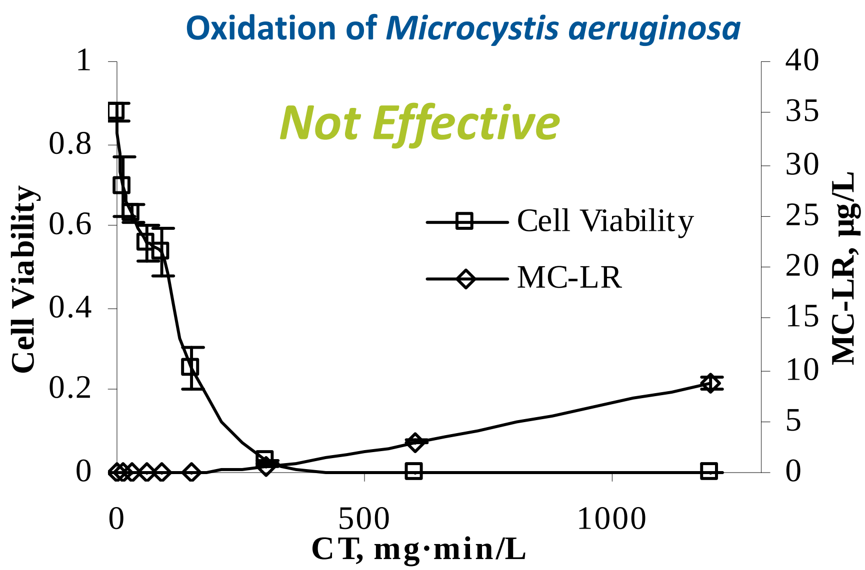
Sulfuric Acid
Premixed
(Hydrogen Peroxide &
Sodium Chlorate)

ISSUES WITH CHLORINE DIOXIDE

- **60-70% of applied ClO_2 goes to chlorite ion**
  - ~1.5 mg/L maximum dose
- **Compliance requirements**
- **Chlorite and free chlorine as secondary disinfectant may lead to "cat urine odor"**
- **Marginally effective against *Cryptosporidium***
- **Operating costs**
- **Supply chain issues**

OXIDATION

CHLORINE DIOXIDE EFFECTIVENESS



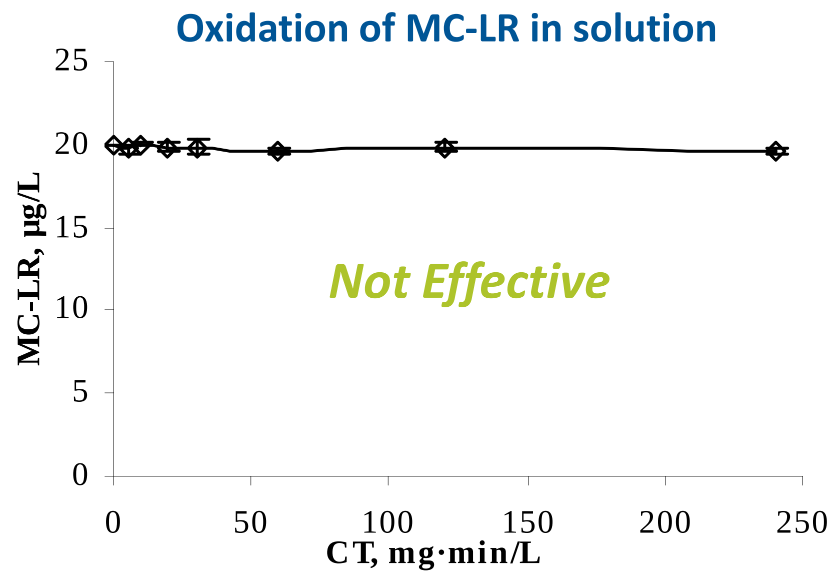


Fig. 10 *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during chlorine dioxide treatment

Source: Ding et al. 2010

CHLORINE DIOXIDE - CONSIDERATIONS

- **Consider stopping during an event**
  - Prevent lysing of cells
  - Must consider other impacts – Mn, preoxidation, CT
- **Must consider chlorite formation**

ADVANCED OXIDATION - SUMMARY

- **Effective**
  - Microcystin, Cylindrospermopsin, Anatoxin
- **Not effective**
  - Saxitoxin??
- **Effective for disinfection and taste and odor**
- **After filtration**
- **High initial cost**
- **High operating cost**

WHAT IS ADVANCED OXIDATION?

- Process that generates reactive species - radicals
  - hydroxyl radicals (●OH)
- Stronger oxidizer than ozone
- Fast kinetics
- Short half-life
- Yield/concentration
- Scavenging potential of water

EXAMPLE PROCESSES/REAGENTS

- Ozone
- Ozone/H_2O_2
- Ozone/UV
- UV/H_2O_2
- UV/PAA
- UV/TiO_2
- UV/Fe/H_2O_2
- Fe/H_2O_2
- UV/S_2O_8
- Ag/S_2O_8
- Fe/S_2O_8
- UV/HSO_5
- Co/HSO_5
- E beam

UV AOP BACKGROUND

UV/H_2O_2 PROCESS

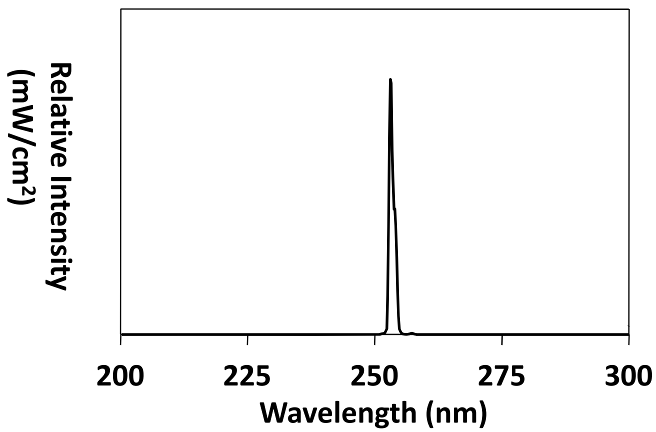
- **UV light absorbed by hydrogen peroxide**

$$H_2O_2 \xrightarrow{h\nu \text{ (energy)}} 2\,\bullet OH$$

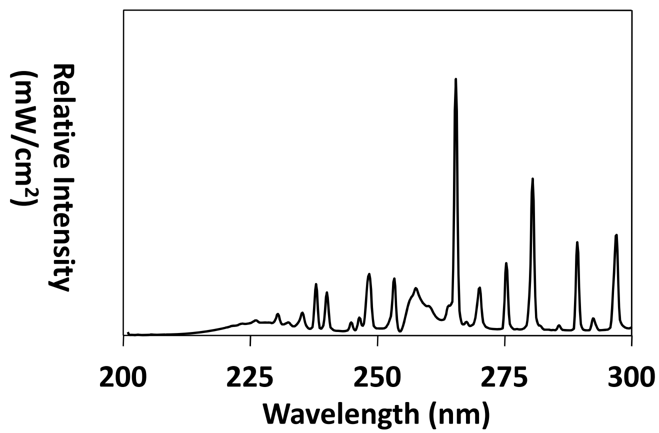
$$P + \bullet OH \xrightarrow{k_{OH,P}} [\text{radical species}] \xrightarrow{O_2} \text{Products}$$

- **Degradation rate depends on:**
  - OH radical rate constant kOH,P
  - H2O2 concentration
  - ●OH radical demand in water
  - Intensity and spectral distribution of the light source
  - Absorption of water background

DIFFERENT TYPES OF LAMPS DISINFECT DIFFERENTLY



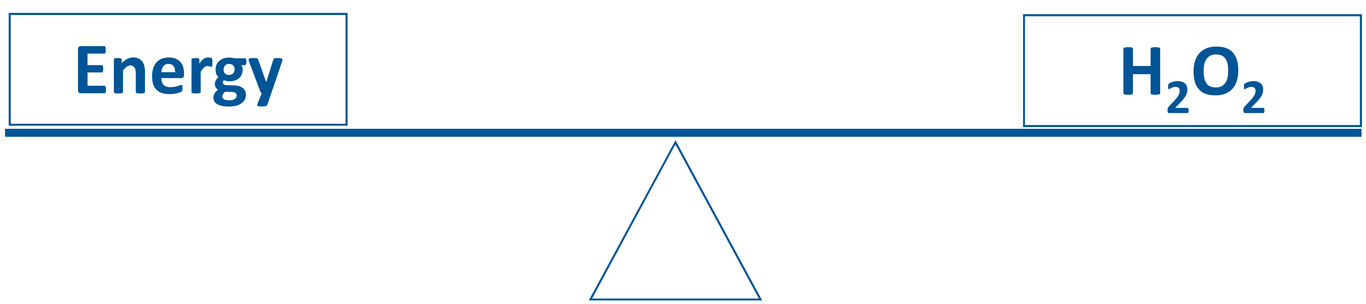
Low Pressure



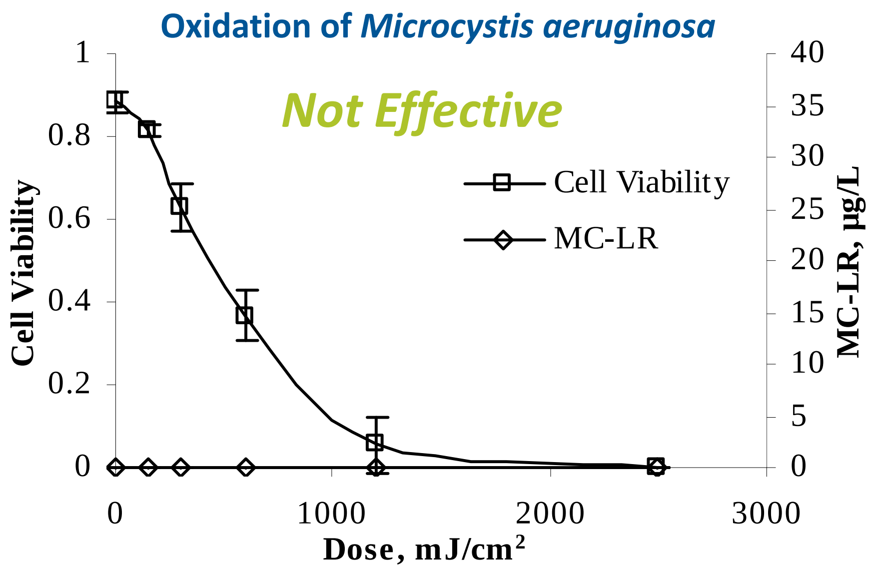
Medium Pressure

MUST BALANCE ENERGY AND HYDROGEN PEROXIDE

- Less peroxide requires more energy
- More peroxide requires less energy
- Diminishing returns?
- Residual hydrogen peroxide



UV EFFECTIVENESS



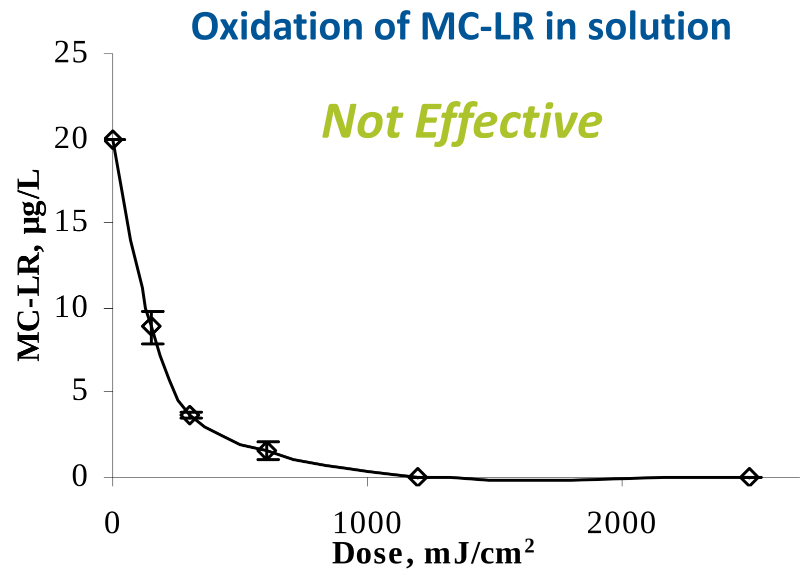


Fig. 16 *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during ultraviolet (UV) treatment

OXIDATION

Source: Ding et al. 2010

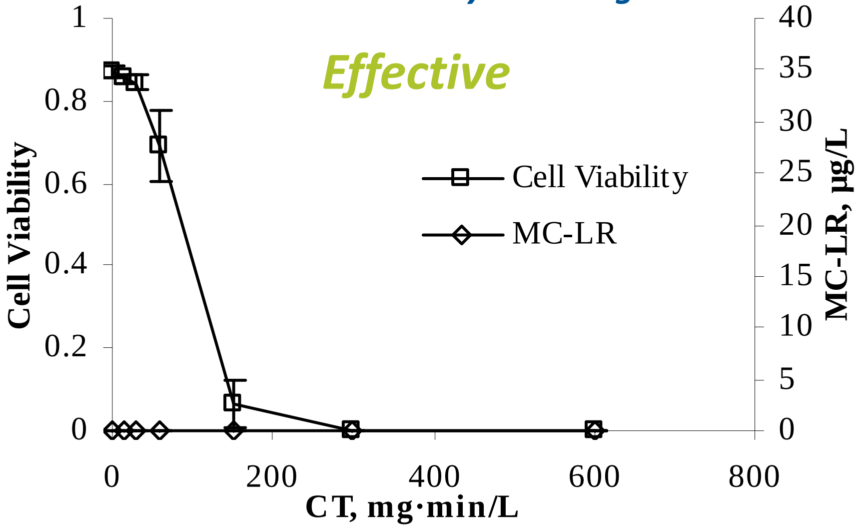
ADVANCED OXIDATION - CONSIDERATIONS

- **Cost effectiveness**
  - Also address T&O or DBPs
- **Meet disinfection requirements**
- **Quenching of residual hydrogen peroxide**
  - High chlorine doses

PERMANGANATE - SUMMARY

- **Effective**
  - Microcystin, Anatoxin
- **Not effective**
  - Cylindrospermopsin, Saxitoxin
- **Does not impact intact cells?**
  - Non-impact has been observed at DAF plants
- **Somewhat simple feed system that is common**
  - Could be used a preoxidant

PERMANGANATE EFFECTIVENESS



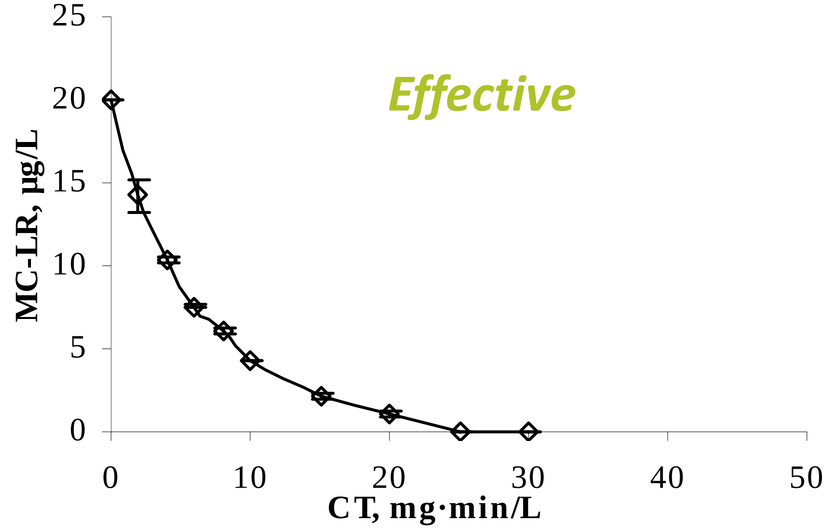


Fig. 11 *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) permanganate (MnO_4^-) treatment

Source: Ding et al. 2010

PERMANGANATE - CONSIDERATIONS

- **Must consider demand**
  - Reliable residual measurement
  - Potential for pink water
- **Fate of manganese in treatment plant**
  - Need a waste point for residuals
- **Handling of dry systems can be problematic**
- **Liquid systems better, but more costly**

EFFECTIVENESS CAN CHANGE WITH MICROCYSTIN VARIANTS

	Half life (minutes)					
Oxidant	MC-LR	MC-RR	MC-LA	MC-LF	MC-LW	MC-YR
Free Chlorine	**29**	12	18	8	0	17
Chlorine Dioxide	>1500	>1500	>1500	>1500	>1500	>1500
Permanganate	6	5	**14**	10	9	6
Ozone	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Monochloramine	>1500	>1500	>1500	>1500	>1500	>1500

Half lives ($t_{1/2}$) (minutes) based on a constant 0.5 mg/L oxidant concentration

Source: Ding et al. 2010

TOOLS FOR OPERATORS

LIMITED PRACTICAL GUIDANCE IDENTIFYING AND TREATING ALGAL TOXINS

- **No simple method for detection**
  - Many different toxins and variants
  - Many require LC/MS (liquid chromatography/mass spec)
  - Some by ELISA (Enzyme-linked immunosorbent assay)
- **Can we use taste and odor?**
  - T&O ≠ toxin
  - Toxin ≠ T&O
- **Can we correlate toxin removal to T&O control?**
  - PAC for MIB/geosmin also removed toxins

REQUIREMENTS FOR EFFECTIVE MANAGEMENT OF T&O (AND TOXINS?)

- Appropriate goals & implementation plans
- Suitable methods of analysis
- Assessment of potential control measures
- Implementation of effective and affordable control measures
- Collection, evaluation, and storage of appropriate monitoring data
- Dedication of sufficient resources to get the job done

DETECTION AND MONITORING

- **Monitoring considerations**
  - Frequency
  - Location
  - Method(s) and cost
  - Other parameters and information, e.g.,
    - Temperature, algal ID & counts, chlorophyll, lake stratification, turbidity
    - HPC, residual chlorine, Cl2:N ratio, Fe & Mn, LSI
- **The importance of consumer complaints**
- **The importance of good record keeping**

SOME PRACTICAL TOXIN INFORMATION

- **YSI sondes**
  - DO, conductivity, temp, pH, depth, chlorophyll a, phycocyanin
  - North Carolina reservoirs
- **General chlorine recommendations (WRF 3148)**
  - pH < 8
  - Residual > 0.5 mg/L after 30 min
  - Chlorine dose > 3 mg/L
  - CT on the order of 20 mg*min/L
- **General ozone recommendations (WRF 3148)**
  - pH > 7
  - Residual > 0.3 mg/L after 5 min
  - CT on the order of 1.0 mg*min/L

CONCLUSIONS

TAKE HOME MESSAGES

- **Oxidation can be effective**
  - No silver bullet for all toxins
  - Consider multiple barrier
- **Consider oxidant and location**
  - Preoxidation may help or hurt
  - Remove cells first
  - Then remove dissolved toxins
- **Operation plan**
  - Source
  - Taste and odor

WHICH OXIDANTS ARE EFFECTIVE?

	Microcystin	Anatoxin-a	Cylindrospermopsin	Saxitoxin
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Chlorine Dioxide	No	No	No	Need data
Advanced oxidation	Yes	Yes	Yes	Need data
Permanganate	Yes	Yes	No	No
Chlorine & Permanganate	Yes	Yes	Yes	Yes
Chlorine & Ozone	Yes	Yes	Yes	Yes

Adapted from Westerick et al. 2010

REFERENCES

- Ding, Shi, Timmons, Adams, "Release and Removal of Microcystins form *Microcystis* during Oxidative-, Physical-, and UV-Based Disinfection" Journal of Environmental Engineering, 136(1), 2-11, 2010
- Westerick, Szlag, Southwell, and Sinclair, "A review of cyanobacteria and cyanotoxins removal/inactivation in drinking water treatment" Anal Bioanal Chem, 397:1705-1714, 2010
- WRF 3148 "International Guidance Manual for the Management of Toxic Cyanobacteria"

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