Cyanotoxin Assessments and Mitigation Plans - Part 2

Marvin Gnagy, P.E.
President
PMG Consulting, Inc.

OTCO Water Workshop

March 8, 2017

Agenda

- Mitigation Plans
- Cyanobacteria and Cyanotoxin Monitoring
- Treatment Using Permanganate Oxidation
- Treatment Using Chlorine Oxidation
- Treatment Using Ozone Oxidation

Agenda

- Treatment Using PAC Adsorption
- Treatment Using GAC Adsorption
- Cyanotoxin Mitigation Strategies
  - No time to cover more complex removal processes
    - Membranes
    - UV/combined oxidants
    - AOP

Mitigation Plans

- Readiness to treat organisms and/or toxins
  - Effective monitoring and detection methods
  - Effective removal processes
  - Effective treatment chemicals and sequencing
  - Effective implementable treatment strategies
  - Capital improvement needs
    - Close gaps found from assessments
  - Effective barriers to exposure
    - Multiple barriers throughout the facilities
  - Nimble self assessment and plan revisions

Mitigation Plans

- Comprehensive knowledge of cyanobacteria and cyanotoxins needed
  - Detection
  - Source water treatment
  - Cell lysing and toxin release
  - Toxin removal chemistries
  - Treatment sequencing and verification techniques
  - Multi-barrier strategies to minimize exposure
  - Regulatory requirements
    - Monitoring
    - Reporting
    - Recordkeeping

Cyanobacteria and Cyanotoxin Monitoring

- Source water
  - Water temperature and pH
  - Bloom observations
    - Masses, oils slicks, scum, green/blue-green/red coloration
  - Chlorophyll-a
  - Dissolved oxygen (DO)
  - Phycocyanin
  - Population identification and counts
  - Quantitative polymerase chain reaction (qPCR)
    - Cyanotoxin production genes, type and potential toxins
  - Nutrients
    - Phosphorus, ammonia, nitrogen

Cyanobacteria and Cyanotoxin Monitoring

- Source water
  - Grab samples and/or data sondes
- Grab samples provide instantaneous monitoring one time

Raw sample from Toledo HAB event 2014

Cyanobacteria and Cyanotoxin Monitoring

- Grab samples
  - Laboratory cyanobacteria detection and counting methods
    - Training available Stone Labs
  - ELISA test kits
    - Microcystin monitoring (some Ohio WTP labs approved)
  - Contract labs
    - Algal toxin monitoring
    - EPA methods 544, 545, 546
      – ELISA (546 total microcystin/nodularin)
      – LC/MS/MS (544 microcystins/nodularin)
      – LC/ESI-MS/MS (545 cylindrospermopsin/anatoxin-a)
      – HPLC-PDA (microcystins, not EPA method list)

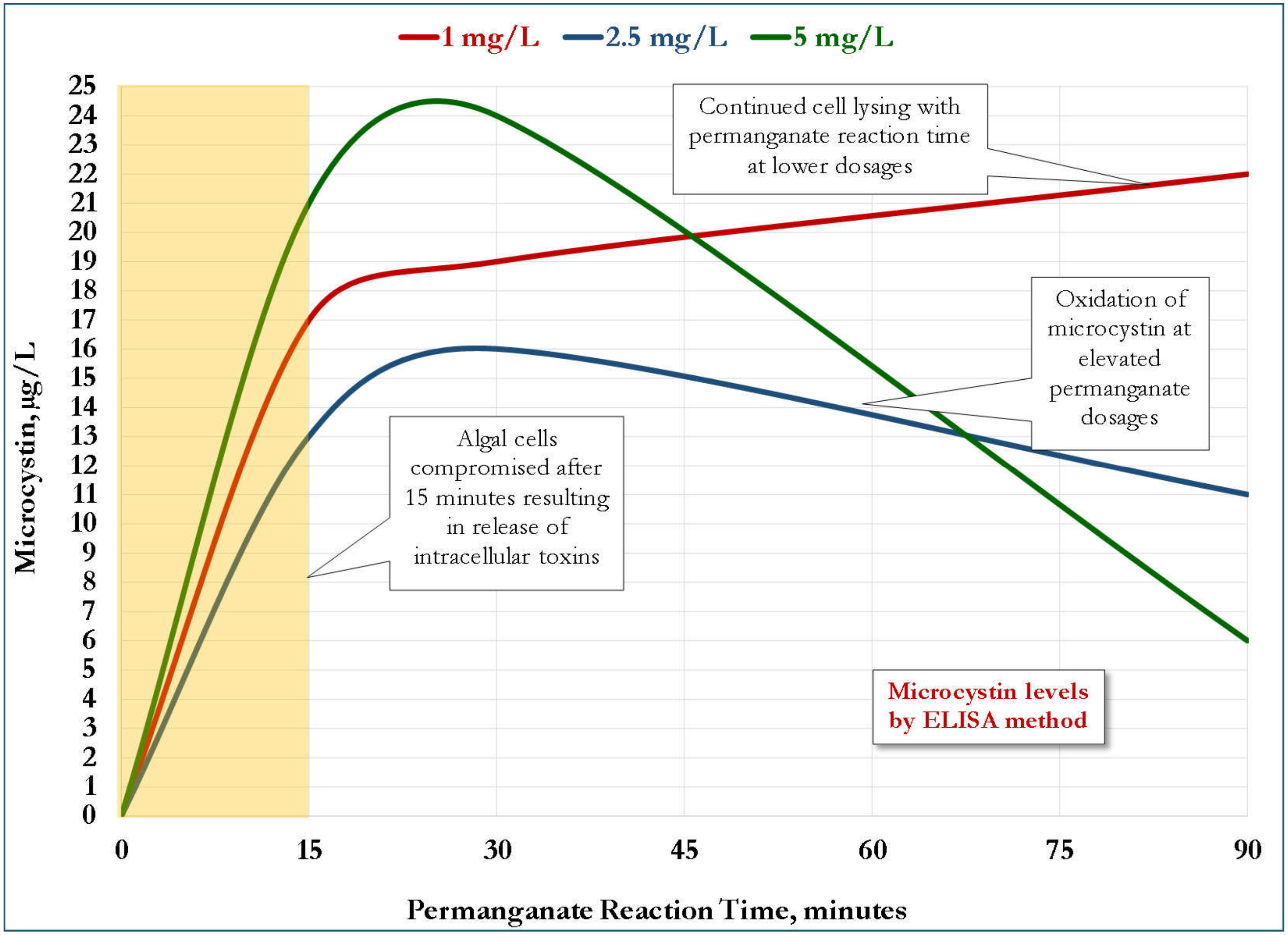
Cyanobacteria and Cyanotoxin Monitoring

- Solar powered
  - No external power availability
- Multiple parameter sondes
  - What you can afford and work with
- Transmitting capabilities
- Located near intake
  - Monitor surface conditions only
  - Severe weather operability
  - Accessible for calibration/maintenance

Treatment Using Permanganate Oxidation

- Generally effective for microcystin and anatoxin-a
- Potassium-based or sodium-based products
  - Manganese dioxide byproducts requires post-coagulation
  - Likely raw water intake feed point
- Dosages as low as 1 mg/L can stress cyanobacteria cells
  - Lysing or not strategies
  - Oxidation dosages may need to be 5 mg/L or greater
  - USEPA data suggested 25 minutes reaction time necessary
    - 1 mg/L, 2.5 mg/L, 5 mg/L dosing

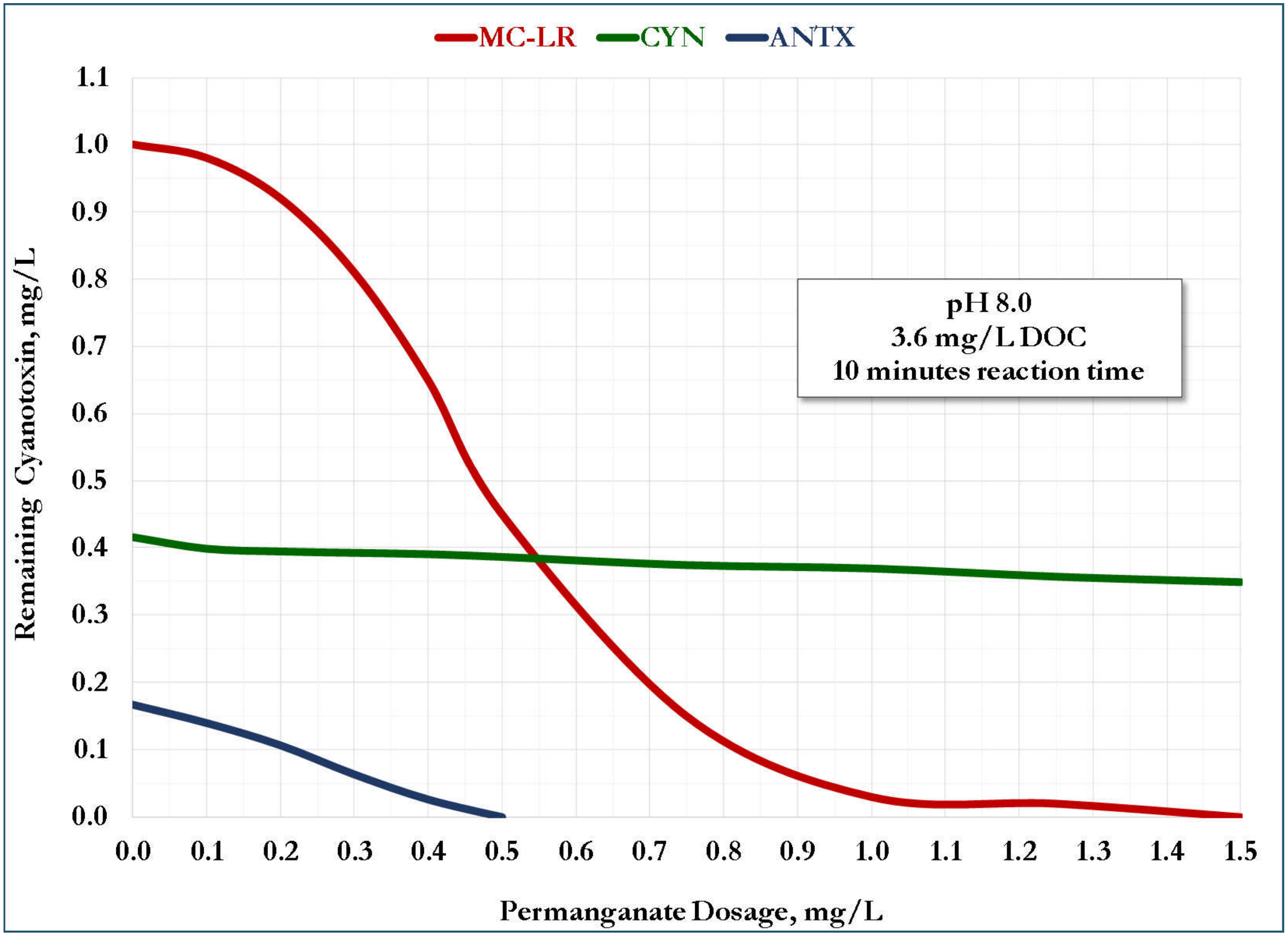
Treatment Using Permanganate Oxidation



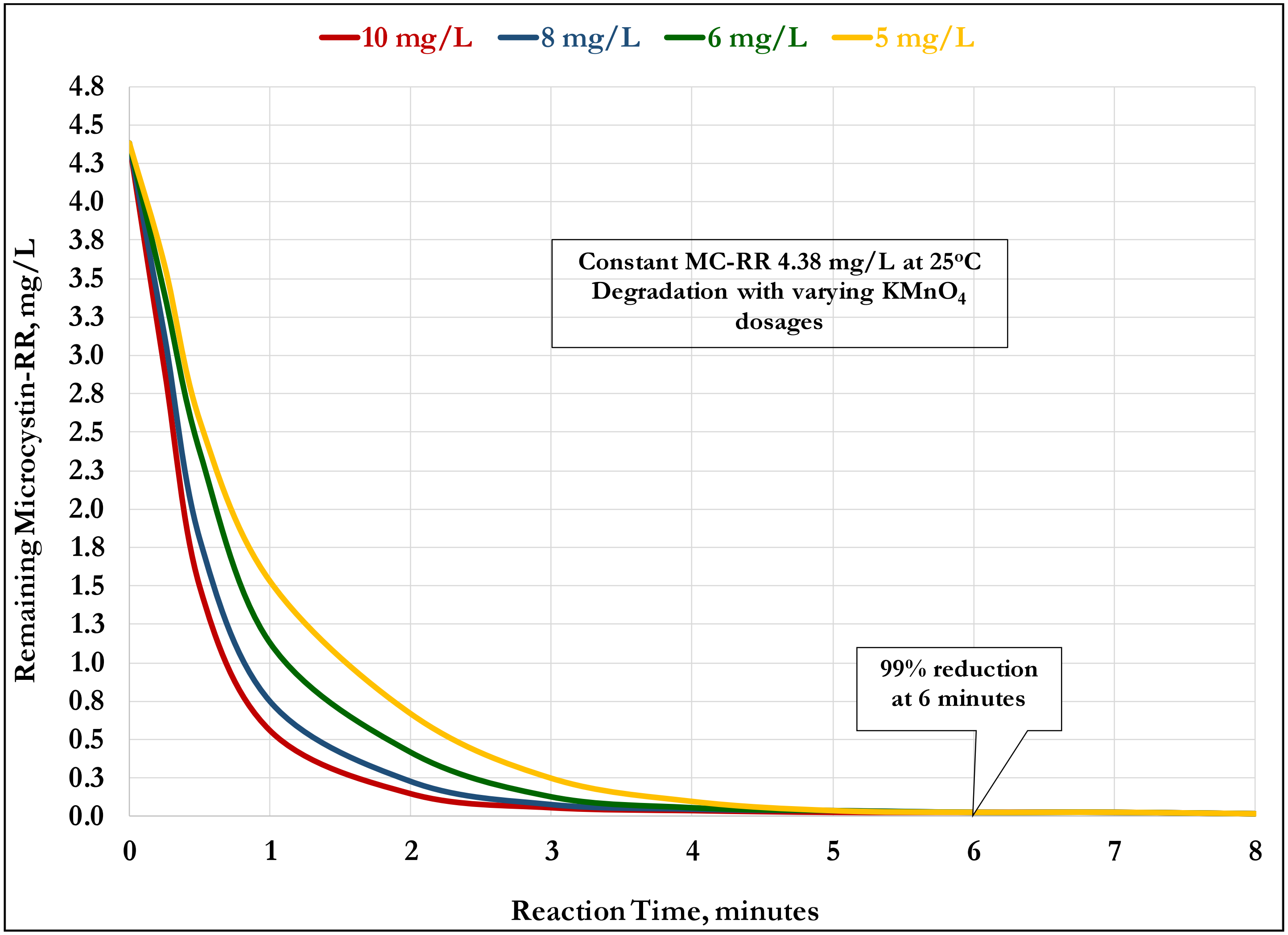
Treatment Using Permanganate Oxidation

- Published reaction rates with permanganate
  - Anatoxin-a, 25,000 $M^{-1}s^{-1}$
  - Microcystin, 375 $M^{-1}s^{-1}$
  - Cylindrospermopsin, 0.45 $M^{-1}s^{-1}$
- Reaction times may vary with dosage
  - Higher dosages reduce reaction time for oxidation
  - Up to 99% reduction found
  - Oxidation to non-toxic metabolites
  - Competition from other sources
    - Iron, manganese, NOM, etc.

Treatment Using Permanganate Oxidation

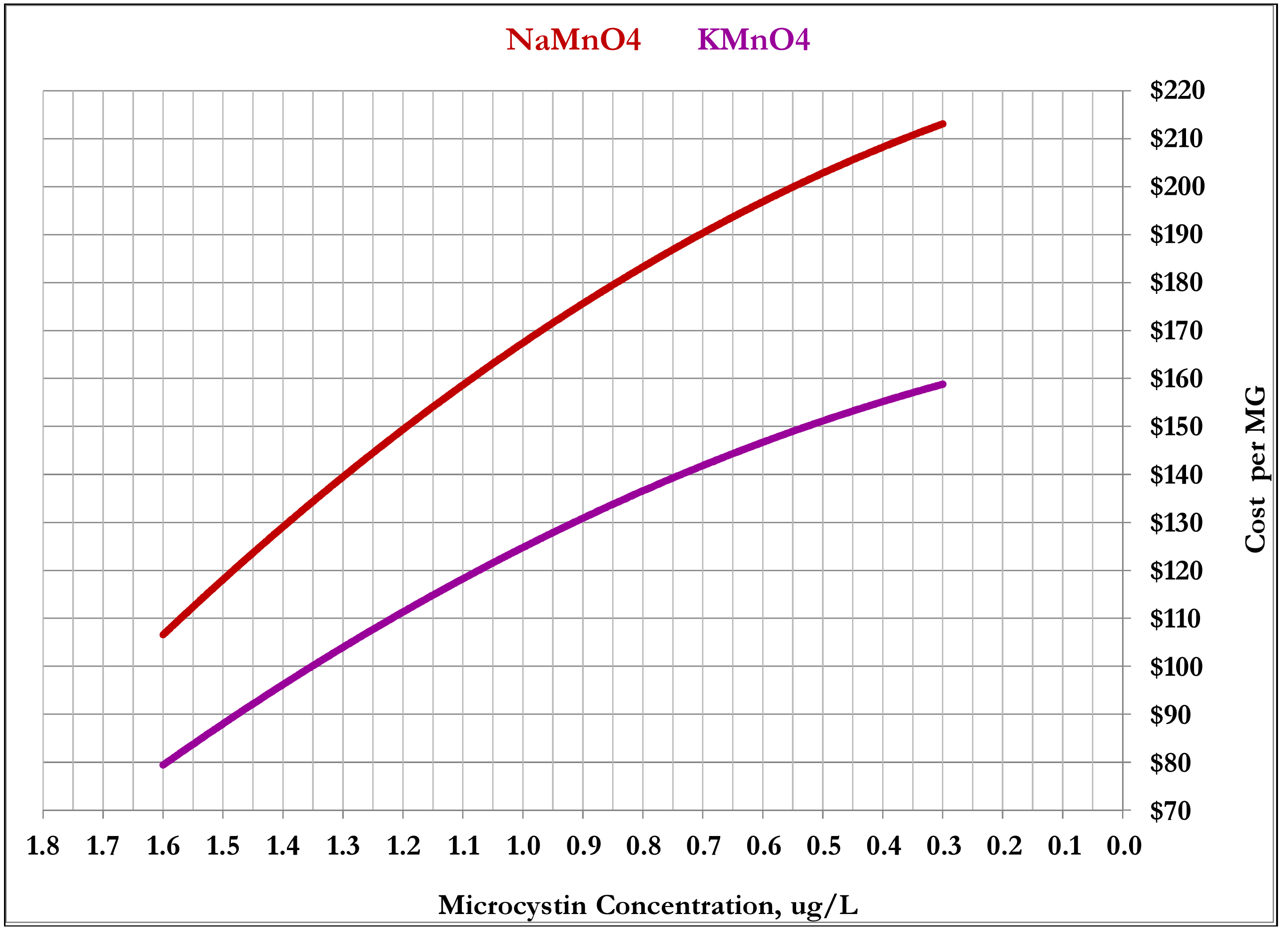


Treatment Using Permanganate Oxidation



Treatment Using Permanganate Oxidation

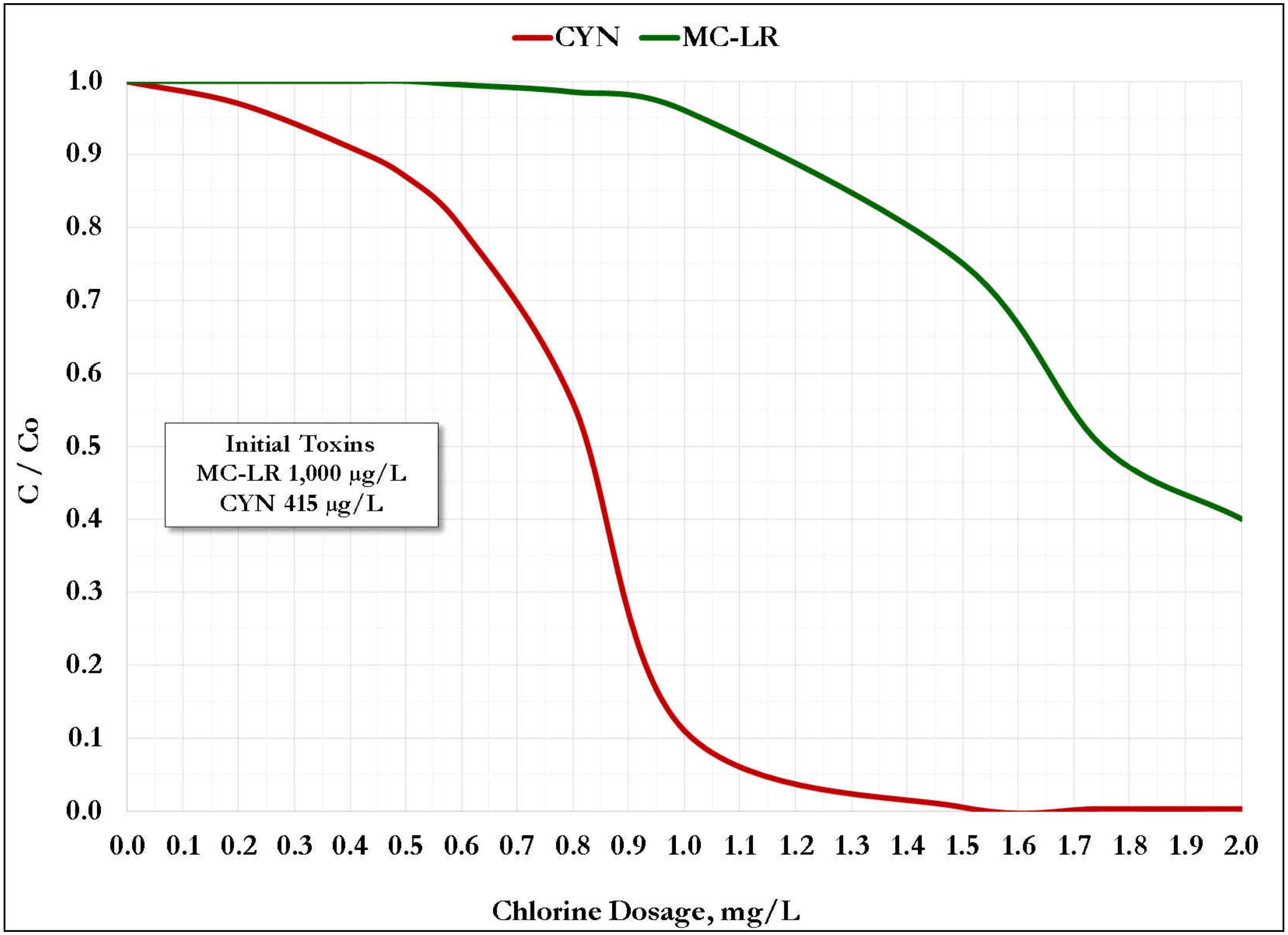
Treatment costs could range from $79 per MG to $213 per MG depending on target level of toxins and type of permanganate



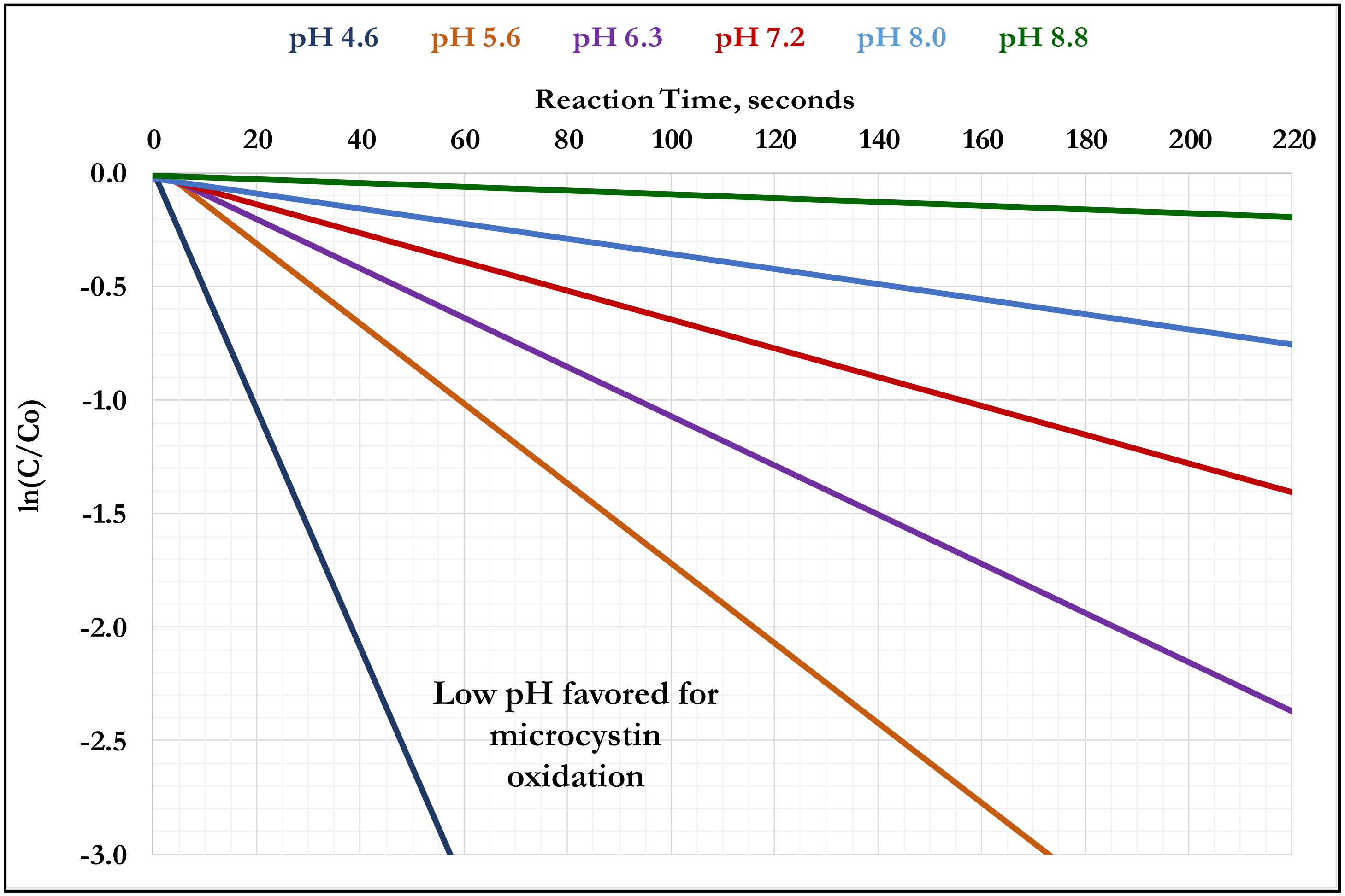
Treatment Using Chlorine Oxidation

- Chlorine addition to raw water not used due to DBPs
- Chlorine application post filtration likely best location
  - Can increase DBP formation depending on pH, dose, and toxin levels
  - CT concept shown to be effective reduction method
  - Likely attacks double bonds resulting in non-toxic metabolites
    - Amino acids from microcystin
    - 5-chloro-cylindrospermopsin or cylindrospermopsic acid
  - Published reaction rates
    - 1,265 $M^{-1}s^{-1}$ cylindrospermopsin
    - 91.5 $M^{-1}s^{-1}$ microcystin

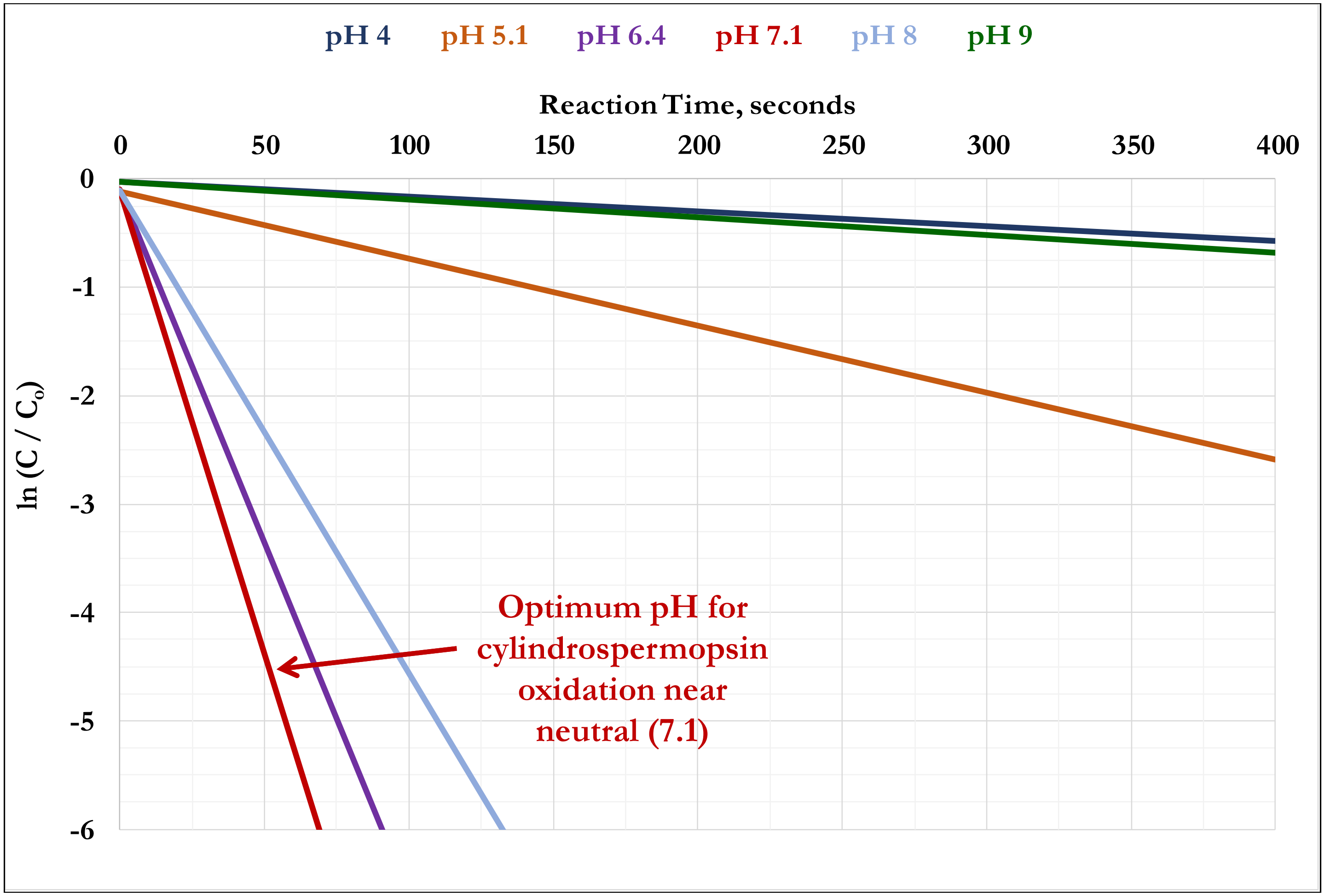
Treatment Using Chlorine Oxidation



Treatment Using Chlorine Oxidation



Treatment Using Chlorine Oxidation



Treatment Using Chlorine Oxidation

- CT concept well known and practiced
  - Added barrier following other treatments
  - Oxidation favors lower pH levels (5 to 8)
  - Competing reactions with iron, manganese, NOM, etc.
- CT values published for microcystin
  - Predict contact time necessary
  - Predict free chlorine residuals needed

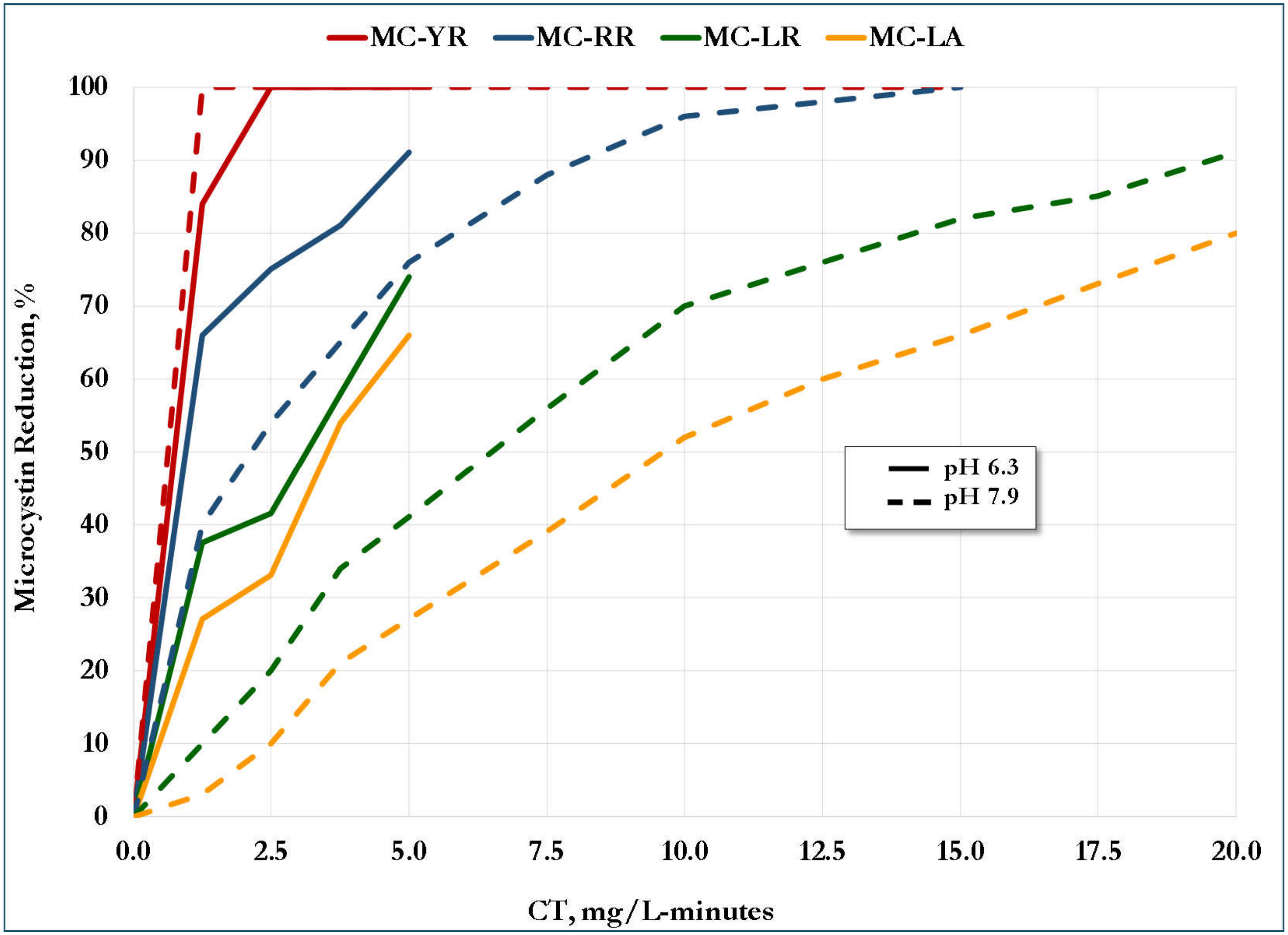
Treatment Using Chlorine Oxidation

50 µg/L Microcystin-LR					10 µg/L Microcystin-LR				
pH	10°C	15°C	20°C	25°C	pH	10°C	15°C	20°C	25°C
6	46.6	40.2	34.8	30.3	6	27.4	23.6	20.5	17.8
7	67.7	58.4	50.6	44.0	7	39.8	34.4	29.8	25.9
8	187.1	161.3	139.8	121.8	8	110.3	94.9	8.23	71.7
9	617.2	526.0	458.6	399.1	9	363.3	309.6	269.8	234.9

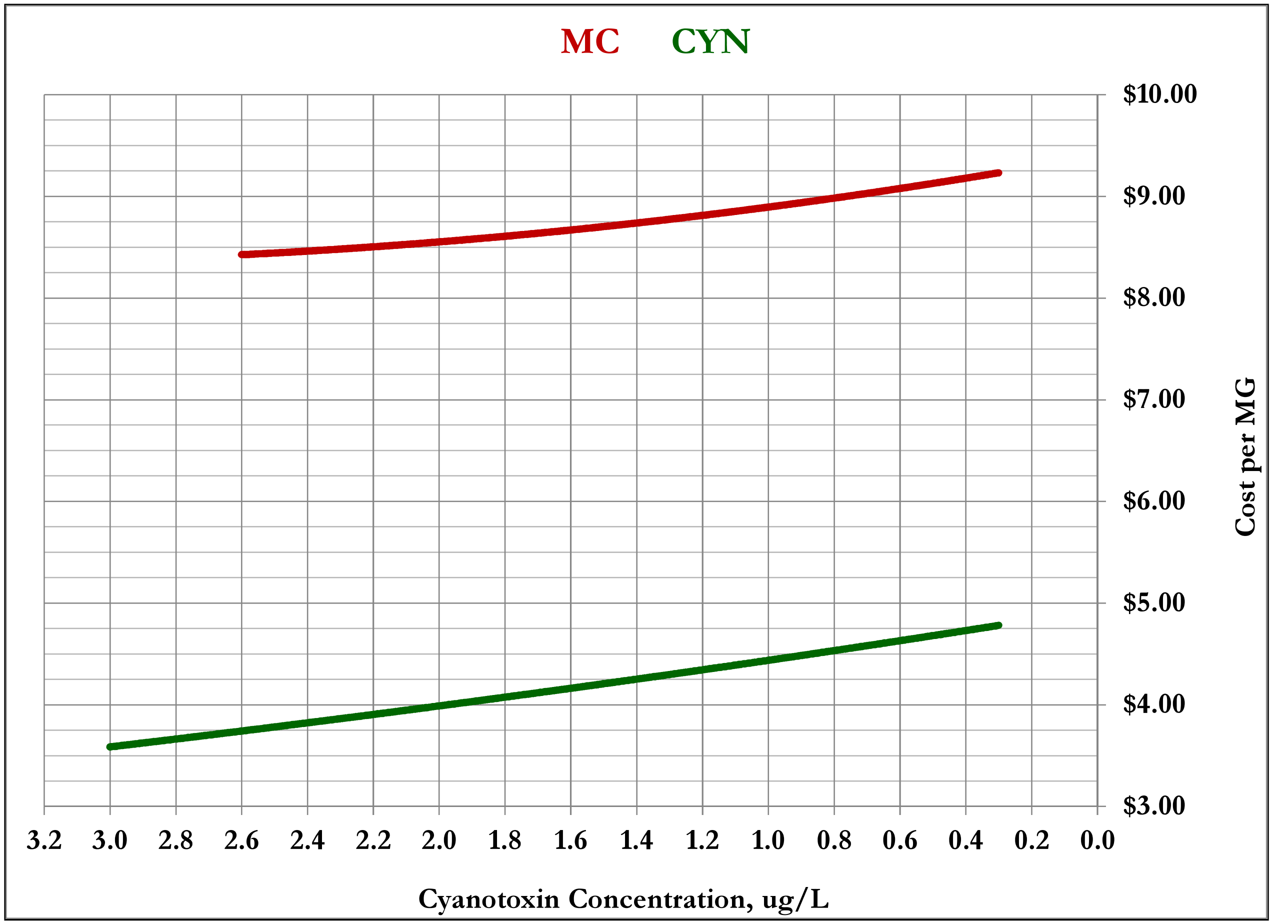
Treatment Using Chlorine Oxidation

50 µg/L Microcystin-LR		10 µg/L Microcystin-LR	
Water pH	7	Water pH	7
Temp, °C	20	Temp, °C	20
Baffling factor	0.5	Baffling factor	0.5
Free chlorine, mg/L	1.5	Free chlorine, mg/L	1.5
CT req, mg/L-min	50.6	CT req, mg/L-min	29.8
Dt, minutes	**67.5**	Dt, minutes	**39.7**

Treatment Using Chlorine Oxidation



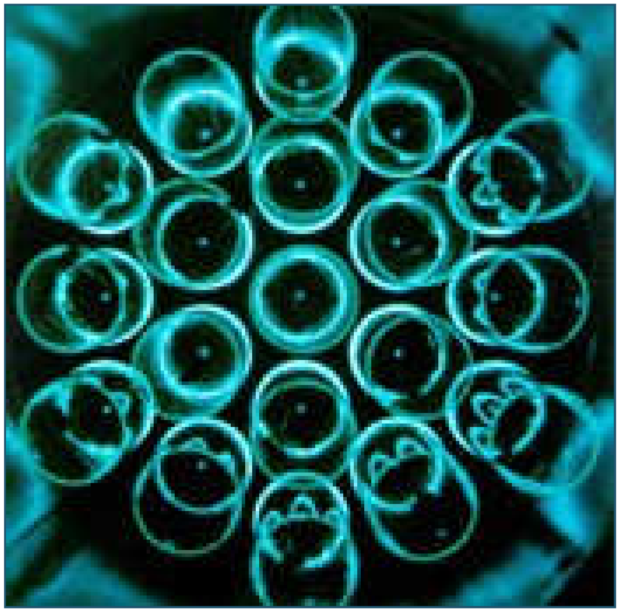
Treatment Using Chlorine Oxidation



Treatment costs could range from $3.60 per MG to $9.25 per MG depending on target level of toxins

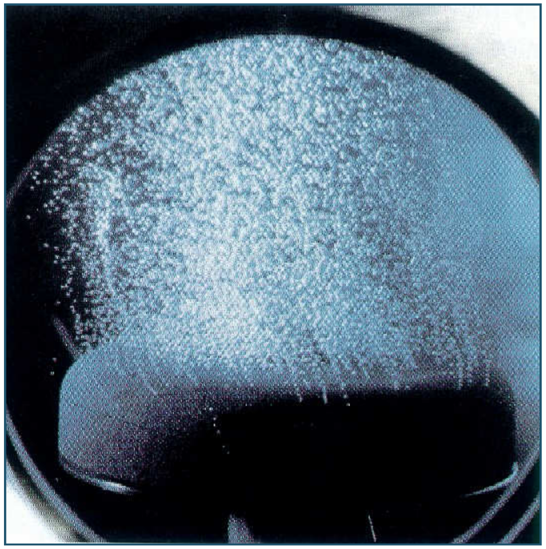
Treatment Using Ozone Oxidation

- Capital-cost intensive treatment process
  - Most powerful oxidant
  - Raw, intermediate, post-filter applications
  - Competing reactions from inorganics, NOM, etc.
  - Other considerations
    - Ozone decay
    - Ozone residuals and quenching
    - Bromate formation
    - Biologically active filtration (BAF) impacts

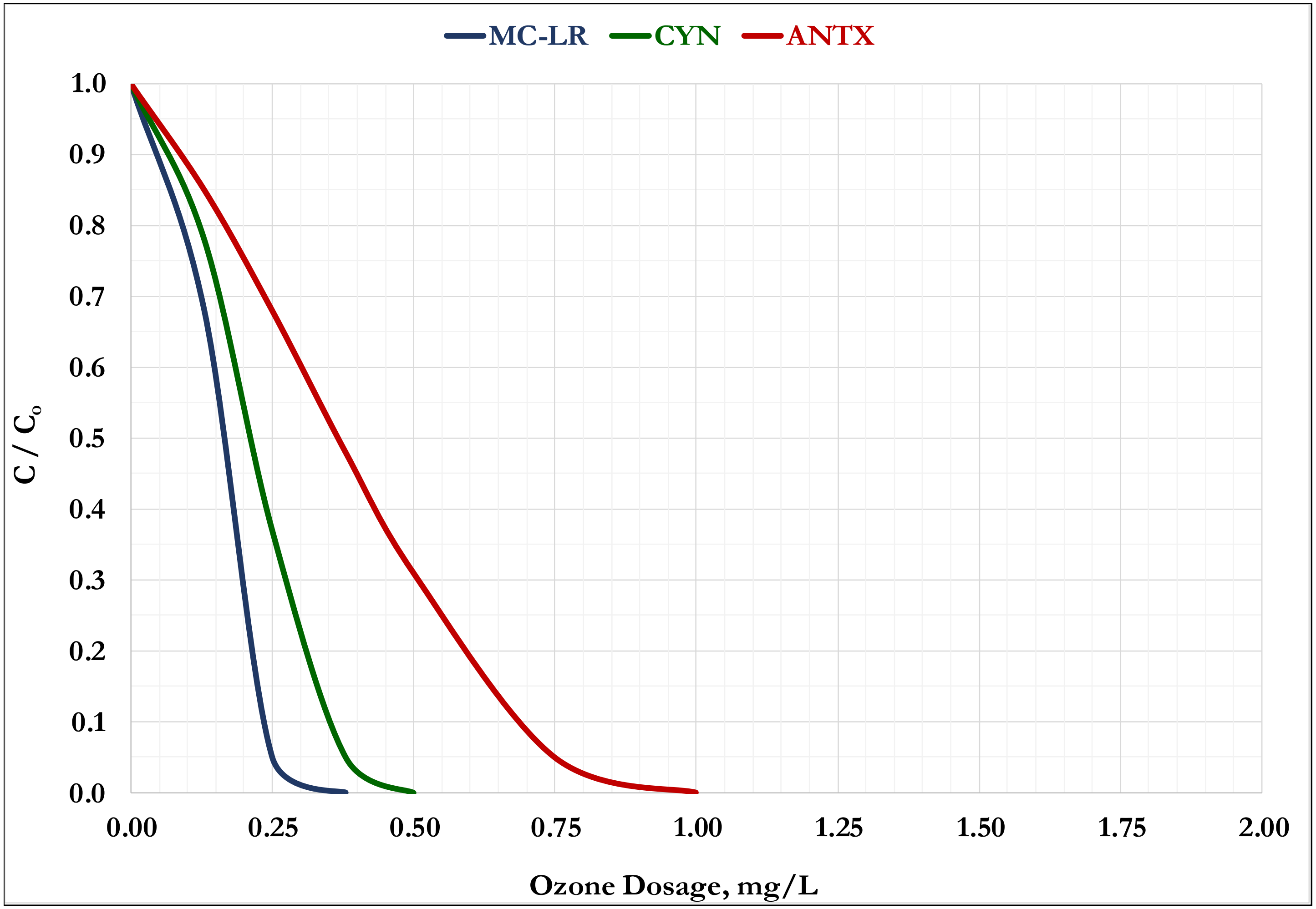


Treatment Using Ozone Oxidation

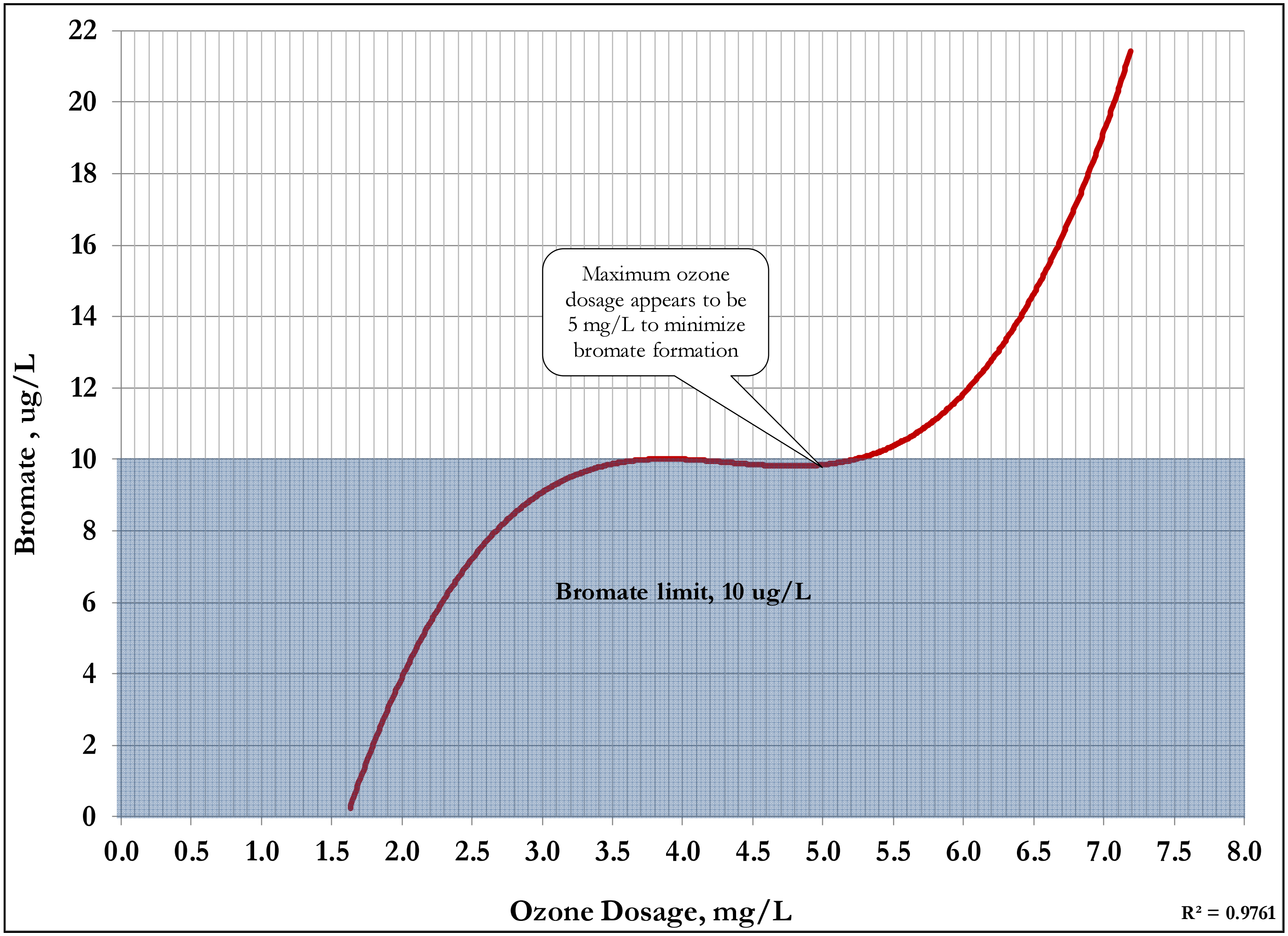
- Ozonation attacks C=O and C=C bonds breaking cyanotoxins into smaller components
  - Degrade generally to aldehydes, ketones, and carboxylic acids
  - 1 mg/L ozone can reduce toxins to very low levels
  - Contact time less than 10 minutes
- Published reaction rates
  - Anatoxin-a, 640,000 $M^{-1}s^{-1}$
  - Microcystin, 410,000 $M^{-1}s^{-1}$
  - Cylindrospermopsin, 340,000 $M^{-1}s^{-1}$
  - Not effective for saxitoxin



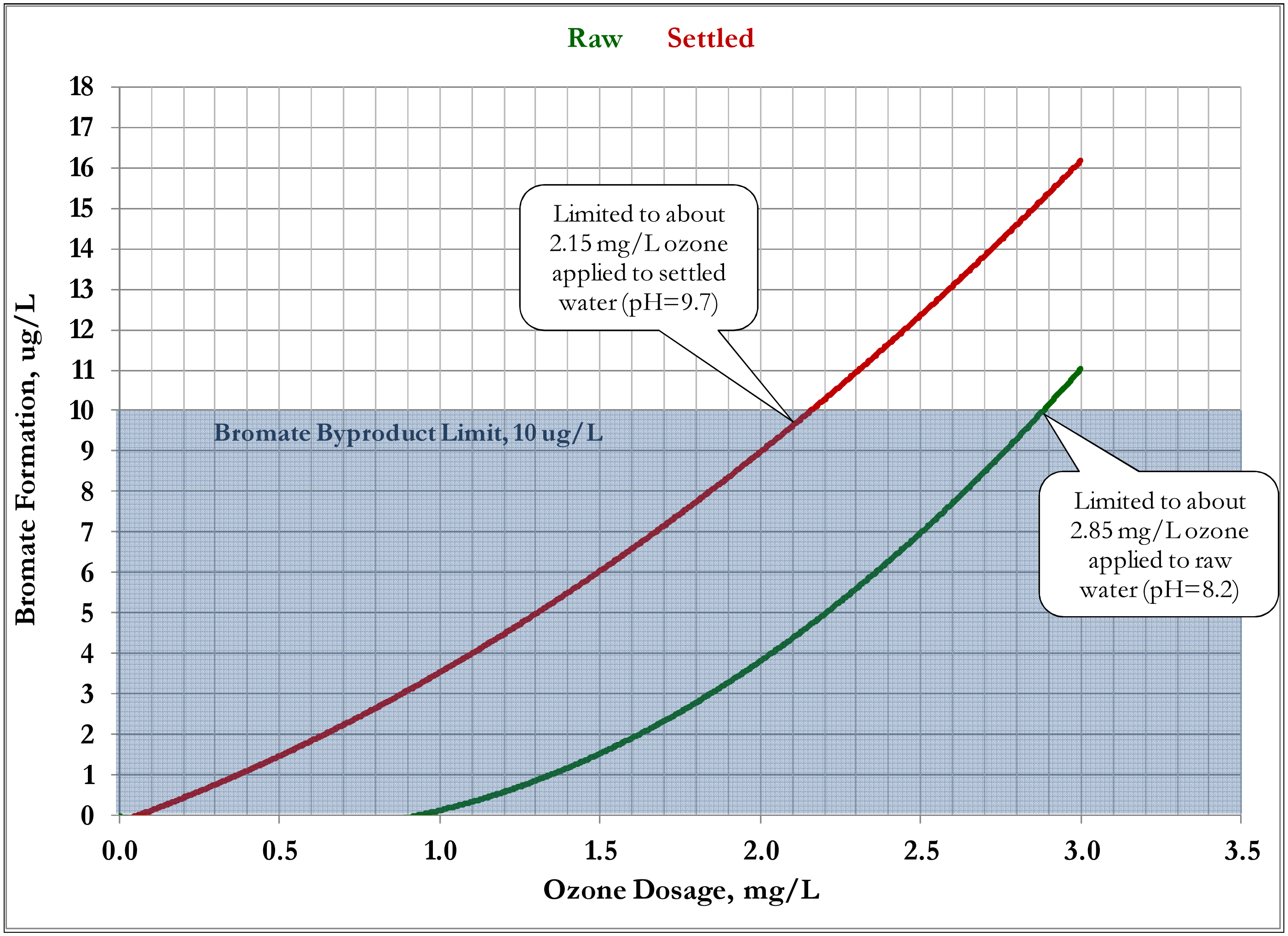
Treatment Using Ozone Oxidation



Treatment Using Ozone Oxidation

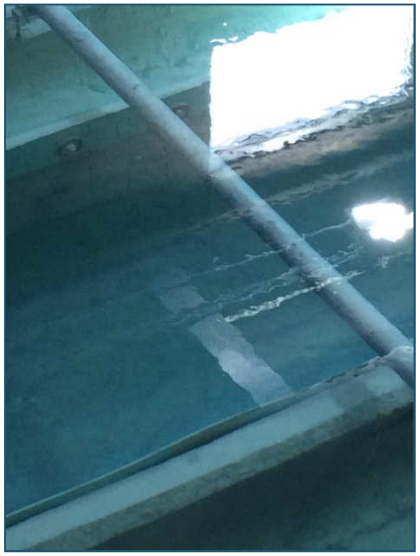


Treatment Using Ozone Oxidation



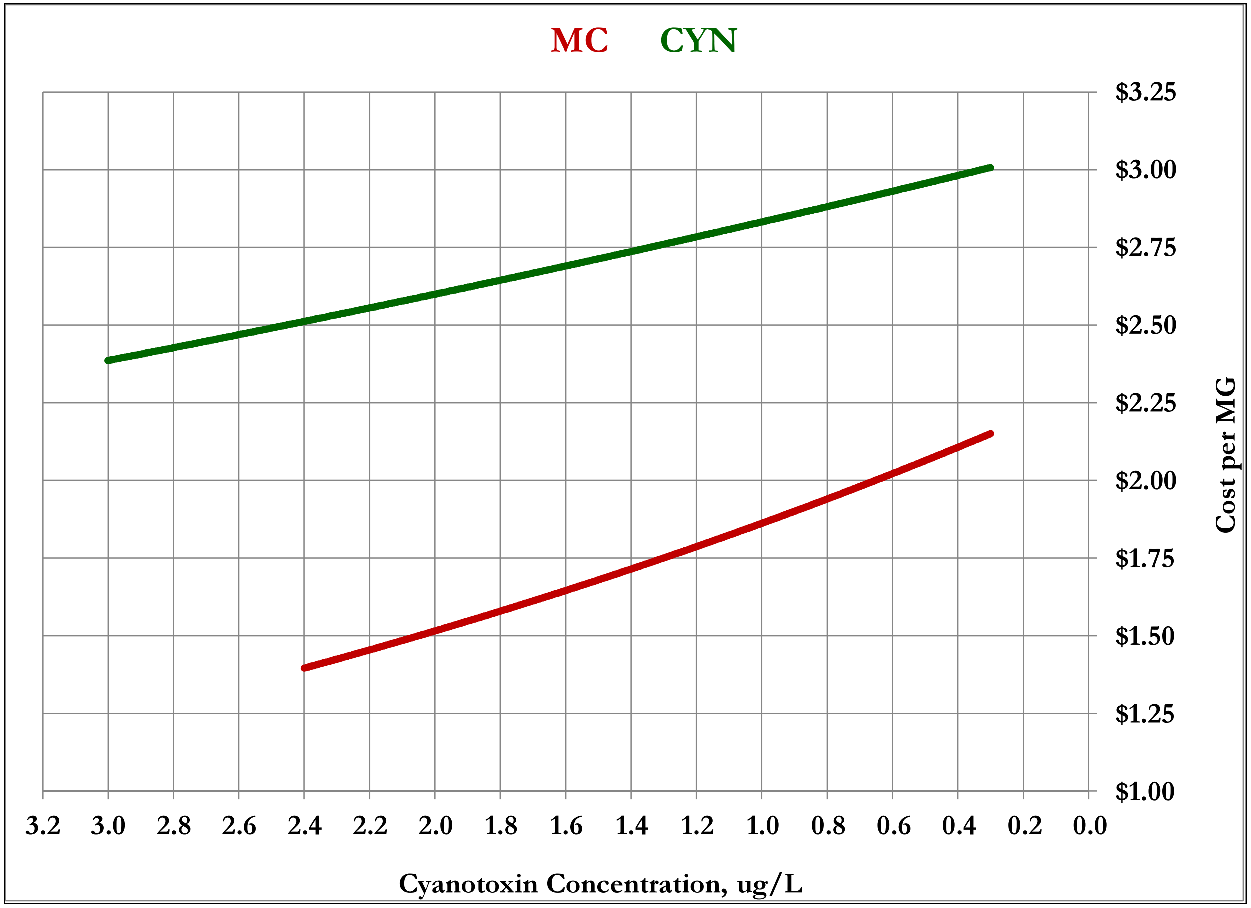
Treatment Using Ozone Oxidation

- Biologically active filtration (BAF)
  - Fits well into intermediate ozonation scheme
  - Ozone creates small molecular weight organics (food)
  - GAC substrate for sustainable bacteria growth
  - Bacteria consume organics (food)
    - Some cyanotoxins may be consumed by BAF (microcystin, cylindrospermopsin, anatoxin-a)
    - Reported microcystin reductions up to 90%, long run times required



Treatment Using Ozone Oxidation

Treatment costs could range from $1.70 per MG to $3.00 per MG depending on target level of toxins

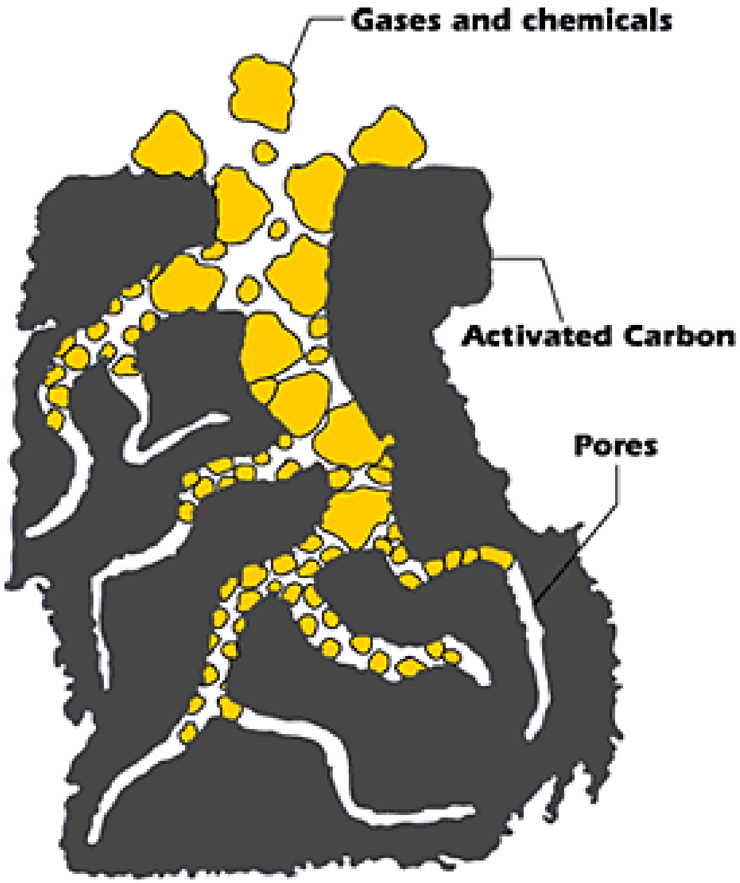


Treatment Using PAC Adsorption

- Effective for removal of cyanotoxins
- Contact times up to 90 minutes might be needed
- Dosing based on isotherms for carbon products
  - 20 mg/L or greater may be needed
  - Wood-based
  - Bituminous-based
  - Coconut-based

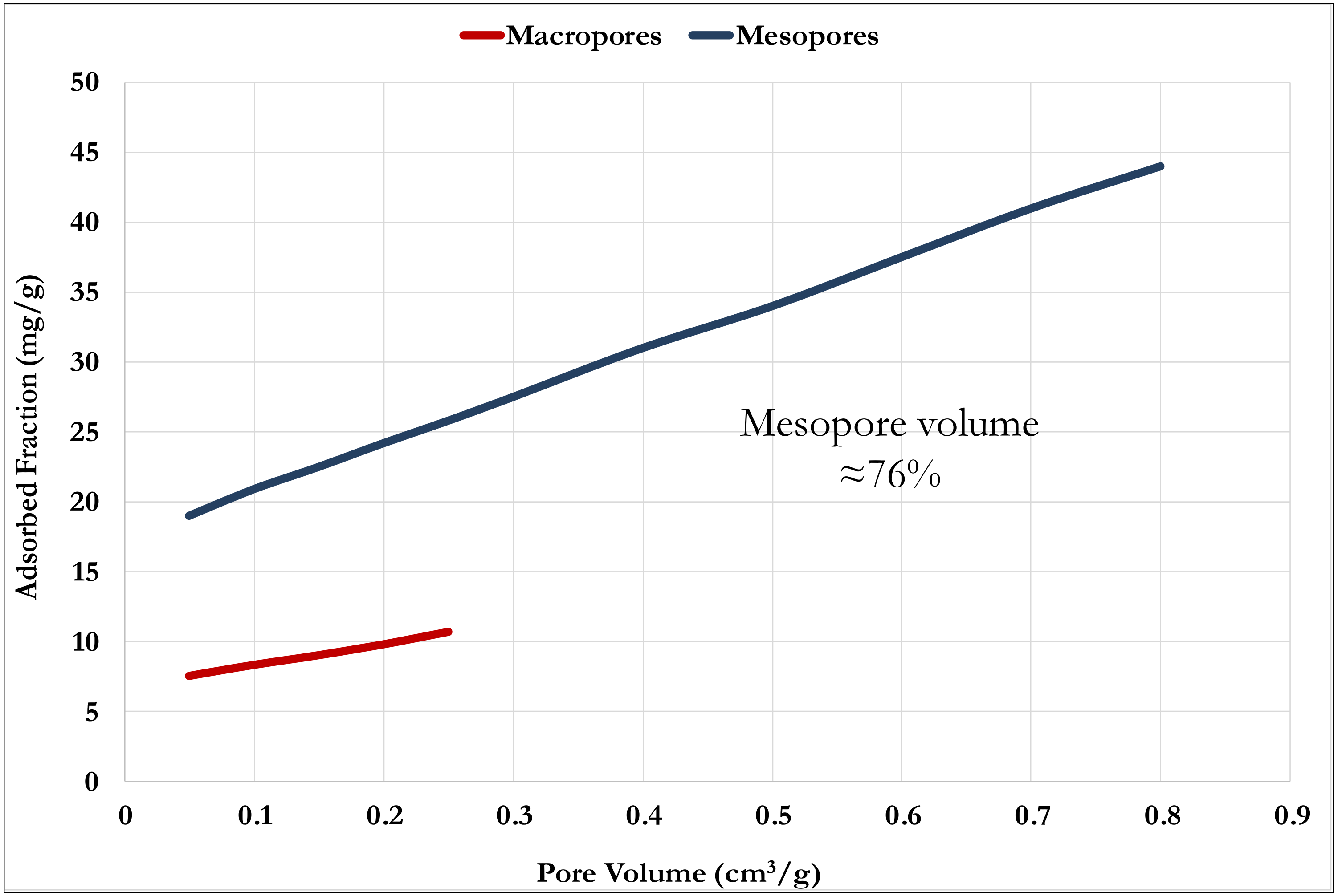
Treatment Using PAC Adsorption

- Carbon consists of pore structures with activated sites
  - Micropores - < 2 nm
  - Mesopores - >2 nm to <50 nm
  - Macropores - >50 nm
  - Related to molecular sizes that will penetrate the pore structure for adsorption at activated sites

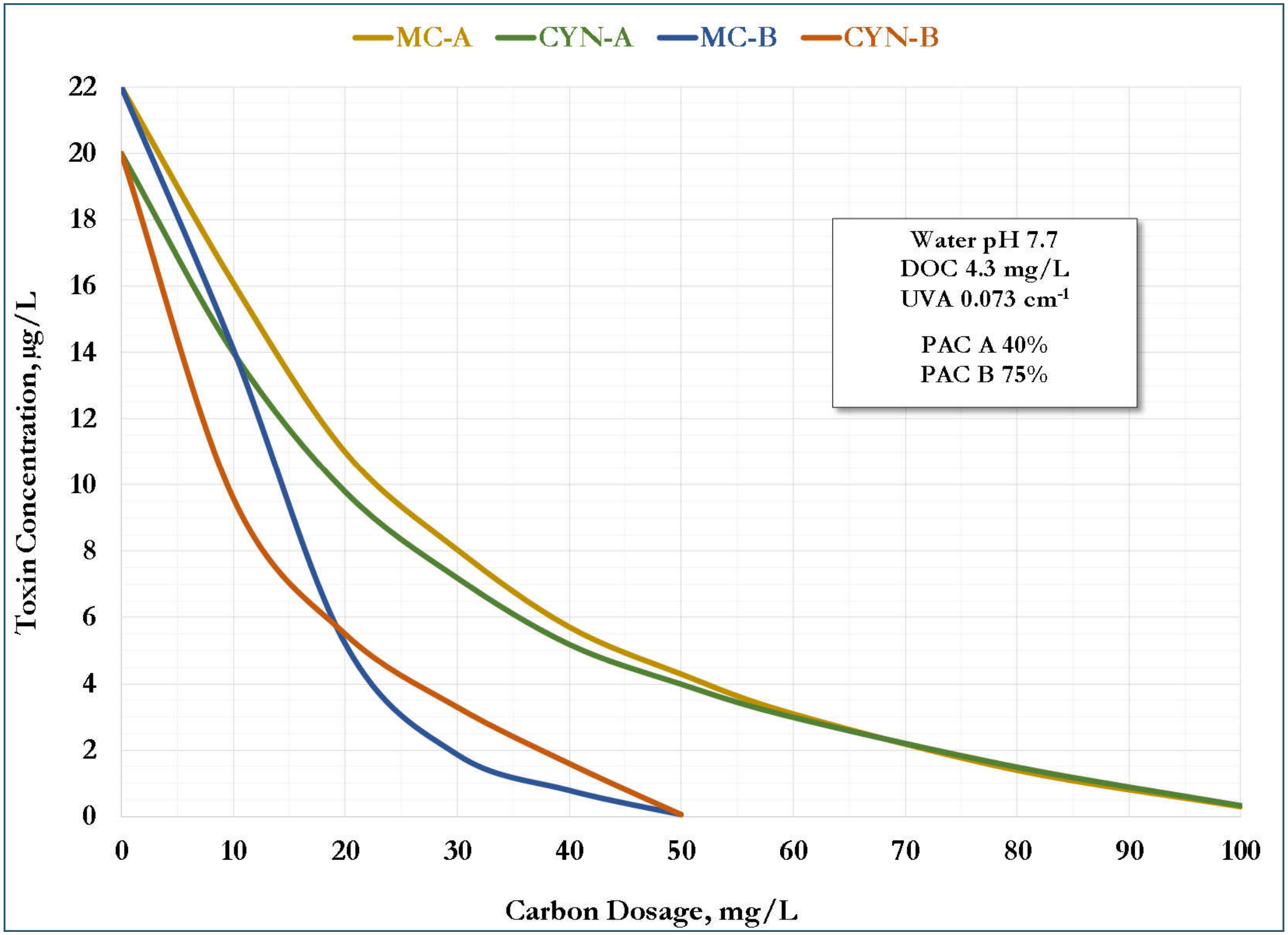


Generic carbon structure

Treatment Using PAC Adsorption



Treatment Using PAC Adsorption



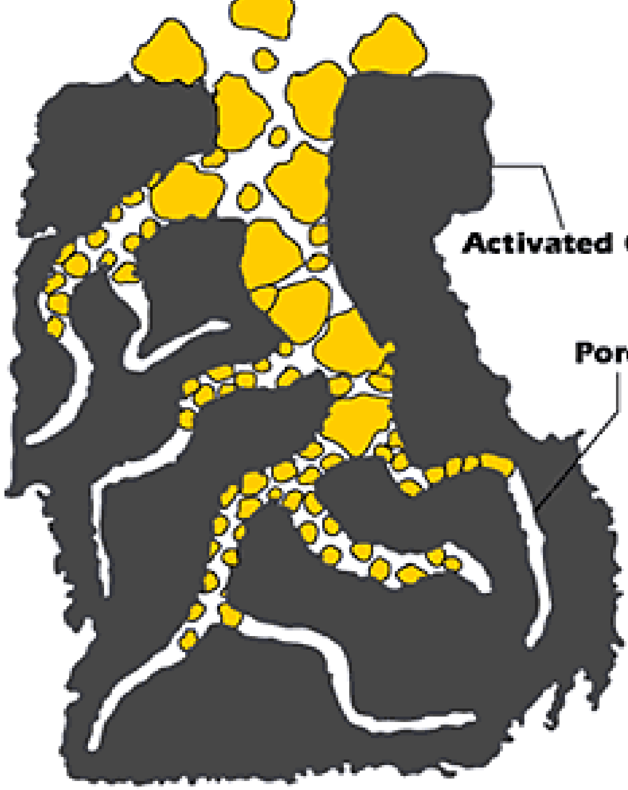
Treatment Using PAC Adsorption

- Adsorption isotherm data from literature defined for some activated carbons
  - K and 1/n values published for general carbon forms
  - Predict carbon dosing based on toxin levels removed and carbon adsorption data

$$q = K C_f^{1/n}$$

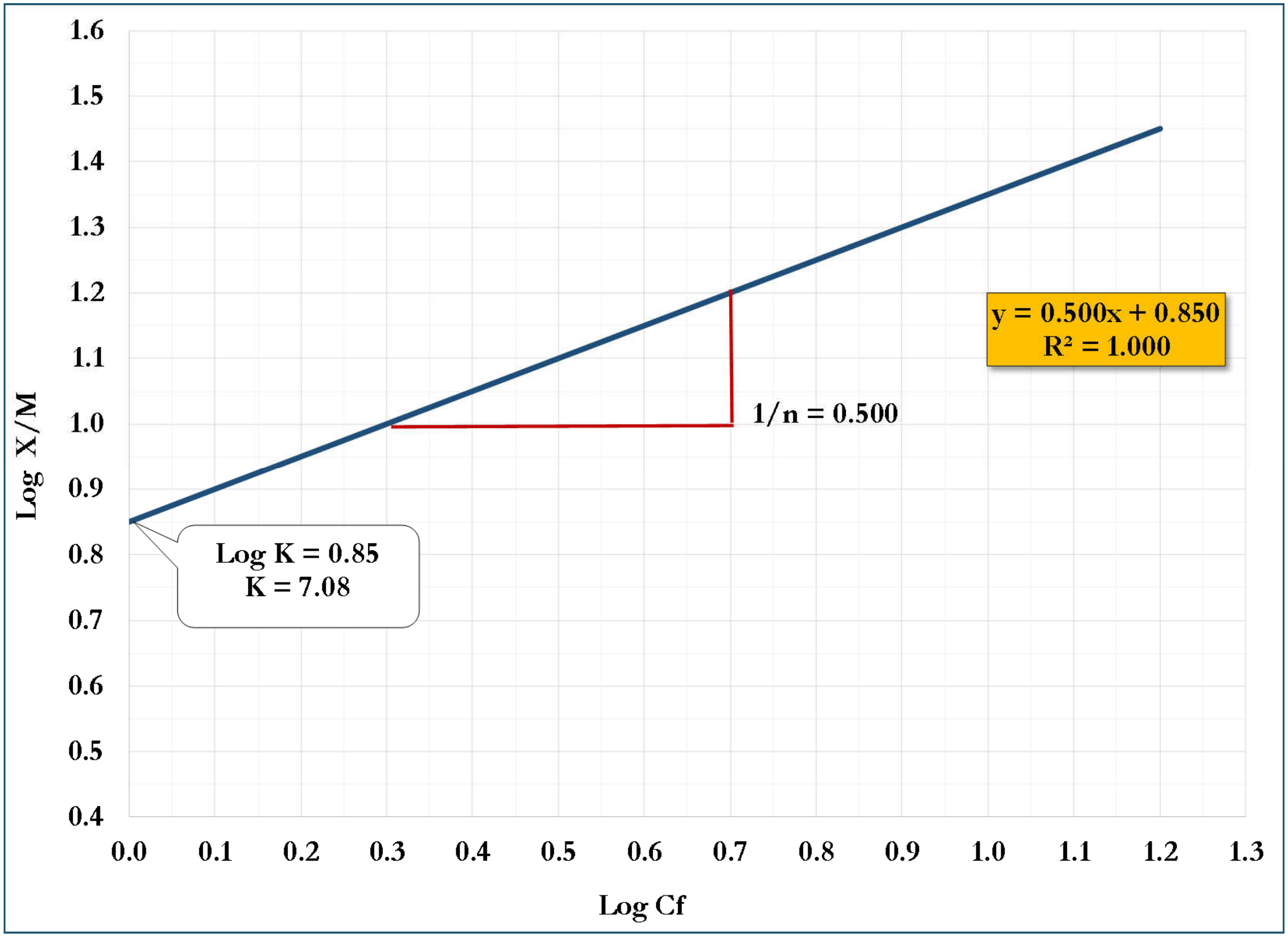
q = toxin adsorption, µg/g
K = adsorptive capacity, (µg/g)(L/µg)$^{1/n}$
C_f = final toxin level, µg/L
$1/n$ = adsorption intensity

$$C_i - C_f / q = dosage$$



Generic carbon structure

Treatment Using PAC Adsorption



Treatment Using PAC Adsorption

Isotherm data from research for select PAC products

"K" and *"1/n"* estimates shown

	Microcystin	
	K_f	1/n
Wood PAC	6,309	0.56
Bituminous PAC	3,630	0.9
Coconut PAC	1,259	1.0

Treatment Using PAC Adsorption

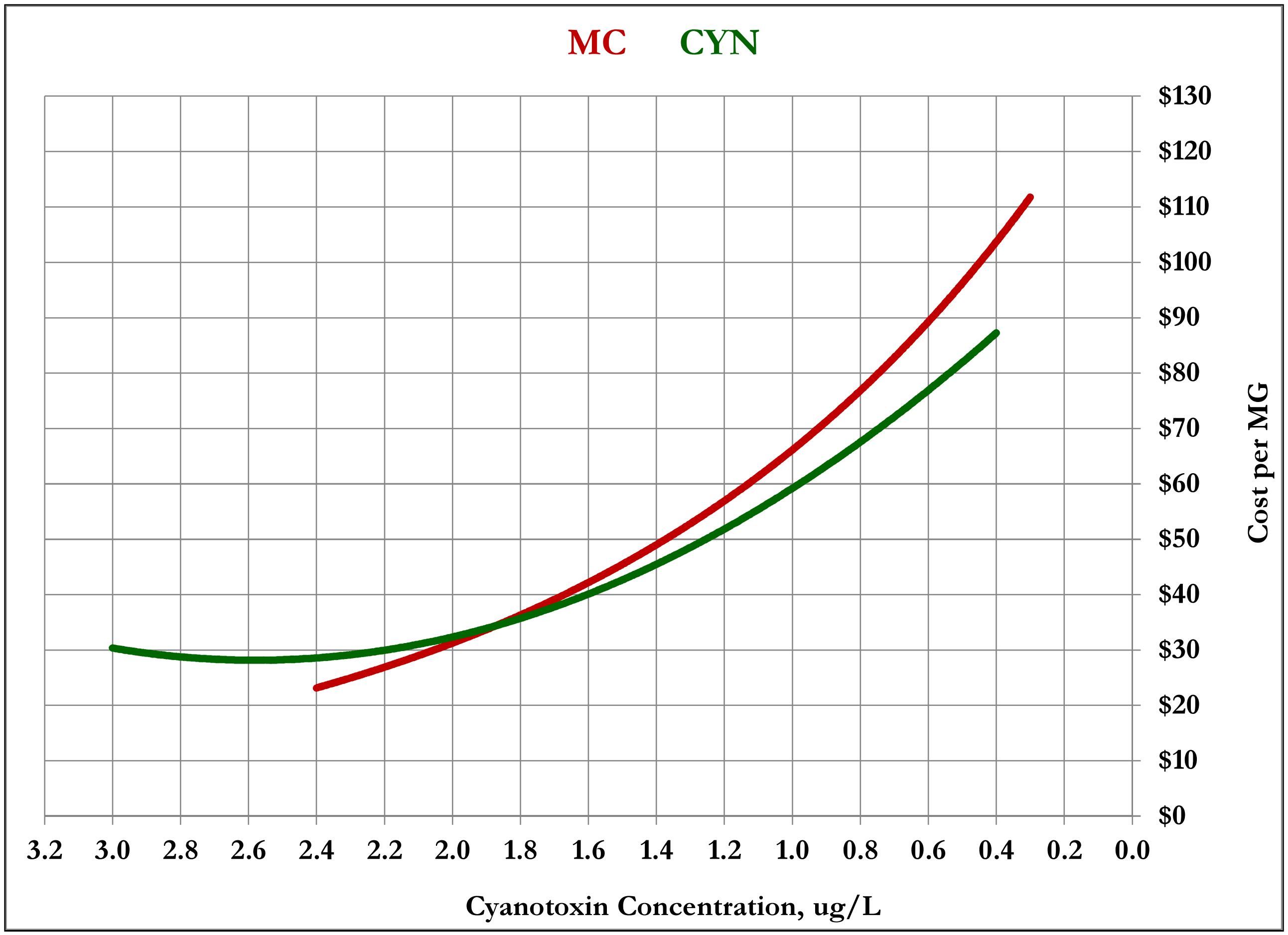
- Assuming no organic matter interferences
  - Same carbon - different microcystin target levels

Wood PAC	K_f - 6309
Initial microcystin, µg/L	50
Final microcystin, µg/L	**1.6**
1/n	0.56
q, µg/g	8,209
Dosage, mg/L	**5.9**

Wood PAC	K_f - 6309
Initial microcystin, µg/L	50
Final microcystin, µg/L	**1.0**
1/n	0.56
q, µg/g	6,309
Dosage, mg/L	**7.8**

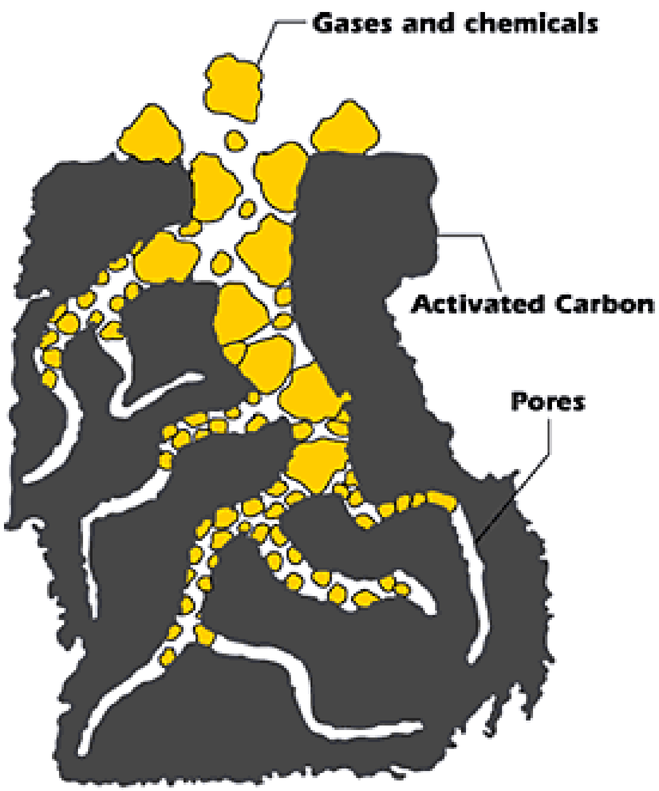
Wood PAC	K_f - 6309
Initial microcystin, µg/L	50
Final microcystin, µg/L	**0.3**
1/n	0.56
q, µg/g	3,215
Dosage, mg/L	**15.5**

Treatment Using PAC Adsorption



Treatment costs could range from $30 per MG to $118 per MG depending on target level of toxins

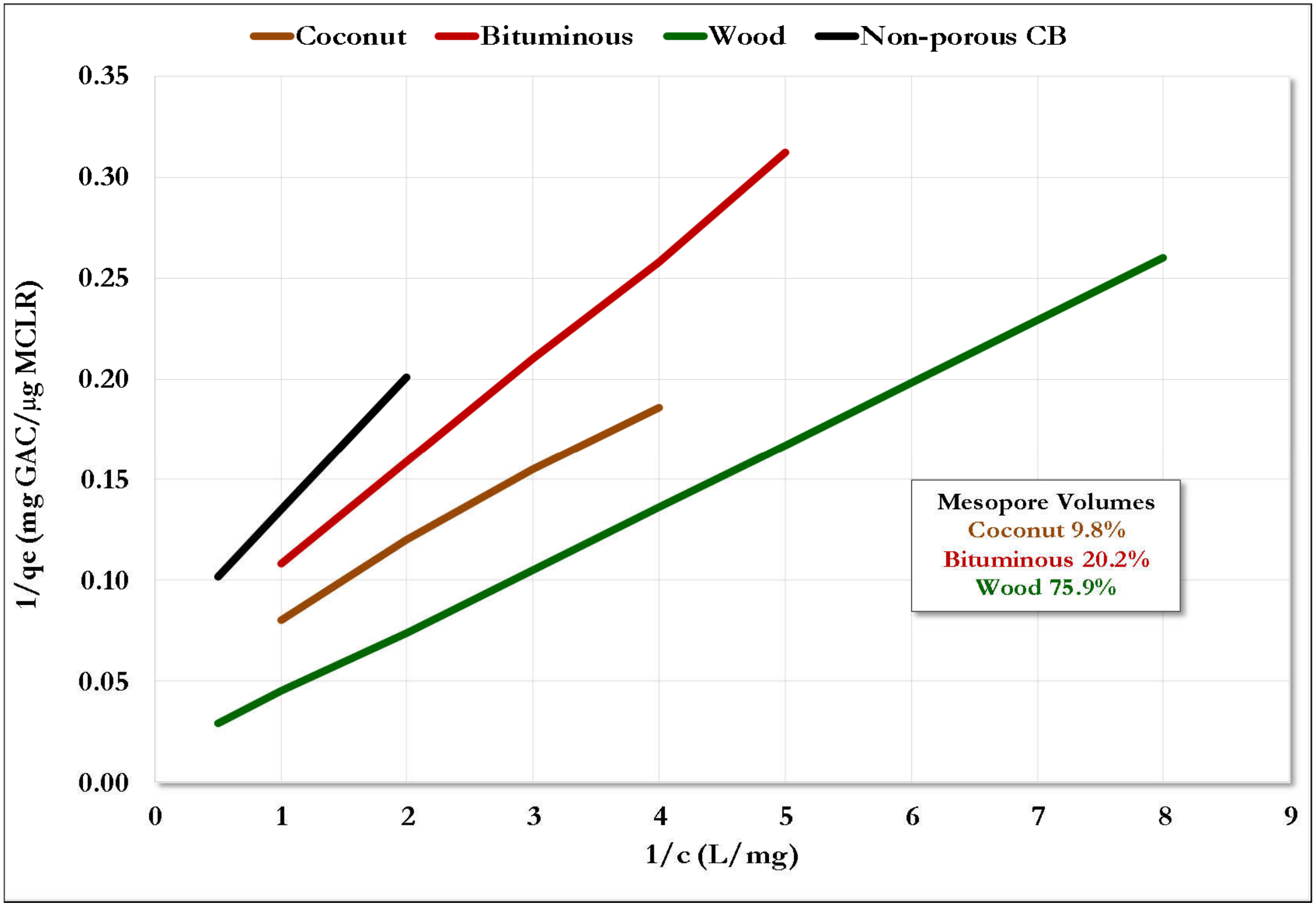
Treatment Using GAC Adsorption



Generic carbon structure

- Effective for removal of cyanotoxins
- EBCT of 10 minutes most common
  - 20 minutes for TOC removals
- Dosing based on isotherms for carbon products
  - Wood-based
  - Bituminous-based
  - Coconut-based
- Pore size distribution important for cyanotoxins
  - Mesopores remove most of toxin materials
- Disinfectant interferences

Treatment Using GAC Adsorption



Treatment Using GAC Adsorption

- Adsorption isotherm data from literature defined for some activated carbons
  - K and 1/n values published for general carbon forms
  - Predict carbon dosing based on toxin levels removed and carbon adsorption data

$$q = K\,C_f^{1/n}$$

q = toxin adsorption, µg/g
K = adsorptive capacity, (µg/g)(L/µg)$^{1/n}$
C_f = final toxin level, µg/L
$1/n$ = adsorption intensity

$$C_i - C_f / q = dosage$$

Treatment Using GAC Adsorption

Isotherm data from research for select PAC products

"K" and *"1/n"* estimates shown

	Microcystins	
	K_f	1/n
Wood GAC	501.2	0.36
Bituminous GAC	512.9	0.36
Coconut GAC	331.1	0.44
Non-activated GC	2.1	1.3

Treatment Using GAC Adsorption

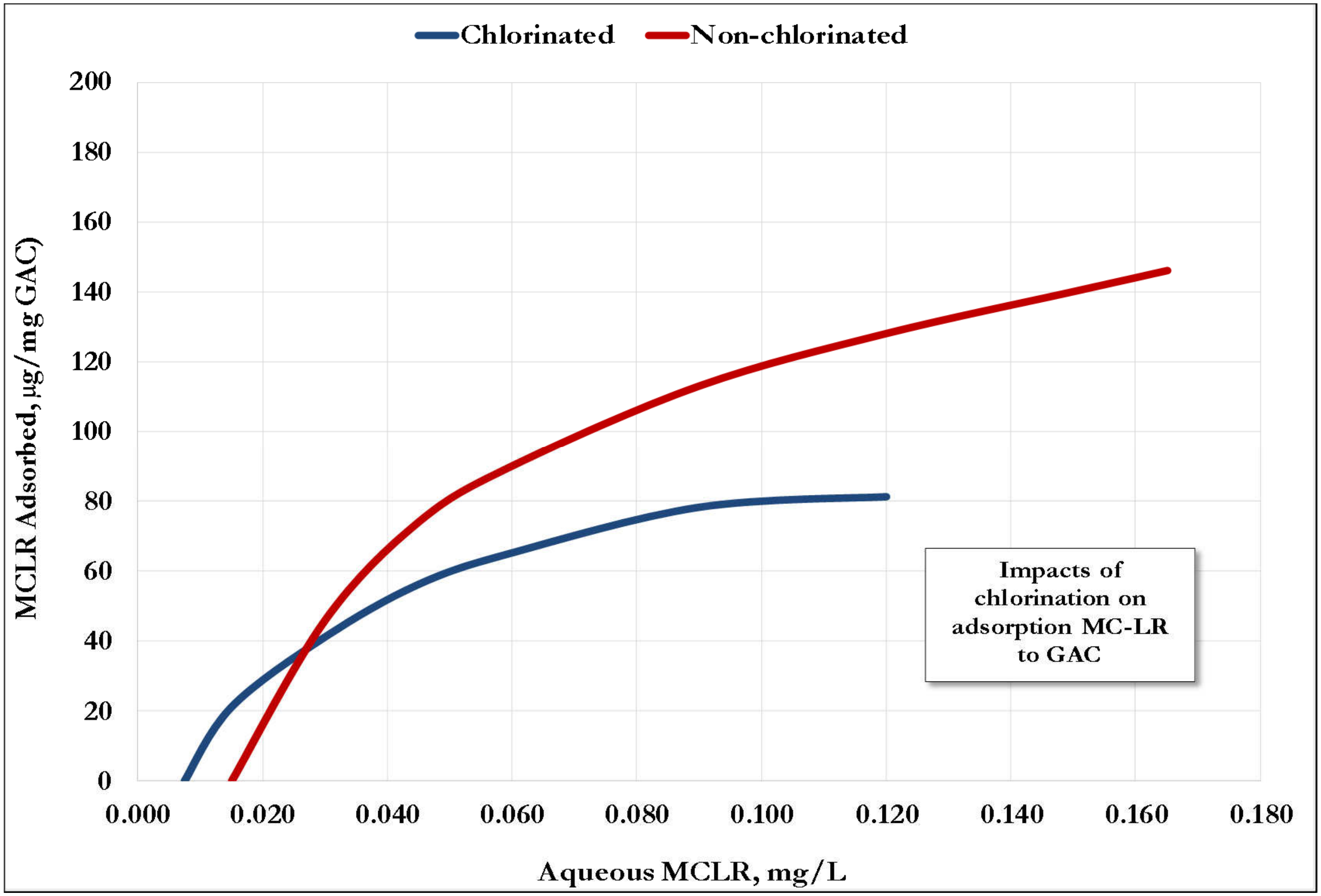
- Assuming no organic matter interferences
  - Same carbon - different microcystin target levels

Bituminous GAC	K_f - 513
Initial microcystin, µg/L	50
Final microcystin, µg/L	**1.6**
1/n	0.36
q, µg/g	608
Dosage, mg/L	**79.7**

Bituminous GAC	K_f - 513
Initial microcystin, µg/L	50
Final microcystin, µg/L	**1.0**
1/n	0.36
q, µg/g	513
Dosage, mg/L	**95.5**

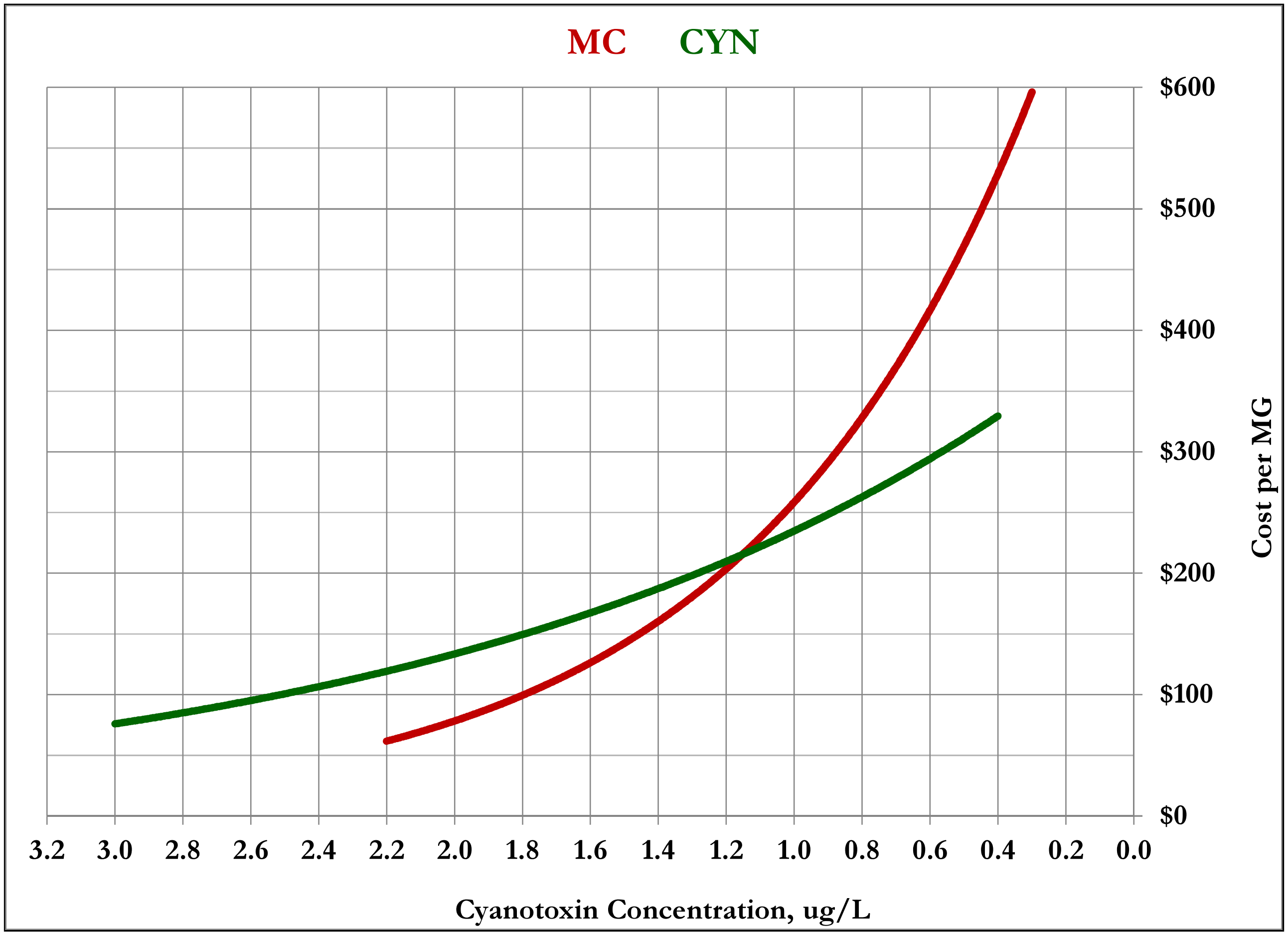
Bituminous GAC	K_f - 513
Initial microcystin, µg/L	50
Final microcystin, µg/L	**0.3**
1/n	0.36
q, µg/g	195
Dosage, mg/L	**149**

Treatment Using GAC Adsorption



Treatment Using GAC Adsorption

Treatment costs could range from $77 per MG to $648 per MG depending on target level of toxins



Cyanotoxin Mitigation Strategies

- Assessments provide current facility capabilities
  - Fill gaps in monitoring or treatment with new technologies or larger dosing capabilities
  - Be mindful of sequencing
    - Avoid interactions between chemicals (-MnO_2 and PAC, PAC and Cl_2)
    - Permanganates form MnO_2 that must be coagulated
    - Intermediate ozonation likely best ozonation method
    - Chlorination of filtered water most likely method to avoid DBP formations
  - Capital improvements need budgeting/scheduling
    - New equipment or technologies may require OEPA demonstration and/or approval
    - Financing of design/construction/start-up necessary

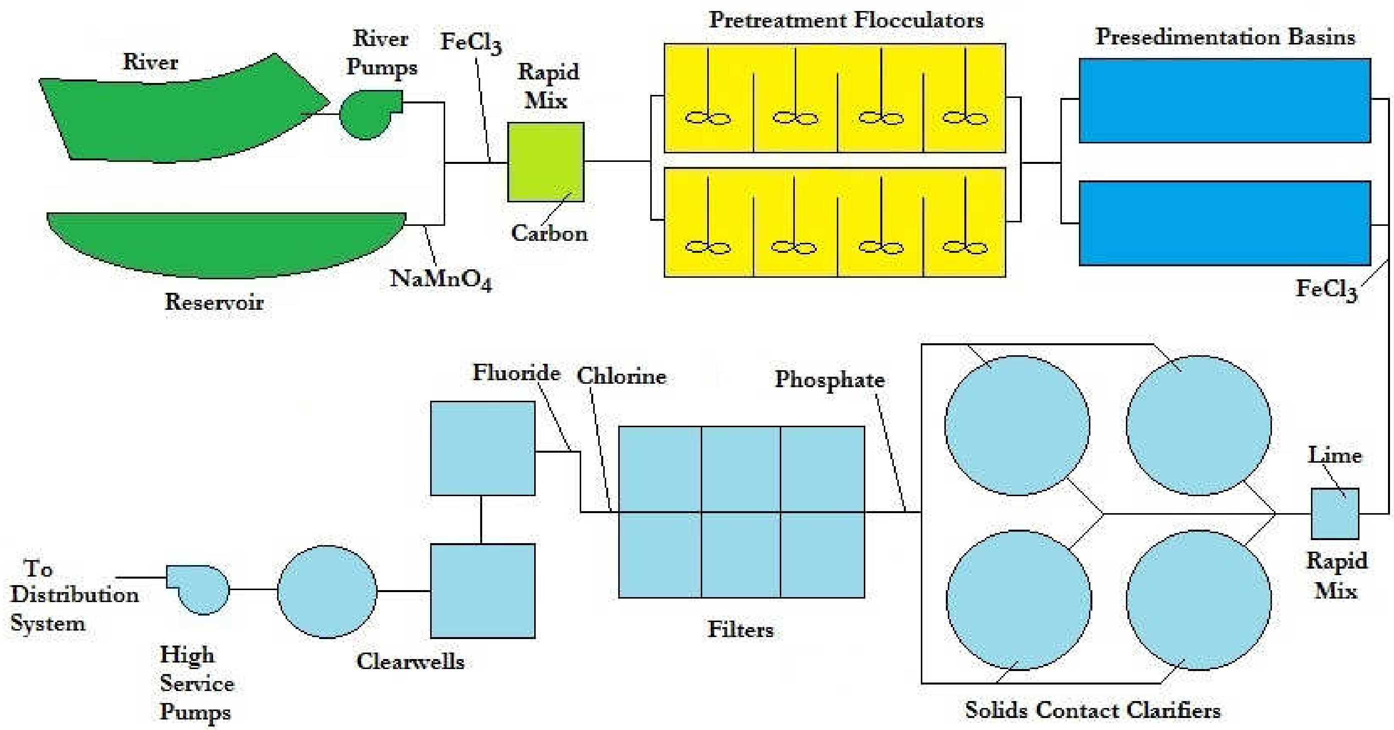
Cyanotoxin Mitigation Strategies

- Rely on multiple barriers to cyanotoxins
  - Process removals are not 100%, synergy needed to reach very low toxin levels
  - Multi-barrier approach should be paramount
- Optimization of existing processes
  - Removing intact cells encouraged by OEPA
  - Increase coagulant dose
  - Optimize PAC dosing
  - More frequent basin cleaning
  - More frequent filter backwash
  - Avoid recycle streams
  - Lower pH in clearwell for CT
  - Increased residuals for CT
  - Reduce plant production rates

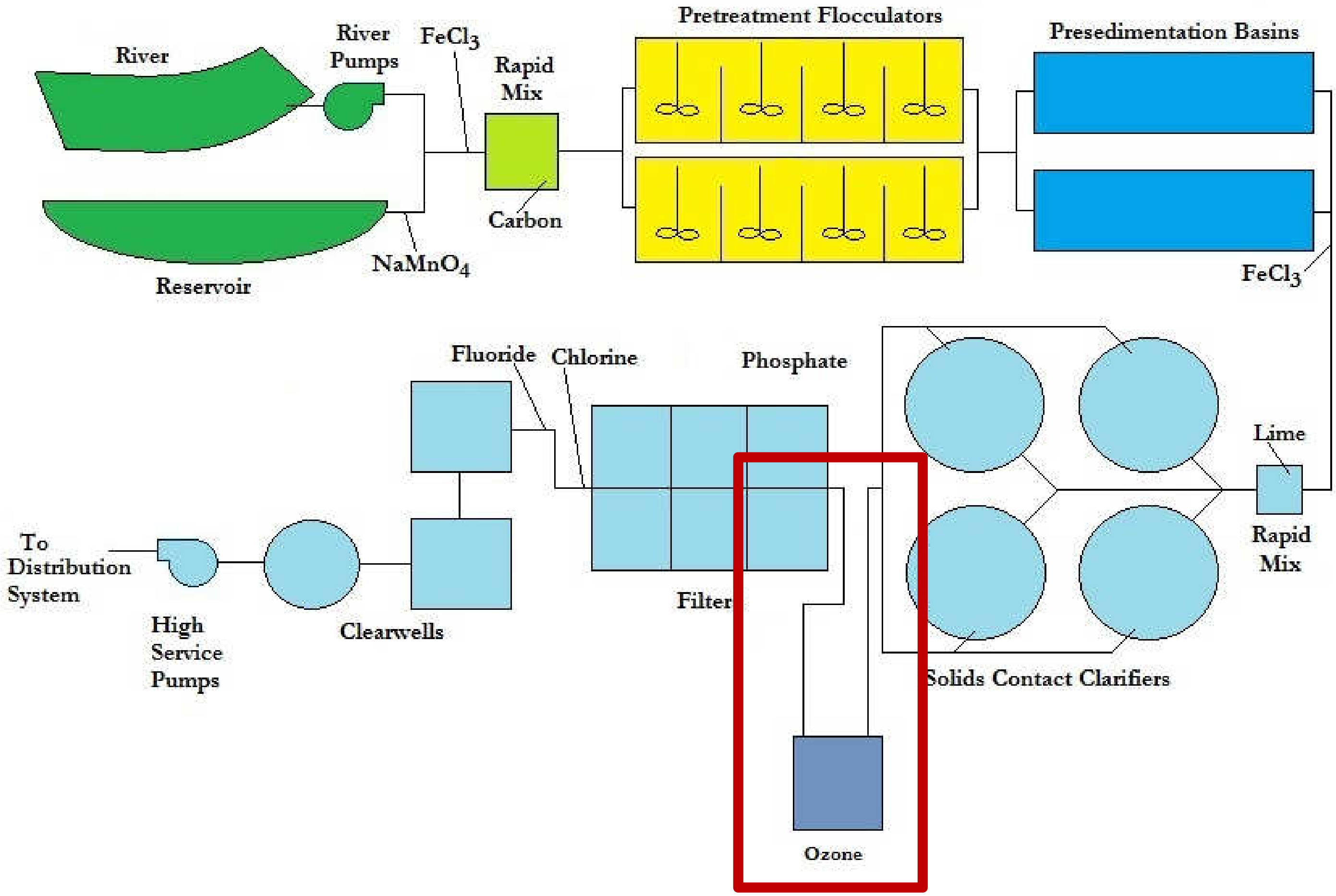
Cyanotoxin Mitigation Strategies

- Treatment Optimization Protocol required under OAC 3745-90-05
  - If microcystin detected in raw or finished water
  - Avoid lysing cells, optimizations to remove intact cells
- Cyanotoxin General Plan required under OAC 3745-90-05
  - If microcystin detected in finished water or system
  - If microcystin found >1.6 μg/L in raw water
  - Outline short-term and long-term mitigation plans to prevent microcystin exceedances

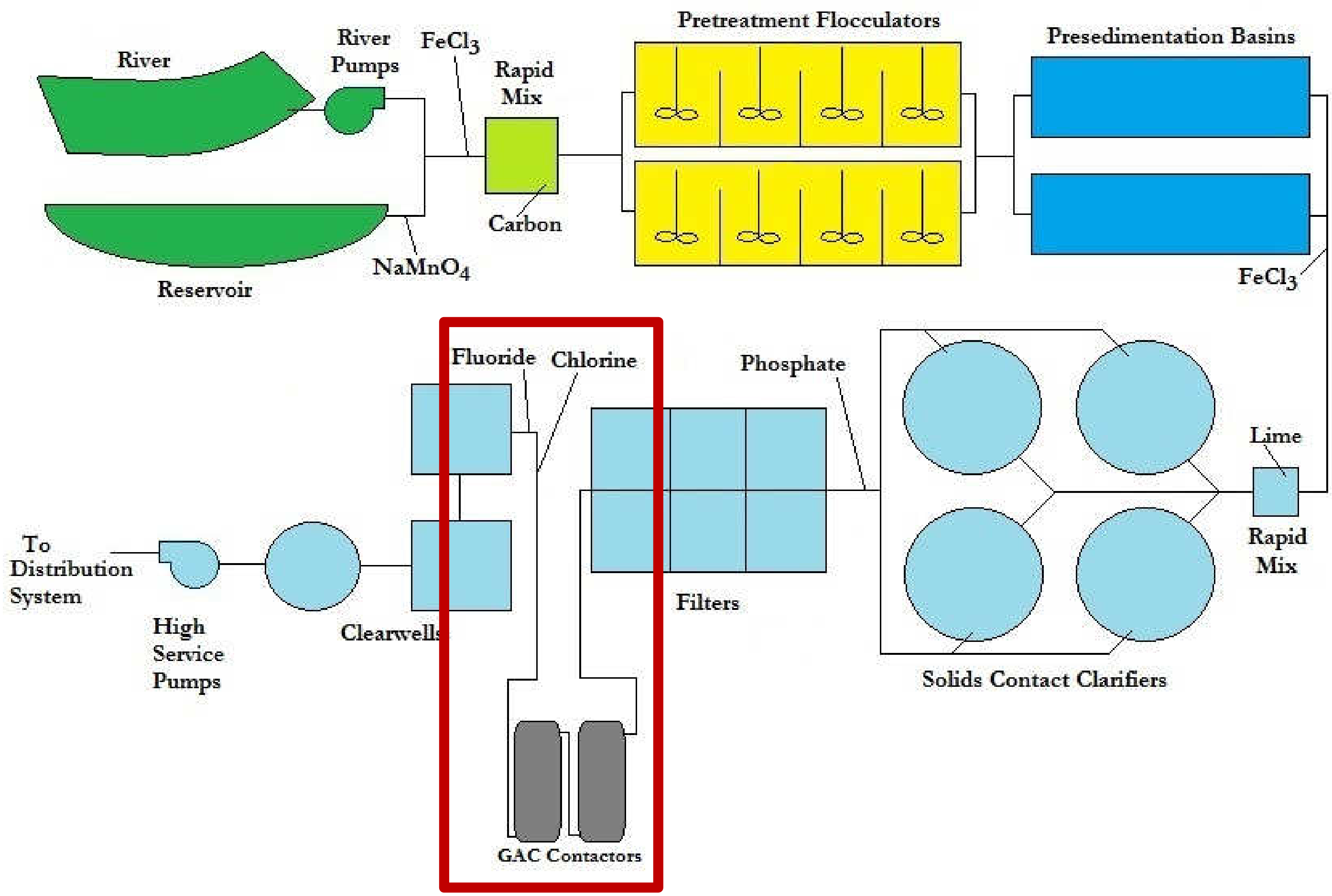
Capital Improvement Potential



Capital Improvement Potential



Capital Improvement Potential



Questions

Marvin Gnagy
pmgconsulting@bex.net
(419) 450-2931