Cyanobacteria Harvesting and Treatment Simulations for Removal of Microcystin from Natural Waters

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OTCO Water Laboratory Webinar

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Agenda

- Harvesting methods
- Concentrating cyanotoxins
- Treatment simulations with permanganates
- Treatment simulations with powdered activated carbon
- Desktop simulations with GAC
- Treatment simulations with chlorine
- Overall HAB planning and treatment activities
- Questions

Harvesting Cyanobacteria

- Concentrated cyanotoxins can be prepared from natural surface water containing cyanobacteria
  - Apparent surface scums and growths
  - Direct microscopic analyses for presence in water
  - Cyanotoxin testing for presence in water
  - Generally water temperatures above 18^{o}C

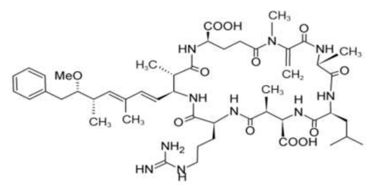
- Collect in phytoplankton net
  - Composite samples from source water into volume needed for treatment simulations
    - 1 liter or 2 liters
  - Preparation of cyanotoxin material
  - Analysis of toxin concentration

Harvesting Cyanobacteria

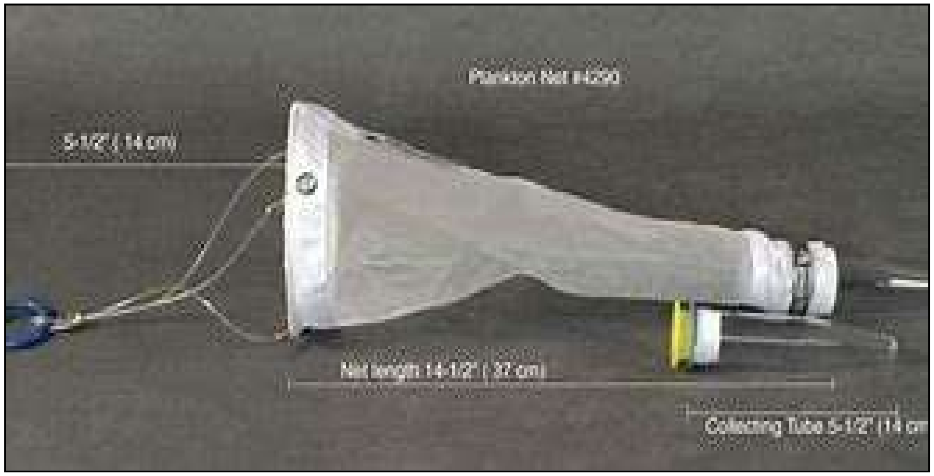
Relative abundance of cyanobacteria in some surface waters

Harvesting Cyanobacteria

- Drag net slowly by boat or off-shore with pole
- Collect in phytoplankton net
  - Composite samples from source water into volume needed for treatment simulations
    - About 2 liters generally used for testing
  - Prepare concentrated cyanotoxin solution
  - Analyze toxin concentration



Harvesting Cyanobacteria



- Phytoplankton nets
  - Inexpensive device
  - Small mesh size (≈80 microns)
  - Three-point drag line
  - Collection bottle
- Net collects cyanobacteria
  - Rinse net with water to push cells downward into sample bottle
  - Pour cyanobacteria sample into composite container

Concentrating Cyanotoxins

- Mix composite sample thoroughly
- Freeze sample container
  - Thaw in warm water bath until liquified
  - Repeat at least 3 cycles
- Freeze/thaw cycles lyse cells and releases toxin material
- Mix final liquid and analyze toxin
  - Microcystin readily tested using customary methods

Concentrating Cyanotoxins

- Final concentrated solution appears dark green
  - Concentrated Microcystin level may range from 900 µg/L to 3,600 µg/L
- Concentrated solution applicable for jar testing dilutions
  - $C_1V_1 = C_2 V_2$ then
  - $V_1 = C_2V_2/C_1$
    - Volume to add to jars

Concentrated Microcystin Solution

Treatment Simulations

- Jar testing most common assessment method
  - Simulates specific treatment based on spiked water samples
  - Oxidant evaluations
    - $KMnO_4$, $NaMnO_4$, Cl_2, ClO_2, O_3, H_2O_2, etc.
  - Adsorption evaluations
    - Powdered activated carbon
  - Coagulation and softening impacts
- GAC adsorption evaluations
  - CUR from WRF (1998)
- Case Studies
  - 6 surface water plants

Permanganate Treatment Simulations

- Concentrated toxin solution used for jar tests
  - $C_1V_1 = C_2V_2$
- Dosages
  - 1 mg/L - 5 mg/L
  - Residual half life in water is about 140 minutes
- Each of 5 jars spiked with ≈50 μg/L microcystin
  - 1 jar used as control (spike)
  - Remaining jars dosed with $KMnO_4$ or $NaMnO_4$ solution

Concentrated microcystin solution

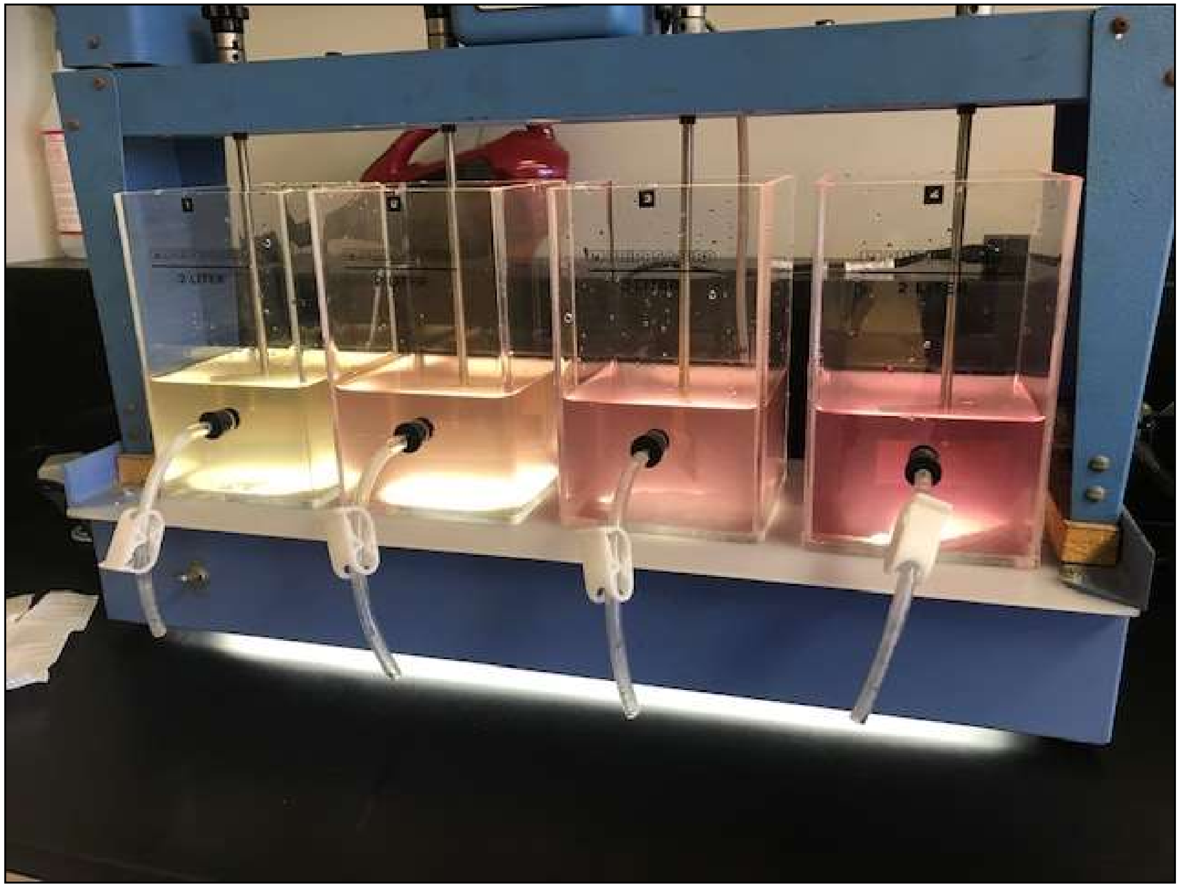
Permanganate Treatment Simulations

$KMnO_4$ Oxidation for Microcystin Reduction - Attica

Permanganate Treatment Simulations

$NaMnO_4$ Oxidation for Microcystin Reduction - Lima

Permanganate Treatment Simulations



$NaMnO_4$ Oxidation for Microcystin Reduction - Defiance

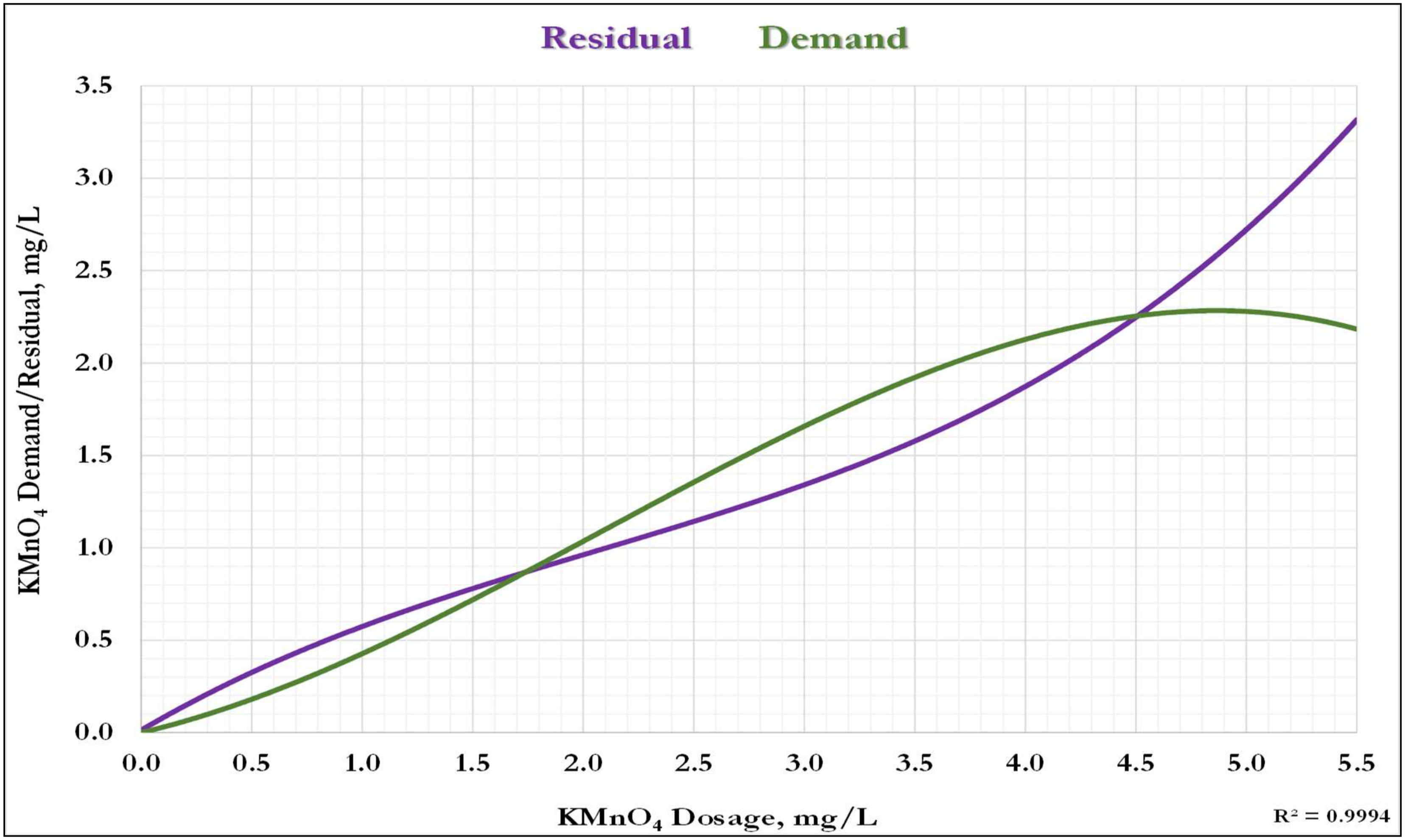
Permanganate Treatment Simulations

$KMnO_4$ Oxidation for Microcystin Reduction - Buffalo

Permanganate Treatment Simulations

- Permanganate residual can be tested after about 10 minutes of reaction
  - DPD method provides oxidant residual in mg/L
  - Multiple by 0.89 to convert to permanganate residual, mg/L
    - Standard Methods technique and discussion
- Once residual and dosage are known, oxidant demand can be calculated

Permanganate Treatment Simulations



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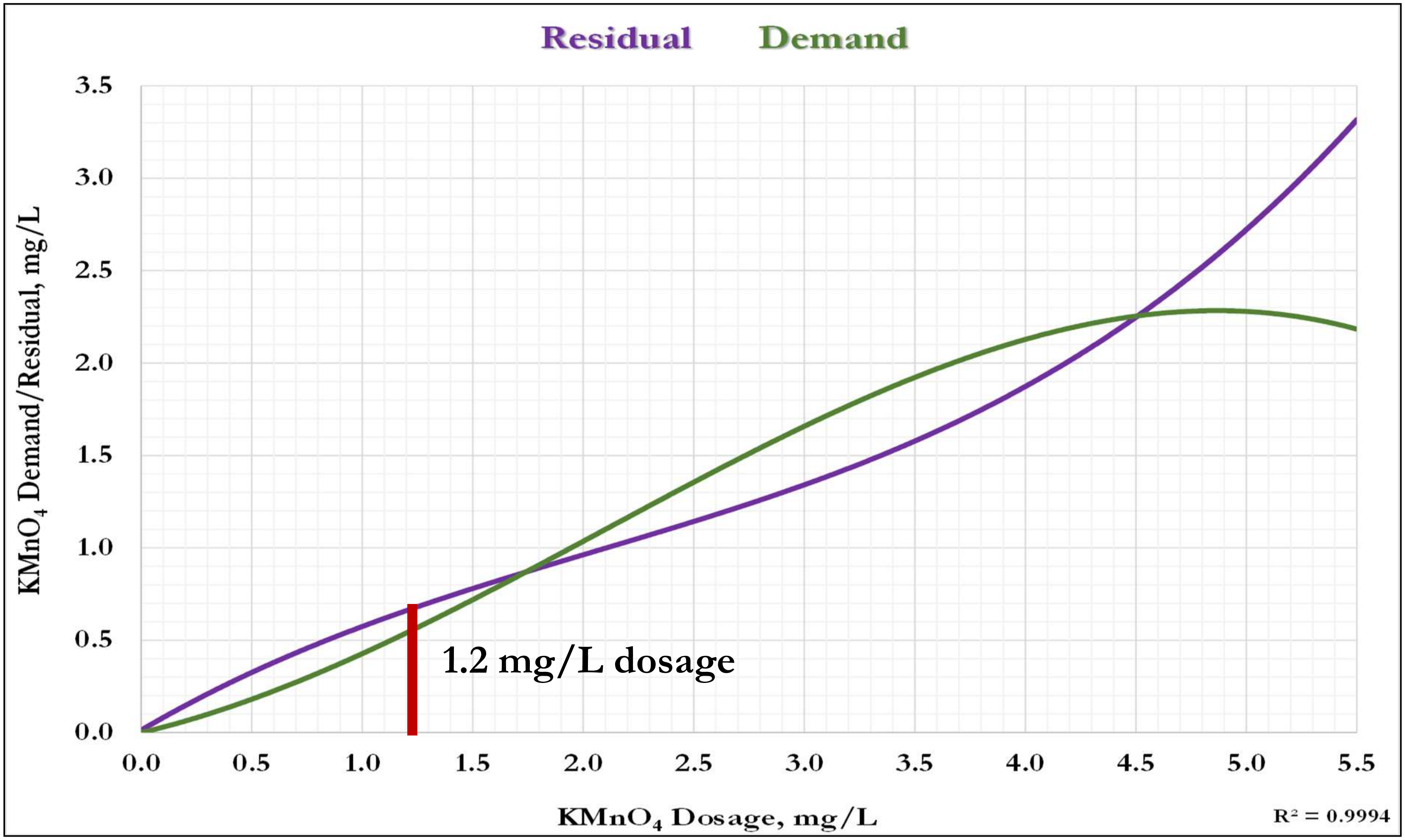
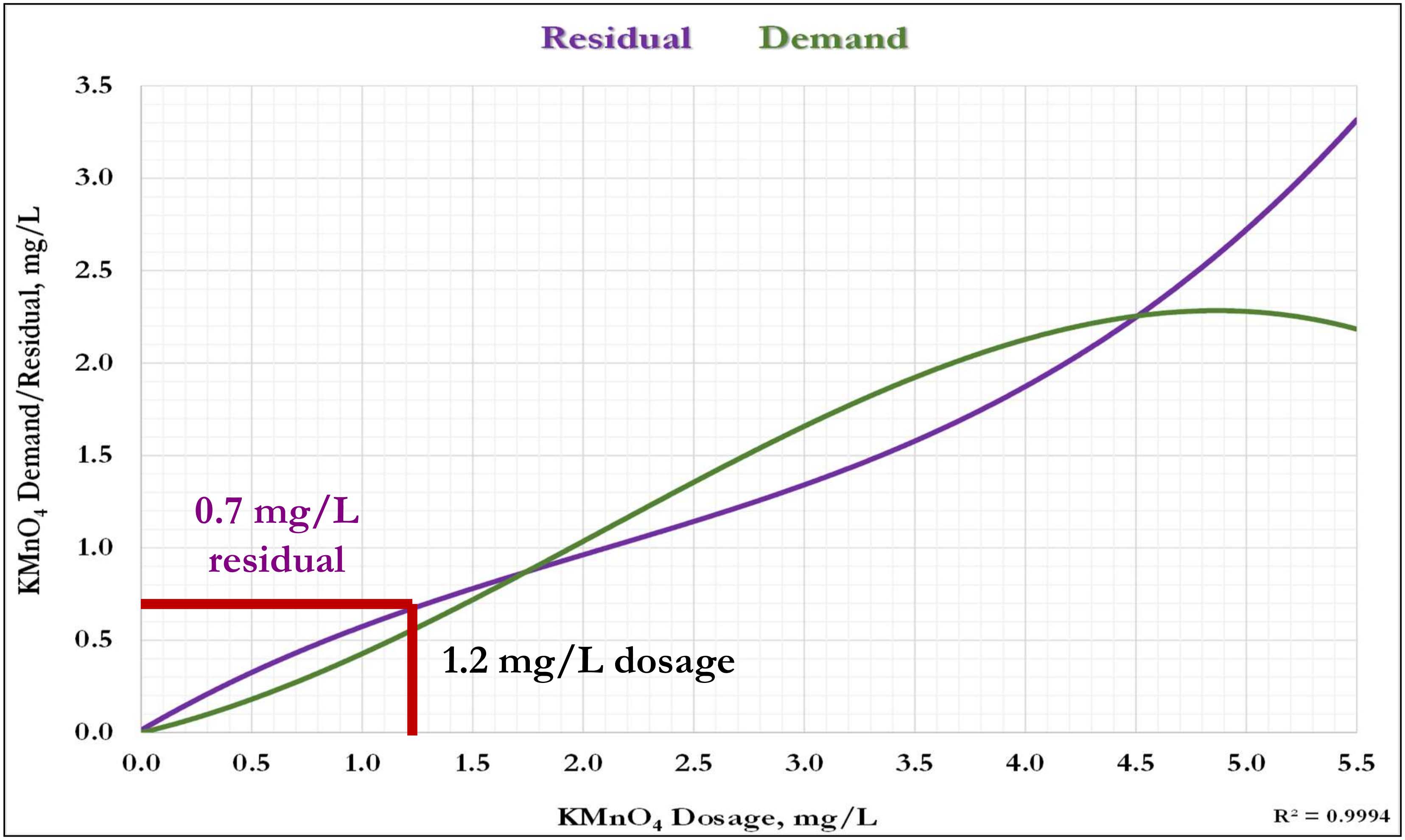
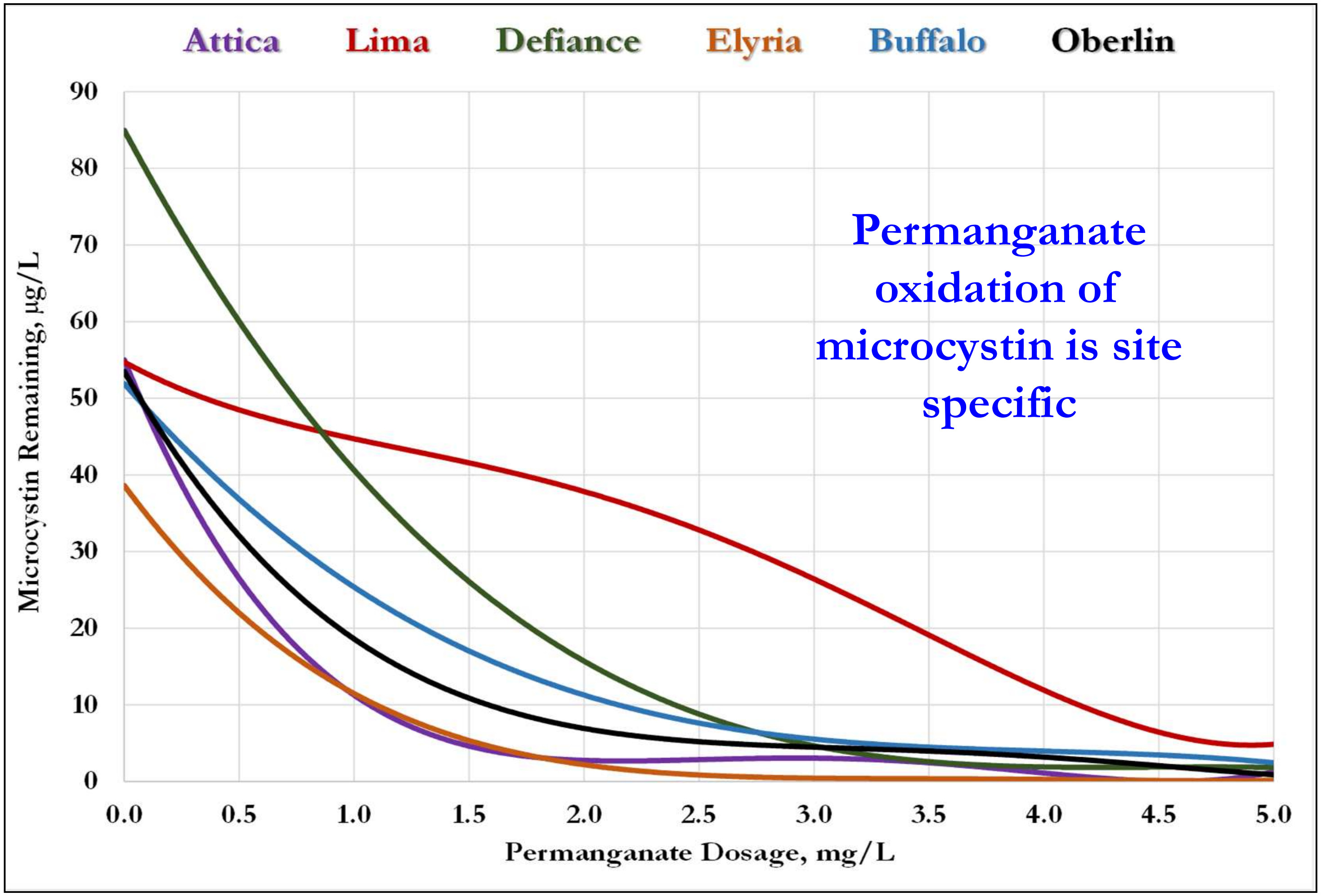


Permanganate Treatment Simulations

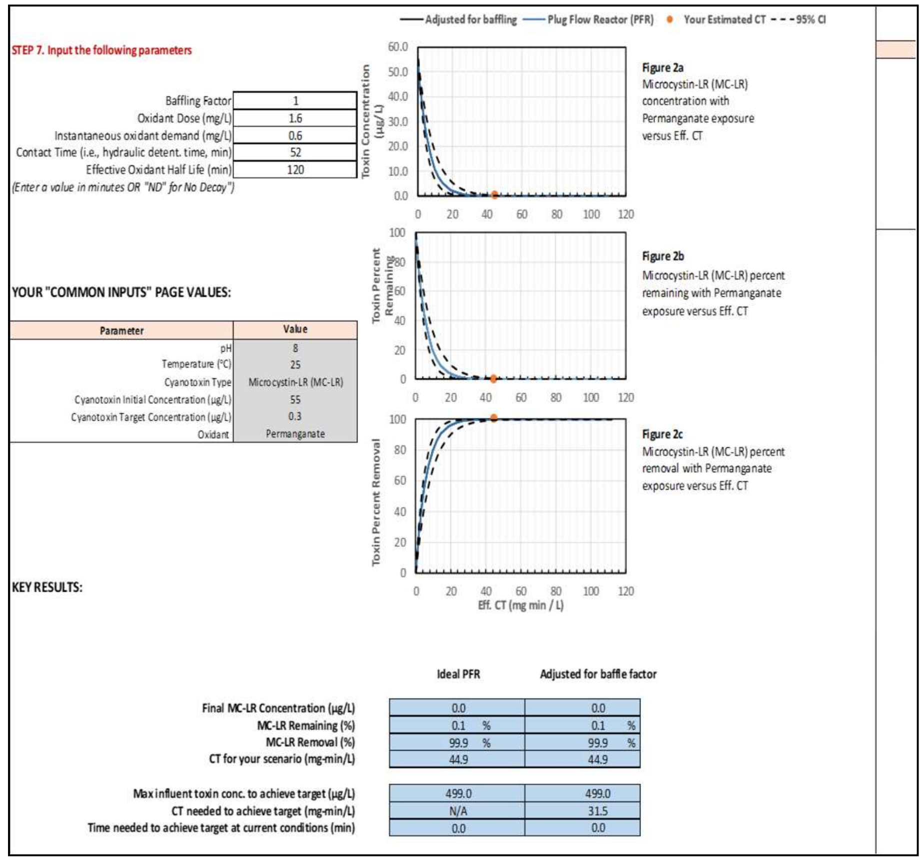


Permanganate Treatment Simulations



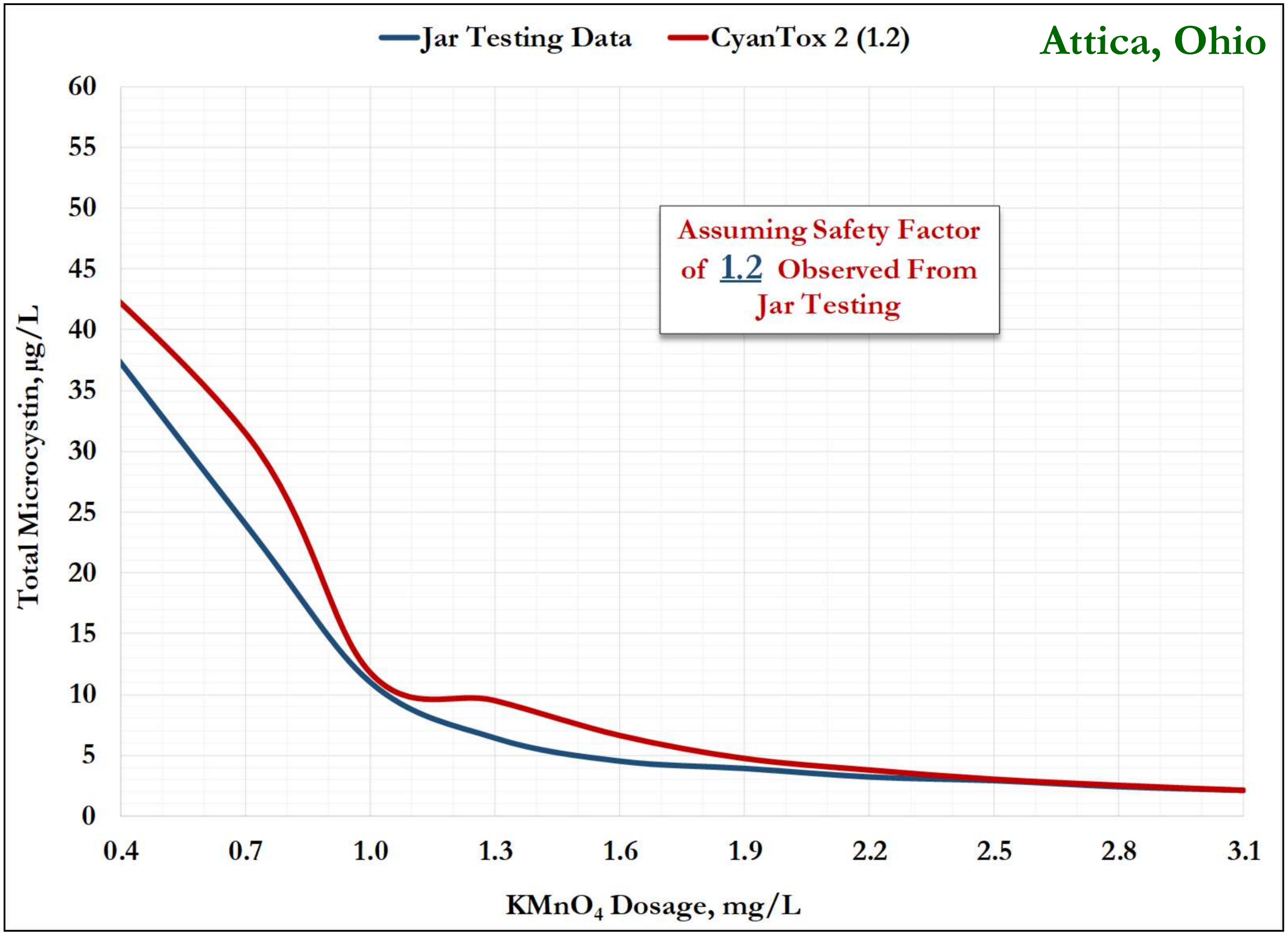
Permanganate Treatment Simulations

- Comparison of jar tests with AWWA CyanoTox2 Model for Cyanotoxins
  - 1st Assumed no safety factor
  - Input actual permanganate demand and dosage ranges
  - Compared model output with experimental data
  - 2cd Identified approximate Safety Factor (site specific)

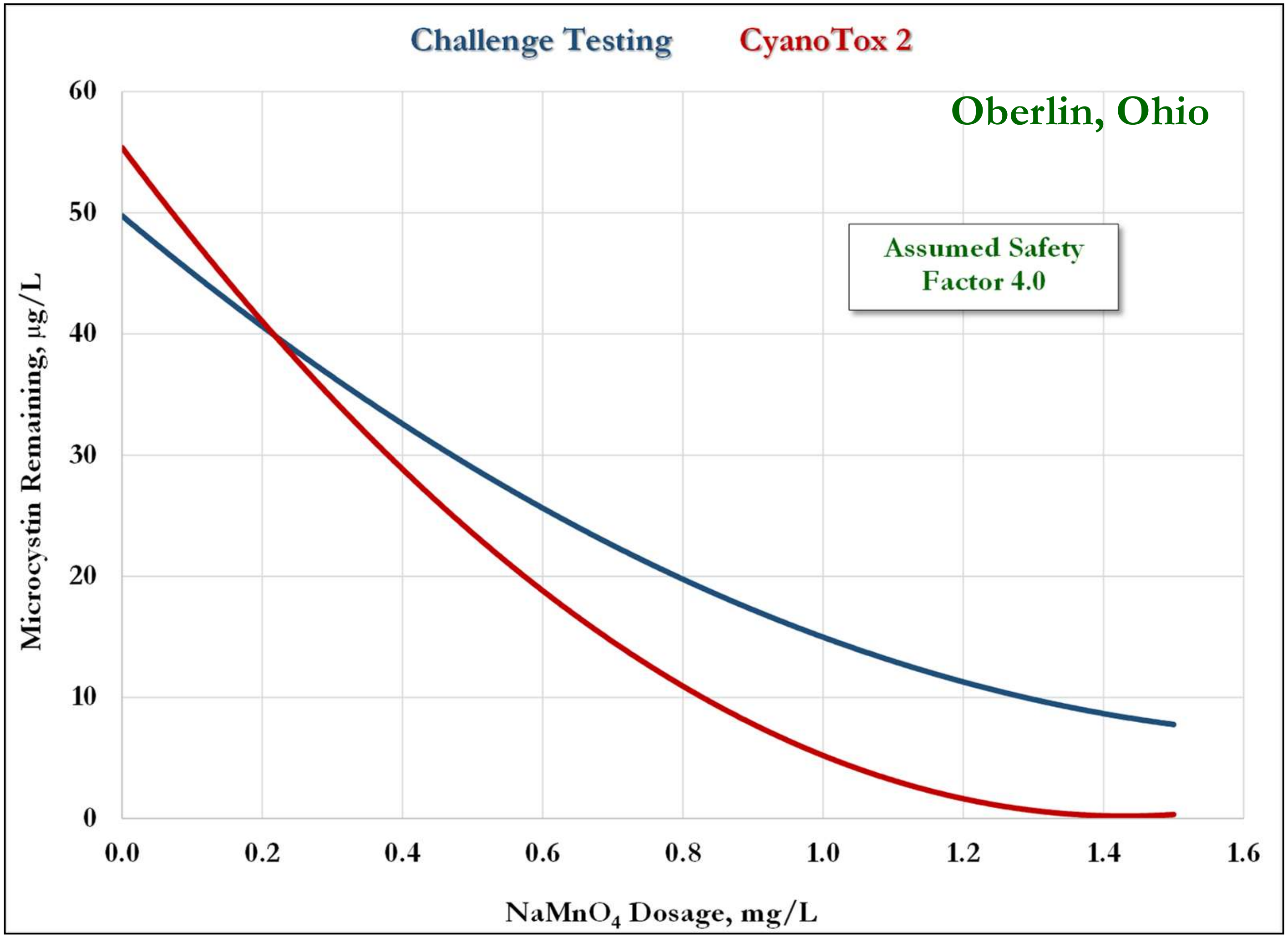


AWWA CyanoTox2 Model

Permanganate Treatment Simulations



Permanganate Treatment Simulations



Permanganate Treatment Simulations

- CyanoTox2 model appears to be useful for some $KMnO_4$ or some $NaMnO_4$ reactions for Microcystin removals
  - Does not correlate well for all water plants
  - Assume reasonable safety factor
    - Actual safety factor determined from correlations to bench-scale tests
- Model reaction kinetics based on $KMnO_4$ addition (Rodriguez, et al)
  - $NaMnO_4$ reaction kinetics likely differ from model equations
  - Assume no reasonable safety factor could be determined if computer modeling shows correlation factor greater than 2.5

Permanganate Treatment Simulations

- Permanganate oxidation effective for Microcystin removals
  - Dosage dependent
  - Reaction time dependent
  - $KMnO_4$ appears to be better than $NaMnO_4$
  - Typical residual range 0.15 mg/L to 0.5 mg/L
- Correlations to AWWA's CyanoTox 2 model possible for some treatment plants

Carbon Treatment Simulations

- Powdered activated carbons (PAC) evaluated
  - Lignite-based (Hydrodarco W)
    - **500** iodine number, high mesopore volume
  - Wood-bituminous blend (WaterCarb 800)
    - **800** iodine number, high mesopore volume
  - WPH bituminous
    - **800** iodine number, high mesopore volume
  - WPH 1000 bituminous
    - **1,000** iodine number, high mesopore volume
  - AquaSorb CB-1-W
    - **1,000** iodine number, high mesopore volume

Carbon Treatment Simulations

- Carbon solutions
  - Prepared from dry samples or obtained from slurry tank
    - Concentration must be known
    - Mix for at least 30 minutes to displace air from carbon pores
  - Generally dosed up to 60 mg/L
    - Simulate carbon contact time in full-scale treatment
    - Long contact times can be adjusted to full-scale if jar tests are shorter contact time

Carbon Treatment Simulations

- Carbon slurry used for testing
- Carbon dosing
  - $C_1V_1 = C_2 V_2$
- Each of 5 jars spiked with ≈50 μg/L microcystin
  - 1 jar used as control (spike)
  - Remaining jars dosed with carbon solution

Concentrated Microcystin Solution

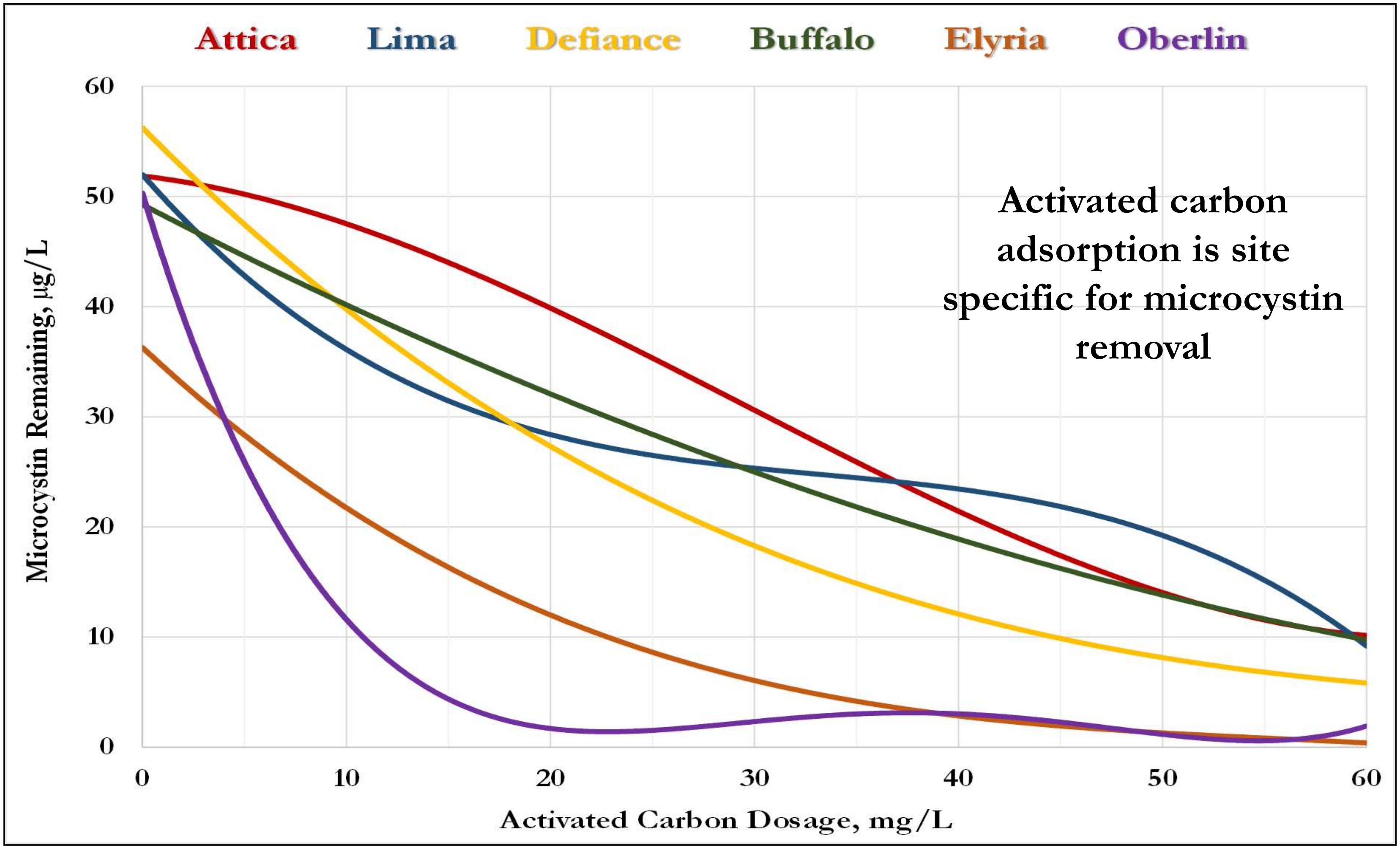
Carbon Treatment Simulations

Activated carbon evaluation for Microcystin reduction - Attica

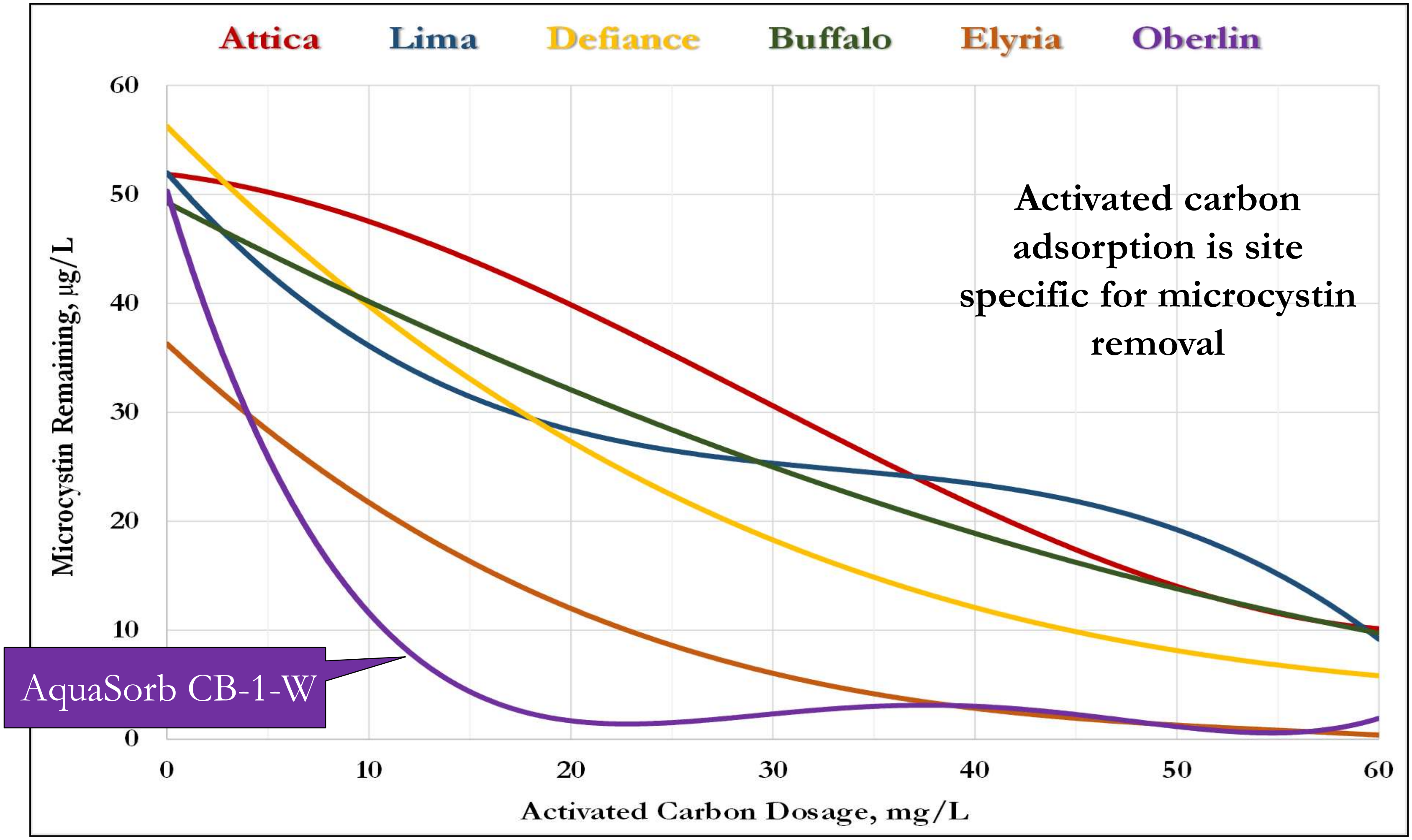
Carbon Treatment Simulations

Activated carbon evaluation for Microcystin reduction - Buffalo

Carbon Treatment Simulations

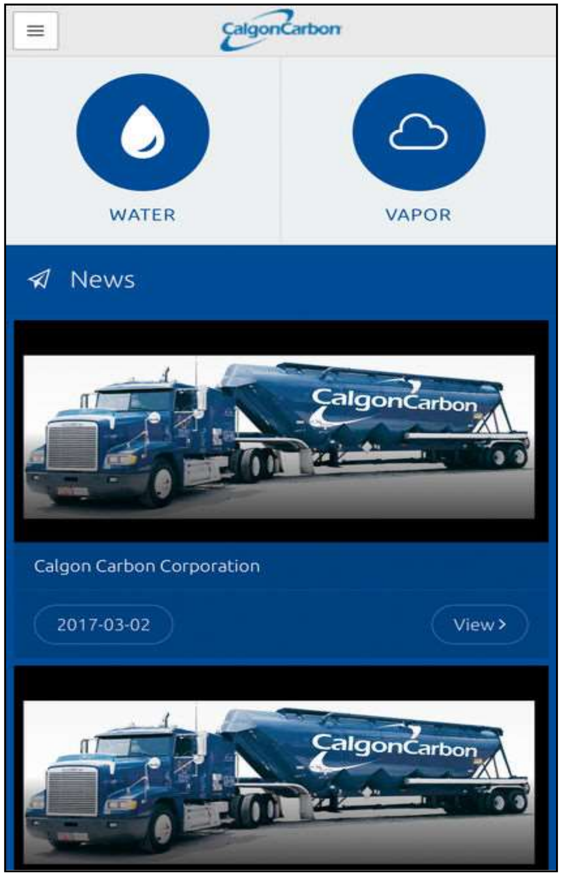


Carbon Treatment Simulations



GAC Treatment Simulations

- GAC contactor desktop evaluations
  - Specific GAC designs
    - 10-min/20-min EBCT
  - Run to TOC breakthrough
  - Up to 2-year life cycle historically
- Carbon usage rate (CUR) for Microcystin-LR
  - CCURE app (assumed safety factor of 2)
    - 0.00648 pounds per 1,000 gallons treated @ 50 µg/L
    - 0.00141pounds per 1,000 gallons treated @ 10 µg/L



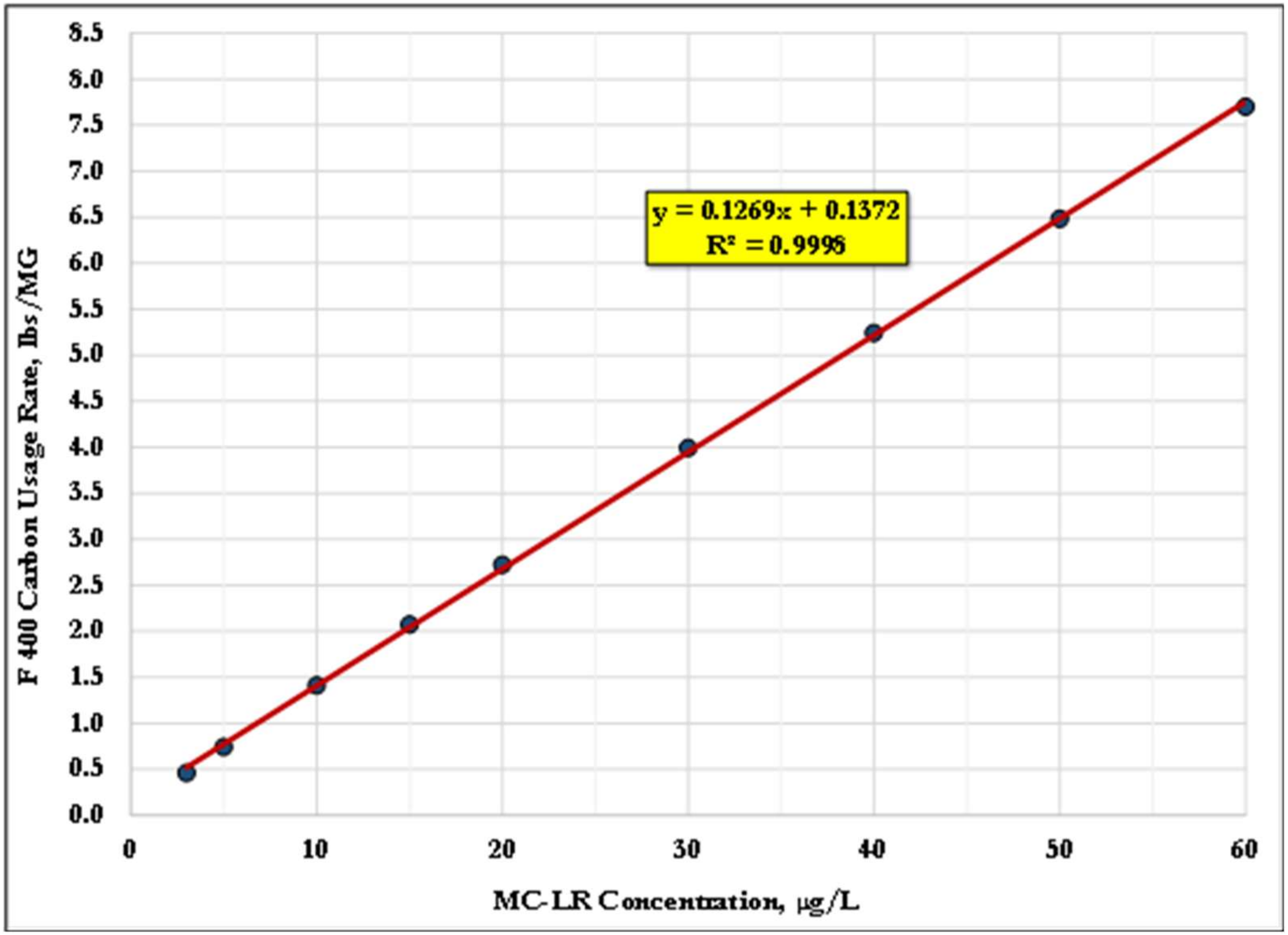
GAC Treatment Simulations

$$CUR, lbs / 1{,}000 gallons = \frac{EBCT * \rho GAC * 10^3}{T * 7.48 * 1{,}440}$$

Where CUR = Carbon Usage Rate, pounds per 1,000 gallons
EBCT= empty bed contact time, minutes
ϱGAC = carbon density, pounds/cubic foot
7.48 = 7.48 gallons per cubic foot
1,440 = 1,440 minutes per day

1998 WRF report - *"Removal of DBP Precursors by GAC Adsorption"*

GAC Treatment Simulations



GAC Treatment Simulations

- Microcystin that would likely enter Lima's GAC contactors
  - Pretreatment reduction with $NaMnO_4$ and activated carbon
- HAB event may reduce GAC life about 20 days every 2-year replacement cycle
  - Negligible impact to GAC treatment for TOC reduction
  - Effluent 0.3 μg/L Microcystin or less

GAC Treatment Simulations

- Microcystin that would likely enter Defiance's planned GAC contactors
  - Pretreatment reduction with $NaMnO_4$ and activated carbon
- HAB event may reduce GAC life about 5 days every 5-month replacement cycle
  - Negligible impact to GAC treatment for TOC reduction
  - Effluent 0.3 µg/L Microcystin or less

GAC Treatment Simulations

- Microcystin that would likely enter Elyria's proposed GAC contactors
  - Pretreatment reduction with $KMnO_4$ and activated carbon
- HAB event may reduce GAC life about 3 days every 9-month replacement cycle
  - Negligible impact to GAC treatment for TOC reduction
  - Effluent 0.3 µg/L Microcystin or less

GAC Treatment Simulations

- Microcystin that would likely enter Oberlin's potential GAC filter caps
  - Pretreatment reduction with $NaMnO_4$ and activated carbon
- HAB event may reduce GAC life about 1 day every 3-month replacement cycle
  - Negligible impact to GAC treatment for TOC reduction
  - Effluent 0.3 µg/L Microcystin or less

Carbon Treatment Simulations

- Activated carbon adsorption effective for Microcystin reduction
  - Pore distribution dependent (carbon selection important)
  - Dosage and EBCT dependent
  - TOC dependent (organic character impacts)
  - PAC contact time dependent (60 minutes minimum)
  - High iodine number tends to reduce carbon dosages and produce greater removals
- Need to evaluate PAC impacts to filtration processes
  - Carbon carryover may limit actual dosages due to impacts identified
    - May limit carbon dosing to about 10 mg/L in conventional treatment
    - Could have minimal impacts if using tube settlers or plate settlers

Chlorine Treatment Simulations

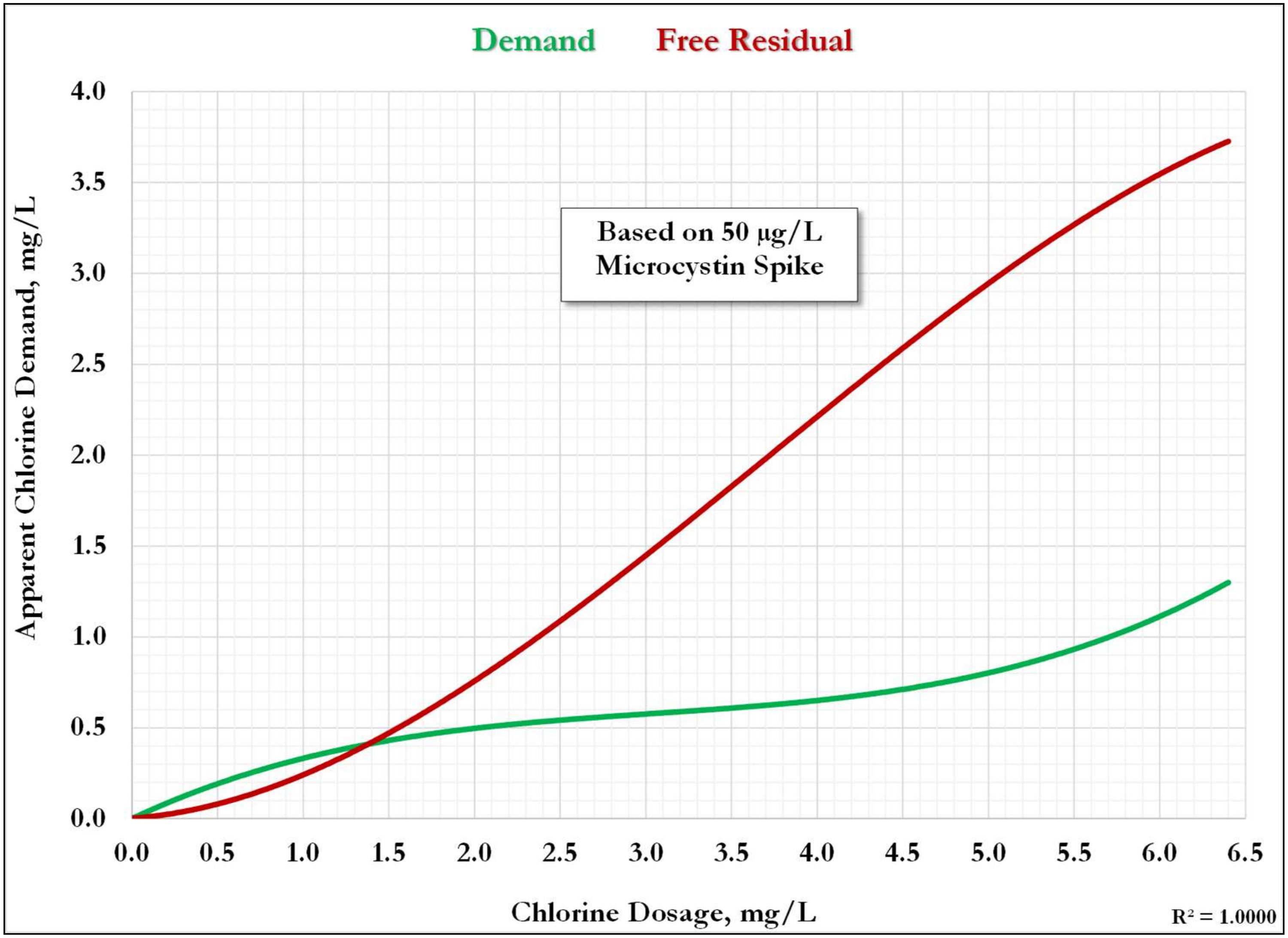
- Concentrated toxin solution used for jar tests
  - $C_1V_1 = C_2V_2$
- Dosages
  - 2 mg/L to 5 mg/L
    - Bracket current chlorine dosing
    - Filtered water used for simulations
- Each of 5 jars spiked with ≈50 µg/L microcystin
  - 1 jar used as control (spike)
  - Remaining jars dosed with chlorine solution

Concentrated microcystin solution

Chlorine Treatment Simulations

- Chlorine residual can be tested after about 10 minutes of reaction
  - DPD method provides chlorine residuals in mg/L
  - Free chlorine and total chlorine needed for evaluations
    - Free chlorine allows calculation of CT values for microcystin removal
- Once residual and dosage are known, chlorine demand can be calculated
- CT simulations demonstrate potential impacts of pH and contact time on microcystin reductions

Chlorine Treatment Simulations



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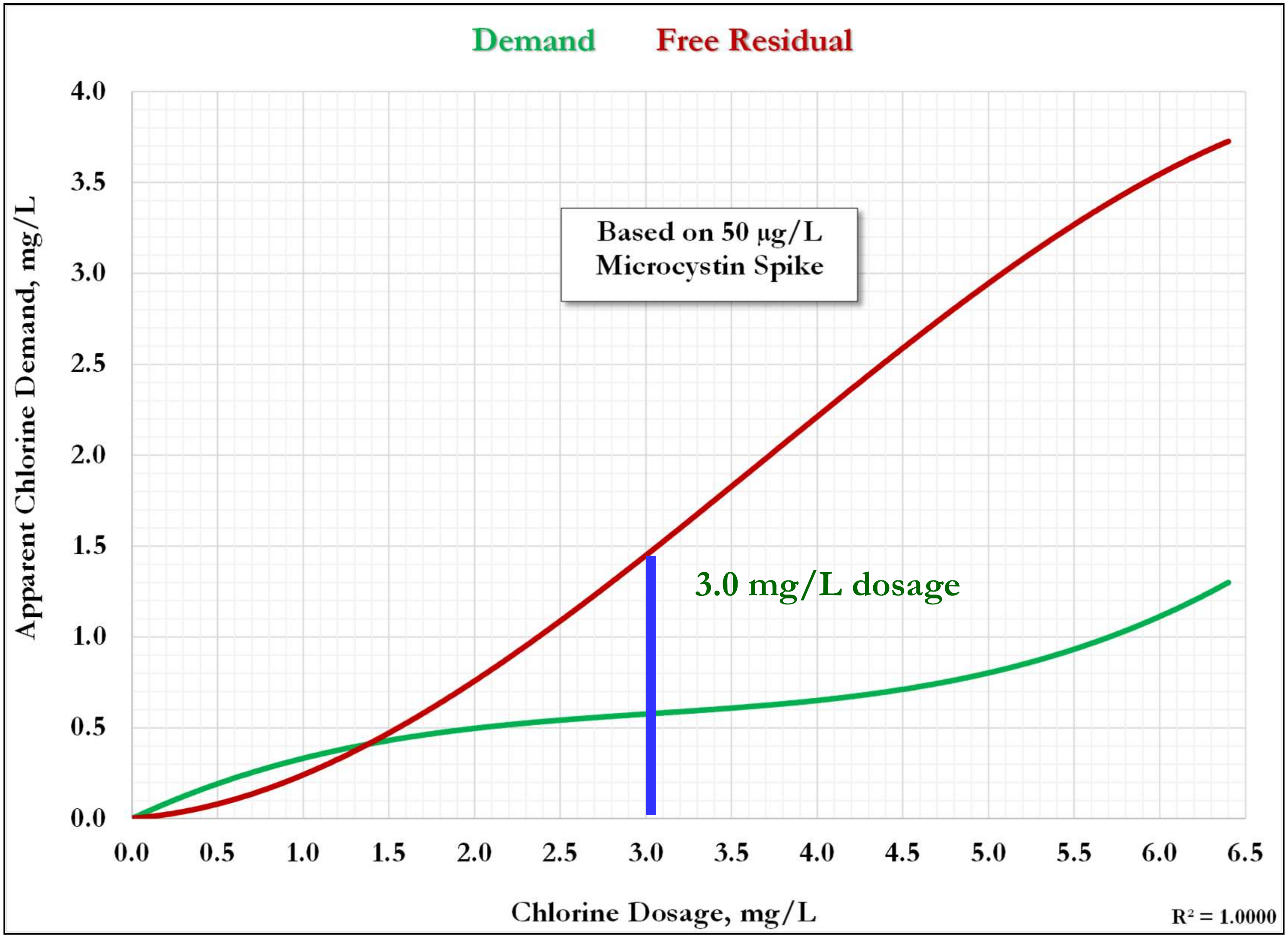

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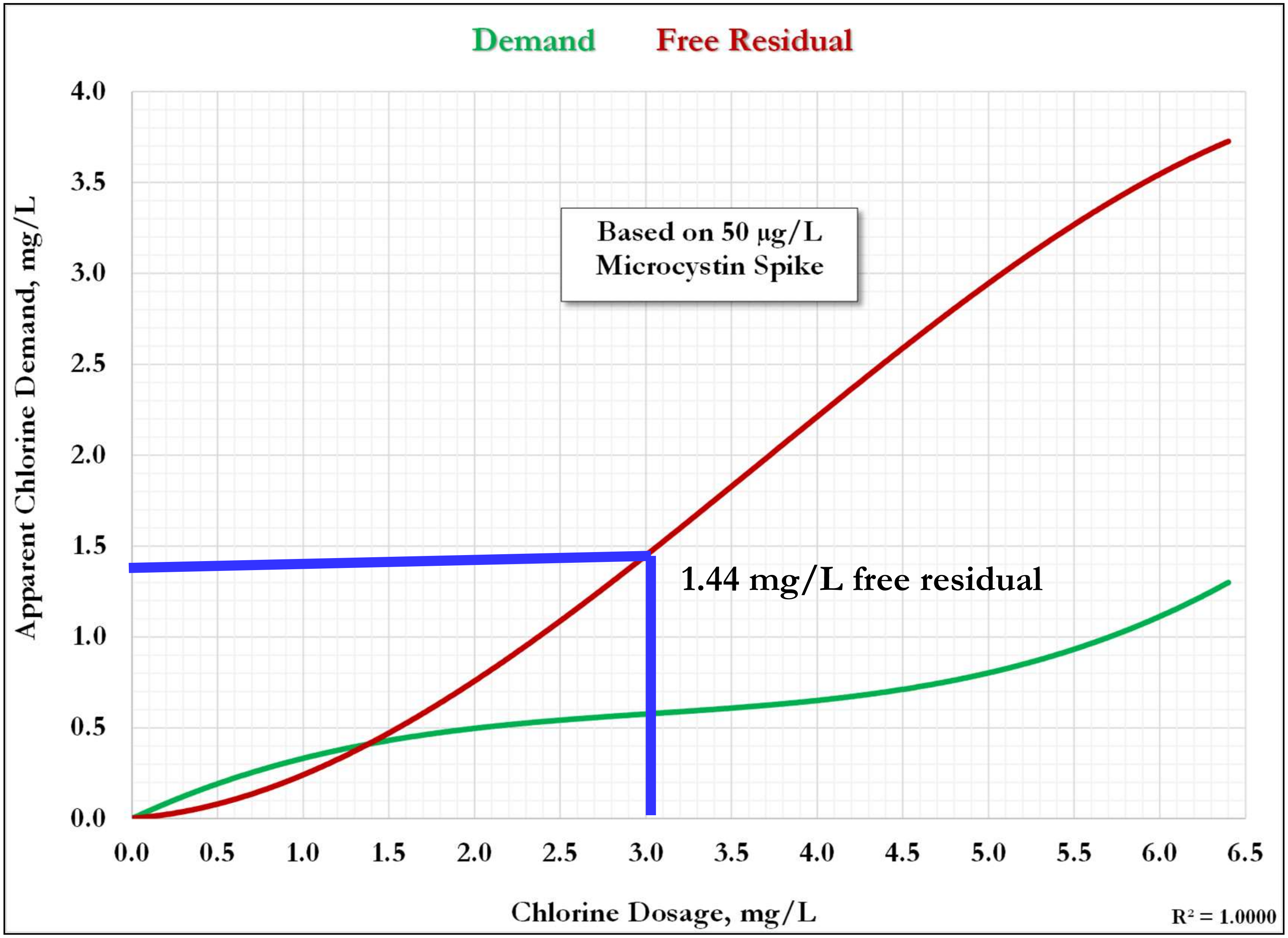

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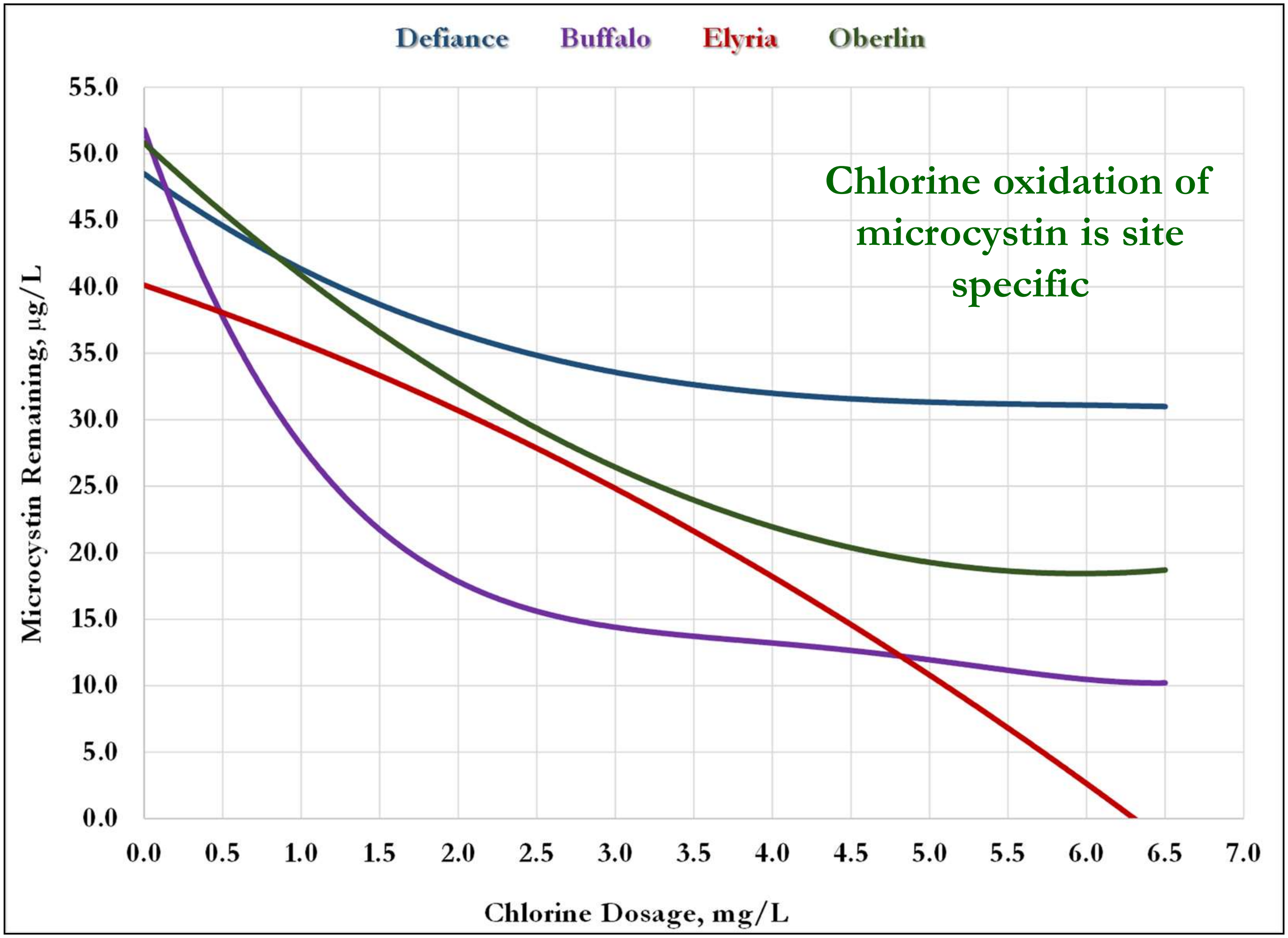

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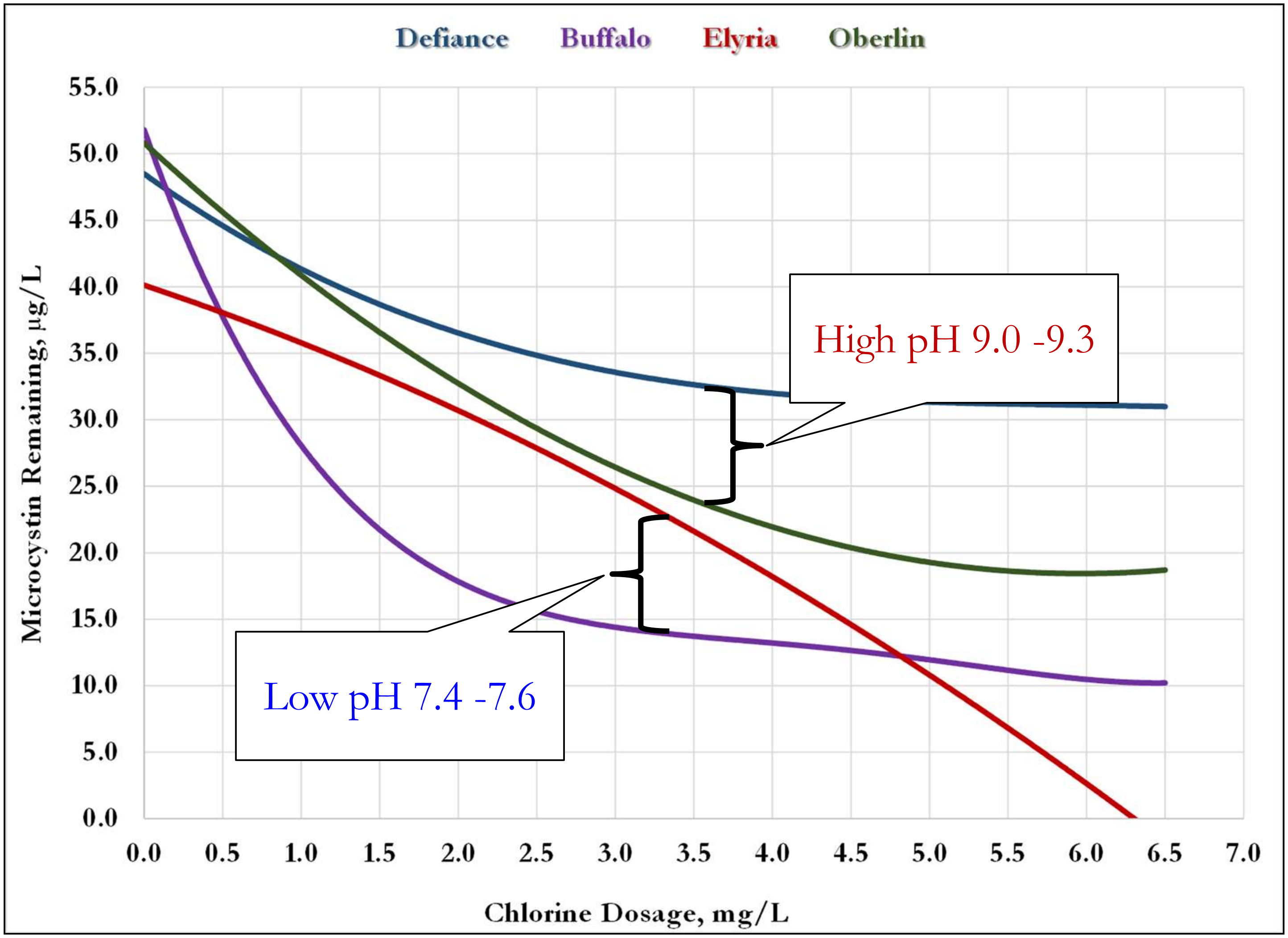
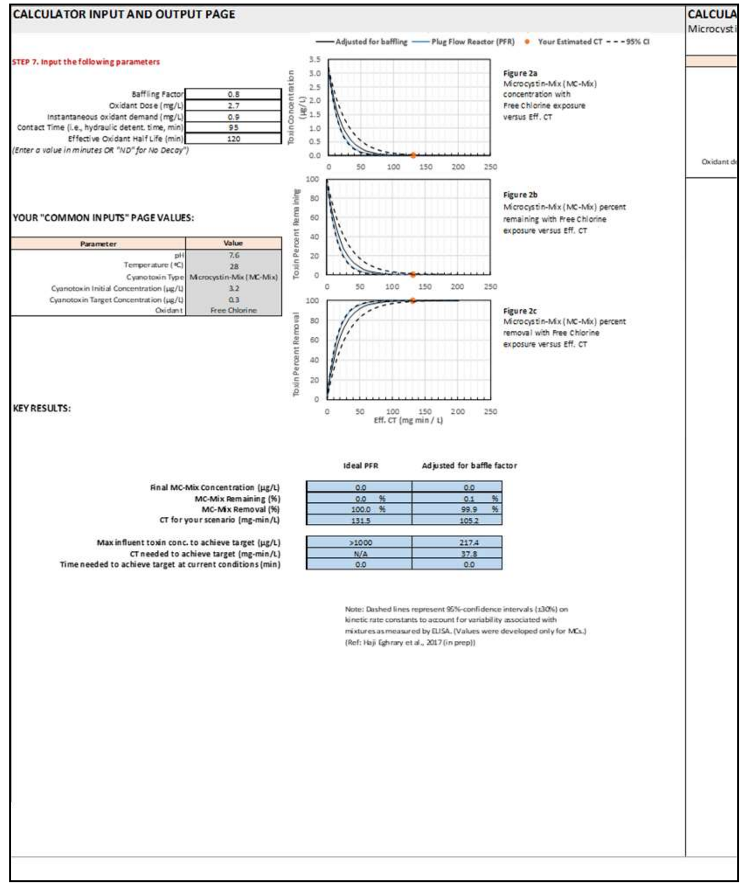


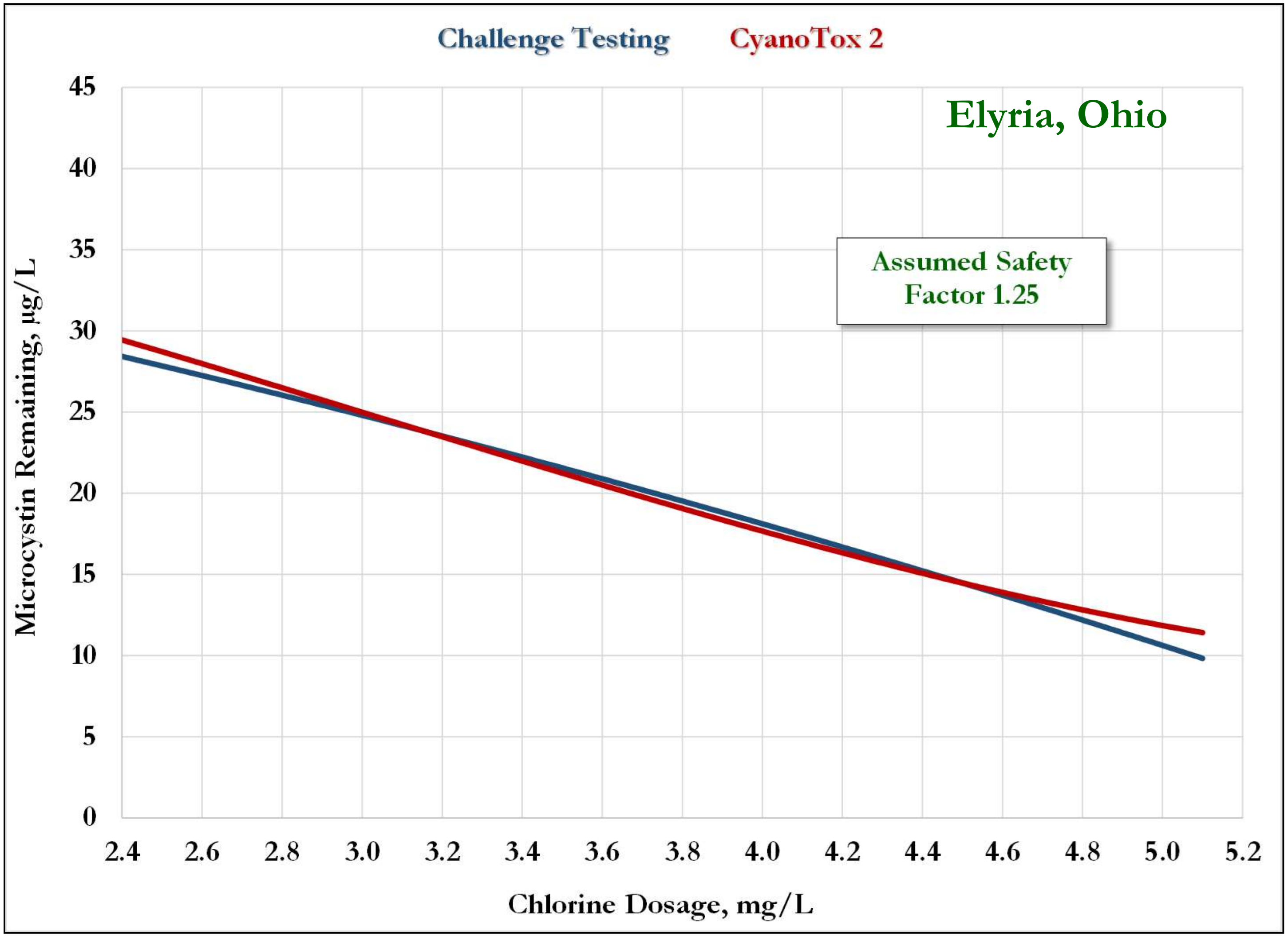
Chlorine Treatment Simulations

- Comparison of jar tests with AWWA CyanoTox2 Model for Cyanotoxins
  - 1st Assumed no safety factor
  - Input actual chlorine demand and dosage ranges
  - Compared model output with experimental data
  - 2cd Identified approximate Safety Factor (site specific)



AWWA CyanoTox2 Model

Chlorine Treatment Simulations



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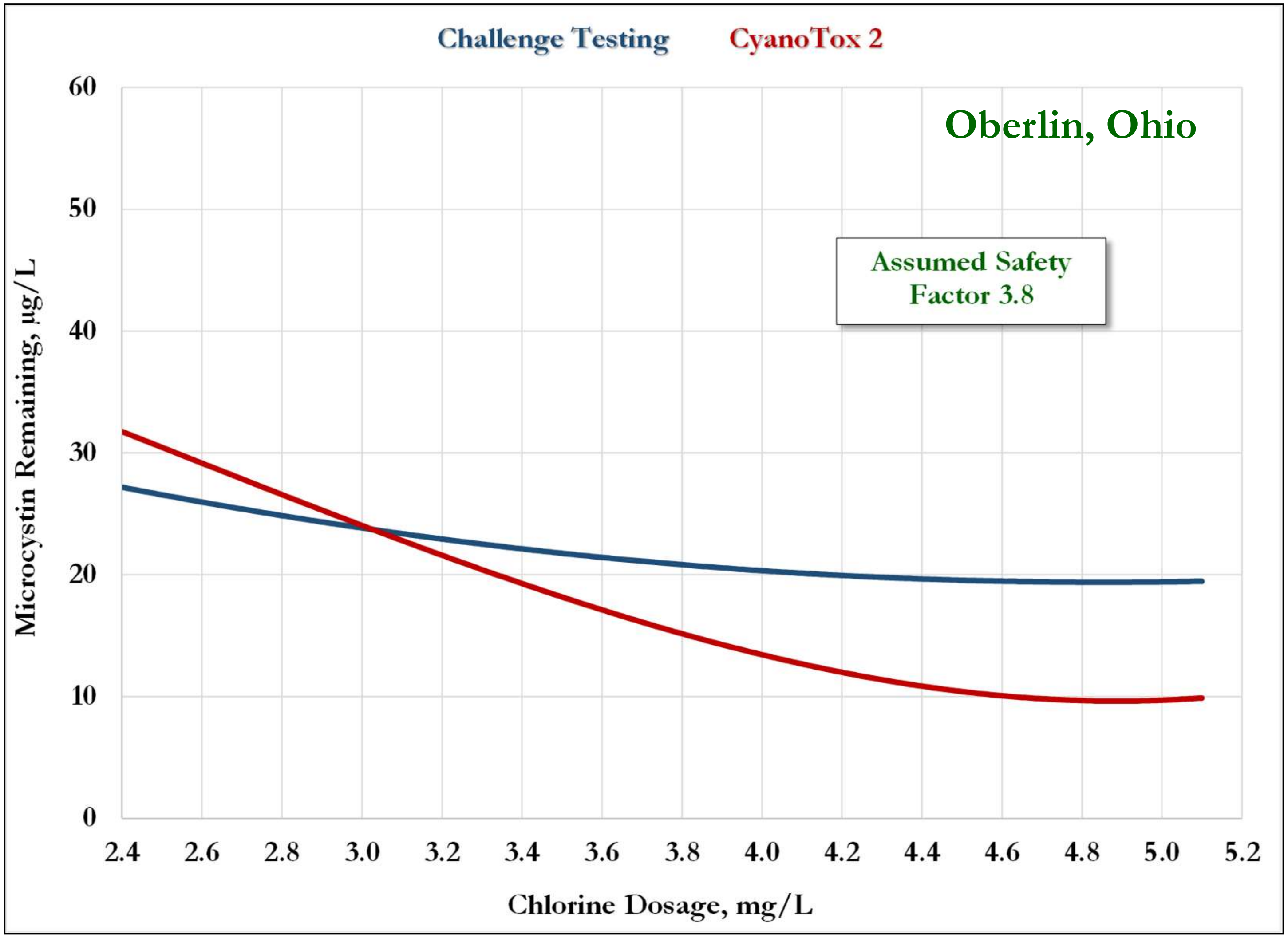

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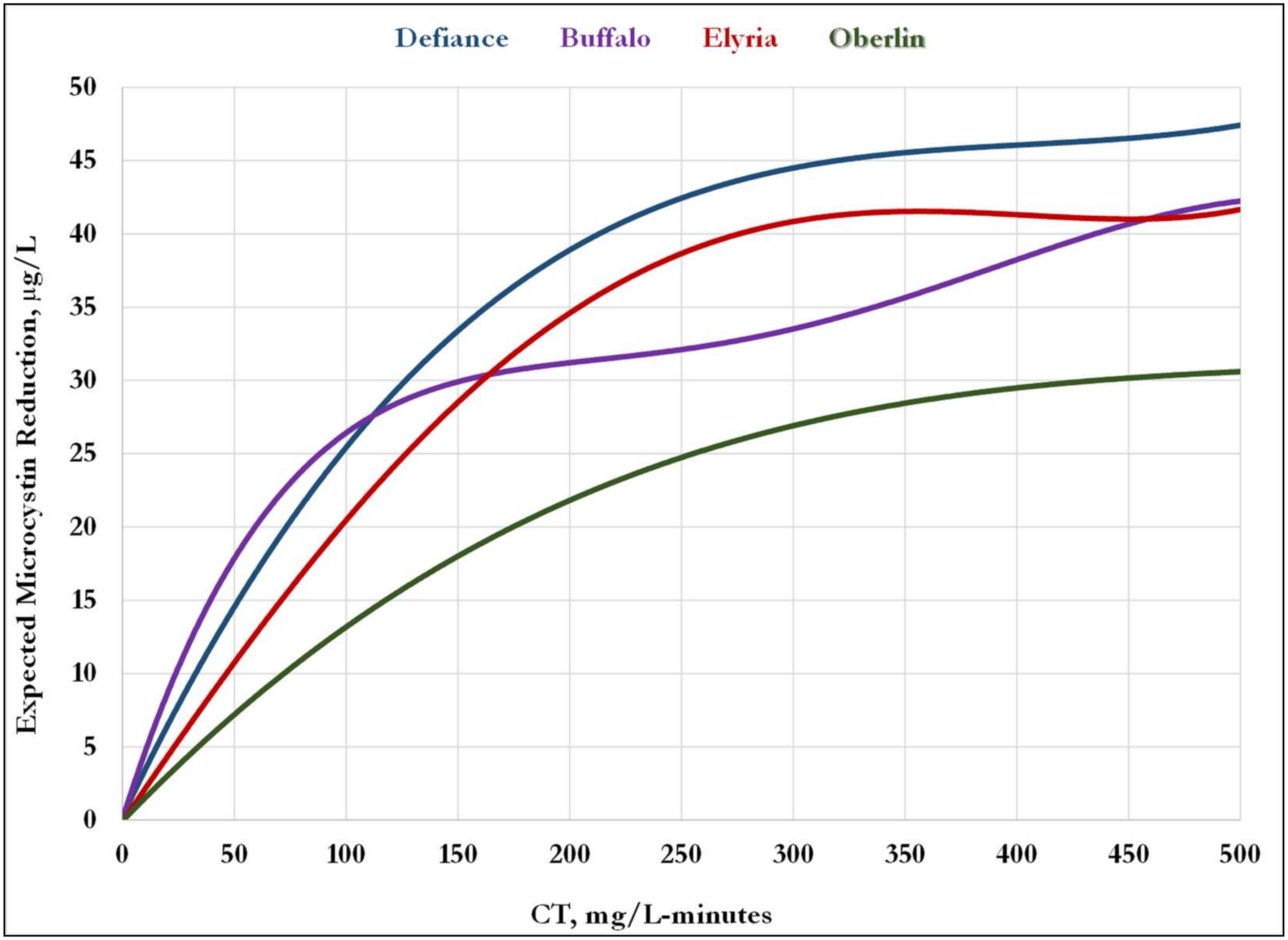

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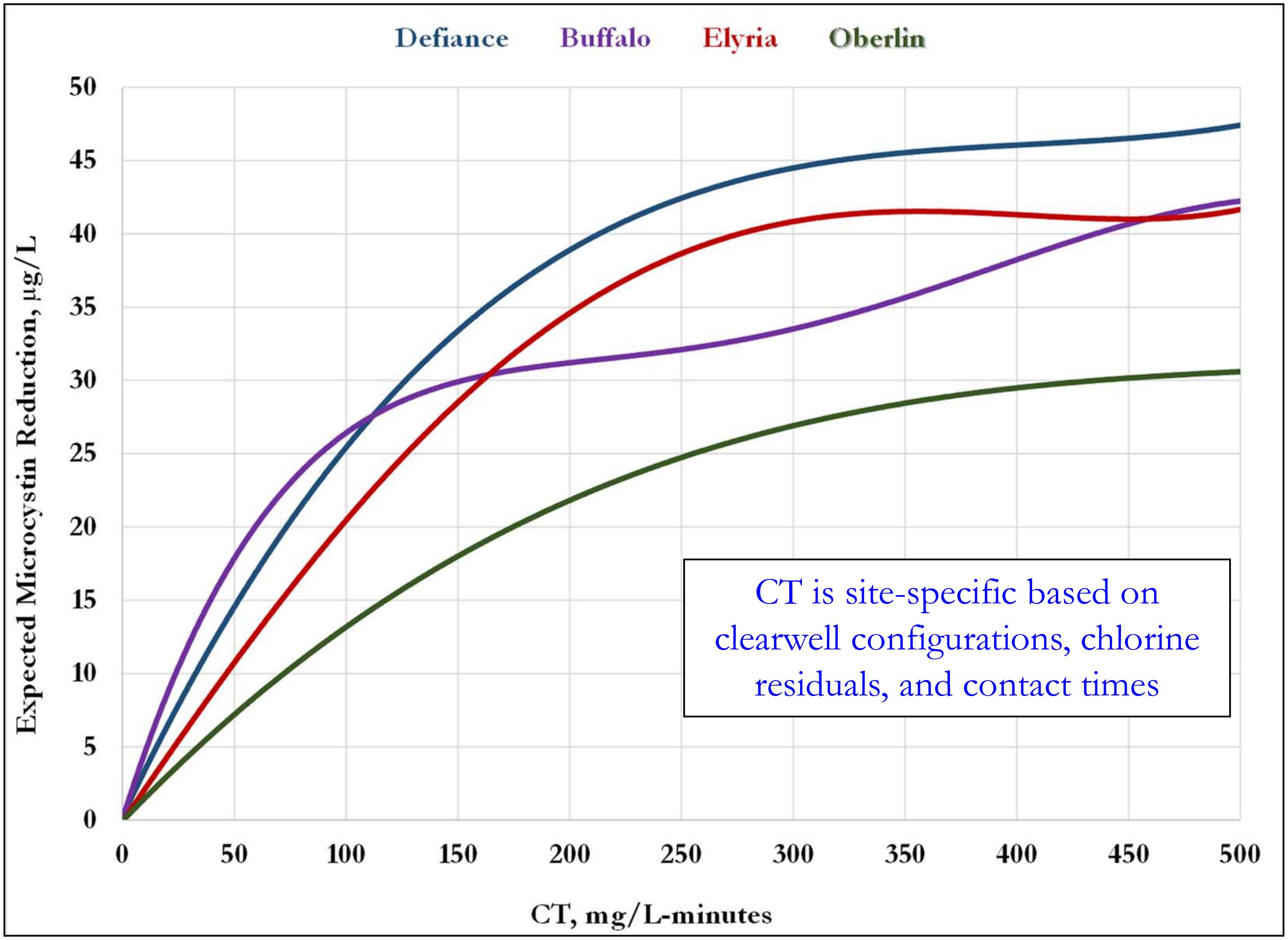
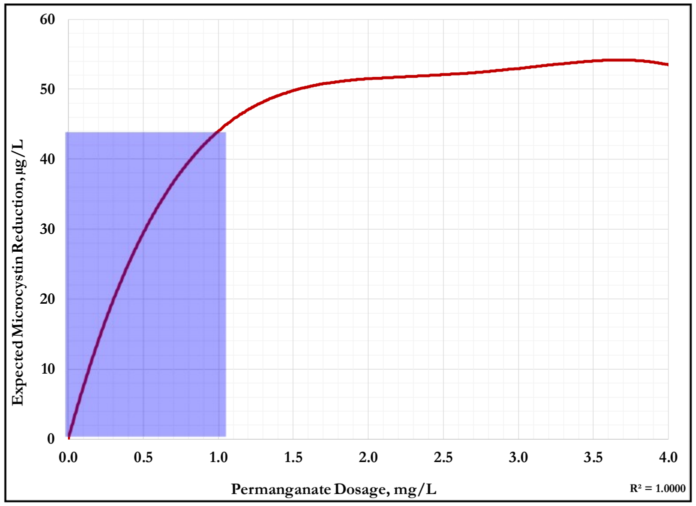


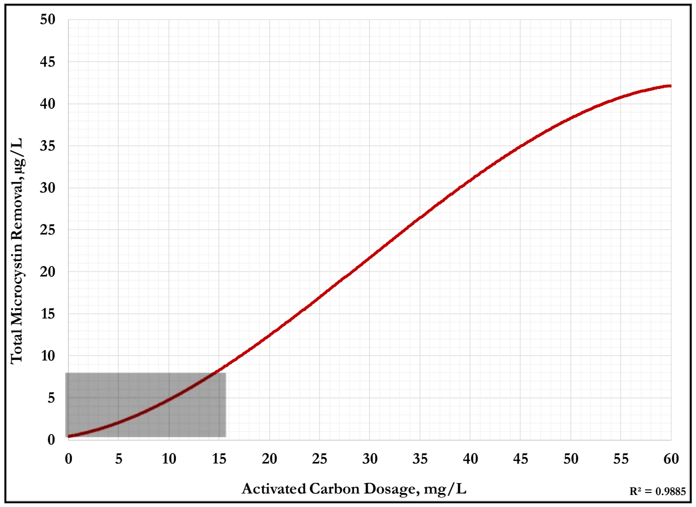
Chlorine Treatment Simulations

- Chlorine oxidation treatment effective for Microcystin reduction
  - Dosage dependent
  - Contact time dependent
  - pH dependent
    - Lower pH generally provides better removals
- Correlations to AWWA's CyanoTox 2 model possible for some treatment plants

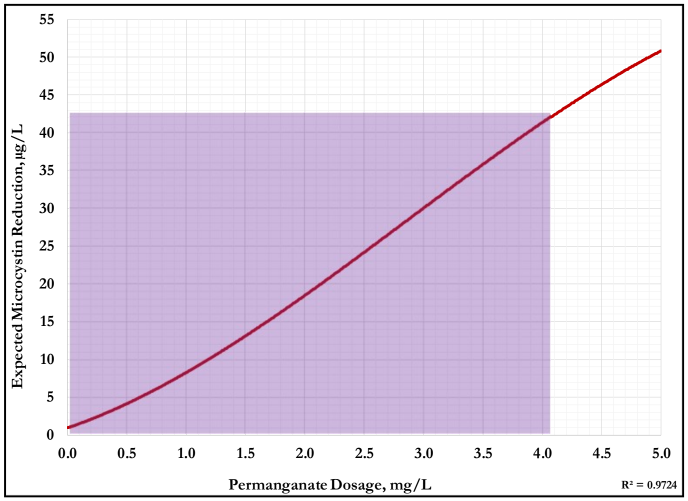
Microcystin Treatment Strategy

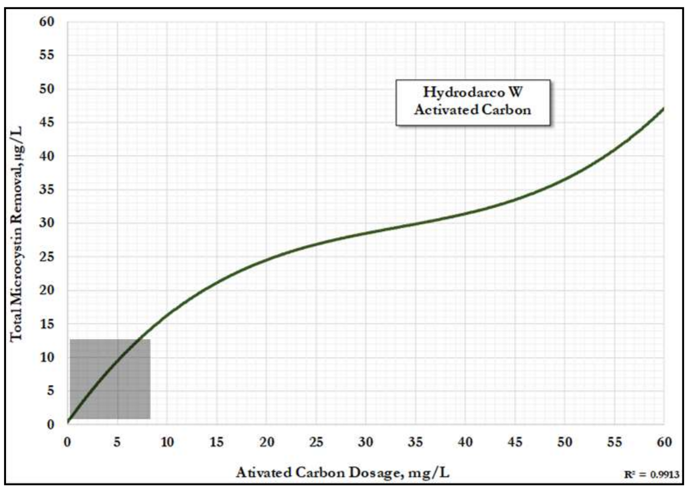
- Attica treatment scenarios
  - Continue to treat reservoir with algaecide to limit Microcystin production
  - 1.1 mg/L $KMnO_4$ pretreatment removes up to 41 μg/L MC
  - 15 mg/L WaterCarb 800 needed for MC adsorption to 0.3 μg/L or less
  - Post filtration chlorine used as extra barrier treatment





Microcystin Treatment Strategy

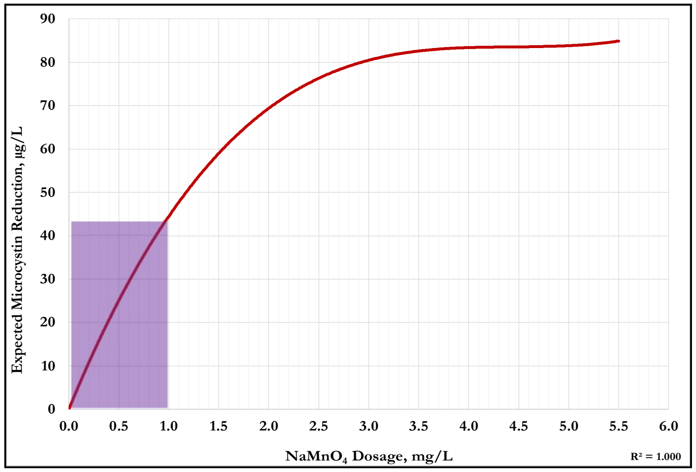


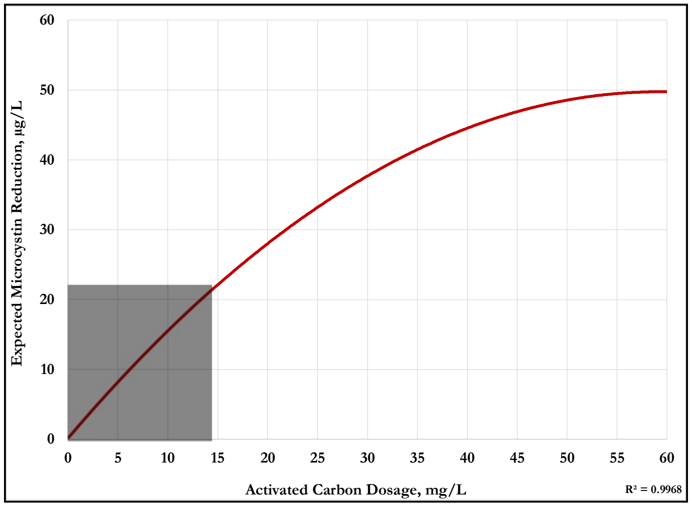


- Lima treatment scenarios
  - 1 mg/L $NaMnO_4$ dosing until MC extracellular
  - Up to 4 mg/L $NaMnO_4$ pretreatment removes up to 41 µg/L MC extracellular
  - 5 mg/L to 8 mg/L Hydrodarco W needed for MC adsorption to 0.3 µg/L or less
  - GAC used as extra barrier
  - Post GAC chlorine used as extra barrier

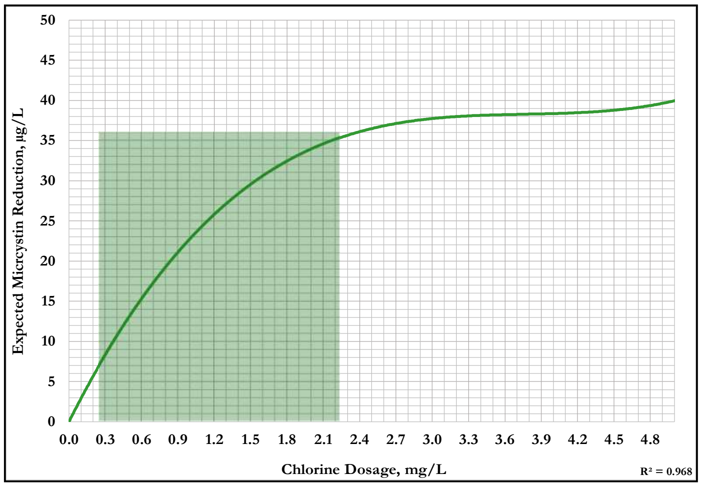
Microcystin Treatment Strategy

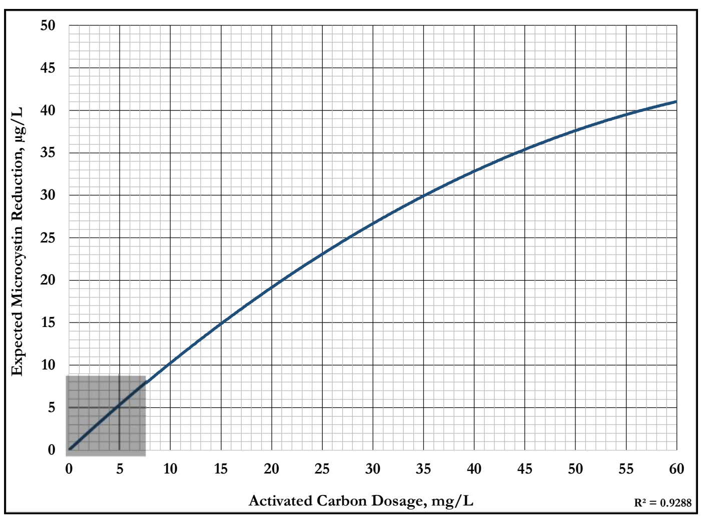
- Defiance treatment scenarios
  - Continue to treat reservoir with algaecide to limit Microcystin production
  - 1 mg/L $NaMnO_4$ pretreatment removes up to 44.5 µg/L MC
  - 8 mg/L Hydrodarco B needed for MC adsorption to 0.3 µg/L or less
  - GAC contactors being installed as extra barrier
  - Post GAC chlorine used as extra barrier
    - Can oxidize up to 15 µg/L at normal dosages





Microcystin Treatment Strategy

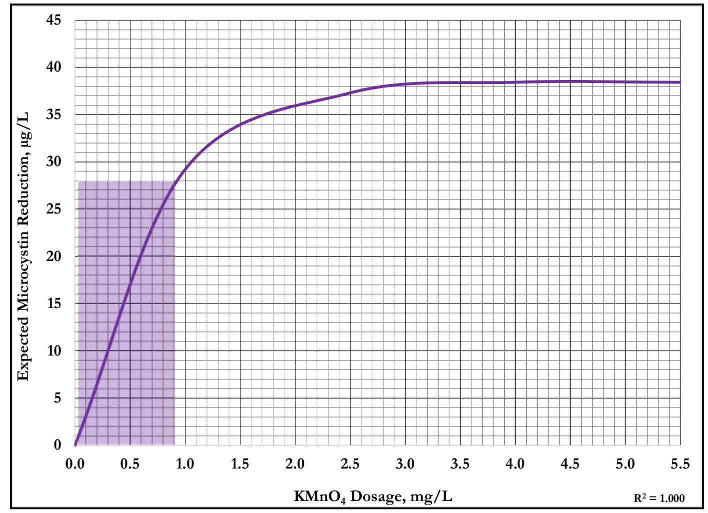


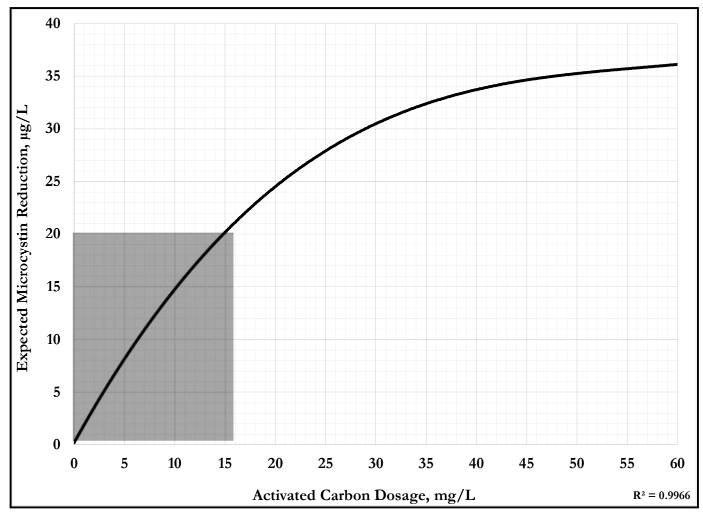


- Buffalo treatment scenarios
  - Routine 2 mg/L pre-chlorination treatment removes up to 35 µg/L MC
    - Low TOC source, no THM issues
  - 15 mg/L WPH needed for MC adsorption to 0.3 µg/L or less
  - Post filtration chlorine used as extra barrier
    - Can oxidize up to 26 µg/L at normal dosages

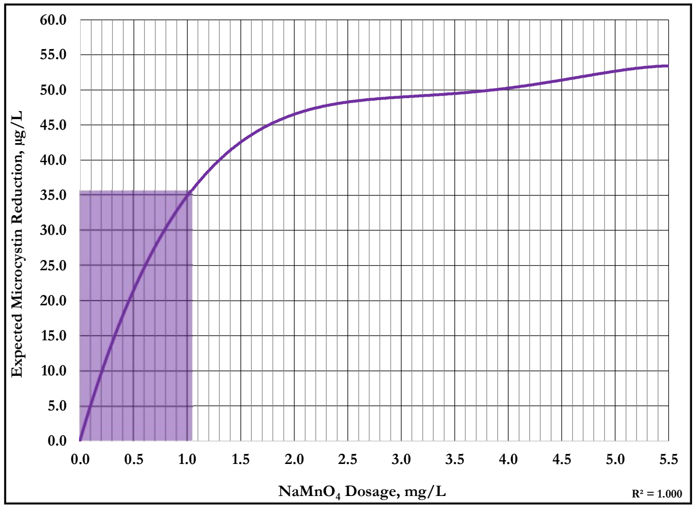
Microcystin Treatment Strategy

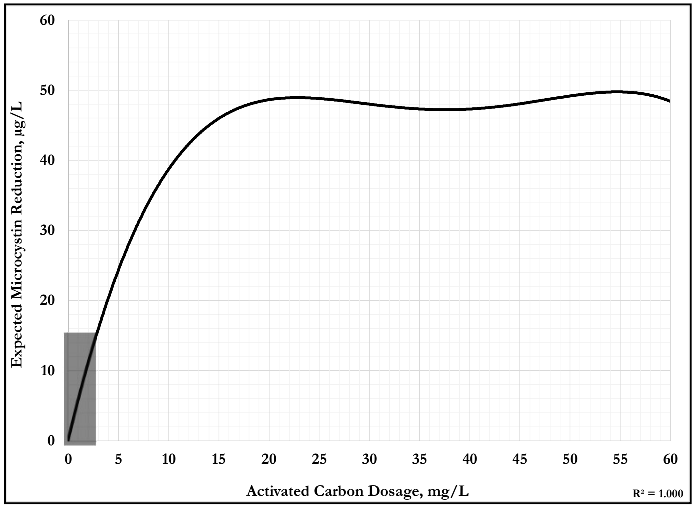
- Elyria treatment scenarios
  - 0.85 mg/L $KMnO_4$ pretreatment removes up to 26.5 µg/L MC
  - 15 mg/L WPH needed to remove up to 21 µg/L MC (48 µg/L combined)
  - Post filtration chlorine used oxidize remaining MC
    - Can remove up to 15 µg/L at normal dosages





Microcystin Treatment Strategy





- Oberlin treatment scenarios
  - 1.0 mg/L $NaMnO_4$ dosing removes up to 35 µg/L MC
  - 3 mg/L to 4 mg/L AquaSorb CB-1-W needed for MC adsorption to 0.3 µg/L or less
  - Post filtration chlorine used as extra barrier
    - Can oxidize up to 27.5 µg/L at normal dosages

Questions

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