Using Rapid Small Scale Column Testing to Evaluate Granular Activated Carbon Adsorption of Cyanotoxins from Drinking Water

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Outline

- Background – cyanotoxins, local conditions, previous research
- Objectives
- RSSCTs (Rapid Small Scale Column Tests)
- Developing RSSCTs and overcoming MC-LR biodegradation
- RSSCT GAC adsorption and the effects of preloading
- UV254/TOC and competitive adsorption
- Biological analysis and practical implications
- Conclusions
- Recommendations for future research

Cyanotoxins

- Cyanotoxins released by cyanobacteria through lysing or cell death (USEPA, 2012)
  - Extracellular toxins
- Health concerns to humans and environment (Falconer 2008)
  - Hypoxia, carcinogenic, organ damage
- Most common (Merel et al. 2013)
  - **Microcystins-LR, RR, LY (100+ congeners exist)**
  - Cylindrospermopsin
  - Anatoxins
  - Saxitoxins
- Guideline of 1.0 µg L^{-1} for MC-LR (WHO, 2011)
- **OH EPA action level of 0.3 µg L^{-1}** (USEPA, 2015a)

Treatment

- Cyanotoxin contamination of drinking water is a growing area of concern
  - Increased nutrient load, population etc.
- Incorrect treatment practices could result in release rather than removal (WRF and AWWA, 2015)
- Intracellular (I)
- Extracellular (E)

- Typical treatment methods include: (WRF and AWWA, 2015)
  - Pretreatment Oxidation (I)
    - Potassium permanganate (E)
  - Coagulation/Sedimentation/Filtration (I)
  - Membranes (I + E)
  - DAF (I)
  - **GAC (E)**
  - PAC (E)
  - Ozone (E)
  - Chlorination (E)

Local Utility

- Worked with a local utility partner on practical questions
- Process
  - Potassium permanganate > Alum > Polymer > Filters > **GAC** > Cl_2
- Three GAC contactors in operation (April 2013)
  - GAC intended for reduction of DBP precursors
  - Carbon is regenerated with 15% virgin makeup
  - Each contactor regenerated twice per year
- What utility wants to know?
  - What is the best way to manage GAC contactors for toxin removal?
  - If the GAC is loaded with NOM…then how effective for toxins?
    - Competition, fouling etc.

William H Harsha Lake

- Toxins detected (Allen 2015)
  - **MC-LR (Max-1.55 ppb)**
  - MC-RR (Max-0.52 ppb)
  - MC-LY (Max-0.19 ppb)
  - 7-desmethylated-MC-LR
- 2014 sampling resulted in max. MC-LR = 3.10 µg L^{-1} (Ohio EPA, 2010-2017)
- Saxitoxin has also been detected (Ohio EPA, 2010- 2017)

Previous Research

- **GAC**
  - Represents an efficient solution for the removal of extracellular toxins (Sorlini and Collivignarelli 2011)
  - GAC + conventional methods very effective (Karner et al. 2001)
  - Mesoporous carbon is more effective at removing cyanotoxins (Westrick 2008)
  - 70-80% TOC in effluent, media replaced (Antoniou et al. 2014)
  - MC adsorption during bloom event may not be viable (Karner et al. 2001)
- **GAC + MC-LR**
  - Flat, long breakthroughs and small steep curves (Huang et al. 2007, Carlile 1994)
  - Bacterial colonization a hindrance and an important mechanism (Wang et al. 2007, Drogui et al. 2012, UKWIR 1996, Wang et al. 2006)
- **RSSCTs**
  - Some work on SBAs (Short Bed Adsorbers)
  - RCT showed 80% after 30,000 BVs (Hall et al. 2000)
- **Research Gaps**
  - Lack of data regarding the performance of GAC in removing cyanotoxins
  - Reliable way to simulate full scale GAC adsorption (RSSCTs)
  - Competitive adsorption of source water NOM and cyanotoxins

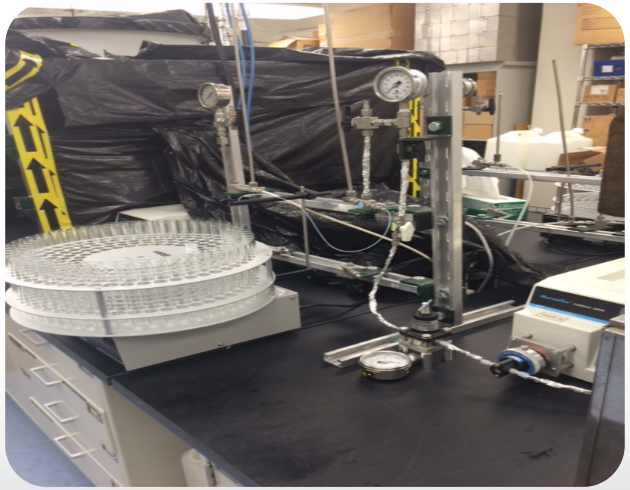
Objectives

- Use RSSCTs to assess the effectiveness of GAC in treating cyanotoxins, particularly MC-LR
- Determine competitive adsorption/inhibition of NOM (TOC) and cyanotoxins
- Use RSSCTs to evaluate the adsorption capacity of GAC in treating cyanotoxins when columns are preloaded with NOM at multiple levels

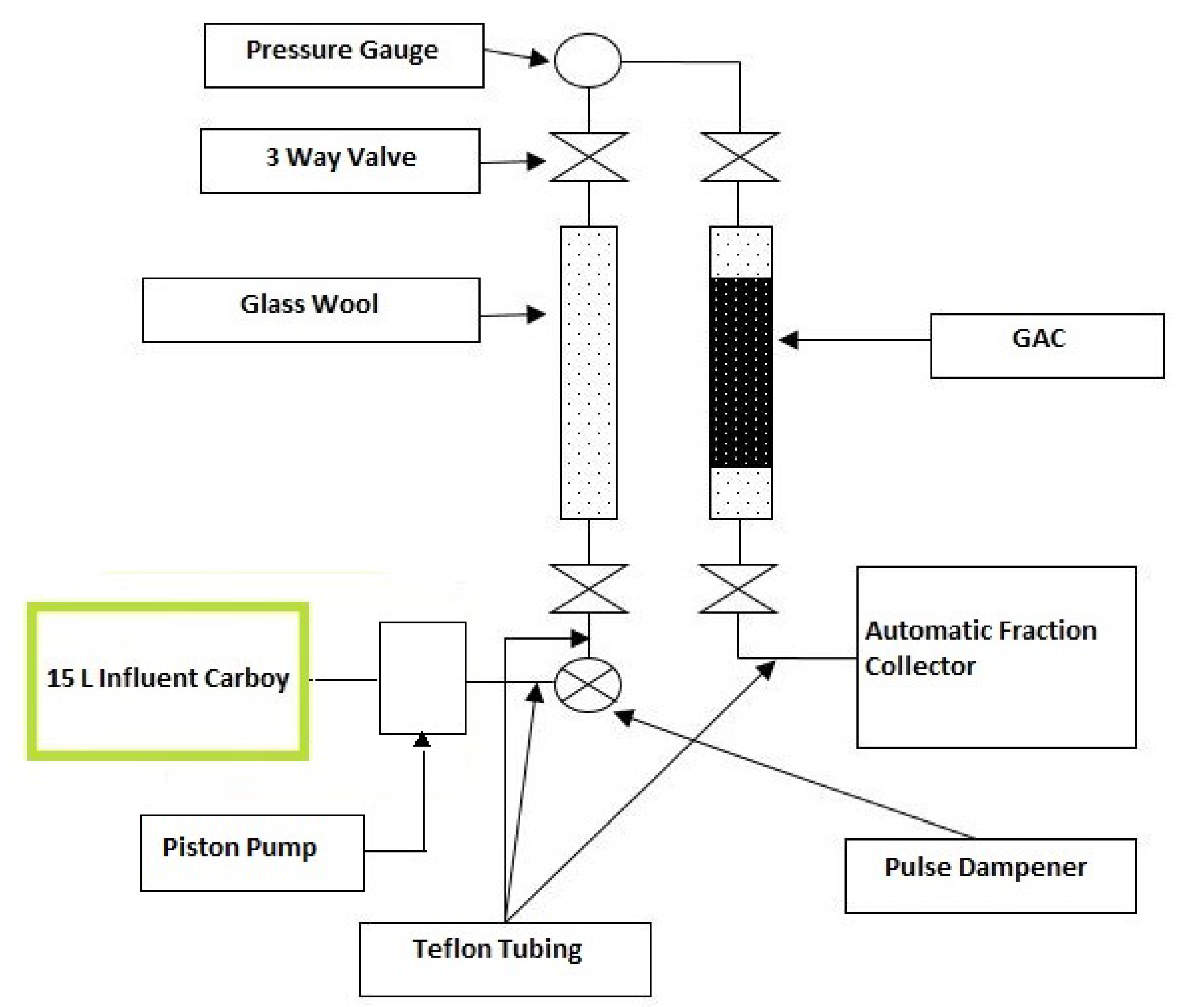
RSSCTs

- RSSCTs are small scale models of full scale processes (Poddar, Nair and Mahindrakar 2013)
  - Reduced time and resources
- Mass transfer methods used to simulate performance (Poddar, Nair and Mahindrakar 2013)
- Carbon ground to reduced sieve size
  - Possibility to overestimate performance of preloaded GAC (Ho and Newcombe 2007)

- Proportional Diffusivity Model (Crittenden et al. 1991)
  - Intraparticle diffusivity changes with particle size
  - Scaling relationship is a function of carbon particle size used in large and small scale



RSSCT Design



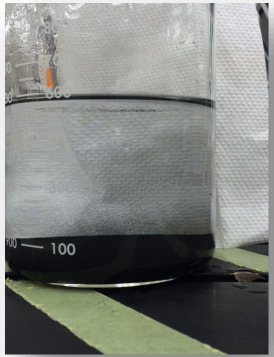
- V= 15 L water
- Estimated RSSCT run time= 33 days
- $EBCT_{sc}$ = 0.84 min
- Hydraulic loading rate (*v*)= 1.73 m h^{-1}
- Flow Rate= 0.32 mL/min
- Sieve size= 100x200
- M_{GAC} = 0.128 g
- RSSCT column diameter= 3.74 mm
- Bed Volume= 0.27 mL
- Bed Length= 2.42 cm
- **$d_{p\,LC}$ = 1.29 mm**
- **$d_{p\,SC}$= 0.11 mm**
- **SF= 11.8**

GAC Prep and GACI (CFE)

- GAC was collected from Clermont County Water Resources Department
  - Regenerated with 15% virgin makeup

- GAC was ground to meet 0.11 mm avg. particle size (100x200 sieve size)

- GAC rinsed to separate "fines" to prevent pressure buildup in column

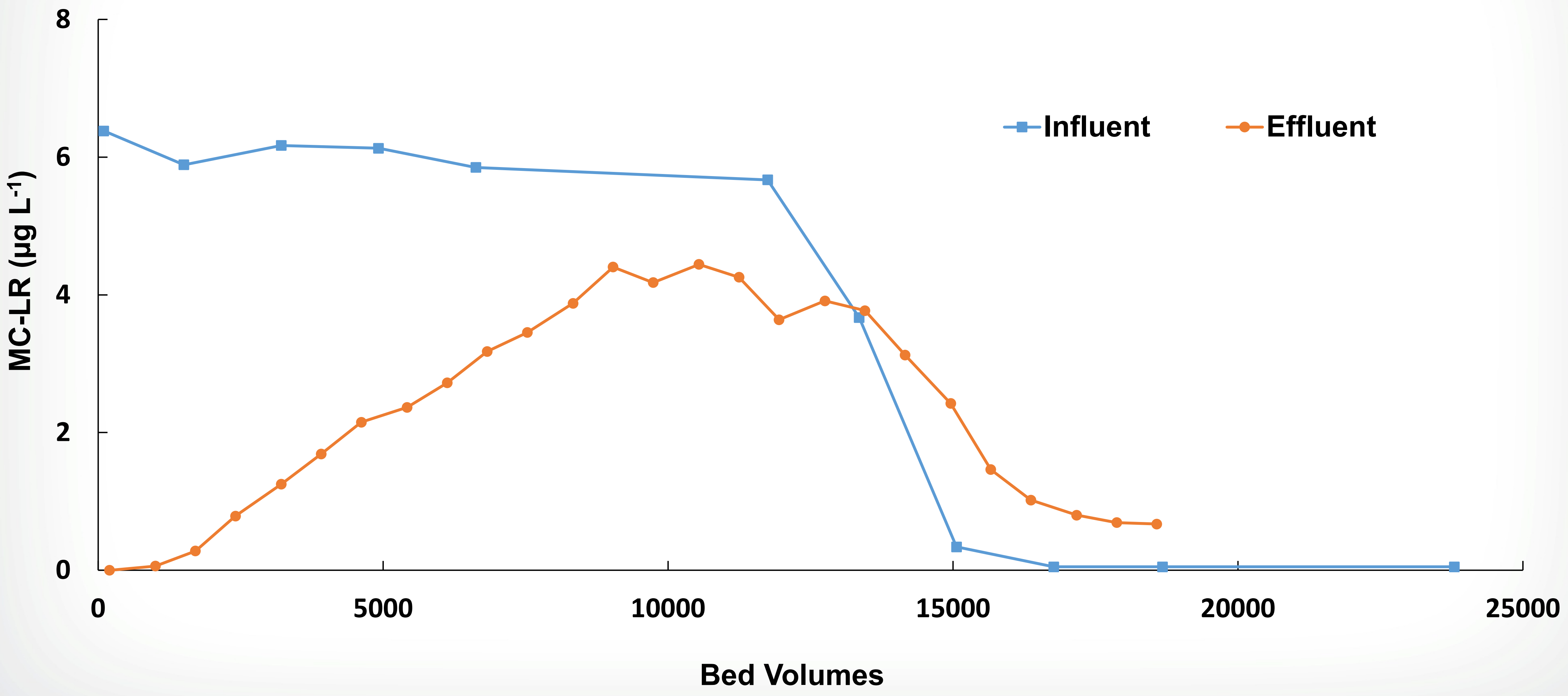


- GACI (CFE) was procured from CCWRD
  - 240 L

Chemicals and Analyses

- **MC-LR**
  - LC/MS/MS
  - USEPA Method 544
- **NOM (Natural Organic Matter)**
  - TOC
    - Combustion Catalytic TOC analyzer (TOC-Vcph Shimadzu Corporation, MD)
    - USEPA method 415.3
  - UV254
    - Analyzed on day of extraction
    - Standard Method 5910
- **MC-LR stock solutions**
  - Beagle Bioproducts (Columbus, OH)
  - Verified by Beagle to be ≥ 95% pure HPLC
  - Provided as dried film in 2 mL vial
  - Dissolved in 1 mL Milli Q water and diluted for analysis of stock via LC/MS/MS
    - USEPA method 544

Initial RSSCT



EPA

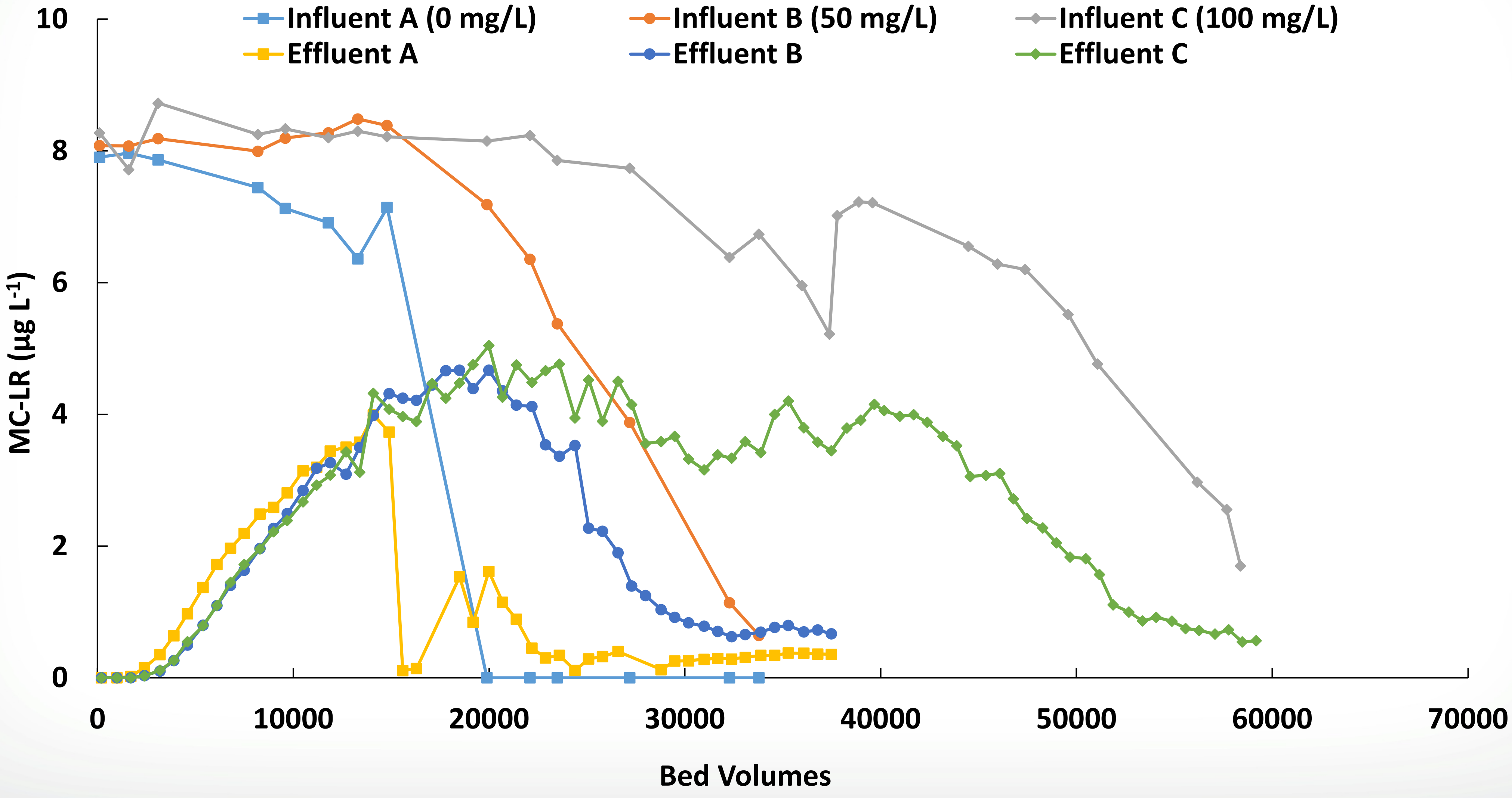
Experiments to Minimize Biological Activity

CLERMONT COUNTY OHIO
WATER RESOURCES DEPARTMENT

University of CINCINNATI

- Refrigeration at 5 °C
- Sodium Azide Inhibition
  - Bottle tests
  - RSSCT tests
- Sterile Techniques

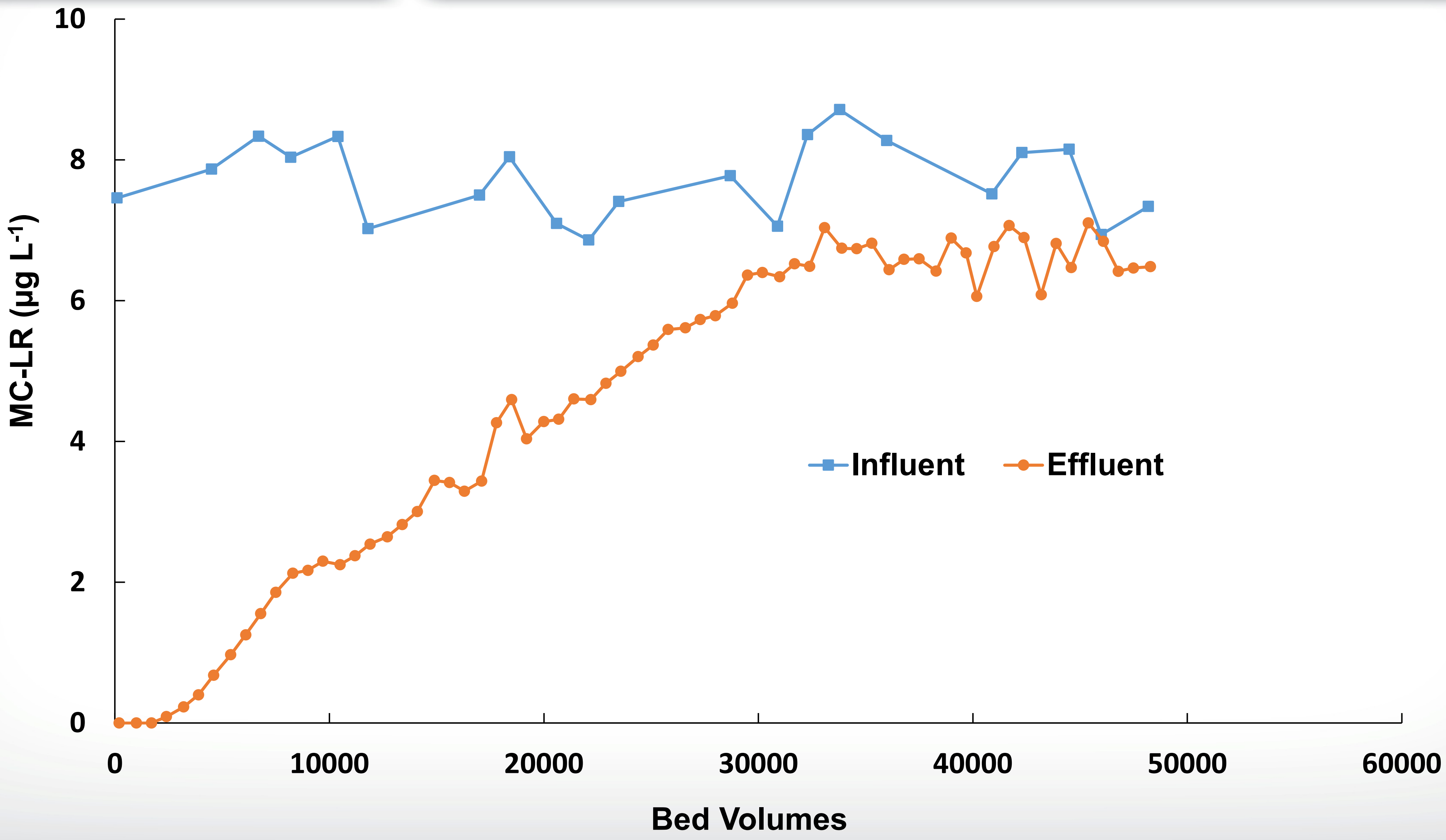
Sodium Azide RSSCT Confirmation Test



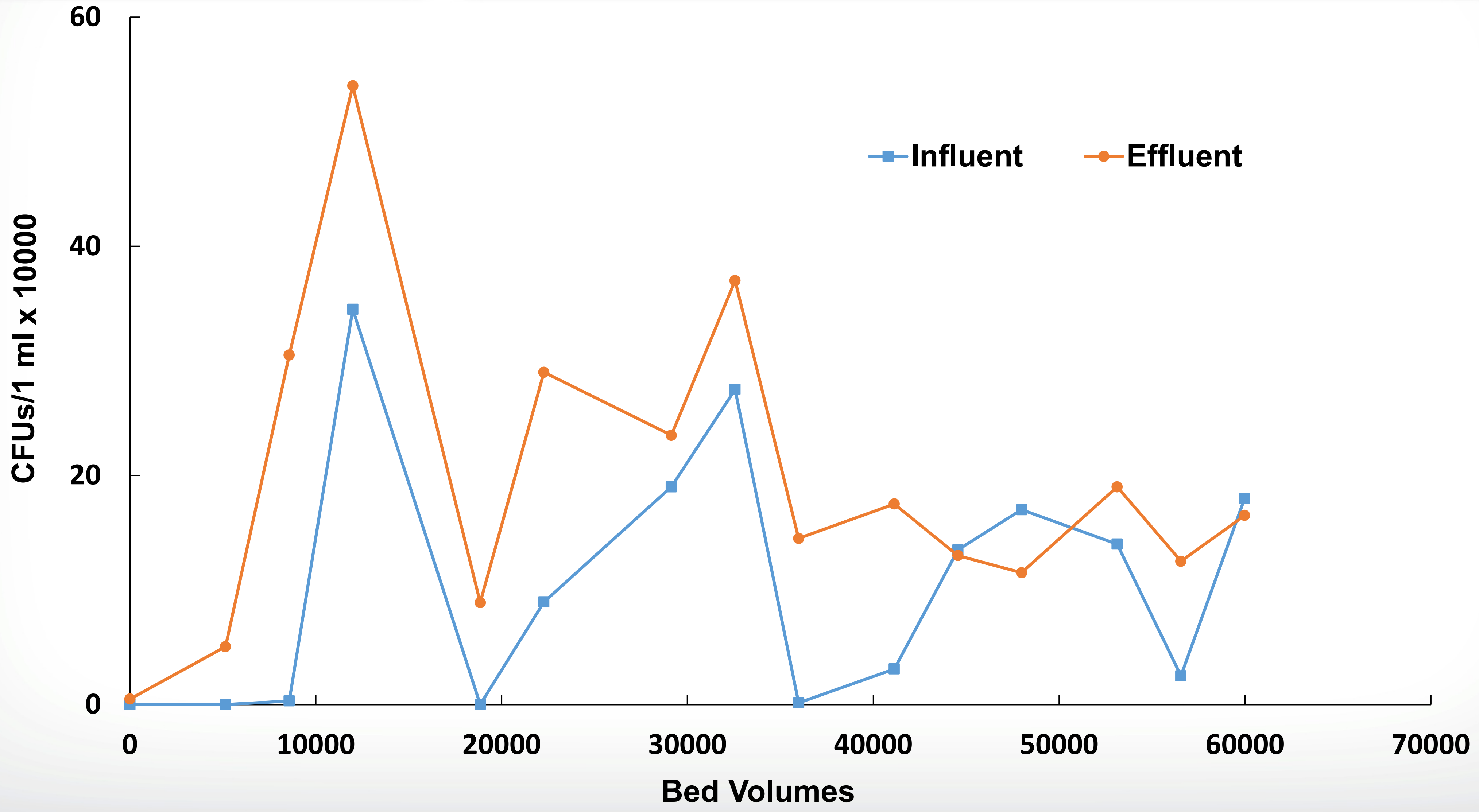
Sterile Techniques

- **Sterile techniques**
  - Autoclaving
  - Filtering (0.2 µm) GACI water collected from CCWRD
  - Teflon tubing, pump, pulse dampener and RSSCT apparatus
    - Cl_2 (10 mg L^{-1})
    - Ascorbic acid purge of Cl_2 (25 mg L^{-1})
    - Milli-Q for 4 days
- **R2A HPCs**
  - Plate counts taken 2-3 times a week
    - Influent and effluent

Partial Sterile RSSCT



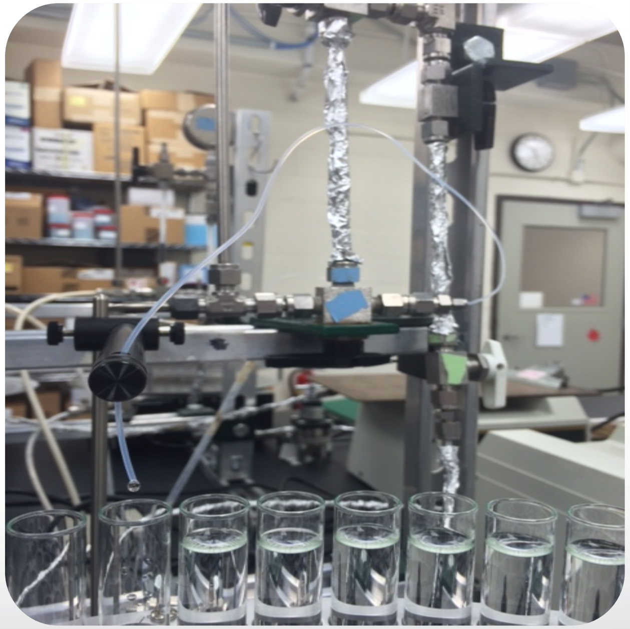
Partial Sterile RSSCT - HPCs



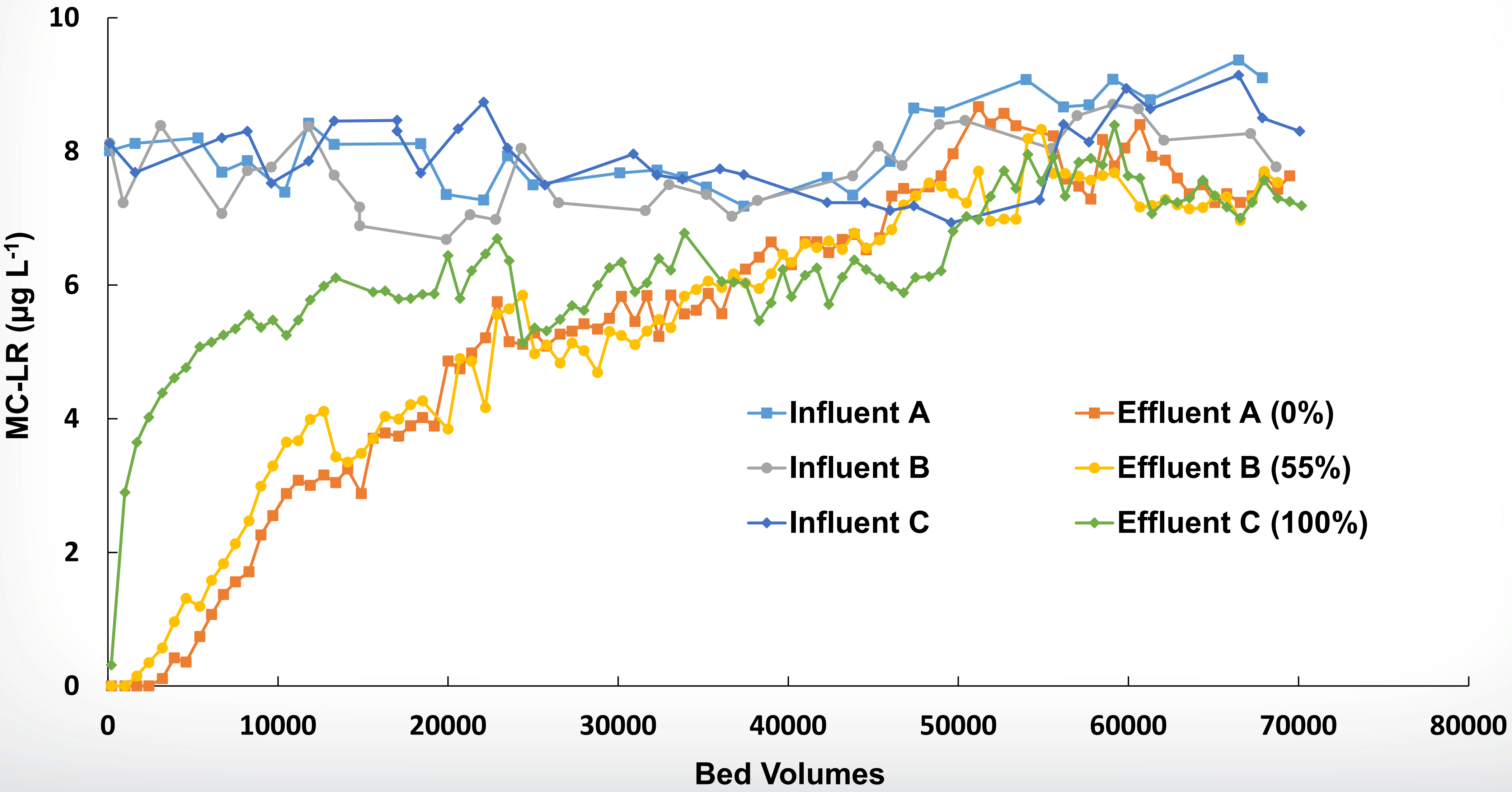
Preloaded RSSCTs

- **Preloaded RSSCTs**
  - Preloading the GAC after grinding to prevent overestimation
  - Design of RSSCTs
    - A – 0% preloaded (control)
    - B – 55% preloaded
    - C – 100% preloaded
  - Columns preloaded with GACI NOM
    - Assumptions based on previous TOC data and current UV254 data
      - NaN_3 contributes to UV254 absorbance!
  - Simulates real-world scenario

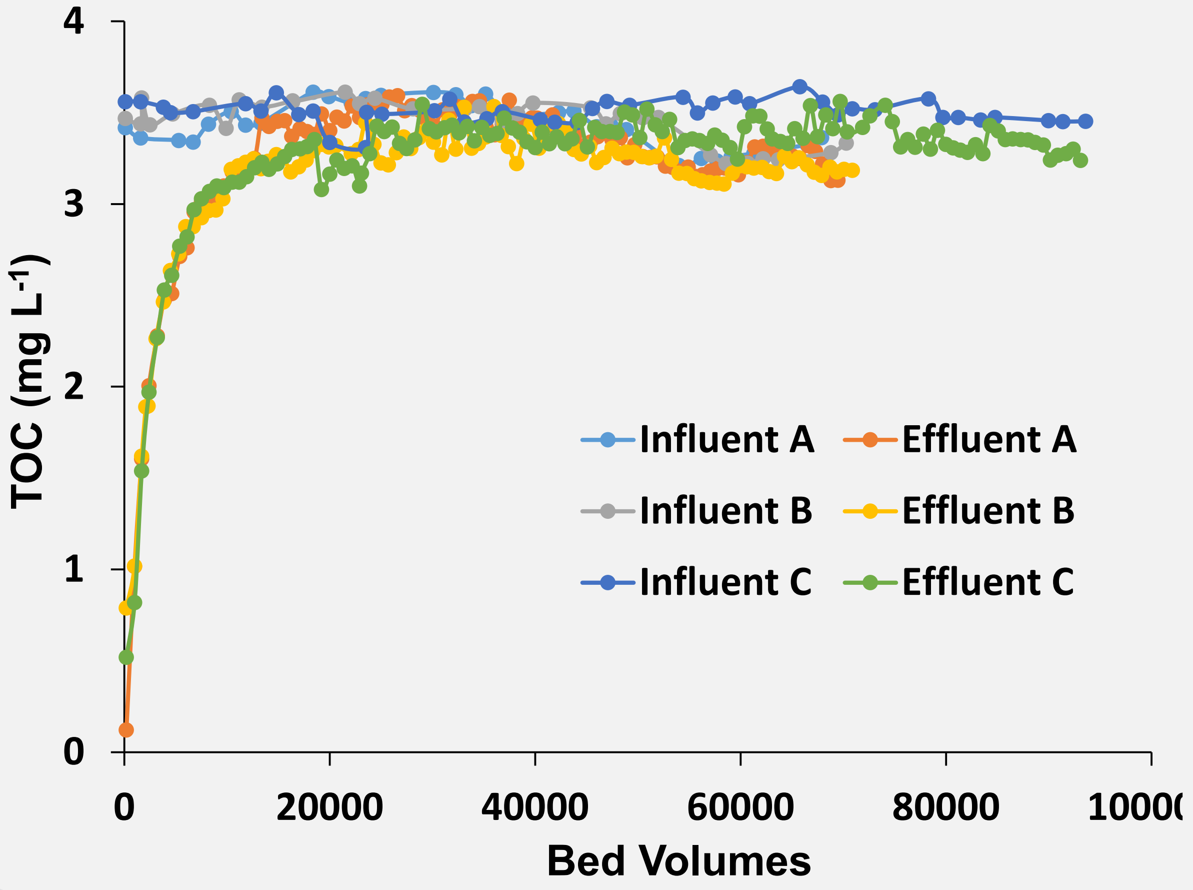
- **Preloading**
  - RSSCT B
    - 55% preloaded with TOC at 2,100 BVs
  - RSSCT C
    - 100% preloaded with TOC at 22,900 BVs

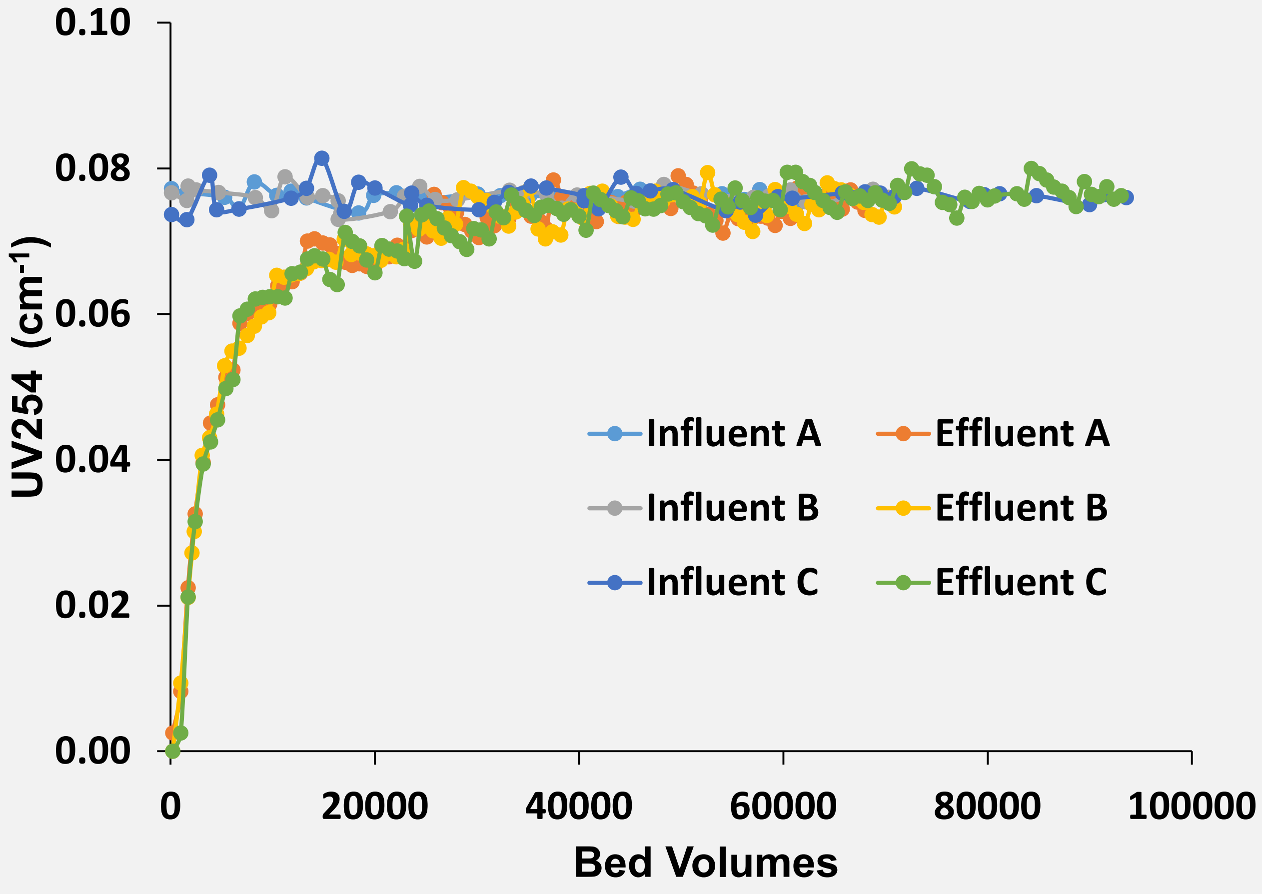


Preloaded RSSCTs

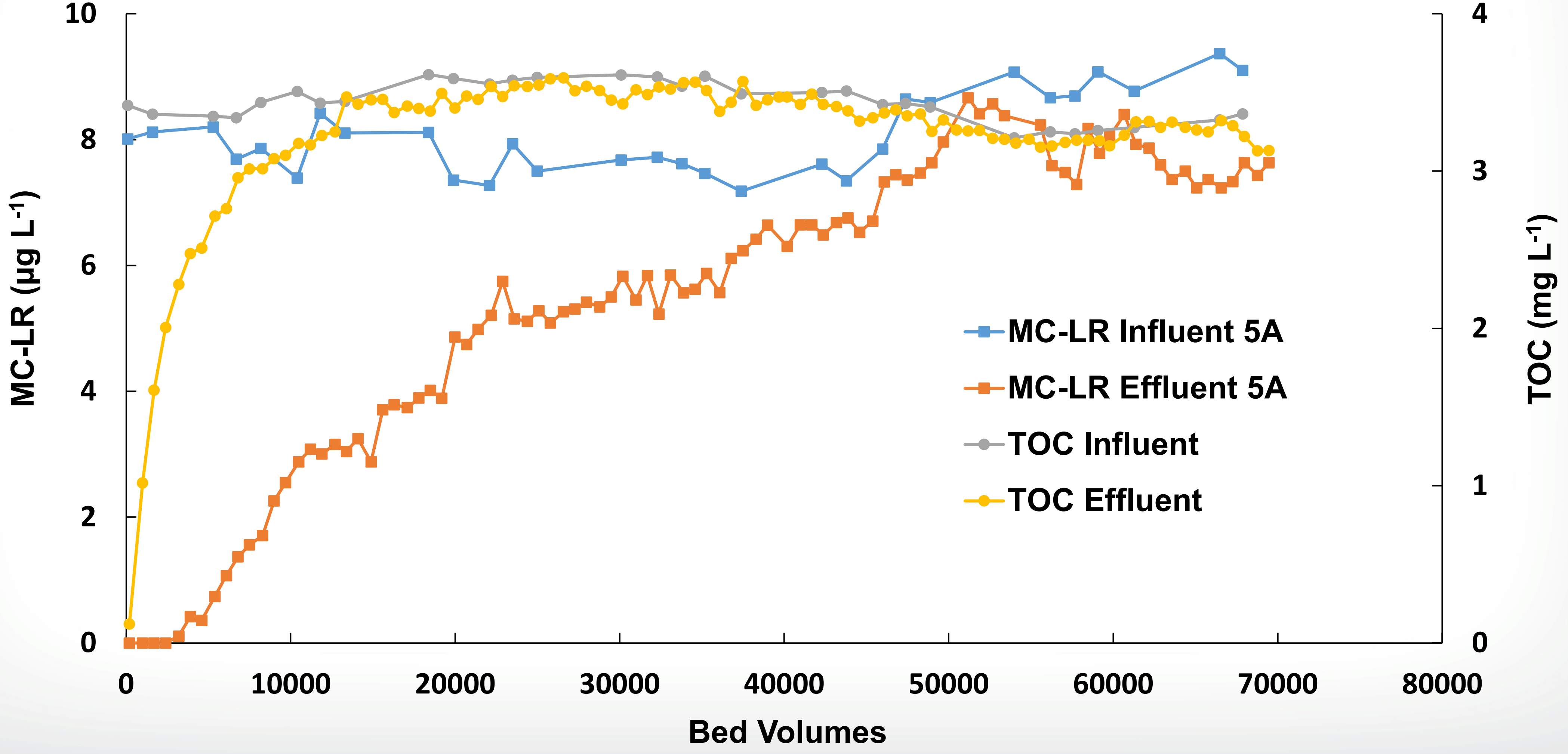


TOC and UV254





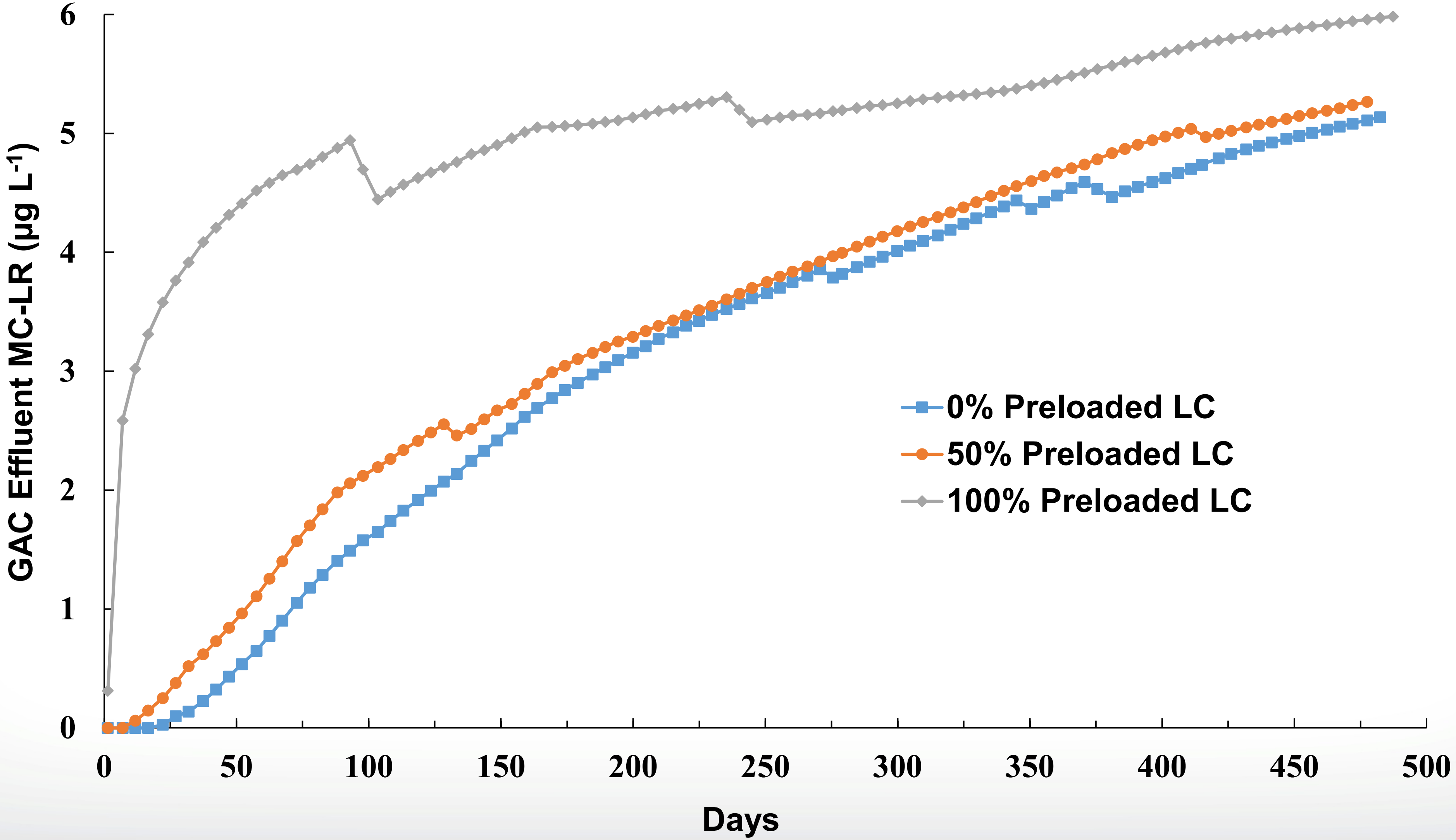
TOC/MC-LR Breakthrough



Biological Parameters

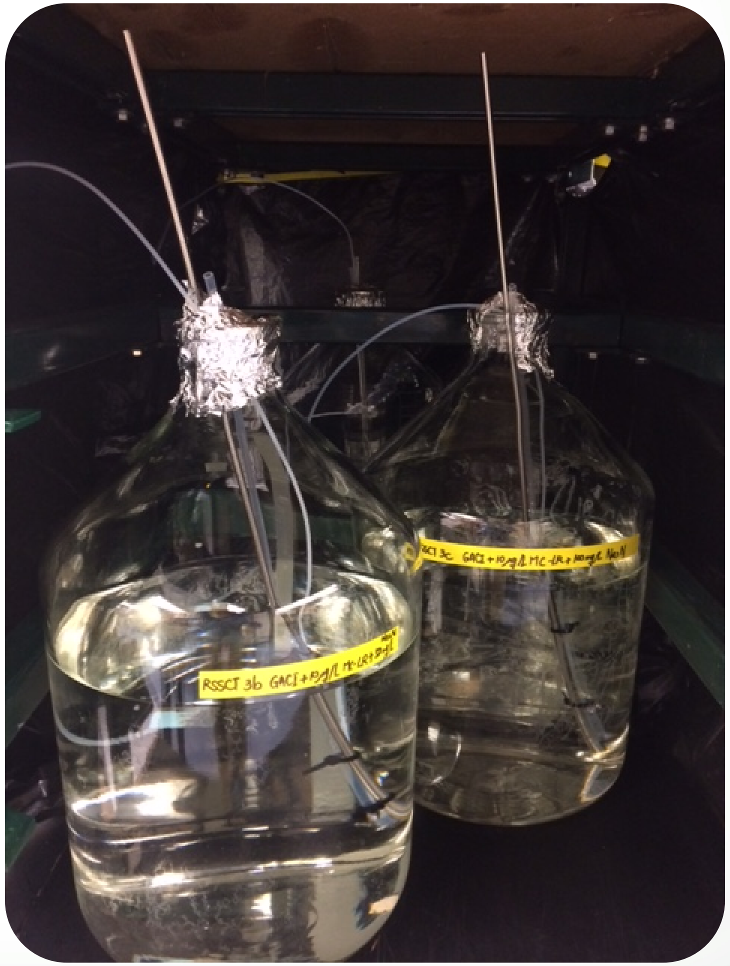
	Temp. (°C)	Lag Phase (days)	k (h^{-1})
Initial	25	6.86	0.07
Low Temp.	5	5.78	0.04
Confirmation	25	8.63	0.05
Inhibition	25	12.75	0.05
Mean	-	8.51	0.05

Practical Implications – Full Scale Simulation



Practical Implications – Biodegradation

- Evaluated simulated biodegradation in full scale using EBCT = 10 min
- Biodegradation within the GAC column reduces MC-LR by 0.03 µg L^{-1}
- Biodegradation within the GAC column is likely not significant at measured rates
- However, in presence of biological activity from WTP intake to distribution system, perhaps some significant biodegradation

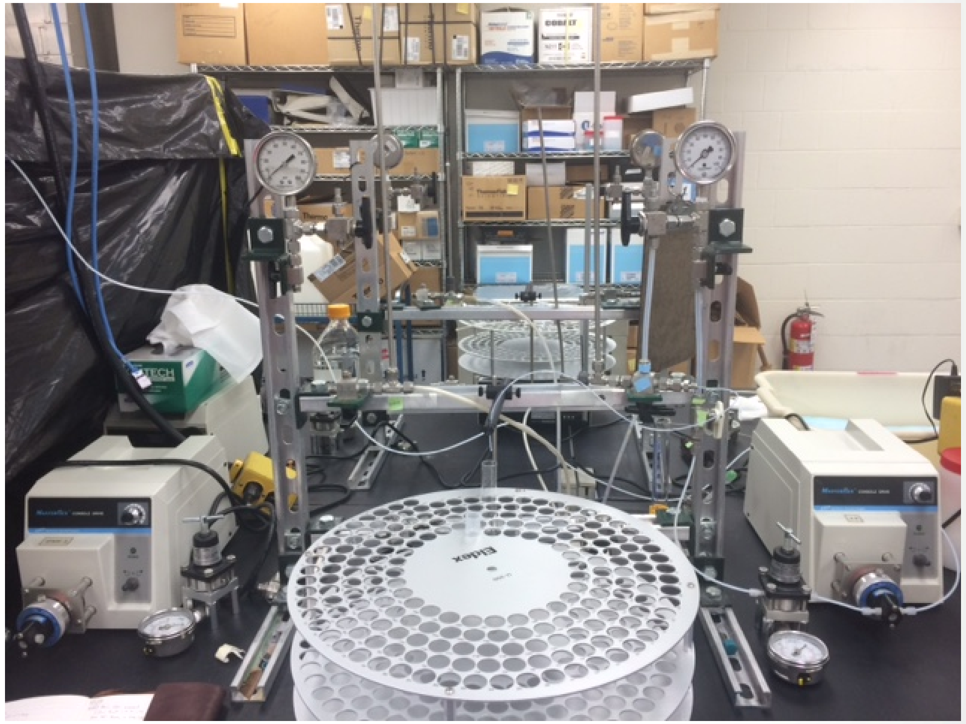


Conclusions

- RSSCTs appear effective and inexpensive for simulating GAC processes with MC-LR
- RSSCTs with natural source water complicated by biodegradation - countermeasures required
- Adsorption only RSSCTs resulted in gradual breakthrough
  - Flat MC-LR breakthrough curve
  - Exceeded OH EPA action level quickly (0.3 µg L^{-1})
- Competitive inhibition (NOM/MC-LR) - NOM preloaded GAC impacts adsorption of MC-LR
- 100% NOM preloaded column resulted in fast and steep MC-LR breakthrough
- However, 50% NOM preload not much different than control
- Biodegradation rates observed in experimental influents relatively insignificant for GAC EBCT

Future Research

- Pilot scale study
- BET/pore surface area analysis on the GAC collected from the water utility
  - Size and distribution of the pores
- Additional investigation of competitive adsorption
- Multiple toxins



Acknowledgments

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