



Evaluation of Distribution System Chemical Water Quality During a Free Chlorine Conversion

Presenter:

David G. Wahman¹

Co-authors:

Matthew T. Alexander², Peyton Woodruff¹, Jatin H. Mistry³, Helen Y. Buse¹,
Christy Muhlen¹, Darren A. Lytle¹, and Jonathan G. Pressman¹

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September 13, 2023

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2020 EPA Regional Applied Research Effort (RARE) Project

- Monitoring **Microbial** and **Chemical** Drinking Water Quality During a Chlorine Maintenance Period

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- Additional EPA project team members:

Chemical

Matthew Alexander
Darren Lytle
Christy Muhlen
Jonathan Pressman
David Wahman
Peyton Woodruff

Microbial

Maura Donohue
Chelsea Hintz
Dawn King
Jingrang Lu
Nathan Sienkiewicz
Ian Struewing



Background

- Chloramines (free chlorine + free ammonia)
 - 2nd most used secondary disinfectant
 - Reduce *regulated* disinfection byproducts (DBPs)
 - Greater stability than free chlorine?
 - Add ammonia in excess to form & ammonia releases during decay/demand

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 - Nitrification risk (ammonia → nitrite → nitrate)
 - Ammonia oxidizing microorganisms (competition of growth versus disinfection)

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 - Ammonia oxidizing microorganisms (competition of growth versus disinfection)
- Free chlorine conversion (FCC)
 - Control nitrification (planned or operational response)
 - Chloramines → free chlorine (~1–2 months) → chloramines
 - Regulated DBP formation ↑ (compliance sampling outside FCC → implications?)
 - Other unintended consequences (e.g., Δ pH or metals)

Objective – Chemical

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 - Greater spatial & temporal coverage than published studies
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- 5. Metals (orthophosphate, copper, lead, iron, & zinc)

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- 24 MGD surface water (97,000 served)
 - 3.3–4.4 mg C/L total organic carbon (TOC)
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Previous RARE (SW-2)

ASCE Journal of Environmental Engineering (2023)

[https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0002062](https://doi.org/10.1061/(ASCE)EE.1943-7870.0002062)

Investigation of Chloramines, Disinfection Byproducts, and Nitrification in Chloraminated Drinking Water Distribution Systems

Gulizhaer Abulikemu¹; Jatin H. Mistry²; David G. Wahman³; Matthew T. Alexander⁴; Alison R. Kennicutt⁵; Jacob D. Bollman⁶; and Jonathan G. Pressman⁷

Water Research (2021)

<https://doi.org/10.1016/j.watres.2021.117689>

Chloramine Concentrations within Distribution Systems and Their Effect on Heterotrophic Bacteria, Mycobacterial Species, and Disinfection Byproducts

Stacy Pfaller^a, Dawn King^a, Jatin H. Mistry^c, Matthew Alexander^b, Gulizhaer Abulikemu^d, Jonathan G. Pressman^a, David G. Wahman^a, Maura J. Donohue^a

Water Research (2021)

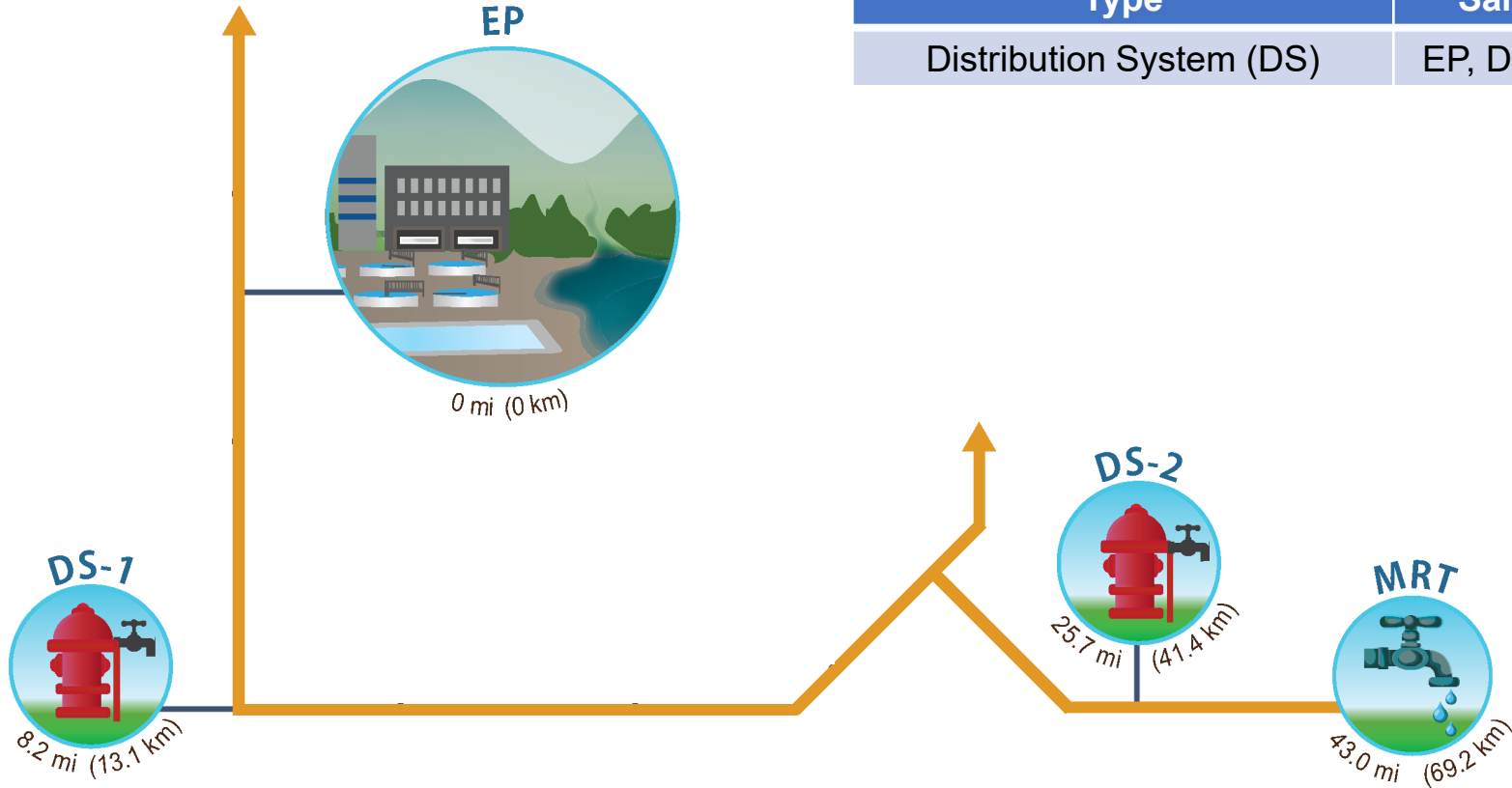
<https://doi.org/10.1016/j.watres.2021.117571>

Legionella and other opportunistic pathogens in full-scale chloraminated municipal drinking water distribution systems

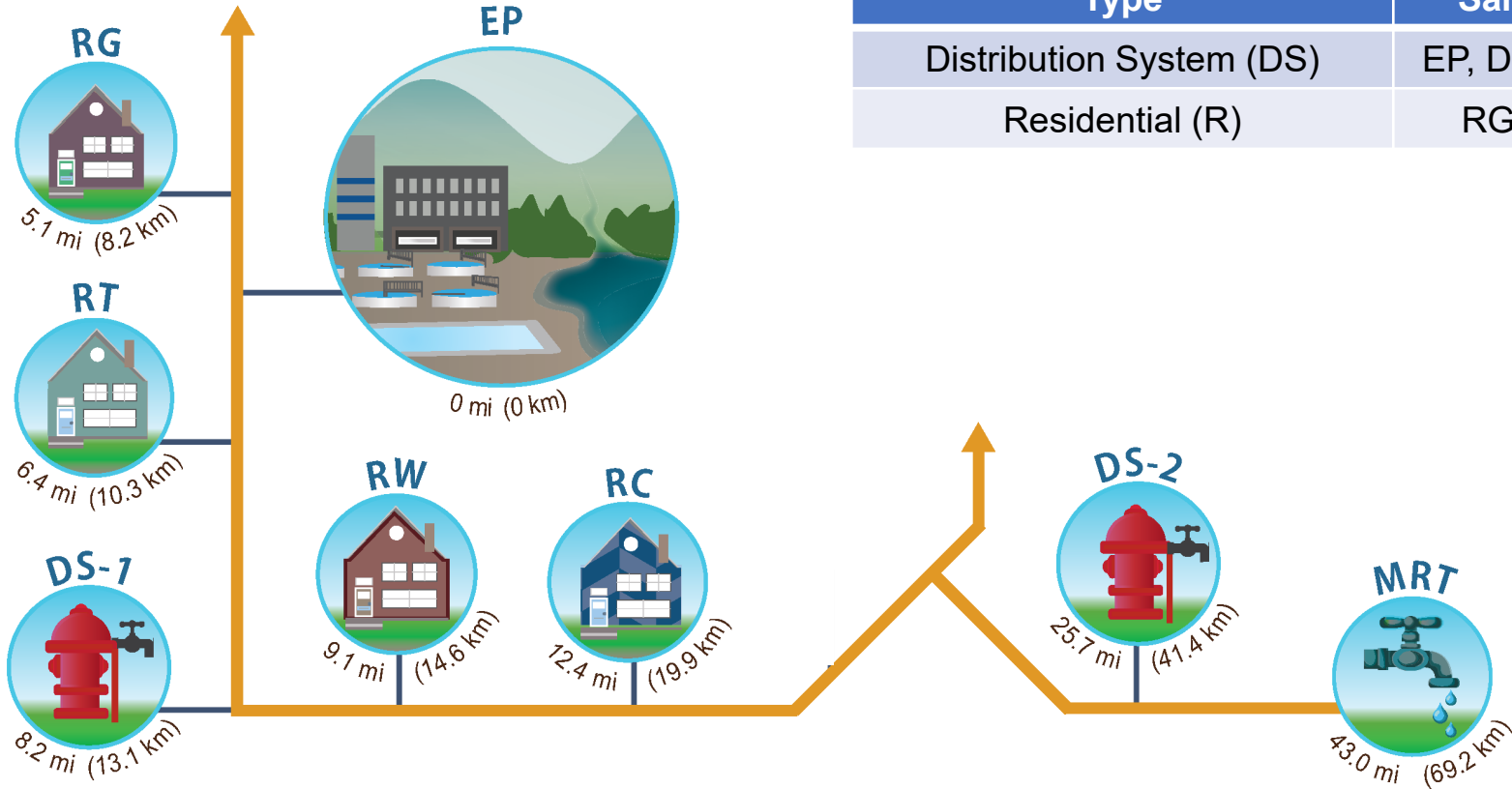
Chiqian Zhang^a, Ian Struewing^b, Jatin H. Mistry^c, David G. Wahman^b, Jonathan Pressman^b, Jingrang Lu^b

Sample Locations

Type	Sample Locations
Distribution System (DS)	EP, DS-1, DS-2, & MRT

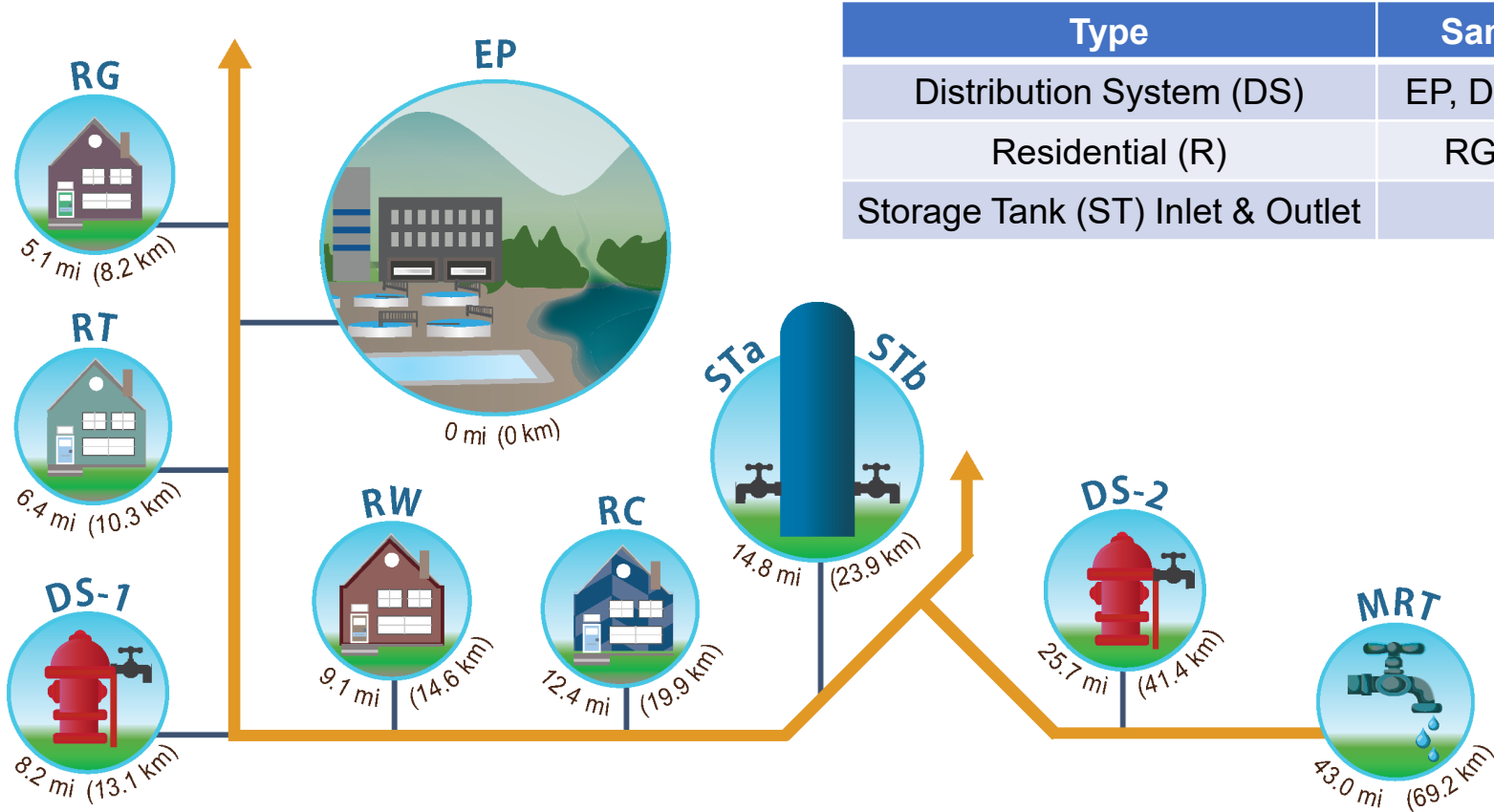


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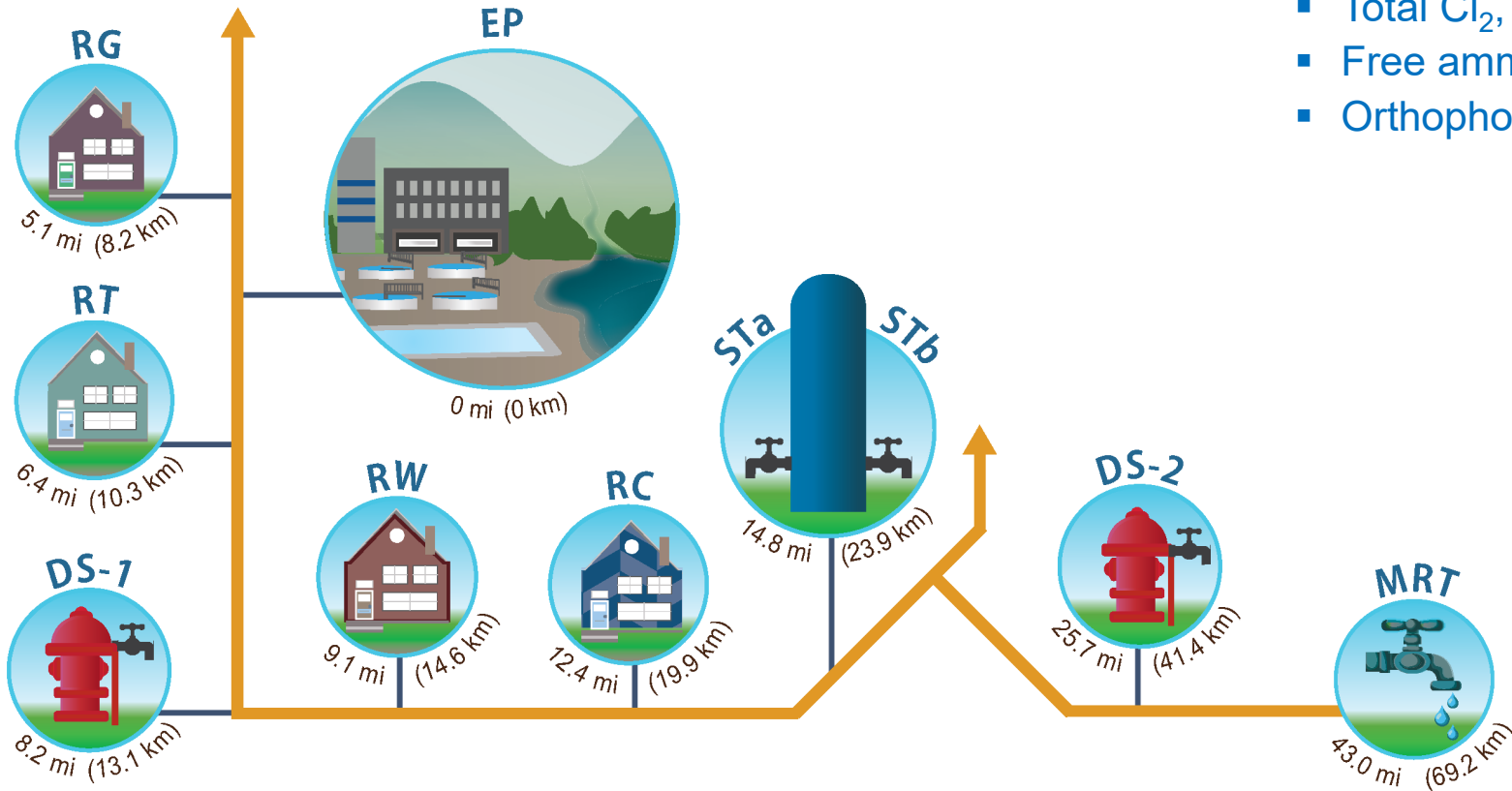
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Storage Tank (ST) Inlet & Outlet	STa & STb

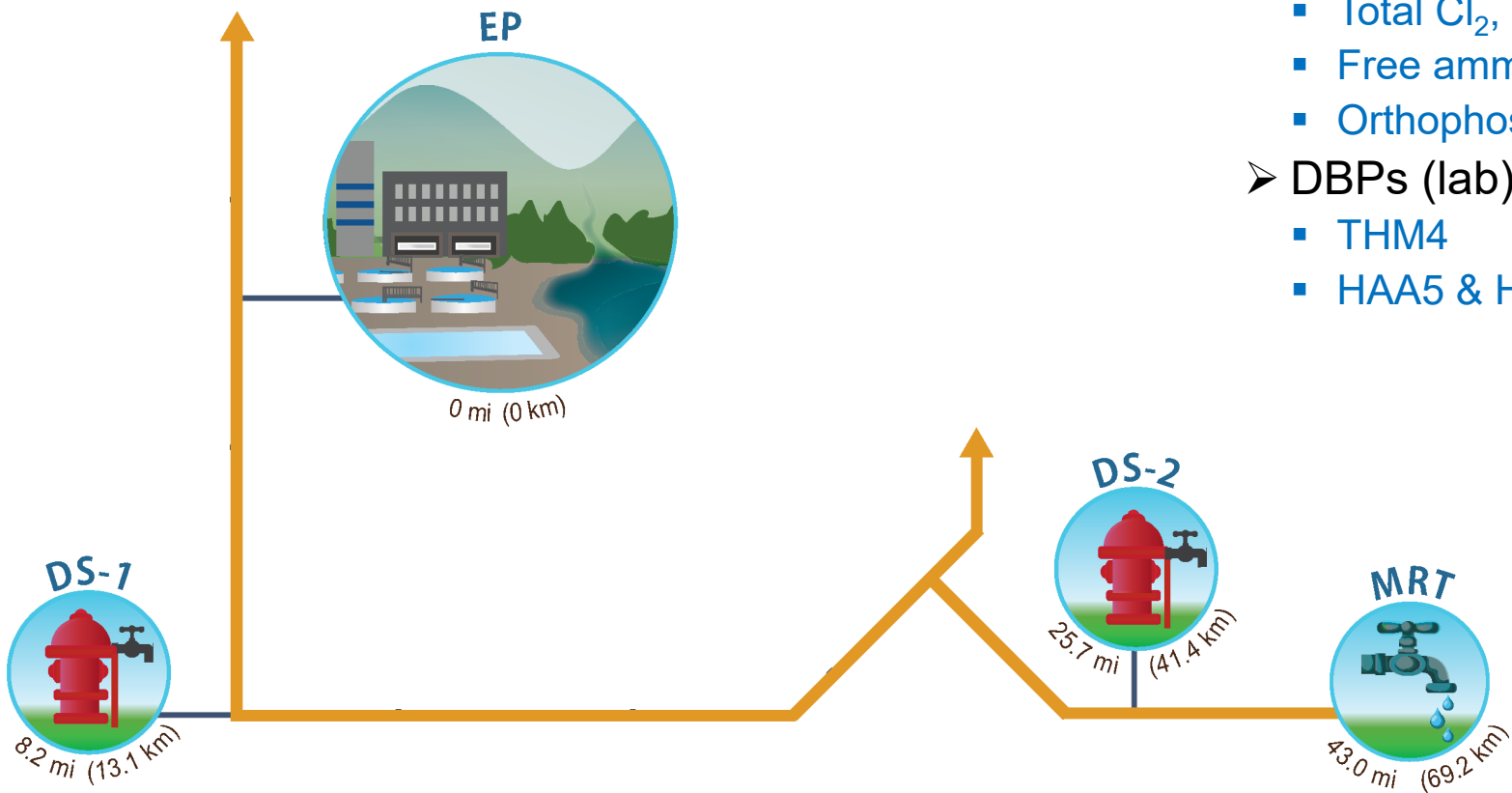
Sample Activities

- All samples (field)
- Temperature & pH
 - Total Cl_2 , mono, & free Cl_2
 - Free ammonia & nitrite
 - Orthophosphate



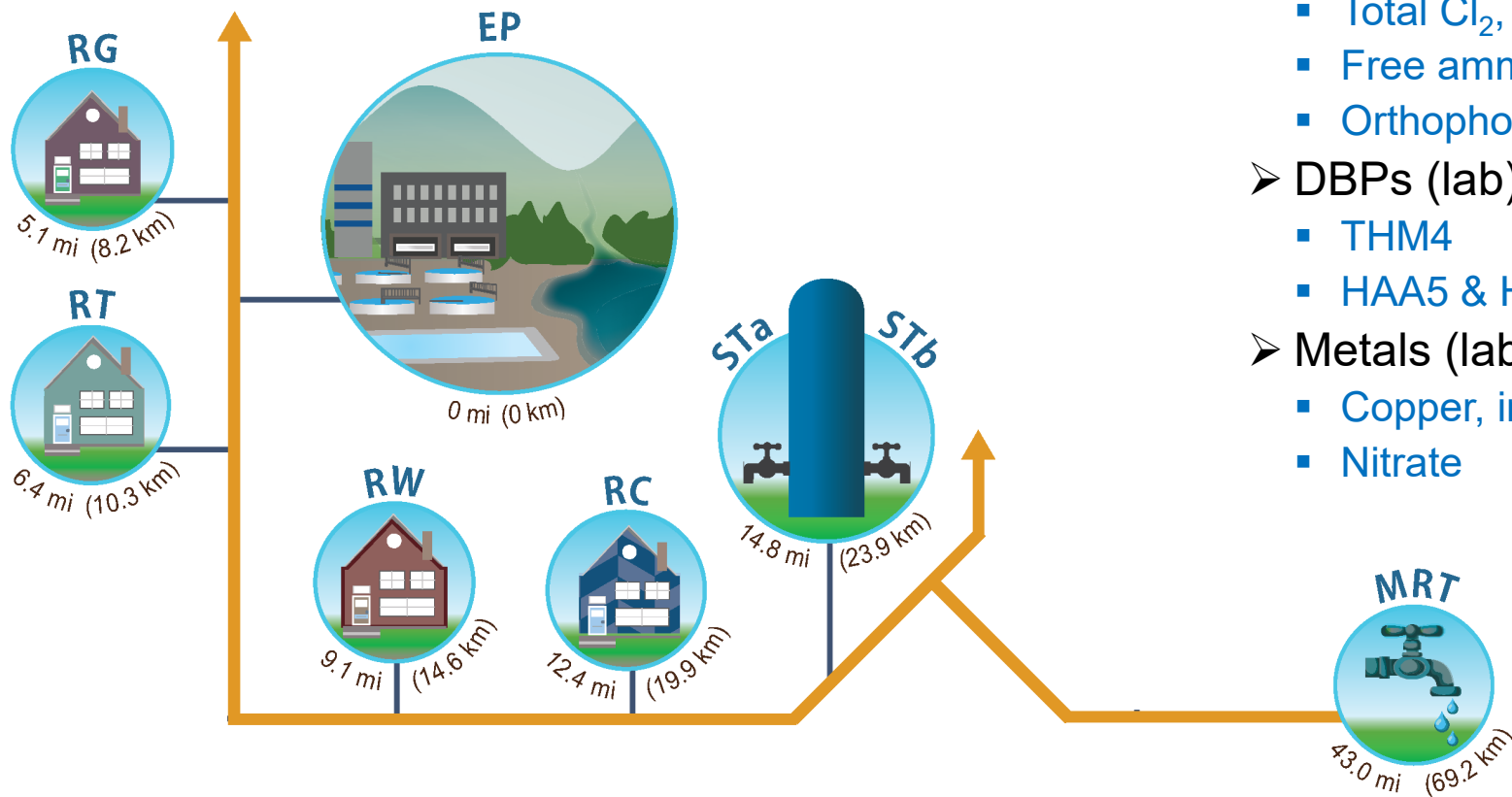
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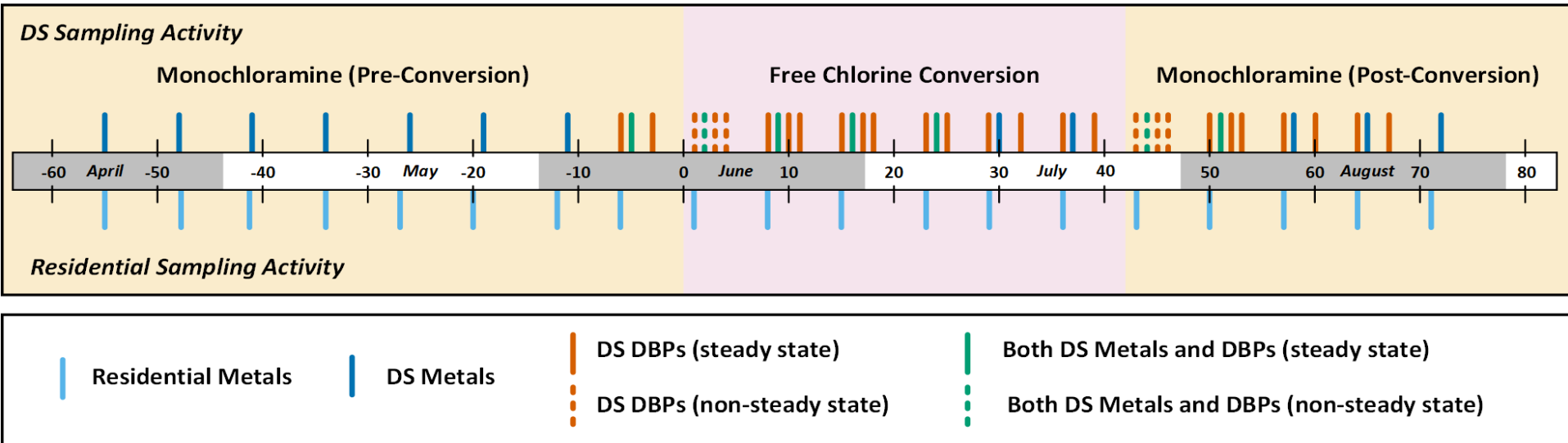


Sample Timeline (April to August 2021)

Day -55 (April 20)

Days 0 to 42 (June 14 to July 26)

Day 72 (August 25)

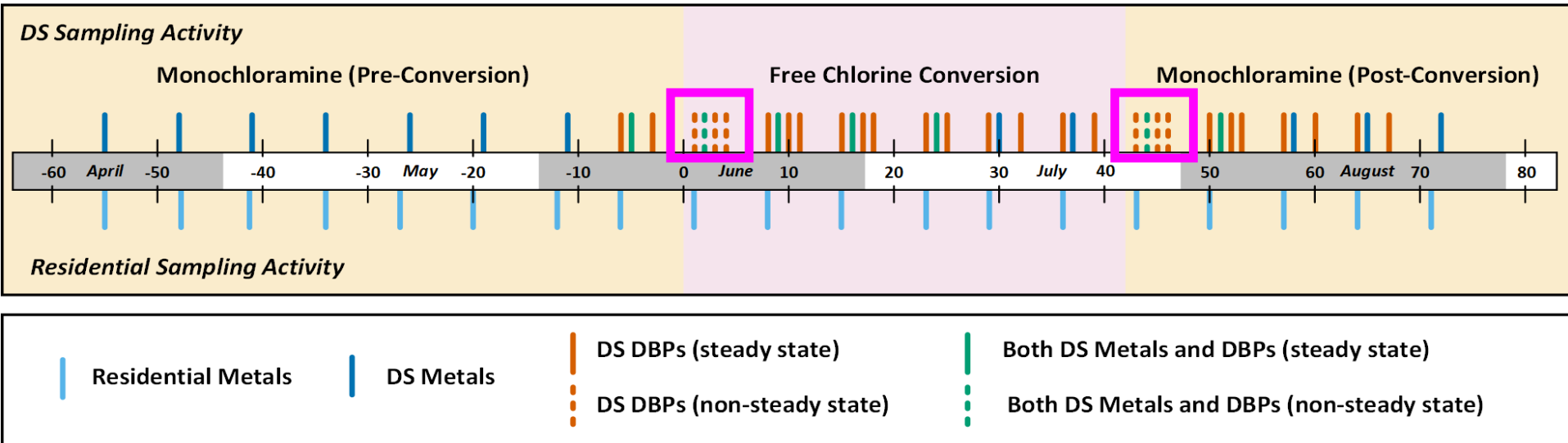


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➤ DS non-steady state

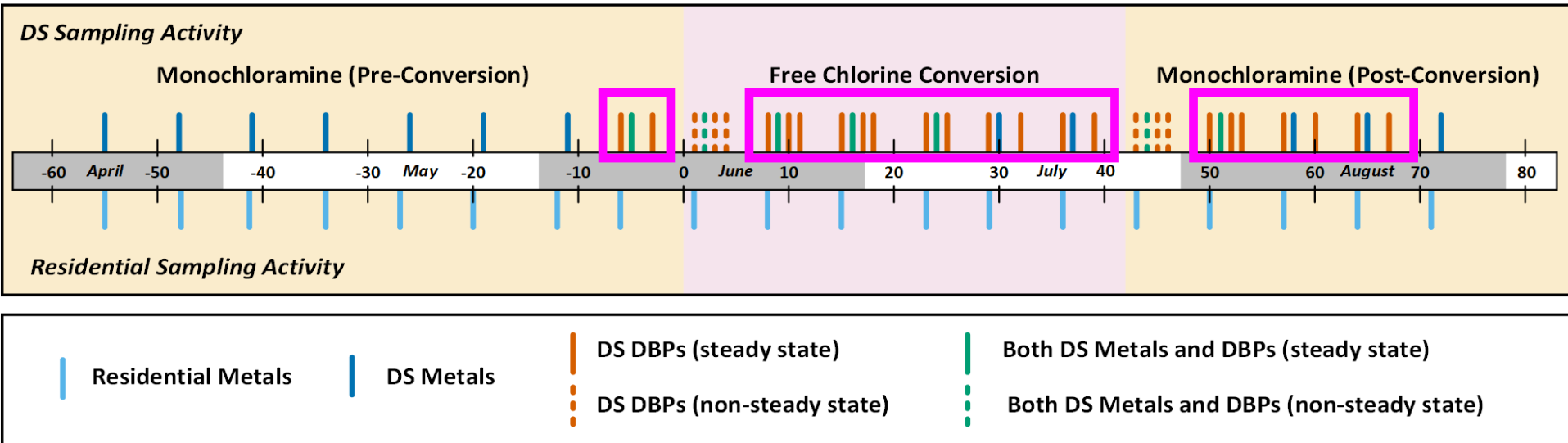
- Temporally variable data
- Shows temporal transients
- 4 days immediately after conversions

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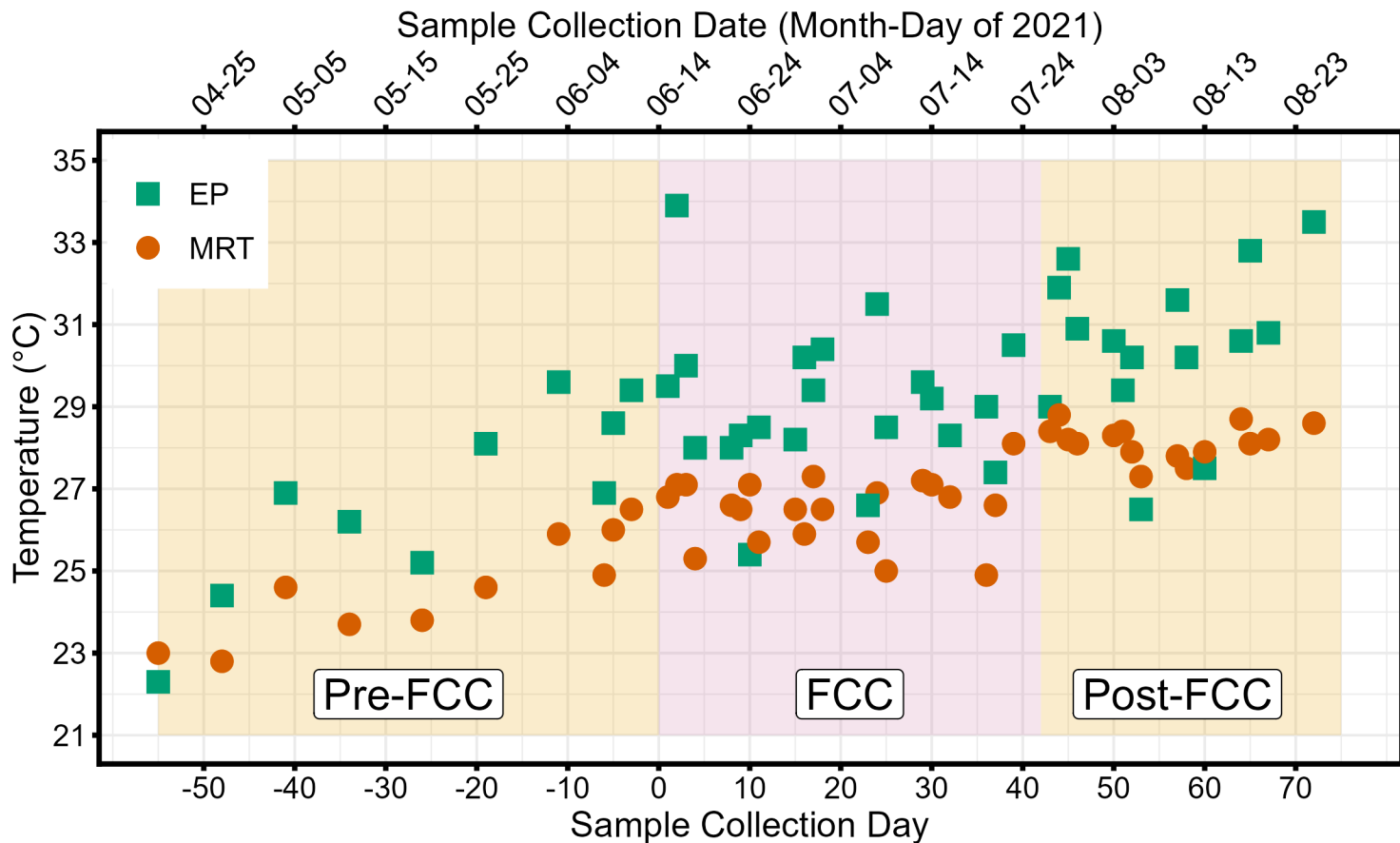
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➤ DS steady-state

- Relatively consistent data
- Averaged data
 - Pre-FCC (Days -6 to 0)
 - FCC (Days 8 to 39)
 - Post-FCC (Days 50 to 67)

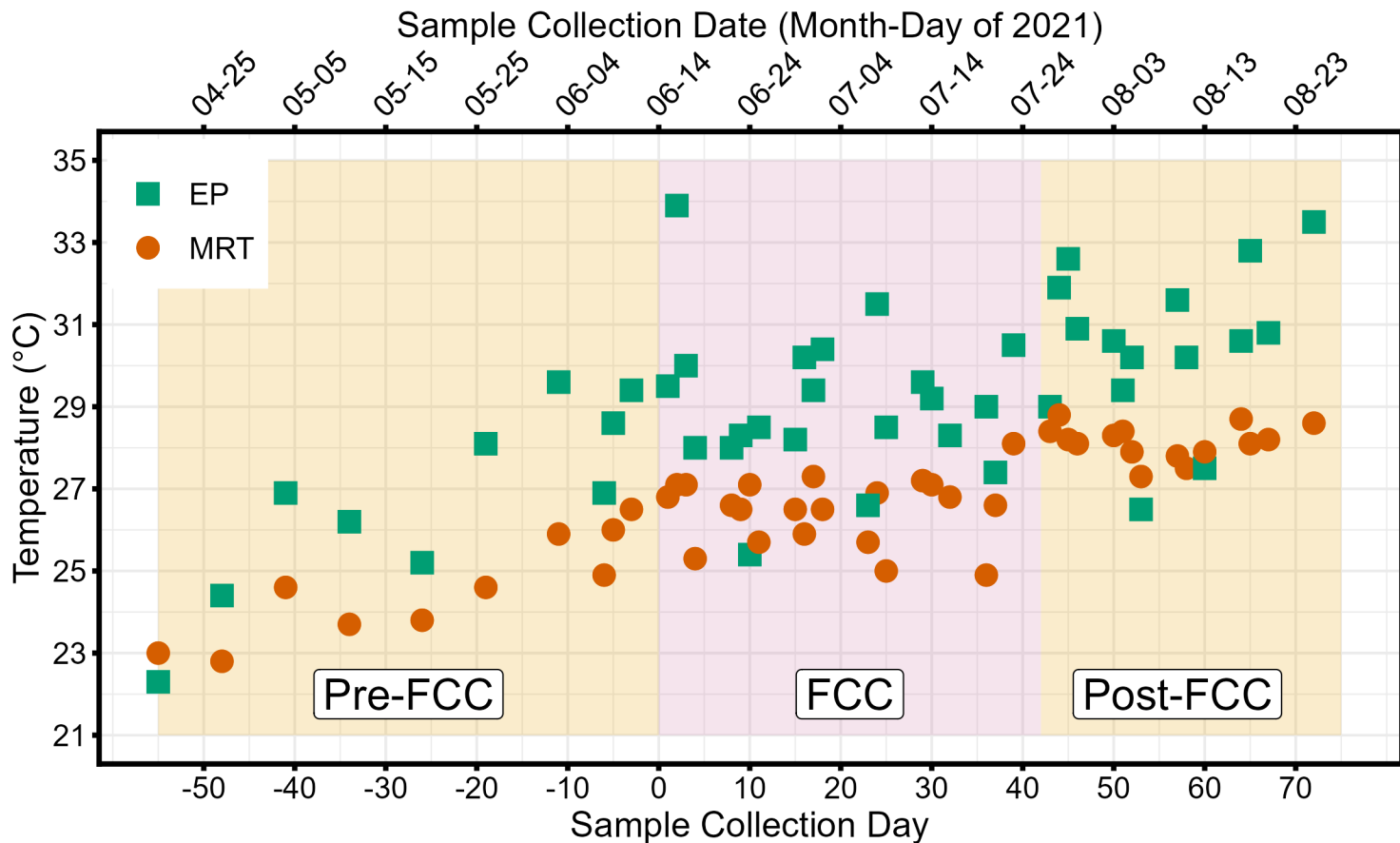
Temperature (All Samples)

➤ Seasonal ↑



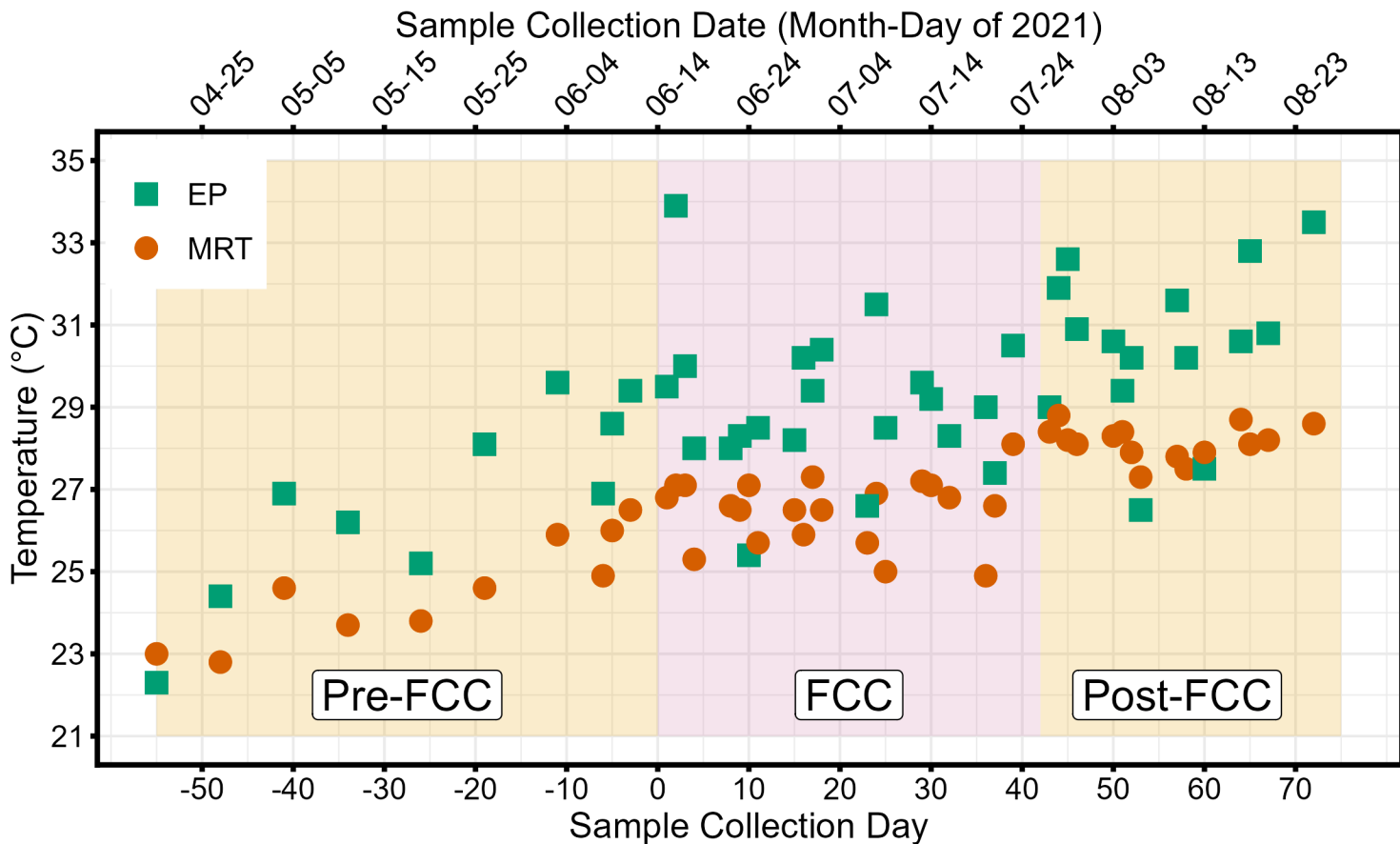
Temperature (All Samples)

- Seasonal ↑
- EP
 - 11°C ↑
 - More scatter



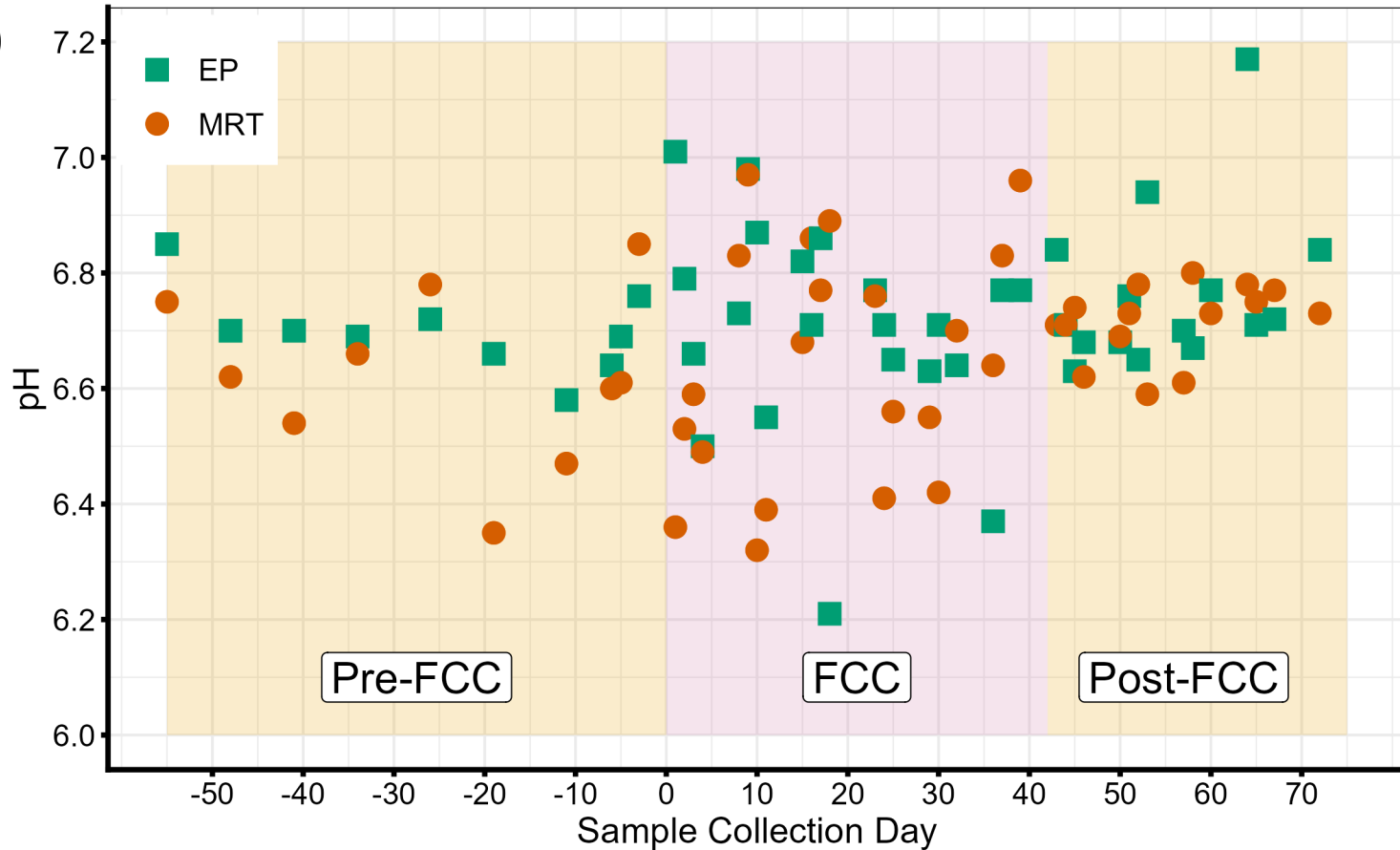
Temperature (All Samples)

- Seasonal ↑
- EP
 - 11°C ↑
 - More scatter
- MRT
 - 6°C ↑
 - Less scatter
 - General ↓ from EP



pH (All Samples)

➤ No trends (scatter)



pH (All Samples)

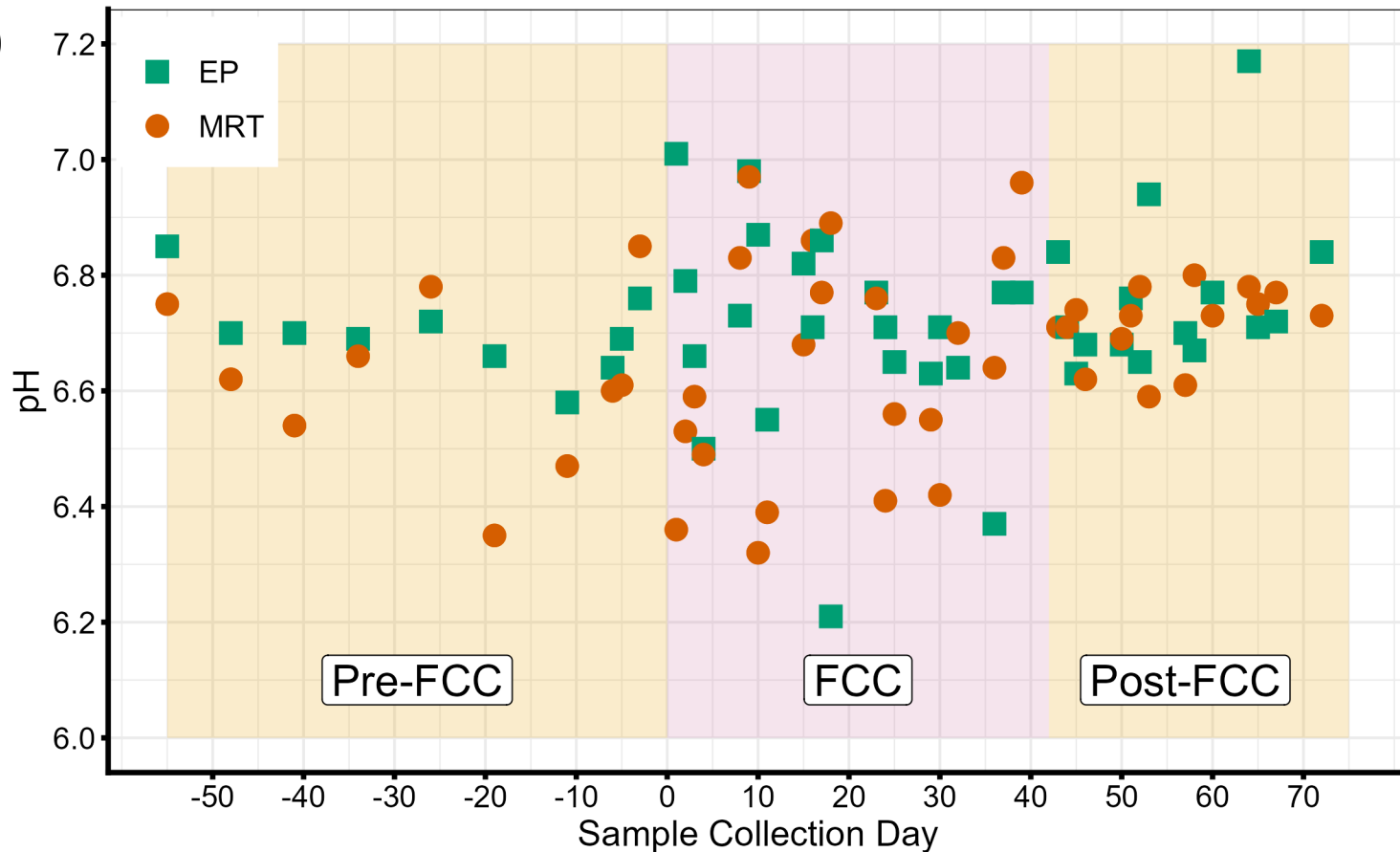
➤ No trends (scatter)

➤ EP

- pH 6.5–7.0

- Less variable

- FCC ↑ variability



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➤ EP

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- Less variable

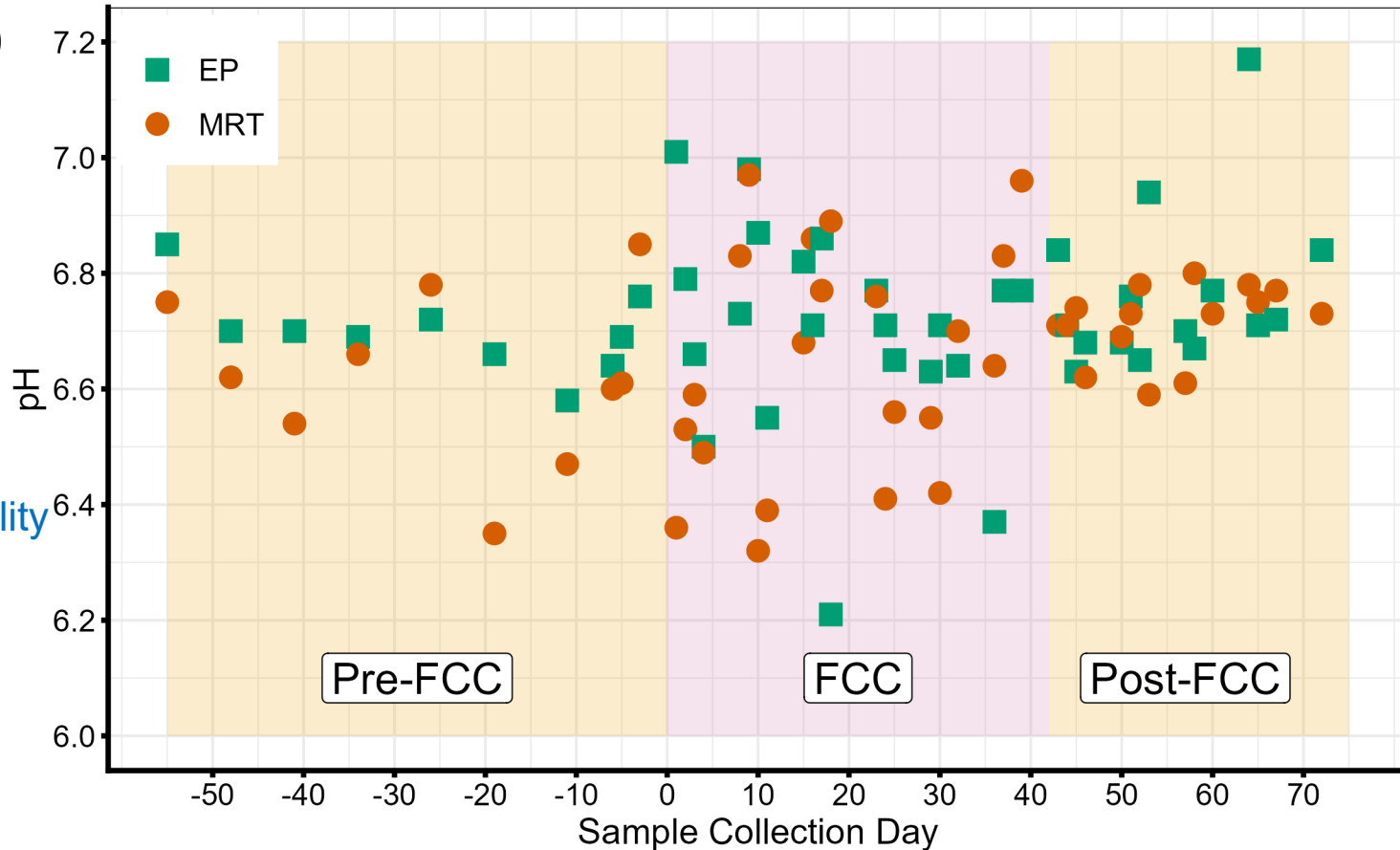
- FCC ↑ variability

➤ MRT

- pH 6.3–7.0

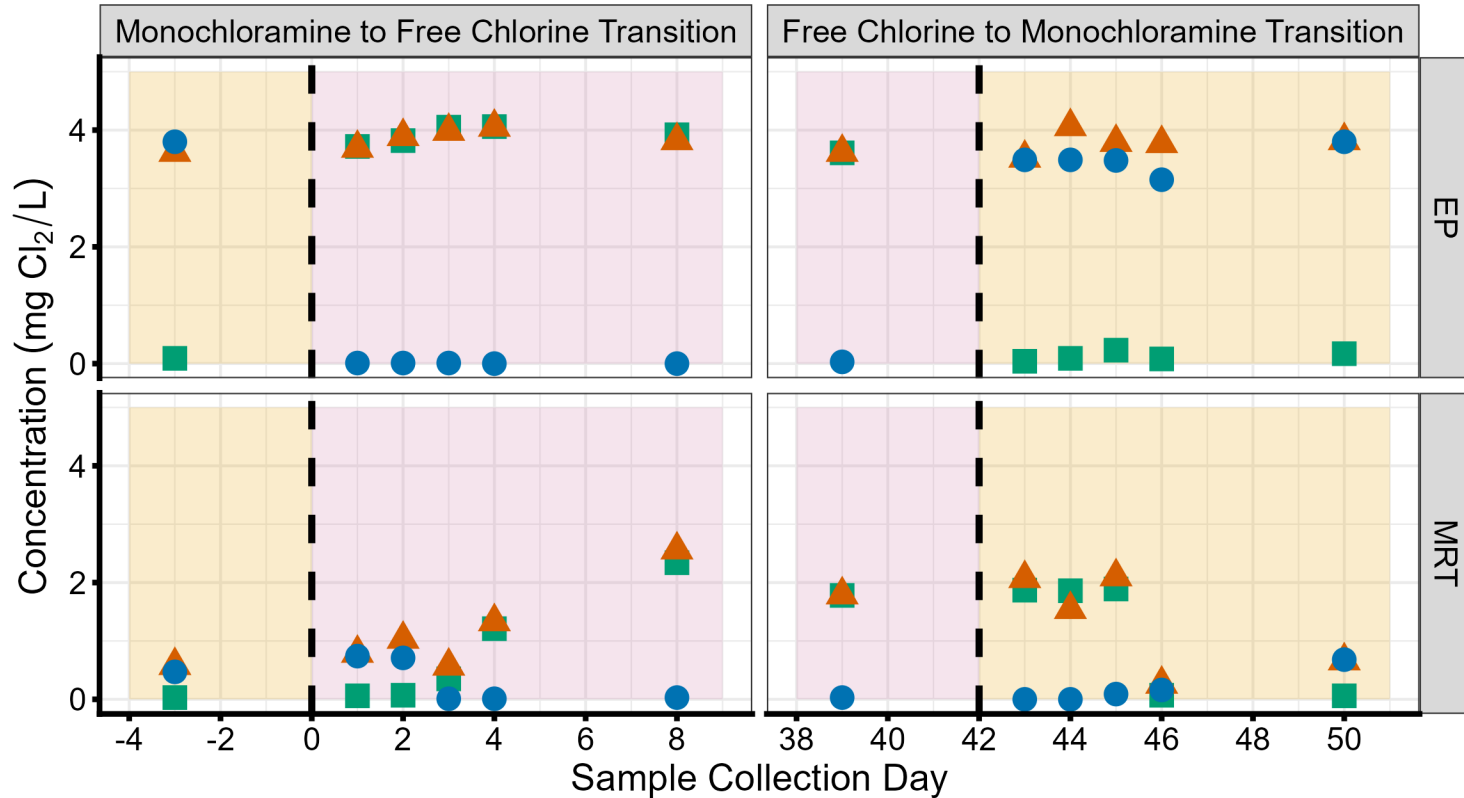
- More variable

- Post-FCC ↓ variability



Disinfectants (Non-Steady State)

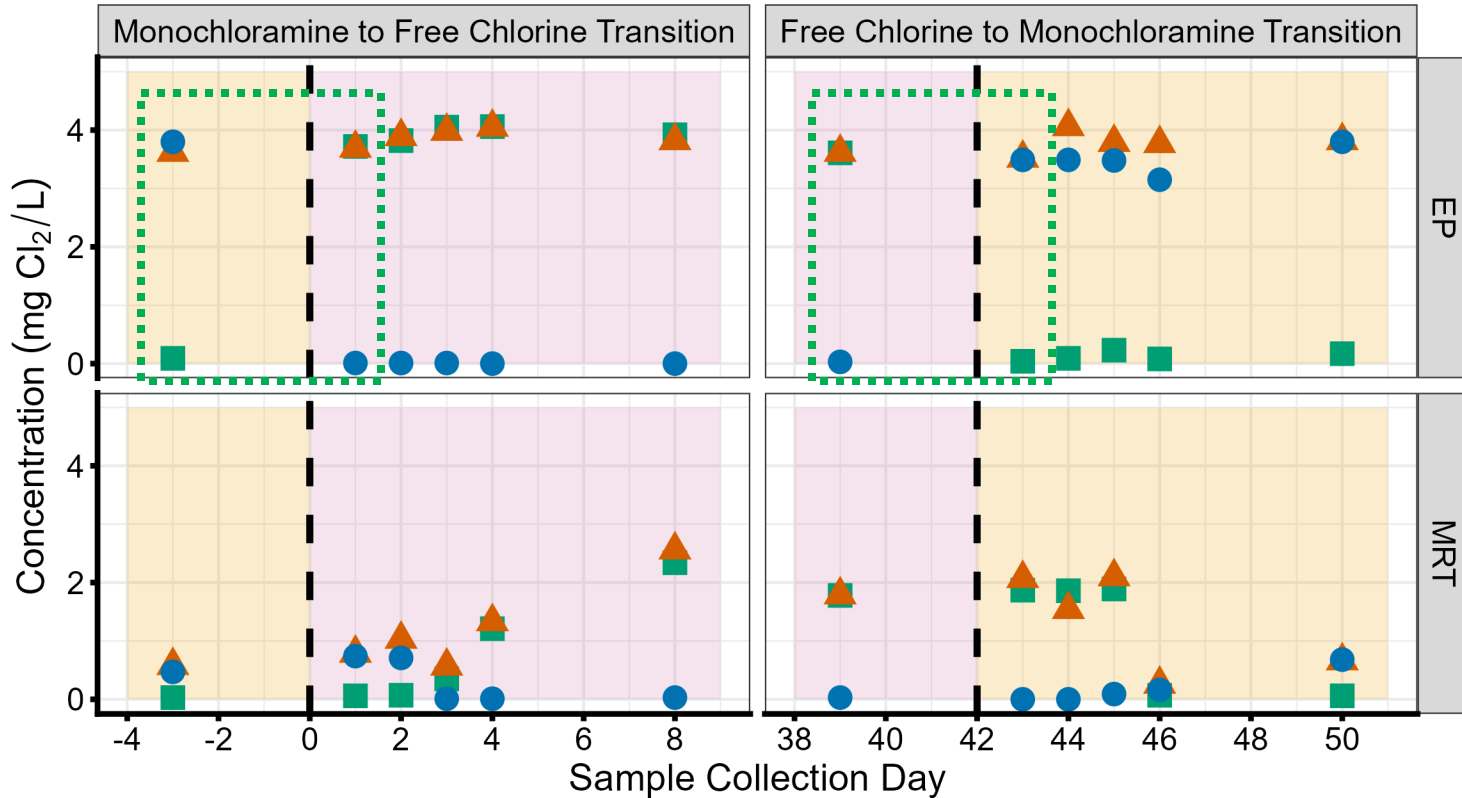
■ Free Chlorine ● Monochloramine ▲ Total Chlorine



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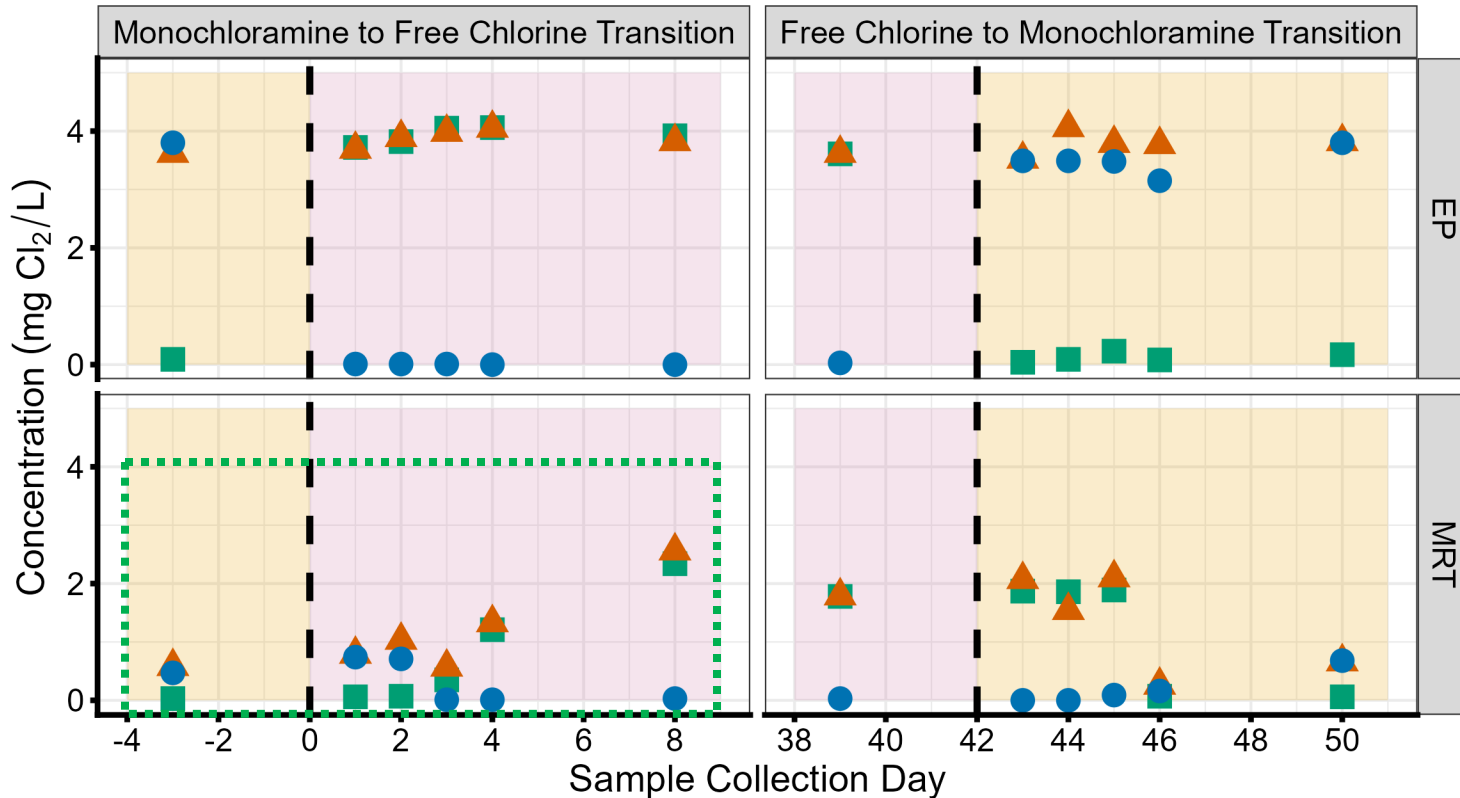
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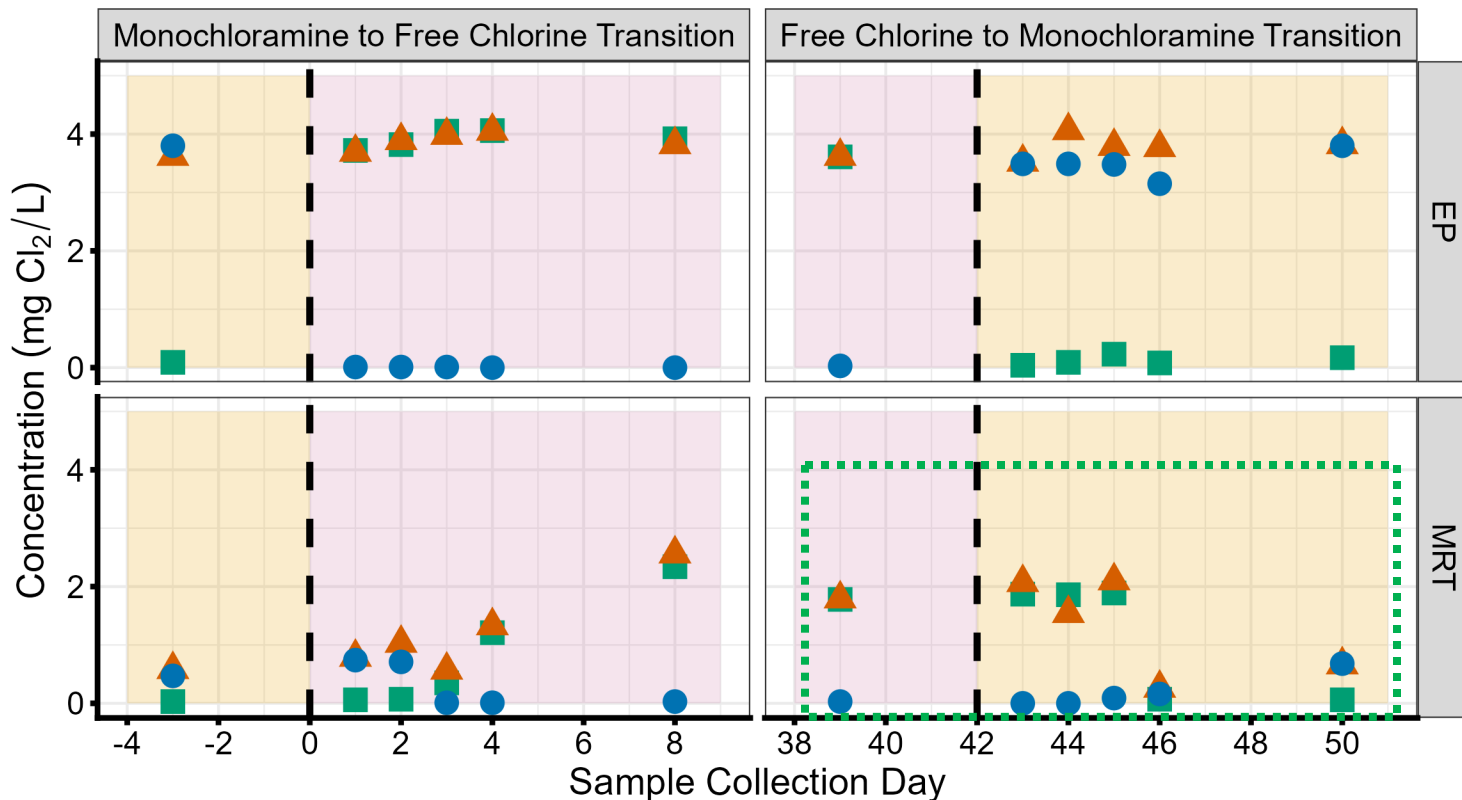
- EP → immediate Δ
- MRT (mono to free)
 - free (3–4 days)
 - stable (8 days)
 - free > mono



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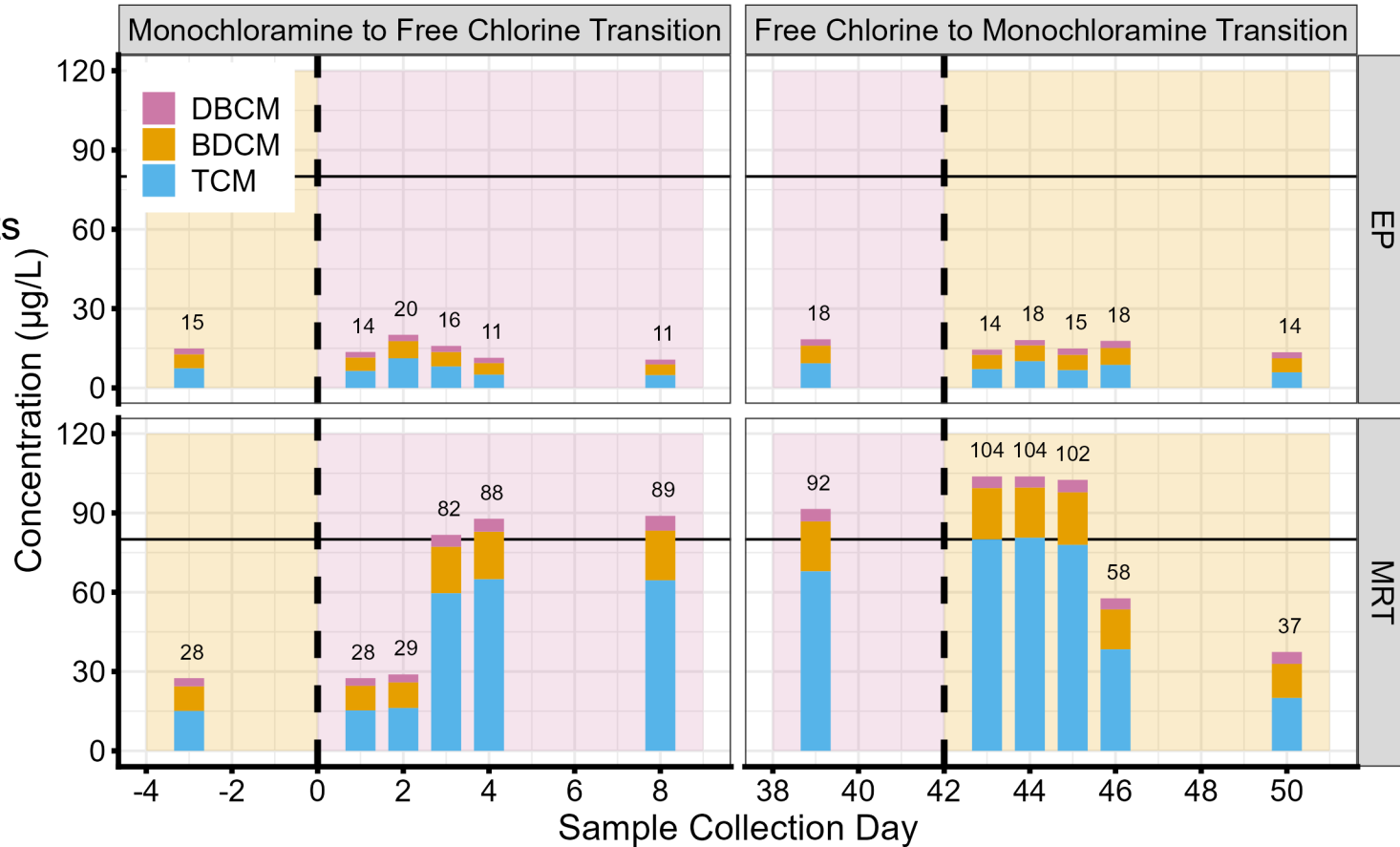
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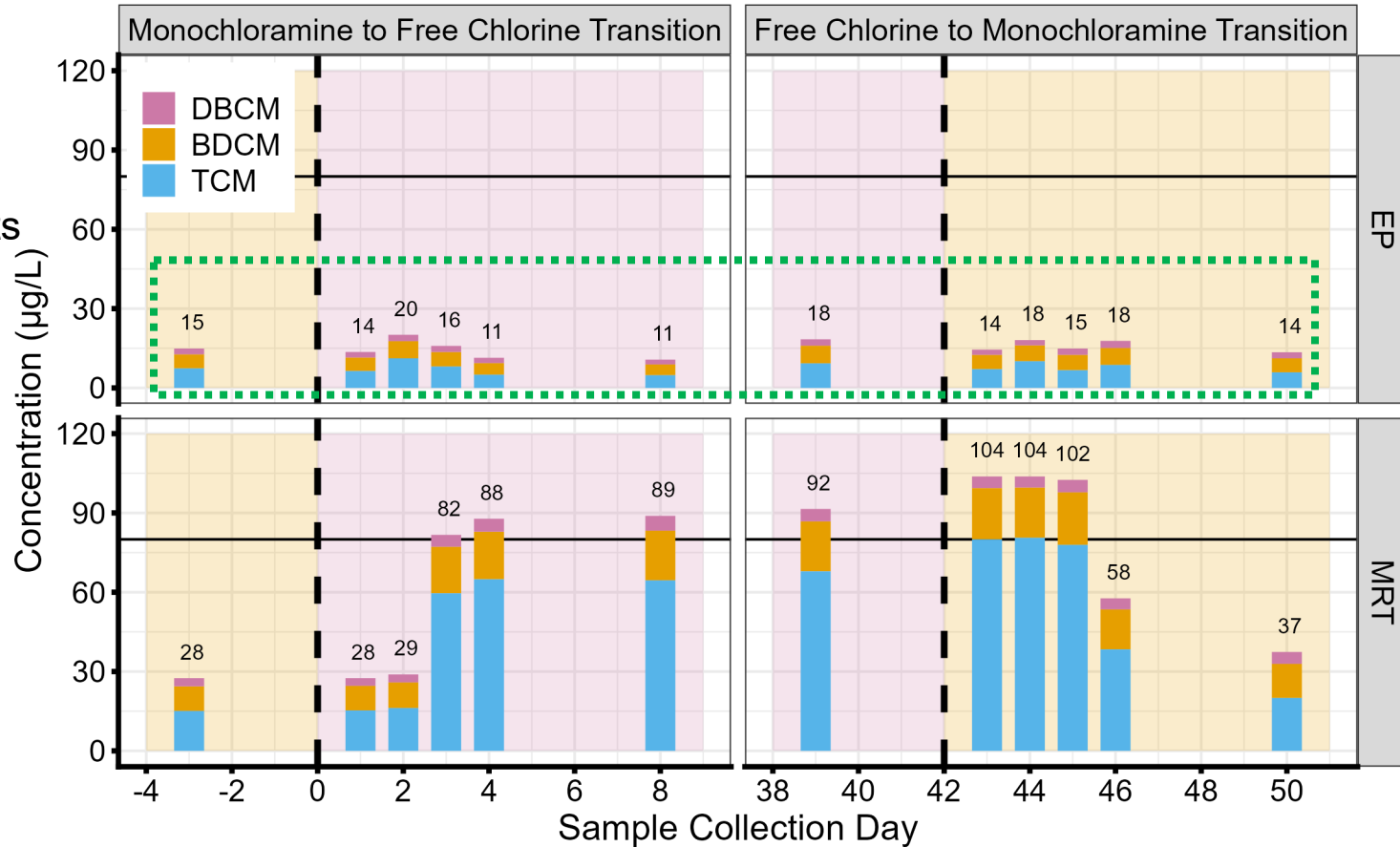
THMs (Non-Steady State)

- No TBM
- Mainly chlorinated
- Parallels disinfectants



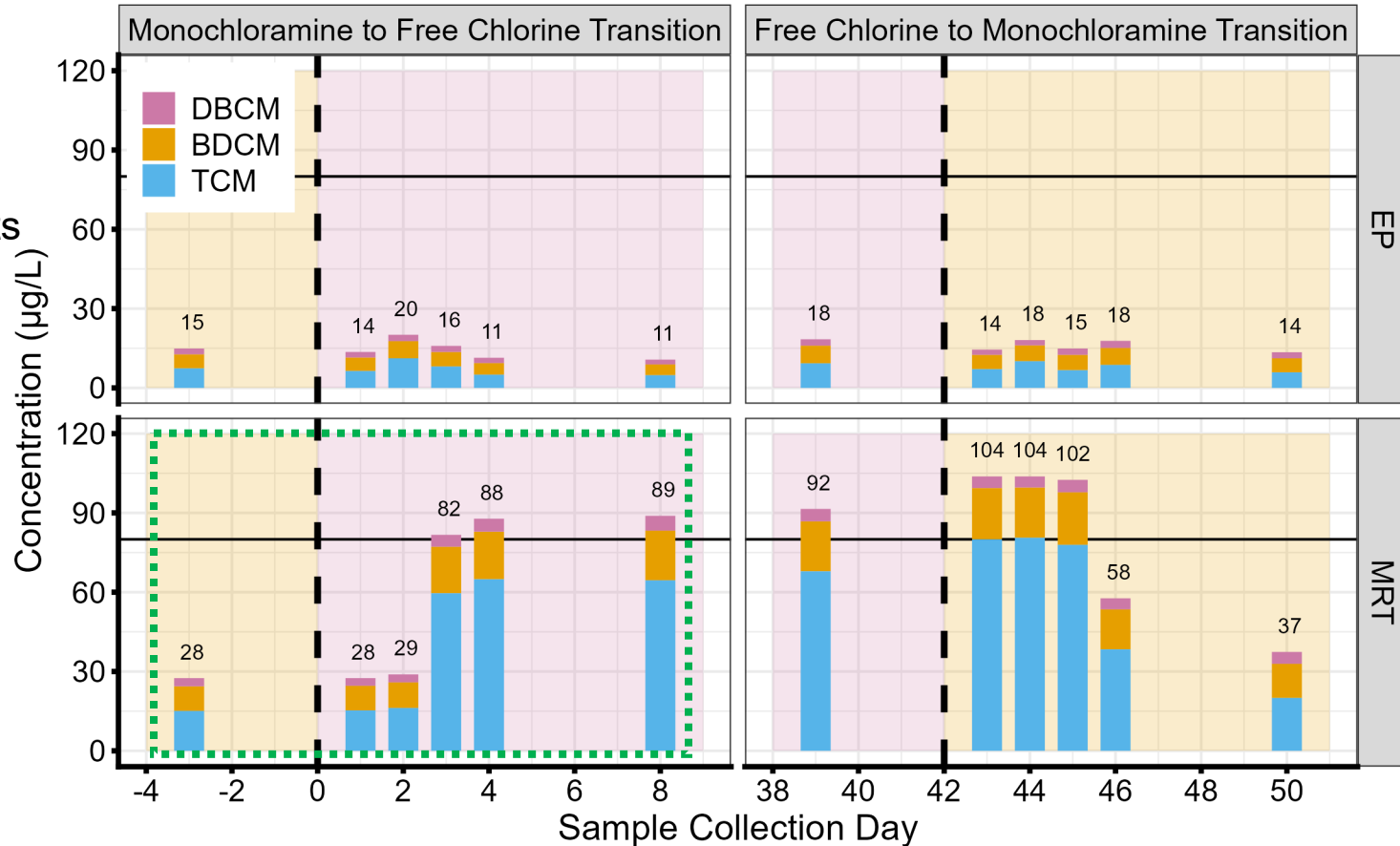
THMs (Non-Steady State)

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- Mainly chlorinated
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- EP not impacted



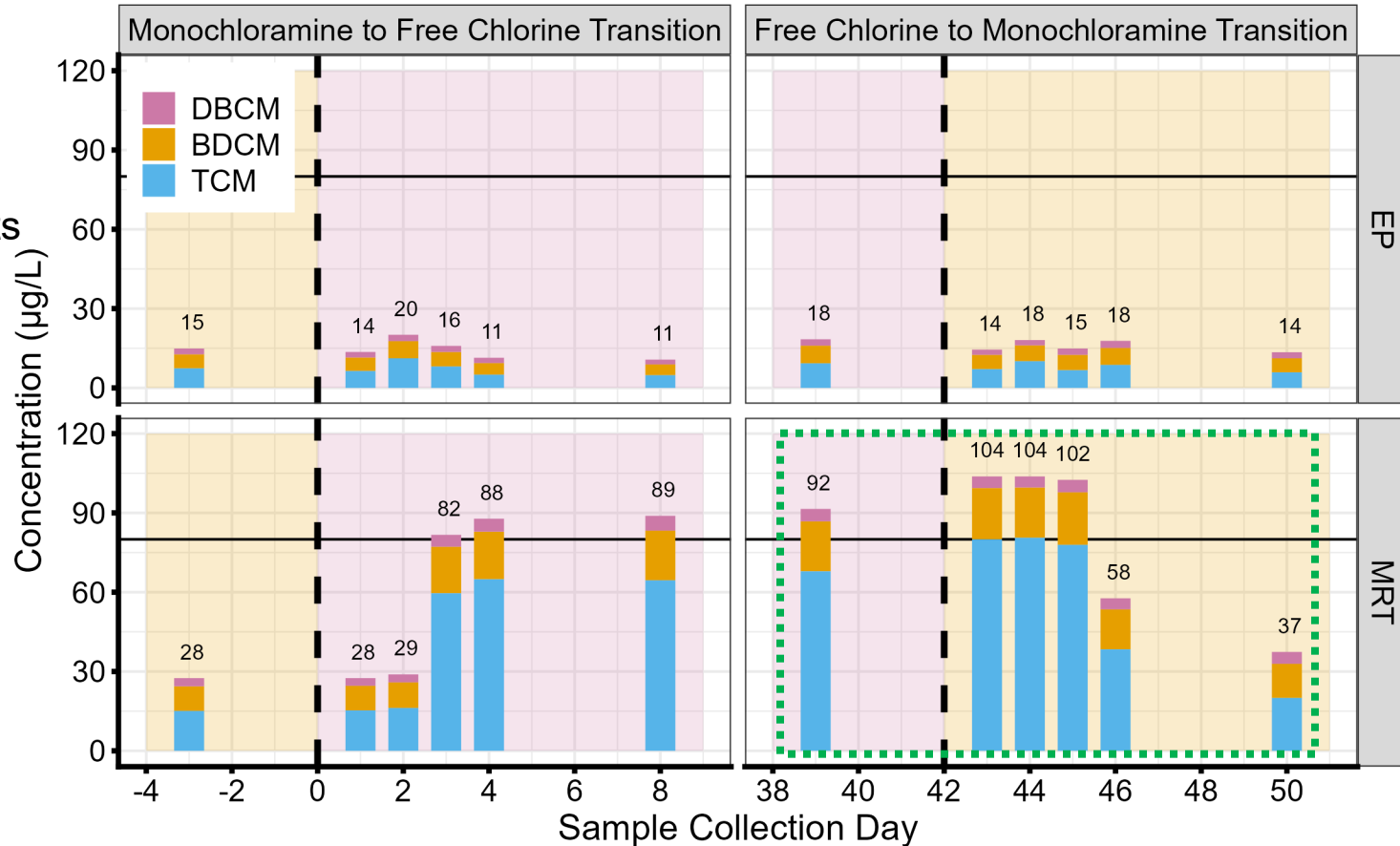
THMs (Non-Steady State)

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 - Mainly TCM ↑
 - Some BDCM ↑
 - Minor DBCM ↑



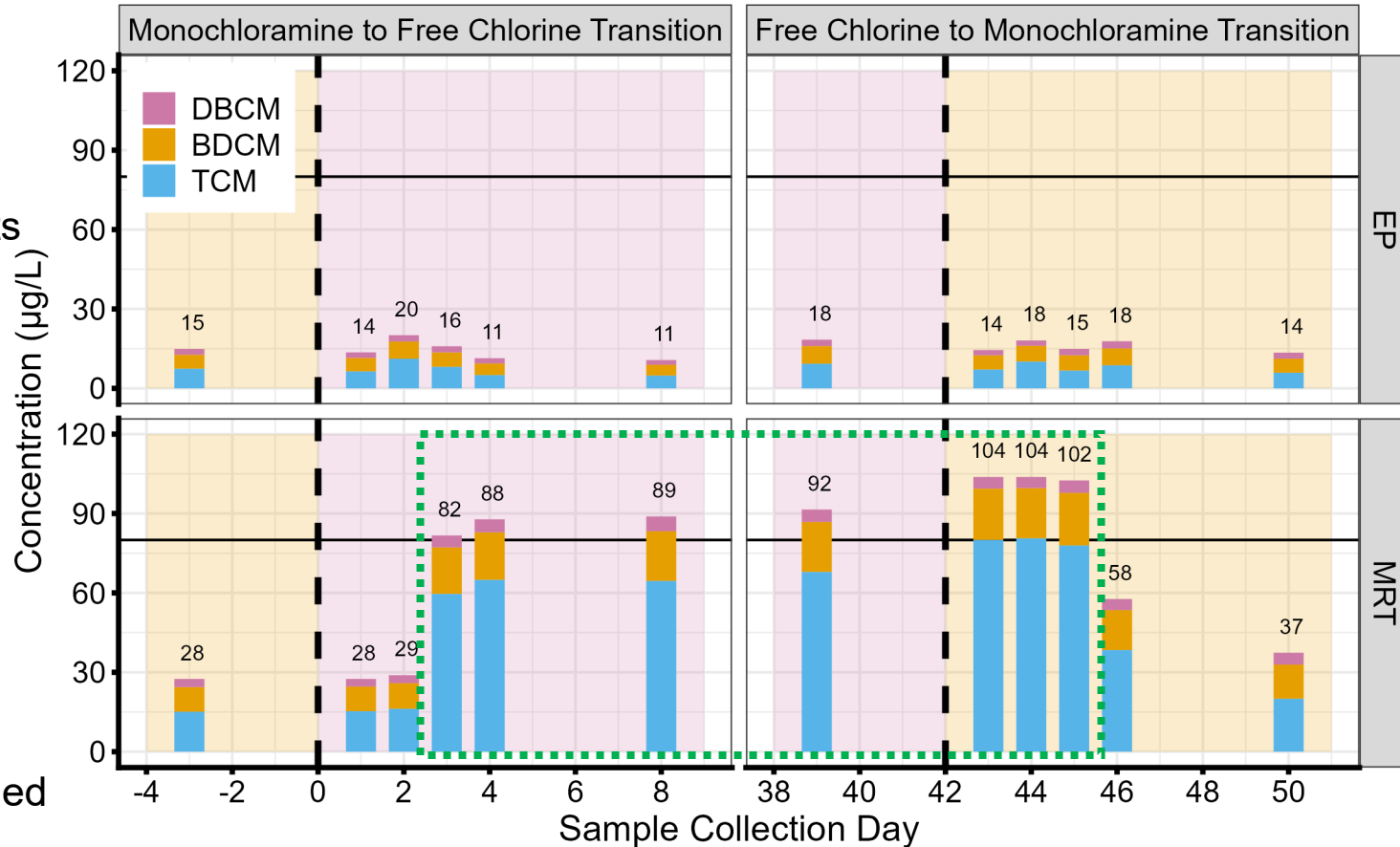
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 - Extra THM4 ↑ (4x)
 - Mainly TCM ↑



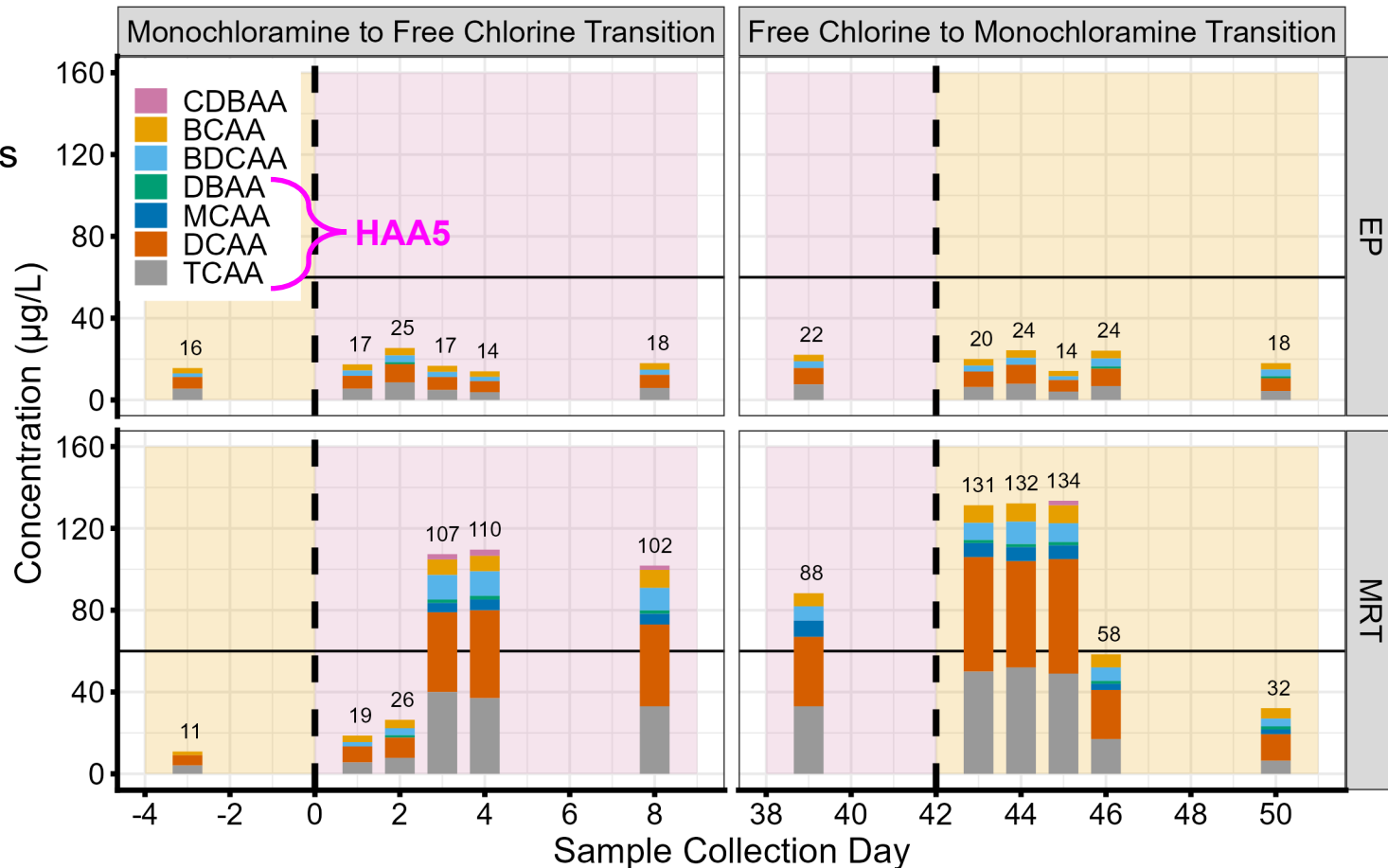
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- MRT (free to mono)
 - Extra THM4 ↑ (4x)
 - Mainly TCM ↑
- 80 µg/L MCL exceeded



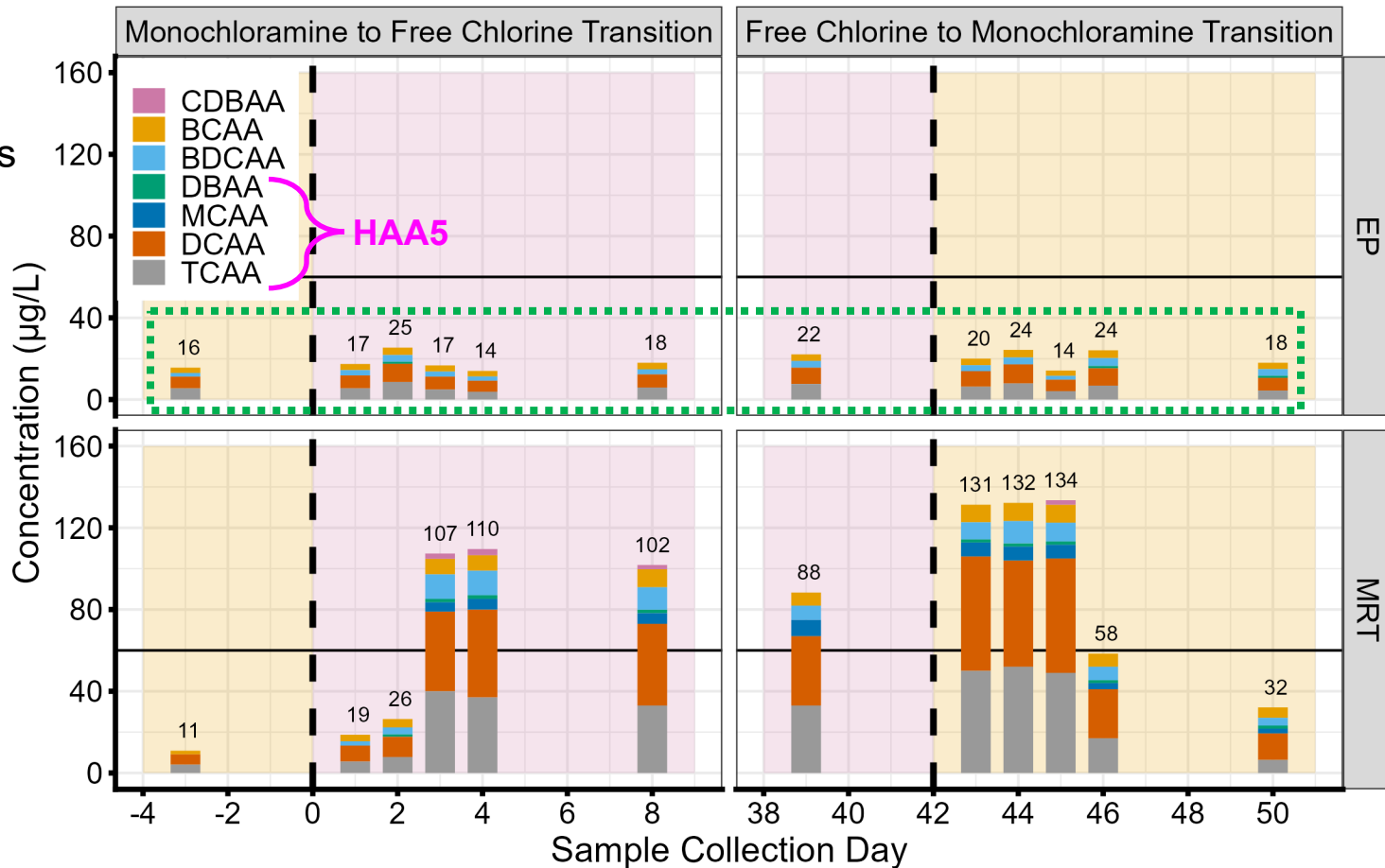
HAA5s (Non-Steady State)

- No MBAA or TBAA
- Mainly chlorinated
- Parallels disinfectants



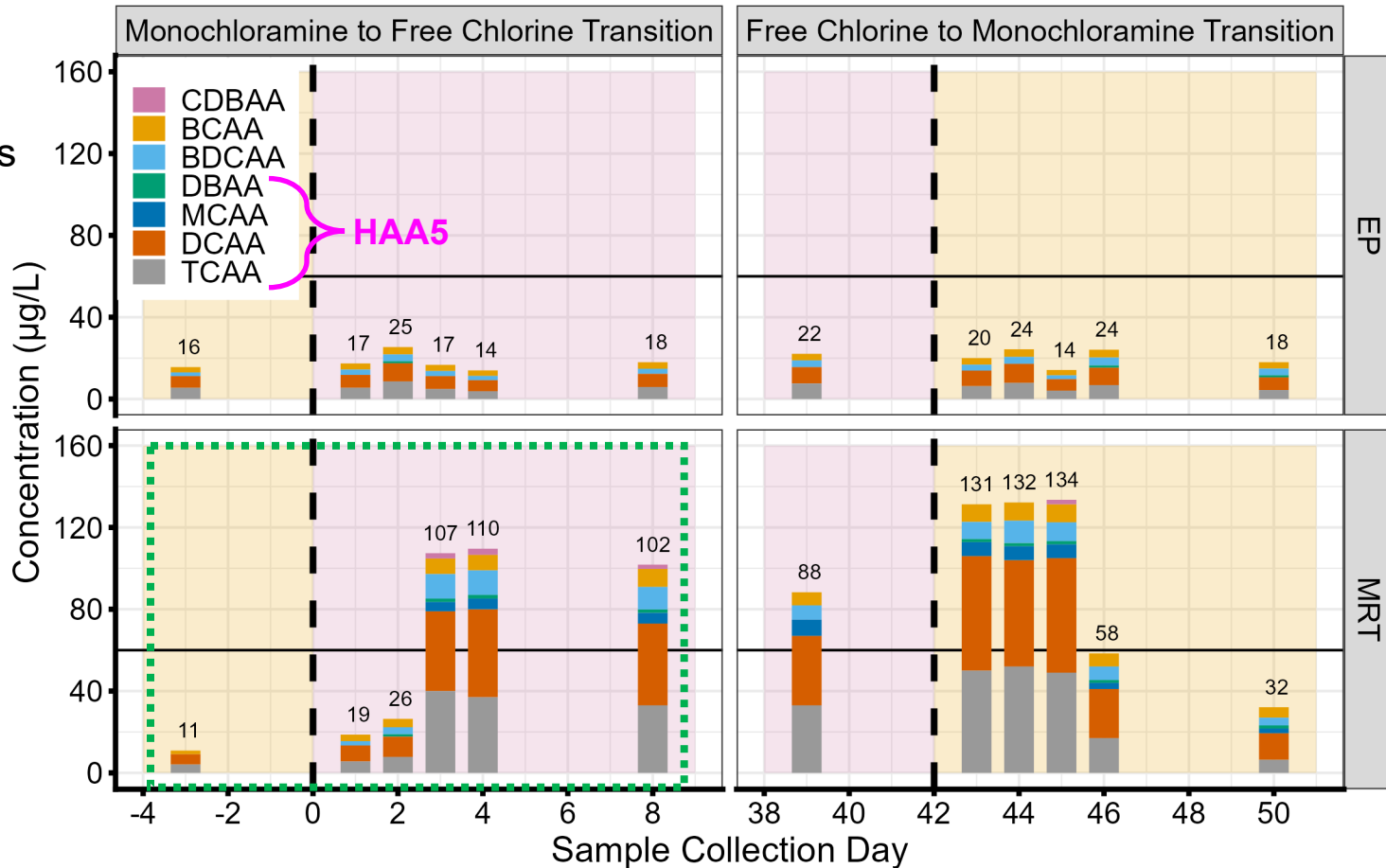
HAAs (Non-Steady State)

- No MBAA or TBAA
- Mainly chlorinated
- Parallels disinfectants
- EP not impacted



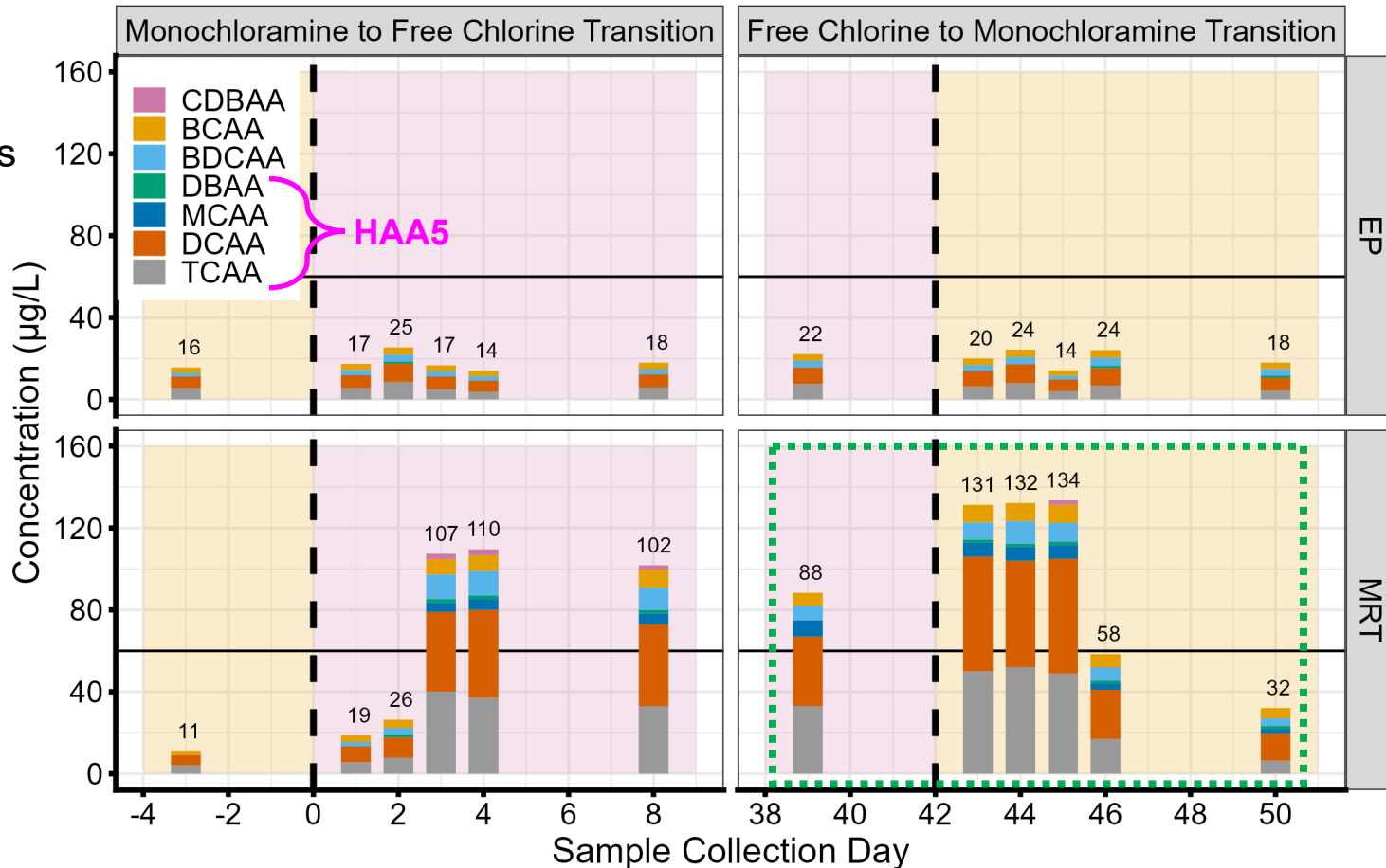
HAAs (Non-Steady State)

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- Mainly chlorinated
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 - HAA5 ↑ (8x)
 - HAA9 ↑ (10x)
 - Mainly chlorinated



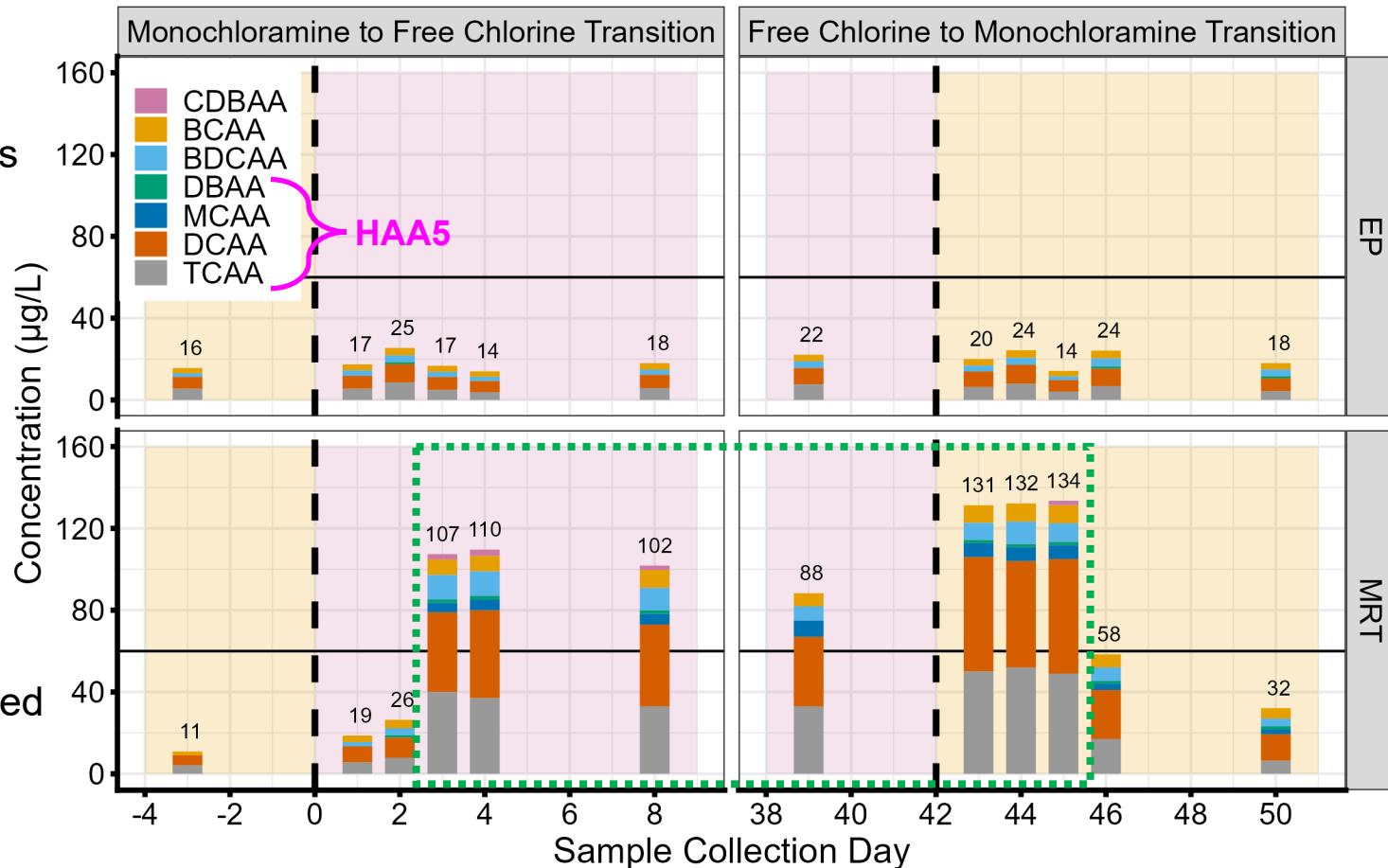
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- MRT (mono to free)
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 - Mainly chlorinated
- MRT (free to mono)
 - Extra HAA5 ↑ (10x)
 - Extra HAA9 ↑ (13x)
 - Mainly chlorinated



HAAs (Non-Steady State)

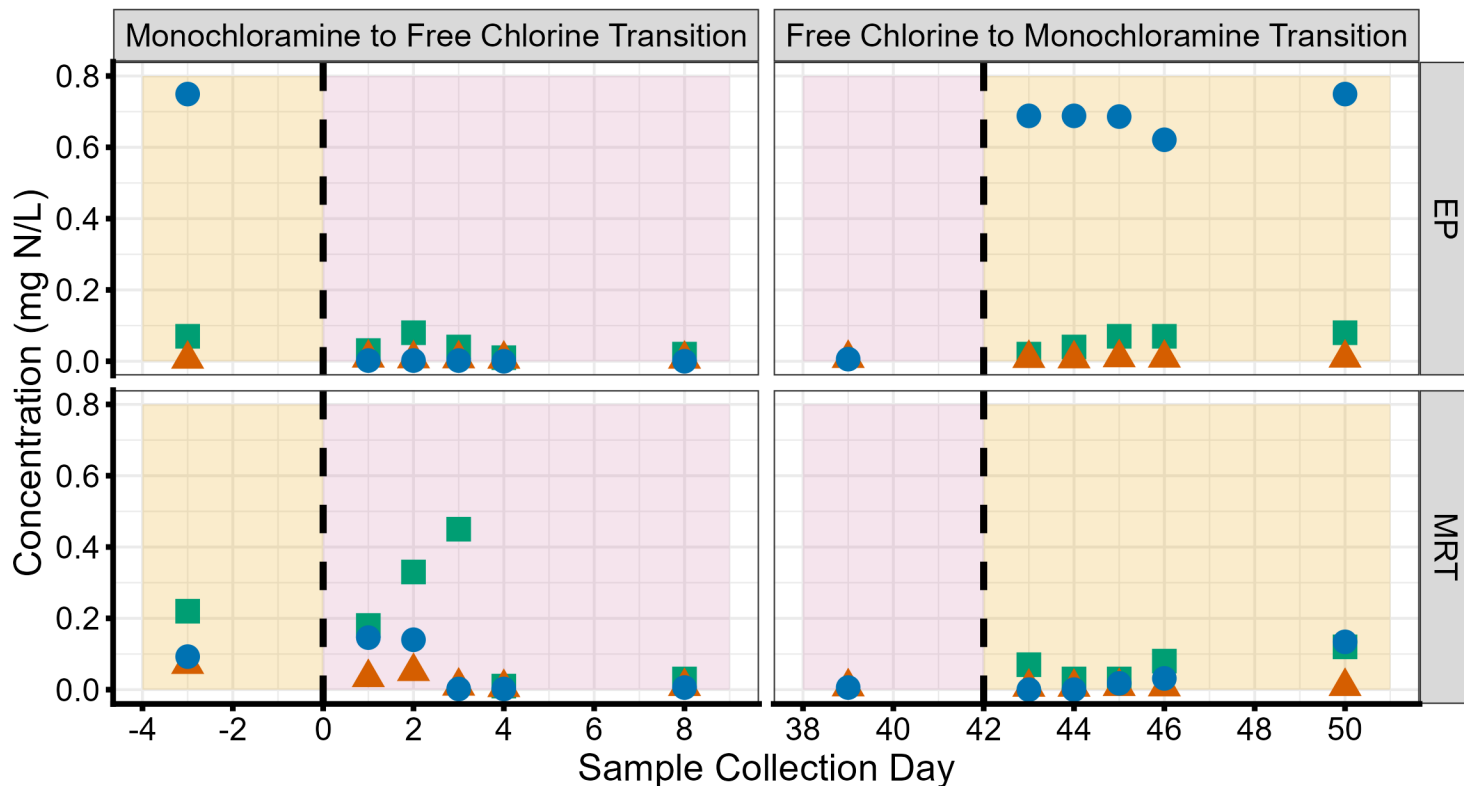
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 - Mainly chlorinated
- MRT (free to mono)
 - Extra HAA5 ↑ (10x)
 - Extra HAA9 ↑ (13x)
 - Mainly chlorinated
- 60 µg/L MCL exceeded



Nitrogen Species (Non-Steady State)

■ Free Ammonia ● Monochloramine ▲ Nitrite

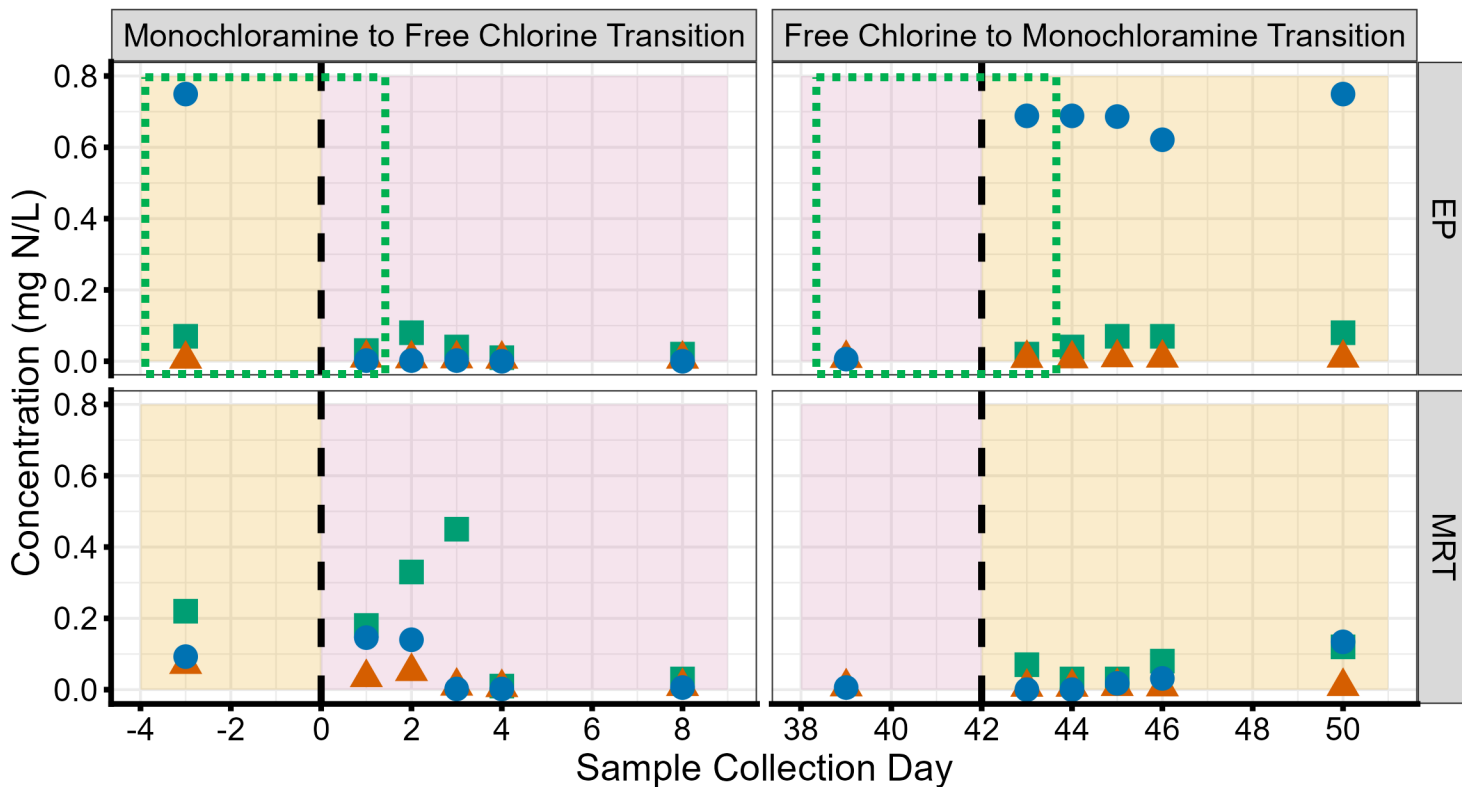
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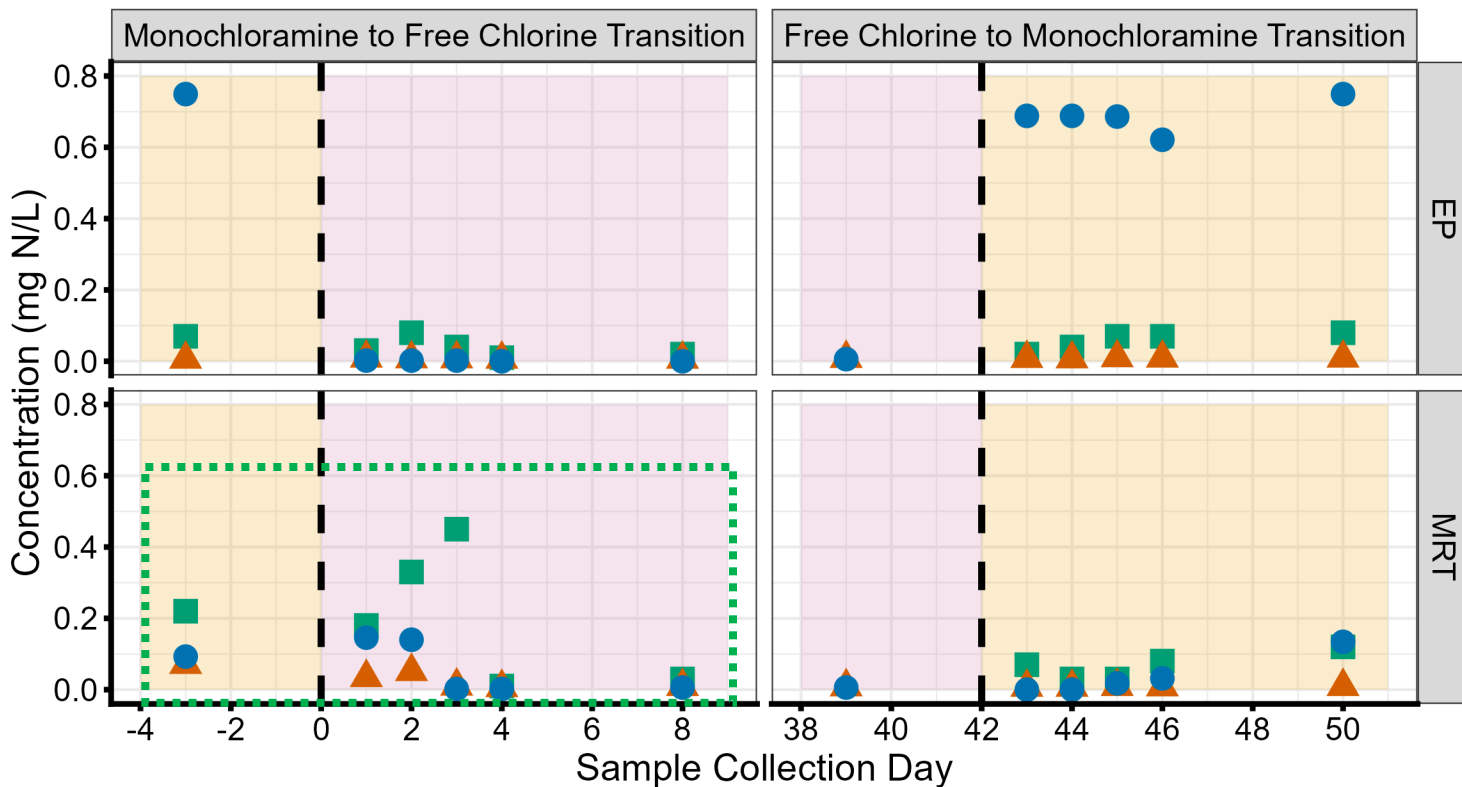
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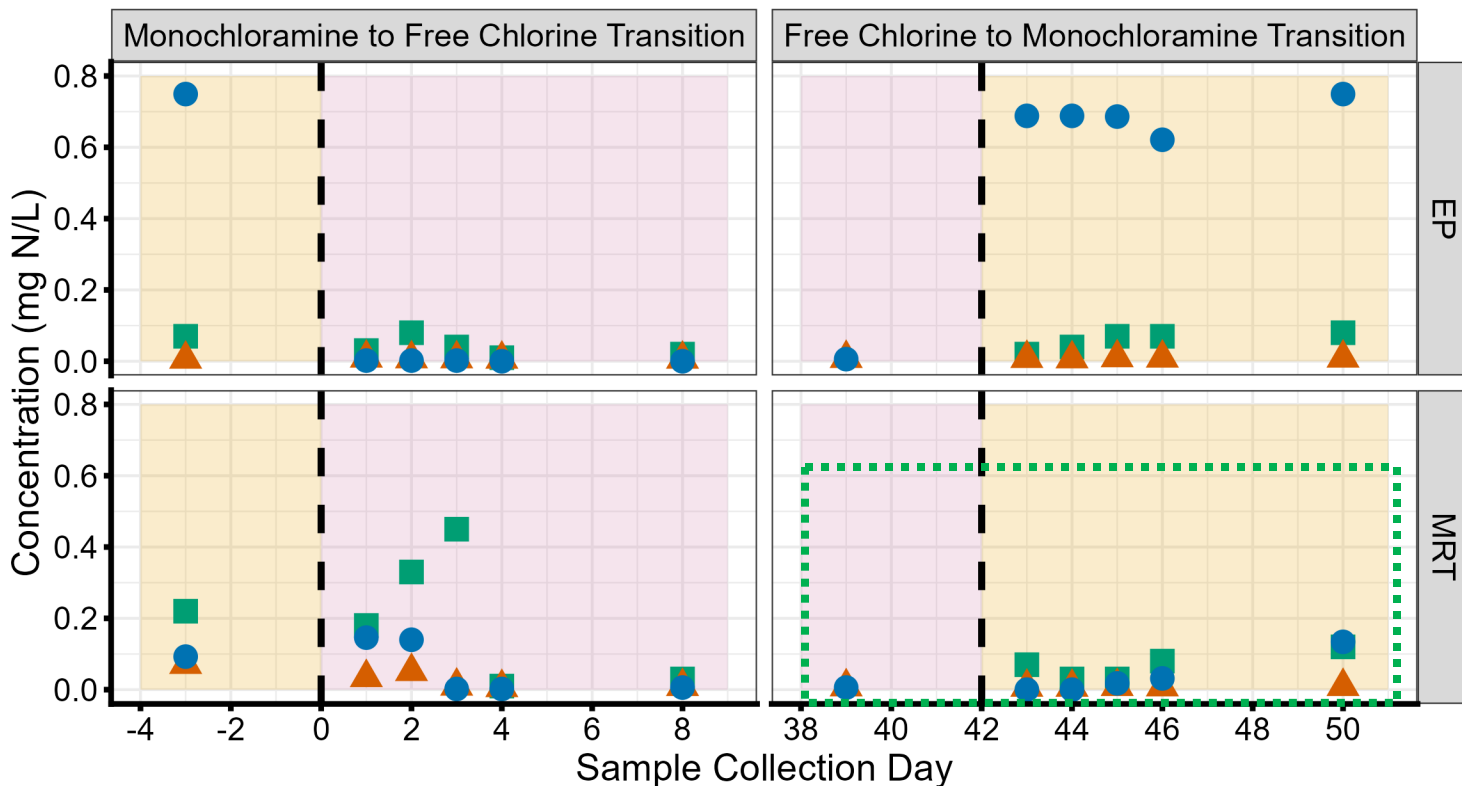
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 - Some nitrite
 - Initial \uparrow ammonia
 - 4 day no ammonia



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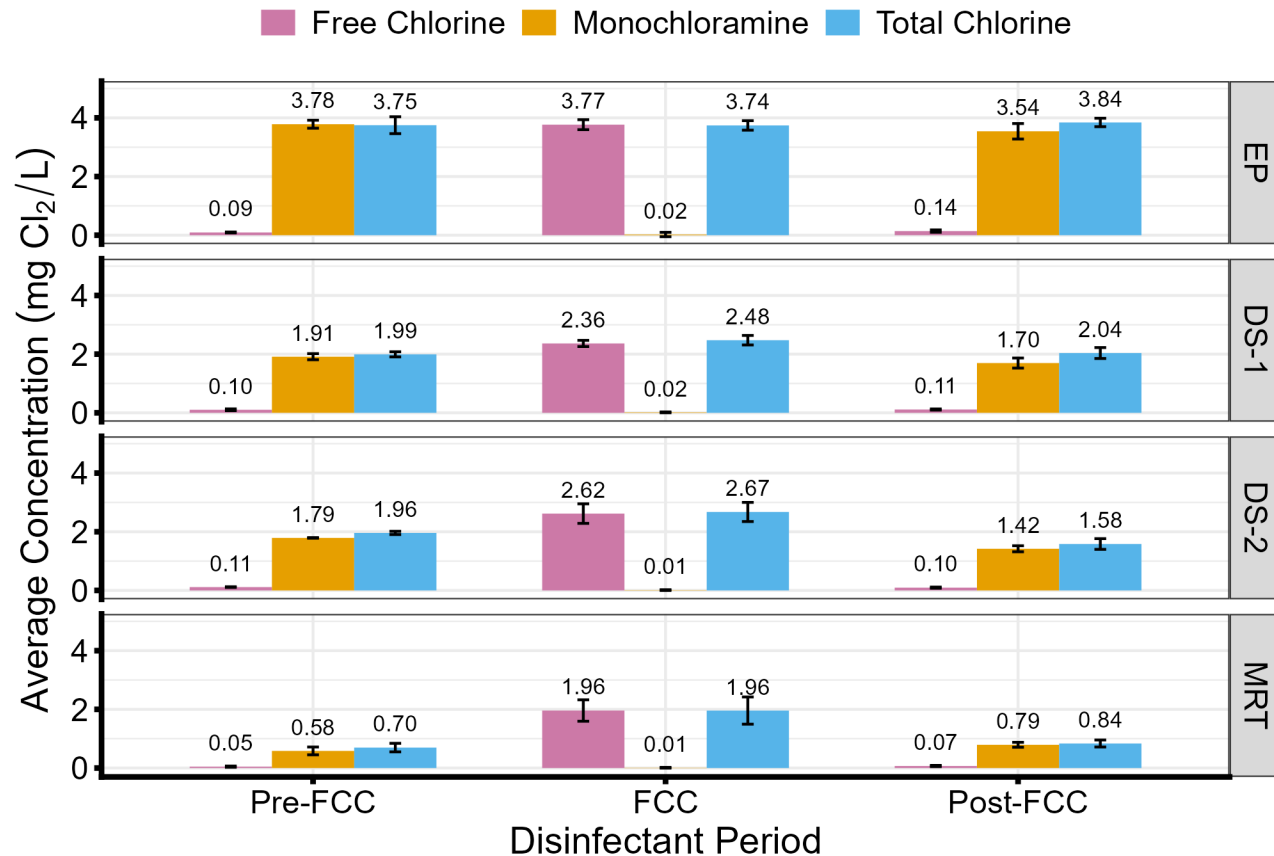
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- MRT (free to mono)
 - No nitrite
 - 4–8 day transition



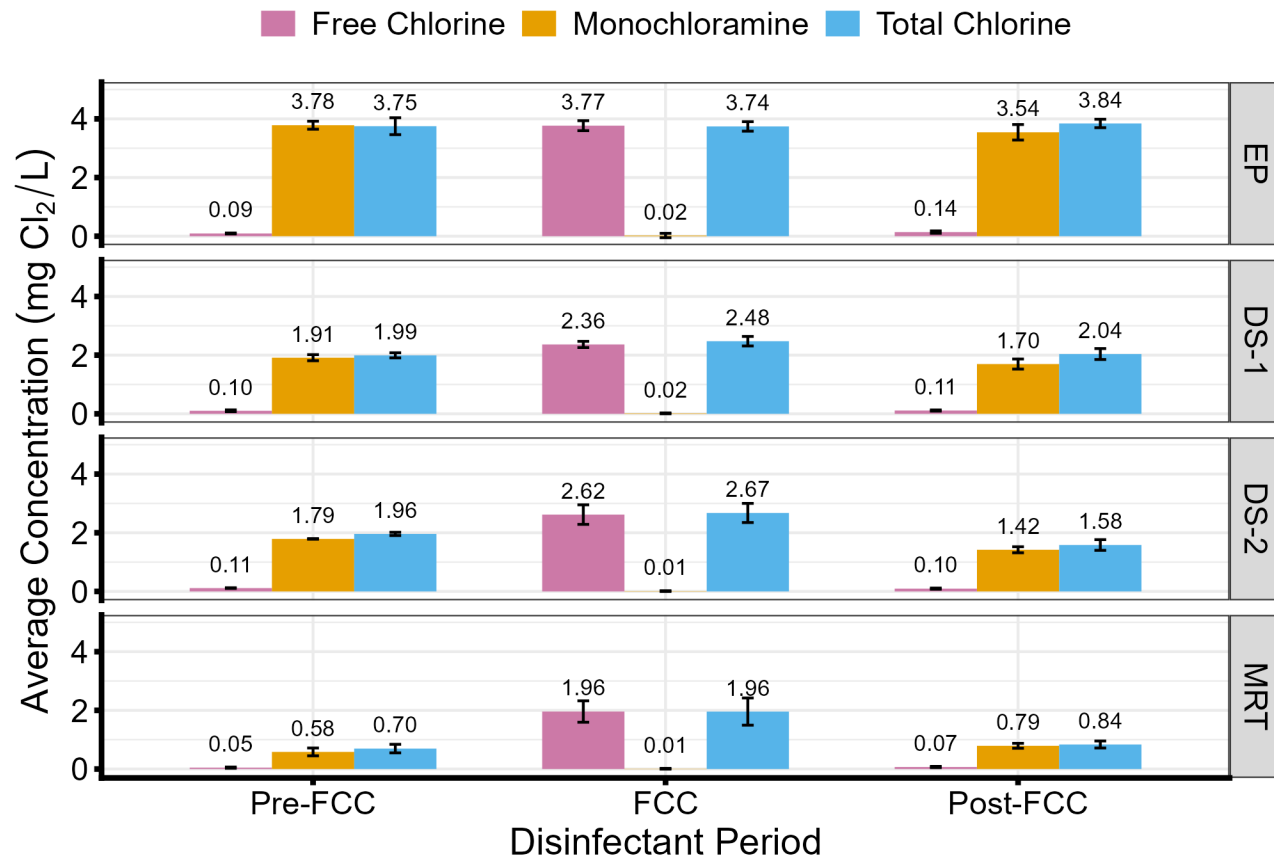
Disinfectants (Steady State)

- Four distribution locations
- EP to MRT = ↑ water age



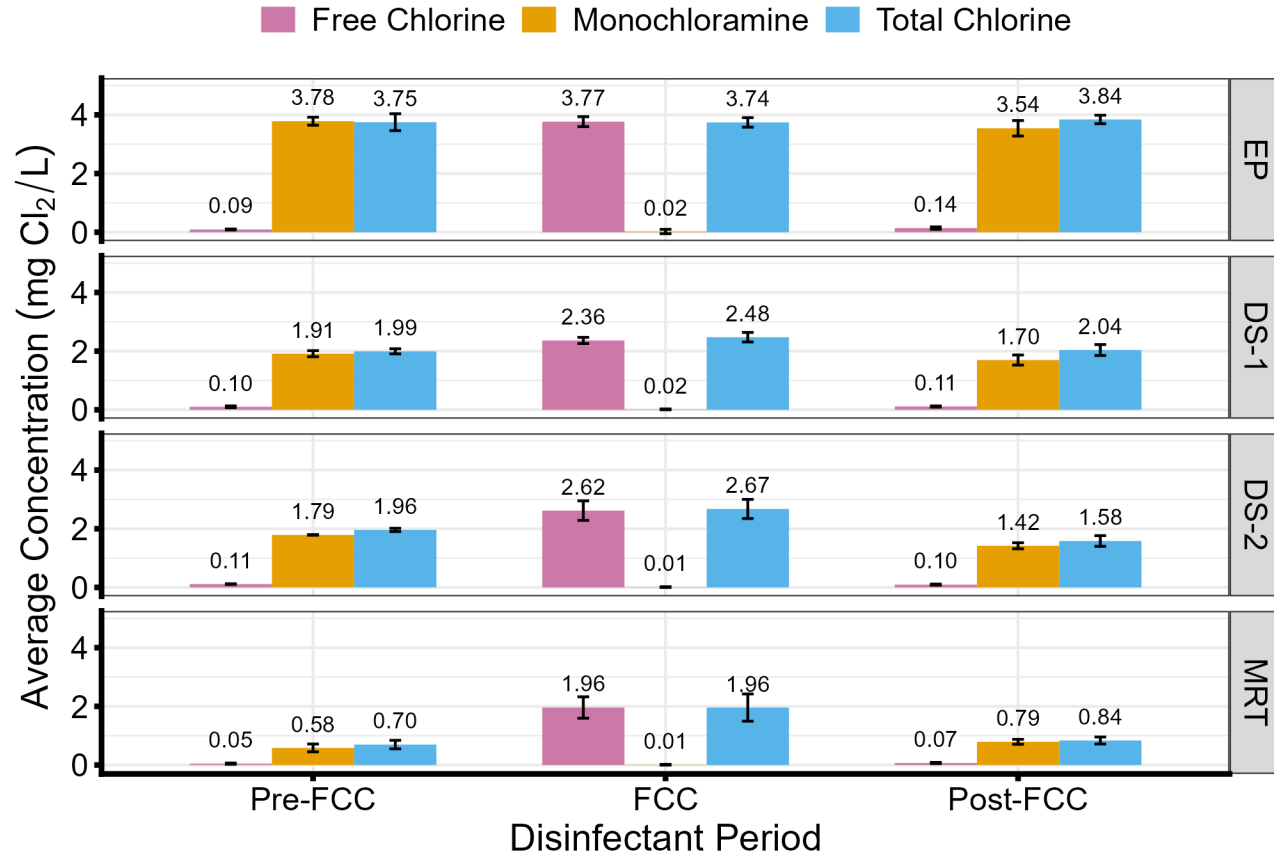
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- EP to MRT = ↑ water age
- ↓ with water age



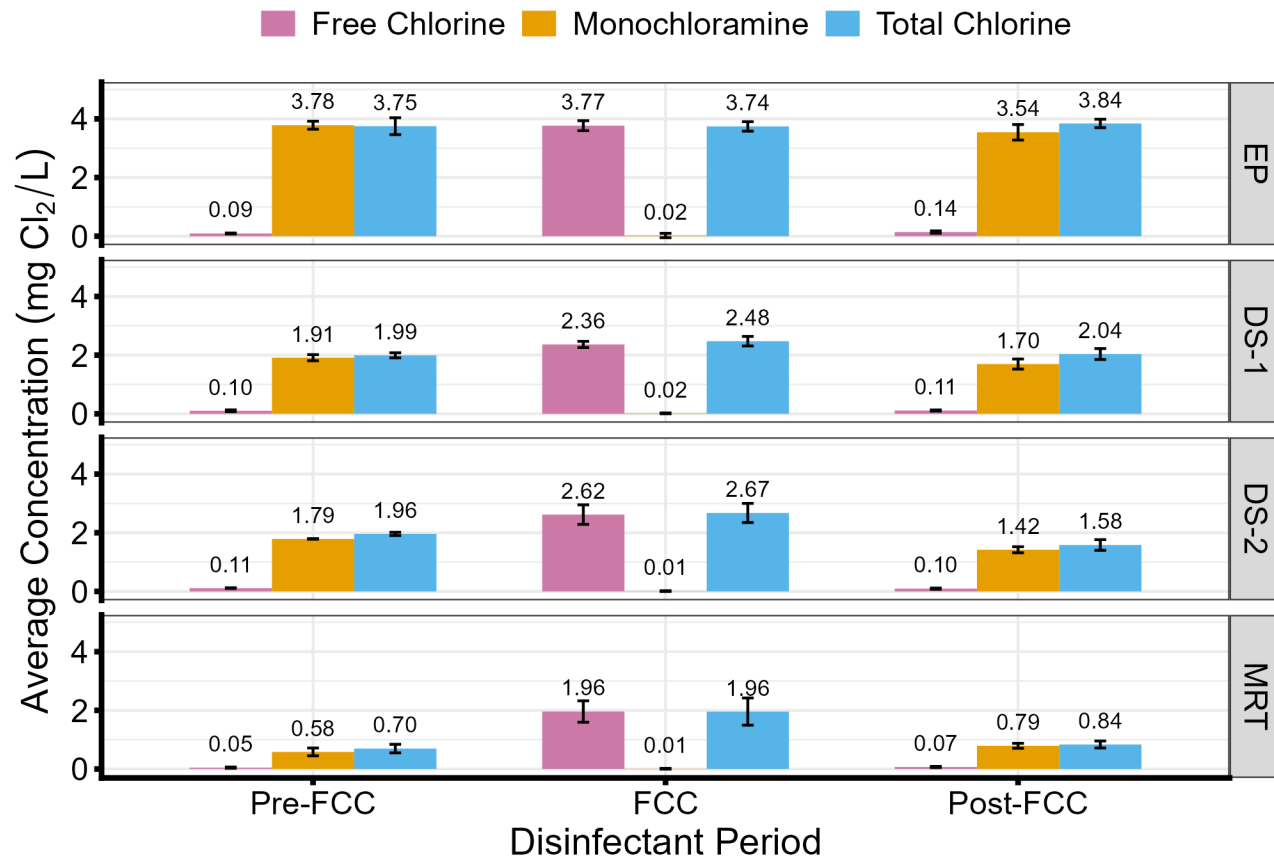
Disinfectants (Steady State)

- Four distribution locations
- EP to MRT = \uparrow water age
- \downarrow with water age
- 0.5 mg Cl_2/L minimum met

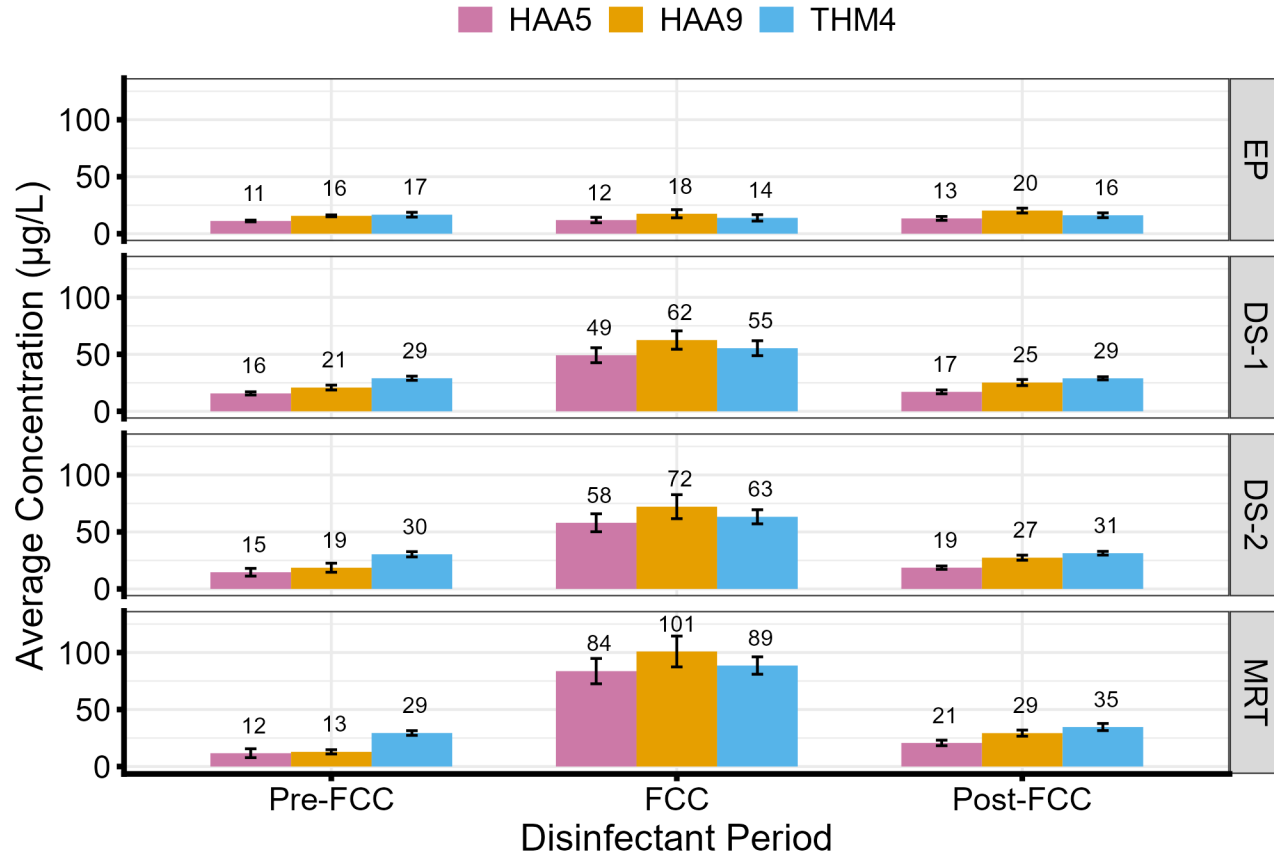


Disinfectants (Steady State)

- Four distribution locations
- EP to MRT = \uparrow water age
- \downarrow with water age
- 0.5 mg Cl_2/L minimum met
- Residual: free > mono (pH)



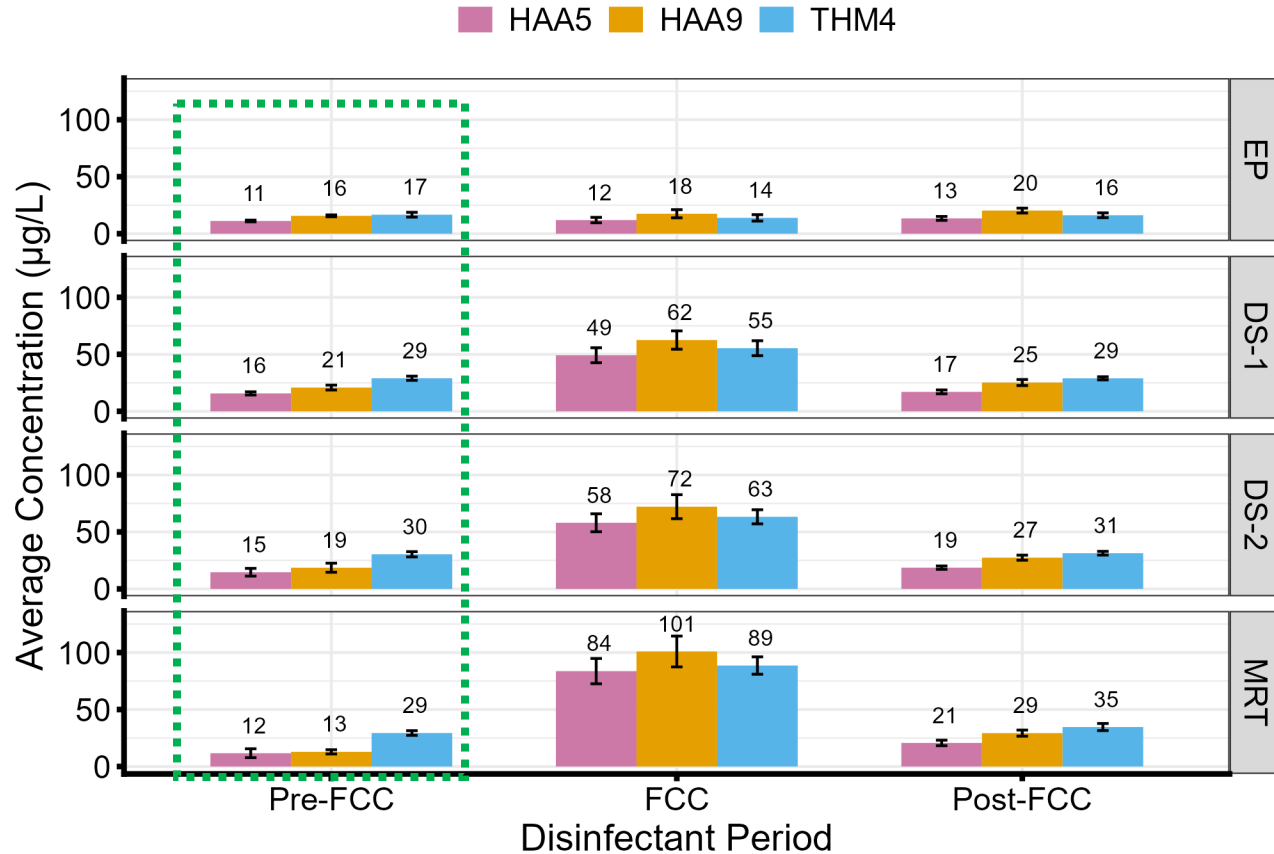
DBPs (Steady State)



DBPs (Steady State)

➤ Pre-FCC

- HAAs: ↑ DS-1 then ↓
- THM4: ↑ DS-1 then ➡
- Biological activity?



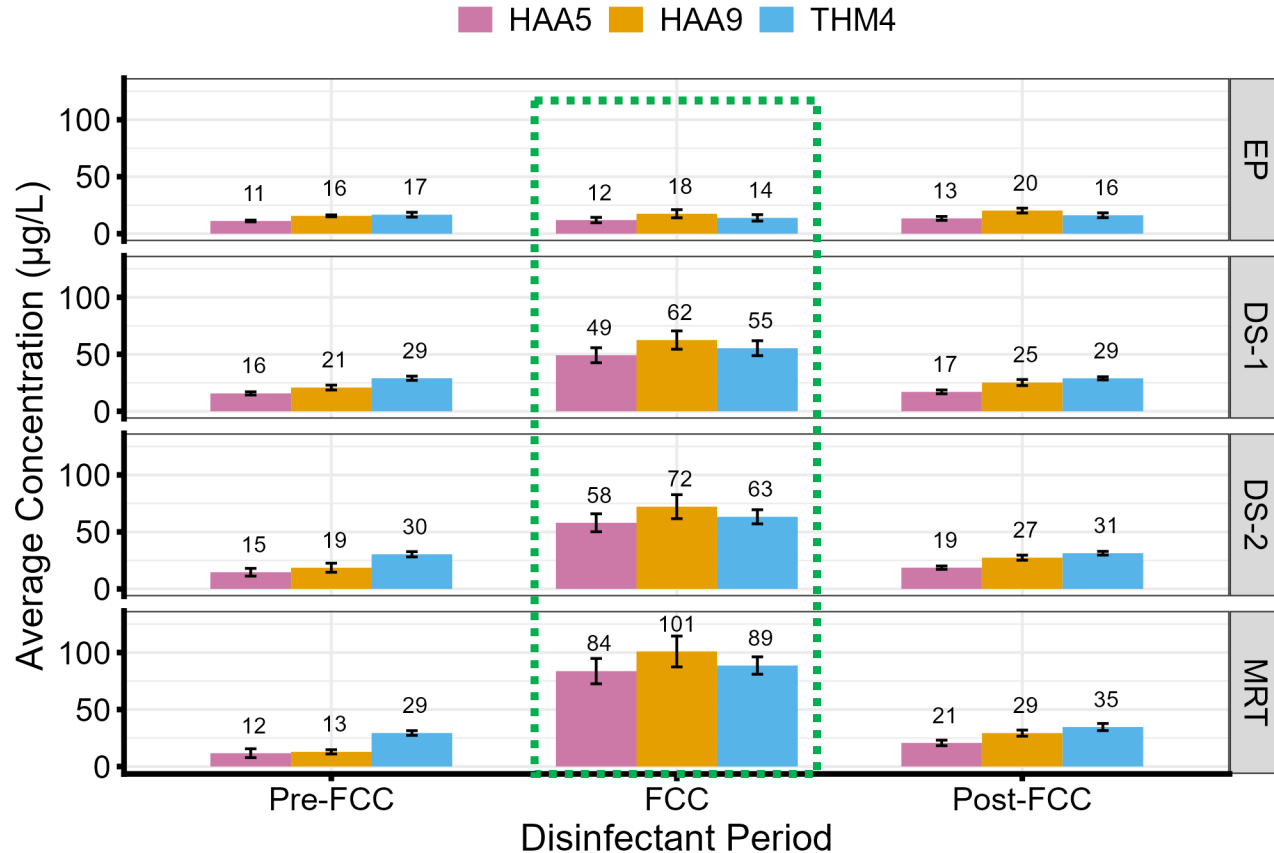
DBPs (Steady State)

➤ Pre-FCC

- HAAs: ↑ DS-1 then ↓
- THM4: ↑ DS-1 then ⇨
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➤ FCC

- All ↑ with water age
- HAAs ↑ (7-8x MRT)
- THM4 ↑ (3x MRT)



DBPs (Steady State)

➤ Pre-FCC

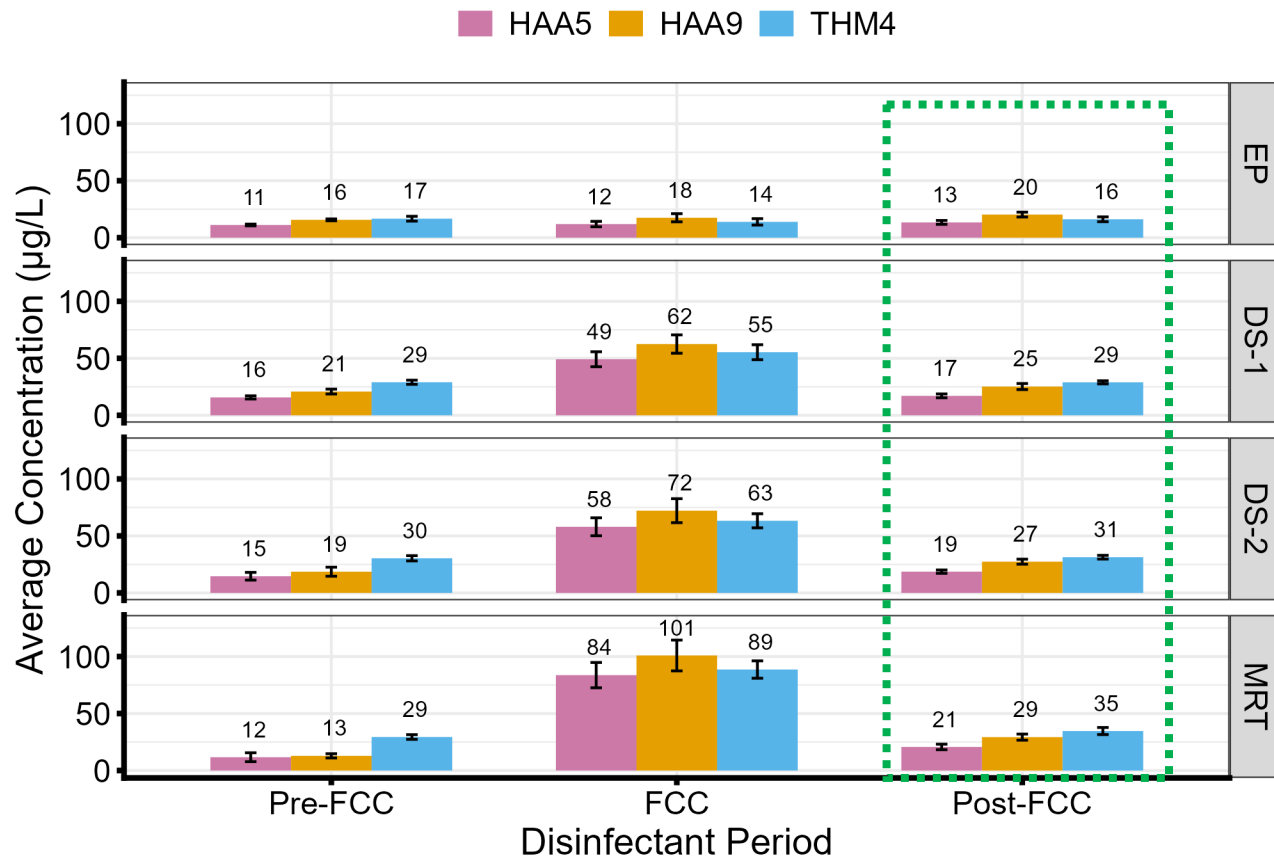
- HAAs: ↑ DS-1 then ↓
- THM4: ↑ DS-1 then ⇨
- Biological activity?

➤ FCC

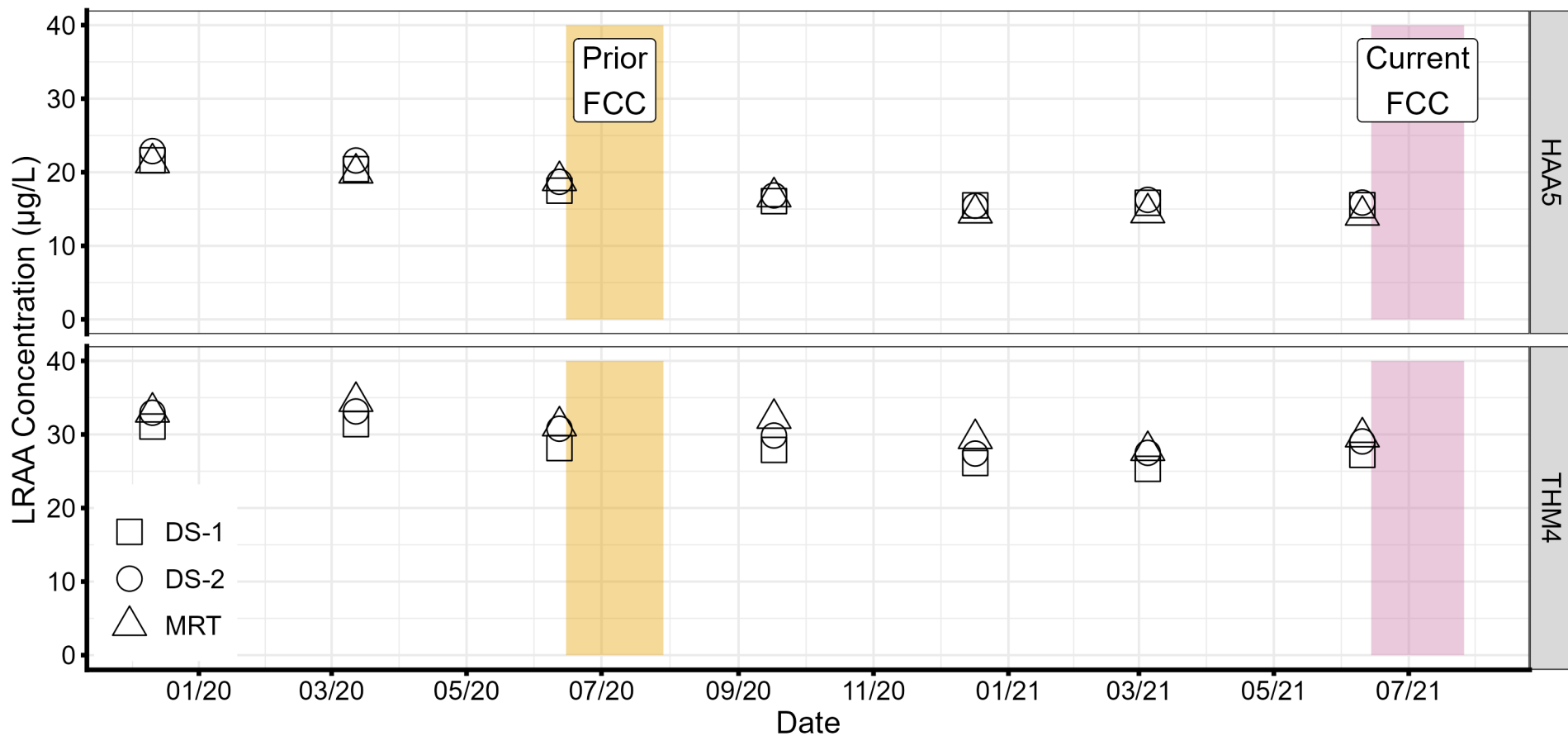
- All ↑ with water age
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- THM4 ↑ (3x MRT)

➤ Post-FCC

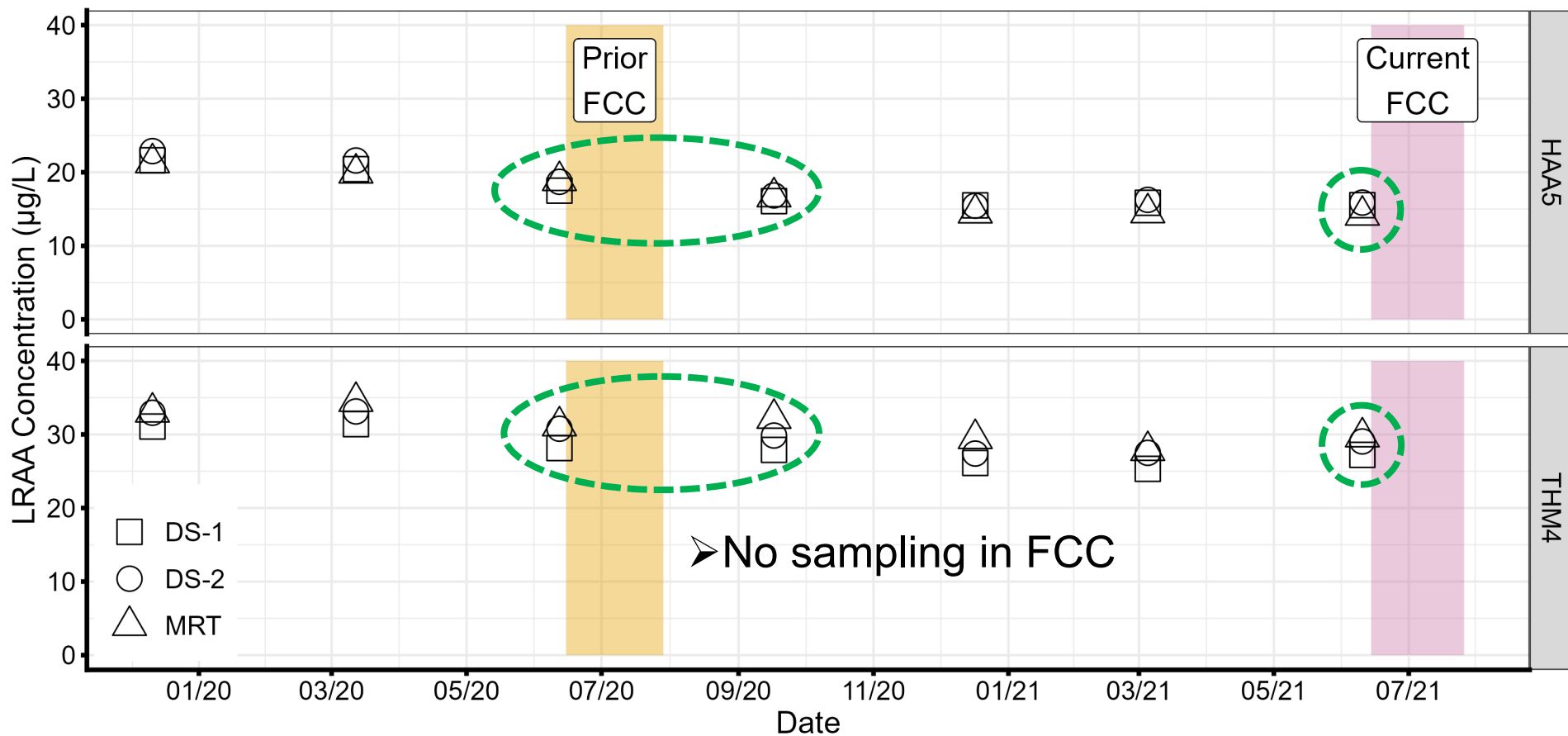
- All ↑ with water age
- Most ↑ vs Pre-FCC
- Temp ↑?
- Biological activity ↓?



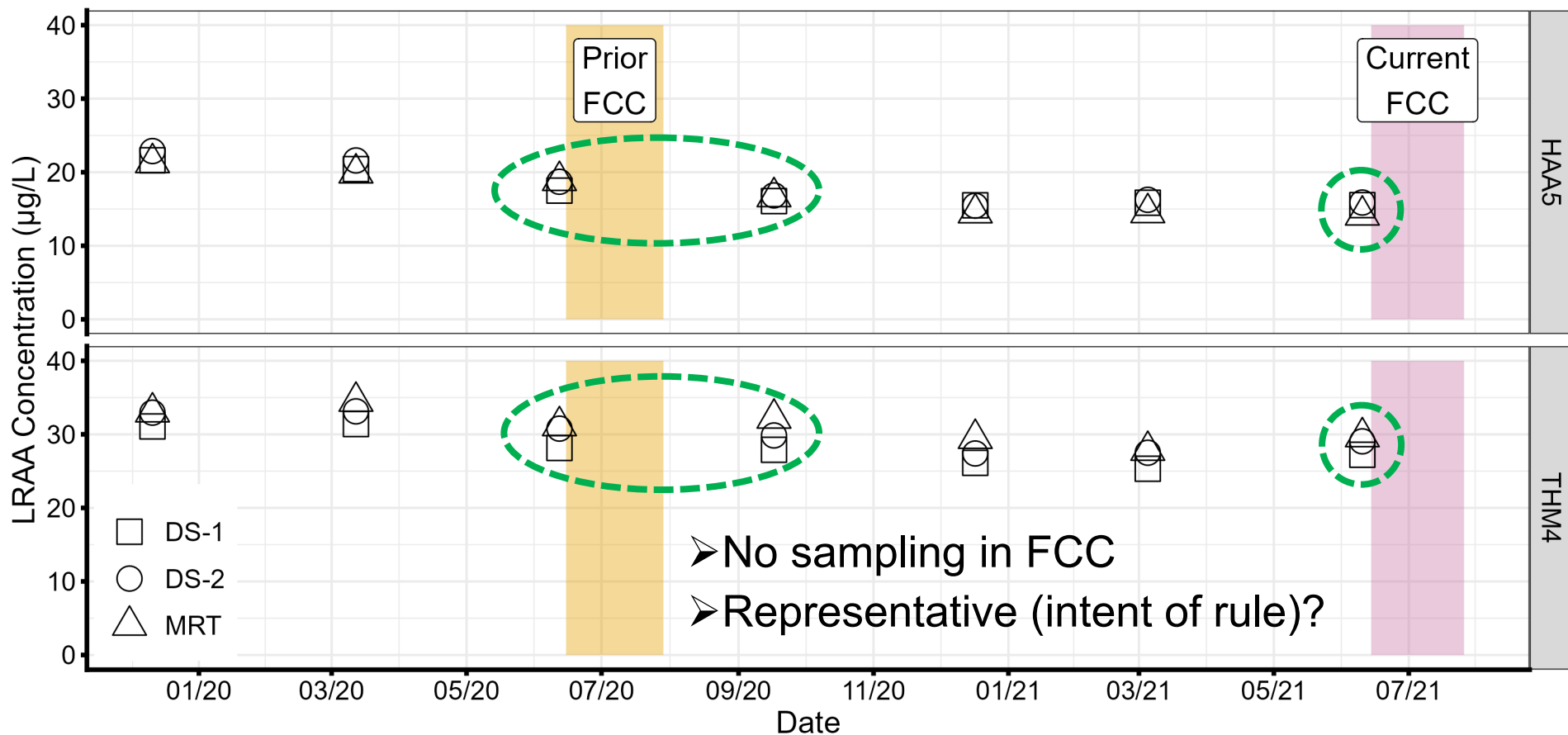
LRAAs & Sampling versus FCCs



LRAAs & Sampling versus FCCs

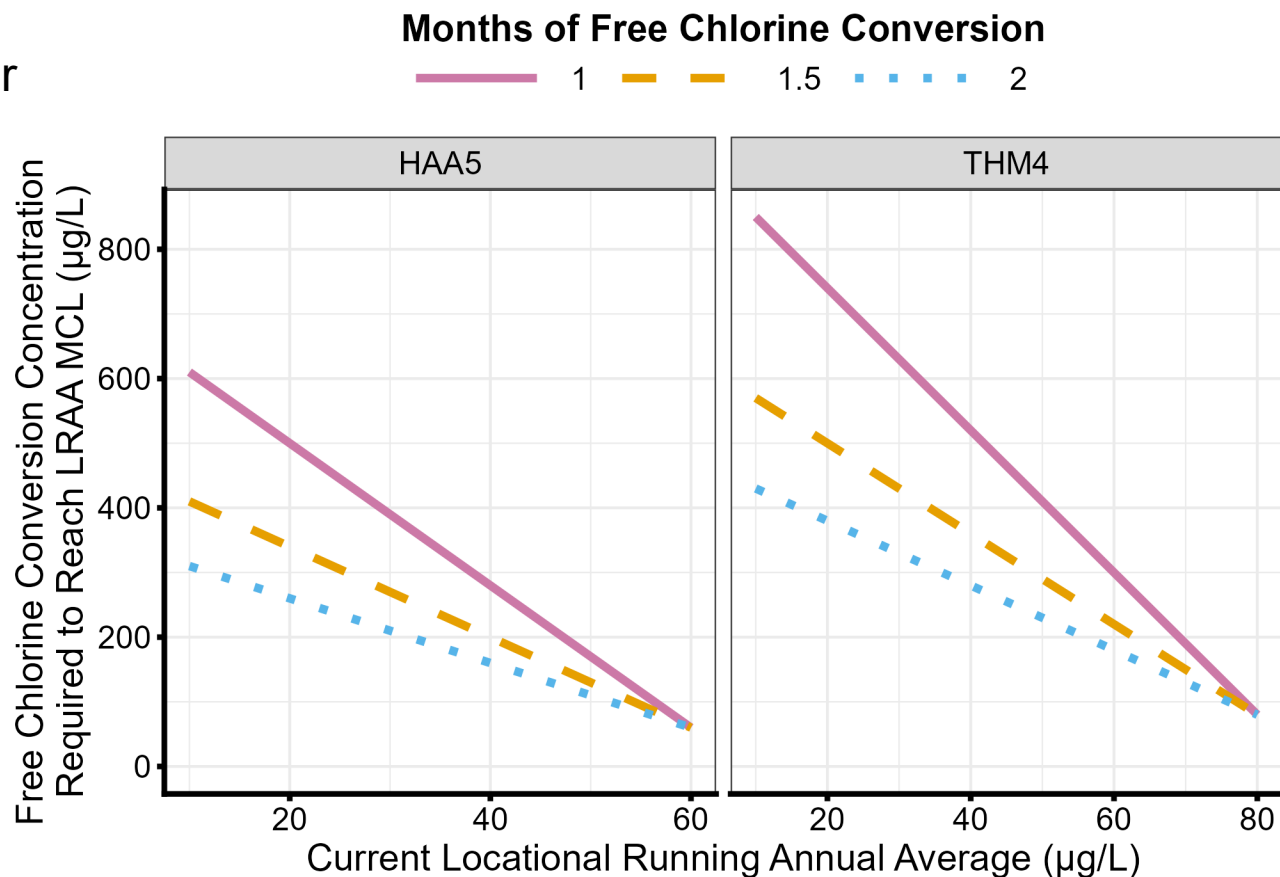


LRAAs & Sampling versus FCCs



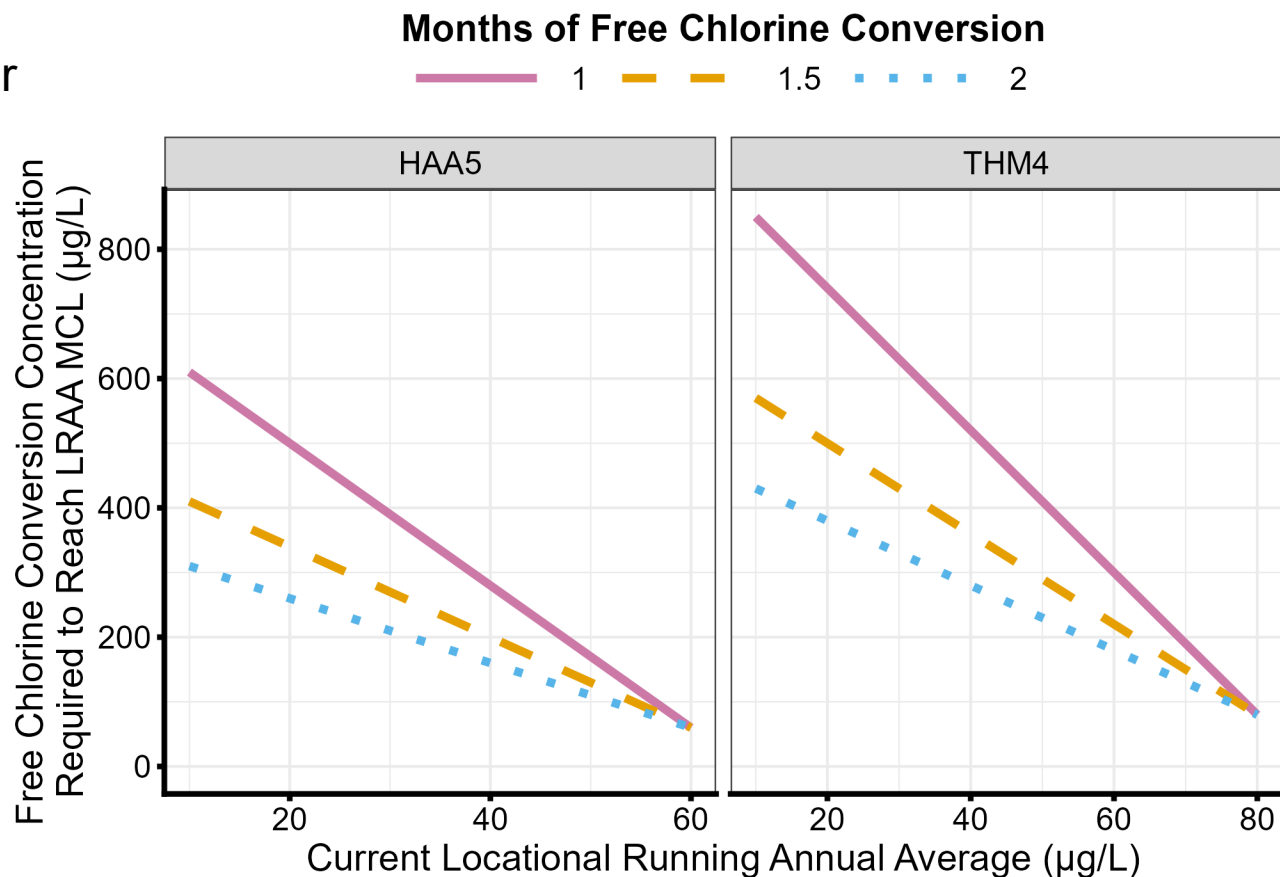
Include FCC (Weighted Average) – MRT?

- modified LRAA (mLRAA)
- Assume one FCC in a year
- Need to know
 - Current LRAA
 - FCC length
 - FCC DBP concentration



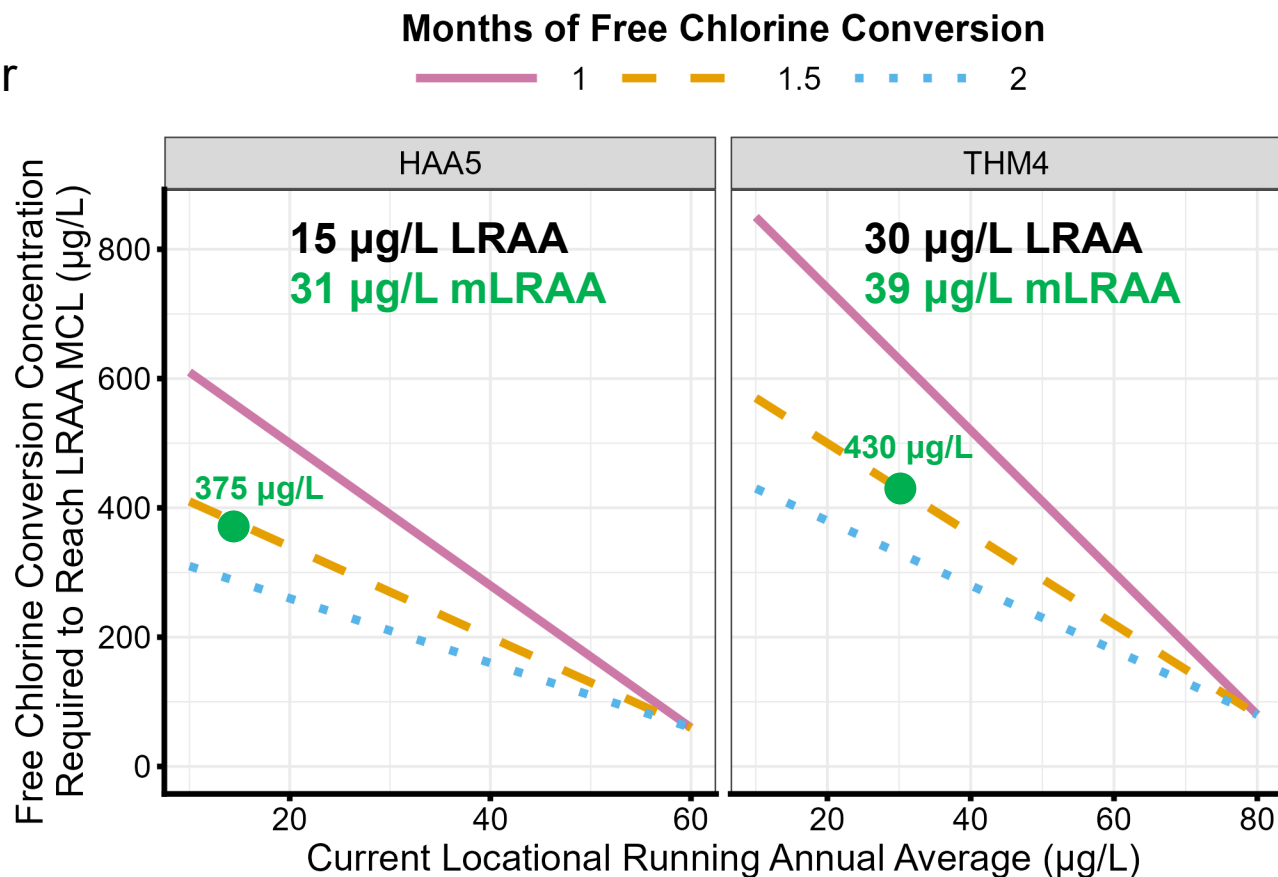
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- Assess potential impact
 - What is too high?
 - What is too long?
 - mLRAA vs LRAA?



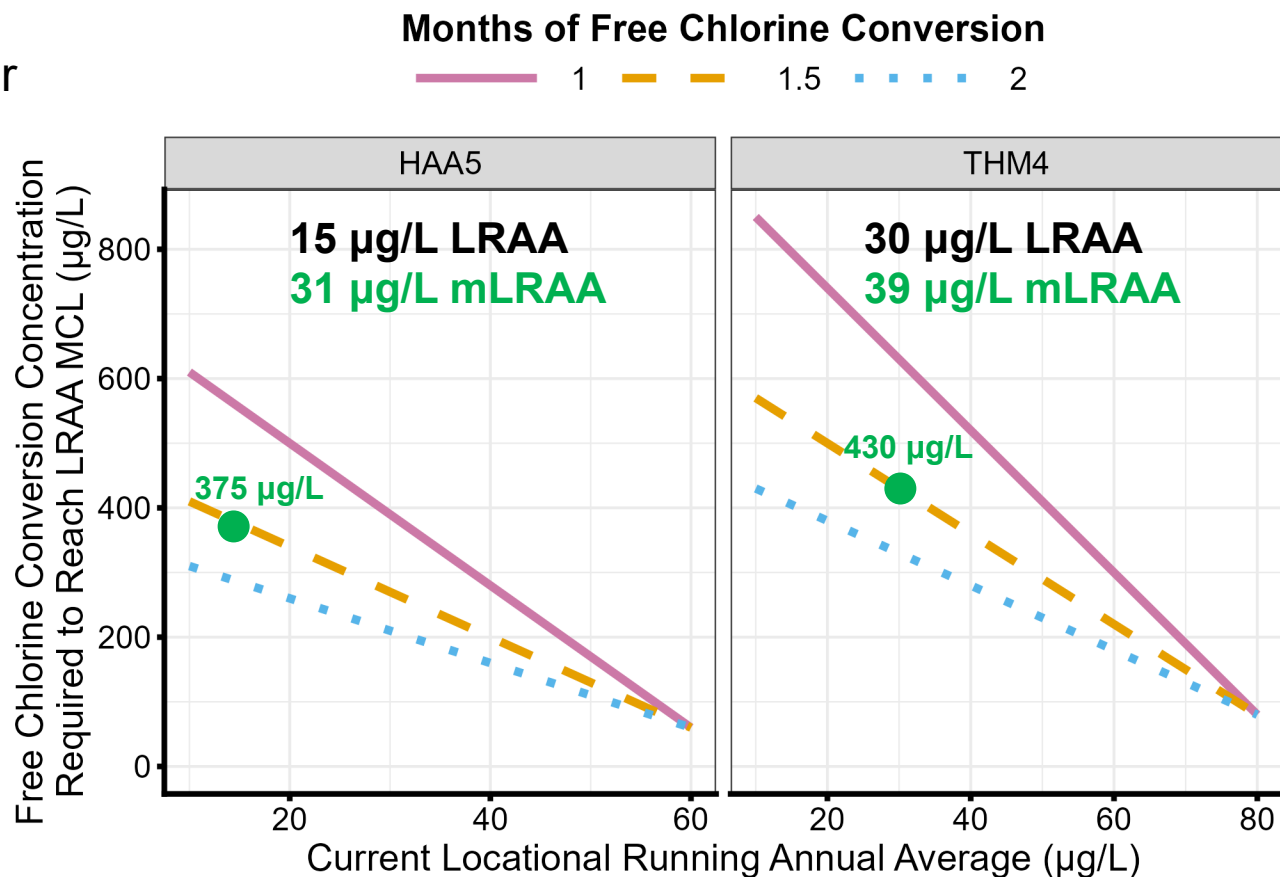
Include FCC (Weighted Average) – MRT?

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 - Low current LRAAs
 - HAA5: 114 vs. 375 µg/L
 - THM4: 104 vs. 430 µg/L

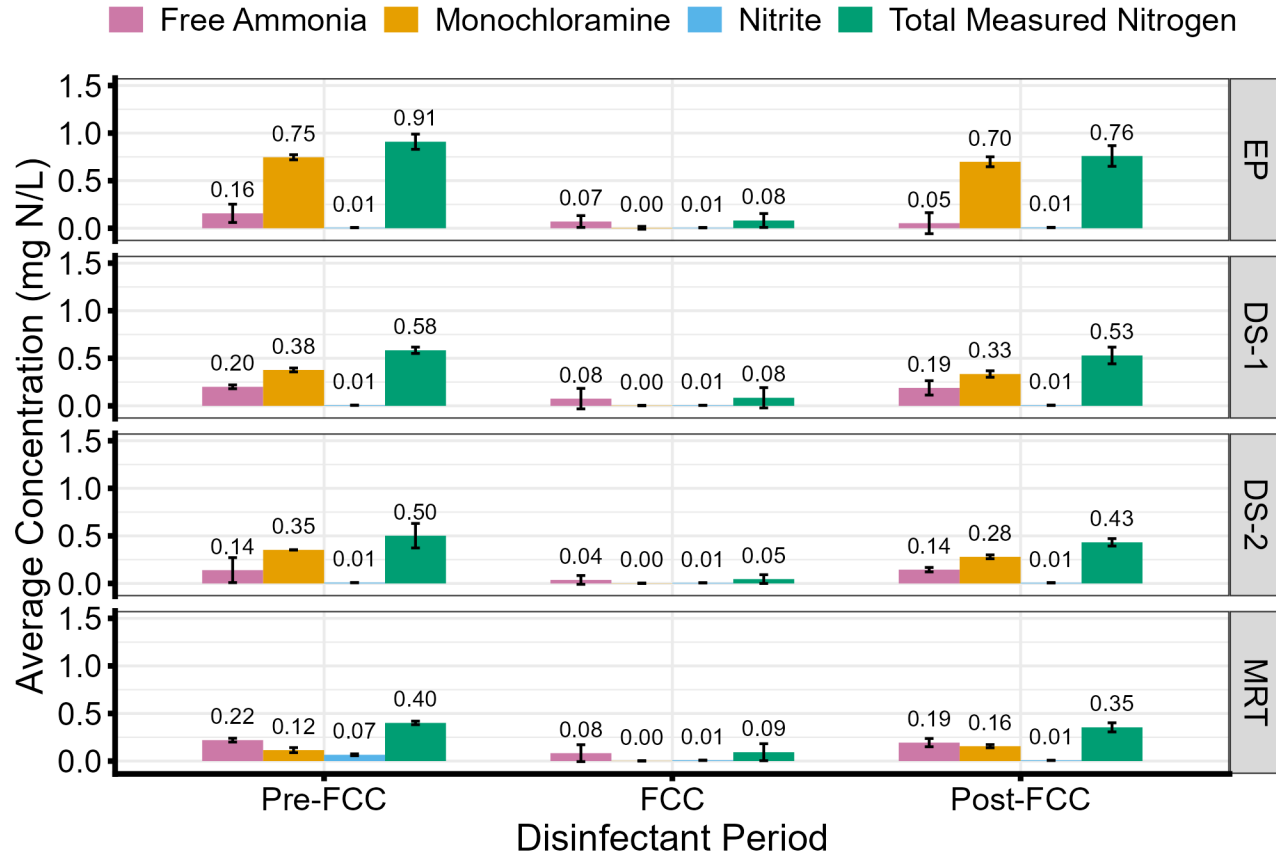


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 - Current LRAA
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 - mLRAA vs LRAA?
- No issue for this system
 - Low current LRAAs
 - HAA5: 114 vs. 375 µg/L
 - THM4: 104 vs. 430 µg/L
- Other systems?



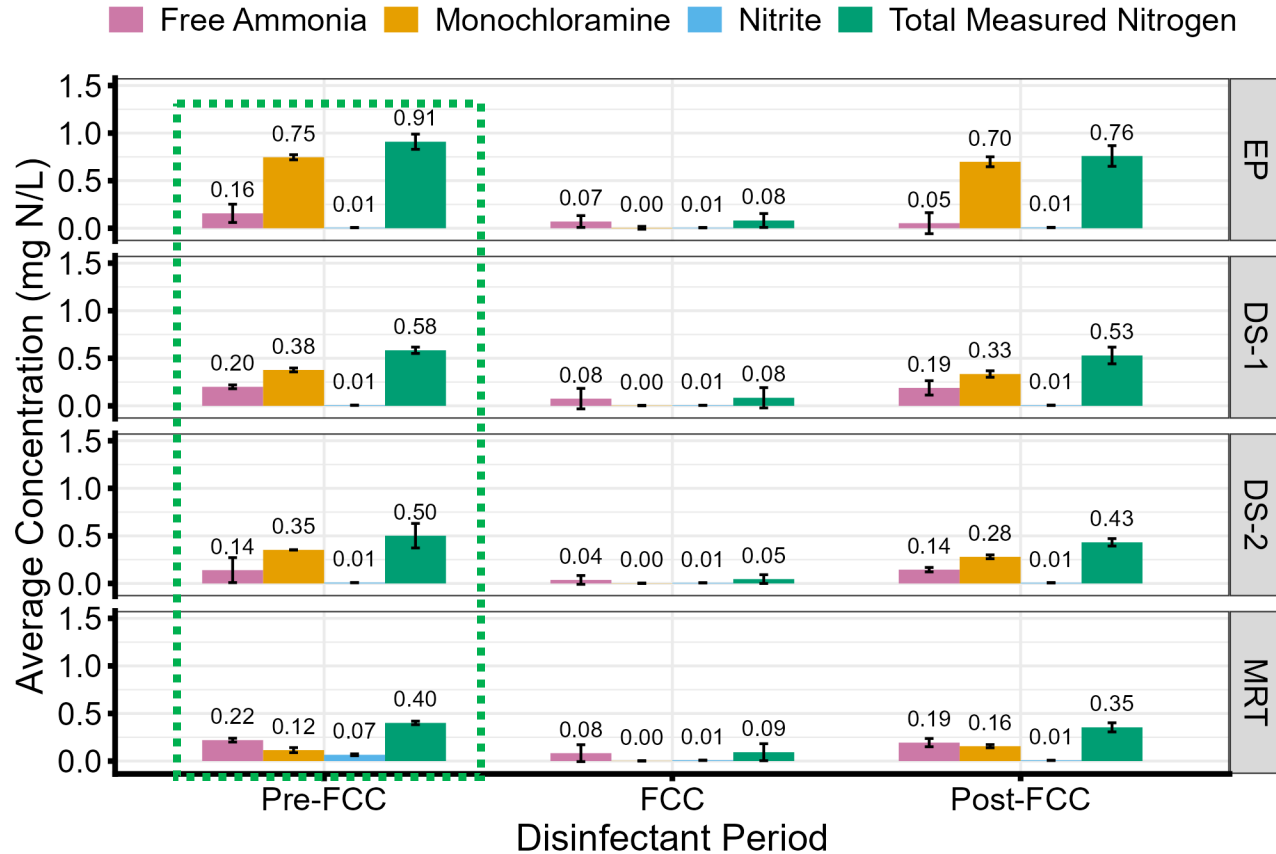
Nitrogen Species (Steady State)



Nitrogen Species (Steady State)

➤ Pre-FCC

- Free ammonia > 0.1 mg N/L
- Nitrite only at MRT (chlorite?)
- Total measured N ↓

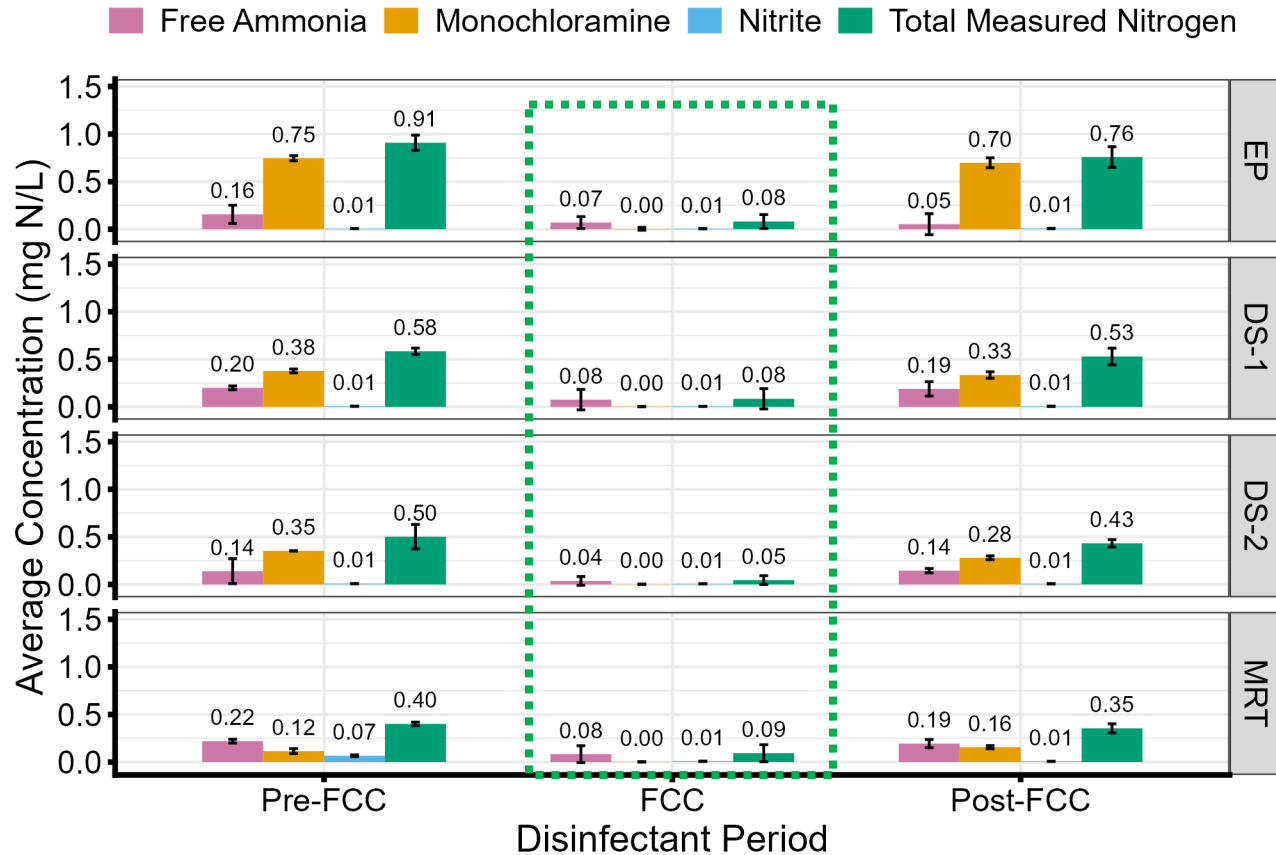


Nitrogen Species (Steady State)

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➤ FCC removed N



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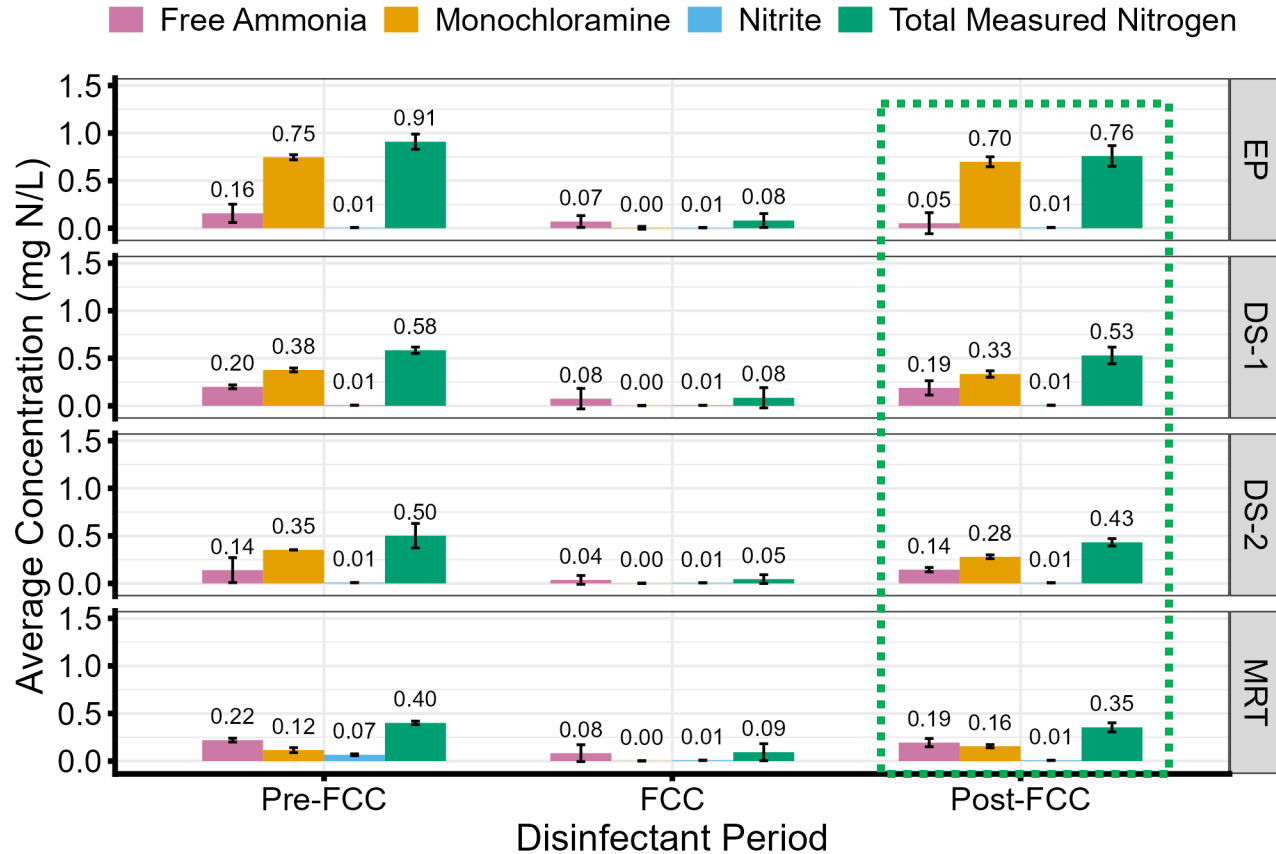
➤ Pre-FCC

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- Total measured N ↓

➤ FCC removed N

➤ Post-FCC

- Like Pre-FCC
- No nitrite at MRT



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- Free ammonia > 0.1 mg N/L
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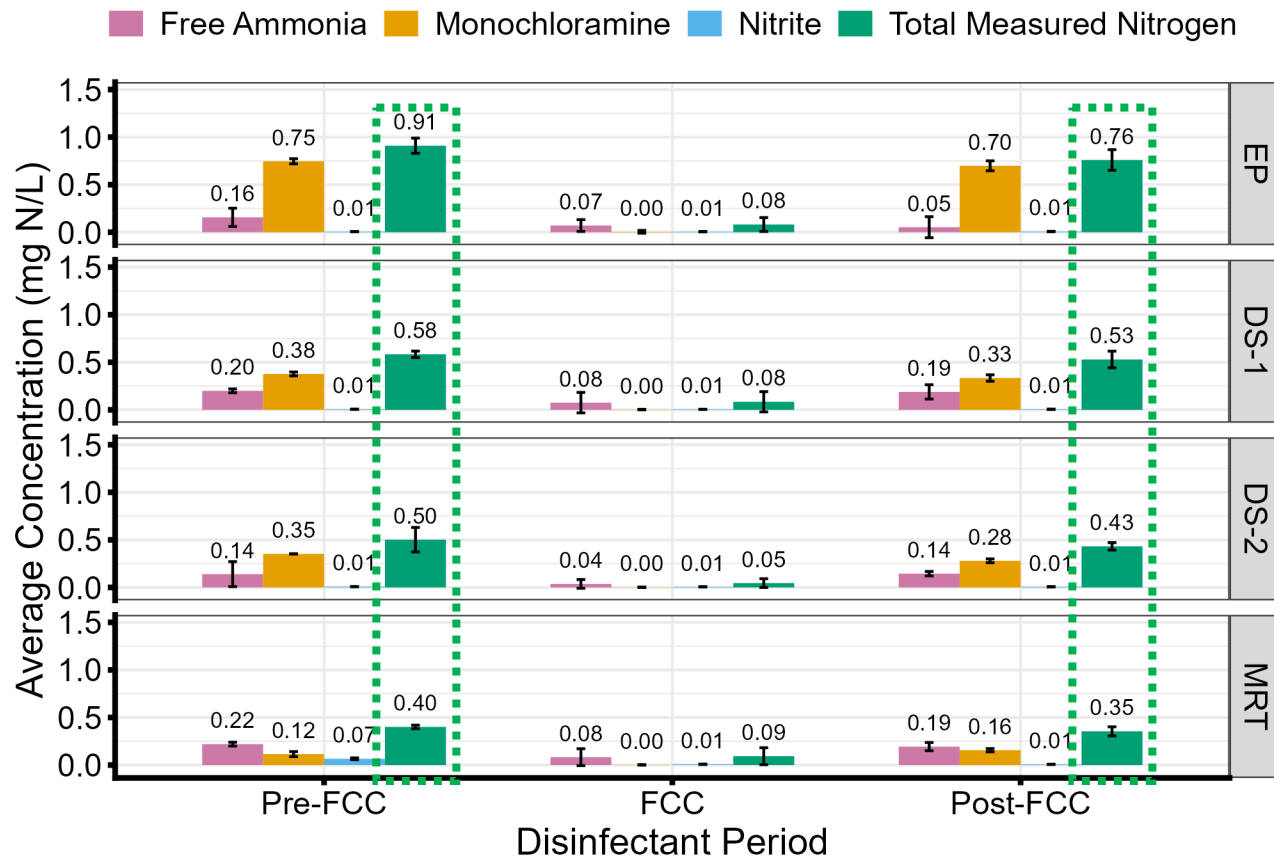
➤ FCC removed N

➤ Post-FCC

- Like Pre-FCC
- No nitrite at MRT

➤ Missing N (0.4–0.5 mg N/L)

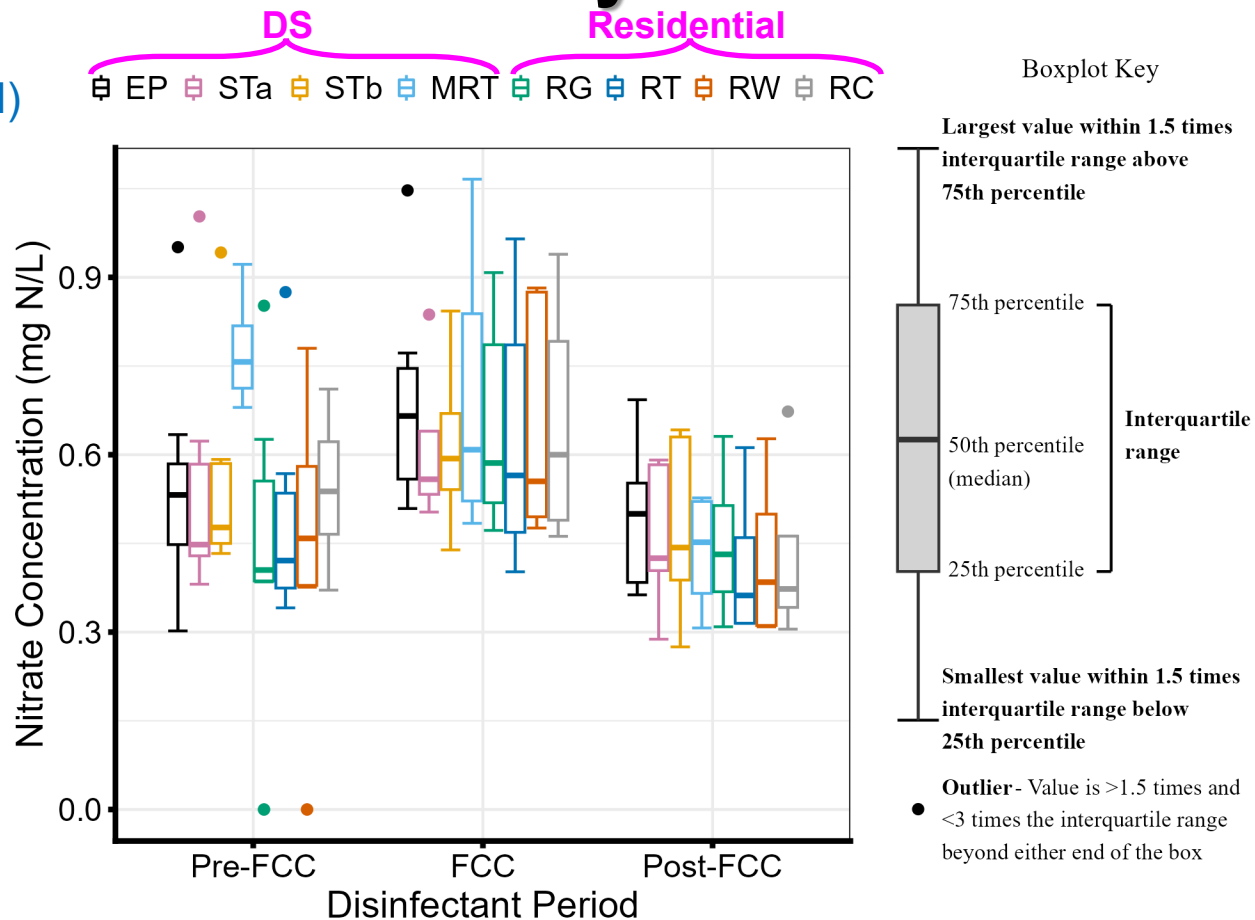
- Nitrate?
 - Complete nitrification?
 - Inorganic nitrite oxidation (pH)?
- Nitrogen gas (mono decay)?



Nitrate Summary

➤ Holding time

- Inorganic nitrite oxidation (pH)
- Nitrite + nitrate?

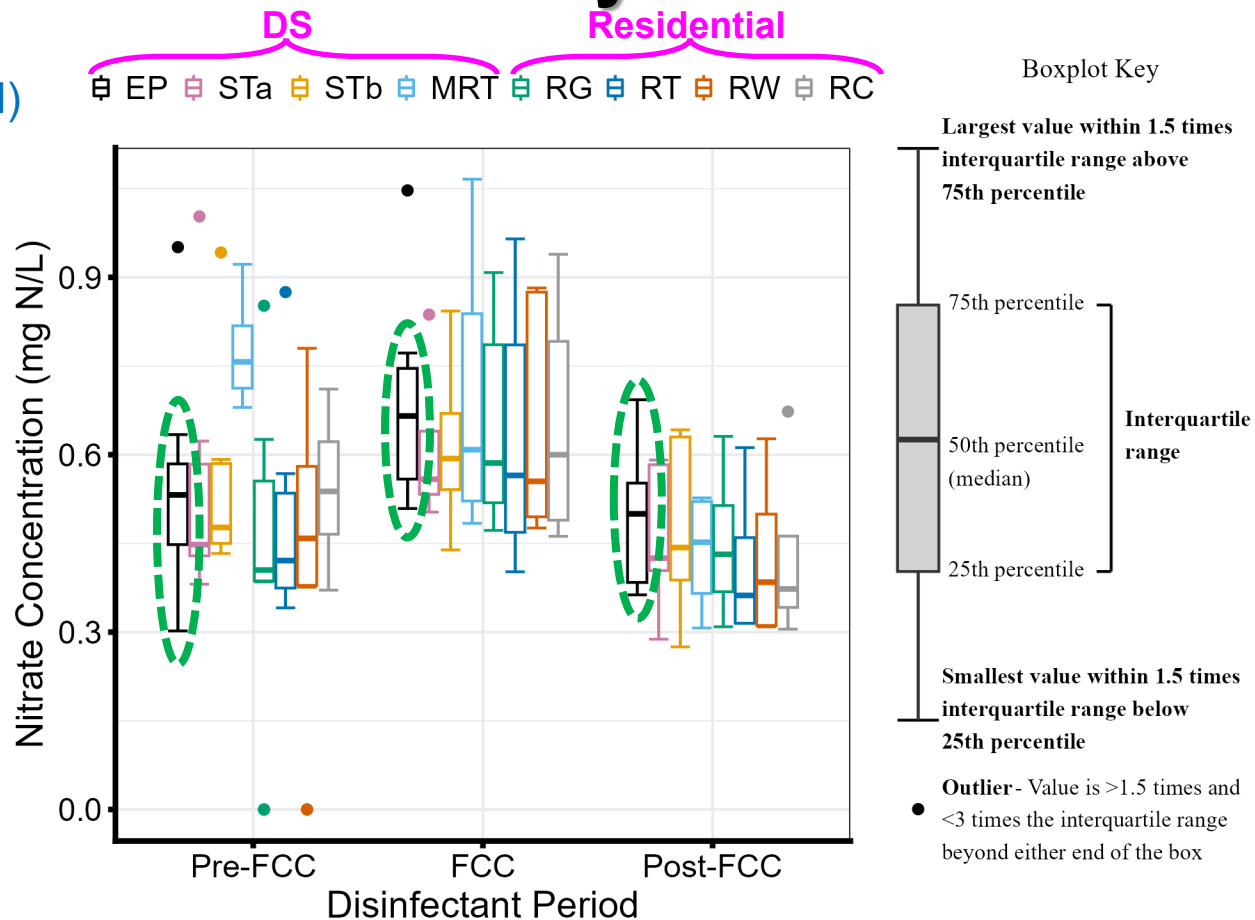


Nitrate Summary

➤ Holding time

- Inorganic nitrite oxidation (pH)
- Nitrite + nitrate?

➤ Variable at EP (0.3–1 mg N/L)



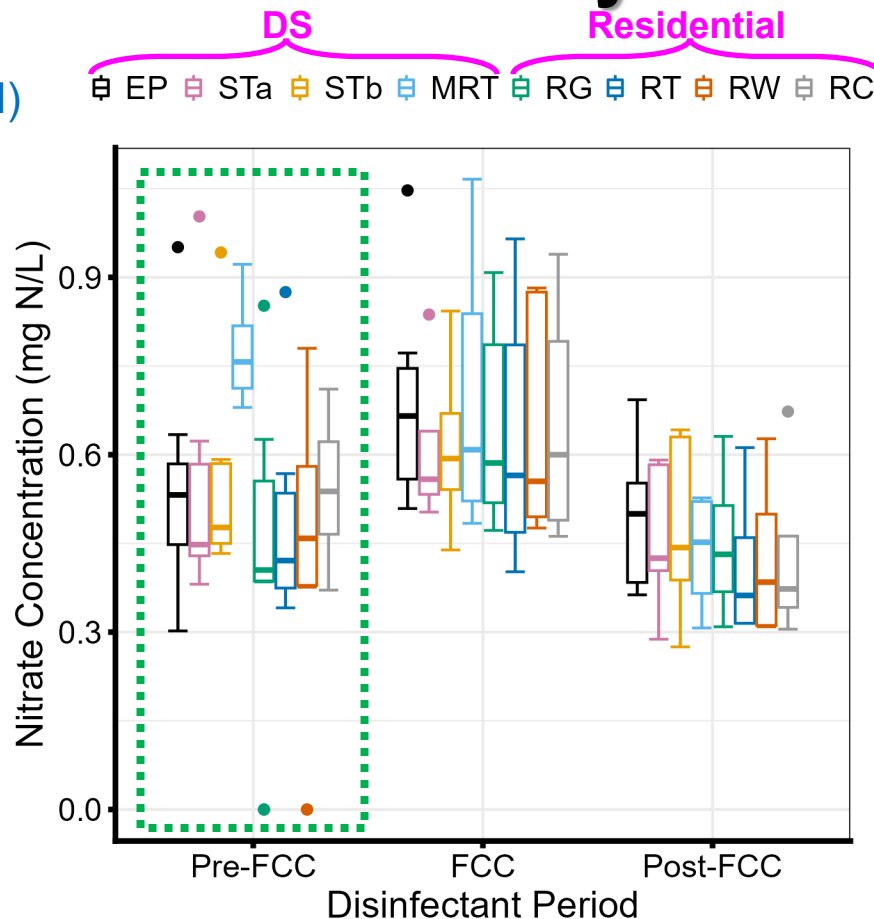
Nitrate Summary

➤ Holding time

- Inorganic nitrite oxidation (pH)
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➤ Pre-FCC



Nitrate Summary

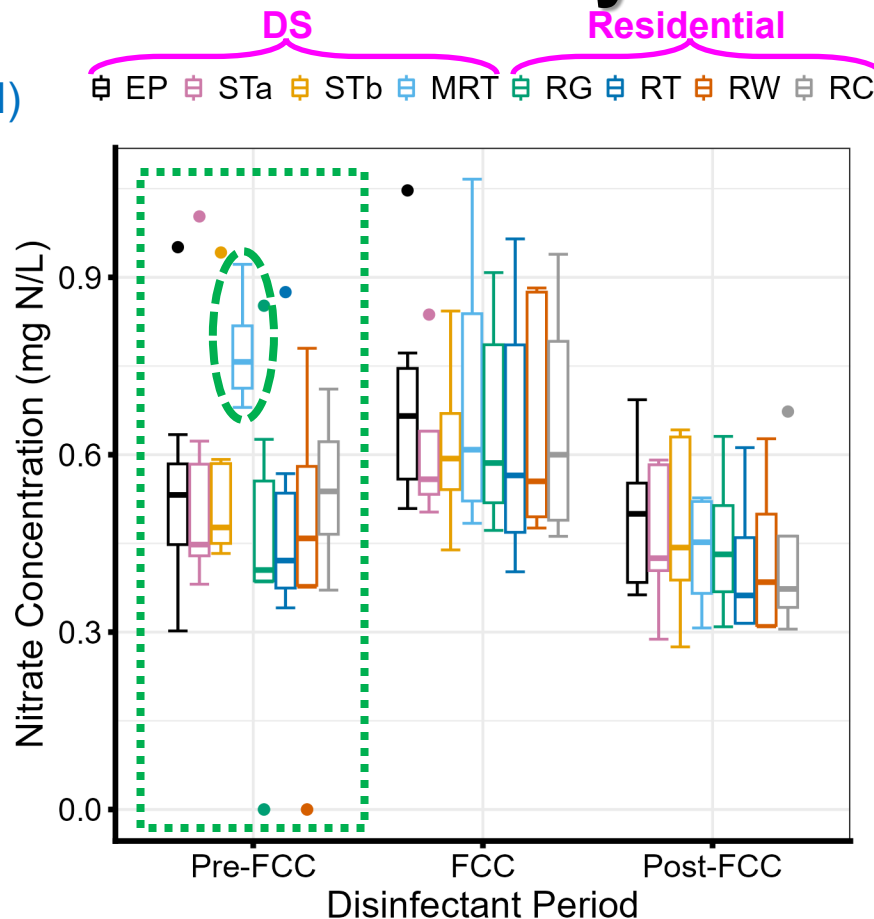
➤ Holding time

- Inorganic nitrite oxidation (pH)
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➤ Variable at EP (0.3–1 mg N/L)

➤ Pre-FCC

- ↑ at MRT



Boxplot Key

Largest value within 1.5 times
interquartile range above
75th percentile

75th percentile

50th percentile
(median)

25th percentile

Interquartile
range

Smallest value within 1.5 times
interquartile range below
25th percentile

● Outlier - Value is >1.5 times and
<3 times the interquartile range
beyond either end of the box

Nitrate Summary

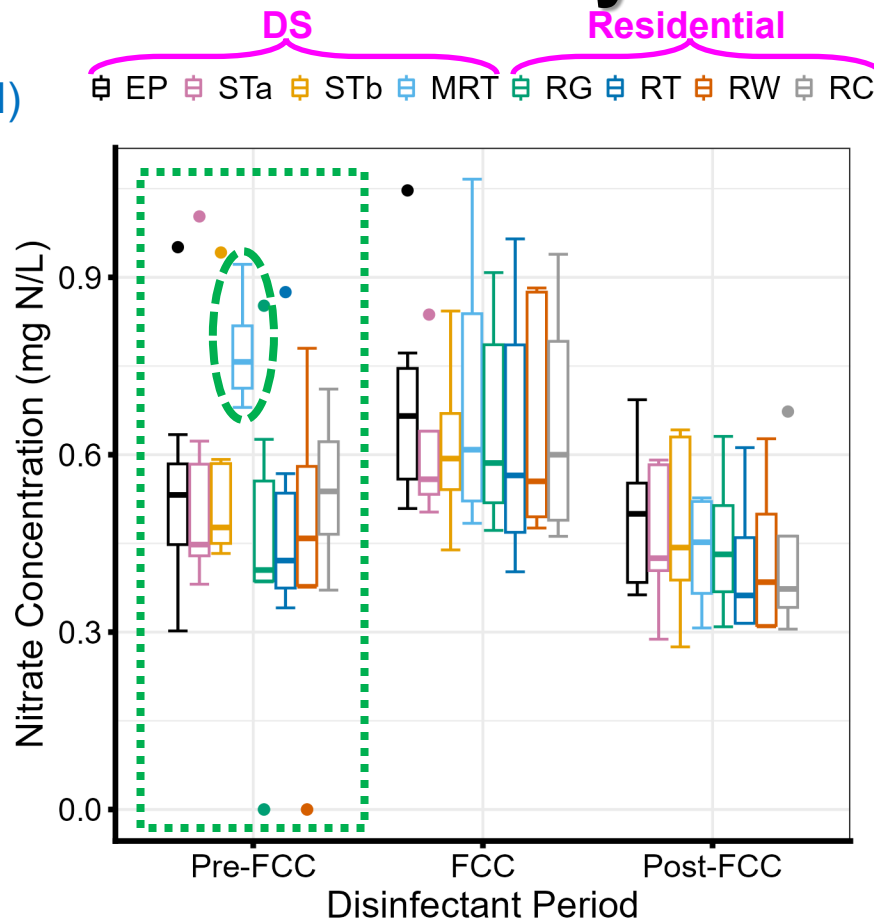
➤ Holding time

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- Nitrite + nitrate?

➤ Variable at EP (0.3–1 mg N/L)

➤ Pre-FCC

- ↑ at MRT
- Only site with nitrite (0.1 mg N/L)
- 0.5 mg N/L gap (without nitrate)
- 0.1–0.2 mg N/L nitrate Δ
- 0.3–0.4 mg N/L gap (with nitrate)



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interquartile range above
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Nitrate Summary

➤ Holding time

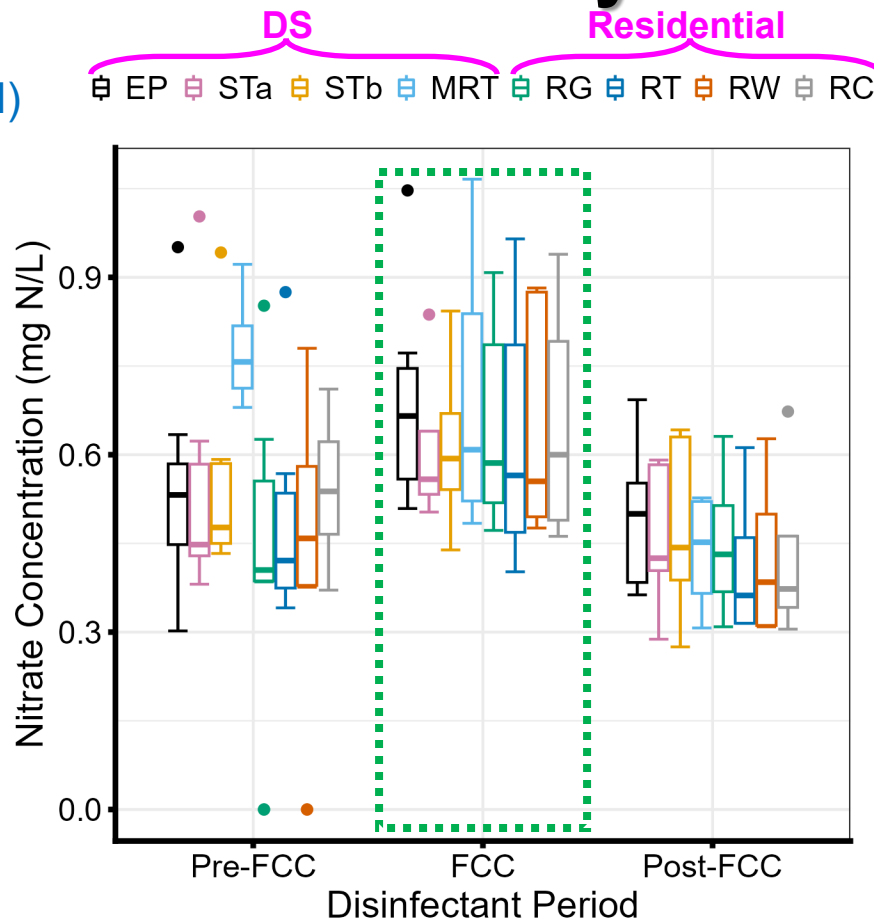
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➤ Variable at EP (0.3–1 mg N/L)

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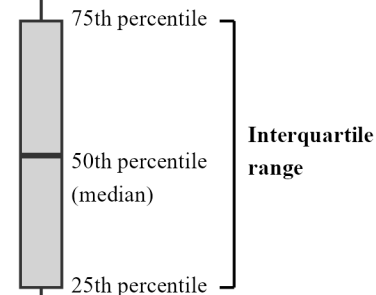
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- 0.3–0.4 mg N/L gap (with nitrate)

➤ FCC no clear ↑



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interquartile range above
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Smallest value within 1.5 times
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- Inorganic nitrite oxidation (pH)
- Nitrite + nitrate?

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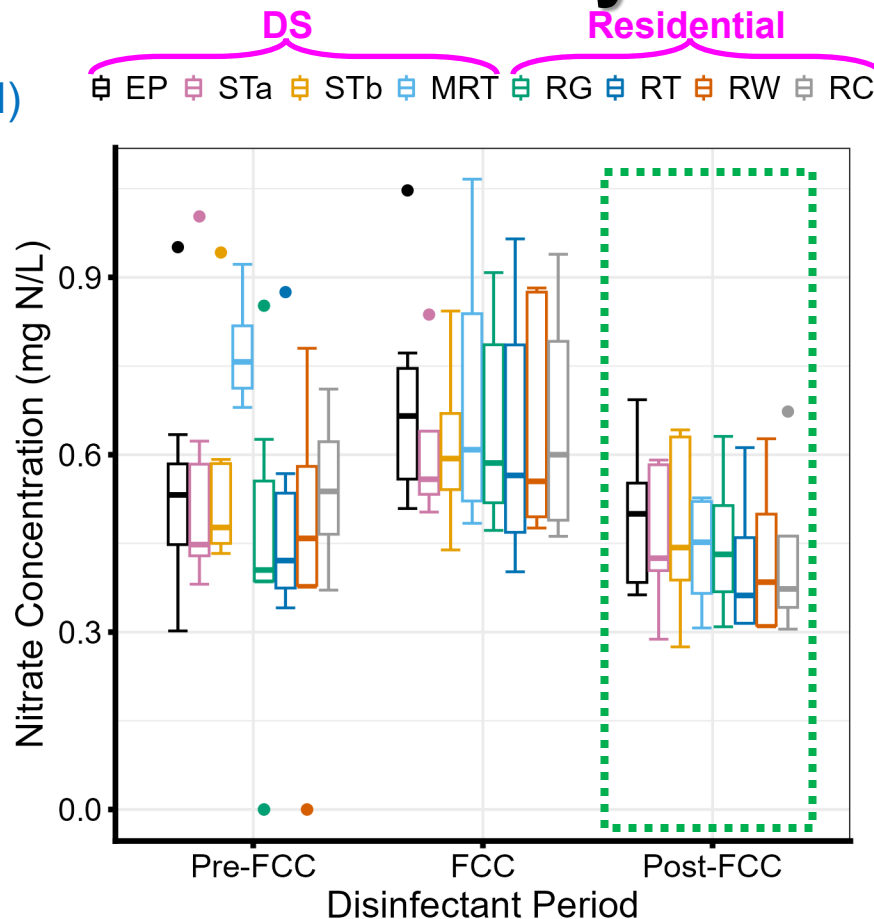
➤ Pre-FCC

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➤ FCC no clear ↑

➤ Post-FCC no clear ↑

- Like FCC trend
- 0.4 mg N/L gap (with nitrate)



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Largest value within 1.5 times
interquartile range above
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50th percentile
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25th percentile

Interquartile
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Smallest value within 1.5 times
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25th percentile

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Nitrate Summary

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- Inorganic nitrite oxidation (pH)
- Nitrite + nitrate?

➤ Variable at EP (0.3–1 mg N/L)

➤ Pre-FCC

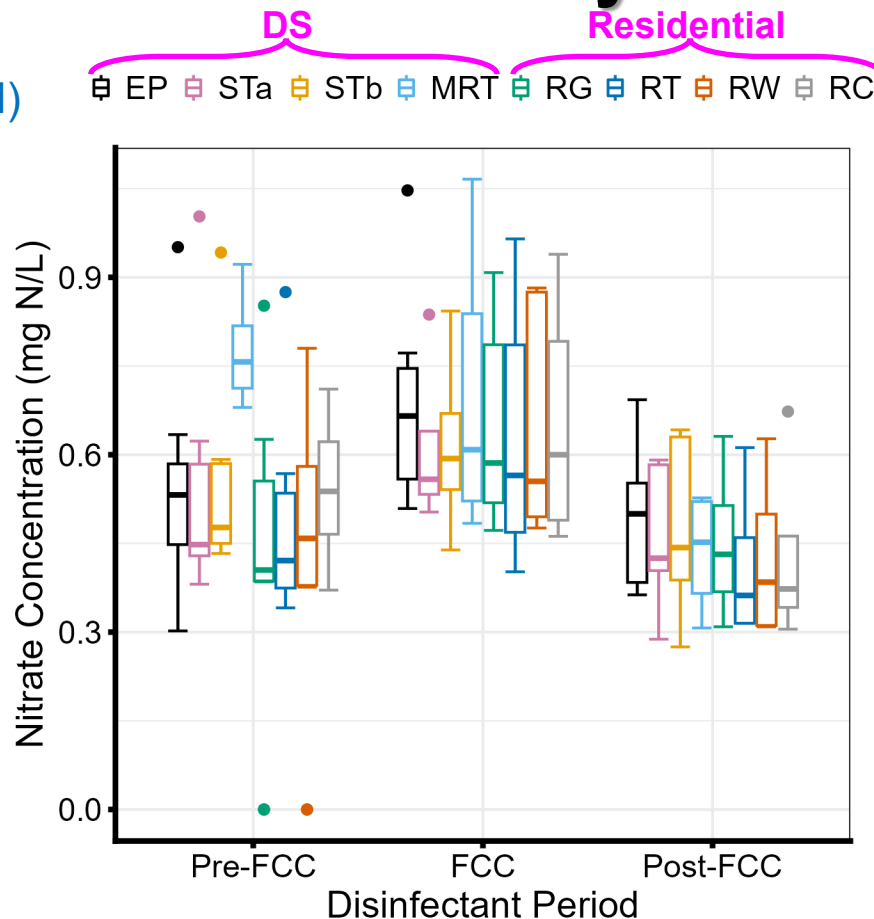
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➤ FCC no clear ↑

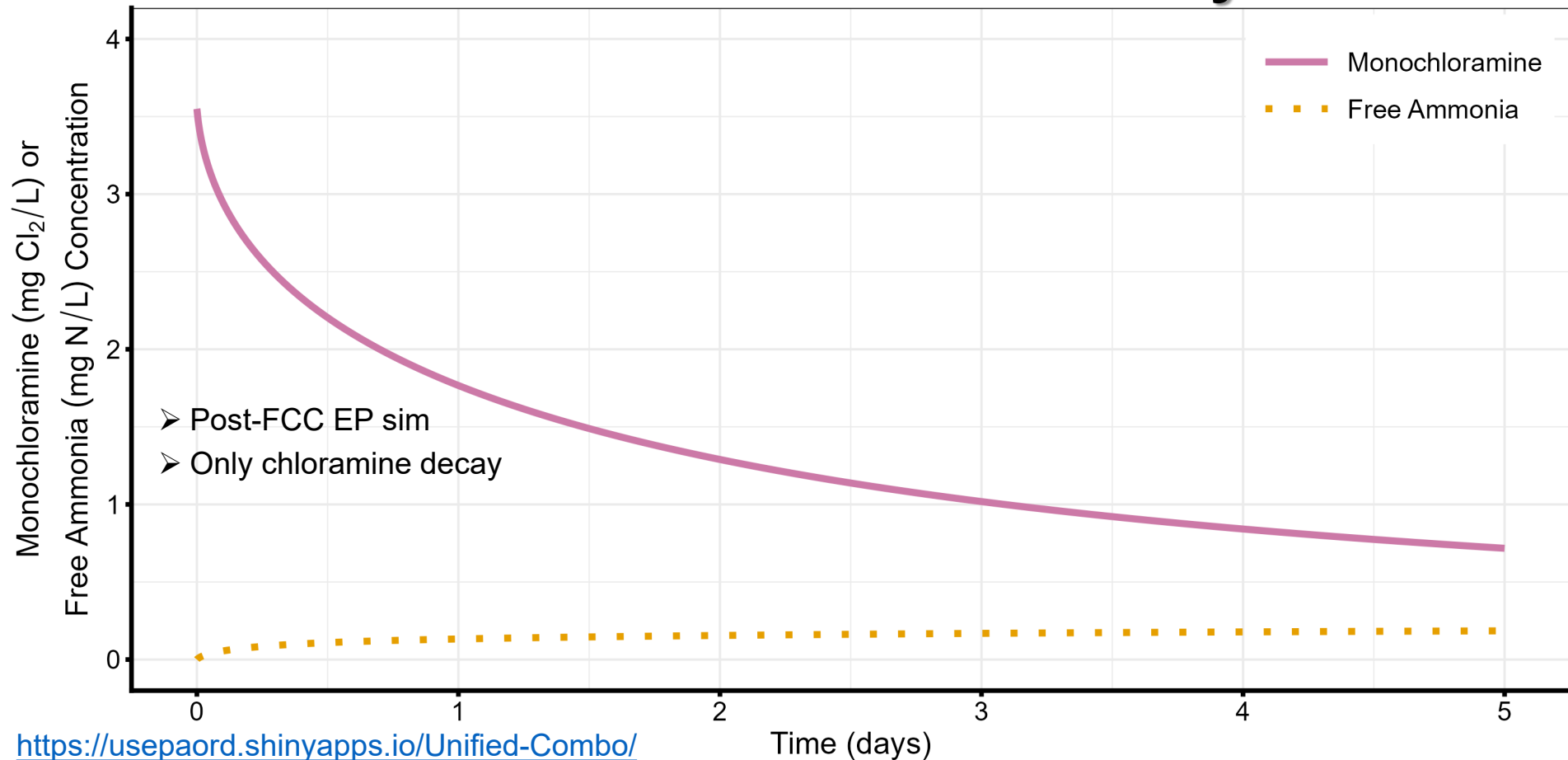
➤ Post-FCC no clear ↑

- Like FCC trend
- 0.4 mg N/L gap (with nitrate)

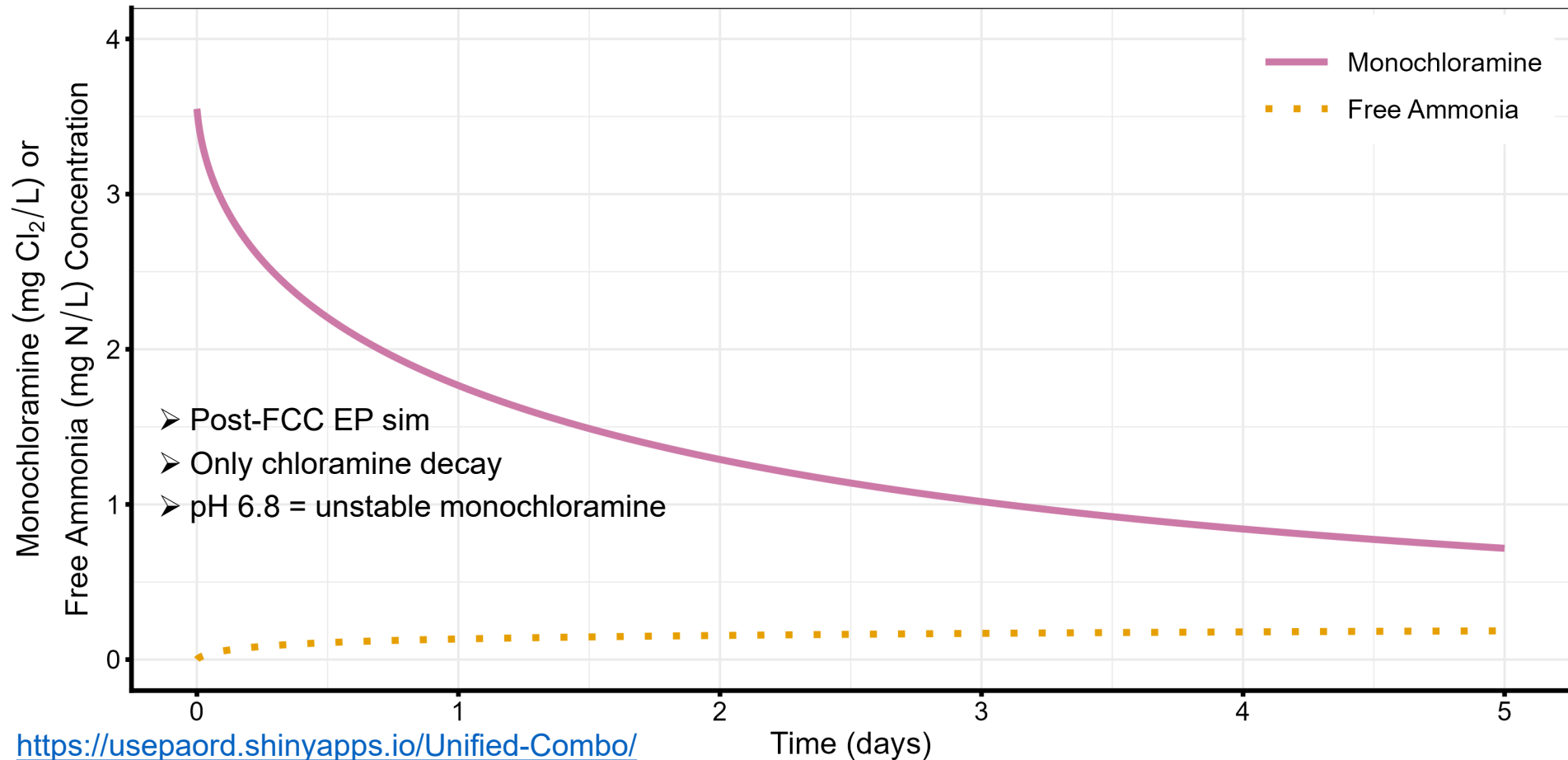
➤ Implies nitrogen gas (decay)



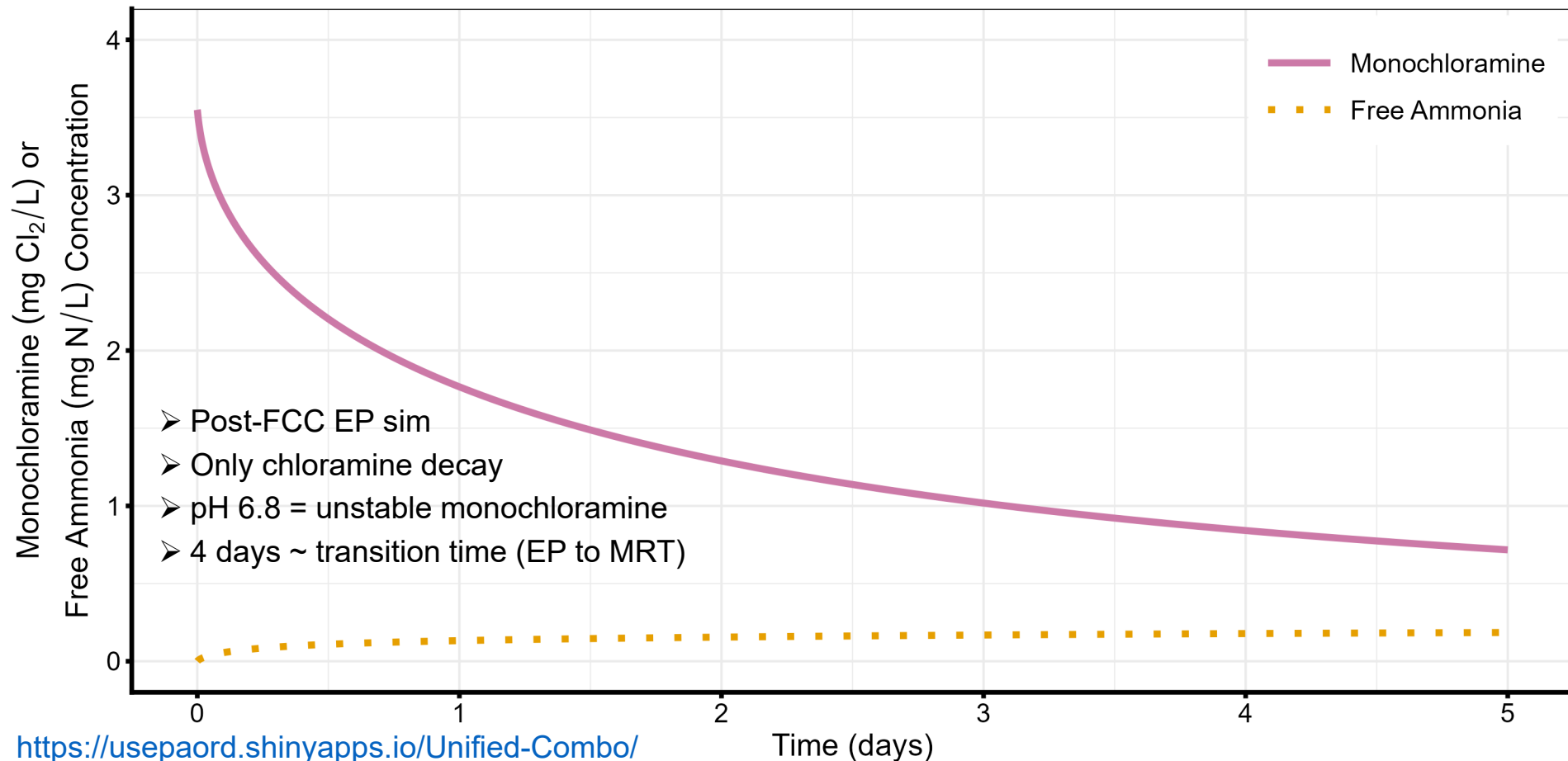
Simulated Chloramine Stability



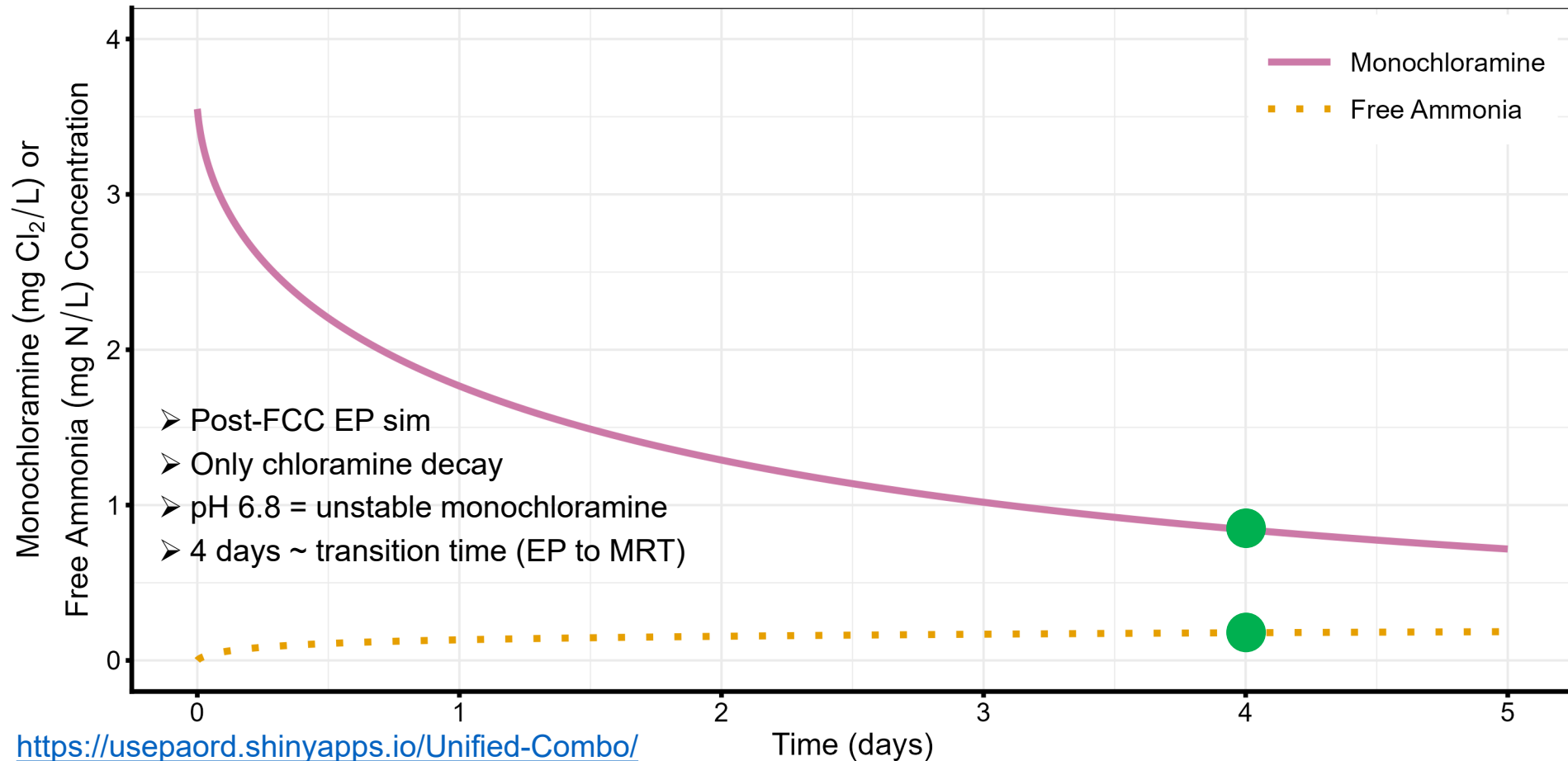
Simulated Chloramine Stability



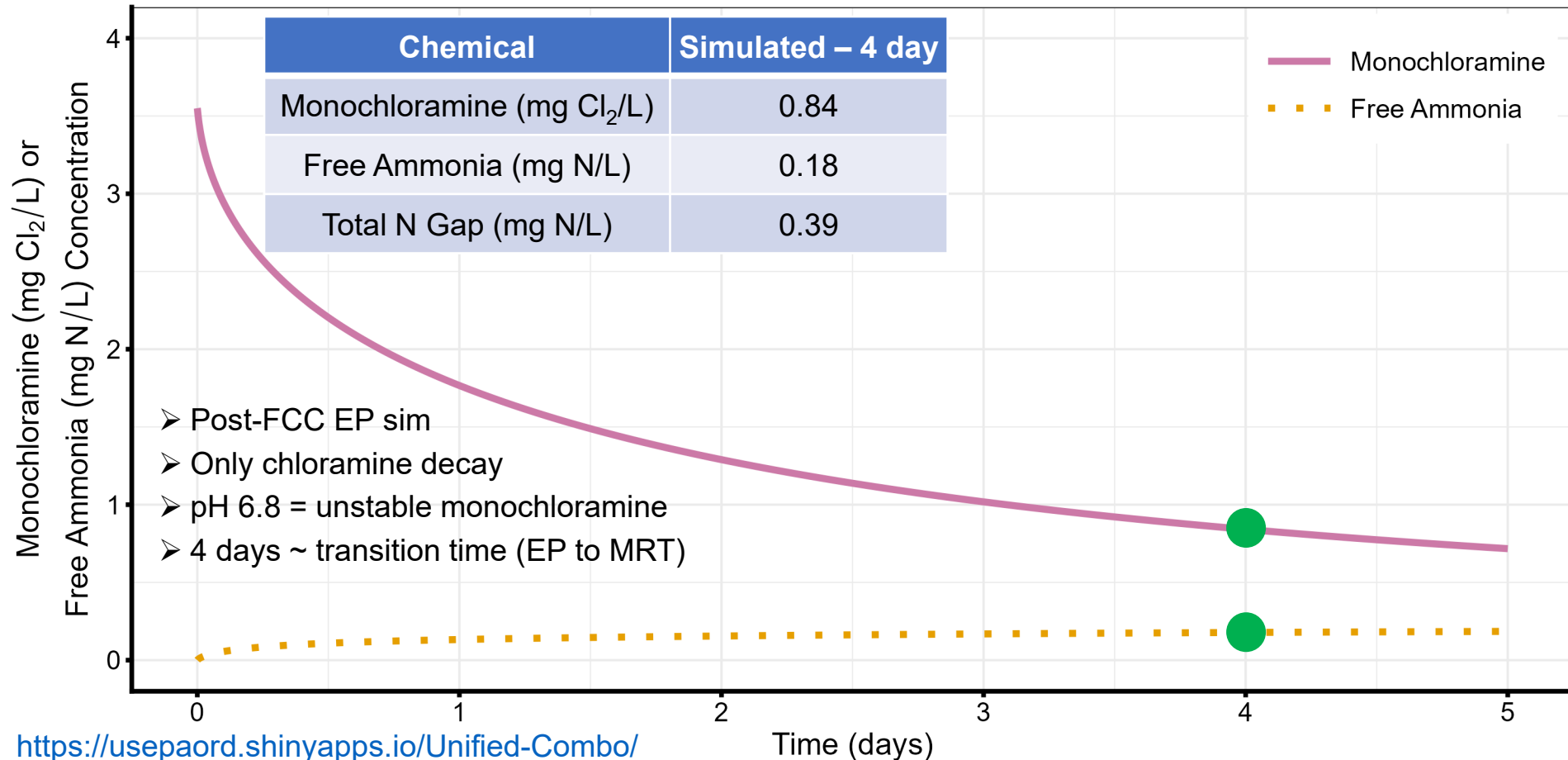
Simulated Chloramine Stability



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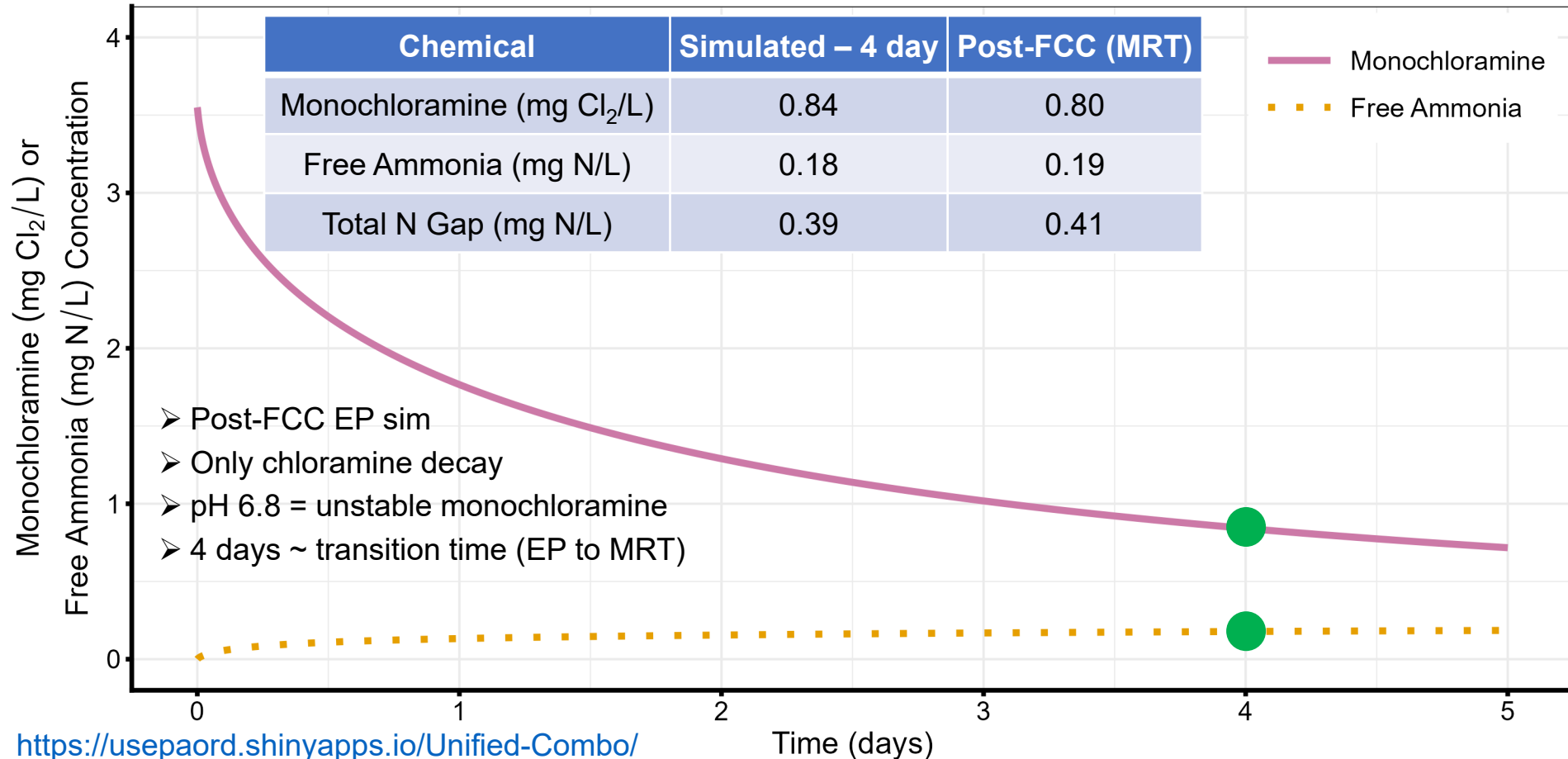


Simulated Chloramine Stability



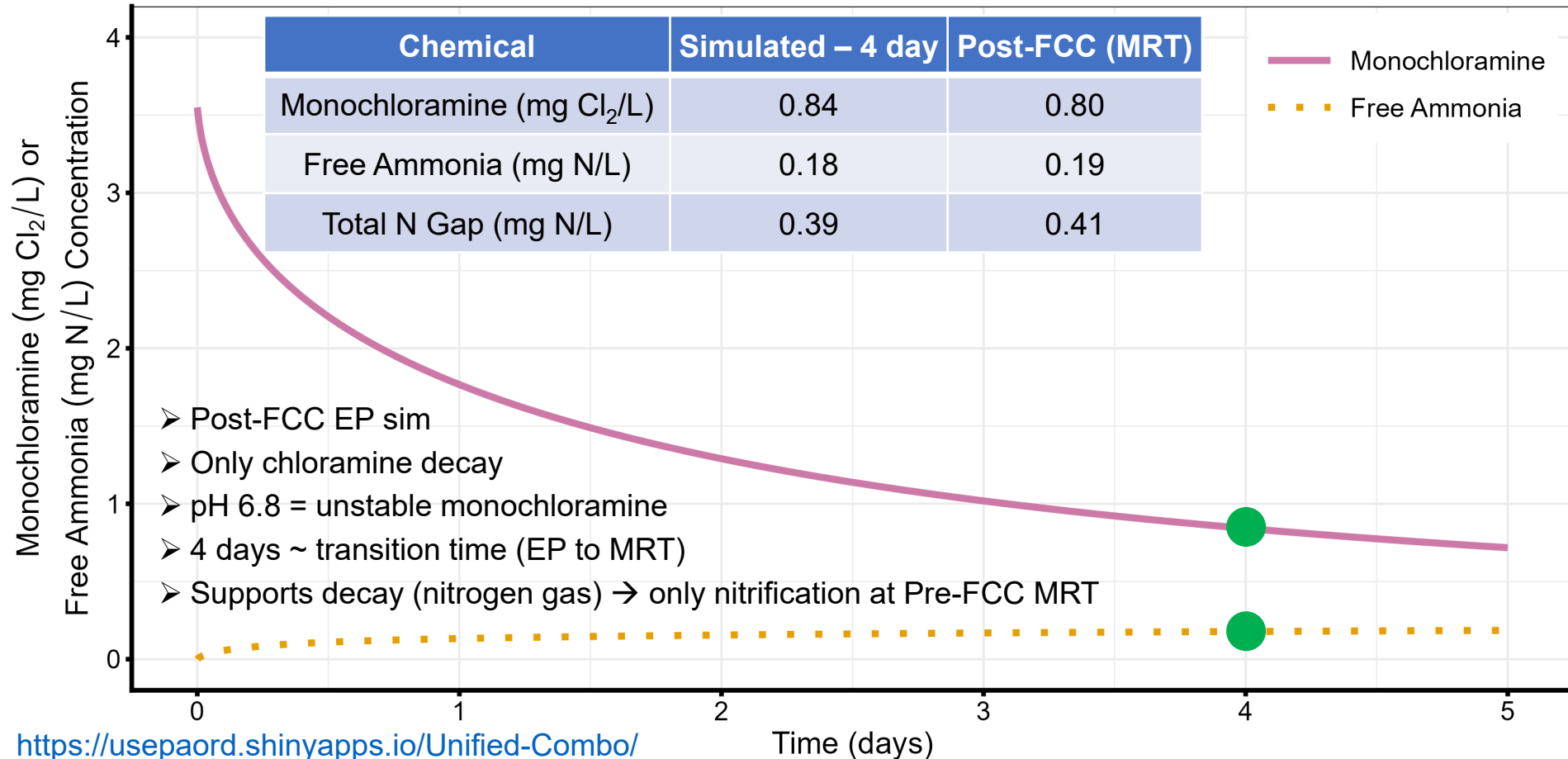
<https://usepaord.shinyapps.io/Unified-Combo/>

Simulated Chloramine Stability



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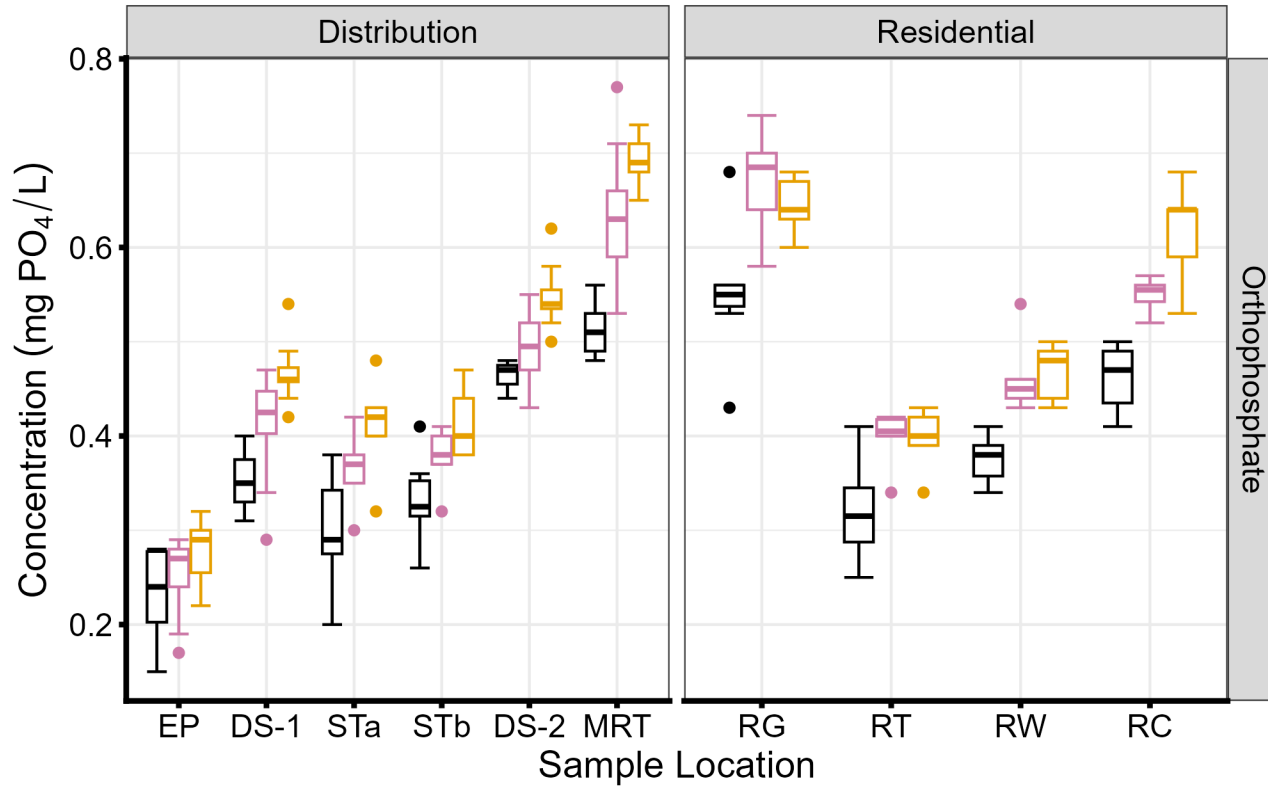
Simulated Chloramine Stability



<https://usepaord.shinyapps.io/Unified-Combo/>

Orthophosphate

Pre-FCC FCC Post-FCC



Boxplot Key

Largest value within 1.5 times interquartile range above 75th percentile

75th percentile

50th percentile (median)

25th percentile

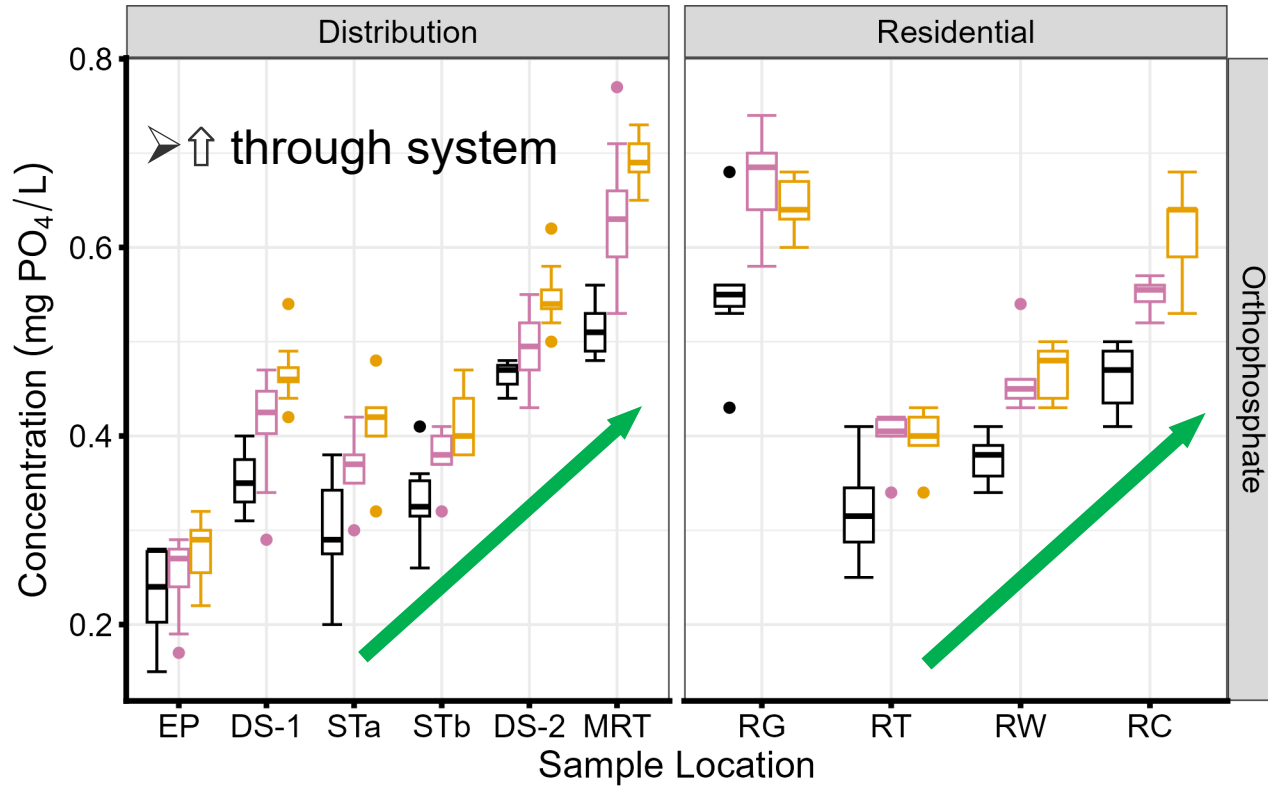
Interquartile range

Smallest value within 1.5 times interquartile range below 25th percentile

Outlier - Value is >1.5 times and <3 times the interquartile range beyond either end of the box

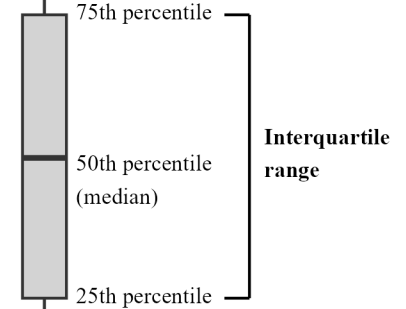
Orthophosphate

Pre-FCC FCC Post-FCC



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Largest value within 1.5 times interquartile range above 75th percentile

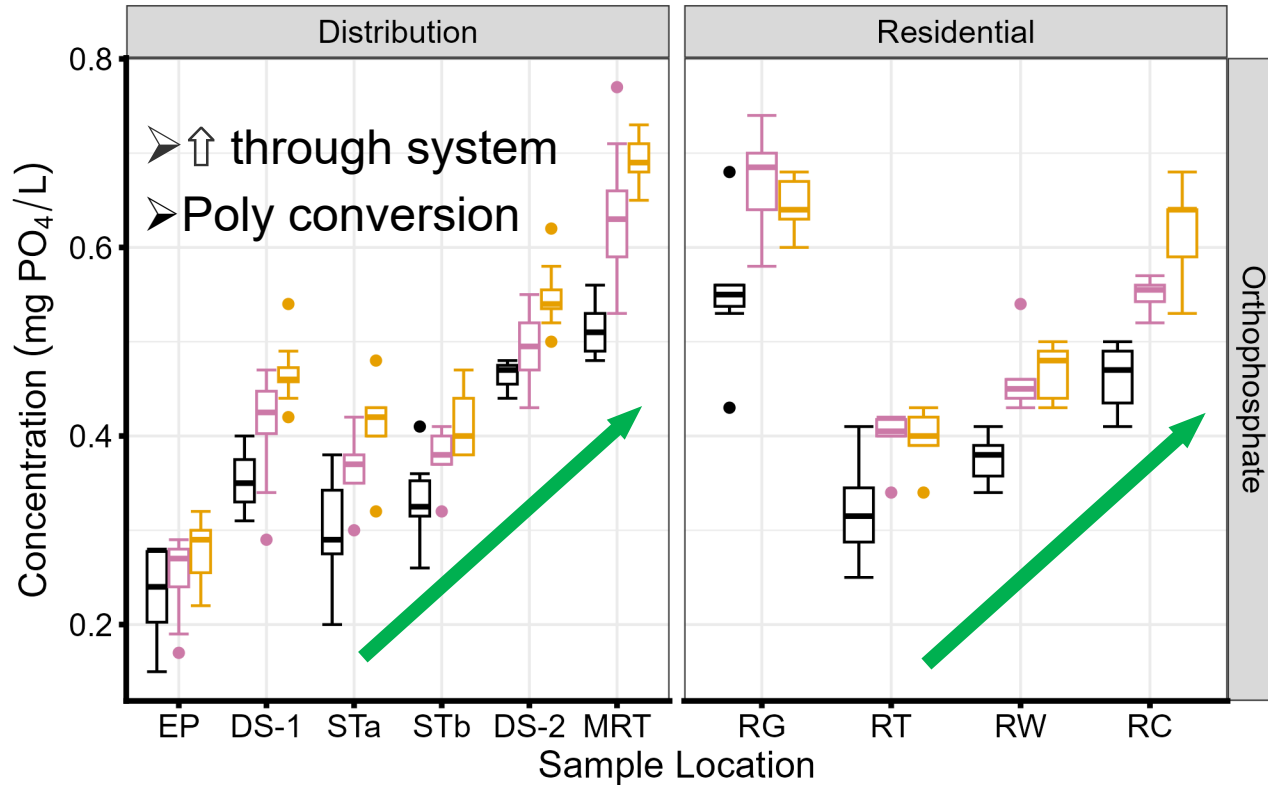


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Orthophosphate

Pre-FCC FCC Post-FCC



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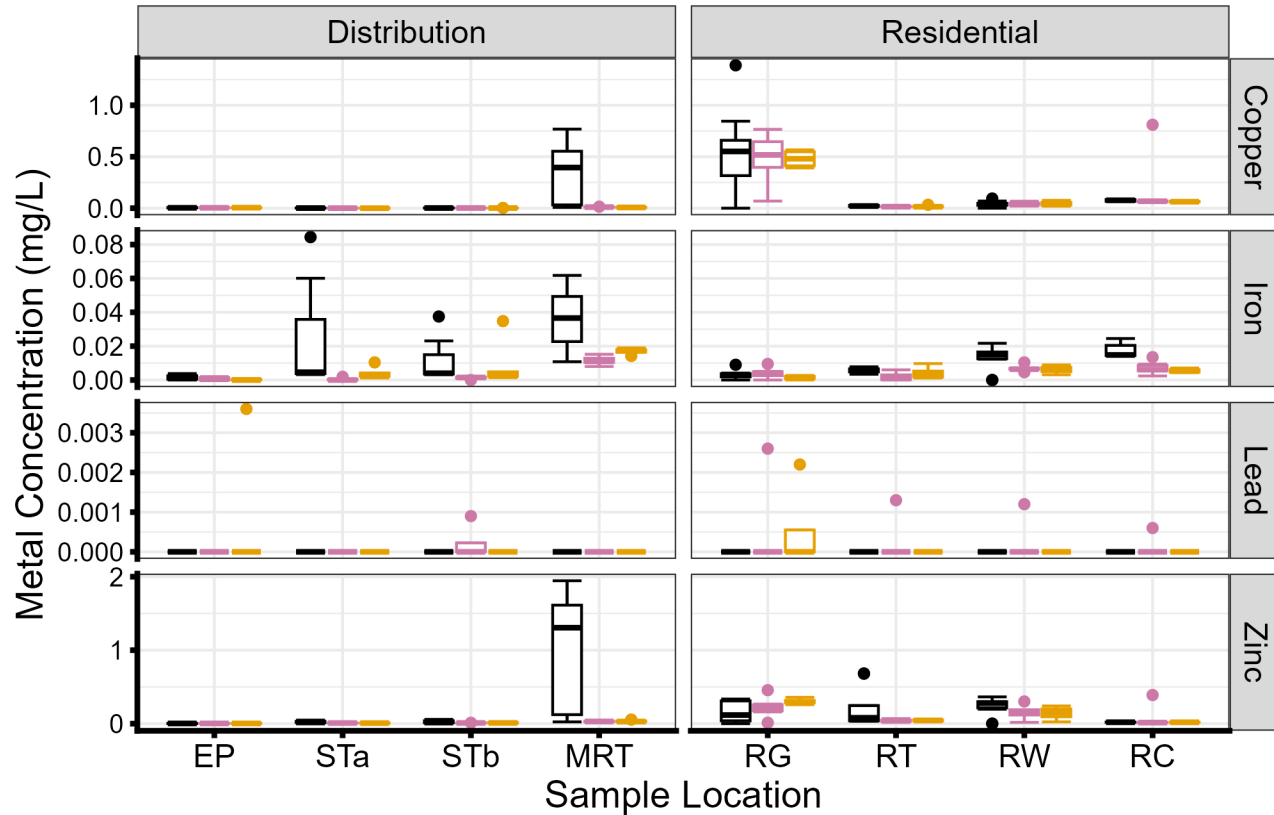
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Metals

Pre-FCC FCC Post-FCC

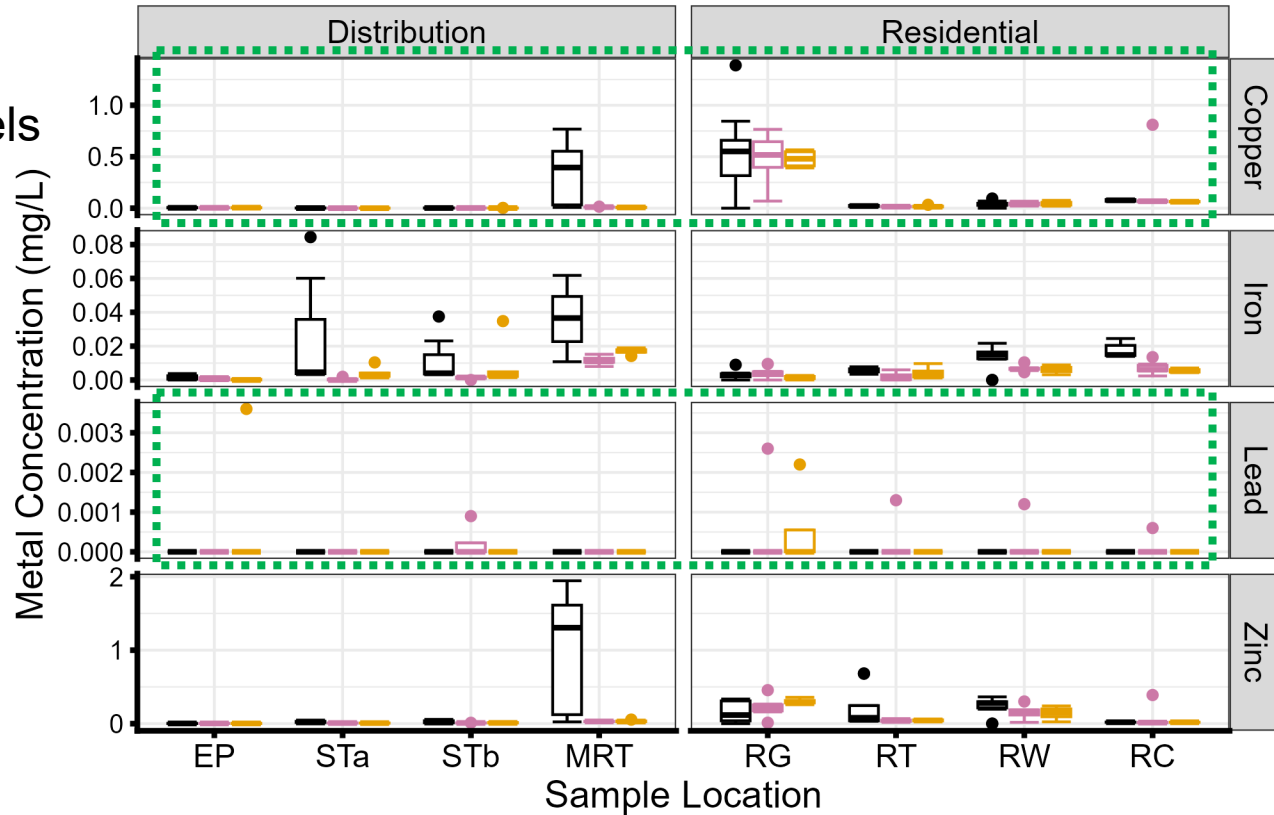
➤ Generally low metals



Metals

Pre-FCC FCC Post-FCC

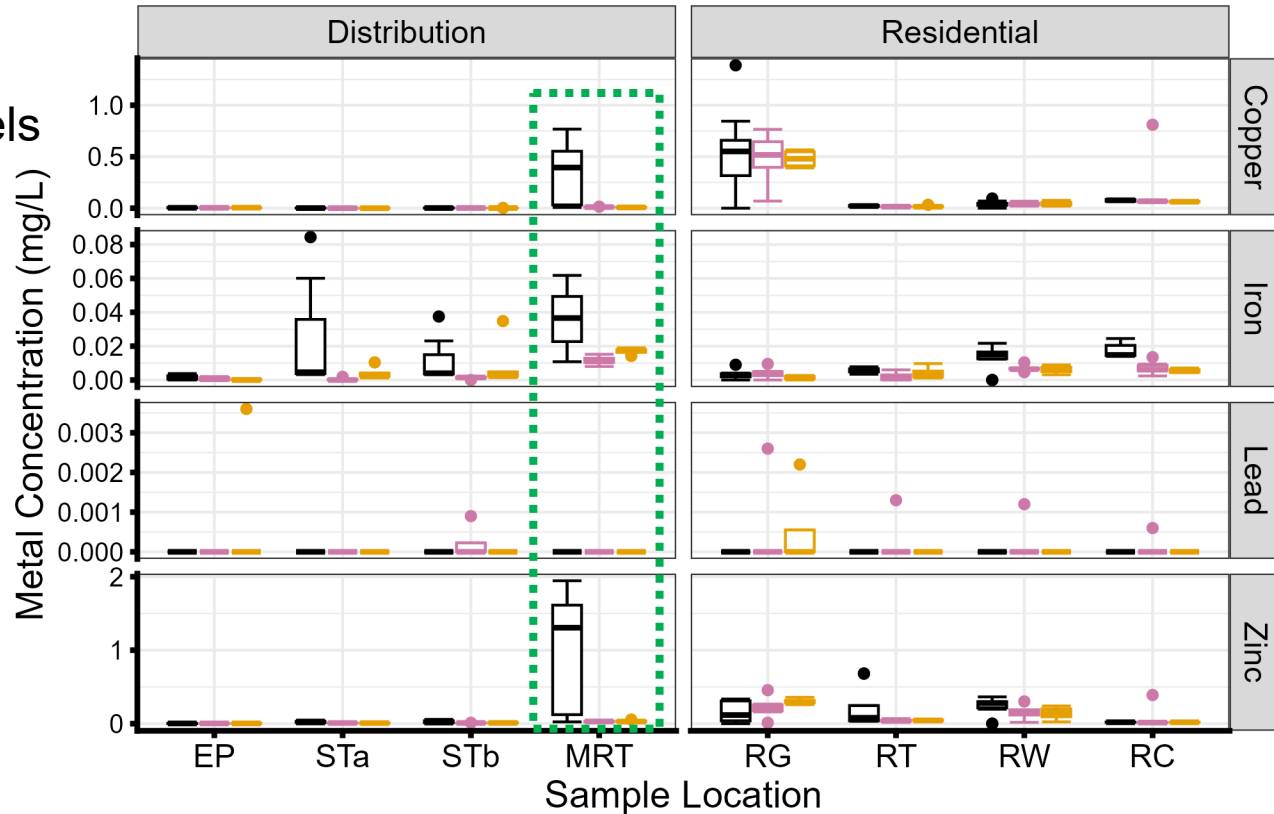
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- Copper & lead < action levels



Metals

Pre-FCC FCC Post-FCC

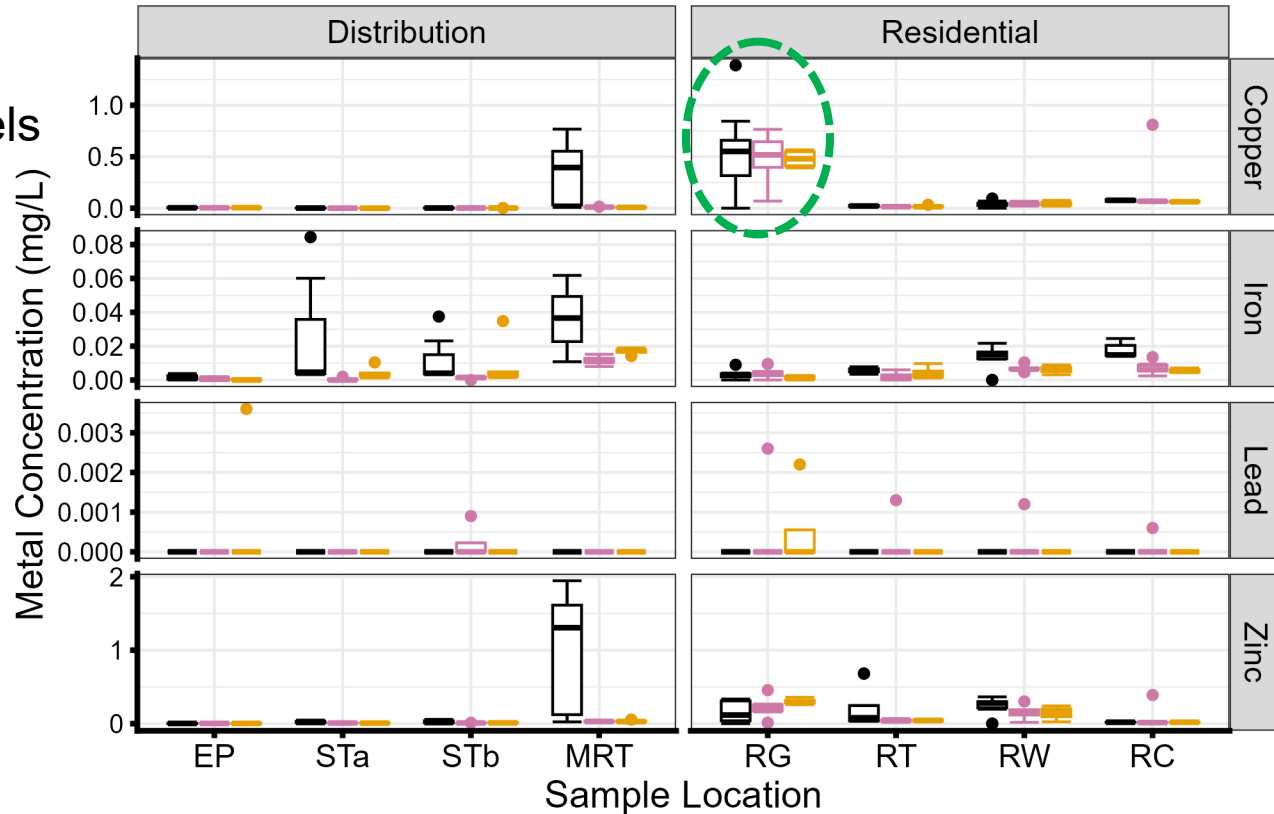
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- MRT ↓ with FCC



Metals

Pre-FCC FCC Post-FCC

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- RG consistent copper



Summary

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- MRT DBPs (µg/L) – paralleled disinfectant transition

DBP Group	Pre-FCC	FCC (Avg.)	FCC (Max.)	Post-FCC
THM4	29	89	104	35
HAA5	12	84	114	21
HAA9	13	101	134	29

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 - Implications are system dependent (DBP conc., FCC duration, ex. LRAA)

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- mLRAA calculation
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 - Implications are system dependent (DBP conc., FCC duration, ex. LRAA)
- Nitrification evidence only at Pre-FCC MRT
- Minor impact to metals

Questions?

Acknowledgements

- Anonymous utility
- Anonymous primacy agency

Contact Information

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wahman.david@epa.gov