28 April 2022

The Impact of Bromide on Chlorine Decay and Disinfection Byproduct Formation

Kyle Shimabuku, PhD, PE
Tarrah Henrie

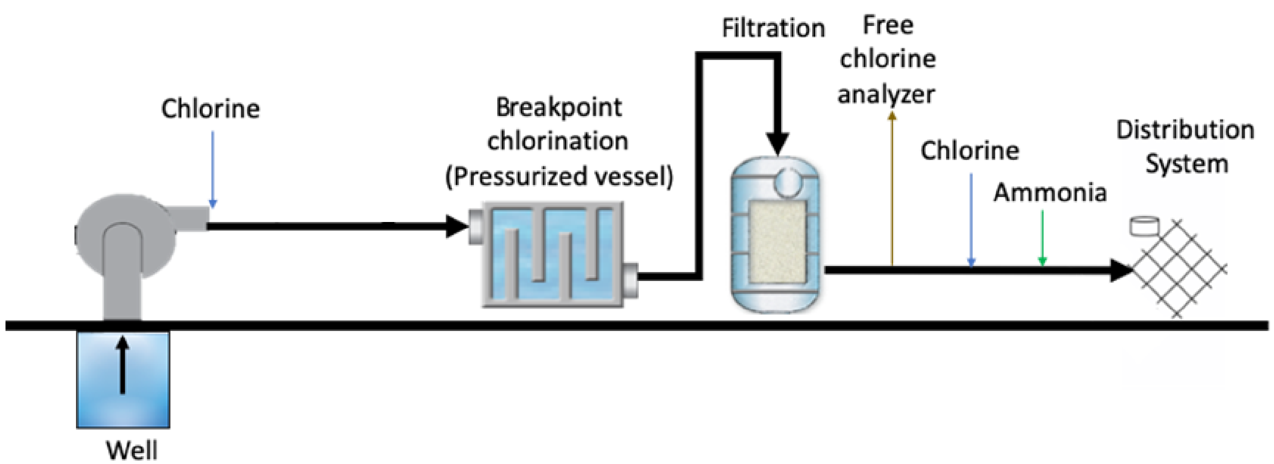
GONZAGA
UNIVERSITY

Motivation

- Chloraminated water system in California fed by groundwater was experiencing blackwater events
  - Wells contained high levels of ammonia and manganese
  - Nitrification and undetectable chlorine levels in the distribution system
  - Insufficient breakpoint chlorination was suspected

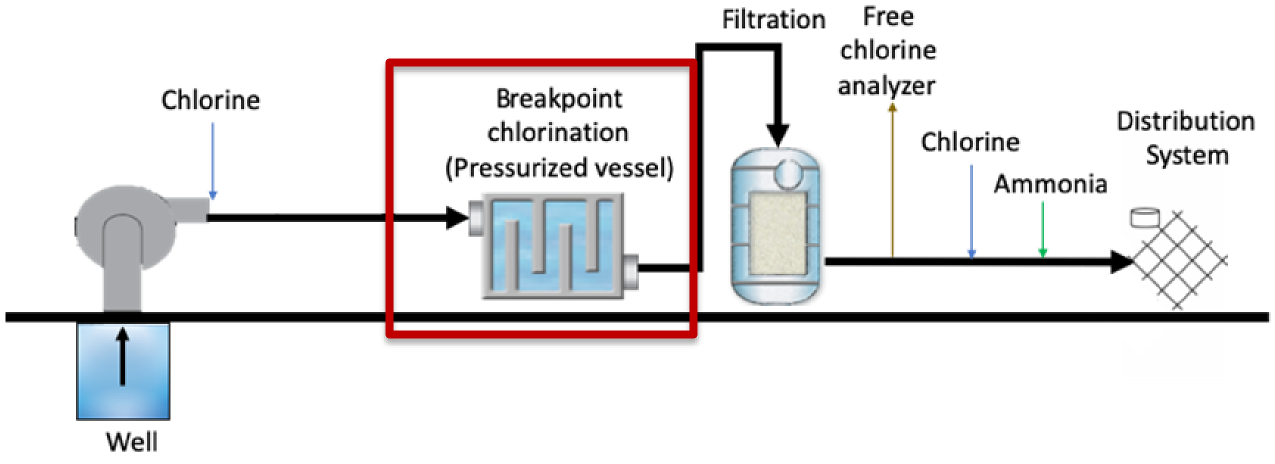
Goal

- For >10 wells containing ammonia:
  1. Determine optimal breakpoint conditions
     - Chlorine dose
     - Chlorine contact time
  2. Remove manganese with oxidation and filtration
  3. Ensure in simulated distribution system testing
     - Total chlorine residual ≥1.5 mg/L
     - TTHMs and HAA5s below 60 and 54 µg/L, respectively

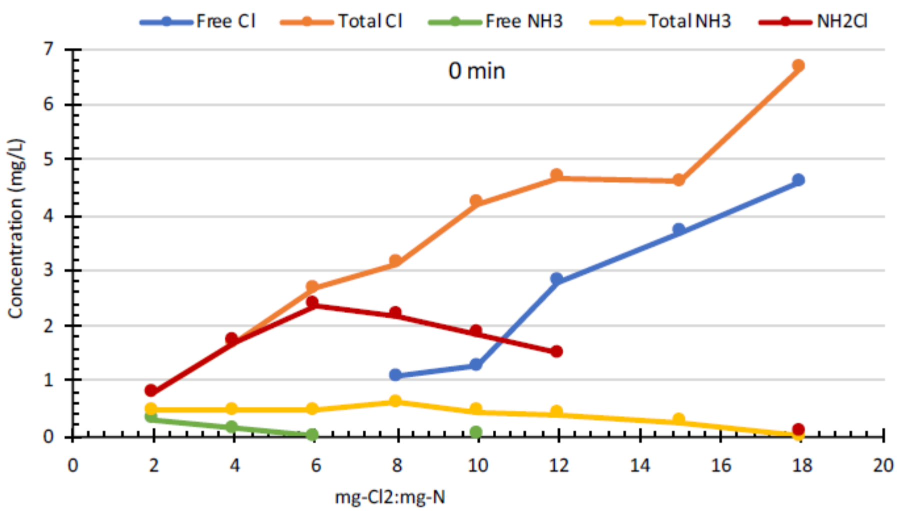


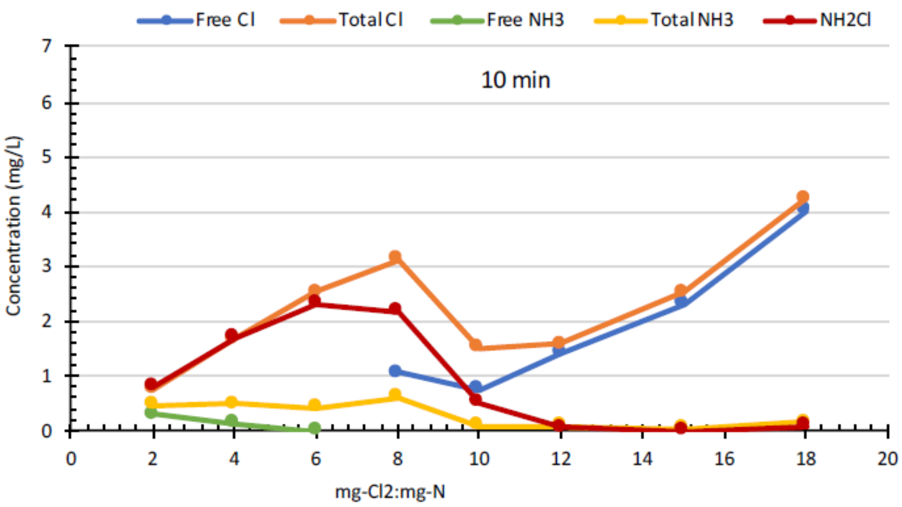
Bench-scale testing approach

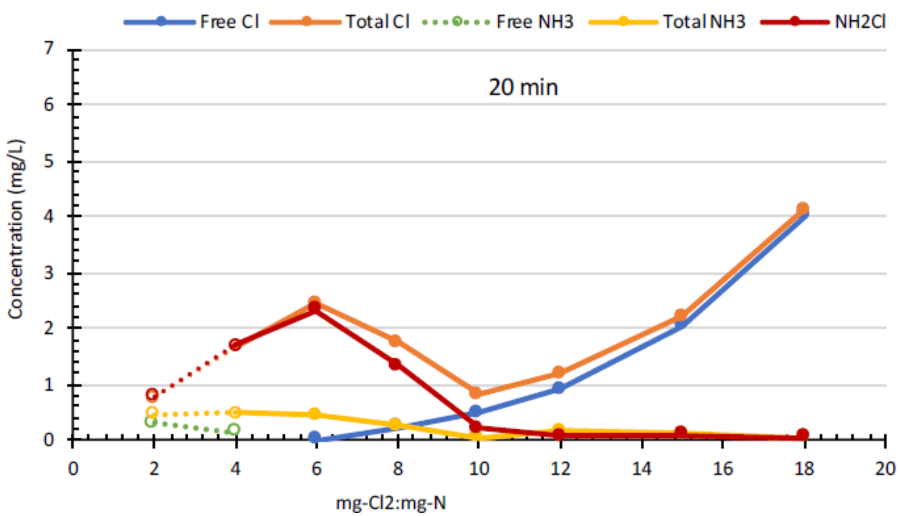
- Study focused on breakpoint chlorination as existing contact times were insufficient
- Testing involved:
  - Adding chlorine at increasing Cl_2:NH_3 ratios (e.g., from 2:1, 4:1, 6:1 etc.)
  - Measure Total Cl_2, Free Cl_2, Total NH_3, Free NH_3, and NH_2CL using a Hach SL-1000 every 10 minutes
  - Target complete NH_3 removal, a >2.5 mg/L free chlorine residual, and free and total Cl within +/- 10 %

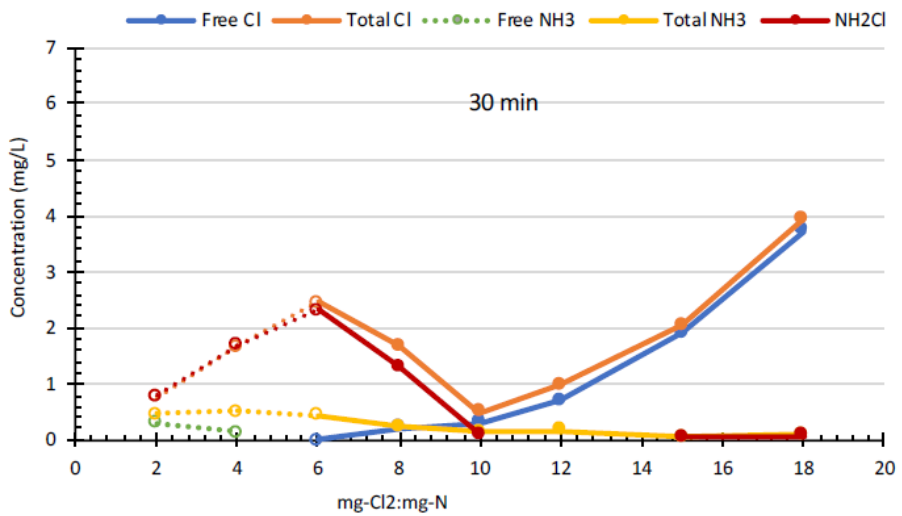


Example breakpoint curves





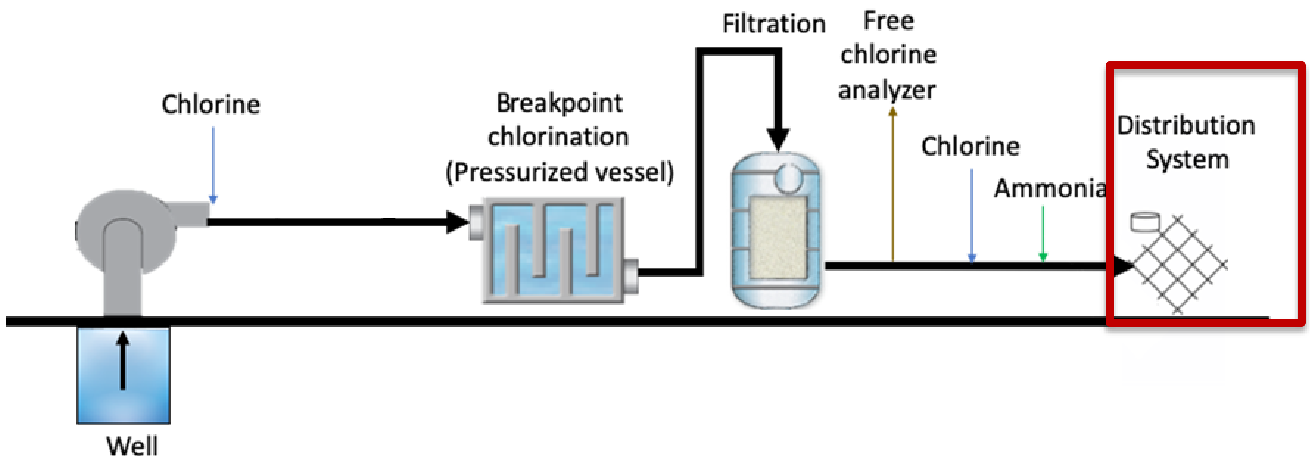




- 10-20 minutes and >14:1 Cl_2:NH_3 appears to be sufficient
- Anticipated breakpoint testing results were found

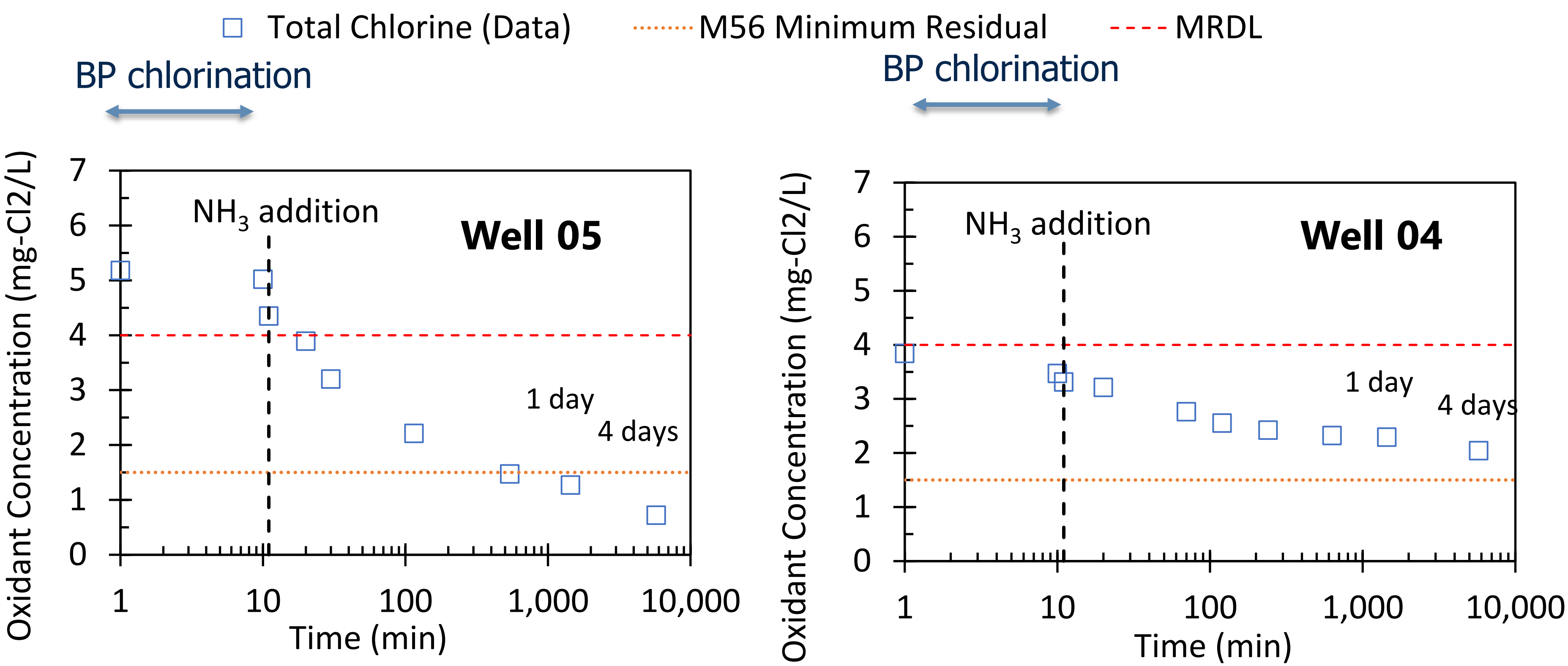
Simulated Distribution System (SDS) testing

- Dose ammonia to target a ≥4.7:1 Cl_2:NH_3 ratio after breakpoint chlorination
- Filter chloraminated samples through 0.45 μm filters
- Measure relevant constituents field parameters before and after ammonia addition
- Sample after filtration for TTHMs and HAA5s
- Store in headspace free amber bottles in the dark
- Sample at 18 to 24 hours and 4 to 5 days



SDS testing results

- Of the 12 wells tested, only one well, "Well 05", could not satisfy total chlorine goal
  - Also had highest levels of DBPs
  - "Well 04" did not show same issues (even though it was only a few hundred feet away)



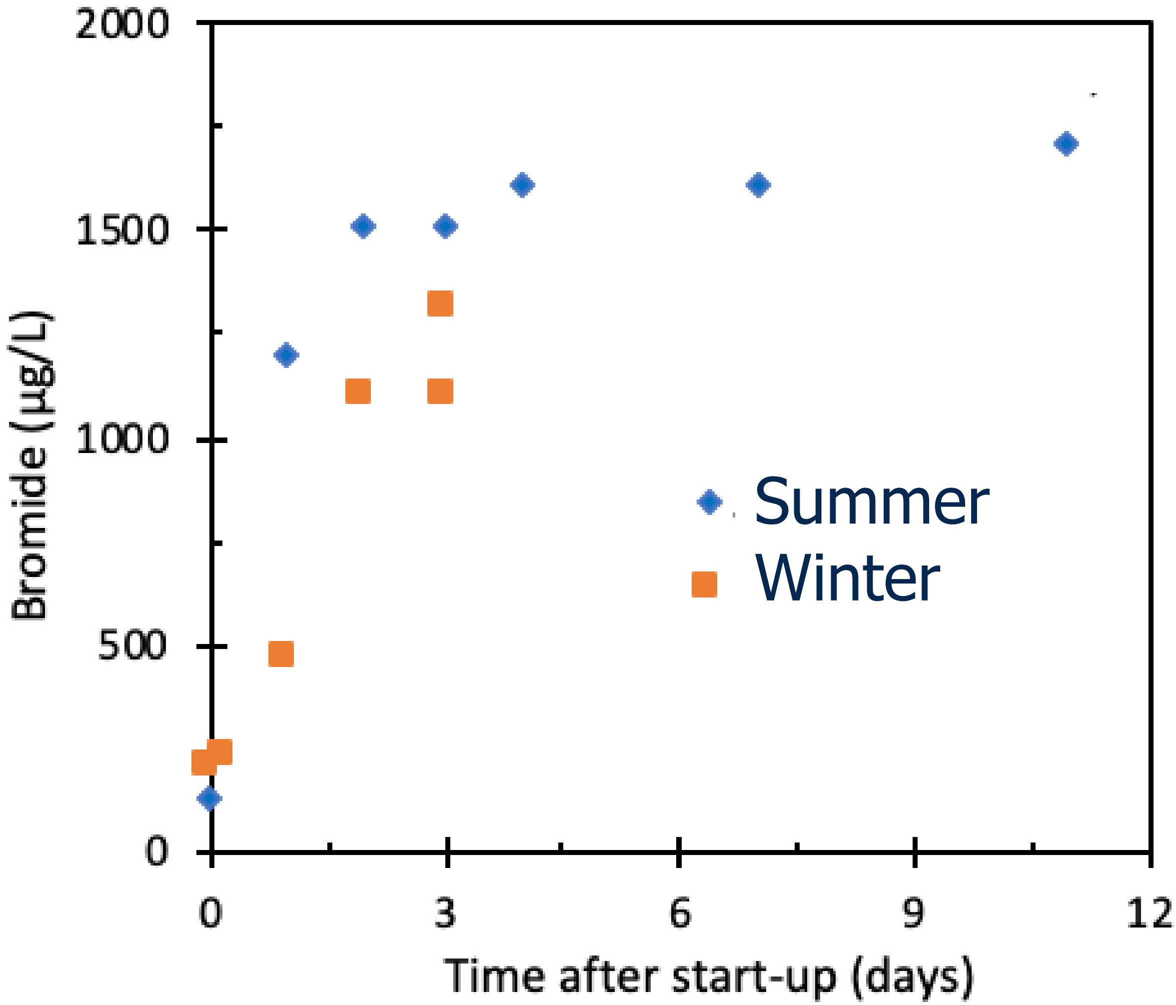
Raw water quality

- Water quality was largely similar in wells except of bromide

Parameter	Well 04	Well 05
Alkalinity (mg-$CaCO_3$/L)	177	150
Ammonia (mg-N/L)	0.12	0.26
Bromide (µg/L)	530	1,700
Chloride (mg/L)	73	240
DO (mg/L)	0.2	0.5
pH	7.9	8
Total Manganese (mg/L)	0.040	0.087
TOC (mg/L)	0.5	1.0
UV_{254} (cm-1)	0.008	0.015
SUVA (L/mg-C/m)	1.6	1.5

Raw water quality

- Variability in bromide concentration after well start-up also made diagnosing the problem difficult



Cause of "Total Cl" decay in Well 05

- High bromide in Well 05 is likely the cause of observed total Cl decay

$$HBr + NaOCl \rightarrow HOBr + NaCl$$

$$HOBr + NH_3 \leftrightarrow NH_2Br + H_2O$$

- Multiple bromamines (e.g., $NHBr_2$) and bromochloramine (NHBrCl) can also form which are less stable than NH_2Cl

Bromamines formation and decomposition

b1	$HOBr + NH_3 \rightarrow NH_2Br + H_2O$
b2	$NH_4^+ \leftrightarrow NH_3 + H^+$
b3	$NH_2Br + NH_2Br \rightarrow NHBr_2 + NH_3$
b4	$NHBr_2 + NH_3 \rightarrow NH_2Br + NH_2Br$
b5	$NH_2Br + NHBr_2 \rightarrow$ products
b6	$NHBr_2 + NHBr_2 \rightarrow$ products + HOB
16	$NH_2Br + Br^- + H^+ \rightarrow NH_3 + Br_2$
17	$NH_2Br + Br_2 \rightarrow NHBr_2 + Br^- + H^+$

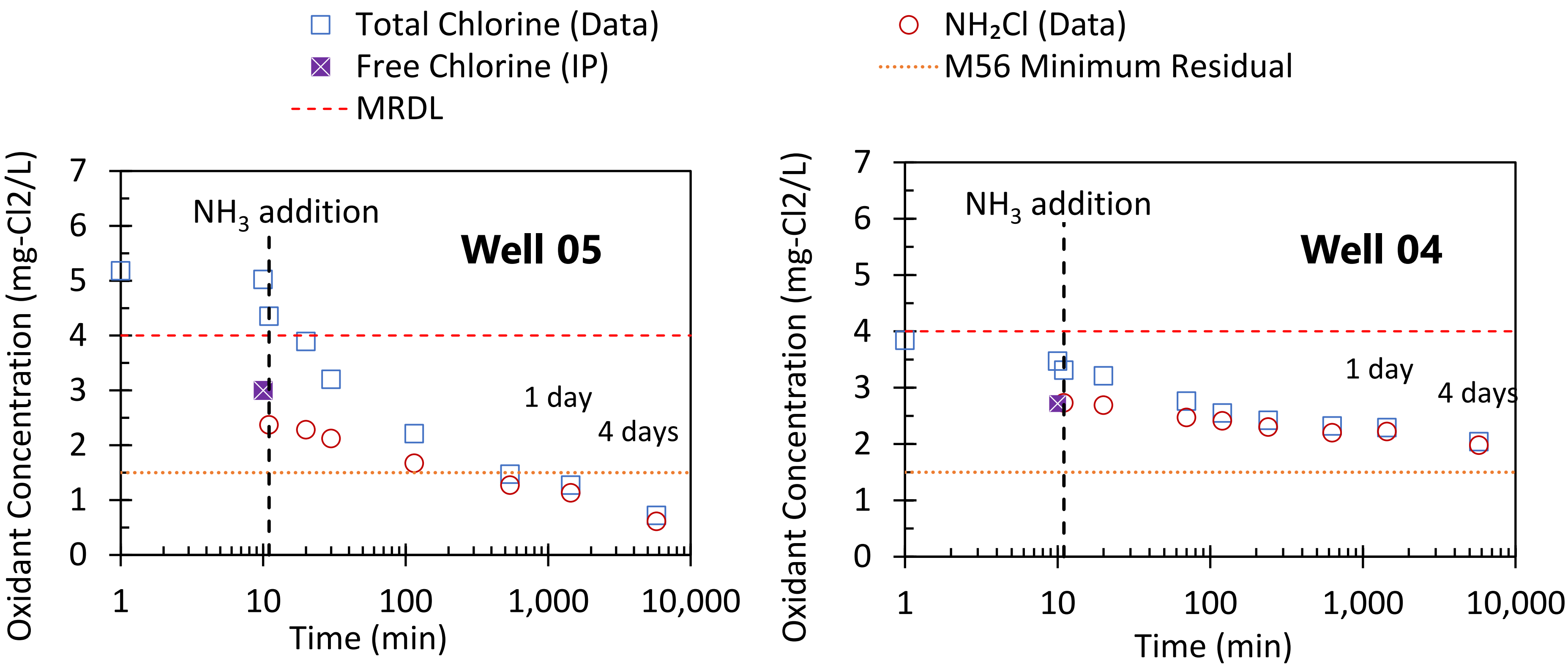
Bromochloramine formation

7	$NH_2Cl + Br_2 \rightarrow NHBrCl + Br^- + H^+$
18	$NH_2Cl + Br_3^- \rightarrow NHBrCl + 2Br^- + H^+$
19	$NH_2Cl + HOBr \rightarrow NHBrCl + H_2O$
20	$NH_2Cl + OBr^- \rightarrow NHBrCl + OH^-$
21	$NH_2Cl + NH_2Br + H^+ \rightarrow NHBrCl + NH_3$
22	$NH_2Cl + NHBr_2 \rightarrow NHBrCl +$ products

Luh, J., & Mariñas, B. J. (2014). Kinetics of bromochloramine formation and decomposition. *Environmental science & technology*, *48*(5), 2843-2852.

- Hach's total chlorine method detects both:
  - Non-brominated oxidants (e.g., HOCl, NH_2Cl)
  - Brominated oxidants (e.g., HOBr, NH_2Br, NHBrCl)
- Brominated oxidants that, are relatively unstable, can appear to be unstable chlorine

SDS testing results: chlorine detection methods

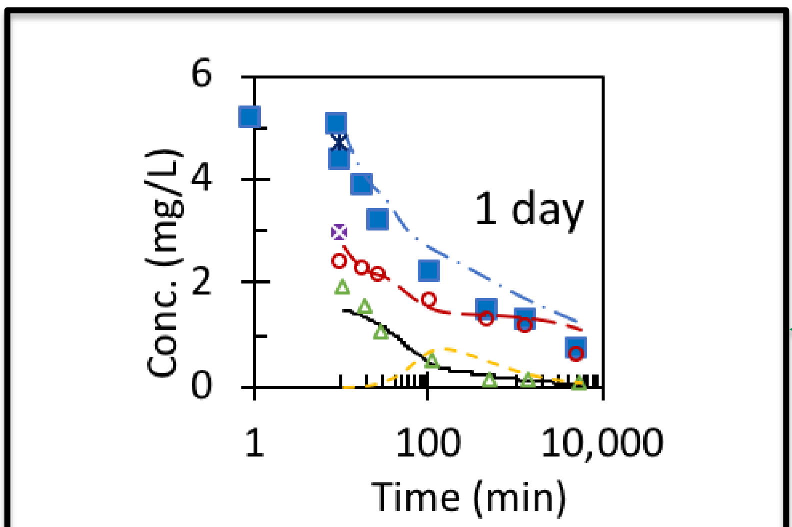


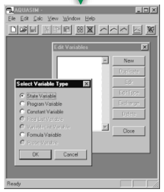
- Hach monochloramine method only detects monochloramine
  - Relies on indophenol (IP) chemistry
  - IP formation is highly specific to NH_2Cl, does not experience interference from bromine containing oxidants
- Indophenol (IP) free chlorine method does not experience HOBr interference
- Difference in total chlorine and NH_2Cl likely a result of brominated oxidants

Modeling bromamine formation/decay

- To further validate bromide was the cause of chlorine decay, modeling was performed using
  - Reaction kinetics software AQUASIM
  - Chlorine, ammonia, and bromine reaction rate constants from Luh and Marinas, 2014

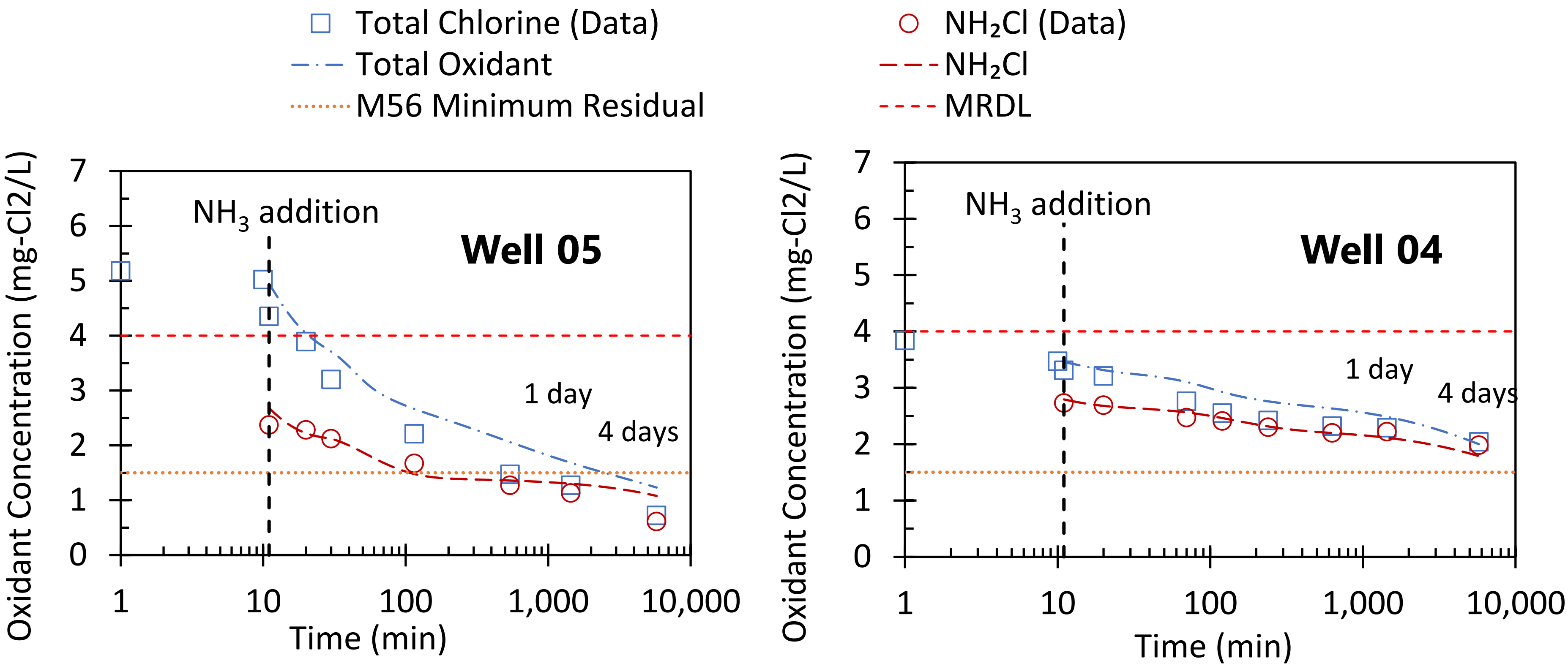
Luh, J., & Mariñas, B. J. (2014). Kinetics of bromochloramine formation and decomposition. *Environmental science & technology*, *48*(5), 2843-2852.





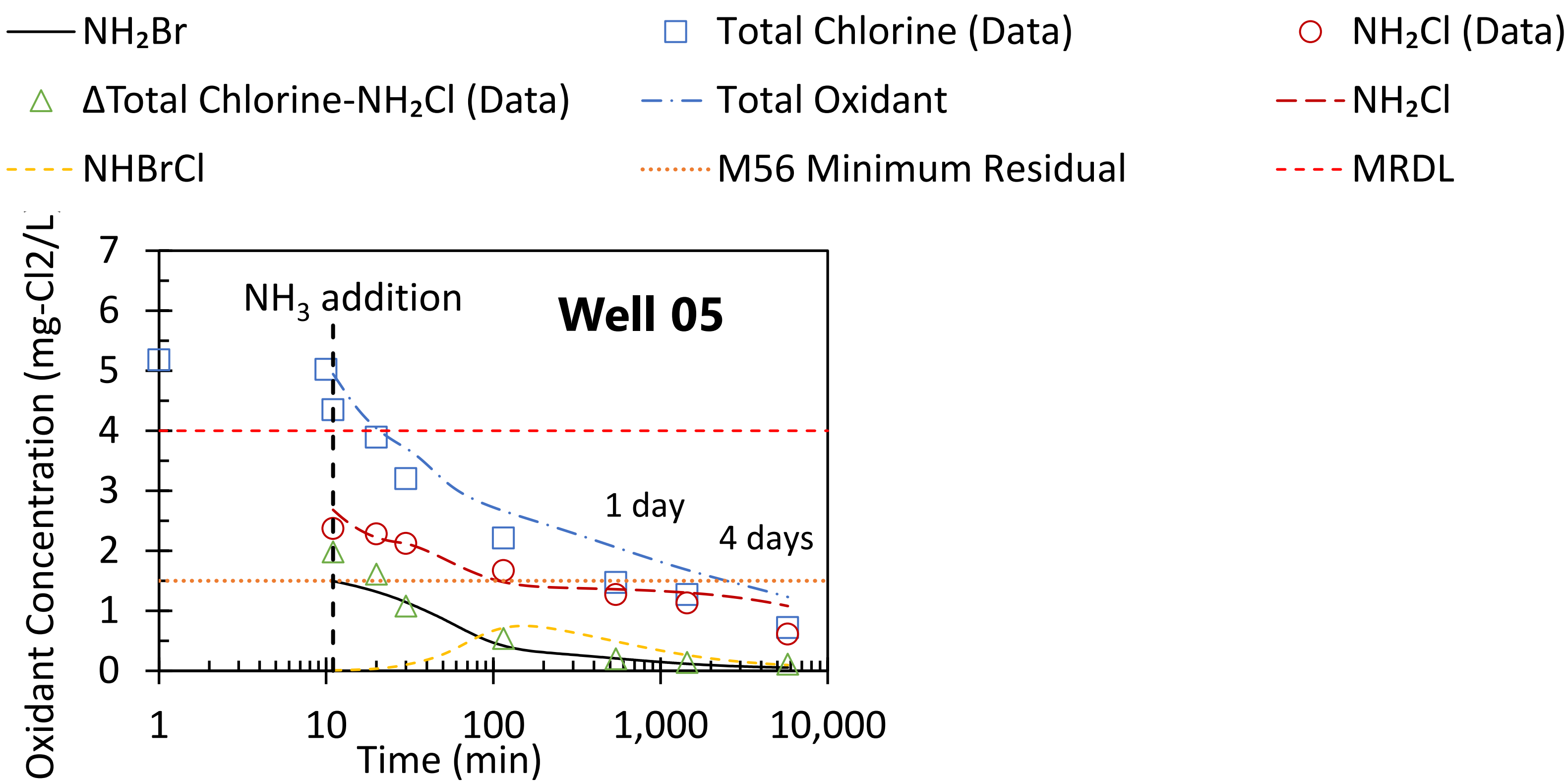
AQUASIM

SDS testing results: modeling



- Lines = model simulations
  - Model accounts for for the presence of bromamines & bromochloramine
- Bromamines are unstable
  - Decays mostly in a few hours
- Model assumes no TOC is present
  - Likely source of model deviations from data

SDS testing results: chlorine detection methods

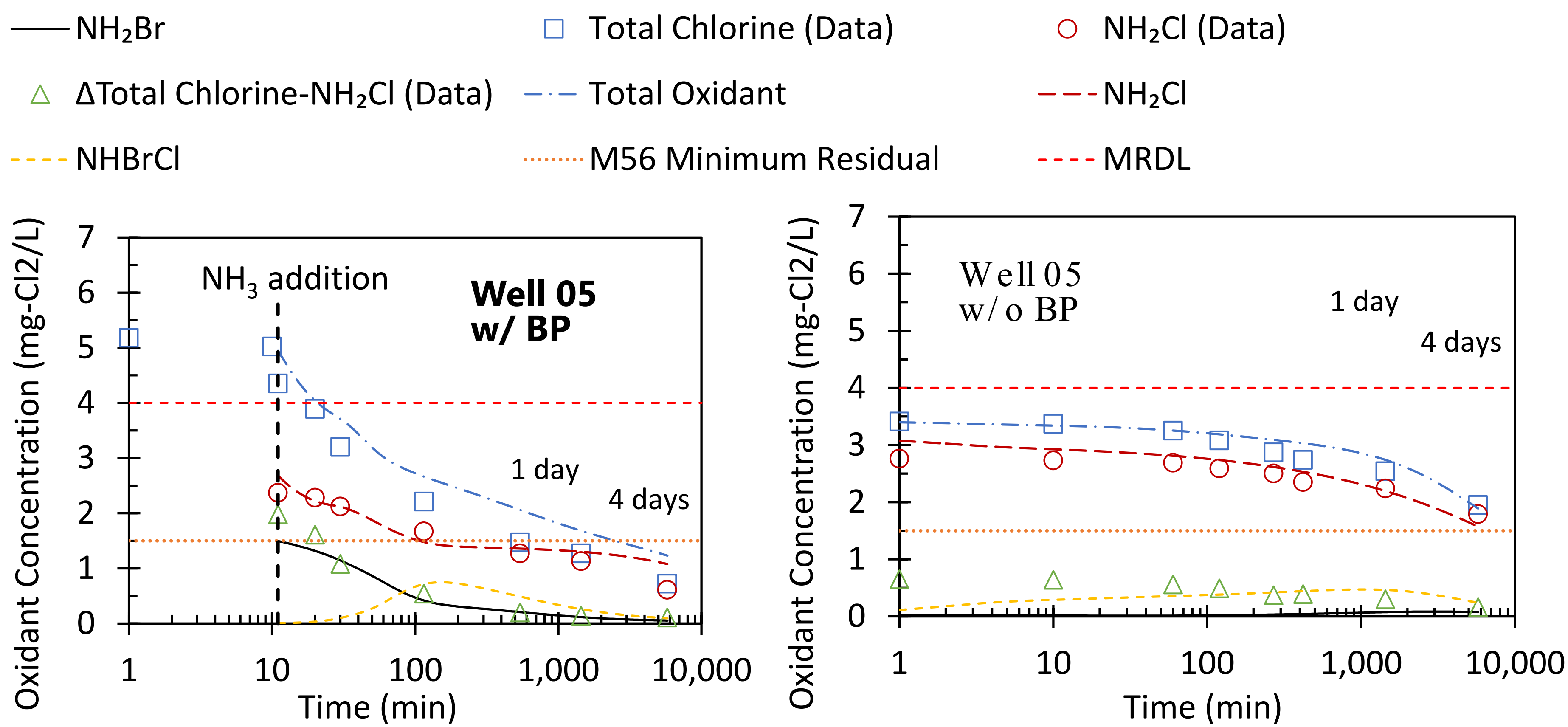


- Total chlorine - NH_2Cl = brominated oxidants (e.g., NH_2Br)
- More raw water bromide makes total chlorine measurement unstable because:
  1. Unstable NH_2Br is formed instead of more stable NH_2Cl

     $HBr + NaOCl \rightarrow HOBr + NaCl$ → $HOBr + NH_3 \leftrightarrow NH_2Br + H_2O$

  2. NH_2Br attacks NH_2Cl, making the NH_2Cl that is present, less stable

SDS testing results: chlorine detection methods

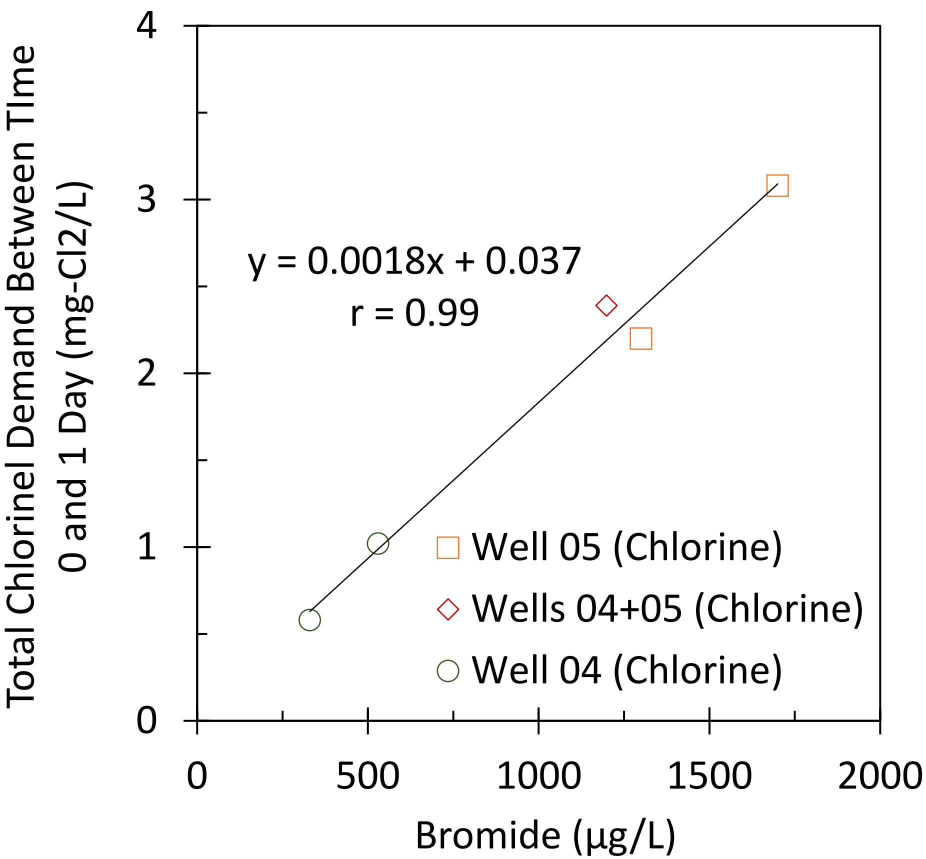


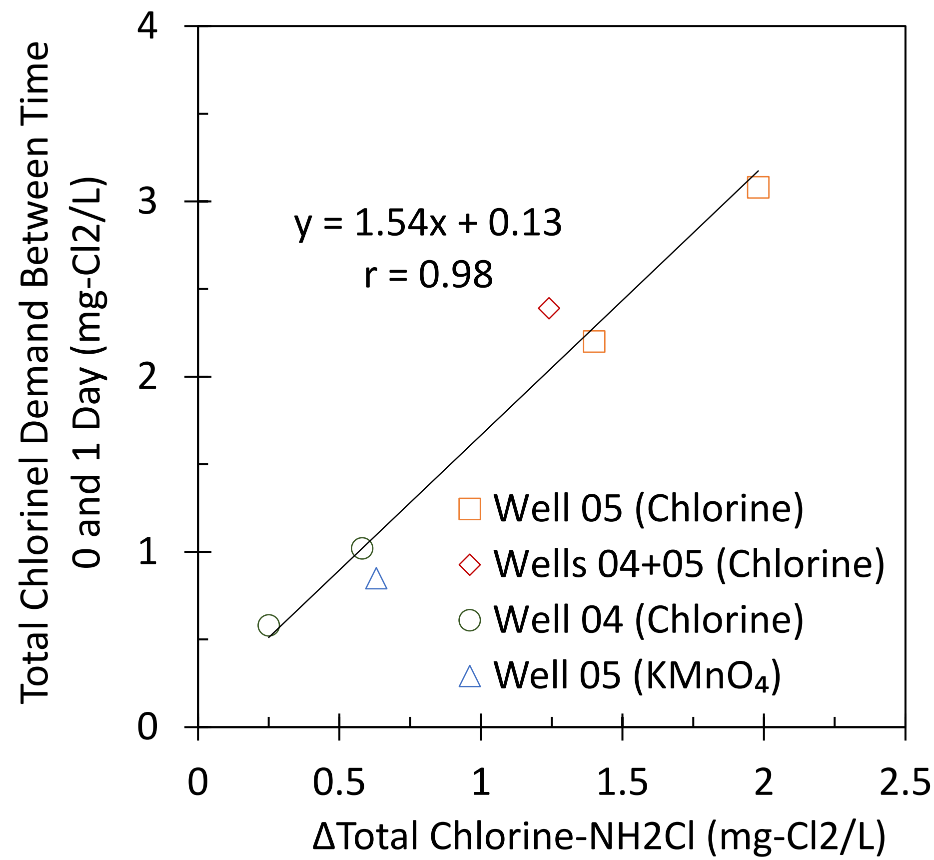
- Adding ammonia before chlorine to form chloramines makes total chlorine measurement more stable
  - HOCl reacts faster with NH_3 relative to Br^-

$HBr + NaOCl \nrightarrow HOBr + NaCl$ $\nrightarrow$ $HOBr + NH_3 \leftrightarrow NH_2Br + H_2O$

  - Some bromamines will form, but much less (e.g., $Br^- + NH_2Cl \rightarrow NH_2Br$ is slow)

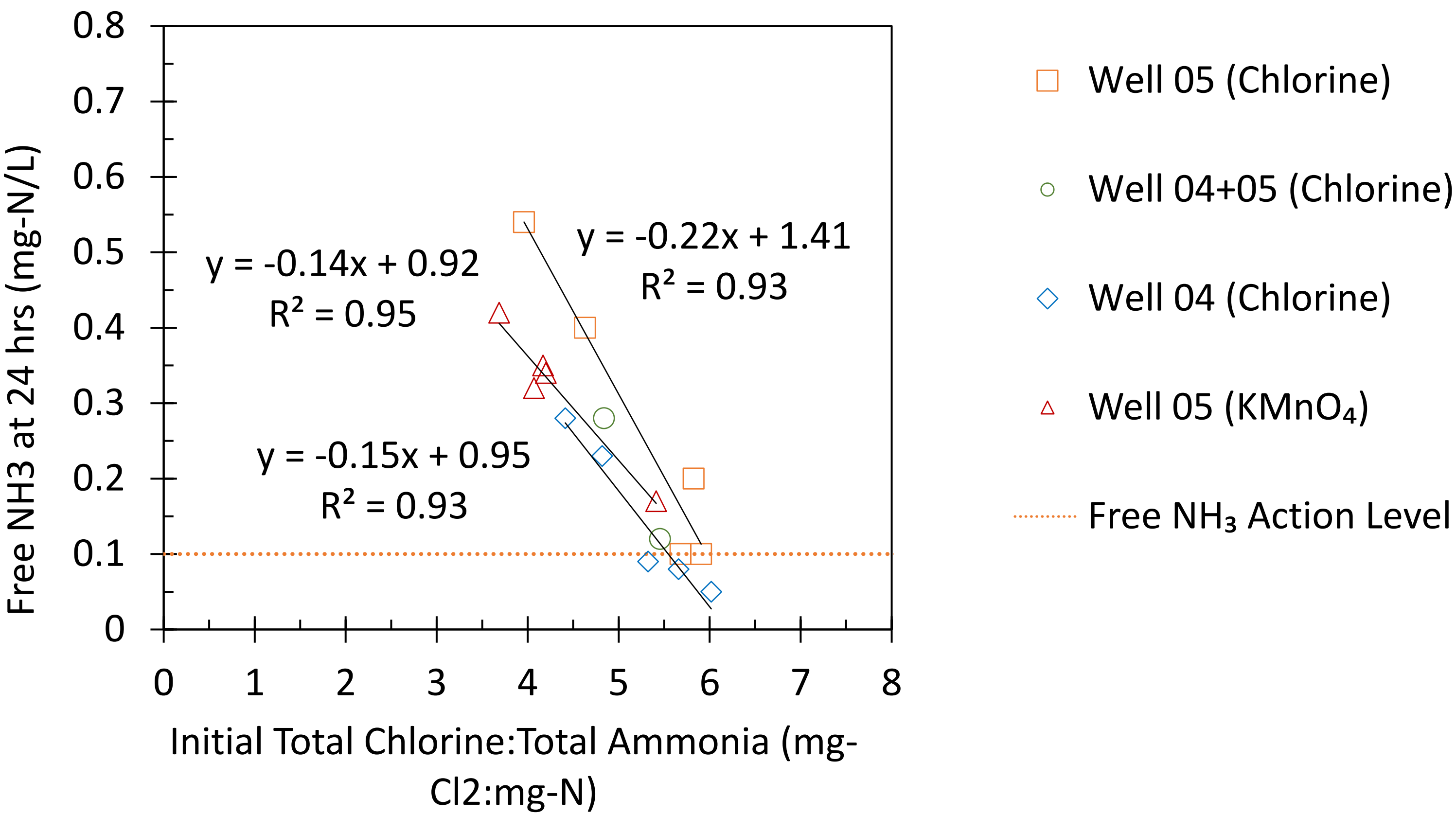
SDS testing results: bromide vs chlorine demand





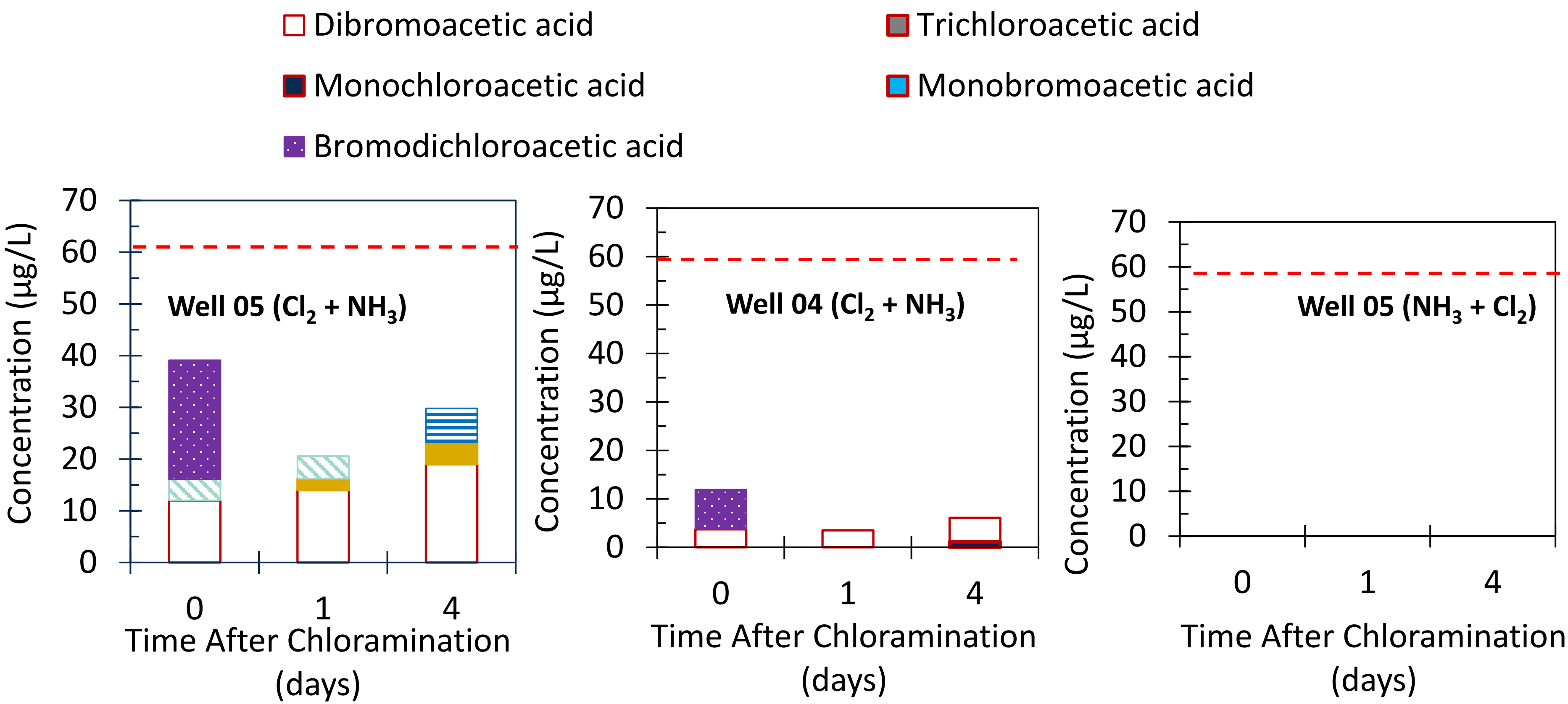
- Chlorine demand caused by bromide can be predicted based on:
  - Raw water bromide concentrations
  - Total chlorine - NH_2Cl = brominated oxidant concentration measured right after chloramine formation

SDS testing results: free ammonia



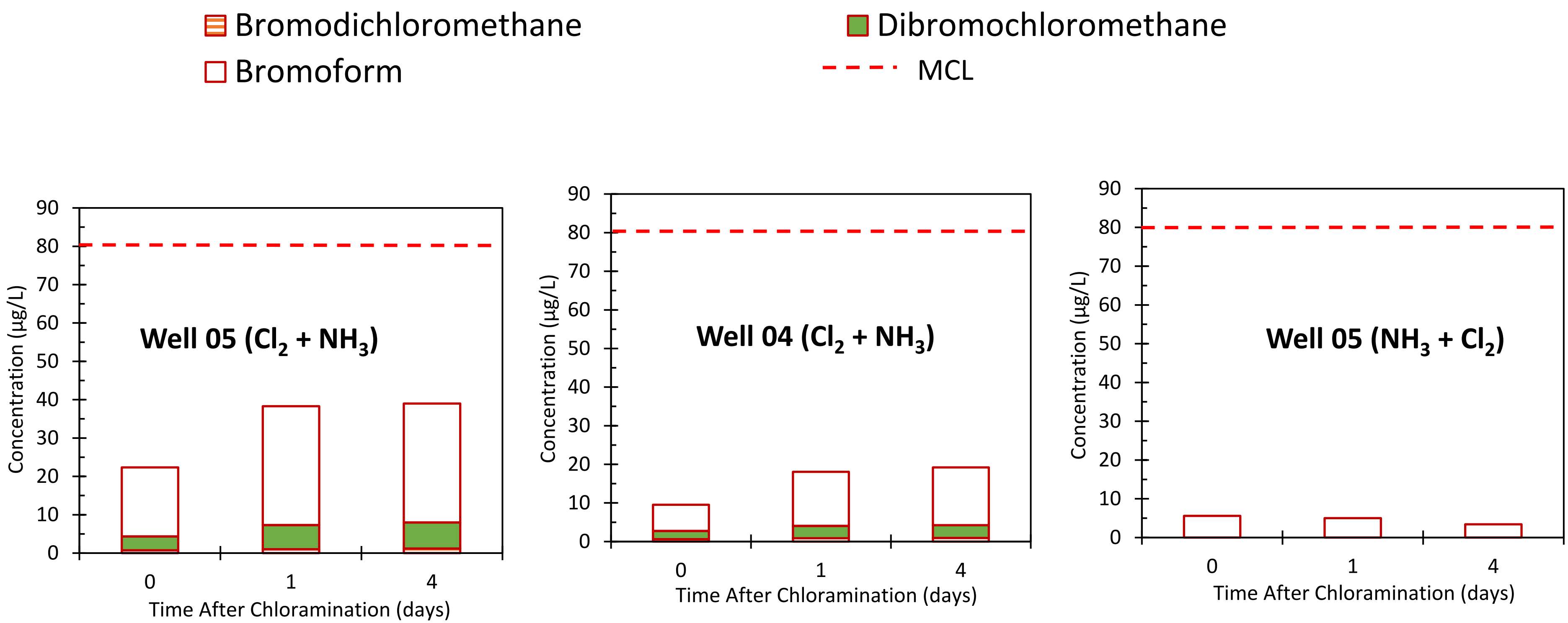
- Bromide also causes more free ammonia to be released
- High Cl:NH_3 ratios should be targeted:
  - Around 5:1
  - Higher than 5:1?

SDS testing results: HAAs



- More HAAs formed in high bromide water
- Adding NH_3 before Cl_2 inhibited HAA formation even in high bromide water

SDS testing results: THMs



- More THMs formed in high bromide water
- Adding NH_3 before Cl_2 limited THM formation in high bromide water

Study Takeaways

- Bromide makes measured total chlorine unstable in chloraminated systems because:
  - Unstable brominated oxidants can form in place of NH_2Cl
  - Hach's total chlorine method detects brominated oxidants
  - Brominated oxidants degrade NH_2Cl

Study Takeaways

- Brominated oxidant formation can be managed with simple process modifications, but planning is needed, e.g.,
  - Adding NH_3 before HOCl to form chloramines
    - Adding $KMnO_4$ to achieve Mn removal via greensand filtration allowed NH_3 to be added first without forming brominated oxidants
  - Chlorine measurements may need reevaluation (total chlorine vs IP chlorine vs NH_2Cl measurements)
  - Greater free NH_3 release and nitrification may be more of an issue

Thank you!

Kyle Shimabuku, PhD, PE

Assistant Professor, Civil Engineering Gonzaga University

shimabuku@gonzaga.edu