18 years of applying MOS solutions to cooling towers and our experiences at higher pH

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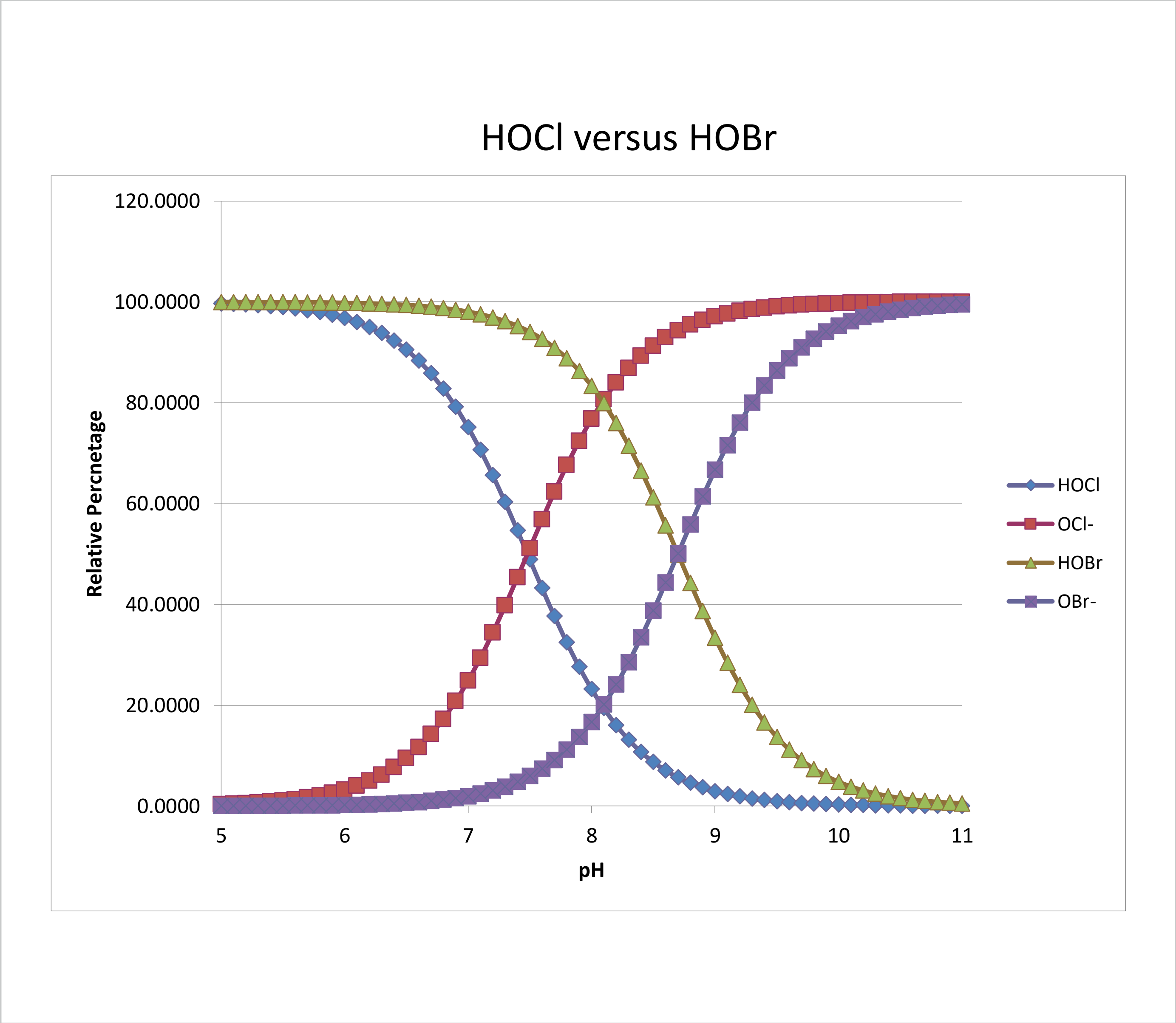
18 years of application to cooling towers

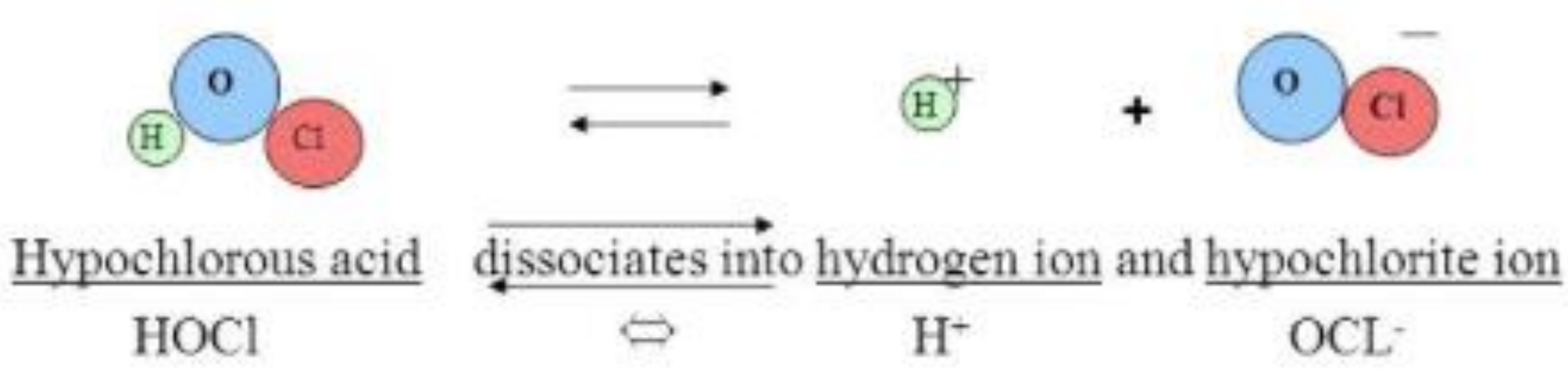
- First application in 2004 (Chicago)
    - 15 lb/day unit
    - 400,000 gallons per day make up to tower
- >20 applications treating over 5,000,000 gallons per day (at peak) load

Water Treatment Bias 101 – the chart

- Bromine (Hypobromous) versus chlorine (hypochlorous) versus pH
- Hypobromous pKa = 8.70
- Hypochlorous pKa = 7.48

Ergo as pH increases bromine chemistry is favored as a more effective biocide





Based on that pKa data alone it would appear that bromine is always the more effective biocide versus chlorine at higher pH

The chart is “static” however and fails to consider Le Chatelier’s Principle on dynamic response of a system at equilibrium

Cooling towers are unique from an oxidizing biocide perspective

Cooling towers continuously cascade the water over an air stream to complete the evaporation process. This results in a loss mechanism that removes the **gaseous species** versus the **ionic species**

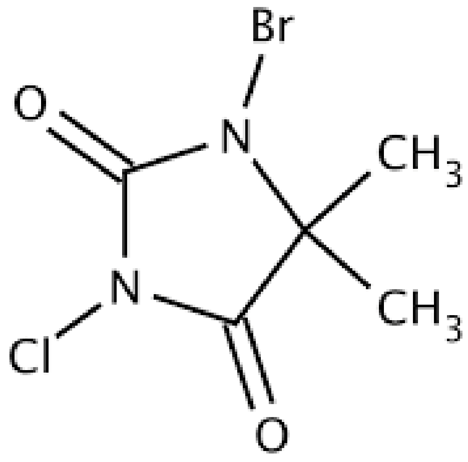
The fraction of a volatile gas, such as hypochlorous acid (HOCl), which is removed by stripping is determined by Henry's constant H for that gas: H = XG/XL, where XG is the mole fraction of the gas in the air and XL is the mole fraction of the gas in the water

We found H = 0.076 for HOCl, compared to 0.71 for NH3, at 20°C. At 40°C, H was about 2.5-fold larger for HOCl. This means that 10–15% of the HOCl is stripped from cooling water on each passage through a typical cooling tower. The measured flashoff of free available chlorine (HOCl + OCl−) was markedly pH-sensitive with a pK of 7.5, exactly as expected if HOCl is volatile but OCl− is not.[1]

[1] Water Research Volume 18, Issue 11, 1984, Pages 1421-1427

Stabilized chemistries

- The loss mechanism from Henry's Law coupled with the increased profit and "static" improvements that appear to be gained from bromine chemistry led to the development of stabilized bromine products
  - BCDMH (1-Bromo-3-chloro-5,5-dimethylhydantoin)
    - Solid product - bromine donor
    - Generates HOBr
    - Can be difficult to dissolve and control residuals
    - https://envirotech.com/wp-content/uploads/2016/01/NACE-Bromine-Chemistry-Review-1.pdf

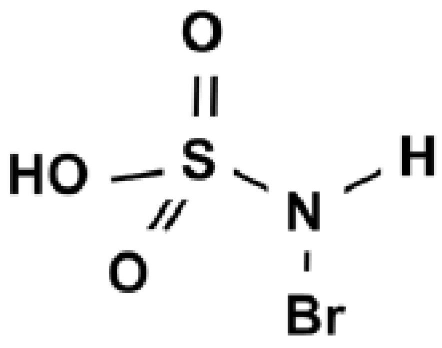


(11) $BCDMH + H_2O \longleftrightarrow CDMH + HOBr$ fast

(12) $CDMH + H_2O \longleftrightarrow DMH + HOCl$ slow

Stabilized chemistries

- The loss mechanism from Henry's Law coupled with the increased profit and "static" improvements that appear to be gained from bromine chemistry led to the development of stabilized bromine products
  - Stabilized Bromine
  - NaBr + HOCl + sulfamic acid →NaCl + HOBr/sulfamic acid



N-bromosulfamic acid

Stabilized chemistries

- Stabilized chemistry can also mitigate the loss of either HOCl or HOBr within cooling towers by forming the sulfamic acid complexes
- Advantages of stabilized chemistry
  - Less loss over cooling tower
  - Easier to handle relative to generating bromine
- Disadvantages
  - Sulfamic acid slows down reaction time
  - Build up of of sulfamic acid as oxidant is consumed can result in “overstabilizing” and slow reaction rates to the point of ineffectiveness

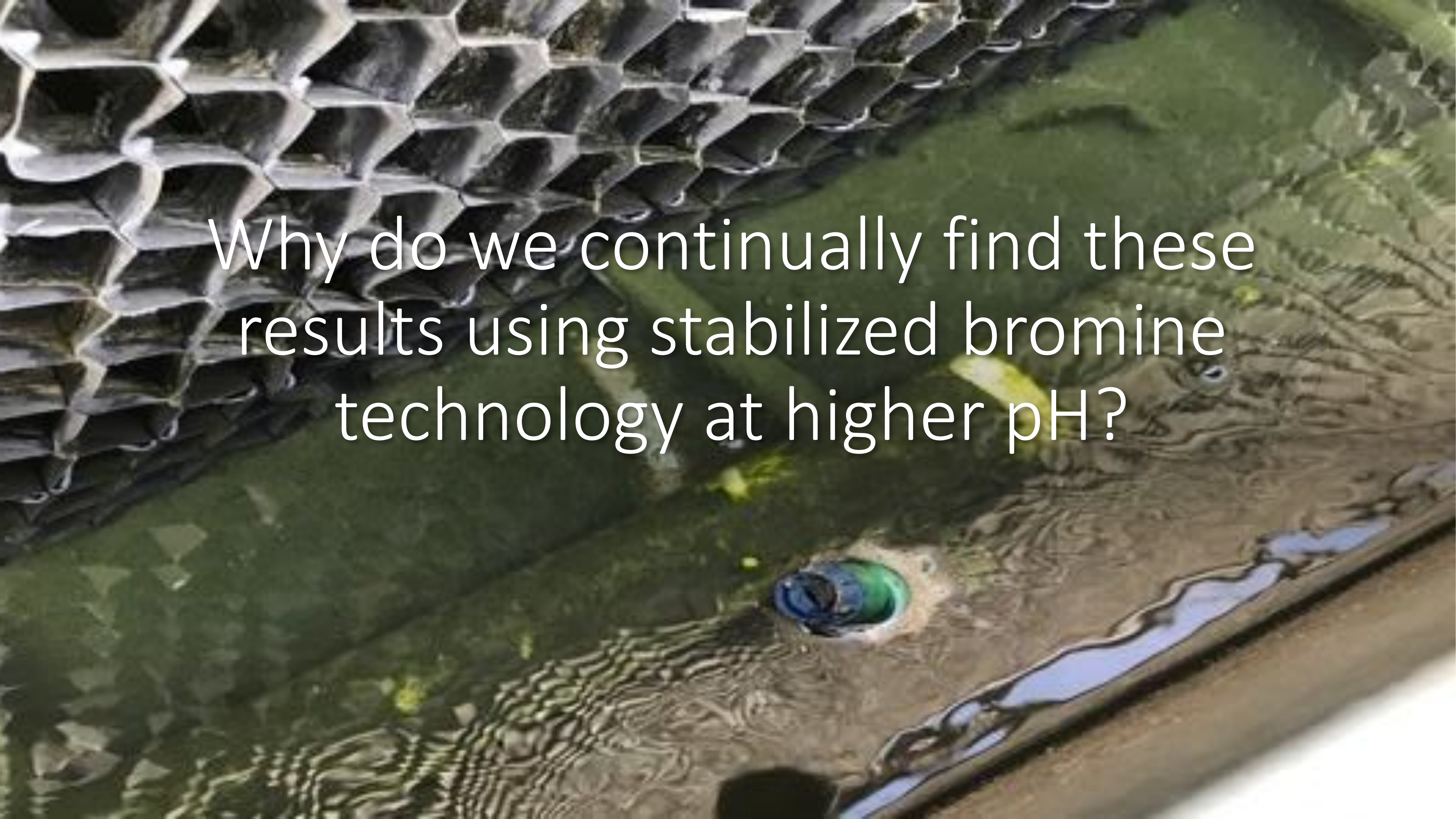
This all leads us to the logical conclusion that in cooling towers bromine is the preferred biocide for elevated pH (>8.3)

But is this what we find in the field?

Does chlorine fail miserably at elevated pH?

Why would MOS solutions work at elevated pH?

Why do we continually find these results using stabilized bromine technology at higher pH?



Let's consider this argument in a different context

- Hypochlorous Acid is a stronger oxidant versus Hypobromous Acid
  - This is independent of pH
- In a cooling tower at higher pH's the dominant form of Hypochlorous acid is OCl^-
  - OCl^- is not volatile like HOCl (or HOBr which is also volatile but due to the higher molecular weight not as volatile)
  - So, for chlorine the OCl^- acts as "built in" stabilizer
  - At higher pH there is more OCl^- versus OBr^- so there is a larger "reserve" of material to convert back to HOCl as the HOCl is consumed or lost
    - This is of course only true if you are continuously maintaining a residual of chlorine

MOS applications

The MOS solution is primarily sodium hypochlorite with reported small quantities of other oxidants - hydrogen peroxide has been suggested.

Application to cooling towers across a broad pH range (7.5 to 9.4) has not shown a demonstratable difference in efficacy in terms of

- Bacterial control (HPC)
- Visual biofilm
- Algae
- Legionella

MOS controlled between 0.3 ppm and 1.0 ppm on a continuous basis

How does dosage of MOS relate to pH?

- The take home message is, as expected, lower pH results in higher applied MOS dosages.

Site	Chicago	Phoenix	Minneapolis
Years in Service	18	7	8
Average MOS FAC lbs/day	10 to 14	6 to 10	16 to 20
pH	8.8	9.2	7.8
Residual	0.5 to 1.0	0.5 to 1.0	0.25 to 0.5
Water Usage (gallons/day)	400,000	550,000	450,000

How does dosage of MOS relate to Bleach under identical conditions?

- Take home comparison – we use less MOS. It is not clear if this is due to bleach (12.5%) degradation or due to MOS advantage

Site	Chicago	Chicago
	MOS	Bleach
Average FAC lbs/day	30 to 32	40
pH	8.8	8.8
Residual	0.5 to 1.0	0.5 to 1.0
Water Usage (gallons/day)	400,000	400,000

Bacterial Data Comparisons

Biocide	MOS	Bleach	Stabilized Bromine	BCDMH
Residual maintained	0.25 to 1.0 ppm	0.5 to 1.0 ppm	Intermittent (feeding 1 time/day) to a minimum of 1 ppm Total	1.0 to 5.0 ppm Total, 0.1 to 0.5 ppm Free
HPC (cfu/ml) – average planktonic	<100 cfu/ml	100 to 1,000 cfu/ml	500 to 50,000 cfu/ml	100 to 1,000 cfu/ml
Algae (present/not present)	None in wetted areas	None in wetted areas	Present in 10 to 25% of sites in wetted areas	Present in 20 to 25% of sites in wetted areas
Legionella (Detected/Not Detected)	Not Detected[1]	Detected less than 2% of samples[2]	Detected in 10% of samples[3]	Detected in 20% of samples [4]
	[1] We have not detected positive Legionella in systems with detectable free chlorine when feeding MOS, systems that have had MOS but then have had issues with feed have had detectable levels.	[2] Out of 30 samples using continuous bleach feed we have had 1 system with positive Legionella with two positives on the same tower with chlorine levels up to 1.0 ppm	[3] Multiple samples from stabilized bromine have had positive results with multiple systems. These results were done in systems we managed but did not control. Many of these were feeding intermittently versus continuously	[4] 1 of five towers tested positive this summer, multiple times with 2 to 5 ppm of Total. 10 total samples, 2 positives on same tower. Similar experiences with towers that we manage but don't control

What have we learned?

- The common practice of applying bromine at higher pH does not translate into measurably better results and our studies show it does not work as well as bleach or MOS at higher pH
  - This is further exacerbated by both over stabilizing AND under dosing due to intermittent feed. Intermittent feed is often practiced with bromine chemistry due to cost concerns
- The bleach or MOS solutions are "self-stabilized" at higher pH due to the equilibrium reaction between HOCl and OCl^-.
  - As long as the bleach or MOS solution are continuously applied
- The MOS solution continues to be the most effective biocide in our studies

What we still need to learn

- This data suggests that stabilized bromine solutions may be as or more effective at near neutral pH (7 to 8) versus higher pH
  - Can’t overstabilize
  - Potential to feed less overall material versus MOS or bleach due to decreased volatility
  - Impact on biofilm and algal growth