Drinking Water Inorganic Chloramine Chemistry

David G. Wahman
Research Environmental Engineer
National Risk Management Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio, United States

EPA Region 6 Workshop
May 21, 2019

wahman.david@epa.gov

Courses

- 101 – Initial ***formation*** & subsequent ***decay***
  - Drinking water
    - ≤ 4 mg Cl_2/L total chlorine
    - 6.5–9.0 pH
    - ≤ 5:1 Cl_2:N mass ratios
  - No or low (< 0.1 mg/L) bromide
  - 25°C
  - Important reactions (Unified Model) → plug (pipe) flow
- 201 – Demand (organics, nitrification), temperature
- 301 – Breakpoint (Cl_2:N > 5:1)
- 401 – Bromide

After this presentation, you will

1. Know relevant chloramine reactions & pH and Cl_2:N importance

2. Understand chloramine formation

3. Understand chloramine decay

4. Know of two chloramine chemistry simulators

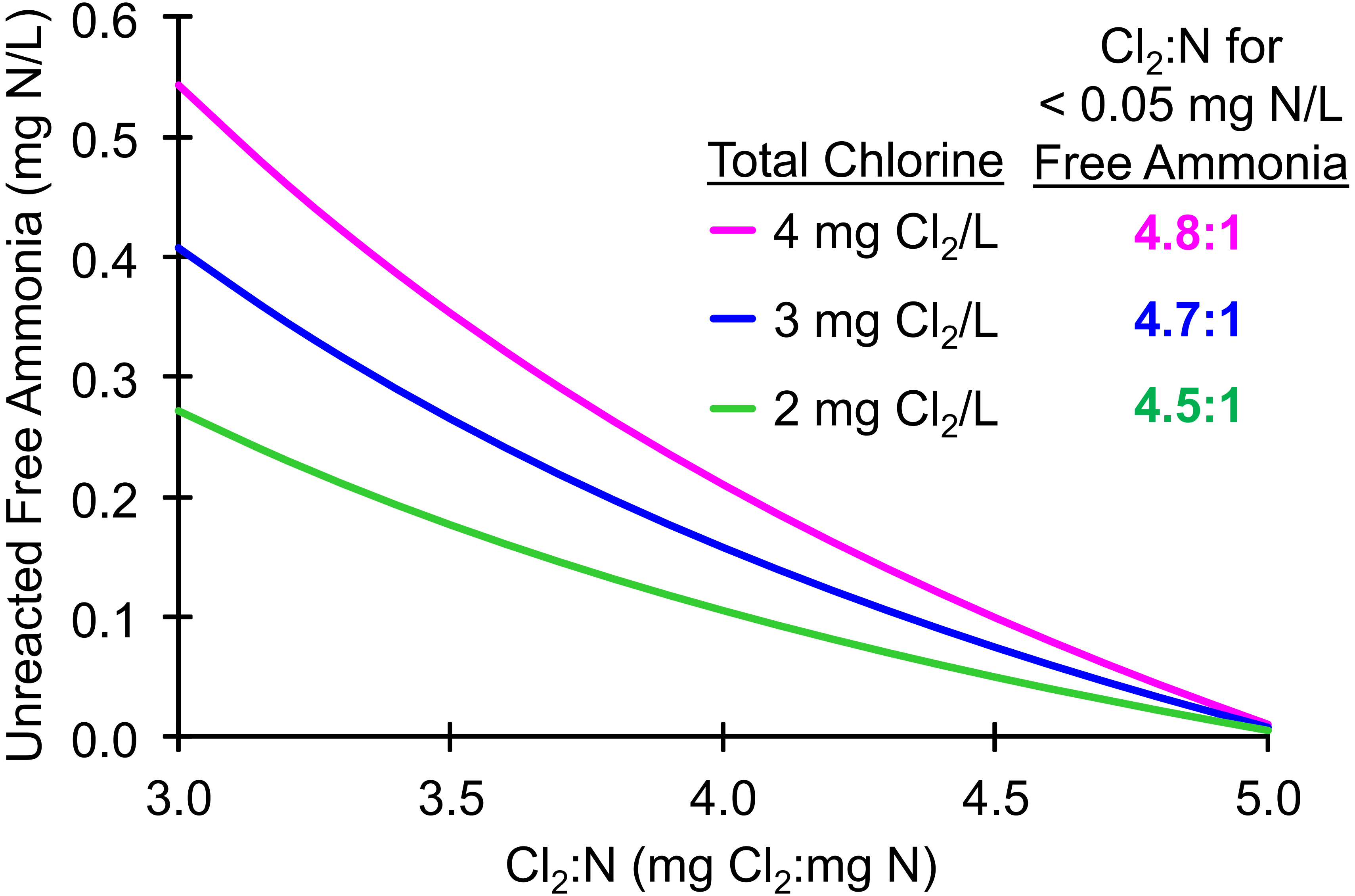
Chloramines

- 2^{nd} most used secondary disinfectant
  - Free ammonia (NH_4^+ and NH_3)
  - Free chlorine (HOCl and OCl^-)
- ↓ regulated DBPs & ↑ residual stability
- 3 inorganic species
  - **Mono**chloramine (NH_2Cl)
  - **Di**chloramine ($NHCl_2$)
  - **Tri**chloramine (NCl_3)
- Total chlorine = free chlorine + chloramines

Drinking Water Chloramine Chemistry

- Formation & decay (will happen, baseline)
  - Chlorine to ammonia–nitrogen ratio (Cl_2:N) ≤ 5:1
    - Free chlorine = 2.0 mg Cl_2/L
    - Free ammonia = 0.5 mg N/L
    - } 4:1 Cl_2:N
    - Concentrations when mixed (not dosed)
    - Source water ammonia
  - pH 6.5 to 9
  - Mixing, temperature
- Demand (will happen if present)
  - Natural organic matter
  - Nitrification related → nitrite, cells, degradation
  - ↓ formation & ↓ stability

Unreacted Free Ammonia (Cl_2:N)



Reaction Scheme (Unified Model)

Mono Formation & Hydrolysis	1.	$HOCl + NH_3 \rightarrow Mono + H_2O$
	2.	$Mono + H_2O \rightarrow HOCl + NH_3$
Di Formation #1 & Hydrolysis (slow)	3.	$HOCl + Mono \rightarrow Di + H_2O$
	4.	$Di + H_2O \rightarrow HOCl + Mono$
Di Formation #2 & Back (slow)	5.	$Mono + Mono \rightarrow Di + NH_3$
	6.	$Di + NH_3 \rightarrow Mono + Mono$
Di (Chloramine) Loss	7.	$Di + H_2O \rightarrow I$
Chloramine Loss: 8&9 fast, 10 slow	8.	$I + Di \rightarrow HOCl + N_2 + HCl$
	9.	$I + Mono \rightarrow H_2O + N_2 + HCl$
	10.	$Mono + Di \rightarrow N_2 + 3HCl$
Breakpoint Reactions, Slow for Cl_2:N ≤ 5:1	11.	$HOCl + Di \rightarrow Tri + H_2O$
	12.	$Di + Tri + 2H_2O \rightarrow 2HOCl + N_2 + 3HCl$
	13.	$Mono + Tri + H_2O \rightarrow HOCl + N_2 + 3HCl$
	14.	$Di + 2HOCl + H_2O \rightarrow NO_3^- + H^+ + 4HCl$

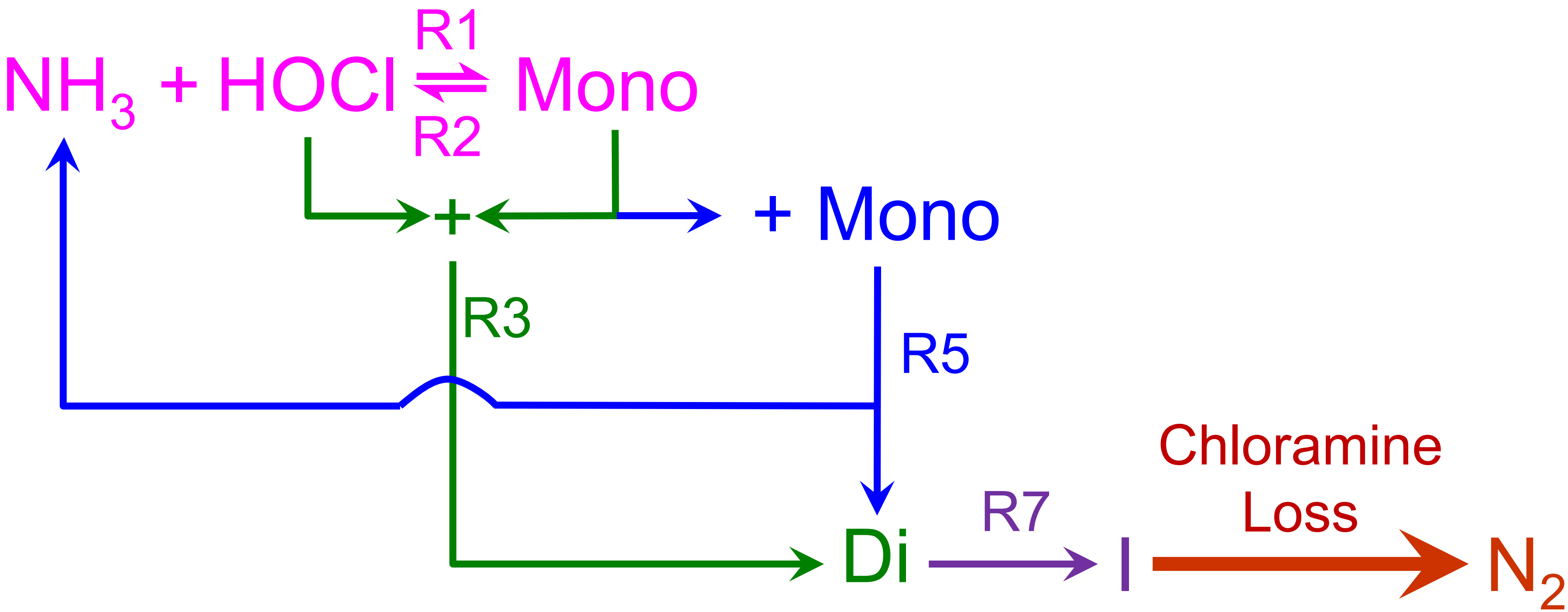
Five kinetically relevant reactions: 1, 2, 3, 5, & 7

Reactions (pH & Cl_2:N Importance)

#	Reaction (What happens?)	Chloramine Impact	Rate Expression (How fast?)	pH (Important?)	Cl_2:N (Important?)
1	$HOCl + NH_3 \rightarrow Mono + H_2O$	↑ Mono	k_1**[HOCl][NH_3]**	✓	✓
2	$Mono + H_2O \rightarrow HOCl + NH_3$	↓ Mono	$k_2[Mono]$		
3	$HOCl + Mono \rightarrow Di + H_2O$	Mono → Di	k_3**[HOCl]**[Mono]	✓	✓
5	$Mono + Mono \rightarrow Di + NH_3$	Mono → Di	k_5**[H^+]**$[Mono]^2$	✓	
7	$Di + H_2O \rightarrow I$	↓ Di ↓ Total Cl_2	$k_7[Di]$**[OH^-]**	✓	

- If rate expression contains:
  - HOCl or NH_3 → pH & Cl_2:N important
  - H^+ or OH^- → pH important

“Simplified” Reaction Scheme



Formation (R1&R3): Competition for free chlorine (HOCl)

Decay (All): Mono → Di → chloramine loss

Overall: 3 Mono → NH_3 + N_2

Demand: Mono → NH_3

After this presentation, you will

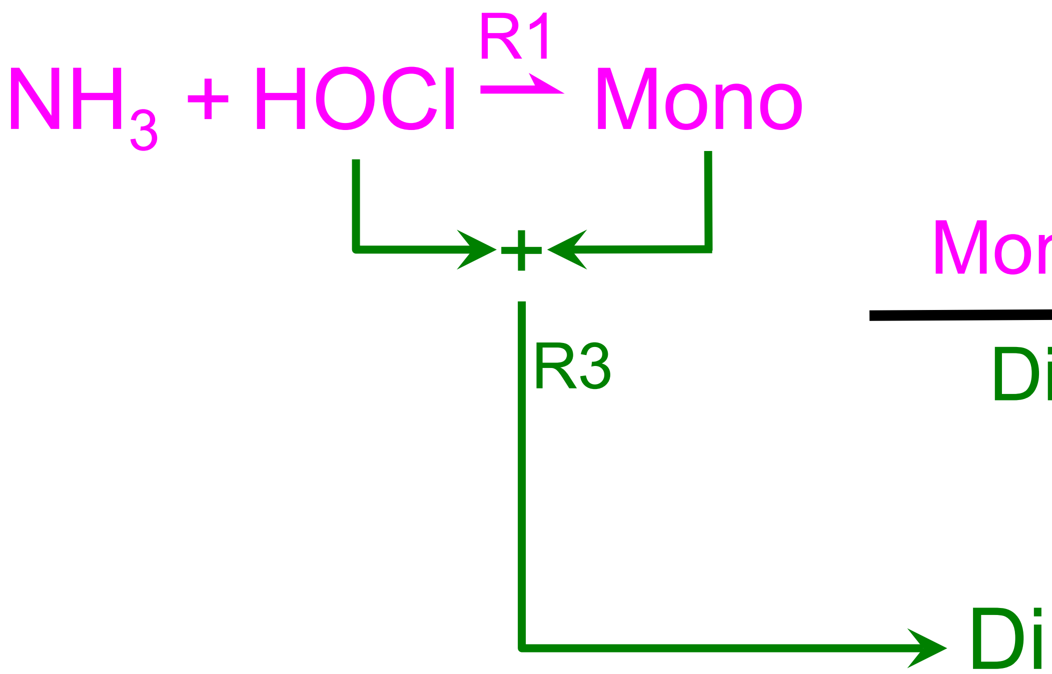
1. Know relevant chloramine reactions & pH and Cl_2:N ratio importance

Monochloramine Formation (25°C)

Cl_2:N Mass Ratio (X:1)	4.8	4.8	4.5	1.3
Total Chlorine (mg Cl_2/L)	2	4	4	14
pH	99% Monochloramine Formation (seconds)			
6.5	191	96	58	1.2
7.0	73	36	22	0.45
7.5	35	18	11	0.22
8.0	24	12	7.2	0.15
8.4 (Fastest)	22	11	6.6	0.14
9.0	27	13	8.1	0.17

Assumes only Reaction 1 is occurring ($Rate_1 = k_1[HOCl][NH_3]$)

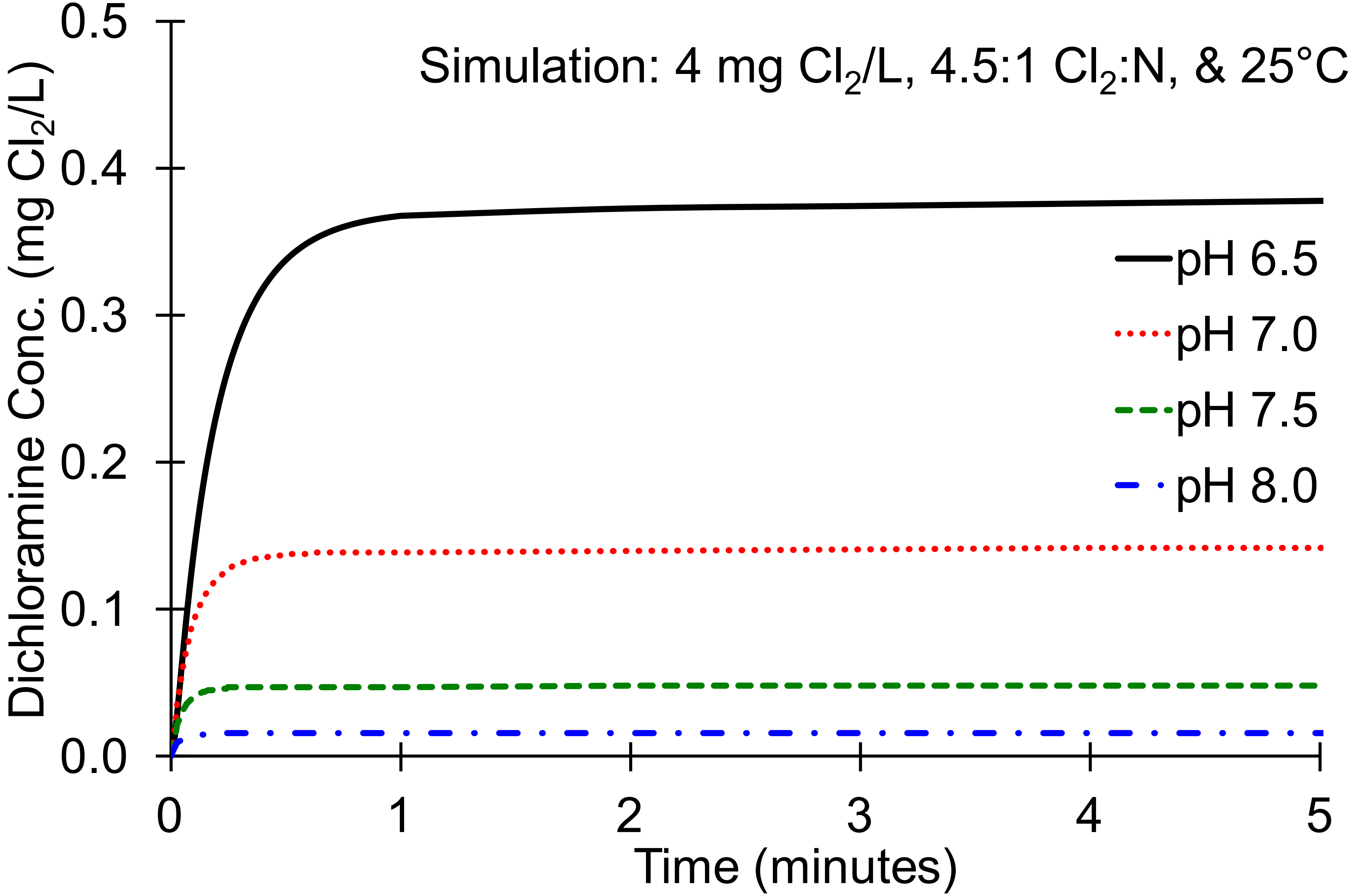
Chloramine Formation (R1 & R3)
Competition for free chlorine (HOCl)



$$\frac{\text{Mono Rate}}{\text{Di Rate}} \propto \frac{[NH_3]}{[\text{Mono}]}$$

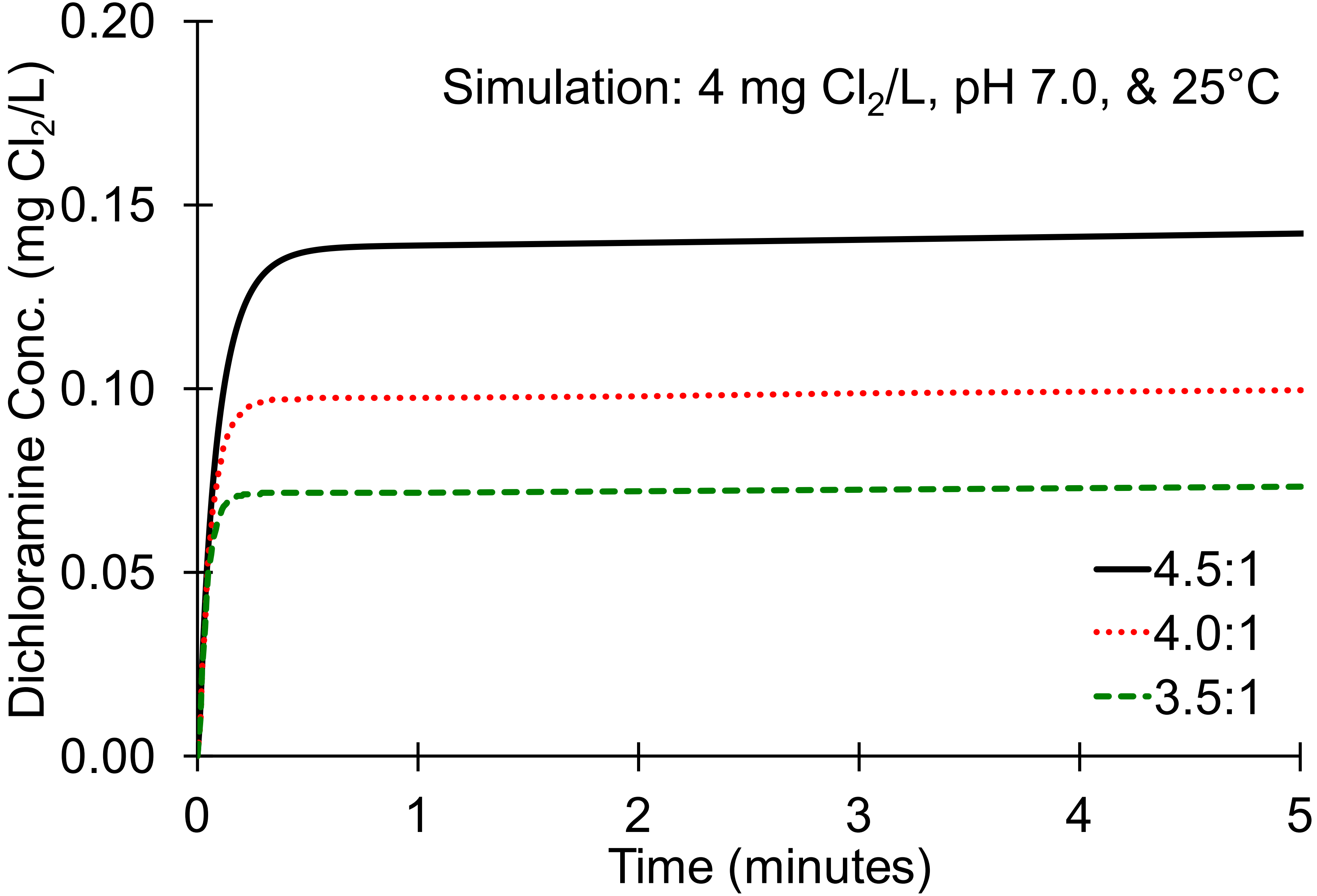
- ↑ pH or ↓ Cl_2:N
  - ↑ NH_3 relative to Mono
  - ↑ Mono formed = ↓ Di formed

↑ pH → ↓ Di = ↑ Mono



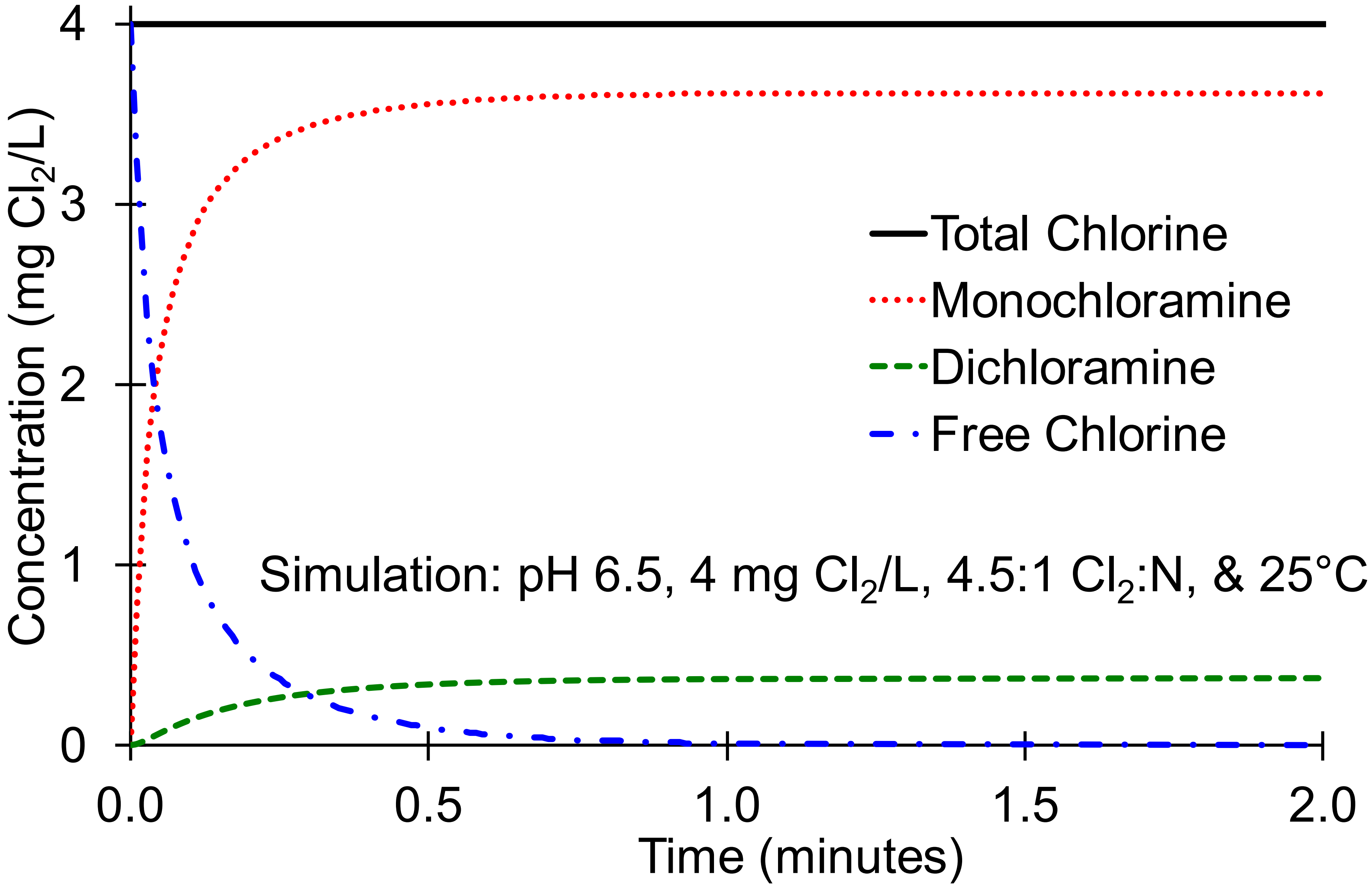
Simulation: 4 mg Cl_2/L, 4.5:1 Cl_2:N, & 25°C
Dichloramine Conc. (mg Cl_2/L)
0.5
0.4
0.3
0.2
0.1
0.0
pH 6.5
pH 7.0
pH 7.5
pH 8.0
0
1
2
3
4
5
Time (minutes)

↓ Cl_2:N → ↓ Di = ↑ Mono

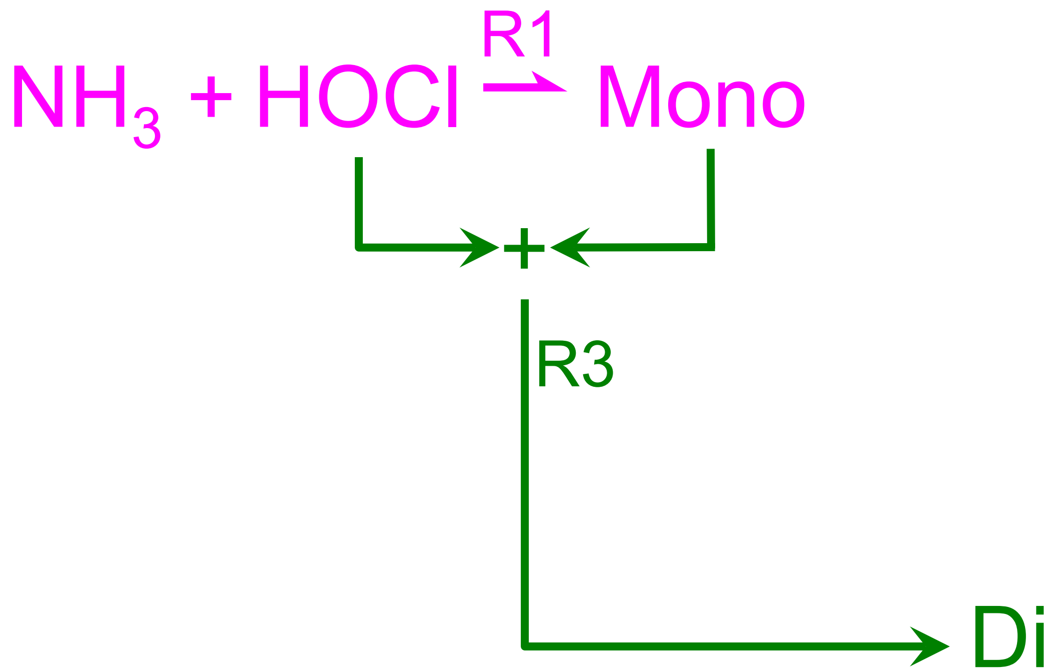


Simulation: 4 mg Cl2/L, pH 7.0, & 25°C
0.20
0.15
0.10
0.05
0.00
Dichloramine Conc. (mg Cl2/L)
0
1
2
3
4
5
Time (minutes)
4.5:1
4.0:1
3.5:1

Summary (Initial Minutes)



Chloramine Formation Summary



- R1 & R3 → competition for free chlorine (HOCl)
- ↑ pH or ↓ Cl_2:N favors Mono over Di formation
- Mixing → minimize localized:
  - Low pH (chlorine gas, liquid ammonium sulfate)
  - High Cl_2:N ratio (NH_3 depletion, breakpoint)

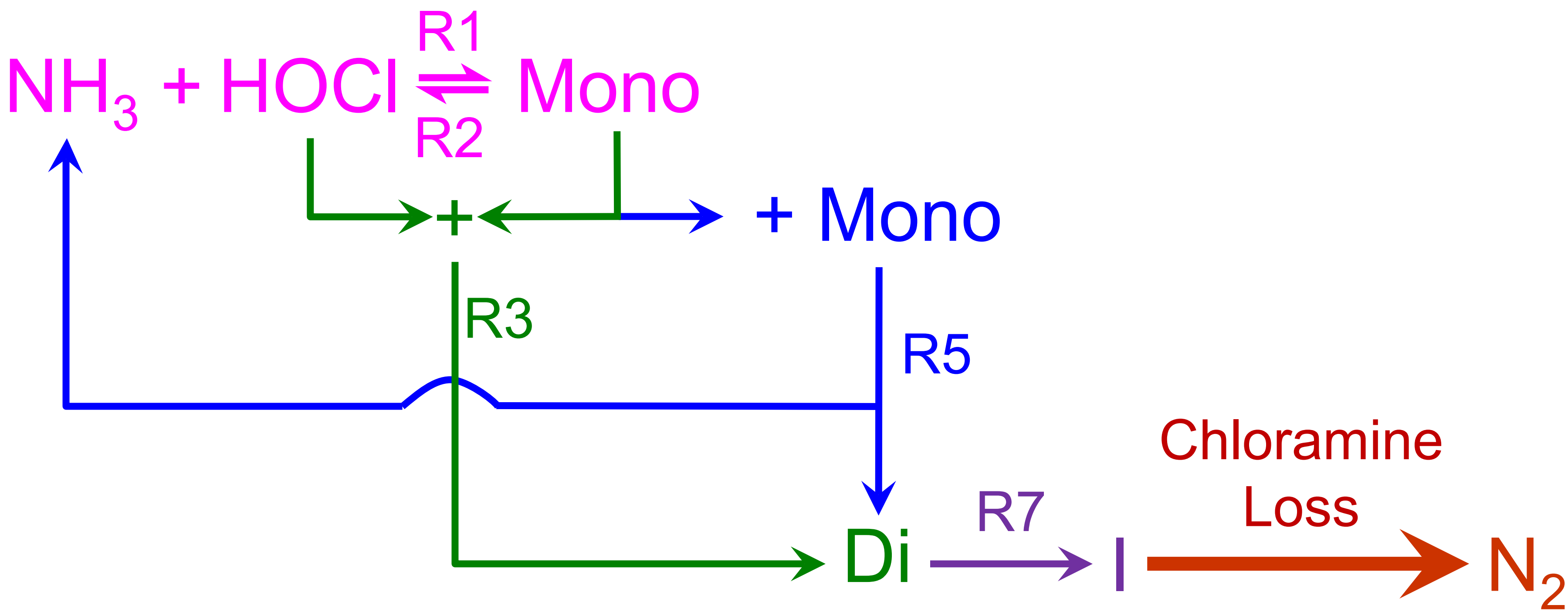
After this presentation, you will

1. Know relevant chloramine reactions & pH and Cl_2:N importance

2. Understand chloramine formation

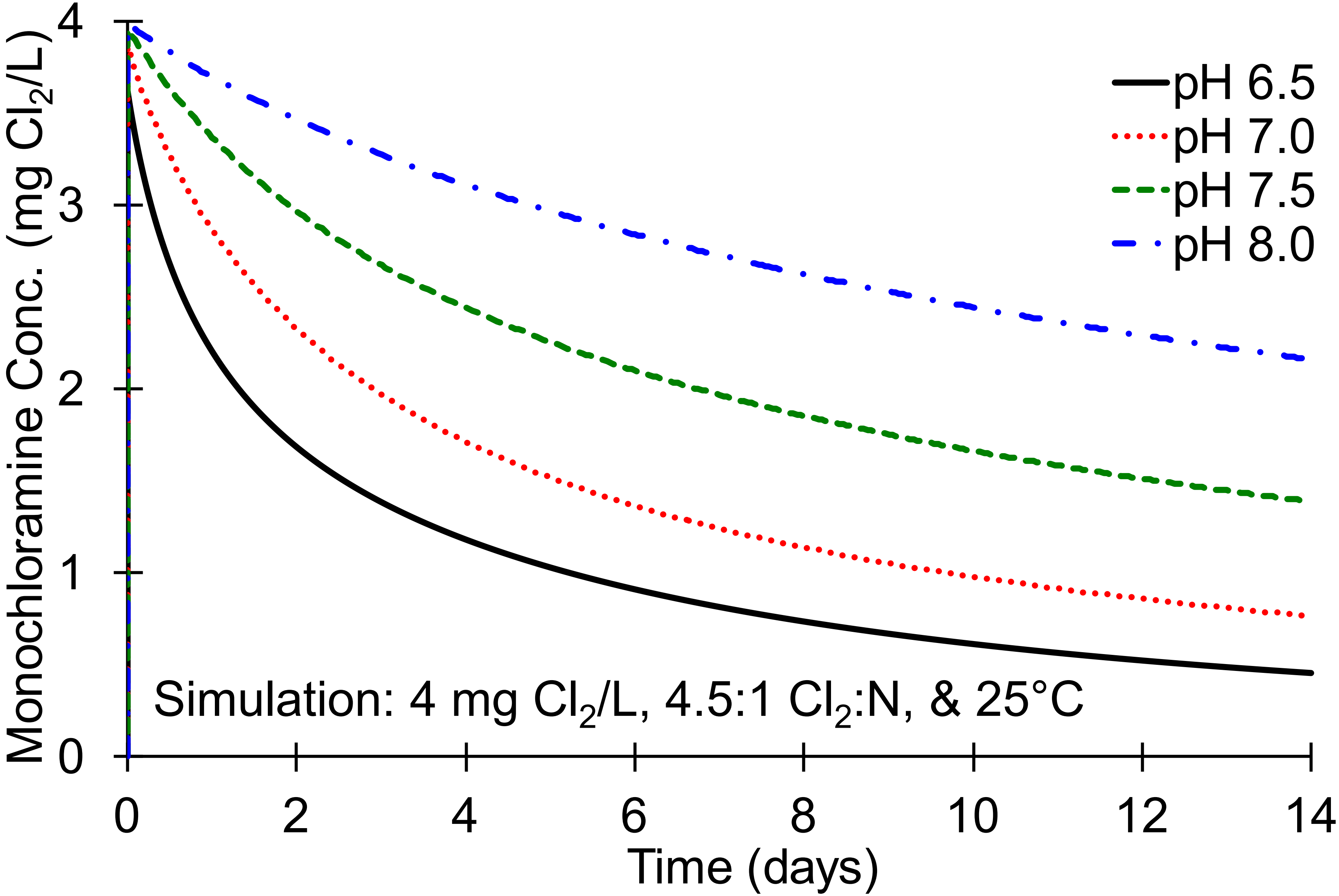
Chloramine Decay (All Reactions)

Mono → Di → chloramine loss

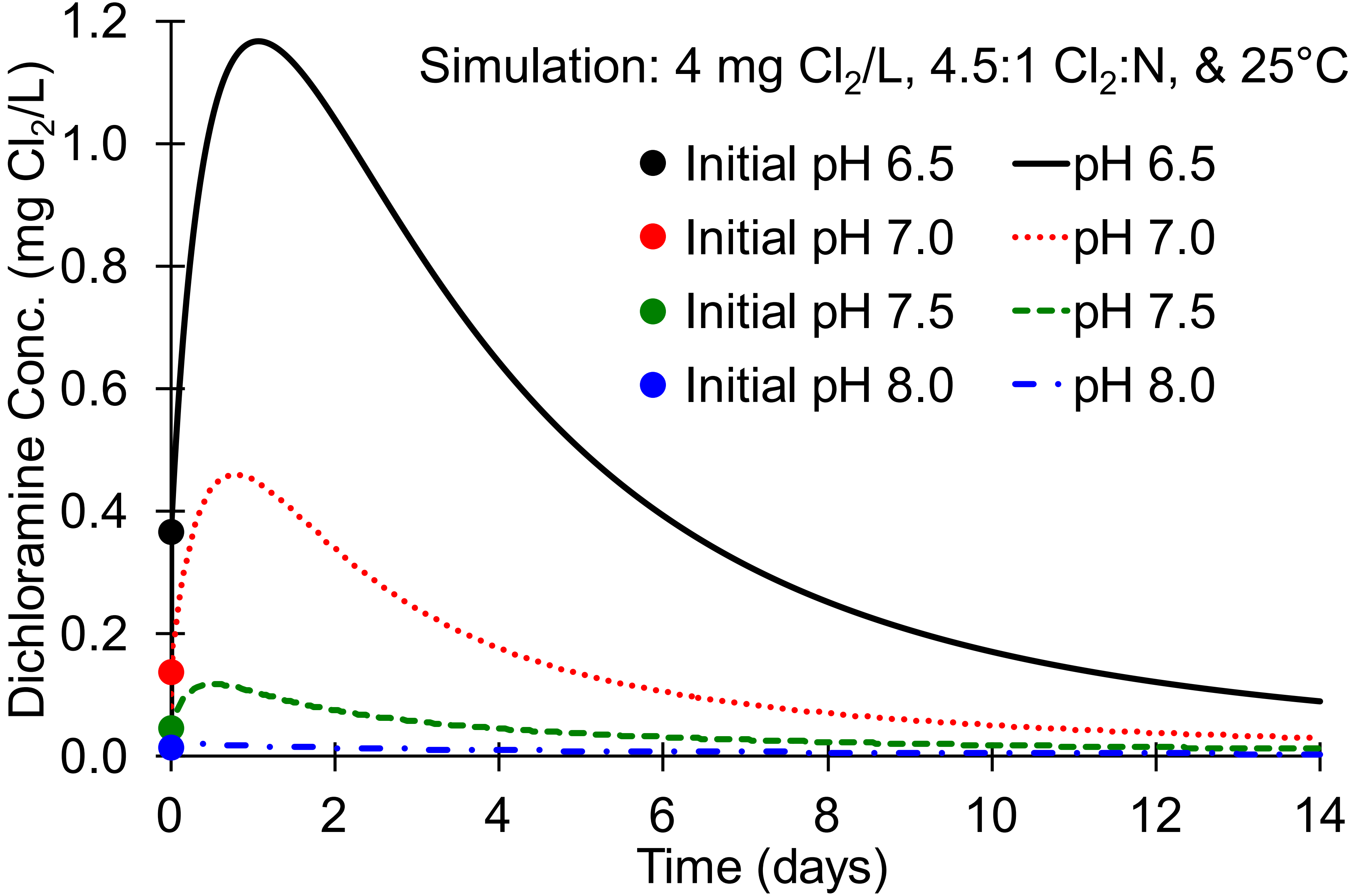


- ↑ pH (R3 & R5 slower, R7 faster)
  - Mono to Di → slower
  - Di accumulation → lower

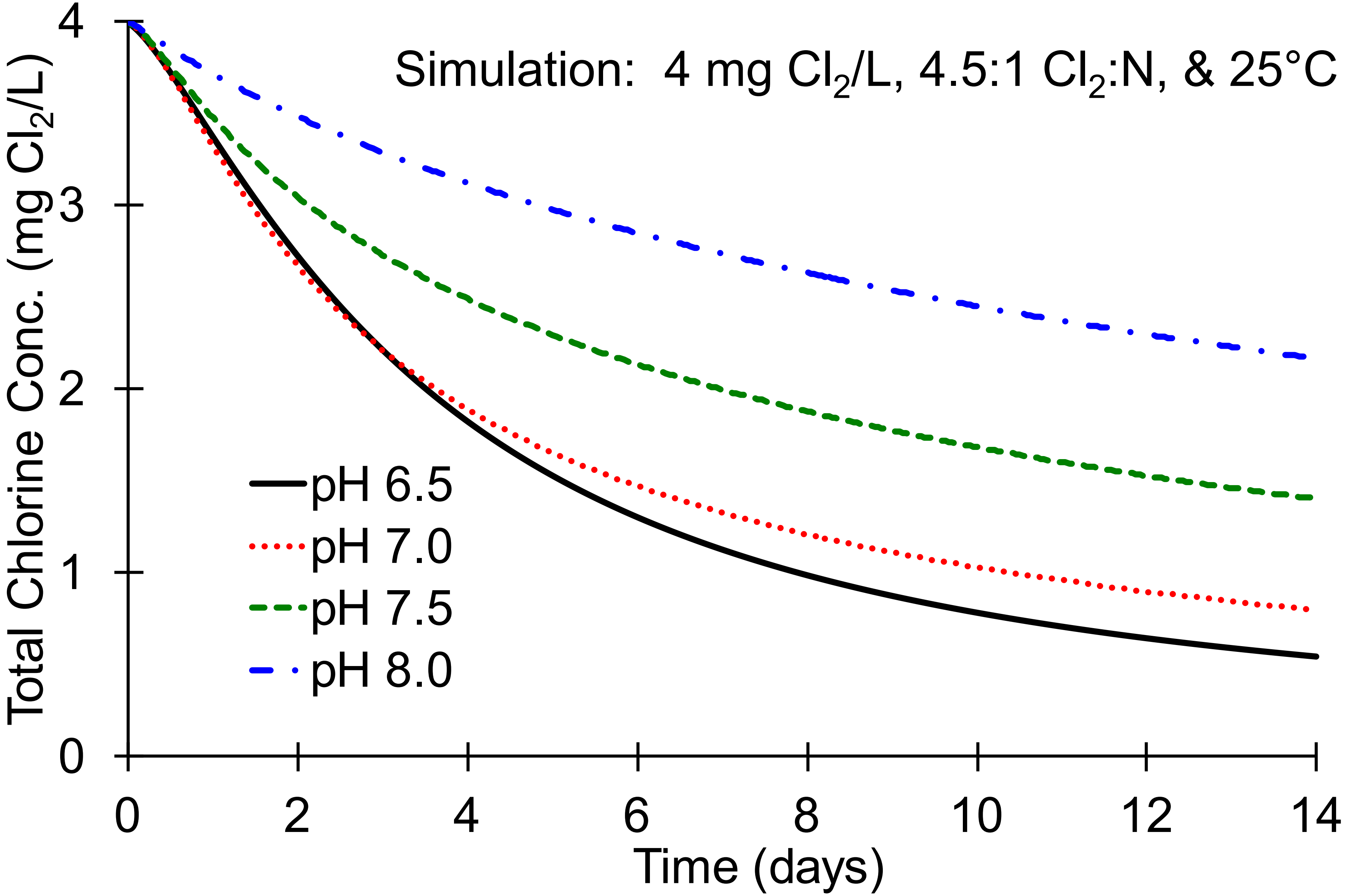
↑ pH → ↑ Mono Stability



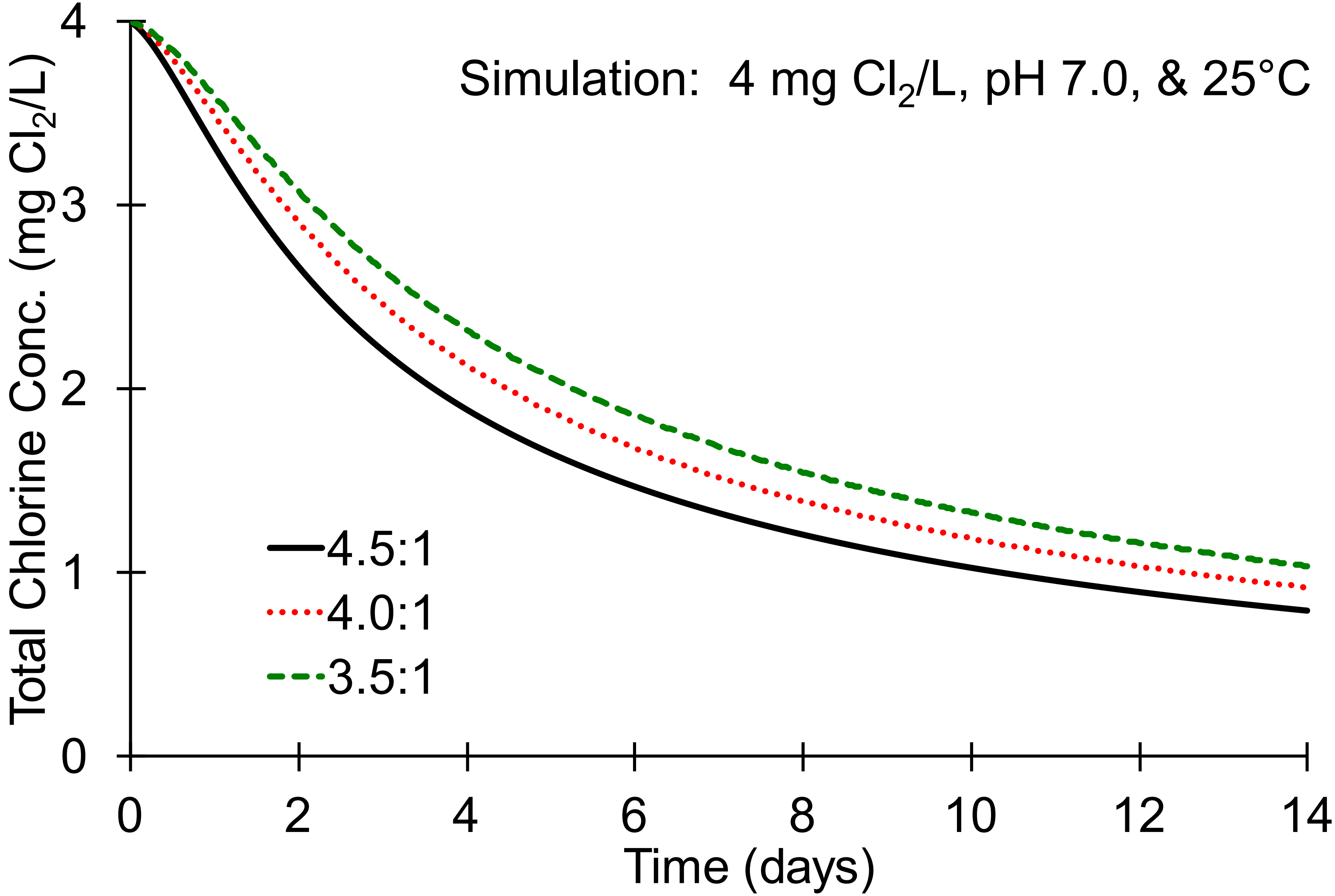
↑ pH → ↓ Di Formation & ↑ Di Loss



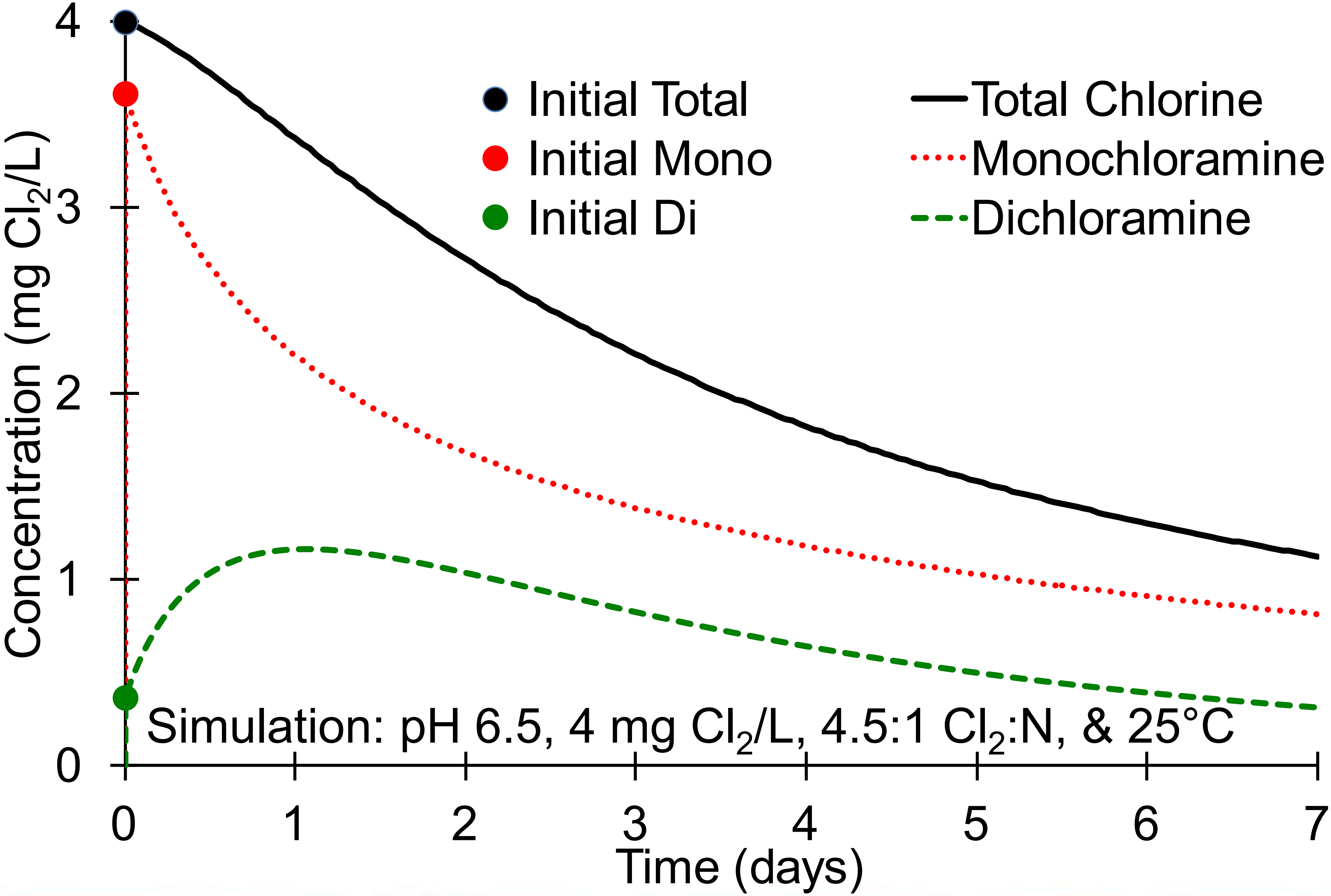
↑ pH → ↑ Total Chlorine Stability



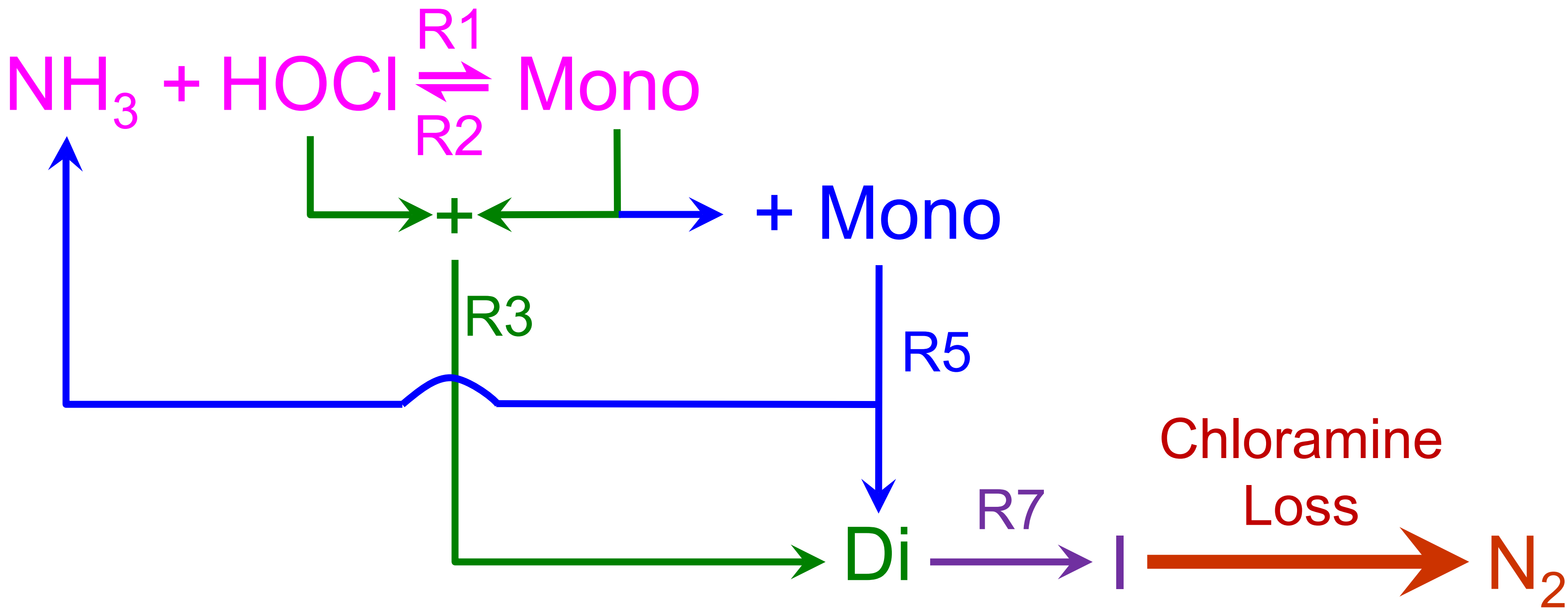
↓ Cl_2:N → ↑ Total Chlorine Stability



Summary (Overall)



Chloramine Decay Summary



- All reactions → unmeasurable free chlorine but present
- Mono → Di → chloramine loss
- ↑ pH or ↓ Cl_2:N favors Mono (total chlorine) stability
- Di is an intermediate & can accumulate
- ↓ pH → measurable Di (pH ≤ 7.5ish)

After this presentation, you will

1. Know relevant chloramine reactions & pH and Cl_2:N importance

2. Understand chloramine formation

3. Understand chloramine decay

Web Based Applications

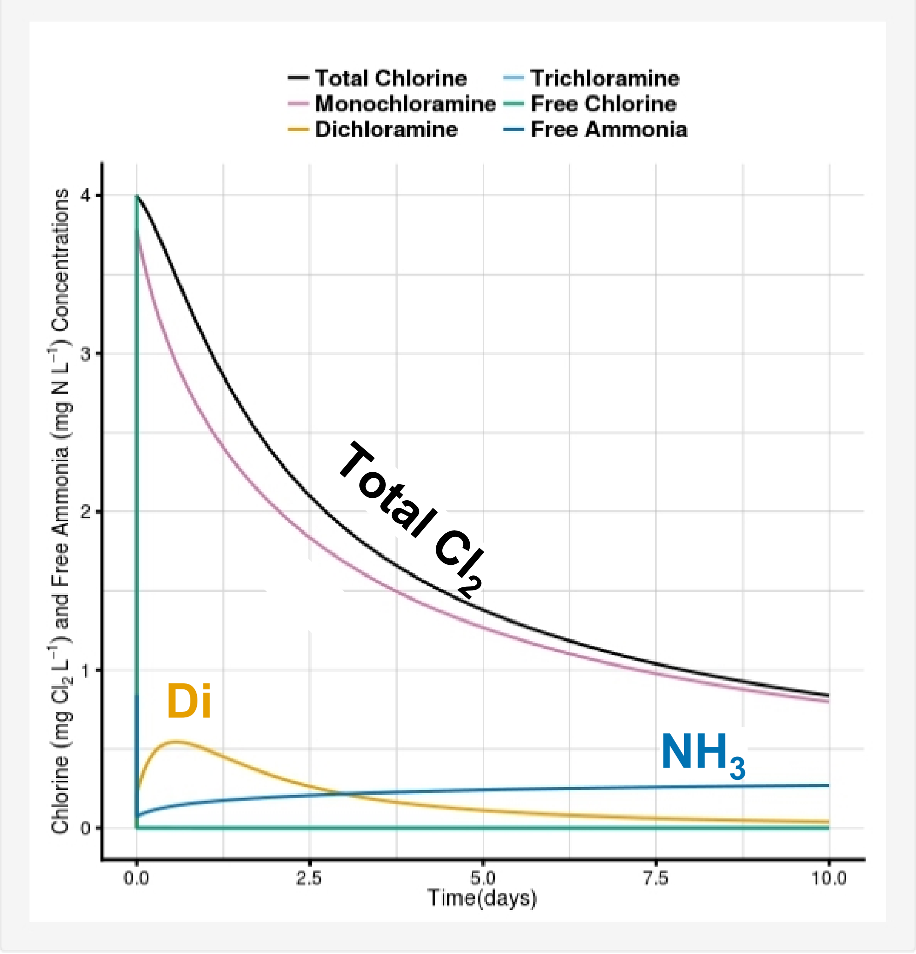
Web-Based Applications to Simulate Drinking Water Inorganic Chloramine Chemistry

DAVID G. WAHMAN[1]

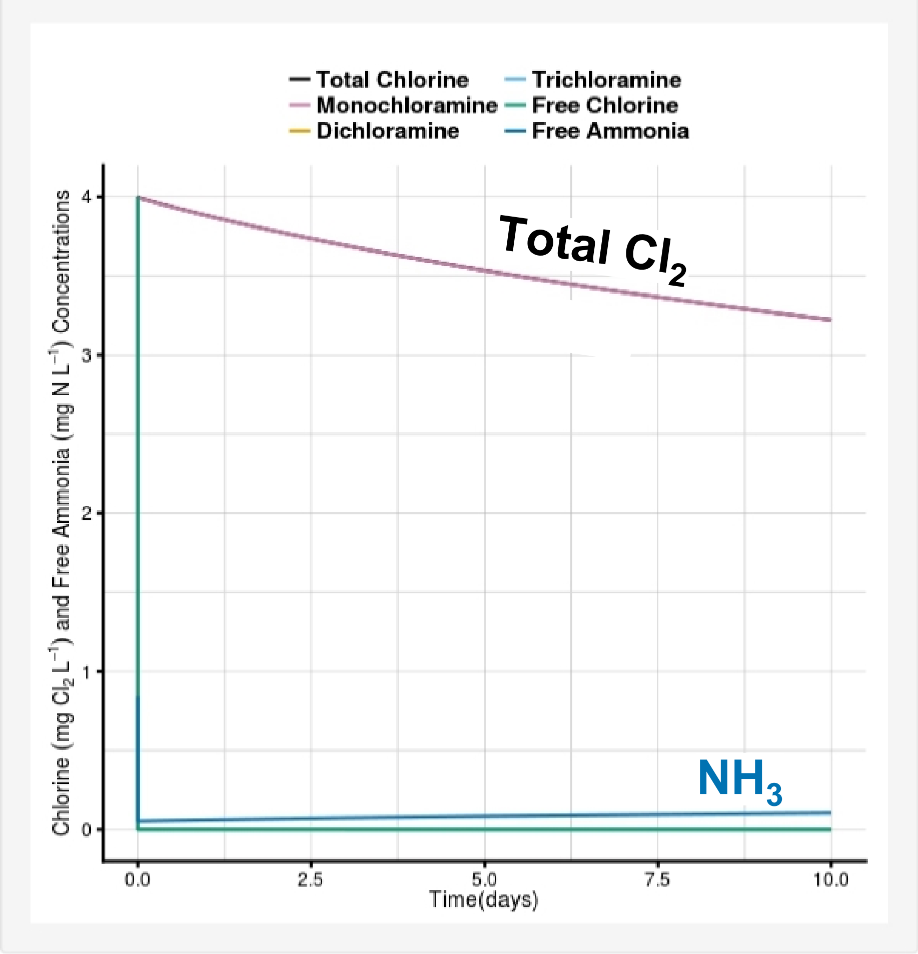
- JAWWA, November 2018, E43–E61
- DOI: https://doi.org/10.1002/awwa.1146
- Learning tools
  - Regulators, engineers, operators, academics, & students
  - No software or modeling expertise
- Simulate your conditions
  - What if scenarios?
  - What is baseline chloramine stability?

Chloramine Formation & Decay App

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

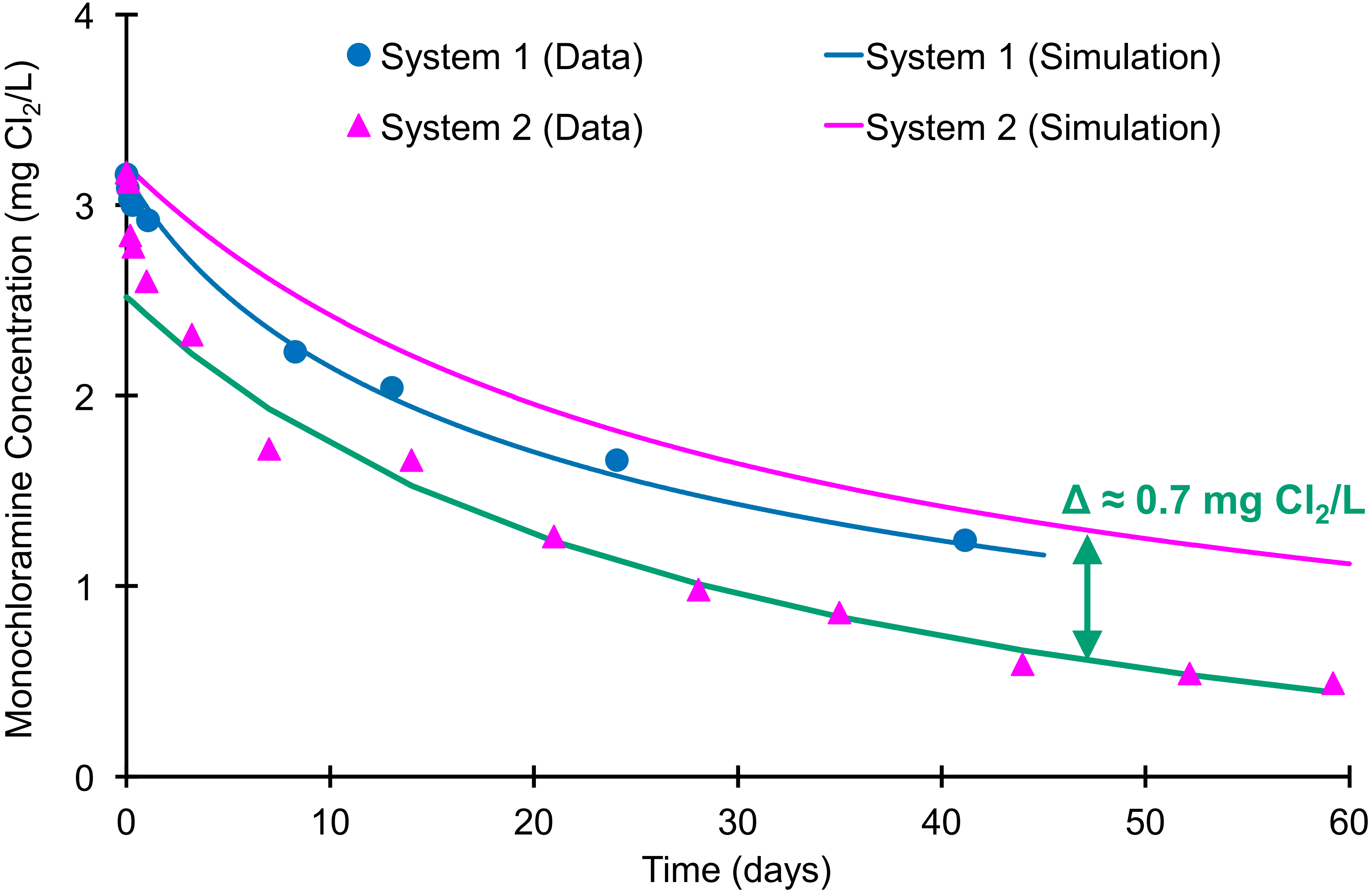


pH 7



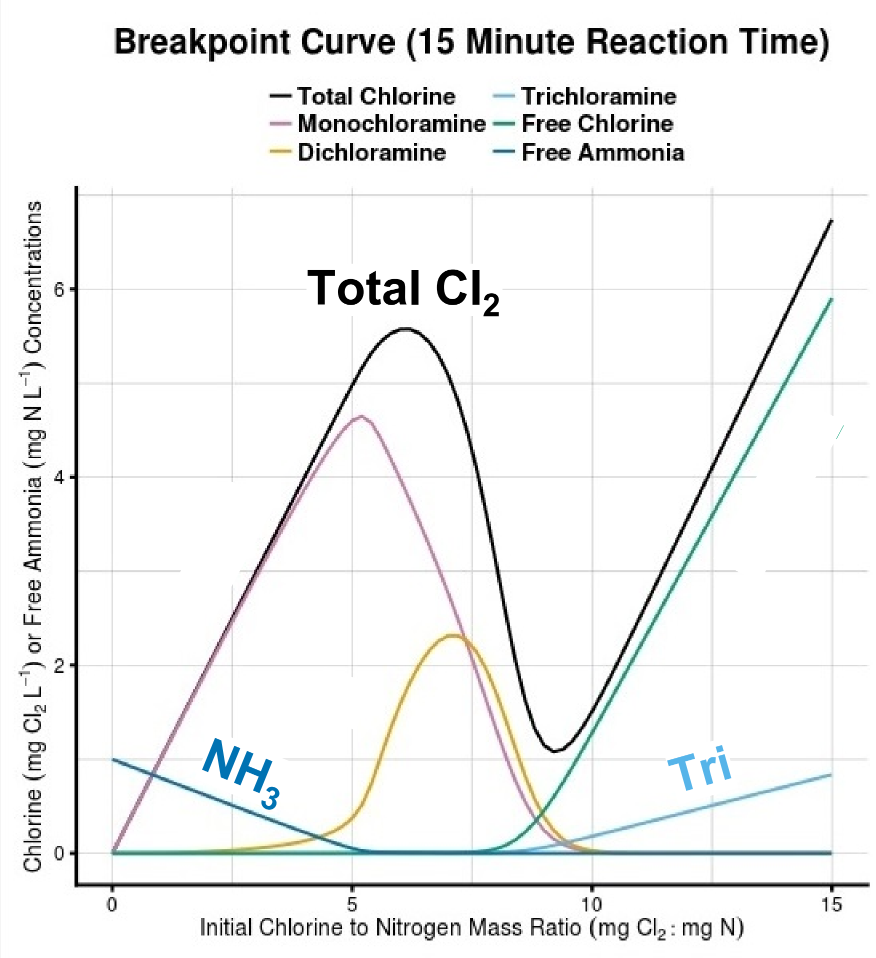
pH 9

Example Use of Web Application

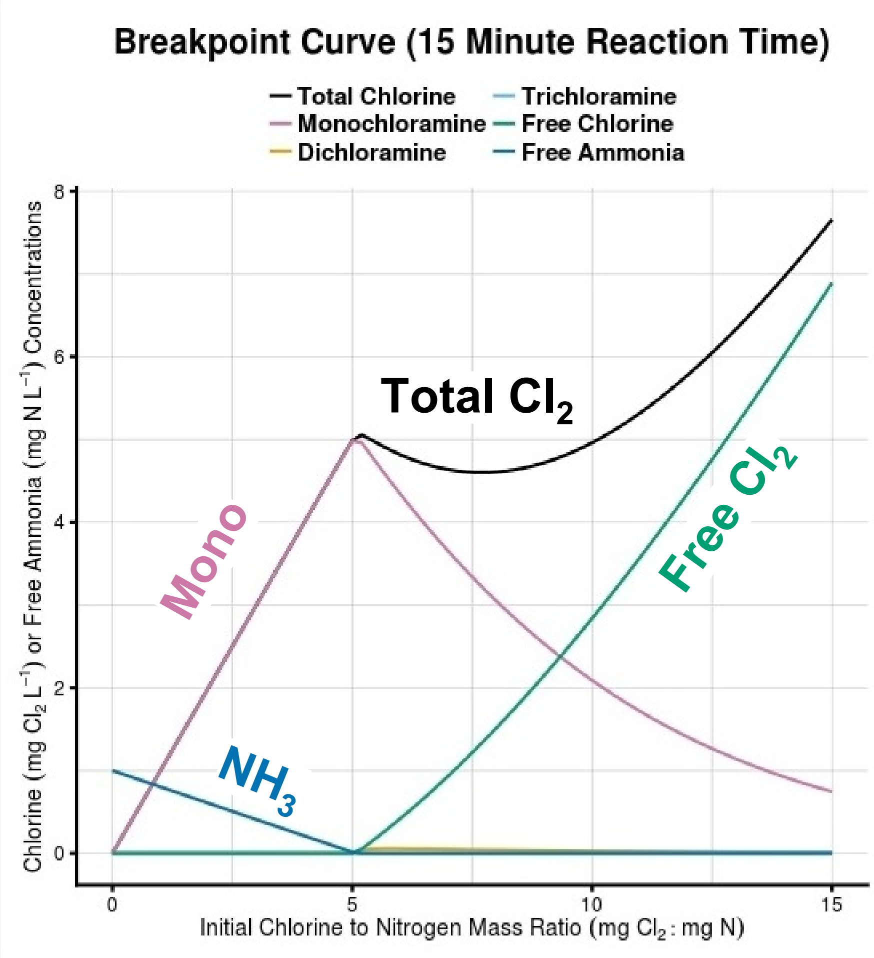


Breakpoint Curve App

https://usepaord.shinyapps.io/Breakpoint-Curve/



pH 7



pH 9

After this presentation, you will

1. Know relevant chloramine reactions & pH and Cl_2:N importance

2. Understand chloramine formation

3. Understand chloramine decay

4. Know of two chloramine chemistry simulators

Take Home Messages

- Free ammonia + free chlorine → chloramines
- Decay vs. Demand → ↓ ammonia release
- Chloramine chemistry
  - First minutes (free chlorine present): Mono/Di formation
  - > minutes: Mono → Di → chloramine loss
- Free chlorine & Di always present (measurable?)
- ↑ pH or ↓ Cl_2:N (pH 6.5–9.0 & $Cl_2:N \leq 5:1$)
  - Favors Mono over Di initial formation
  - ↑ Mono stability = ↑ total chlorine stability
- Di can increase after plant
- Two applications to simulate chloramine chemistry

Additional Resources

American Water Works Association (2013) *Nitrification Prevention and Control in Drinking Water (AWWA Manual M56, 2nd Edition)*. AWWA. Denver, CO.

Jafvert, C.T. and Valentine, R.L. (1992) Reaction Scheme for Ammoniacal Water. *Environmental Science & Technology* 26(3), 577–586.

Ozekin K., Valentine R.L., and Vikesland P.J. (1996) Modeling the decomposition of disinfecting residuals of chloramine. In *Water Disinfection and Natural Organic Matter: Characterization and Control*. Minear, R.A. and Amy, G.L. (eds). American Chemical Society. Washington D.C., pages 115–125.

Qiang Z., and Adams C.D. (2004). Determination of Monochloramine Formation Rate Constants with Stopped–Flow Spectrophotometry. *Environmental Science & Technology* 38(5), 1435–1444.

Vikesland, J.P., Ozekin, K. & Valentine, R.L. (2001) Monochloramine Decay in Model and Distribution System Waters. *Water Research* 35(7), 1766–1776.

Wahman, D.G. and Speitel, G.E. (2012) The relative importance of nitrite oxidation by hypochlorous acid under chloramination conditions. *Environmental Science & Technology* 46(11), 6056–6064.

Web–Based Applications

Breakpoint chlorination simulator: https://usepaord.shinyapps.io/Breakpoint-Curve/

Chloramine formation and decay simulator: https://usepaord.shinyapps.io/Unified-Combo/

Wahman, D.G. (2018) Web–based applications to simulate drinking water inorganic chloramine chemistry. *Journal American Water Works Association* 110(11), E43–E61. DOI: https://doi.org/10.1002/awwa.1146