Web–Based Apps to Simulate Disinfectant Water Chemistry: Development and Practical Uses

David G. Wahman
Research Environmental Engineer
Center for Environmental Solutions & Emergency Response
Office of Research & Development
U.S. Environmental Protection Agency
Cincinnati, Ohio, United States

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After the presentation, you will

1. Know of two chloramine apps:
   - Simulate chemistry (kinetics)
   - Interpret hold studies
   - Interpret real–world observations
2. Know of two chlorinated cyanurate apps:
   - Simulate chemistry (equilibrium)
   - Estimate free chlorine residual

Chloramines

- 2nd most used secondary disinfectant
  - Free ammonia (NH_4^+ and NH_3, Free NH_3)
  - Free chlorine (HOCl and OCl^-, Free Cl_2)
- ↓ regulated DBPs & ↑ residual stability
- 3 inorganic species
  - **Mono**chloramine (NH_2Cl)
  - **Di**chloramine ($NHCl_2$)
  - **Tri**chloramine (NCl_3)
- Kinetically controlled system (time matters)

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 (residual not dose)
    - Source water ammonia
  - pH
  - Mixing, temperature, hydraulics
- Demand (will happen if present)
  - Natural organic matter & inorganics (e.g., iron)
  - Nitrification related → nitrite, cells, degradation
  - ↓ formation & ↓ stability

Chloramine Reaction Scheme

Unified Model
Formation & "Decay"
Jafvert & Valentine (1992)
Vikesland et al. (2001)

1	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$
2	$NH_2Cl + H_2O \rightarrow HOCl + NH_3$
3	$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$
4	$NHCl_2 + H_2O \rightarrow HOCl + NH_2Cl$
5	$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$
6	$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$
7	$NHCl_2 + H_2O \rightarrow I$
8	$I + NHCl_2 \rightarrow HOCl + N_2 + 3H^+ + 3Cl^-$
9	$I + NH_2Cl \rightarrow N_2 + 3H^+ + 3Cl^-$
10	$NH_2Cl + NHCl_2 \rightarrow N_2 + 3H^+ + 3Cl^-$
11	$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$
12	$NHCl_2 + NCl_3 + 2H_2O \rightarrow N_2 + 2HOCl + 3HCl$
13	$NHCl_2 + NCl_3 + H_2O \rightarrow N_2 + HOCl + 3HCl$
14	$NHCl_2 + 2HOCl + H_2O \rightarrow NO_3^- + 5H^+ + 4Cl^-$
15	$NH_2Cl + DOC_1 \rightarrow NH_3 + \text{Products}$
16	$HOCl + DOC_2 \rightarrow \text{Products}$

Example "Demand"
Organic Matter
Duirk et al. (2005)

Motivation & Goals

- Create interactive apps
- Ability to simulate your conditions
  - Impact of changes?
  - What happens outside of normal ranges?
  - What is the baseline chloramine stability?
- Freeware
- Web based
- Users
  - Regulators, engineers, operators, academics, & students
  - No software or modeling expertise

Chloramine Chemistry App

- Formation & decay + organic matter demand
- https://usepaord.shinyapps.io/Unified-Combo/
- Assumptions
  - Batch (plug–flow) → time = water age (pipe–flow)
  - Ideal chemical mixing
  - No pipe wall or additional demand reactions
  - No or low bromide (< 0.1 mg/L)
- Features
  - User–selectable inputs
  - Two side–by–side simulations
  - Three chemical addition scenarios
  - Download simulation data (.csv)

Chloramine Chemistry – Layout

A_2015-04-29_16_44.csv - Excel

	Time_minutes	Time_hours	Time_days	Total_Chlorine_mg_Cl2_L	Monochloramine_mg_Cl2_L	Dichloramine_mg_Cl2_L	Trichloramine_mg_Cl2_L	Free_Chlorine_mg_Cl2_L	Free_Ammonia_mg_N_L
1	0	0	0	4	0	0	0	4	0.842105263
2	0.016666667	0.000277778	1.16E-05	3.999966864	2.003168617	0.023836689	0.000140768	1.97282079	0.444753264
3	0.033333333	0.000555556	2.31E-05	3.999880266	2.676448537	0.052583197	0.000498708	1.270349824	0.309131674
4	0.05	0.000833333	3.47E-05	3.999775143	3.009085291	0.076167219	0.000912214	0.91361042	0.241183201
5	0.066666667	0.001111111	4.63E-05	3.999665334	3.205129669	0.095206058	0.001316188	0.698013418	0.200616483
6	0.083333333	0.001388889	5.79E-05	3.99955565	3.333153036	0.110763851	0.001688287	0.553950476	0.173807169
7	0.1	0.001666667	6.94E-05	3.999447755	3.422574969	0.123660578	0.002021892	0.451190315	0.154873897
8	0.116666667	0.001944444	8.10E-05	3.999342143	3.488073812	0.134487183	0.002316548	0.374464601	0.140864166
9	0.133333333	0.002222222	9.26E-05	3.999238869	3.537772588	0.143672144	0.00257426	0.315219877	0.130133912
10	0.15	0.0025	0.000104167	3.999137824	3.576521076	0.15153247	0.002797956	0.268286323	0.12169543
11	0.166666667	0.002777778	0.000115741	3.999038857	3.607388361	0.15830788	0.002990806	0.23035181	0.114919736
12	0.183333333	0.003055556	0.000127315	3.998941813	3.632408242	0.164183382	0.003155917	0.199194272	0.109387387
13	0.2	0.003333333	0.000138889	3.998846554	3.652979987	0.169304372	0.003296207	0.173265987	0.104807973
14	0.216666667	0.003611111	0.000150463	3.998752965	3.670096734	0.173786957	0.003414352	0.151454922	0.100974071
15	0.233333333	0.003888889	0.000162037	3.998660948	3.684482075	0.177725146	0.003512775	0.132940952	0.097733599
16	0.25	0.004166667	0.000173611	3.998570427	3.69667522	0.181195994	0.003593659	0.117105553	0.094972518
17	0.266666667	0.004444444	0.000185185	3.998481336	3.707085864	0.18426333	0.003658958	0.103473184	0.092603646
18	0.283333333	0.004722222	0.000196759	3.998393625	3.716030624	0.186980524	0.00371042	0.091672057	0.090559195
19	0.3	0.005	0.000208333	3.99830725	3.723757872	0.189392565	0.003749606	0.081407208	0.088785673
20	0.316666667	0.005277778	0.000219907	3.998222179	3.730465039	0.191537654	0.003777908	0.072441577	0.087240309
21	0.333333333	0.005555556	0.000231481	3.99813838	3.736310952	0.193448437	0.003796571	0.06458242	0.085888501
22	0.35	0.005833333	0.000243056	3.998055829	3.741424737	0.195152968	0.003806702	0.057671422	0.084701963
23	0.366666667	0.006111111	0.00025463	3.997974505	3.74591238	0.196675478	0.003809292	0.051577356	0.083657355
24	0.383333333	0.006388889	0.000266204	3.997894388	3.749861632	0.198036988	0.003805225	0.046190544	0.082735256
25	0.4	0.006666667	0.000277778	3.997815461	3.753345702	0.199255805	0.003795289	0.041418665	0.081919383
26	0.416666667	0.006944444	0.000289352	3.997737706	3.756426113	0.200347934	0.00378019	0.037183469	0.081195989
27	0.433333333	0.007222222	0.000300926	3.997661109	3.759154902	0.201327406	0.003760557	0.033418243	0.080553398
28	0.45	0.0075	0.0003125	3.997585653	3.761576334	0.202206562	0.003736952	0.030065804	0.079981634
29	0.466666667	0.007777778	0.000324074	3.997511325	3.763728269	0.202996278	0.003709879	0.0270769	0.079472132
30	0.483333333	0.008055556	0.000335648	3.99743811	3.765643241	0.203706164	0.003679785	0.02440892	0.079017507
31	0.5	0.008333333	0.000347222	3.997365993	3.767349334	0.204344727	0.003647073	0.022024858	0.078611359
32	0.516666667	0.008611111	0.000358796	3.99729496	3.768870895	0.204919515	0.003612102	0.019892449	0.078248125

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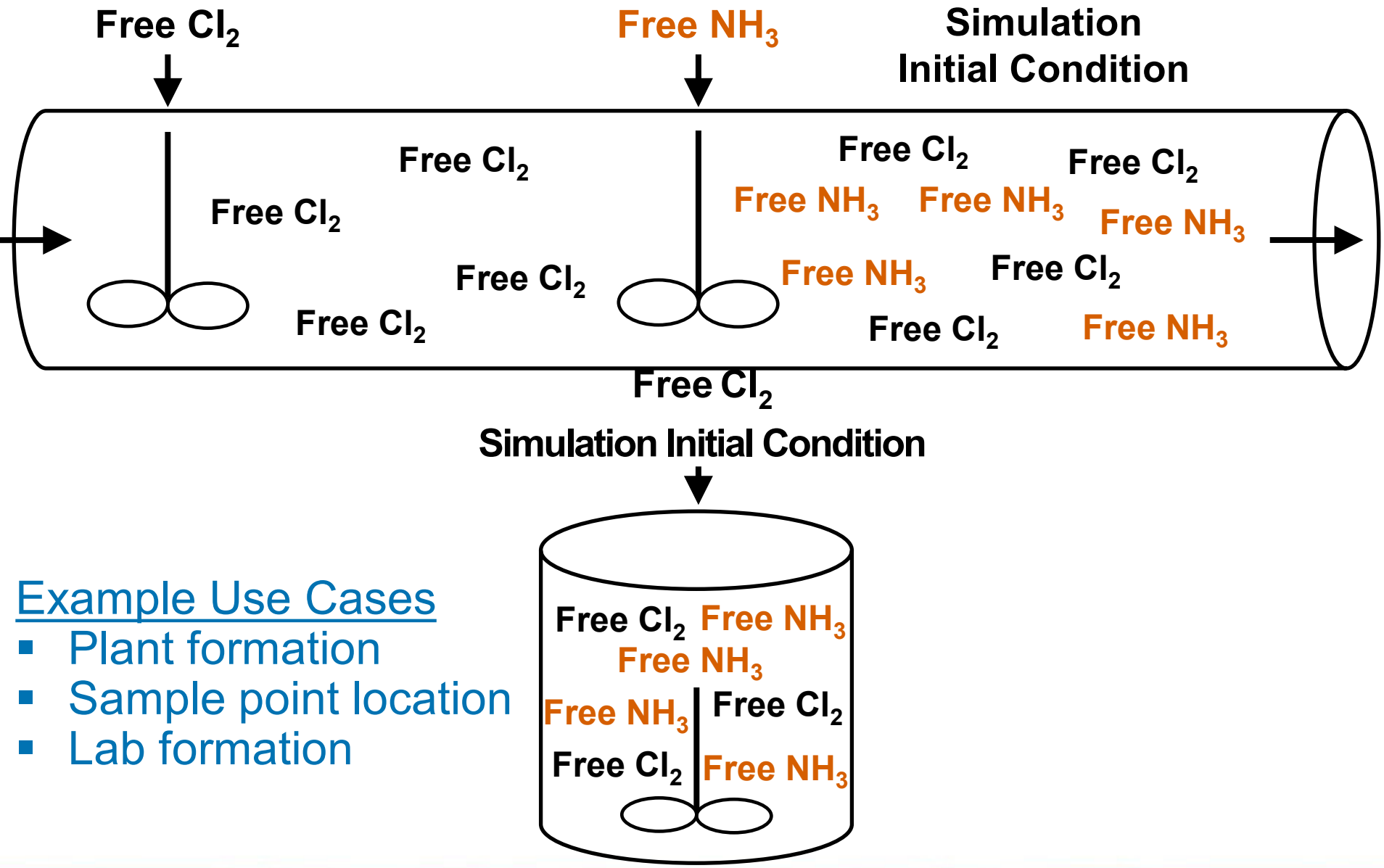
Simultaneous Addition (Plant Formation)

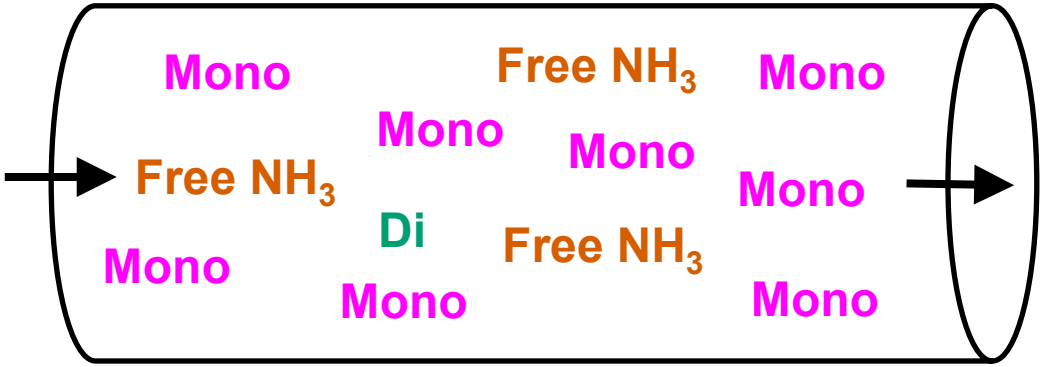


Example Use Cases

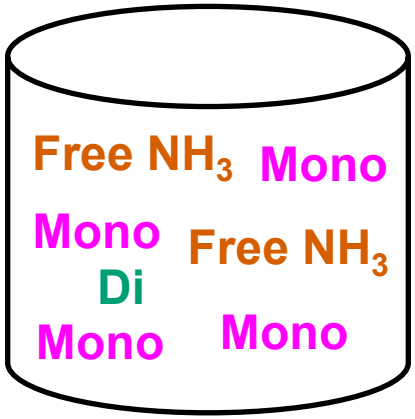
- Plant formation
- Sample point location
- Lab formation

Preformed Chloramines (DS Sample)

Simulation Initial Condition



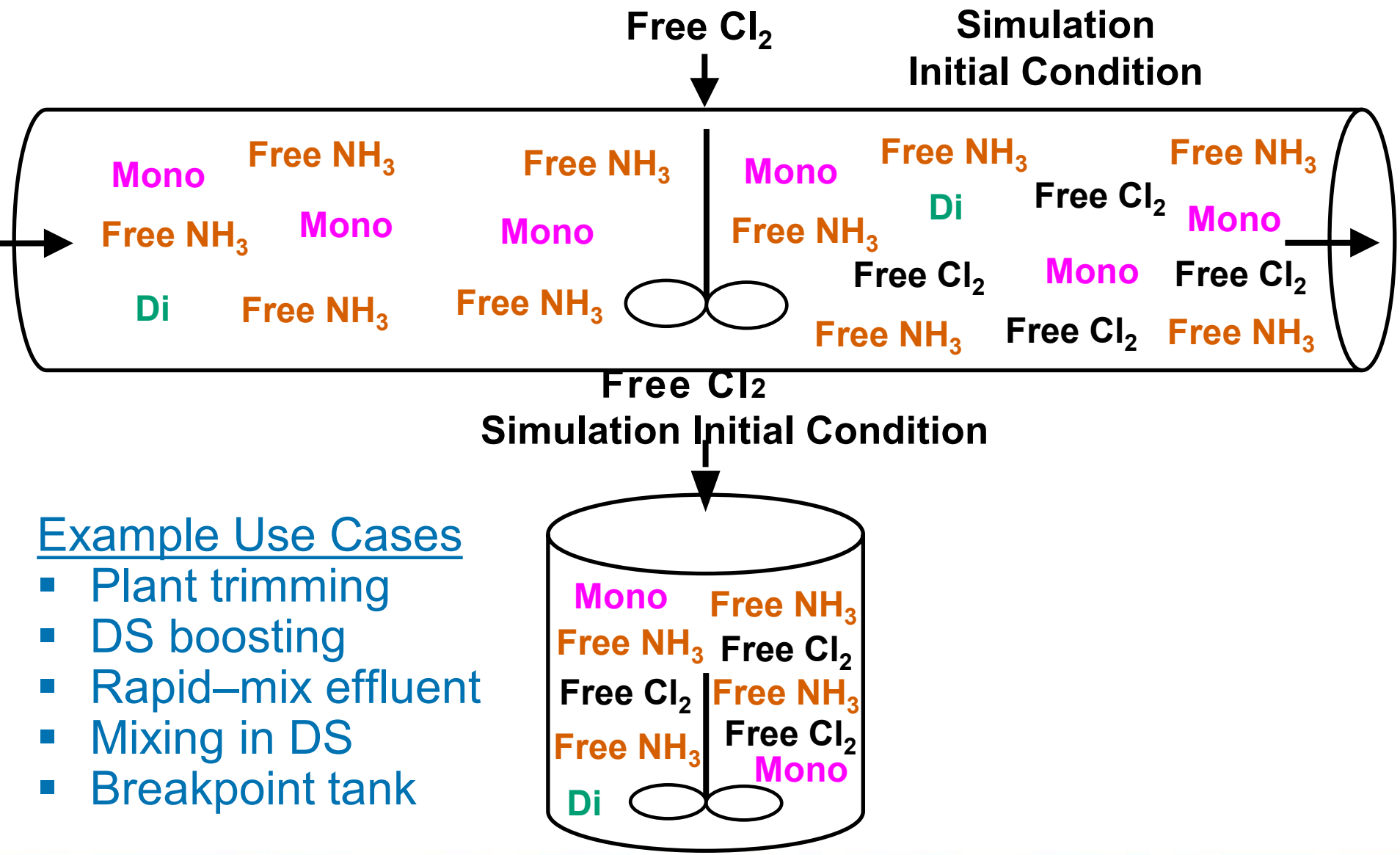
Simulation Initial Condition



Example Use Cases

- Hold study
- Lab stock dosing

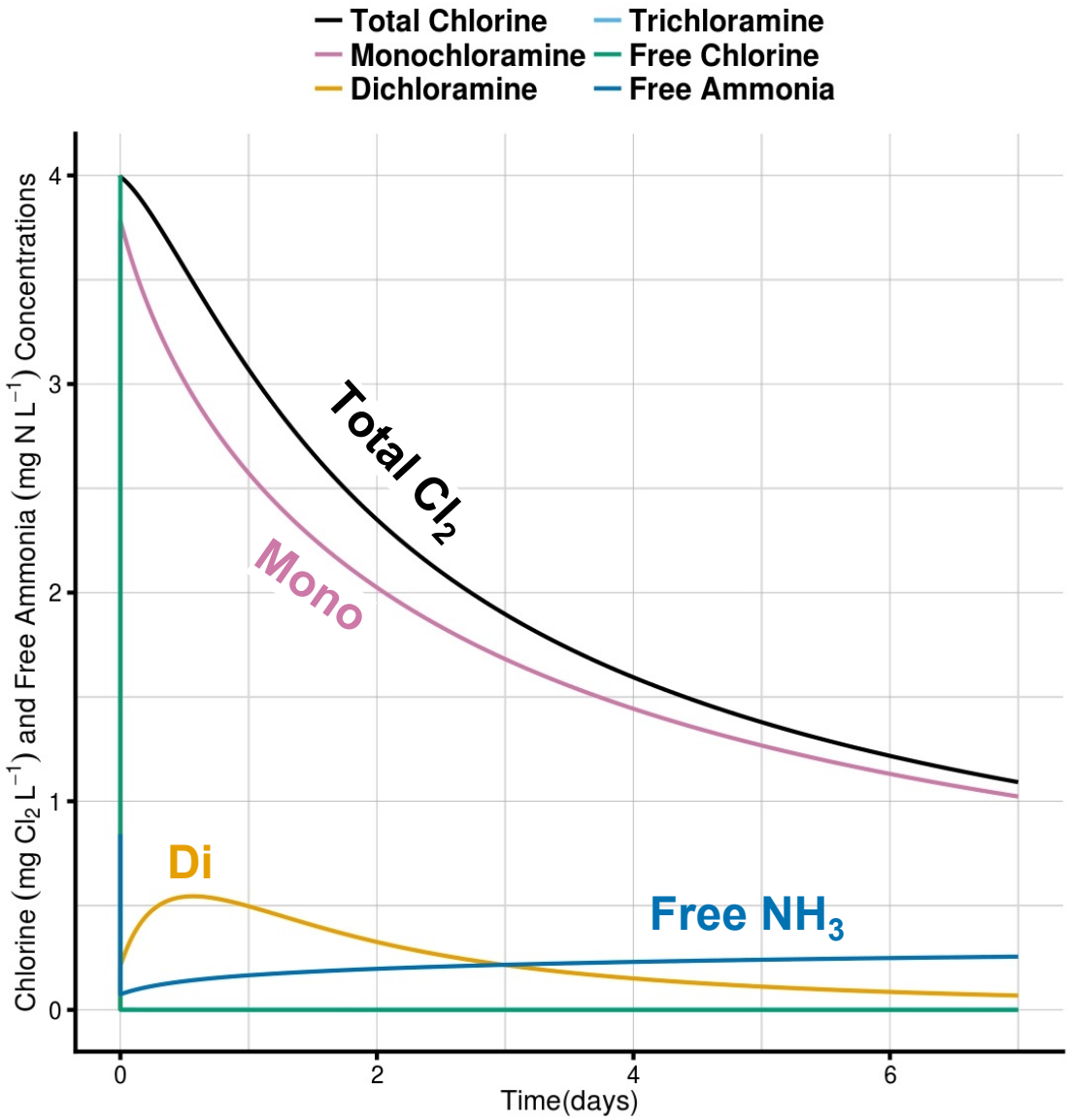
Booster Chlorination (Plant or DS)



Example Use Cases

- Plant trimming
- DS boosting
- Rapid–mix effluent
- Mixing in DS
- Breakpoint tank

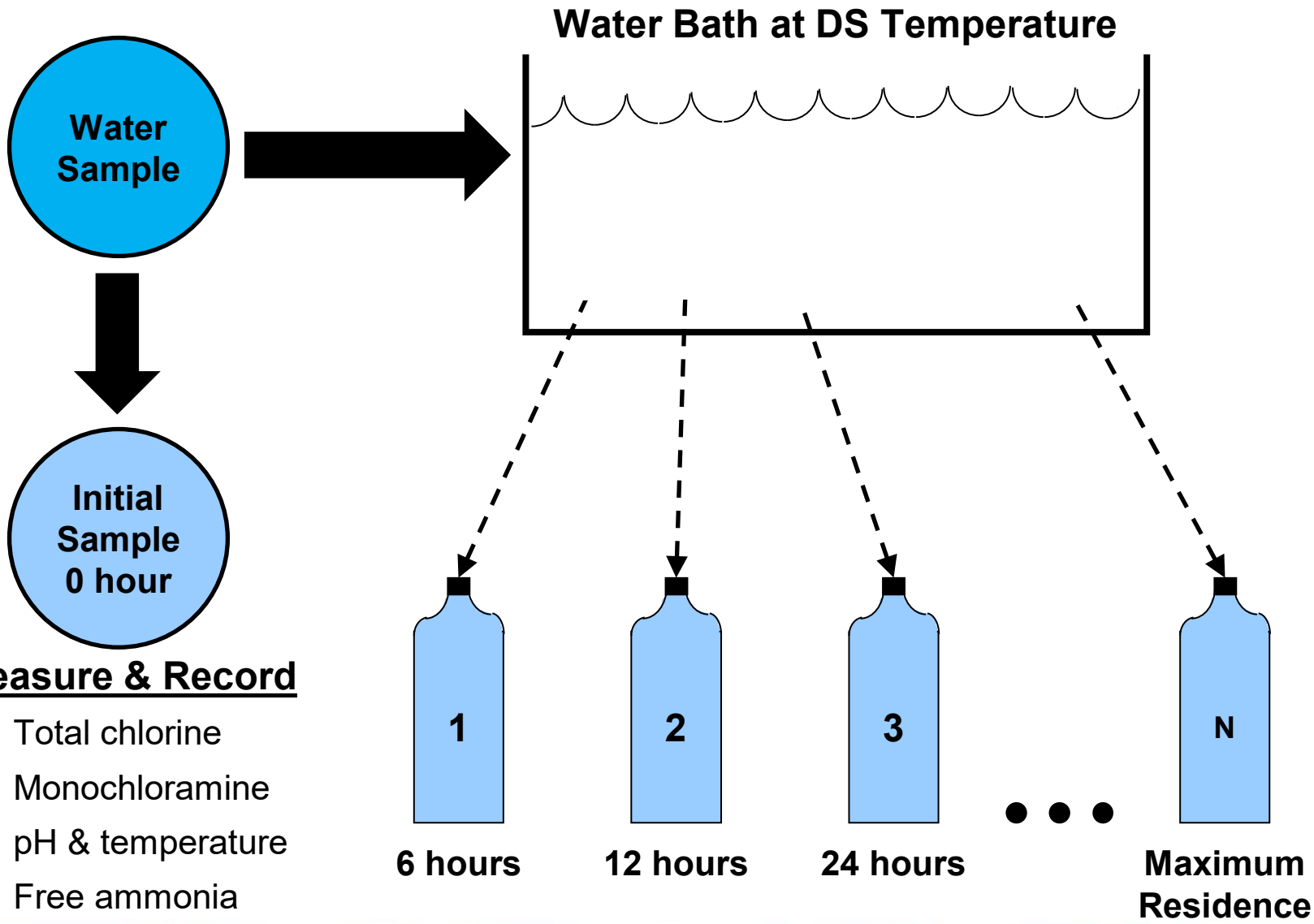
Chloramine Chemistry – Output Plot



Hold Study Use Case – Overview

- *Opflow* publications
  - Alexander et al., May 2019, 16–19, https://doi.org/10.1002/opfl.1187
    - "Use a Hold Study to Assess Distribution System Influent Water Quality"
  - Alexander et al., June 2020, 20–23, https://doi.org/10.1002/opfl.1383
    - "Use a Hold Study and a Web-Based App to Assess Chloramine Demand"
- Water sample
  - Within treatment plant
  - Distribution system influent
  - Master meter
- Measure residual over time → assess bulk water stability
- Bottle study → no hydraulic or material impacts
  - Chlorine demand free
  - Size based on sample volume (1 liter)
  - Protect from light → amber glass, foil wrapped, cabinet
  - Headspace free

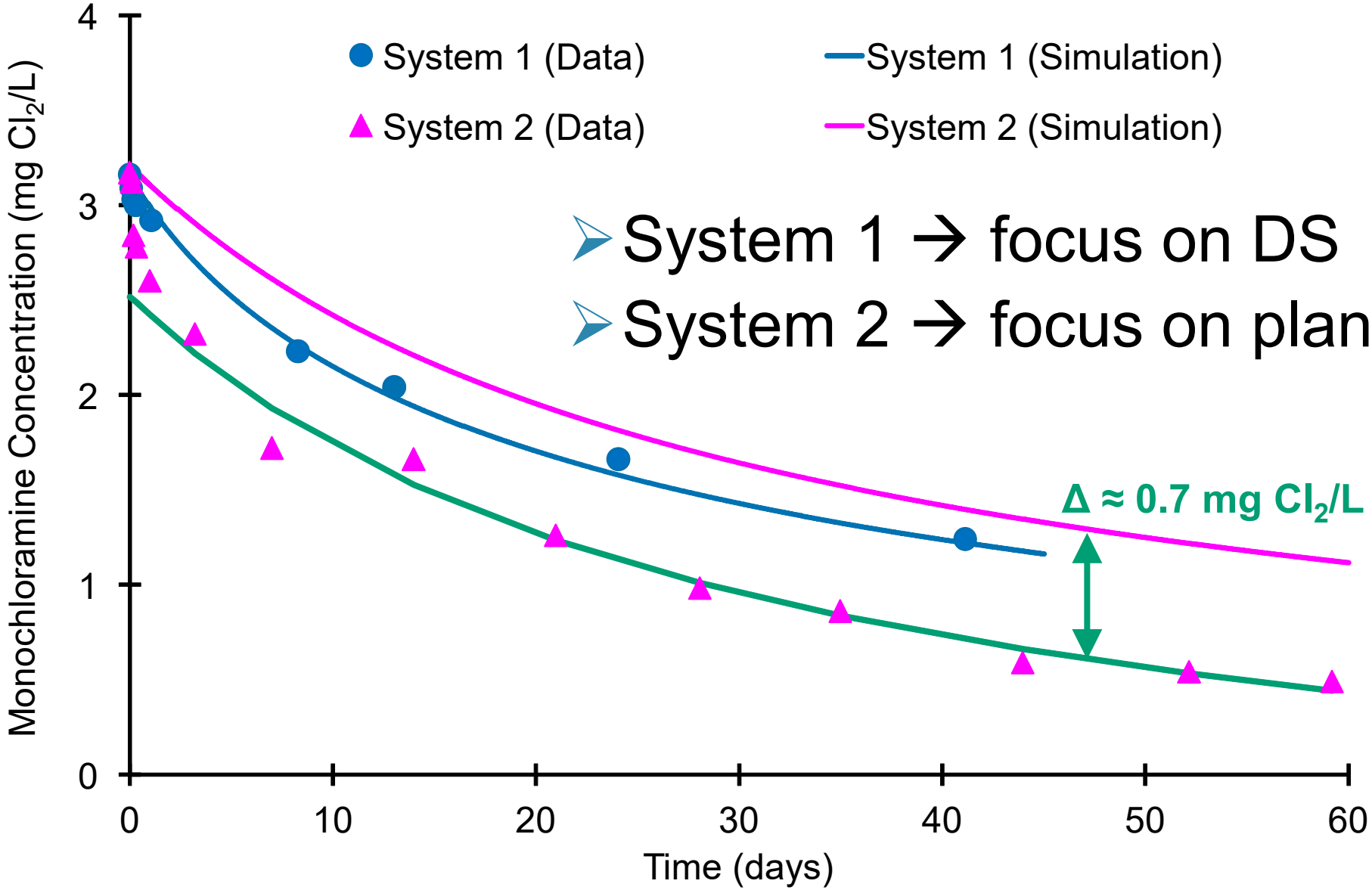
Hold Study – Approach



Measure & Record

- Total chlorine
- Monochloramine
- pH & temperature
- Free ammonia

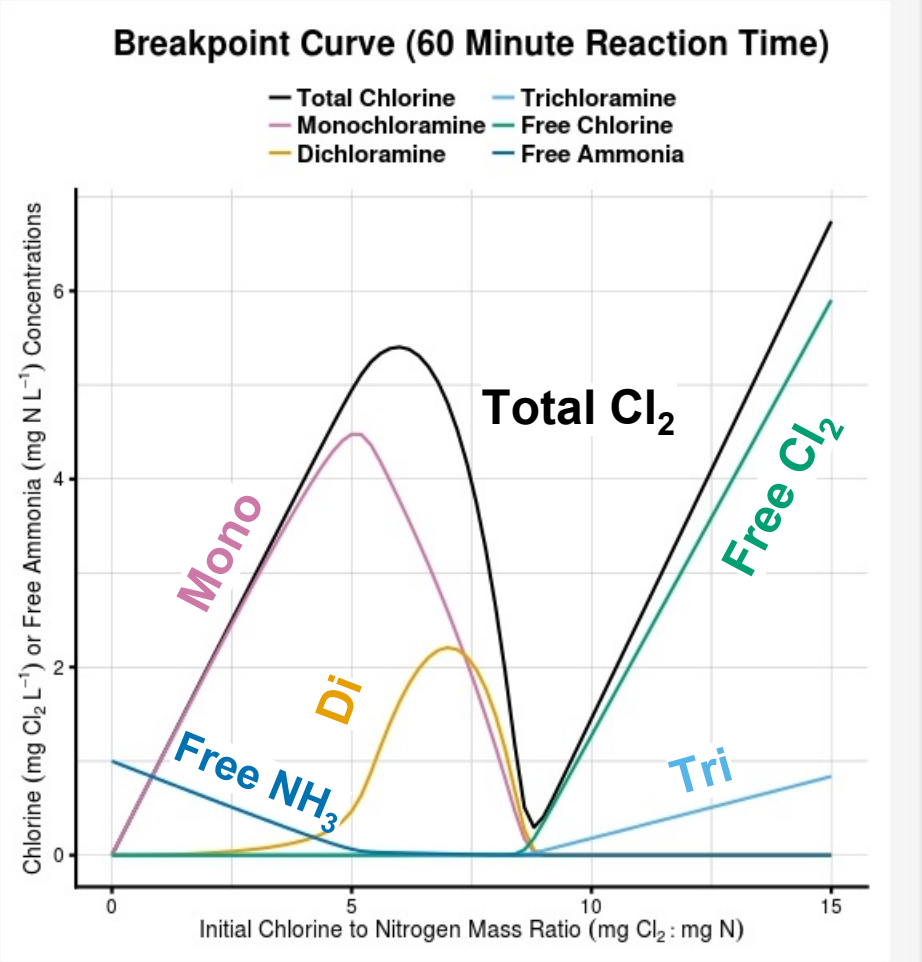
Hold Study – Example Use Case



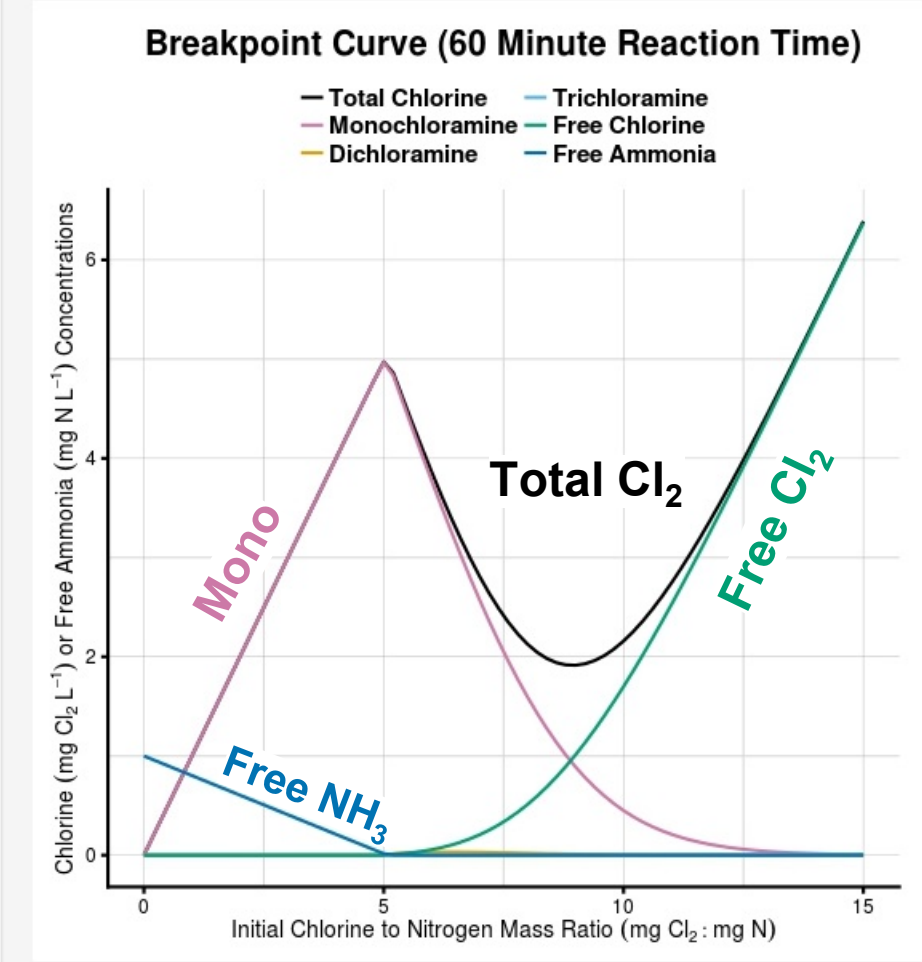
- System 1 → focus on DS
- System 2 → focus on plant

Breakpoint Curve App – Add Chlorine

- https://usepaord.shinyapps.io/Breakpoint-Curve/
- Remove 1 mg N/L free ammonia (add free chlorine)



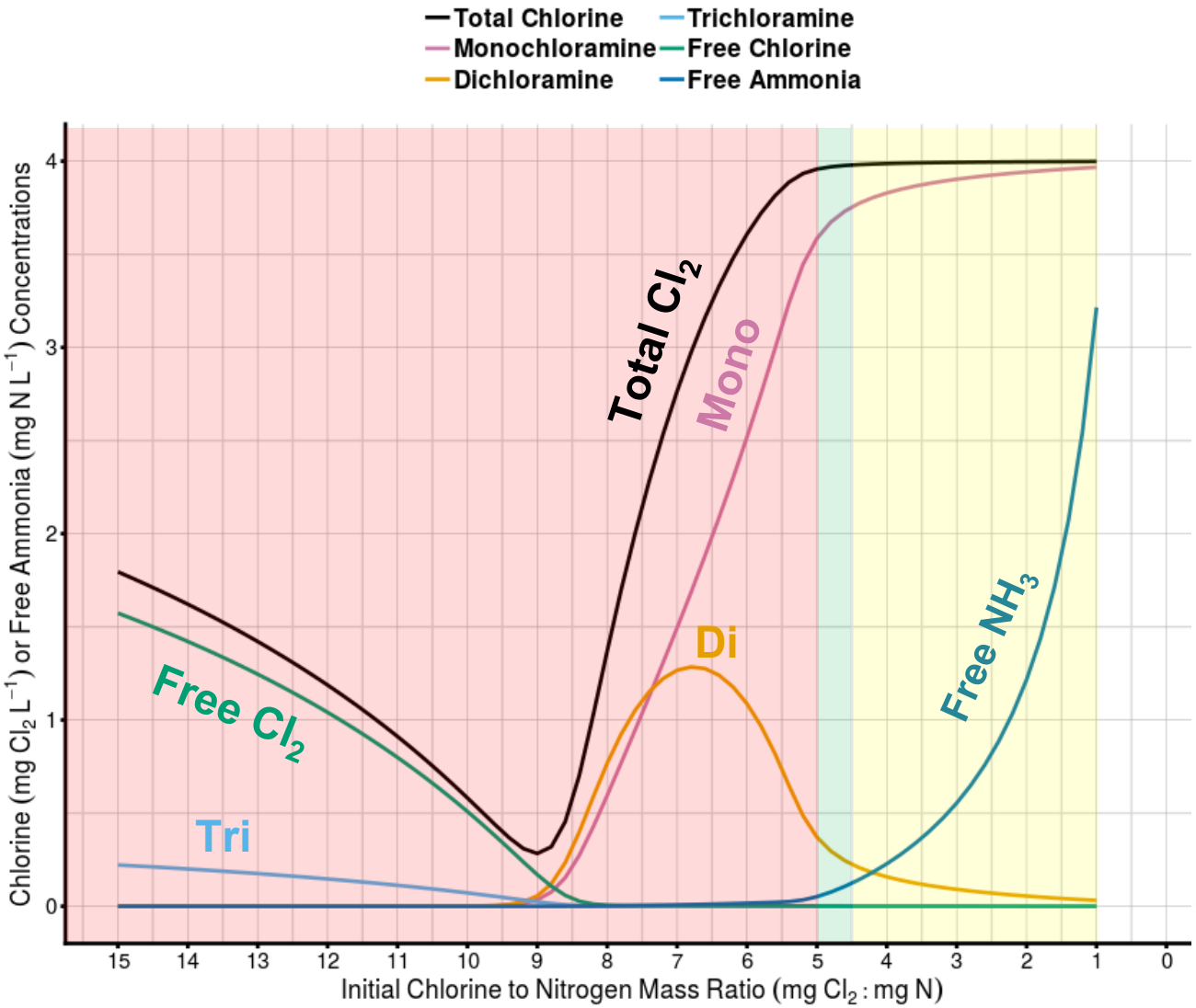
pH 7



pH 9

Breakpoint Curve App – Add Ammonia

- Chloramine formation (add free ammonia)
- Impact of Cl_2:N (4 mg Cl_2/L, pH 7, 60 minute)



After the presentation, you will

1. Know of two chloramine apps:
   - Simulate chemistry (kinetics)
   - Interpret hold studies
   - Interpret real–world observations

Web-Based Applications to Simulate Drinking Water Inorganic Chloramine Chemistry

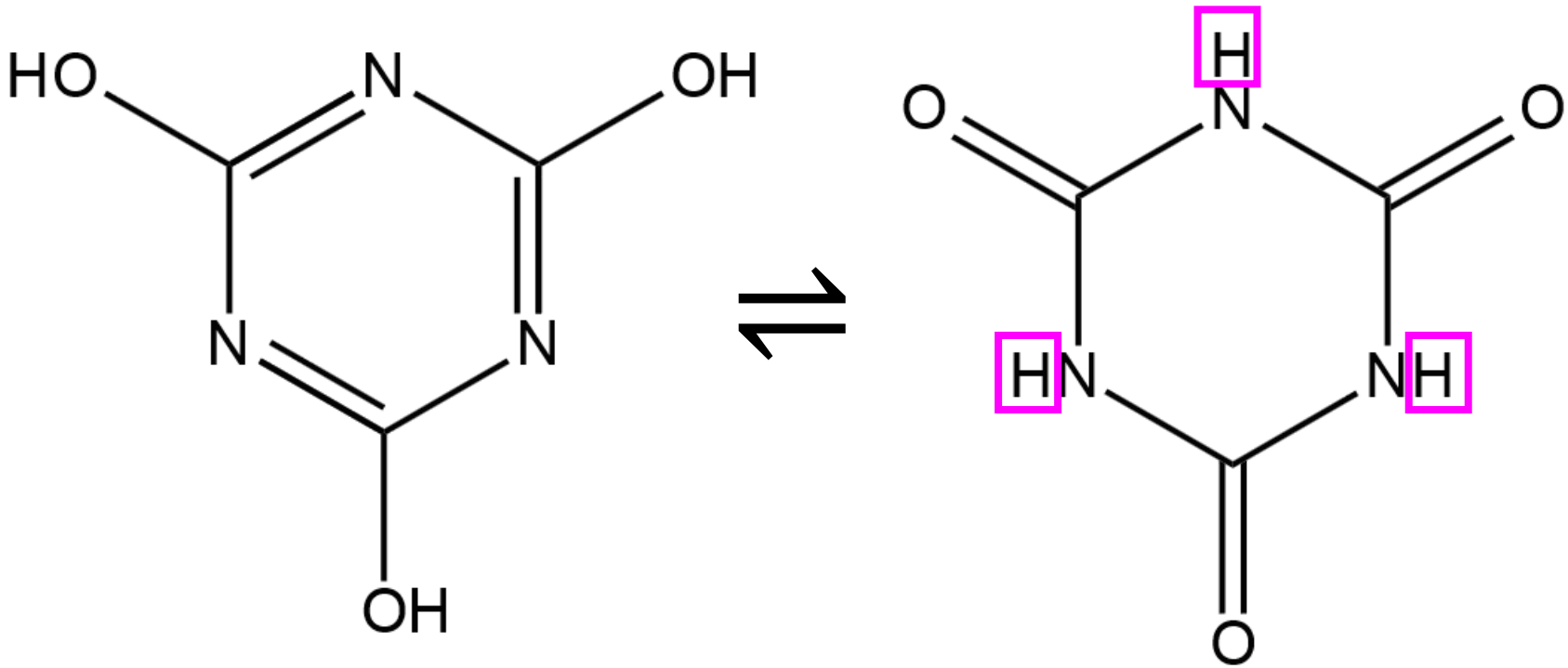
DAVID G. WAHMAN[1]

- *JAWWA*, November 2018, E43–E61
- DOI: https://doi.org/10.1002/awwa.1146

Free Chlorine & Sunlight

- Free chlorine
  - Hypochlorous acid (HOCl) + hypochlorite ion (OCl^-)
  - Absorbs ultraviolet (UV) light → decomposes
- Wavelengths > ~280 nm reach Earth's surface
  - Peak absorbance (λ_{max}): OCl^- = 292 nm & HOCl = 235 nm
  - 30 minute half–life
- Cyanuric acid → outdoor pools since 1958
  - "Stabilizes" free chlorine
  - Forms chlorinated cyanurates
    - Lowers free chlorine concentration
    - "Reservoir" of free chlorine → releases back into water
    - λ_{max} = 215–220 nm → more stable in sunlight

Cyanuric Acid (H_3Cy)



Cyanuric Acid
(enol form)

Isocyanuric Acid
(keto form)

- "Cy" = $C_3N_3O_3 \rightarrow H_3Cy$

Chlorinated Cyanurate Equilibrium System

Trichlor $\boxed{Cl_3Cy}$

$\rightleftarrows$

$HCl_2Cy \rightleftharpoons \boxed{Cl_2Cy^-}$ **Dichlor**

$\rightleftarrows \qquad \rightleftarrows$

$H_2ClCy \rightleftharpoons HClCy^- \rightleftharpoons ClCy^{2-}$

$\rightleftarrows \qquad \rightleftarrows \qquad \rightleftarrows$

Cyanuric Acid $\boxed{H_3Cy} \rightleftharpoons H_2Cy^- \rightleftharpoons HCy^{2-} \rightleftharpoons Cy^{3-}$

$HOCl \rightleftharpoons OCl^-$

Chlorinated Cyanurates

↑ Free Chlorine Added

↑ pH →

- Cy + free chlorine ⇌ chlorinated cyanurates
- Total (available) chlorine (TOTCl) = 8 species with Cl
- Total cyanurate (TOTCy) = 10 species with Cy
- Free chlorine is disinfectant → no approved methods work

Drinking Water Dichlor/Trichlor

- Federal Insecticide, Fungicide, and Rodenticide Registration Act (FIFRA)
  - 1st approval, July 2001 → Oxychem Corporation
  - Routine treatment of drinking water
- Manufacturer NSF 60 Certification
  - Function → disinfection & oxidation
  - 6, 10, or 30 mg/L max
  - 7 dichlor[1] & 10 trichlor[2] manufacturers
- World Health Organization (WHO) guidelines
  - Sodium dichloroisocyanurate (Dichlor): 50 mg/L
  - Cyanuric acid: 40 mg/L
- SDWA primacy agency may approve use
- Benefits → ease of use (solid chlorine form, no Ca^{2+})

[1] http://info.nsf.org/Certified/PwsChemicals/Listings.asp?ChemicalName=Sodium+Dichloroisocyanurate
[2] http://info.nsf.org/Certified/PwsChemicals/Listings.asp?ChemicalName=Trichloroisocyanuric+Acid

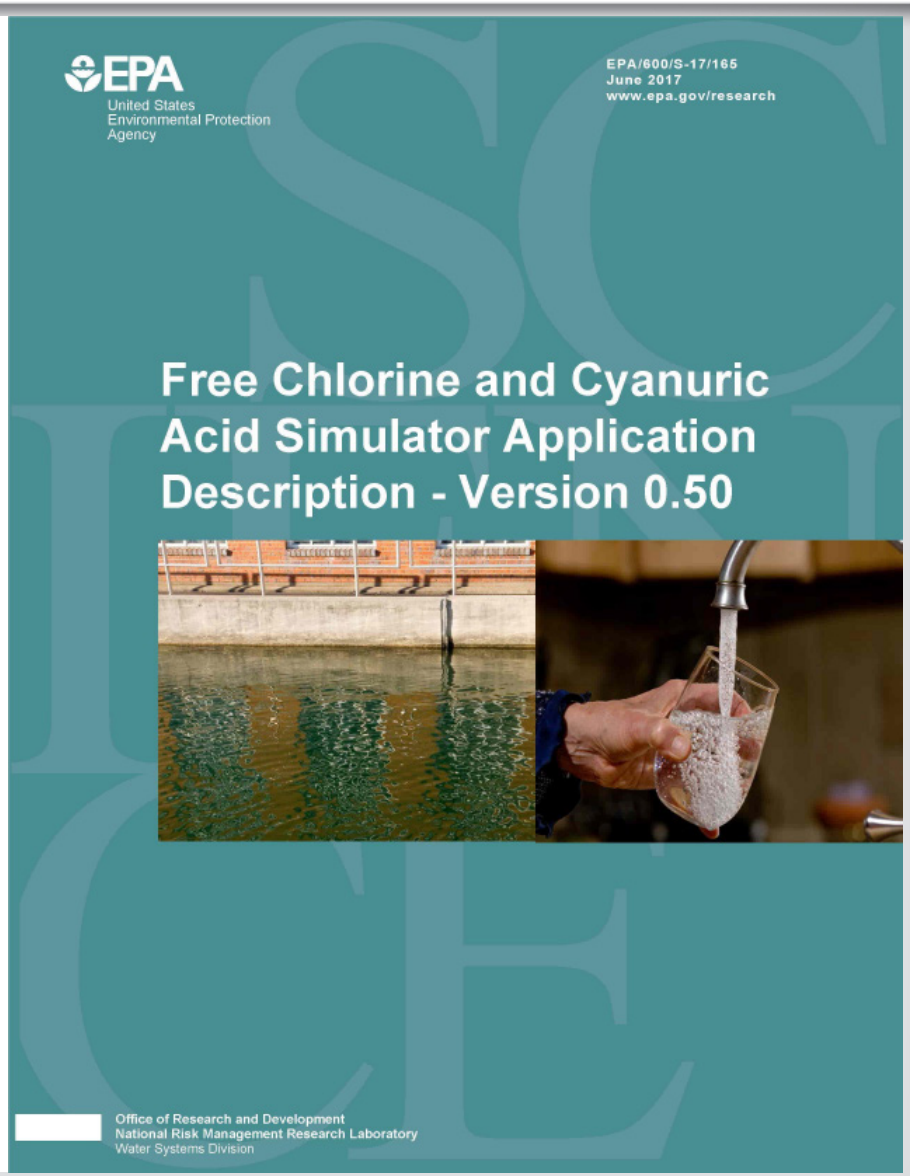
Free Chlorine Measurement

- Cy + free chlorine ⇌ chlorinated cyanurates
  - Fast equilibrium
  - Cannot react with free chlorine (or chlorinated cyanurates)
  - Cannot change pH
- What does not work?
  - DPD & amperometric titration (Wajon & Morris 1980)
  - Indophenol & ChemKeys (Wahman et al. 2019)
  - Currently, no approved method
- What could? → Water chemistry estimate from sample?
  - O'Brien (1972) → equilibrium system (25°C only)
  - Need to know:
    - pH → directly measure
    - Total chlorine (TOTCl) → free chlorine DPD
    - Total cyanurate (TOTCy) → estimate from chemical dosing

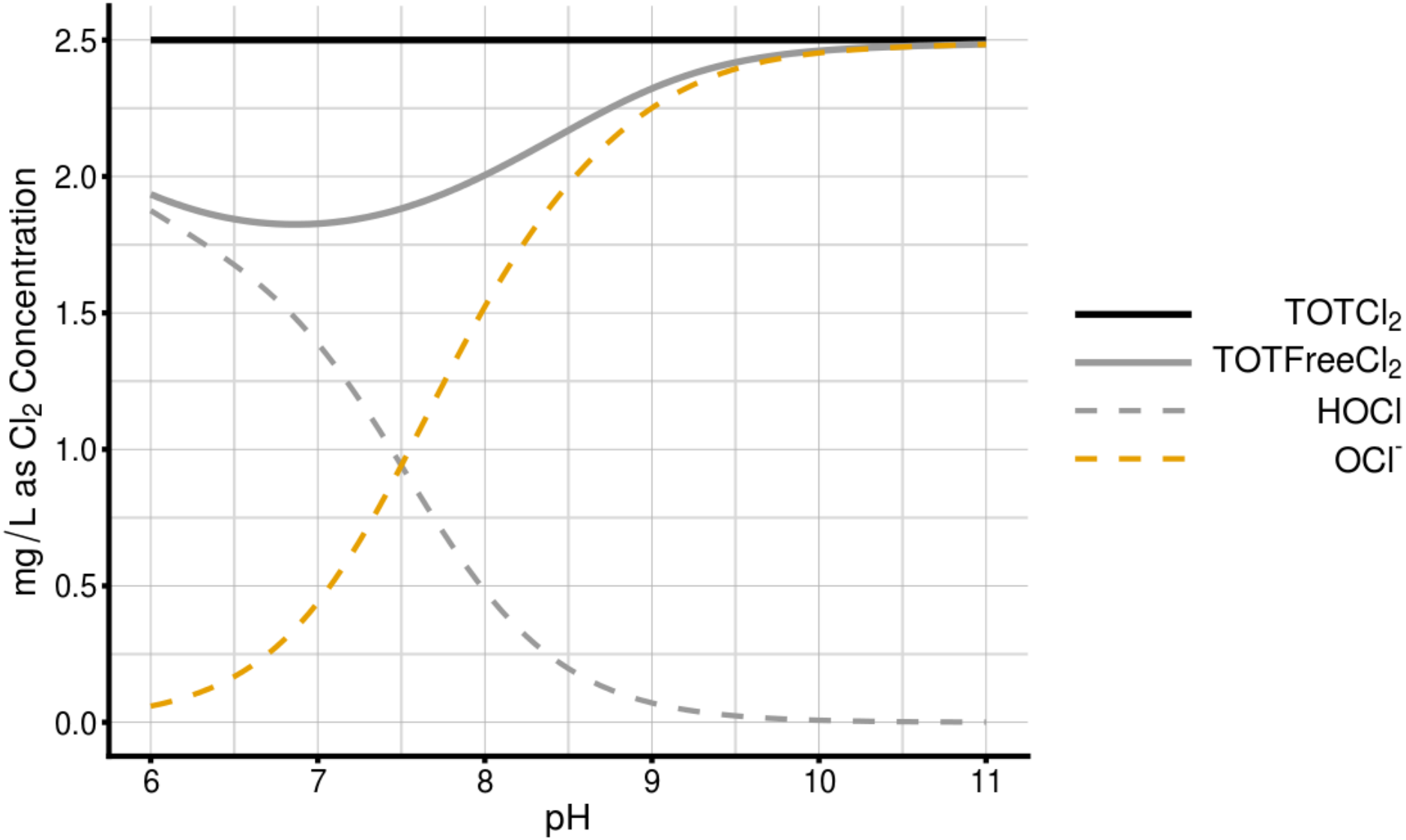
Free Chlorine & Cy App

https://usepaord.shinyapps.io/cyanuric/

- Assumptions
  - Full O'Brien model → 25°C
  - Know total chlorine
  - Know total cyanurate
  - Know pH range
- Features
  - User–selectable inputs
  - Two side–by–side simulations
  - Chemical addition scenarios
  - Download simulation data (.csv)
- App Description
  - https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100S368.txt



App Output (25°C)



Practical Issue – Temperature

$$
\begin{array}{ccc}
 & & Cl_2Cy^- \\
 & & \rightleftarrows \\
 & & HClCy^- \\
 & & \rightleftarrows \\
H_3Cy & \rightleftharpoons & H_2Cy^- \\
HOCl & \rightleftharpoons & OCl^-
\end{array}
$$

- Simple model
  - 12 species → 6 species
  - 10 equilibria → 4 equilibria
  - Temperature → 3 equilibria
- Experiments → temperature

Simple Model Estimator

https://shiny.epa.gov/fcedts/

Inputs for Free Chlorine Estimate

Temperature (Celsius) - Measured

5 — 25 — 35

5 8 11 14 17 20 23 26 29 32 35

pH - Measured

6.5 — 8 — 9.5

6.5 6.8 7.1 7.4 7.7 8 8.3 8.6 8.9 9.2 9.5

Total Chlorine (mg Cl_2/L) - Measured with a free chlorine method (see Application Documentation)

0.05 — 3 — 10

0.05 1.05 2.05 3.05 4.05 5.05 6.05 7.05 8.05 9.05 10

Total Cyanurate (mg/L as cyanuric acid) - Estimated from chemical dosing (see Application Documentation)

0.05 — 3 — 10

0.05 1.05 2.05 3.05 4.05 5.05 6.05 7.05 8.05 9.05 10

Estimated free chlorine concentration = 1.44 mg/L as chlorine

Additional Information

https://doi.org/10.1002/awwa.1086

Literature Review

JournalAWWA

Chlorinated Cyanurates: Review of Water Chemistry and Associated Drinking Water Implications

David G. Wahman

https://doi.org/10.1002/aws2.1133

Practical Issues

AWWA WATER SCIENCE

Chlorinated cyanurates in drinking water: Measurement bias, stability, and disinfectant byproduct formation

David G. Wahman, Matthew T. Alexander, Alison G. Dugan

https://doi.org/10.1039/C8EW00431E

Model Development

Environmental Science: Water Research & Technology

First acid ionization constant of the drinking water relevant chemical cyanuric acid from 5 to 35 °C

David G. Wahman

https://doi.org/10.1089/ees.2018.0387

Model Development

Environmental Engineering Science

A Drinking Water Relevant Water Chemistry Model for the Free Chlorine and Cyanuric Acid System from 5°C to 35°C

David G. Wahman and Matthew T. Alexander

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Acknowledgements

- App Development & Testing
  - Matt Alexander, Alicia Diehl, Alison Dugan, Richard Falk, Vadim Malkov, Jonathan Pressman, & Jerry Speitel
- App Deployment
  - Kudeha Atila, Velez Childress, Jamie Falik, Michael Hillard, Jeff Hollister, Michelle Ibarra, Thom Johnson, Kim Lyons, Ethan McMahon, Caroline Parton, Michelle Sims, Becky Taylor, Ann Vega, & Dalroy Ward

Breakpoint Chlorination:

External hosted location: https://usepaord.shinyapps.io/Breakpoint-Curve/

EPA cloud.gov hosted location: https://shiny.epa.gov/cbcs/

Source code: https://github.com/USEPA/Chlorine_Breakpoint_Curve_Simulator

Chloramine Formation and Decay:

External hosted location: https://usepaord.shinyapps.io/Unified-Combo/

EPA cloud.gov hosted location: https://shiny.epa.gov/cfd/

Source code: https://github.com/USEPA/Inorganic_Chloramine_-Formation_and_Decay_Application

Chloramine Apps Webinar (Start at 33 min): https://www.youtube.com/watch?v=s6Kxn1Atff4&feature=youtu.be

Chlorinated Cyanurates (25° C):

External hosted location: https://usepaord.shinyapps.io/cyanuric/

EPA cloud.gov hosted location: https://shiny.epa.gov/fccas/

Source code: https://github.com/USEPA/Free_Chlorine_and_Cyanuric_Acid_Simulator

Chlorinated Cyanurates (Simple Model, 5–35° C):

EPA cloud.gov hosted location: https://shiny.epa.gov/fcedts/

Source code: https://github.com/USEPA/Free-Chlorine-Estimator-for-Dichlor-and-Trichlor-Systems

Chlorinated Cyanurates Webinar: https://www.youtube.com/watch?v=ljgxqfiuoXk&feature=youtu.be