Dichlor & Trichlor
Water Chemistry Implications

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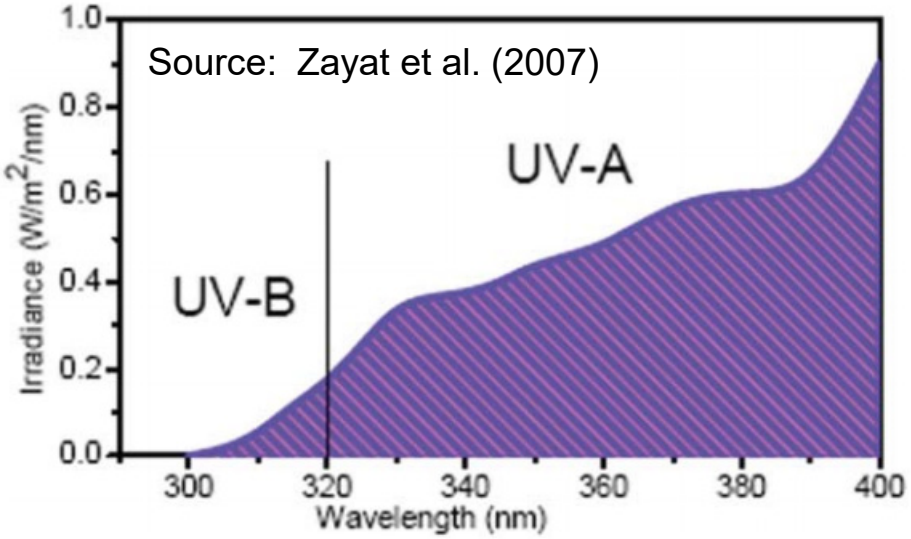
After this presentation:

1. Familiar with chlorinated cyanurates & use
2. Understand water chemistry & implications
3. Aware of things to consider in practice
4. Familiar with web–based application

Free Chlorine & Sunlight (Pools)

- 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



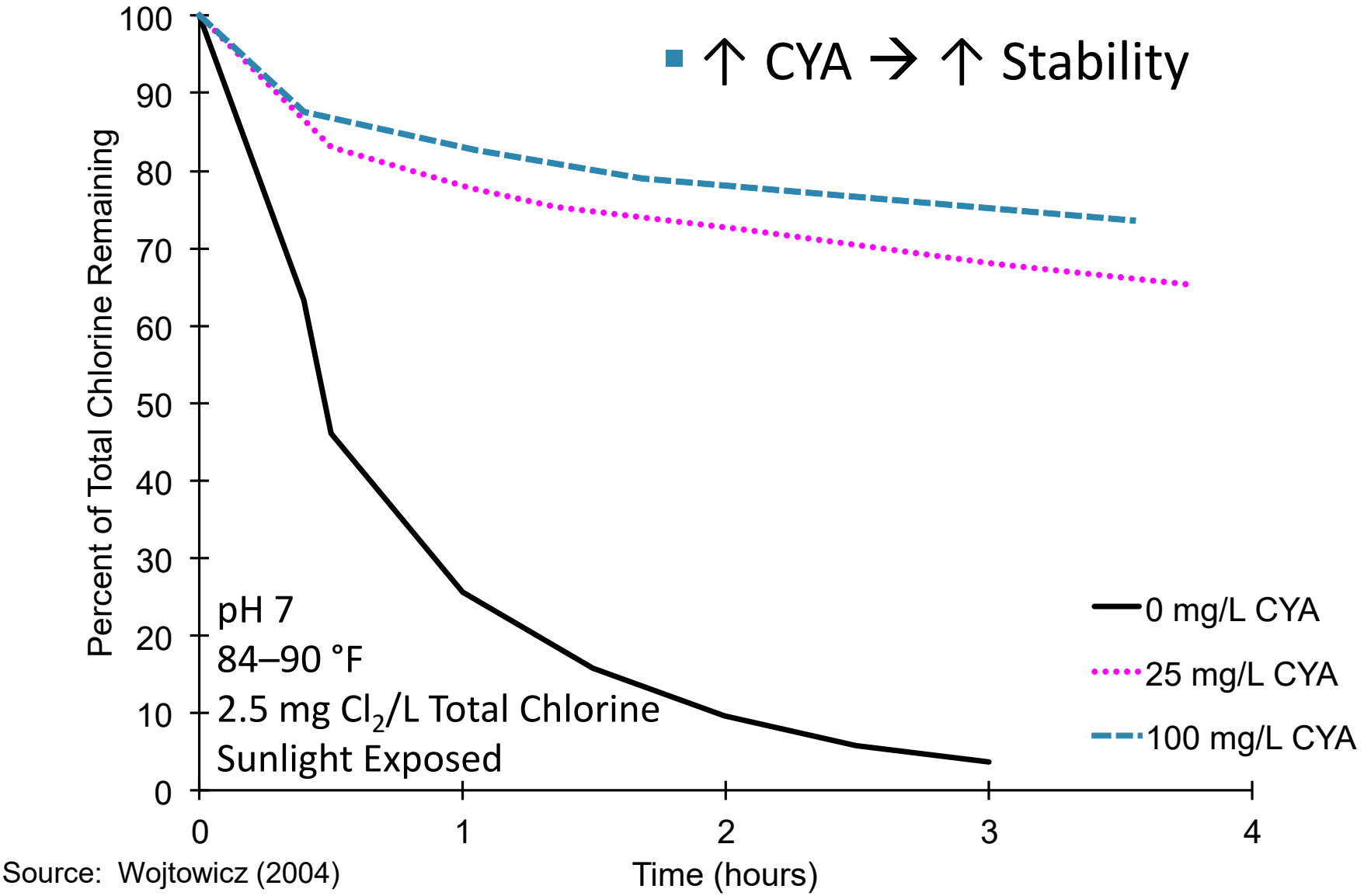
Cyanuric Acid Addition (Pools)

- Cyanuric acid (CYA)
  - Not related to cyanide
  - Outdoor pools since 1958
  - Added to “stabilize” 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

- Public pool concentrations (ANSI/APSP 2009)

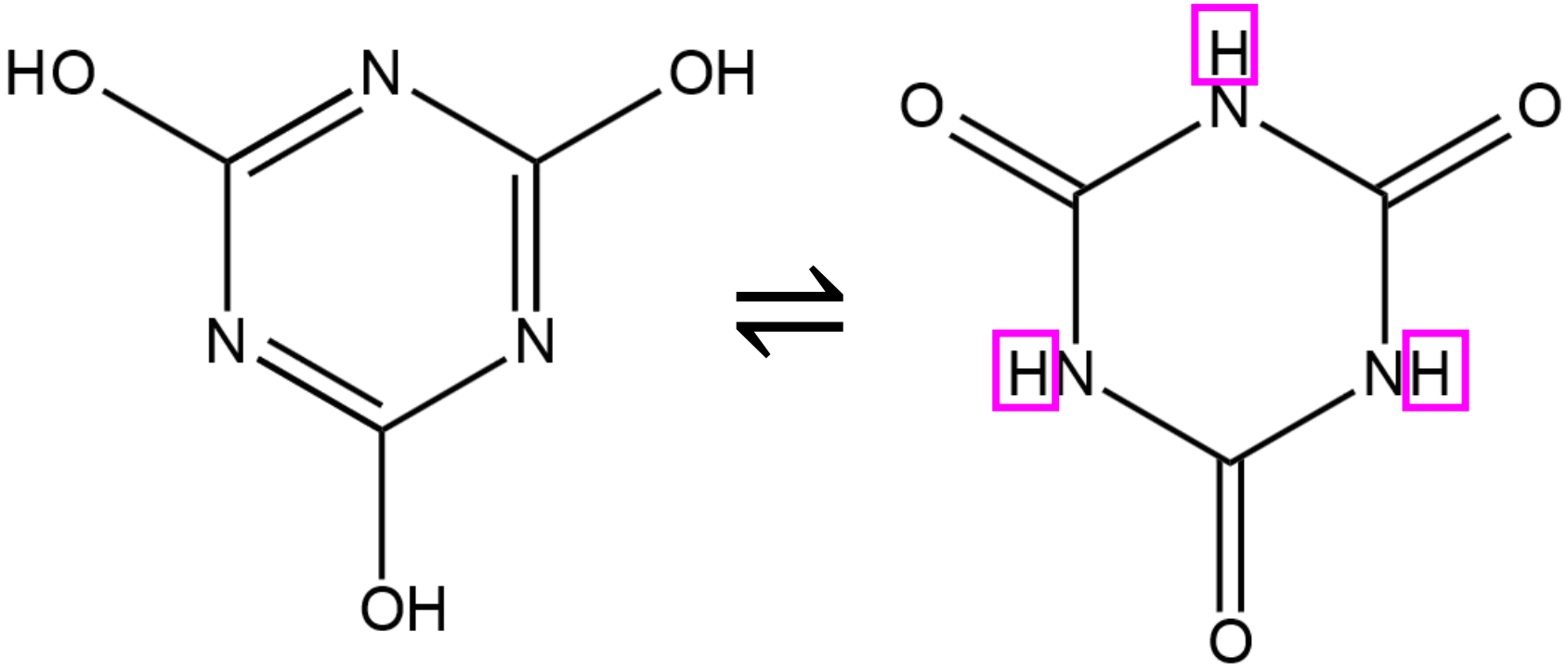
Parameter	Minimum	Ideal	Maximum
Total (Available) Chlorine (mg Cl_2/L)	1	2–4	4
Cyanuric Acid (mg/L)	N/A	30–50	100

CYA Stabilization (Concentration)



Source: Wojtowicz (2004)

Cyanuric Acid (H_3Cy)

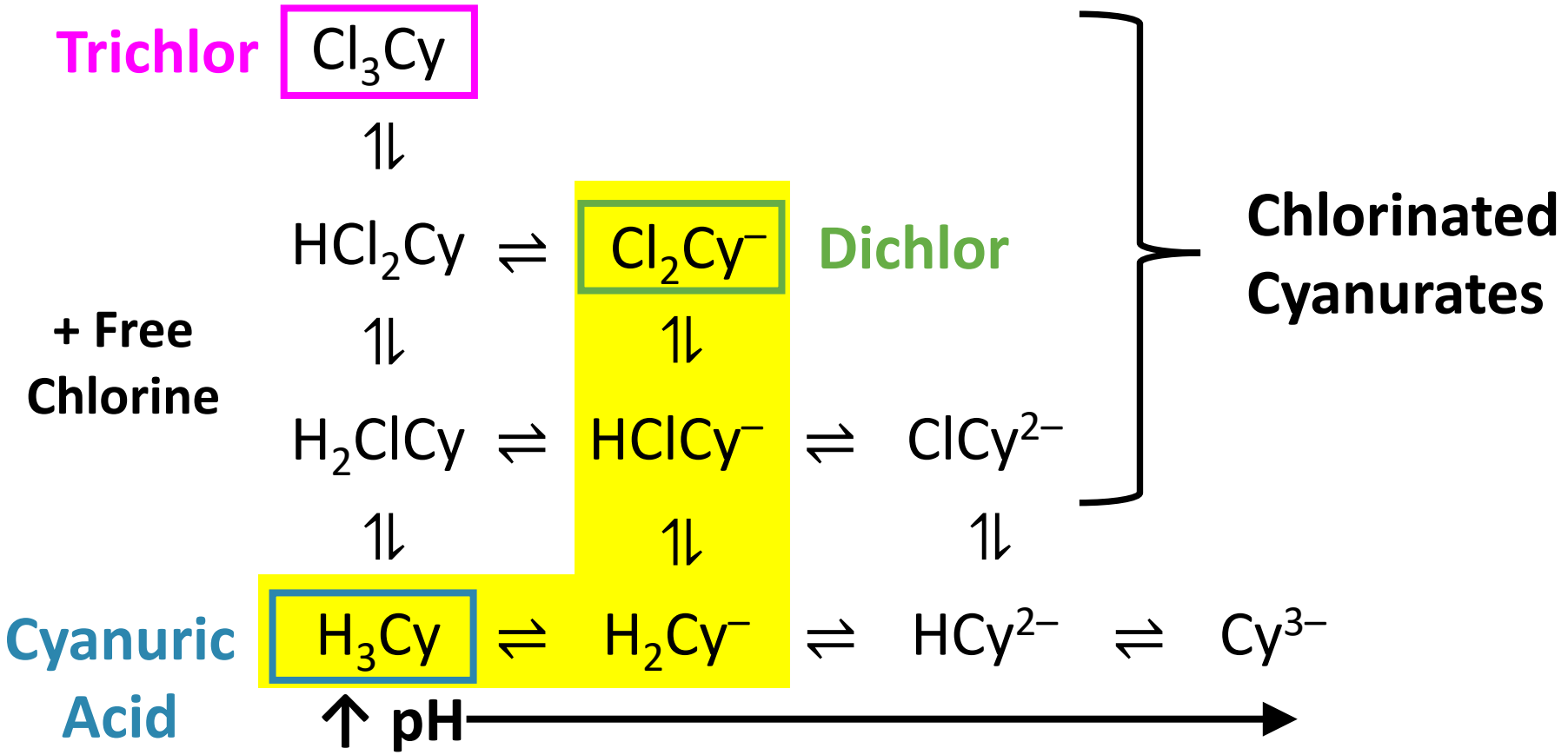


Cyanuric Acid
(enol form)

Isocyanuric Acid
(keto form)

- "Cy" = Cyanurate structure → H_3Cy

Chlorinated Cyanurates



- Cy + free chlorine ⇌ chlorinated cyanurates
- Free chlorine is disinfectant

Terminology

- No ammonia present (i.e., no chloramines)
- Free chlorine = hypochlorous acid + hypochlorite ion
- Available chlorine = six chlorinated cyanurates
- Total (available) chlorine (TOTCl) = free chlorine + available chlorine

$$3[Cl_3Cy] + 2[HCl_2Cy] + [H_2ClCy] + 2[Cl_2Cy^-] + [HClCy^-] + [ClCy^{2-}] + [HOCl] + [OCl^-]$$

- Total cyanurate (TOTCy) = 10 species with Cy

$$[Cl_3Cy] + [HCl_2Cy] + [H_2ClCy] + [Cl_2Cy^-] + [HClCy^-] + [ClCy^{2-}] + [H_3Cy] + [H_2Cy^-] + [HCy^{2-}] + [Cy^{3-}]$$

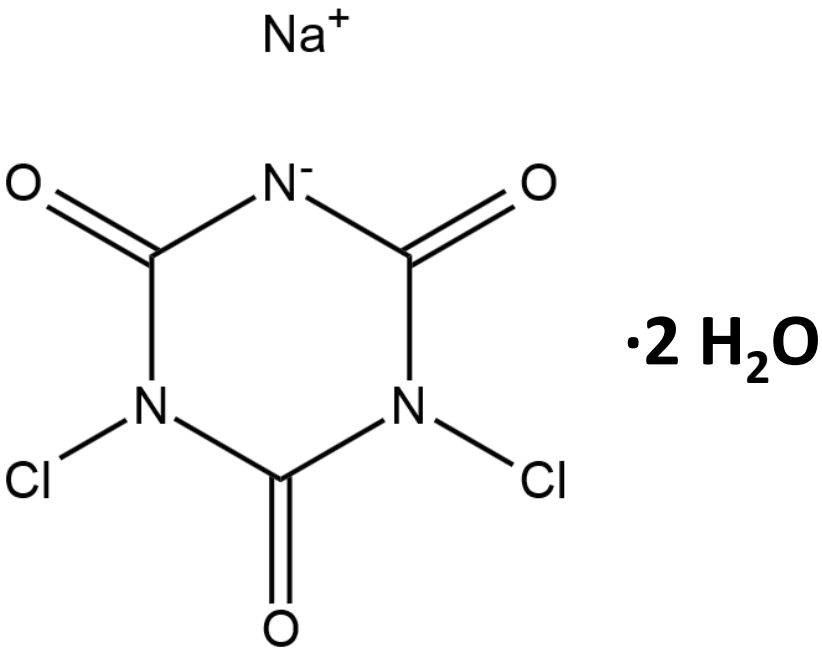
Drinking Water Use

- Federal Insecticide, Fungicide, and Rodenticide Registration Act
  - 1st approval, July 2001 → Oxychem Corporation
  - Routine treatment of drinking water
- Manufacturer NSF 60 Certification
  - Function → disinfection & oxidation (30 mg/L max)
  - Dichlor[1] = 6 (2 others for well cleaning)
  - Trichlor[2] = 7
- World Health Organization (WHO) guidelines
  - Sodium dichloroisocyanurate (Dichlor): 50 mg/L
  - Cyanuric acid: 40 mg/L
- Practical TOTCy concentration
  - 5–10 mg/L maximum
  - 100 mg/L pool maximum
- Safe Drinking Water Act primacy agencies may approve use

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

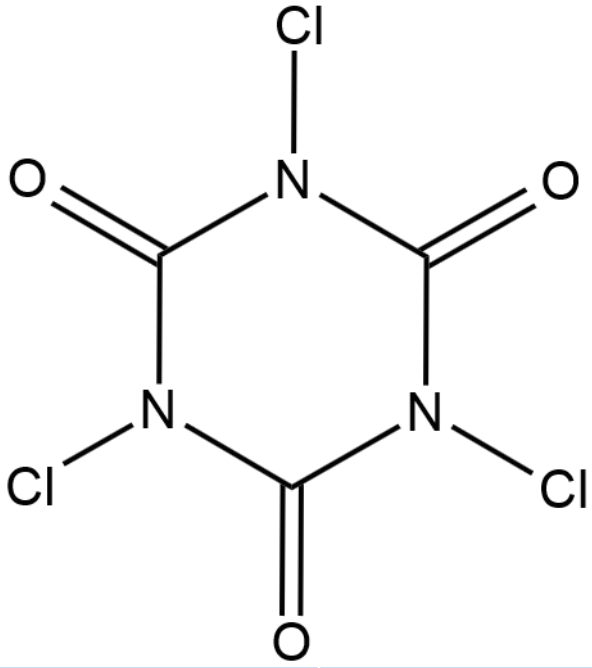
Dichlor & Trichlor

Dichlor Anhydrous (Dihydrate)



·2 H_2O

Trichlor



Property	Dichlor Anhydrous	Dichlor Dihydrate	Trichlor
% Available Chlorine	65	55	92
pH, 1% solution	6.0–7.0	6.0–7.0	3.0
Solubility (25°C, %)	24	28	1.2
Total Chlorine (mg Cl_2/L) per Label	0.81	0.69	0.76
Total Cyanurate (mg/L) per Label	0.73	0.63	0.46

Dichlor & Trichlor Addition

Chemical Addition Scenario Assumes 100% Chemical Purity	Dichlor Anhydrous	Dichlor Dihydrate	Trichlor
$\frac{\text{TOTCl (mg } Cl_2)}{\text{Chemical (mg)}}$	0.65	0.55	0.92
$\frac{\text{TOTCy (mg)}}{\text{Chemical (mg)}}$	0.59	0.50	0.56
$\frac{\text{Chemical (mg)}}{\text{TOTCl (mg } Cl_2)}$	1.54	1.82	1.09
$\frac{\text{TOTCy (mg)}}{\text{TOTCl (mg } Cl_2)}$	0.91	0.91	0.61

Reasons for Use (Free Cl_2)

- Benefits (Kuechler 2009)
  - Easier to handle
    - Tablet or granules
    - Safer than liquids or gases
    - Long storage life (i.e., years)
  - Concentrated chlorine
    - Trichlor → 90%
    - Dichlor → 55–65%
    - Calcium hypochlorite → 65–70%
    - Sodium hypochlorite → 10–15%
  - No calcium addition
  - Dichlor specific
    - Easily dissolves
    - More soluble
    - Neutral pH

After this presentation:

1. Familiar with chlorinated cyanurates & use

- Dichlor & trichlor for drinking water
- Free chlorine source
- FIFRA approved & NSF 60 certified
- Cy + free chlorine ⇌ chlorinated cyanurates

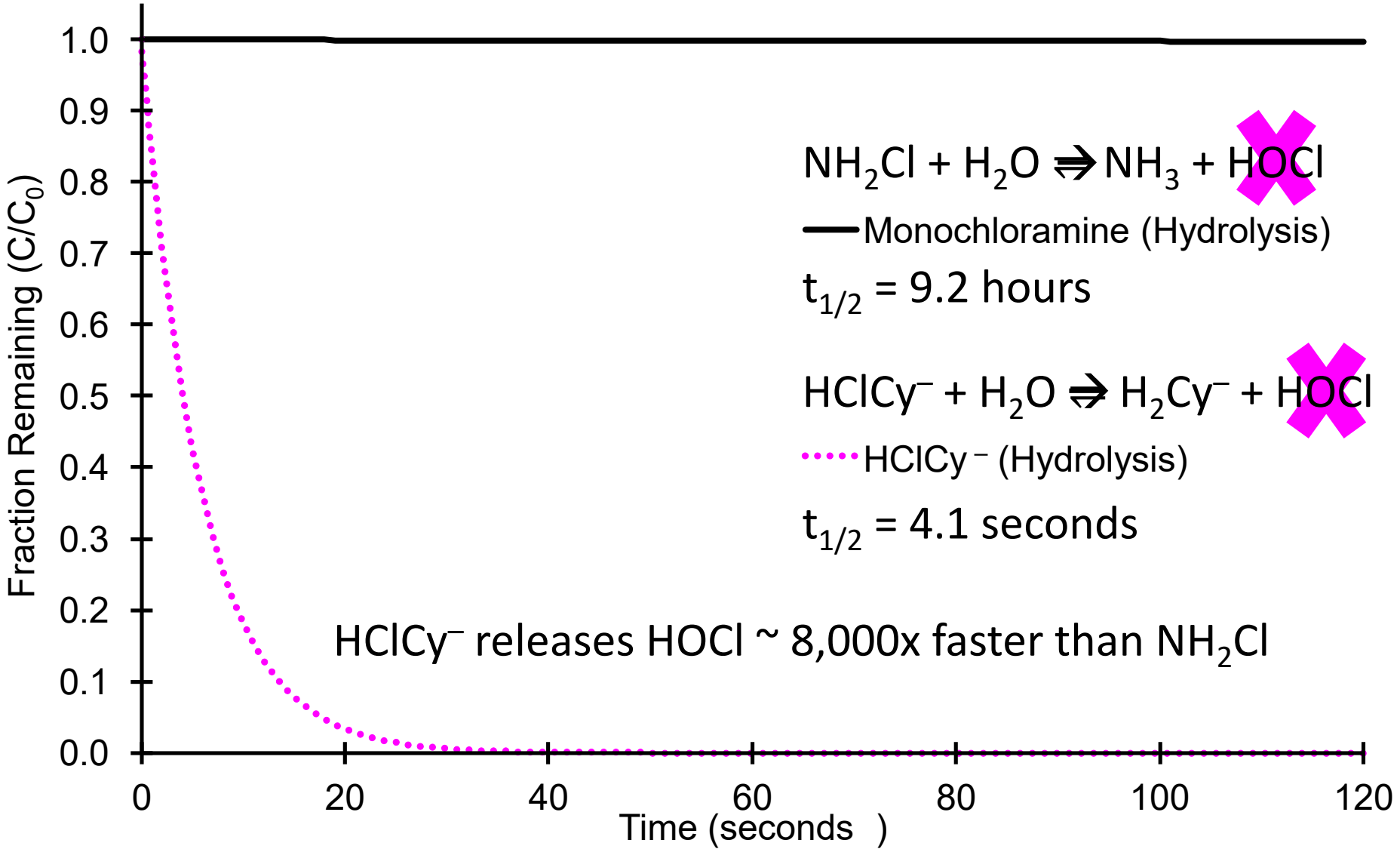
Water Chemistry

- No ammonia present
- Issue → free chlorine measurement bias → measure total
- O'Brien (1972) → equilibrium system (25°C)
- 3 known species: TOTCl, TOTCy, and pH → $[H^+]$
- 12 unknown chemical species

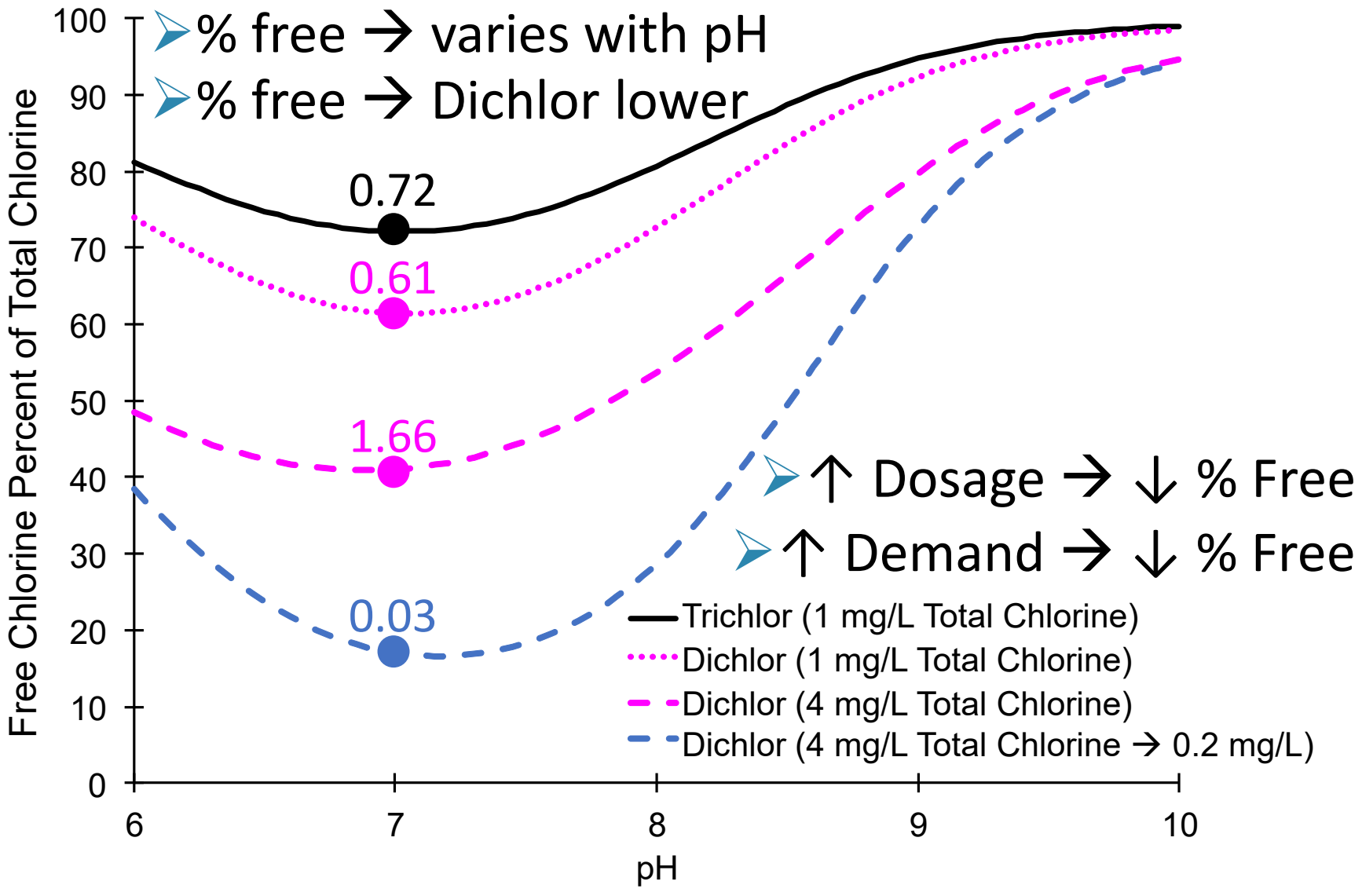
  $[Cl_3Cy], [HCl_2Cy], [H_2ClCy], [Cl_2Cy^-], [HClCy^-], [ClCy^{2-}],$
  $[H_3Cy], [H_2Cy^-], [HCy^{2-}], [Cy^{3-}], [HOCl], [OCl^-]$

- 12 equations
  - TOTCl
  - TOTCy
  - Free chlorine equilibrium
  - 9 cyanurate equilibrium
- Unknowns = Equations → Solvable

Equilibrium – "Fast" System



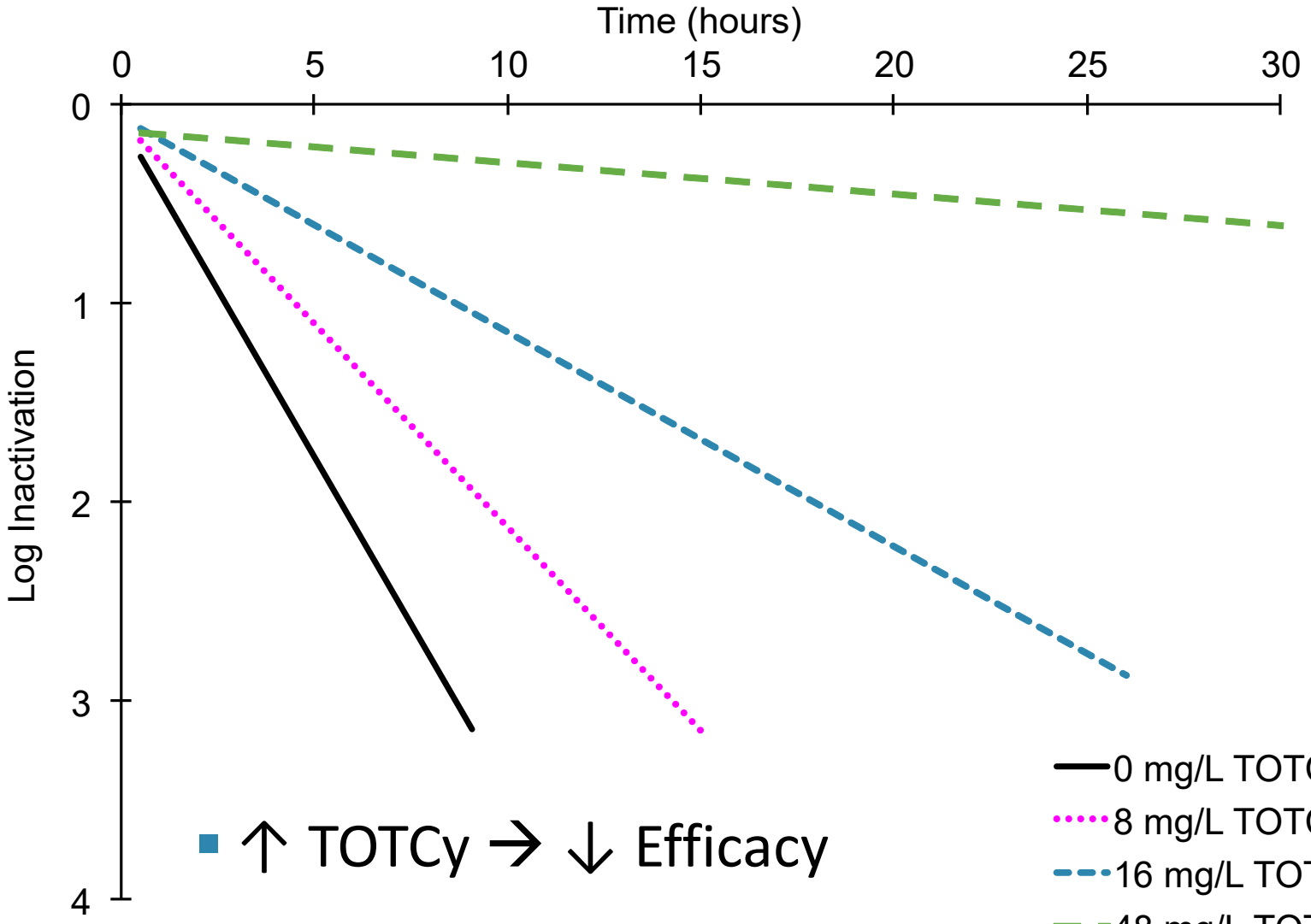
Free Chlorine % Variation



Disinfection

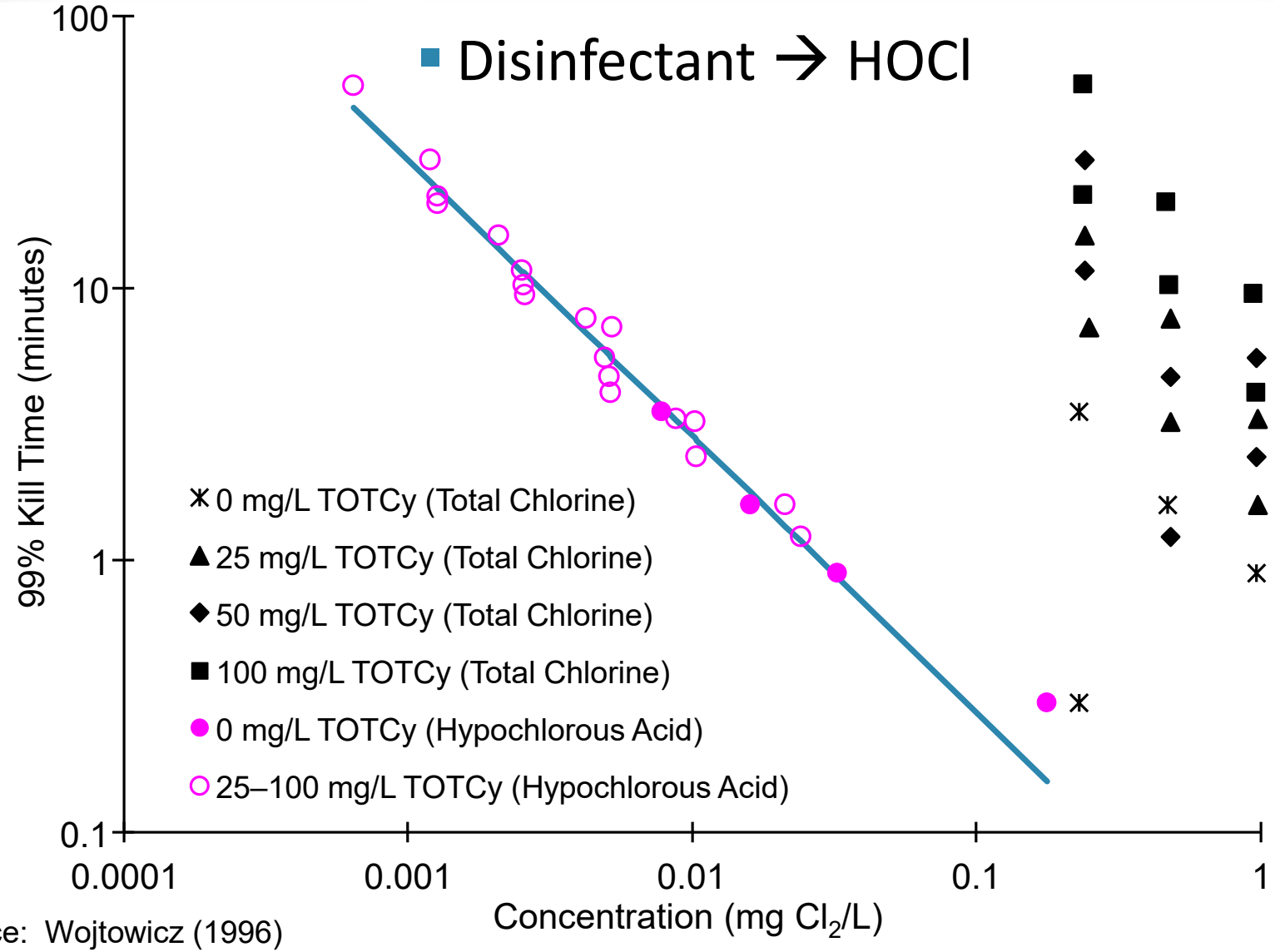
- Disinfection process
  - HOCl reacting with an organism
  - HOCl + Organism → Inactivation
  - Reaction Rate = k_I[HOCl][Organism]
- For same total chlorine
  - ↑TOTCy → ↓[HOCl]
  - ↓ reaction rate (i.e., speed)
  - ↓ disinfection

Disinfection Impacts (*C. parvum*)



Source: Murphy et al. (2015)

Actual Disinfectant (*S. faecalis*)



Source: Wojtowicz (1996)

After this presentation:

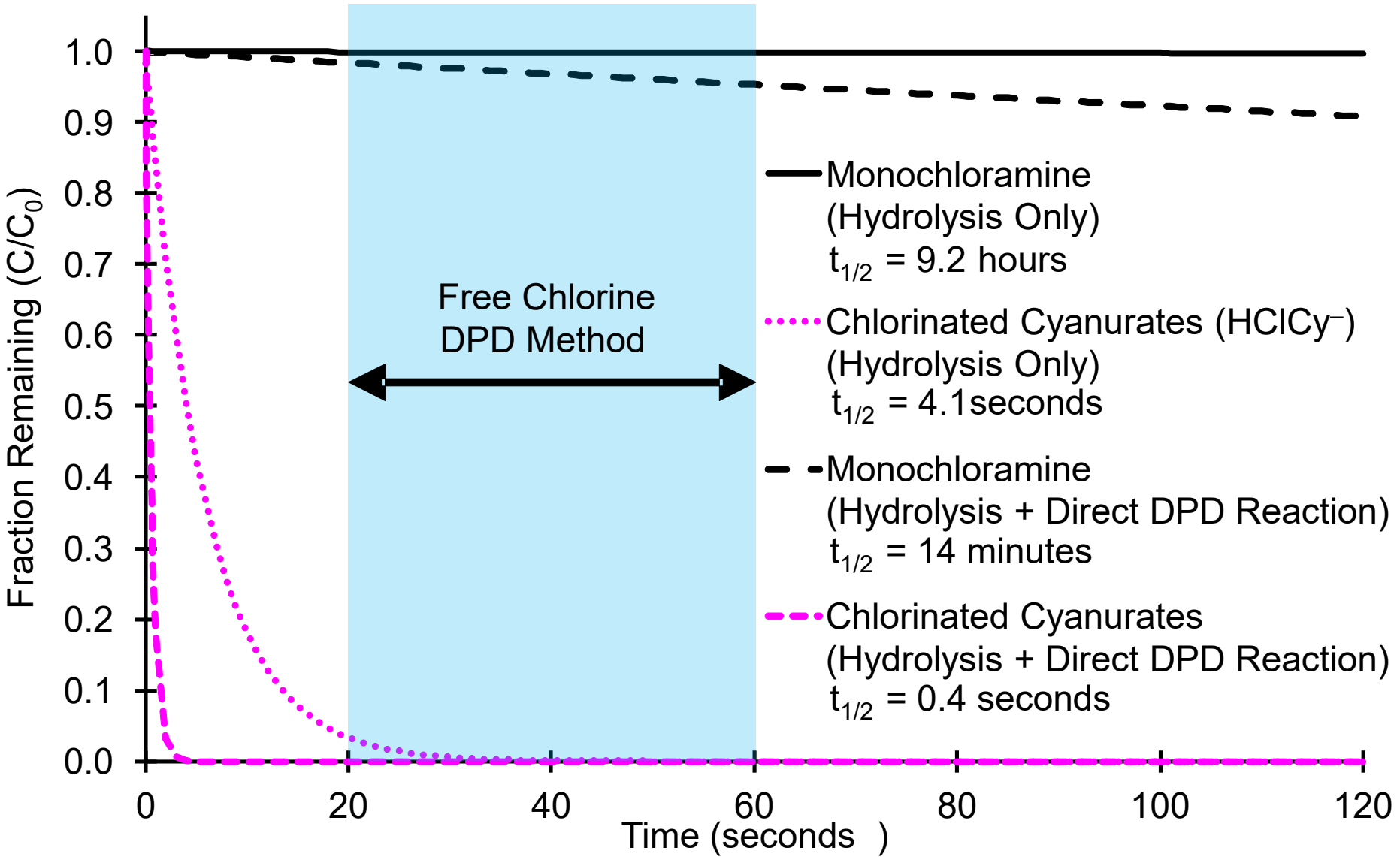
2. Understand water chemistry & implications

- Temperature → only 25°C known
- % Free Cl_2 → varies with pH
- ↑ Dosage or ↑ Demand → ↓ % Free
- HOCl is disinfectant in system

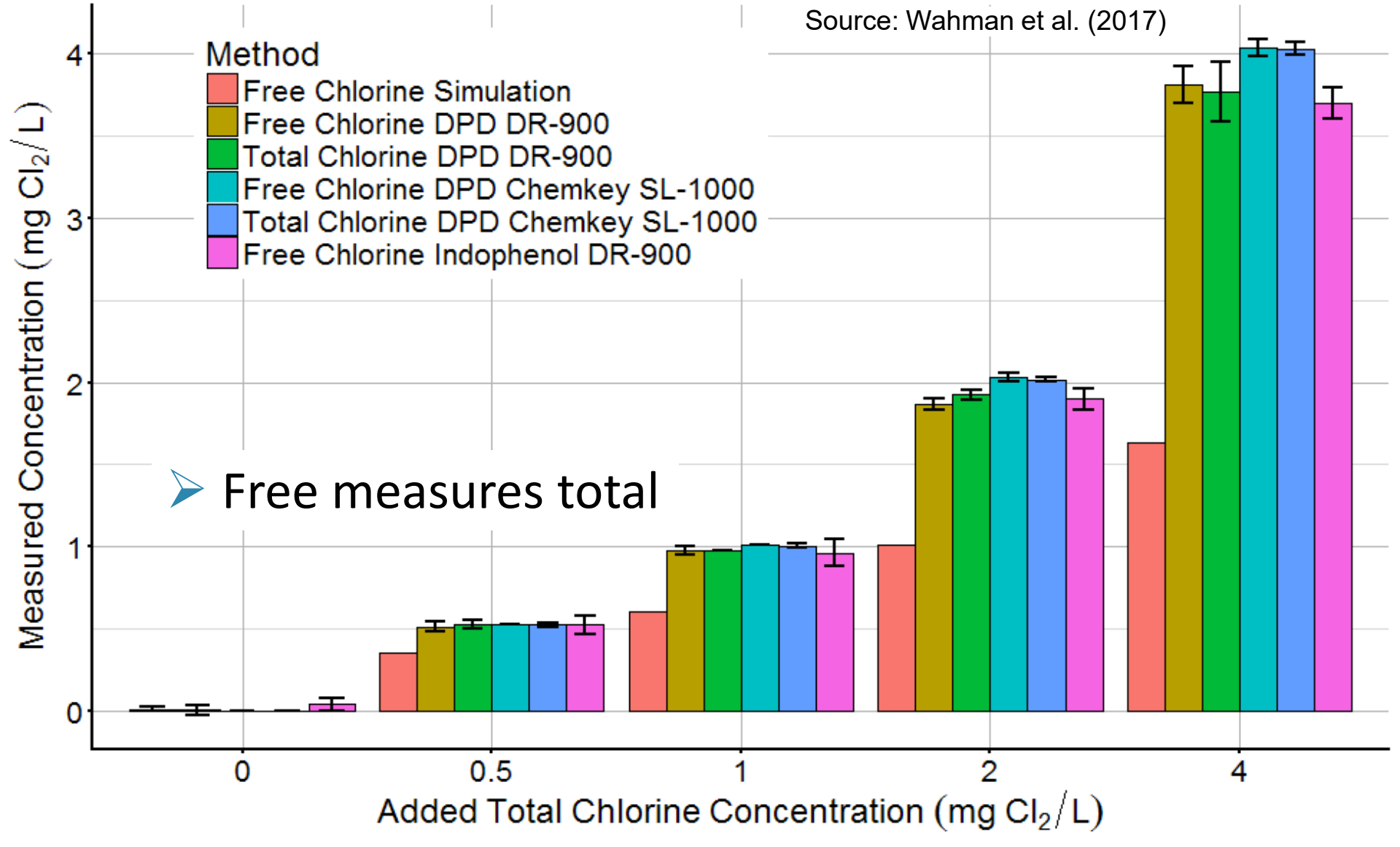
Things to Consider Free Chlorine Measurement

- Cy + free chlorine ⇌ chlorinated cyanurates
  - Fast equilibrium
  - Method cannot react with free chlorine
  - Method cannot change pH
  - Free chlorine test → measures total chlorine
- What does not work?
  - DPD (Whittle 1970; Wajon & Morris 1980)
  - Amperometric titration (Wajon & Morris 1980)
  - Indophenol (Wahman et al. 2017)
  - ChemKeys (Wahman et al. 2017)
  - Currently, no approved method

Hydrolysis & Direct Reaction



Dichlor at pH 7



- Free measures total

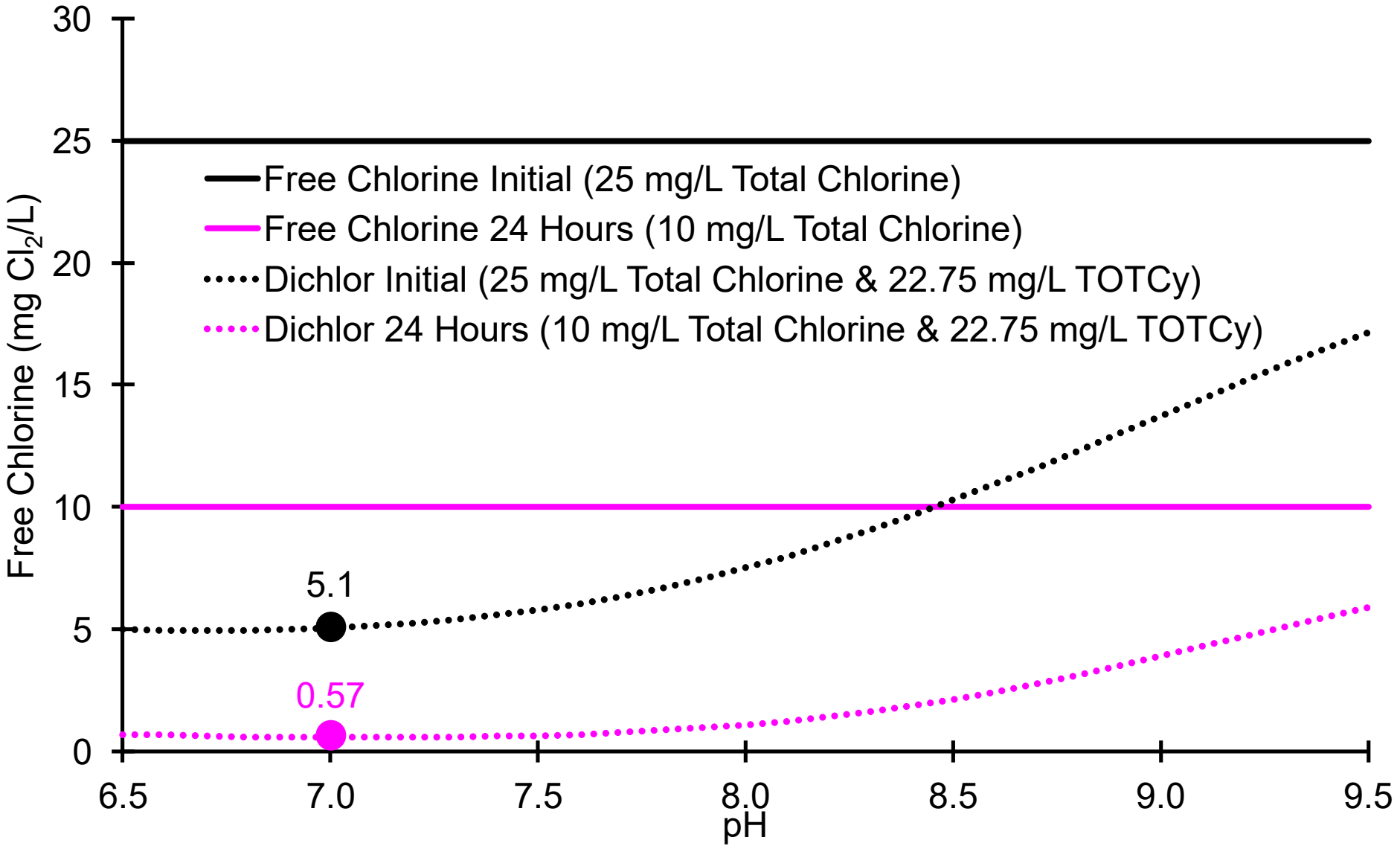
Things to Consider Free Chlorine Measurement

- What could work?
  - Cannot disturb equilibrium → no reaction or Δ pH
  - Direct measurement
- UV absorption → interferences & detection limit
- Amperometric electrode → mixed results
- Water chemistry estimate from actual sample
  - pH → directly measure
  - Total chlorine (TOTCl) → free chlorine DPD
  - Total cyanurate (TOTCy)
    - Current methods for pools (> 5 mg/L TOTCy)
    - Need drinking water field method (0.1–5 mg/L TOTCy)
    - Alternative → estimate from chemical dosing
  - Temperature → only 25°C (10 equilibrium constants)
    - Only known for 25°C
    - 10 equilibrium constants

Other Things to Consider?

- Goal of providing disinfectant residual
  - System integrity indicator
  - Quantifiable target → "detectable" vs. number
  - Microbial barrier (e.g., 0.5 mg Cl_2/L for *N. fowleri*)
- Feed solution degradation
  - TOTCl/TOTCy ratio
    - Decrease with time?
    - Impact on estimating TOTCy dose?
  - Chlorite/chlorate formation (10,000 mg Cl_2/L → ~1% Free)
- Disinfection of mains and/or tanks
  - ANSI/AWWA C652–11 (Water Storage Facilities)
  - ANSI/AWWA C651–14 (Water Mains)
- Chloramines & blending disinfectants
- Cyanurate related DBPs

ANSI/AWWA C651–14 Example (Continuous Feed Method)



After this presentation:

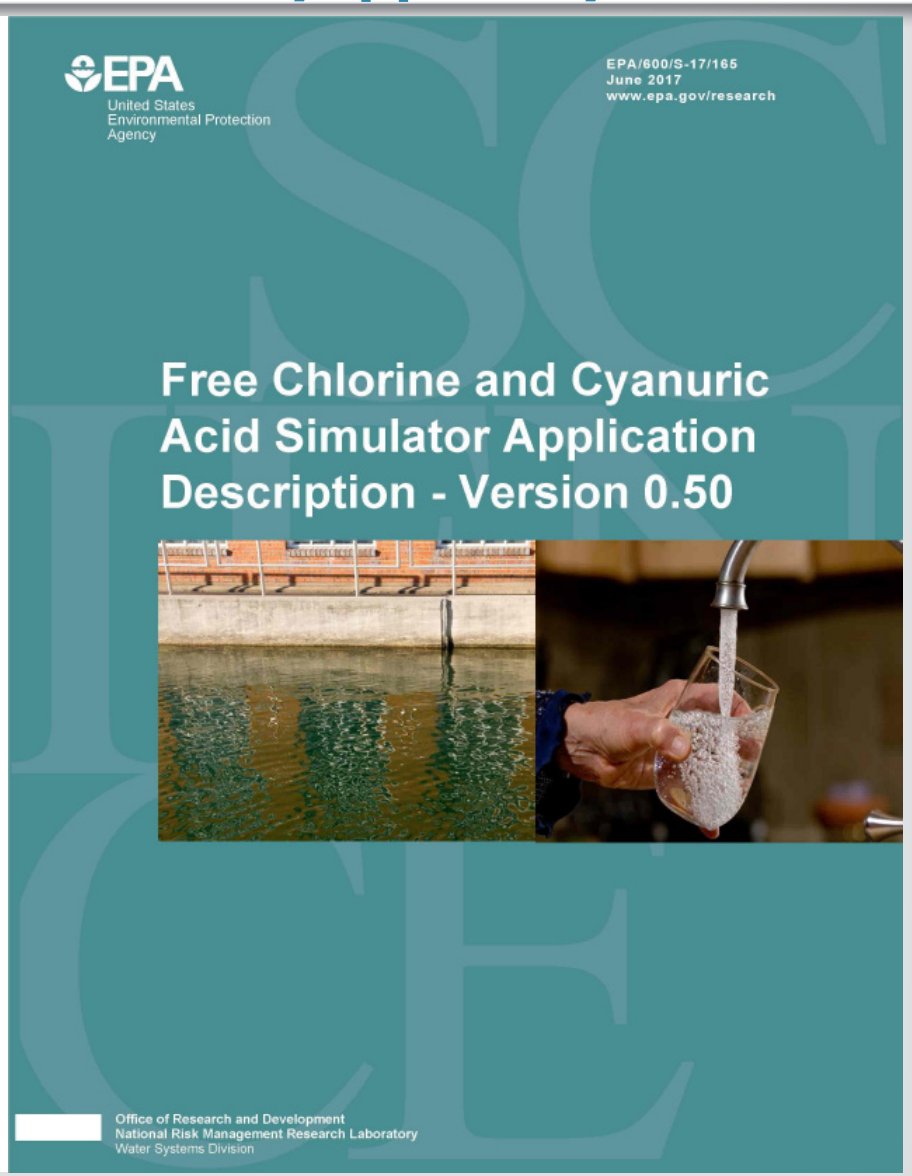
3. Aware of things to consider in practice

- No approved method for free chlorine
- Simulation possible
  - Need TOTCl, TOTCy, pH
  - Temperature limitation
- Other practical issues

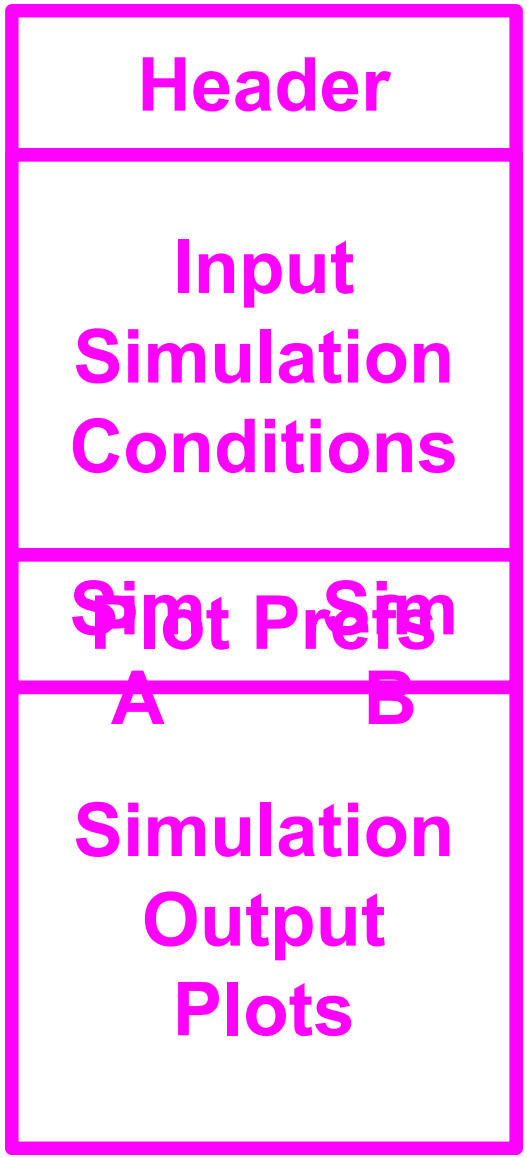
Free Chlorine & Cy App

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)
- Application Description
  - https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100S368.txt



Application Layout



Application Header

Free Chlorine and Cyanuric Acid System Simulator

Version 0.50, Last Updated May 10, 2017

Created by David G. Wahman (wahman.david@epa.gov), United States Environmental Protection Agency

The provided application simulates the water chemistry, at the selected conditions, associated with the free chlorine and cyanuric acid system (i.e., chlorinated cyanurates). The application allows the user to estimate the free chlorine concentration when cyanuric acid is present as is the case when adding chlorine-containing chemicals commonly referred to as Dichlor (anhydrous sodium dichloroisocyanurate or sodium dichloroisocyanurate dihydrate) or Trichlor (trichloroisocyanuric acid) to water. Equilibrium equations and associated constants are for a temperature of 25 degrees Celsius as presented by Obrien et al. (Chemistry of Water Supply, Treatment, and Distribution, 1974, pp 333-358).

To open a document describing the application in a new window, click on the following link: Application Documentation


Water Resources Center
The Ohio State University

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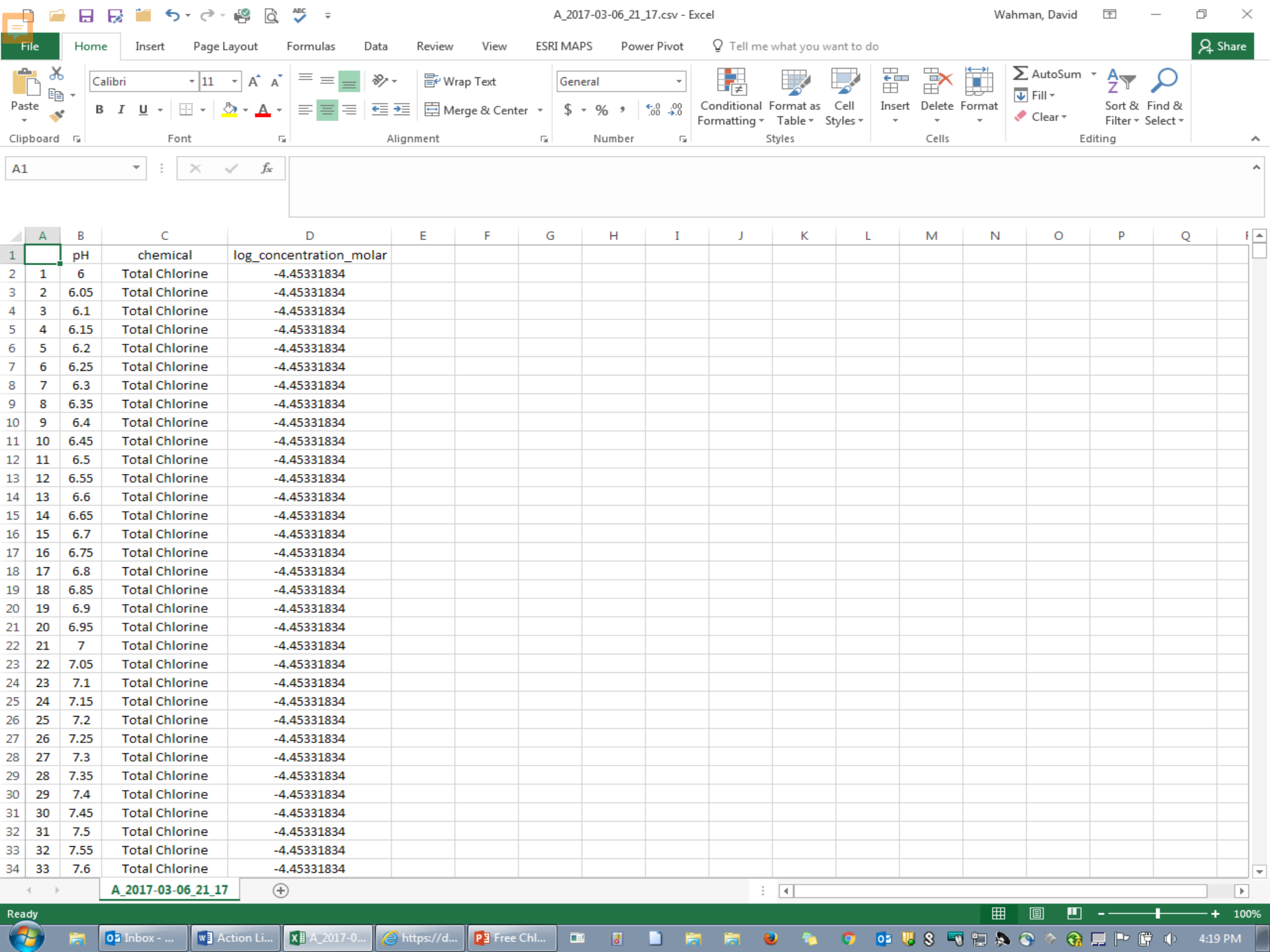
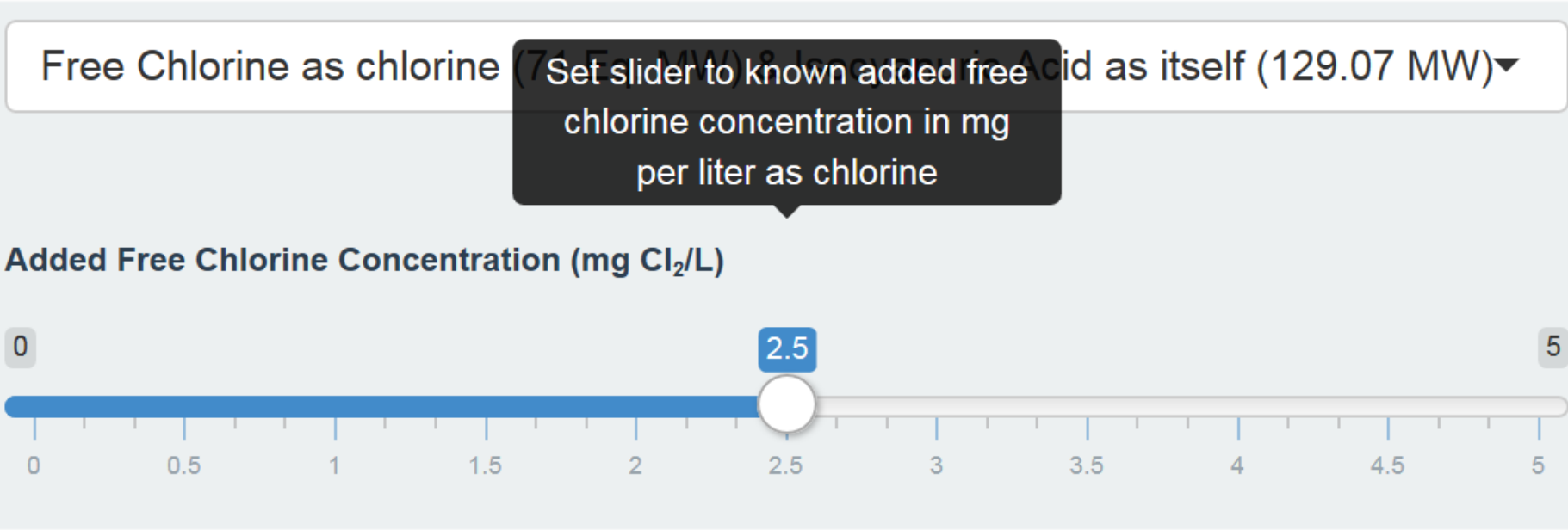


	A	B	C	D
1		pH	chemical	log_concentration_molar
2	1	6	Total Chlorine	-4.45331834
3	2	6.05	Total Chlorine	-4.45331834
4	3	6.1	Total Chlorine	-4.45331834
5	4	6.15	Total Chlorine	-4.45331834
6	5	6.2	Total Chlorine	-4.45331834
7	6	6.25	Total Chlorine	-4.45331834
8	7	6.3	Total Chlorine	-4.45331834
9	8	6.35	Total Chlorine	-4.45331834
10	9	6.4	Total Chlorine	-4.45331834
11	10	6.45	Total Chlorine	-4.45331834
12	11	6.5	Total Chlorine	-4.45331834
13	12	6.55	Total Chlorine	-4.45331834
14	13	6.6	Total Chlorine	-4.45331834
15	14	6.65	Total Chlorine	-4.45331834
16	15	6.7	Total Chlorine	-4.45331834
17	16	6.75	Total Chlorine	-4.45331834
18	17	6.8	Total Chlorine	-4.45331834
19	18	6.85	Total Chlorine	-4.45331834
20	19	6.9	Total Chlorine	-4.45331834
21	20	6.95	Total Chlorine	-4.45331834
22	21	7	Total Chlorine	-4.45331834
23	22	7.05	Total Chlorine	-4.45331834
24	23	7.1	Total Chlorine	-4.45331834
25	24	7.15	Total Chlorine	-4.45331834
26	25	7.2	Total Chlorine	-4.45331834
27	26	7.25	Total Chlorine	-4.45331834
28	27	7.3	Total Chlorine	-4.45331834
29	28	7.35	Total Chlorine	-4.45331834
30	29	7.4	Total Chlorine	-4.45331834
31	30	7.45	Total Chlorine	-4.45331834
32	31	7.5	Total Chlorine	-4.45331834
33	32	7.55	Total Chlorine	-4.45331834
34	33	7.6	Total Chlorine	-4.45331834

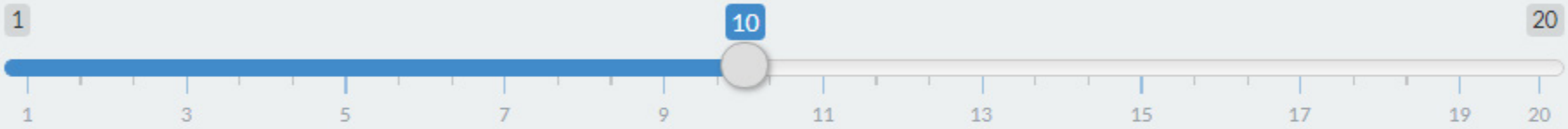
Application Tooltips



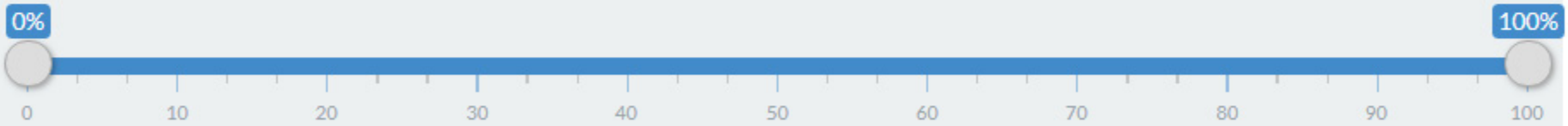
Application Plot Preferences

Simulation A Plot Preferences

Select Range for Y-axis on log Concentration Plots

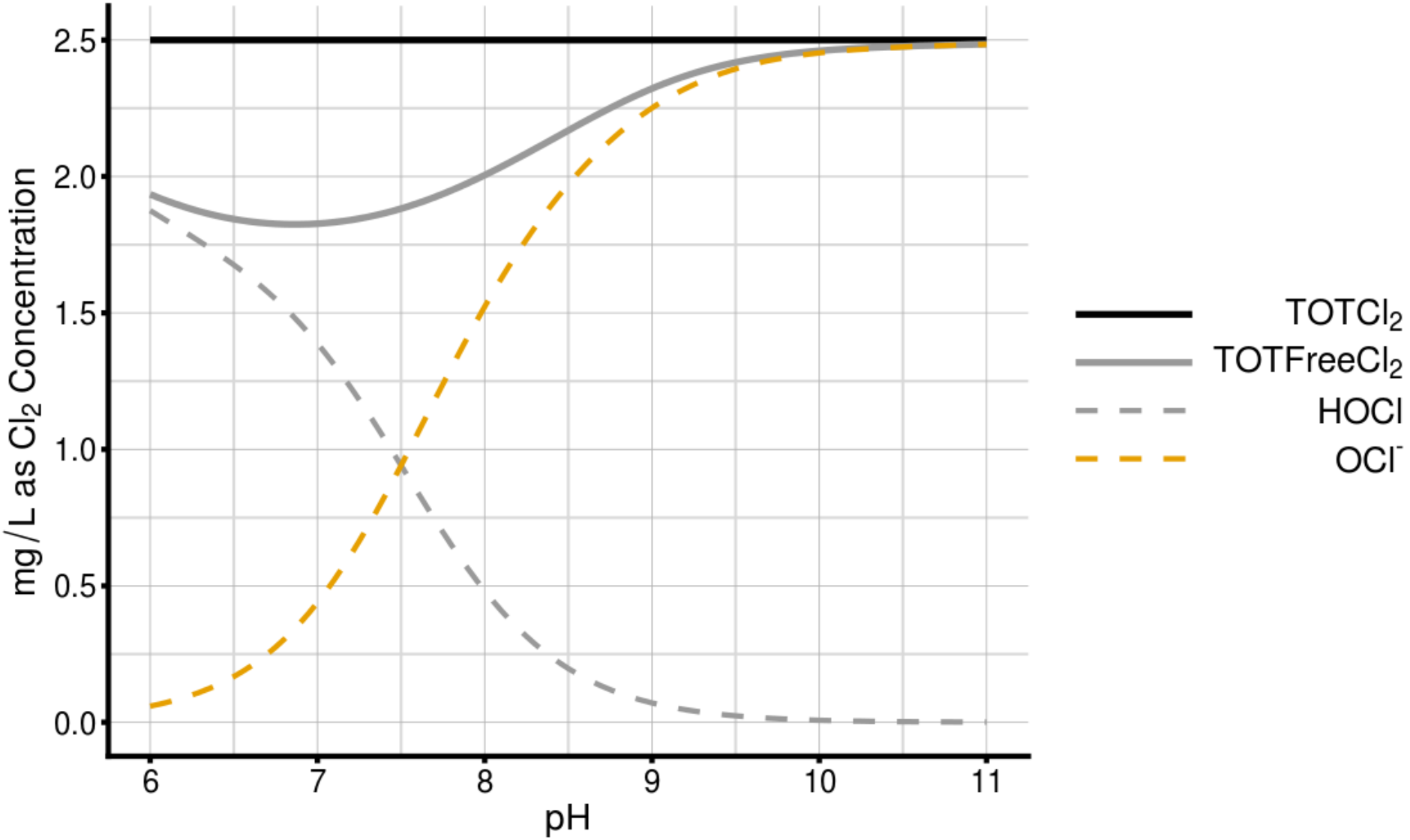


Select the Percent of Total Chlorine to use for the Lower and Upper Limits on the mg/L Plot Y-axis



Update Plots for Simulation A

Application Output Plots



After this presentation:

4. Familiar with web–based application

- Implements O'Brien model (25°C)
- Inputs → TOTCl, TOTCy, pH
- Outputs → All chemical species
- Future update for temperature

References

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Additional Resources

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Web–Based Application

Free Chlorine and Cyanuric Acid Chemistry Simulator: https://usepaord.shinyapps.io/cyanuric/

Free Chlorine and Cyanuric Acid Simulator Application Description - Version 0.50: https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100S368.txt

Questions?

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