Chlorinated Cyanurates (Dichlor & Trichlor) Water Chemistry Implications

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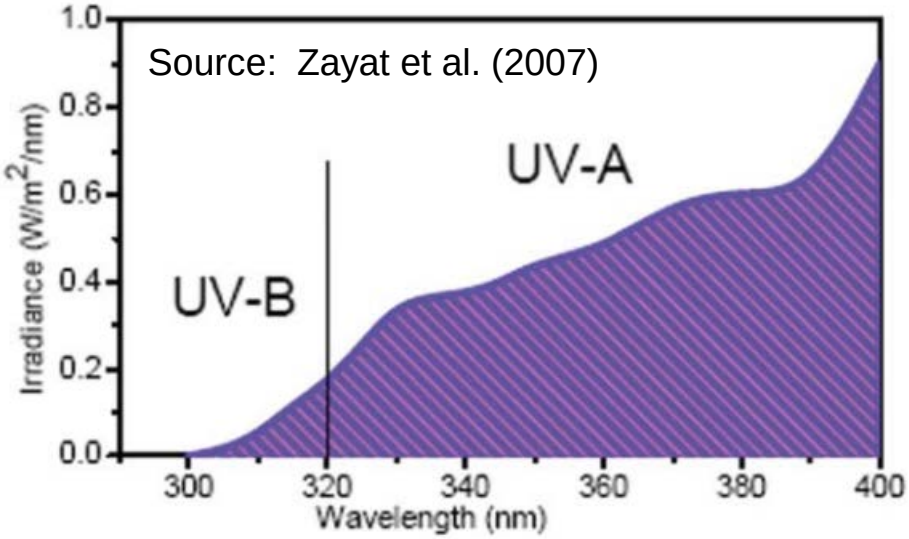
After this presentation:

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

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



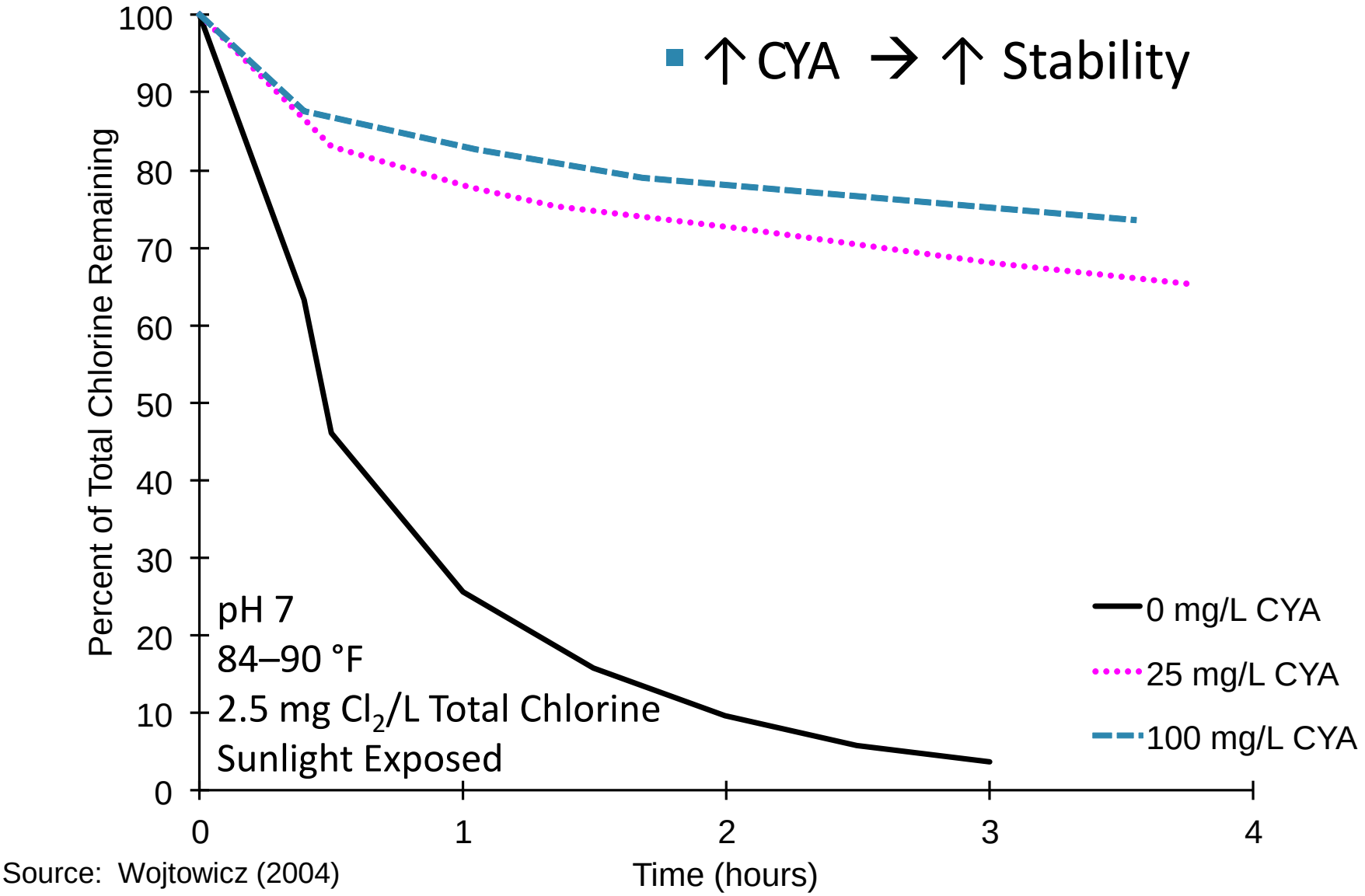
Cyanuric Acid Addition

- 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)

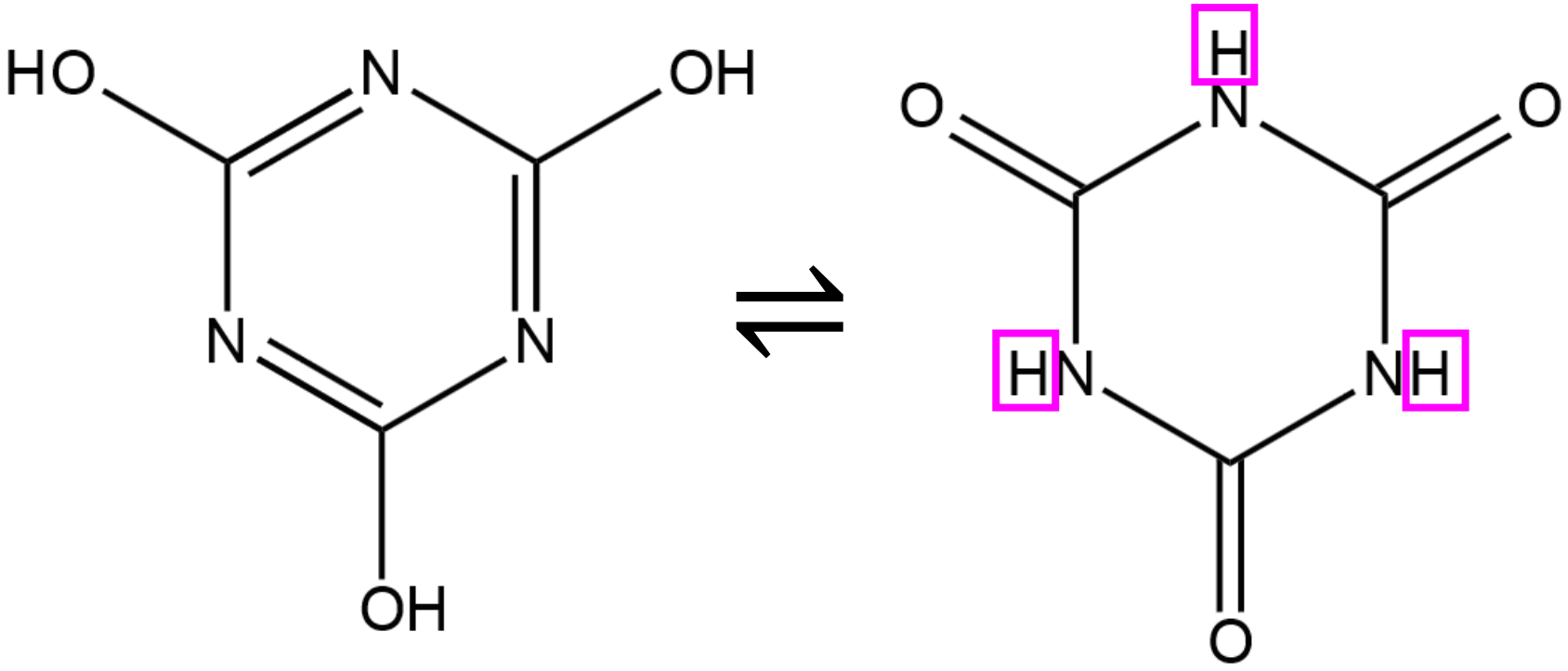
Parameter	Minimum	Ideal	Maximum
Total (Available) Chlorine (mg Cl_2/L)	1	2–4	4
Cyanuric Acid (mg/L)	N/A	30–50	100

CYA Stabilization (Concentration)



Source: Wojtowicz (2004)

Cyanuric Acid (H_3Cy)

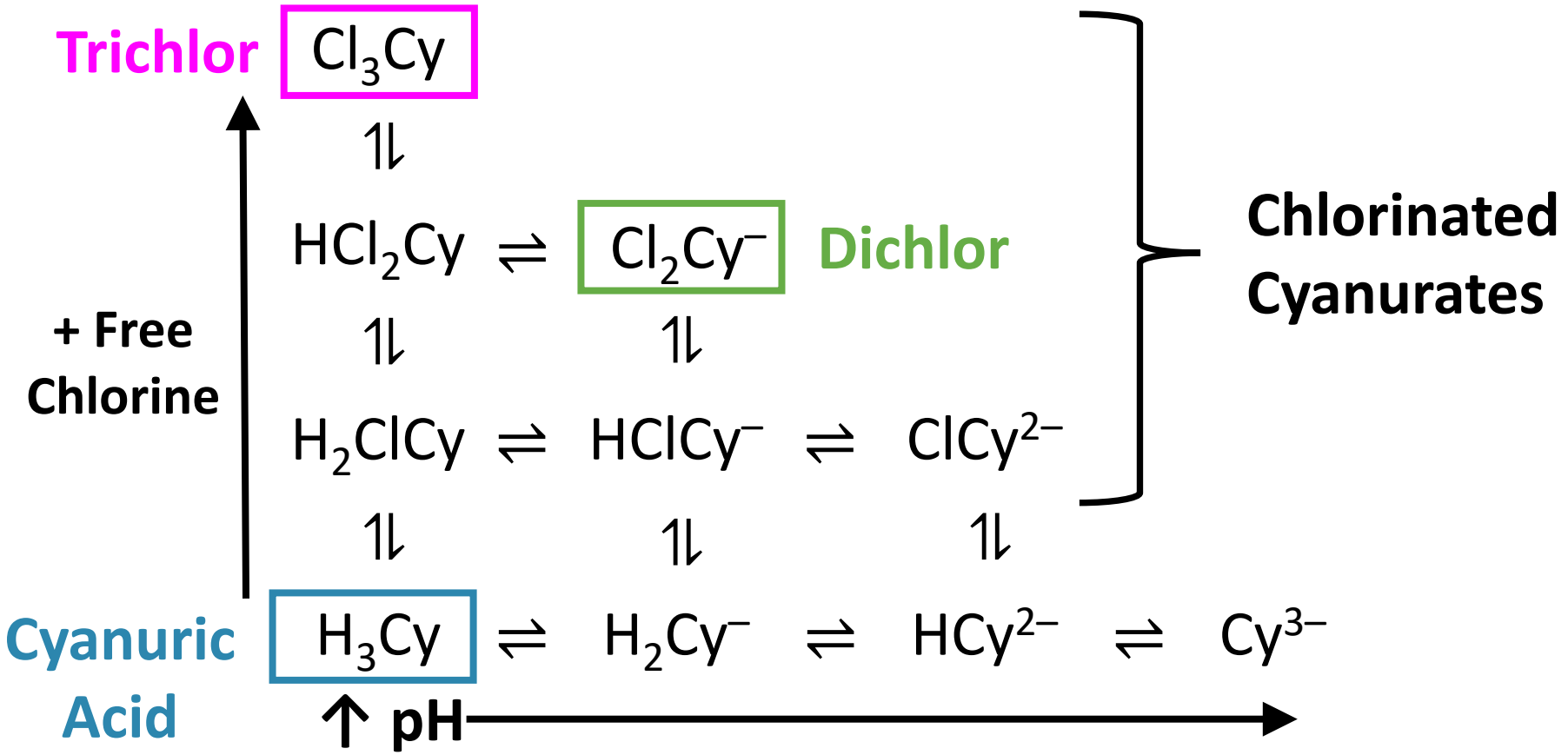


Cyanuric Acid
(enol form)

Isocyanuric Acid
(keto form)

- "Cy" = Cyanurate structure → H_3Cy

Chlorinated Cyanurates



- 10 chemical species (6 with chlorine)
- 12 equilibrium equations (9 independent)
- Cy + free chlorine ⇌ chlorinated cyanurates
- Free chlorine is disinfectant

Terminology

- 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 (FIFRA)

- Federal Insecticide, Fungicide, and Rodenticide Registration Act (FIFRA)
  - 1st approval, July 2001 → Oxychem Corporation
  - Routine treatment of drinking water
- Example Dichlor label (Registration # 935–41):

  "Feed 1 ounce of this product per 6000 gallons of water until a **free available chlorine residual of at least 0.2 ppm is attained throughout the distribution system**. Check water frequently with a chlorine test kit. Bacteriological sampling must be conducted at a frequency no less than that prescribed by the National Interim Primary Drinking Water Regulations. Contact your local Health Department for further details."
- Example Trichlor label (RN 935–59): 6000→9000

Drinking Water Use

- Manufacturer NSF 60 Certification
  - Function → disinfection & oxidation
  - 30 mg/L max
  - Dichlor[1] = 6 (2 others for well cleaning)
  - Trichlor[2] = 7
  - Cyanuric Acid = 0
- 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
- States, tribes, or territories 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

FIFRA & SDWA Quick Guide Developed by OPP & OGWDW

https://www.epa.gov/pesticide-registration/guidance-disinfectant-products-intended-treat-drinking-water

United States Environmental Protection Agency

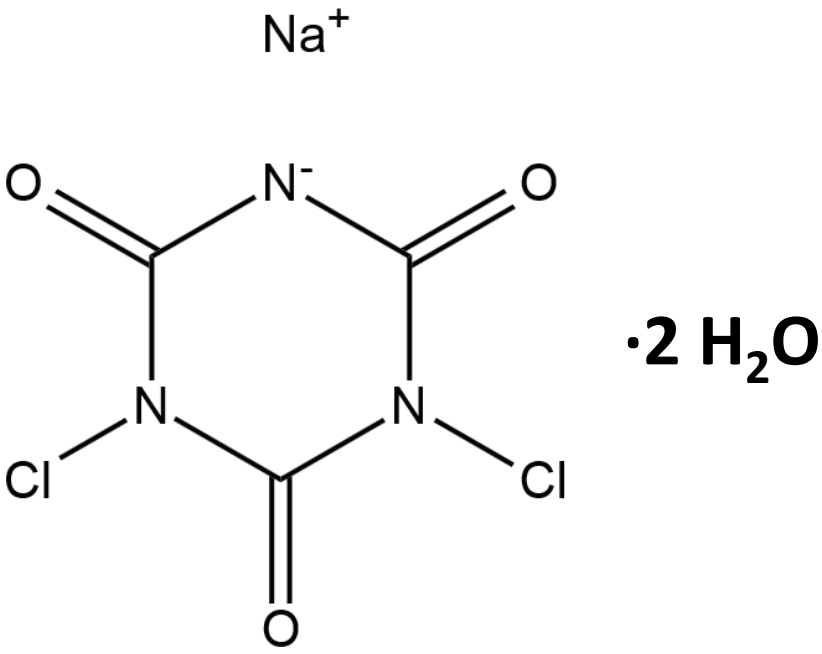
Office of Pesticide Programs
September 2017

Quick Guide for Disinfectant Products for Drinking Water Use by Public Water Systems

Understanding Your Responsibility under FIFRA and How FIFRA Approval Relates to SDWA

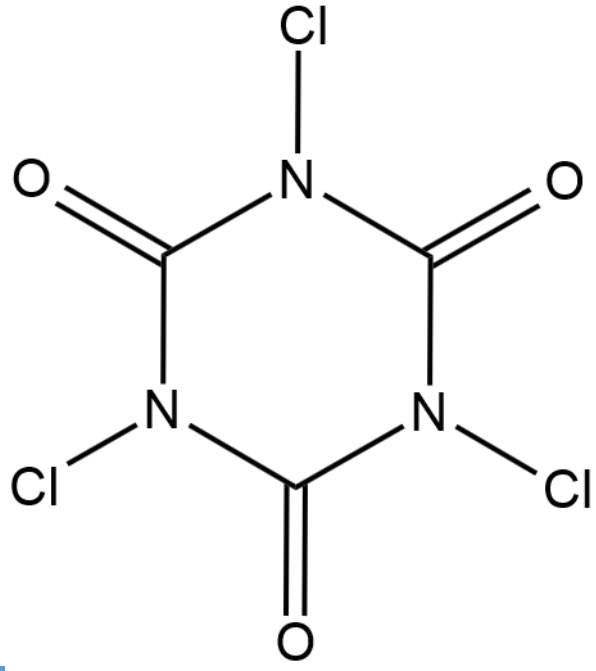
Dichlor & Trichlor

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
TOTCl ($mg\ Cl_2$) Chemical (mg)	0.65	0.55	0.92
TOTCy (mg) Chemical (mg)	0.59	0.50	0.56
Chemical (mg) TOTCl ($mg\ Cl_2$)	1.54	1.82	1.09
TOTCy (mg) TOTCl ($mg\ Cl_2$)	0.91	0.91	0.61

Reasons for Use (Free Cl_2)

- Benefits (Kuechler 2009)
  - 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%
  - Dichlor specific
    - Easily dissolves
    - More soluble
    - Neutral pH
- Greater residual stability?
- Regulated DBP formation?

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

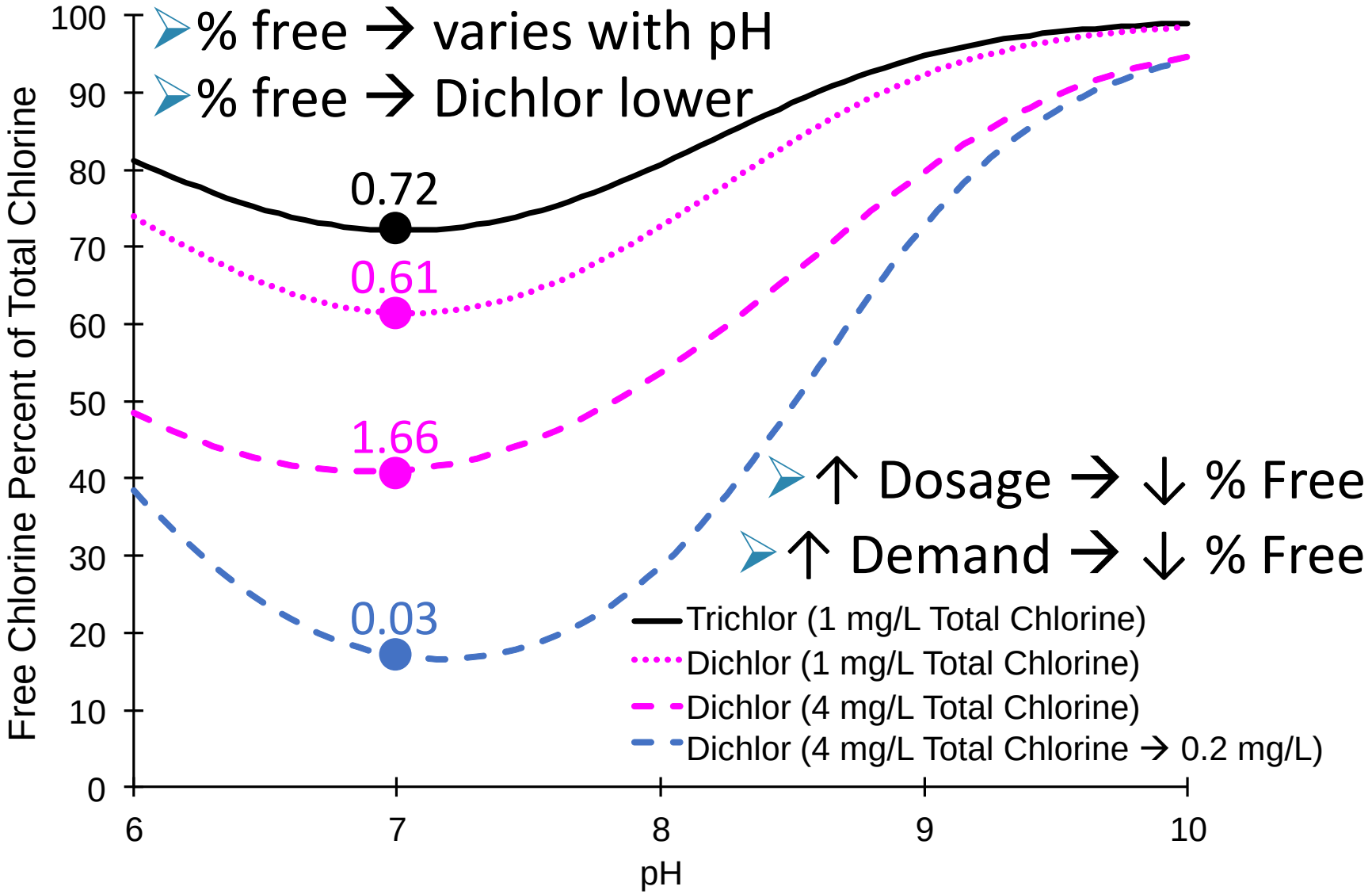
Water Chemistry

- 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

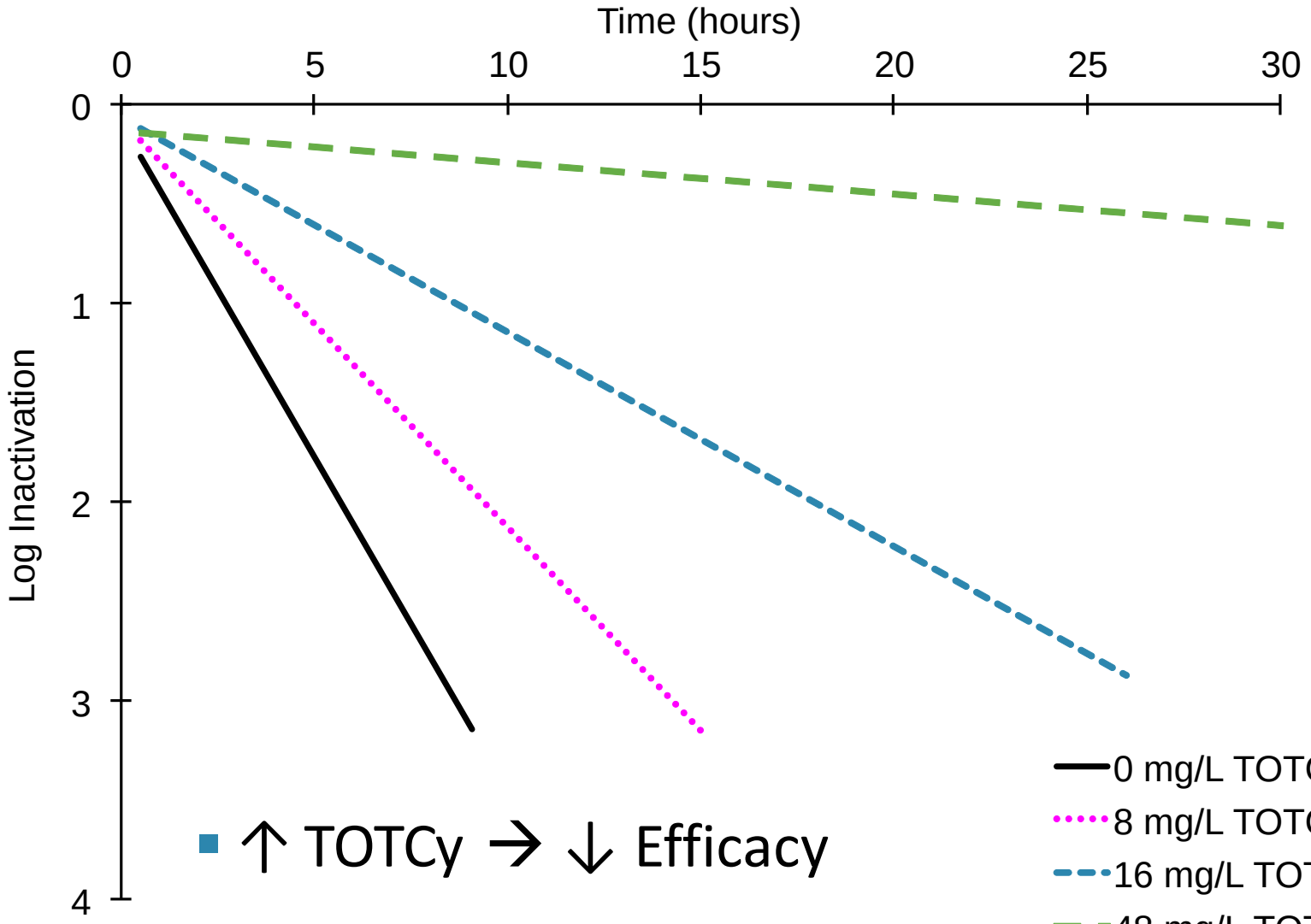
Free Chlorine % Variation



Disinfection & Stability (DBPs)

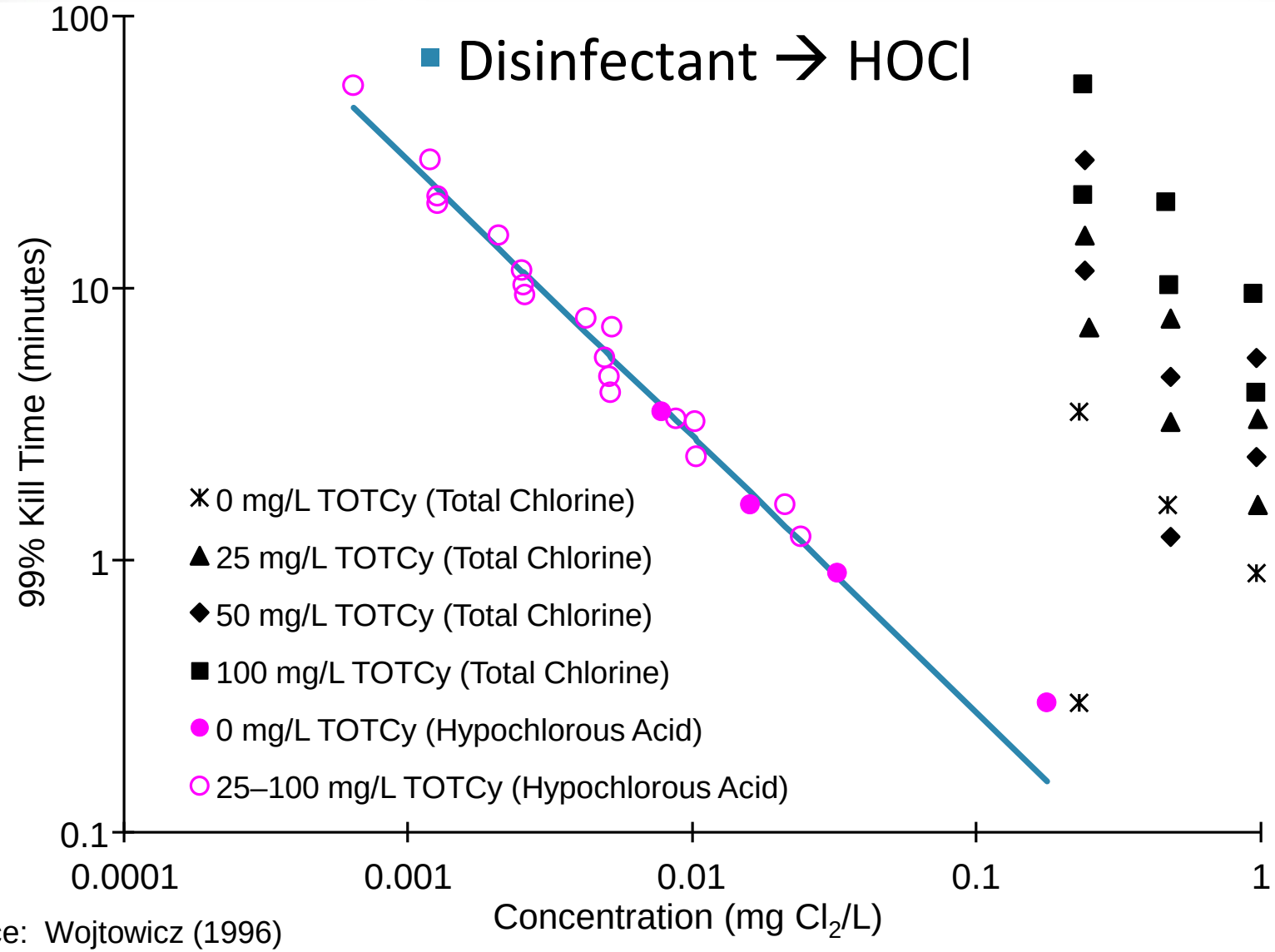
- Disinfection process
  - HOCl reacting with an organism
  - HOCl + Organism → Inactivation
  - Reaction Rate = k_I[HOCl][Organism]
- Stability (DBPs)
  - HOCl reacting with natural organic matter (NOM)
  - HOCl + NOM → DBPs
  - NOM ∝ total organic carbon (TOC)
  - Reaction Rate = k_{TOC}[HOCl][TOC]
- For same total chlorine
  - ↑TOTCy → ↓[HOCl] → ↓ reaction rates (i.e., speed)
  - ↓ disinfection & ↑ stability (↓ DBPs or delay formation)

Disinfection Impacts (*C. parvum*)



Source: Murphy et al. (2015)

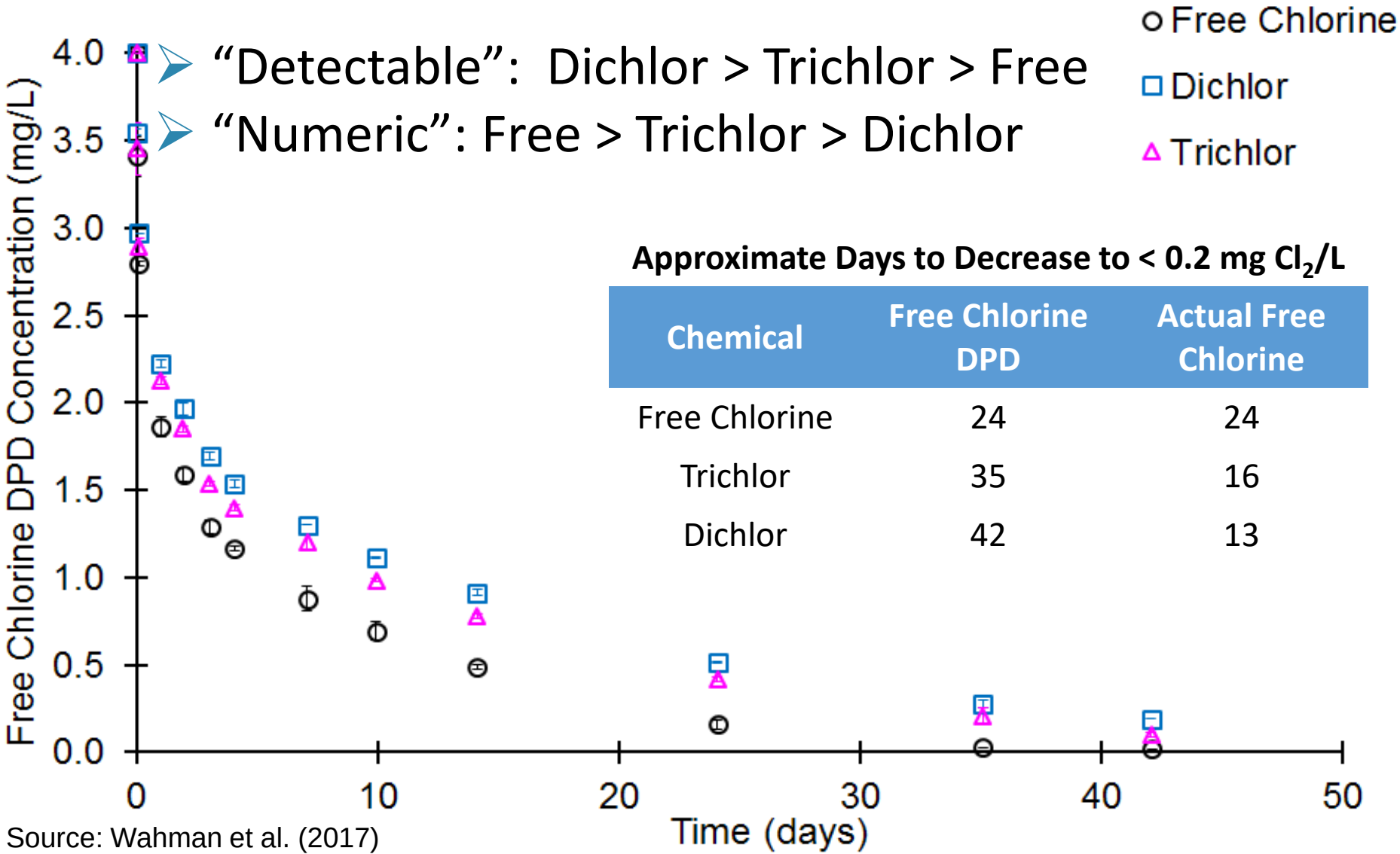
Actual Disinfectant (*S. faecalis*)



Source: Wojtowicz (1996)

Residual Stability Comparison

- "Detectable": Dichlor > Trichlor > Free
- "Numeric": Free > Trichlor > Dichlor



Approximate Days to Decrease to < 0.2 mg Cl_2/L

Chemical	Free Chlorine DPD	Actual Free Chlorine
Free Chlorine	24	24
Trichlor	35	16
Dichlor	42	13

Source: Wahman et al. (2017)

After this presentation:

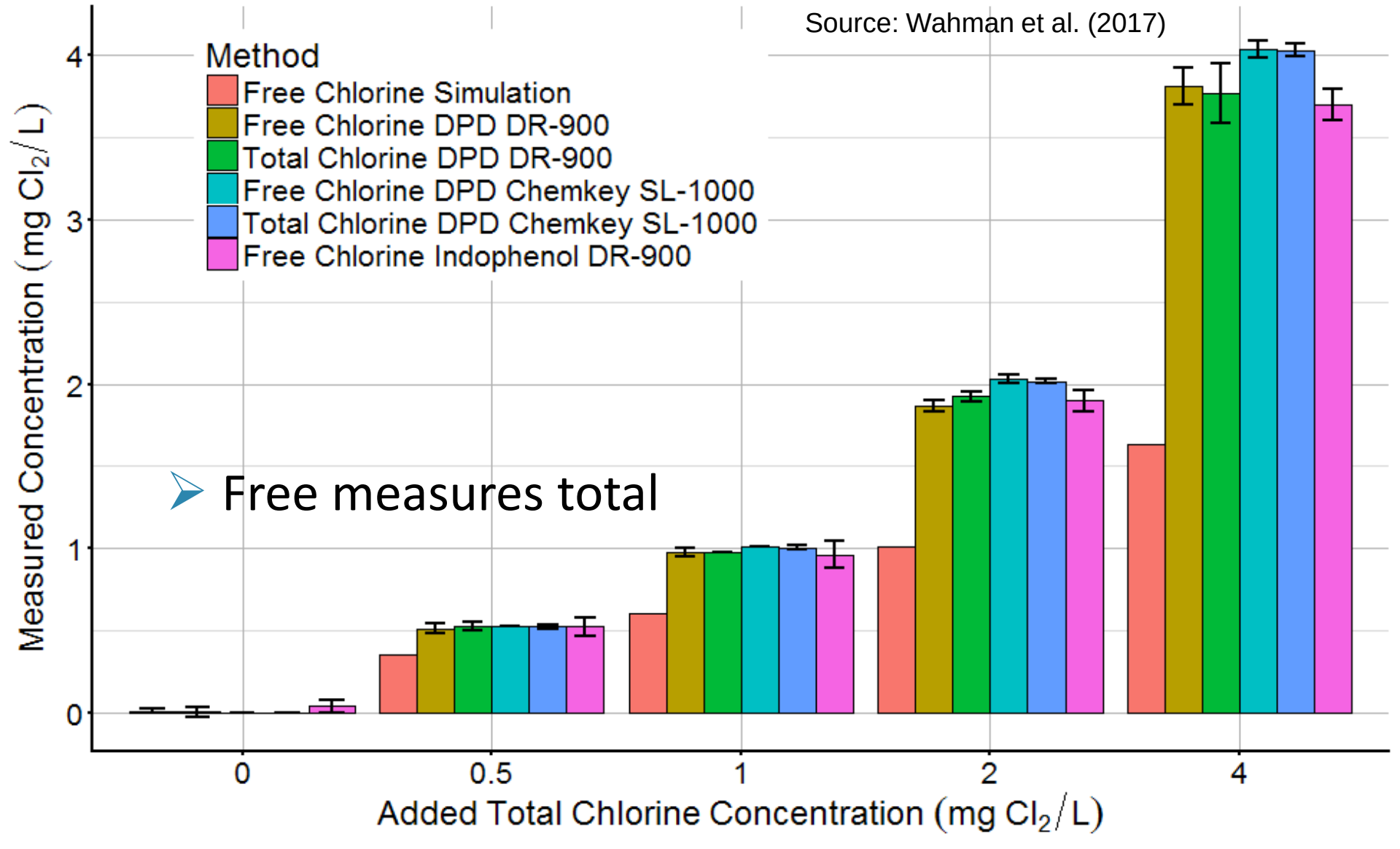
2. Understand water chemistry & implications

- 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

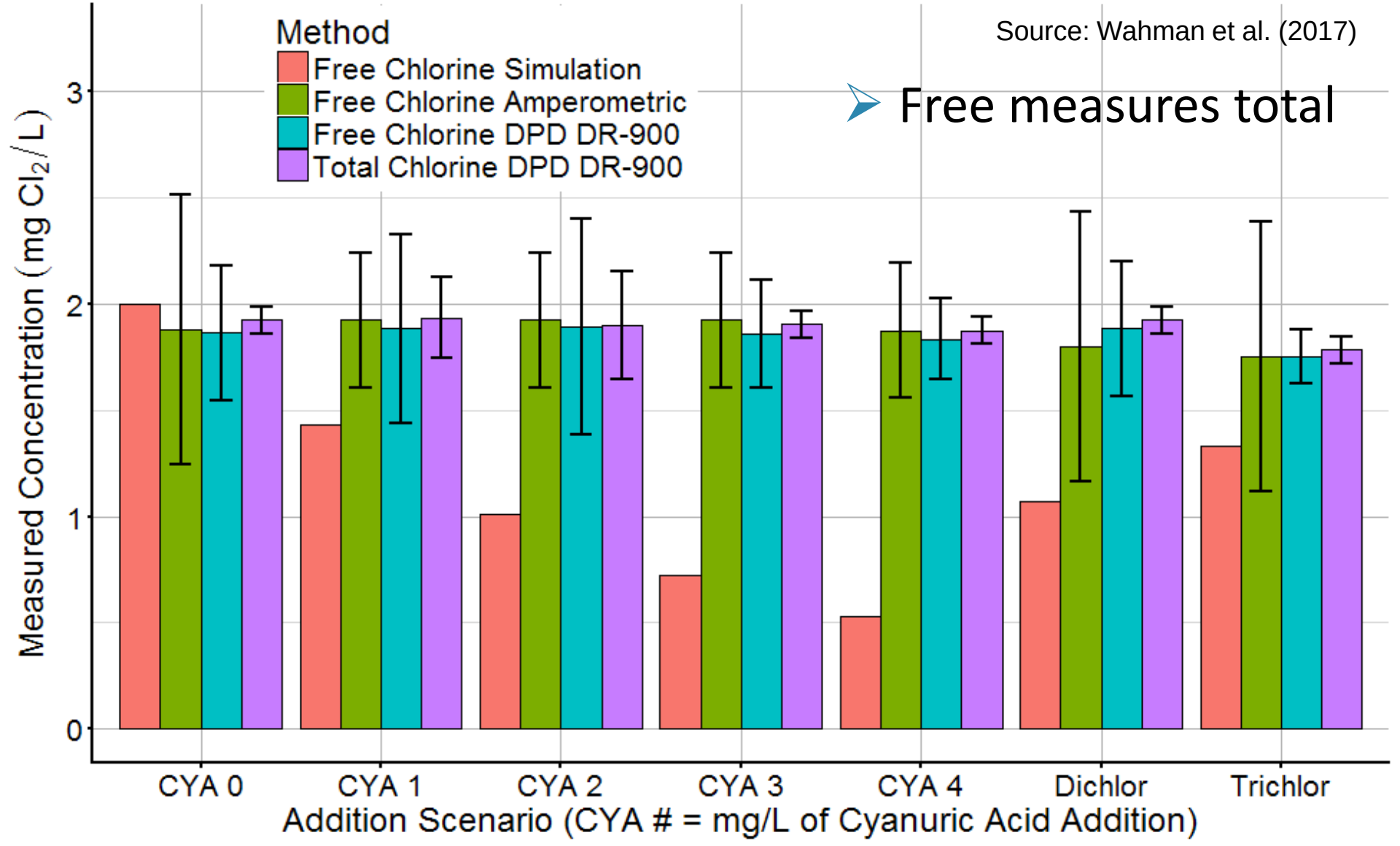
- Cy + free chlorine ⇌ chlorinated cyanurates
  - Fast equilibrium
  - Method cannot react with free chlorine
  - Method cannot change pH
  - Free chlorine test → measures total chlorine
- What does not work?
  - DPD (Whittle 1970; Wajon & Morris 1980)
  - Amperometric titration (Wajon & Morris 1980)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

Dichlor at pH 7



- Free measures total

2 mg Cl_2/L at pH 7.5



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)
- Chlorine trimming or boosting & blending disinfectants
- Cyanurate related DBPs

After this presentation:

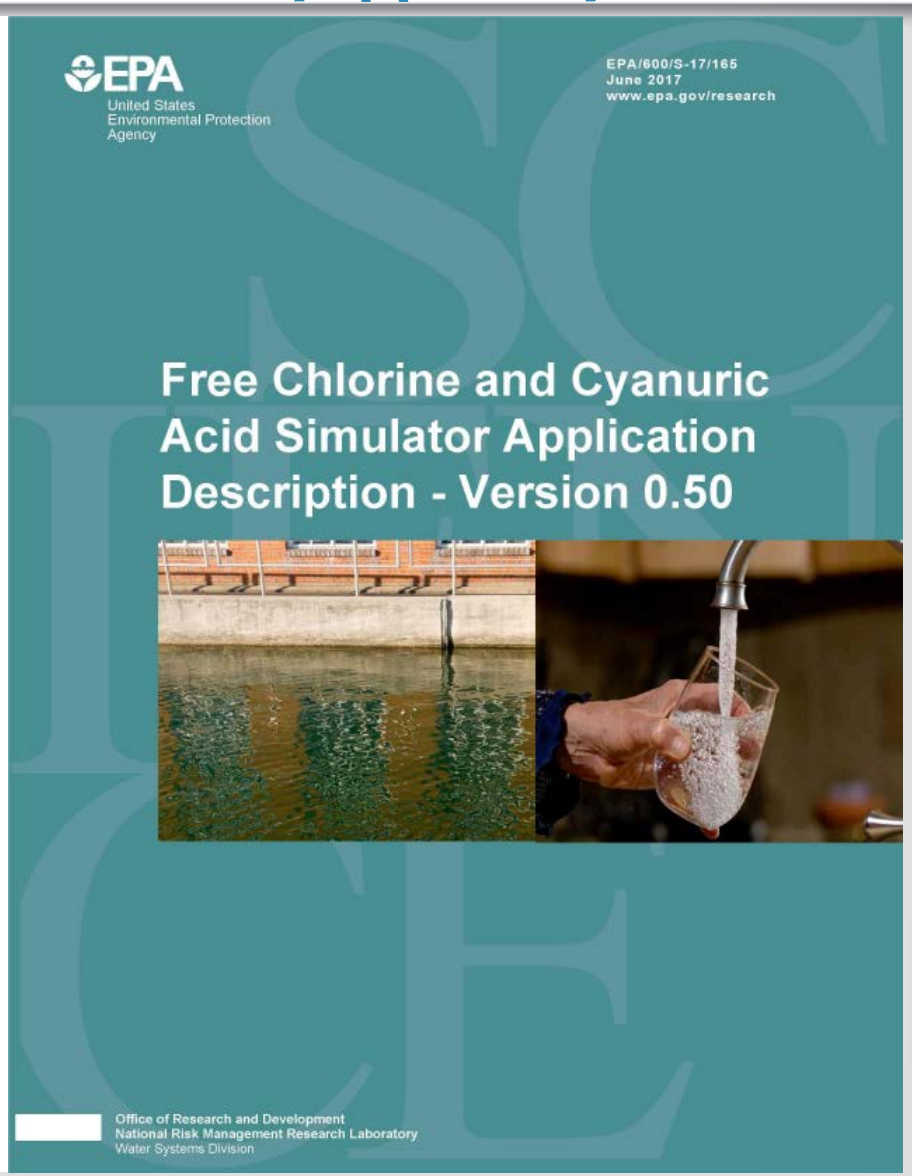
3. Aware of things to consider in practice

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

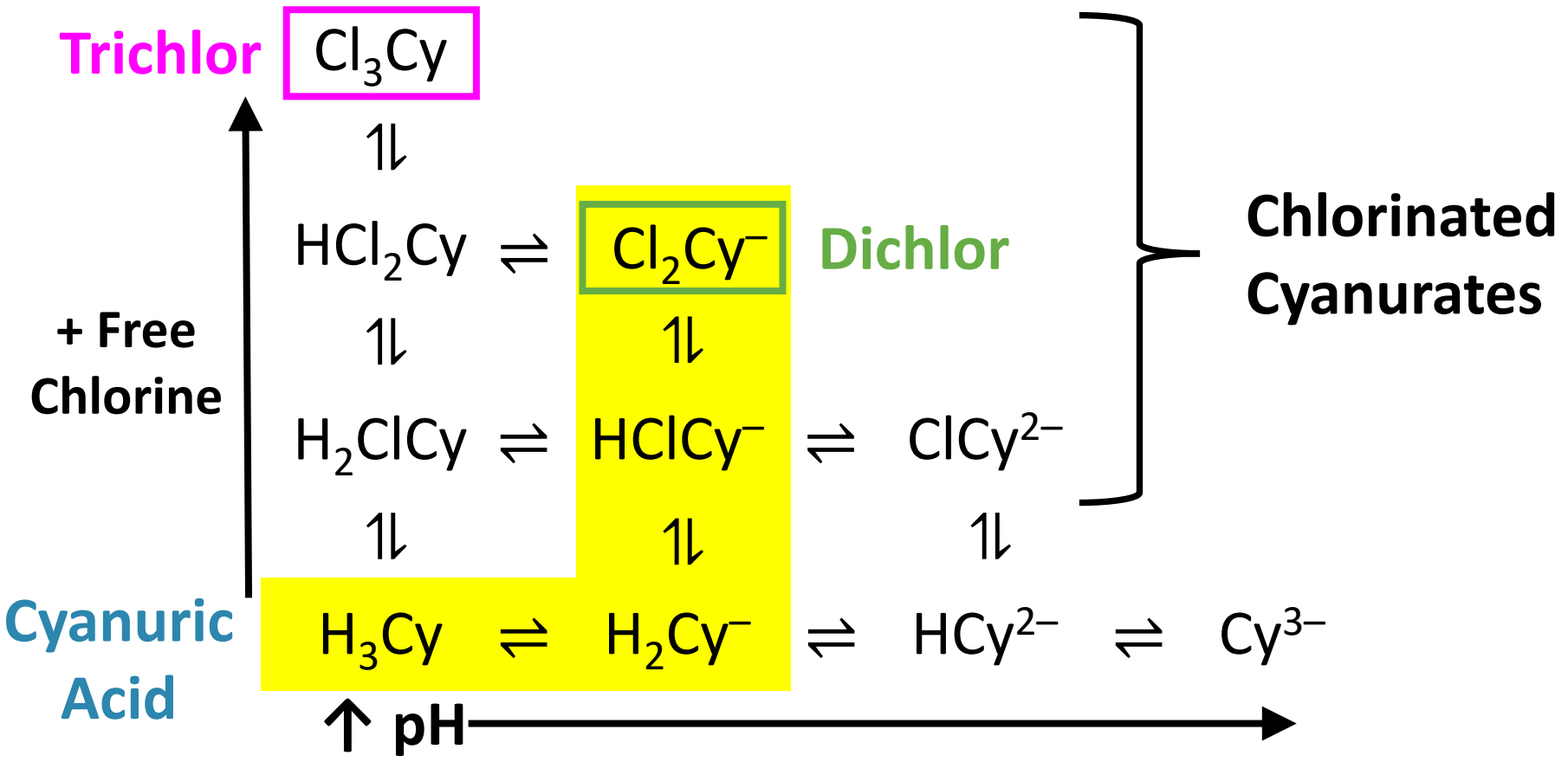
Free Chlorine & Cy App

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

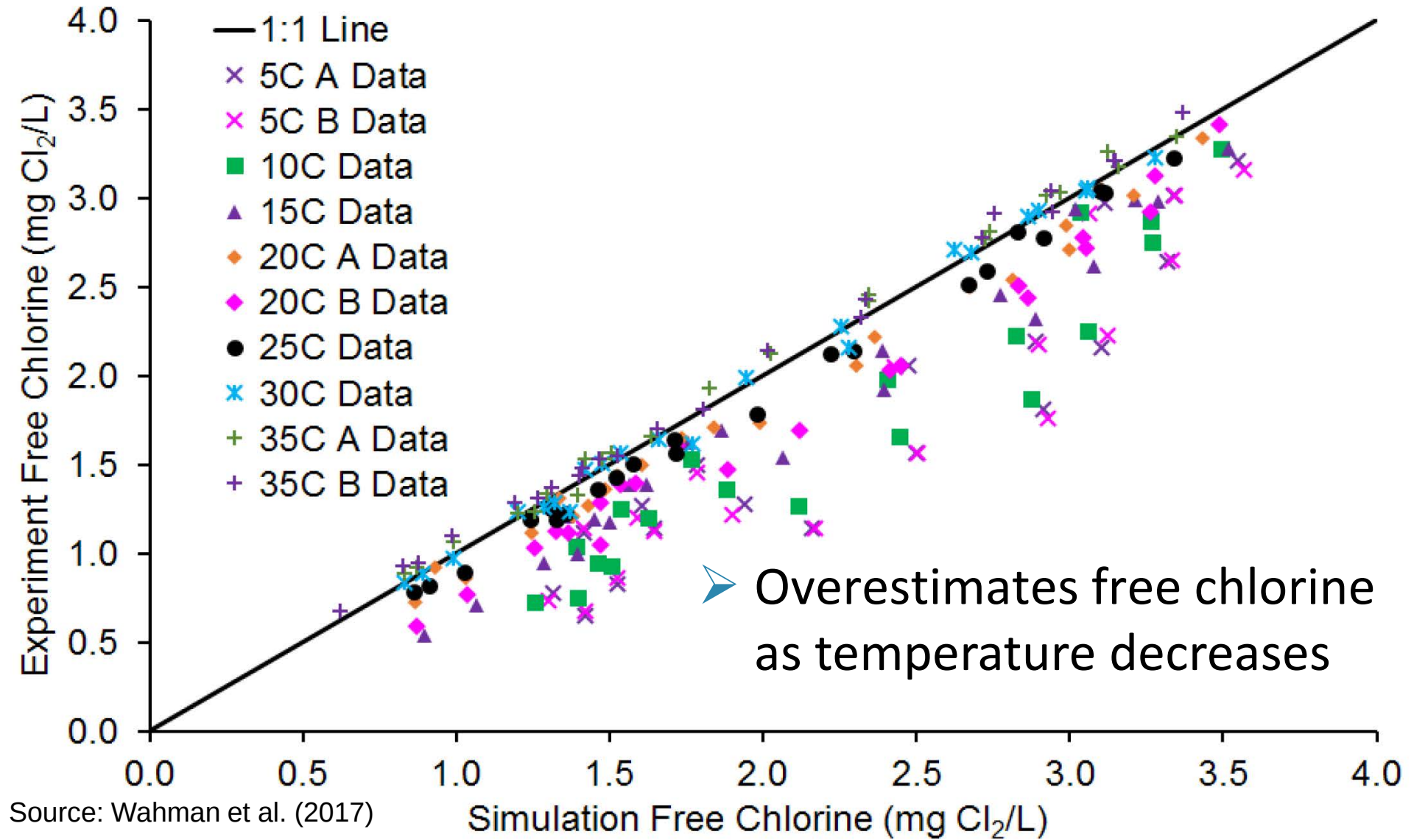


Chlorinated Cyanurates



- Simplified model for drinking water?
  - 12 → 6 chemical species
  - 12 → 6 equations (10 → 4 temperature dependent)

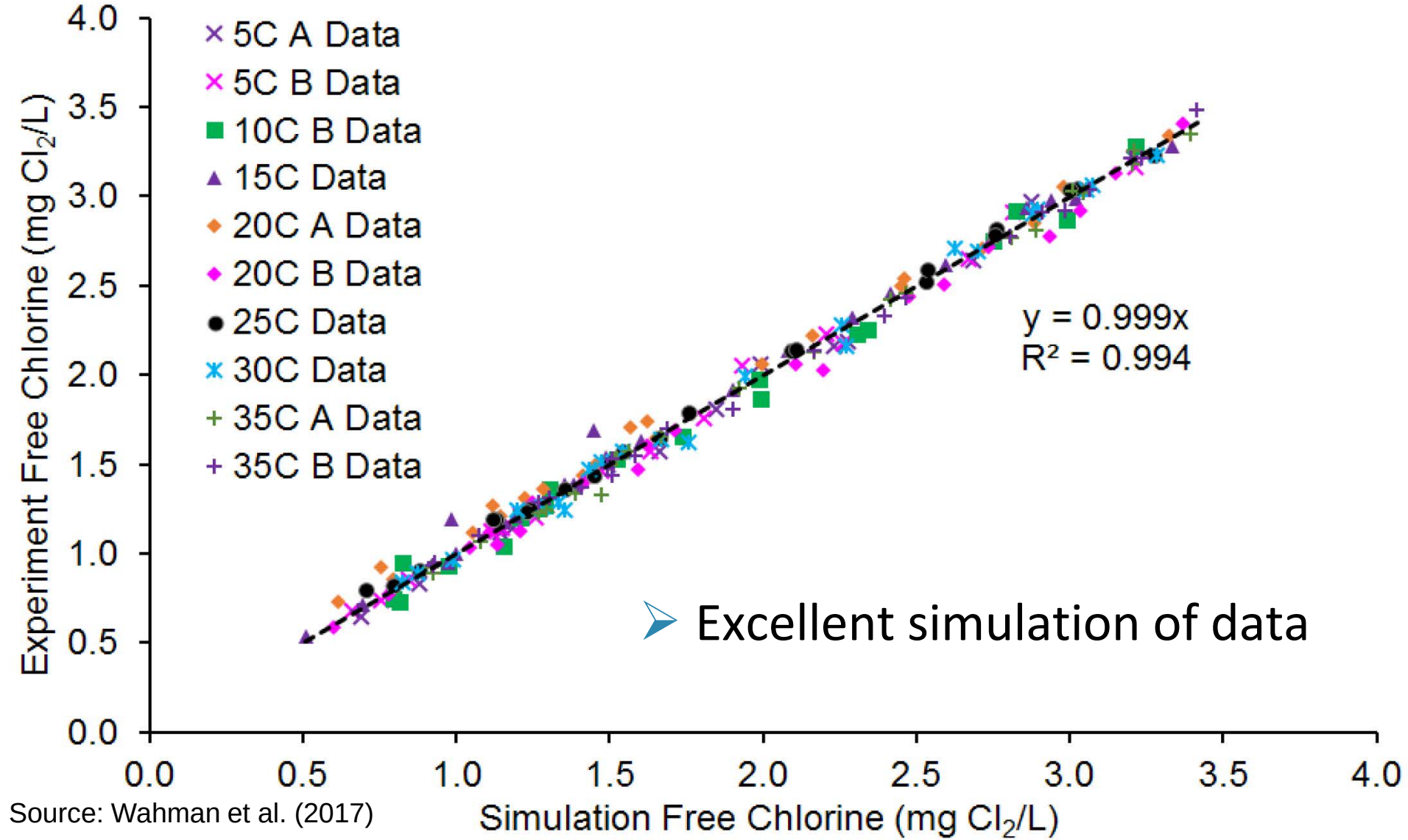
O'Brien Simulations (25°C)



- Overestimates free chlorine as temperature decreases

Source: Wahman et al. (2017)

Simplified Model with Temp.



- Excellent simulation of data

Source: Wahman et al. (2017)

After this presentation:

4. Aware of application & future updates

- Simulate free chlorine concentration
- Web–based application for 25°C
- Research ongoing for 5–35°C update
- Future update to web–based application

References

Cited References

ANSI/APSP, American National Standard for Water Quality in Public Pools and Spas; The Association of Pool and Spa Professionals: Alexandria, VA: **2009**, ANSI/APSP–11.

Kuechler, T. C., Use Of Chlorinated Isocyanurates for Drinking Water Chlorination. Proceedings of the Water Environment Federation 2009, **2009**, (1), 799–806.

Morris, J. C., The acid ionization constant of HOCl from 5 to 35C. *The Journal of Physical Chemistry* **1966,** *70*, (12), 3798-3805.

Murphy, J. L.; Arrowood, M. J.; Lu, X.; Hlavsa, M. C.; Beach, M. J.; Hill, V. R., Effect of cyanuric acid on the inactivation of Cryptosporidium parvum under hyperchlorination conditions. *Environ. Sci. Technol.* **2015**, 49, (12), 7348–7355.

O'Brien, J. E. *Hydrolytic and Ionization Equilibria of Chlorinated Isocyanurate in Water*. Dissertation, Harvard University, Cambridge, Massachusetts, **1972**.

Solastiouk, B. Thermodynamic and kinetic study of the chlorine / cyanuric acid system in aqueous solution. Lorraine National Polytechnic Institute, Nancy, France, 1989.

Wajon, J. E.; Carrell Morris, J., The analysis of free chlorine in the presence of nitrogenous organic compounds. *Environ. Int.* **1980**, 3, (1), 41–47.

Wahman, D. G., Alexander, M. T., and Dugan, A. G. (2017) Chlorinated Cyanurates: Method Interferences and Application Implications. Proceedings of the American Water Works Association 2017 Water Quality Technology Conference, Portland, Oregon, November 12–16, 2017.

Whittle, G. P. Recent advances in determining free chlorine, National Specialty Conference on Disinfection, Amherst, MA, **1970**.

Wojtowicz, J. A., Relative bactericidal effectiveness of hypochlorous acid and chloroisocyanurates. *Journal of the Swimming Pool and Spa Industry* **1996**, 2, (1), 34–41.

Wojtowicz, J. A., Effect of cyanuric acid on swimming pool maintenance. *Journal of the Swimming Pool and Spa Industry* **2004**, 5, (1), 15–19.

Zayat, M.; Garcia-Parejo, P.; Levy, D., Preventing UV-light damage of light sensitive materials using a highly protective UV-absorbing coating. *Chem. Soc. Rev.* **2007,** *36*, (8), 1270-1281.

Additional Resources

O'Brien, J. E.; Morris, J. C.; Bulter, J. N., Equilibria in Aqueous Solutions of Chlorinated Isocyanurate. In Chemistry of Water Supply, Treatment, and Distribution, Rubin, A. J., Ed. Ann Arbor Science Publishers, Inc.: Ann Arbor, MI, **1974**; pp 333–358.

Wojtowicz, J. A., Cyanuric and Isocyanuric Acids. In *Kirk–Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc.: **2000**; Vol. 8, pp 199–219.

Worley, S. D.; Wojtowicz, J. A., N–Halamines. In *Kirk–Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc.: **2000**; Vol. 13, pp 98–132.

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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