Chlorinated Cyanurates: Method Interferences and Application Implications

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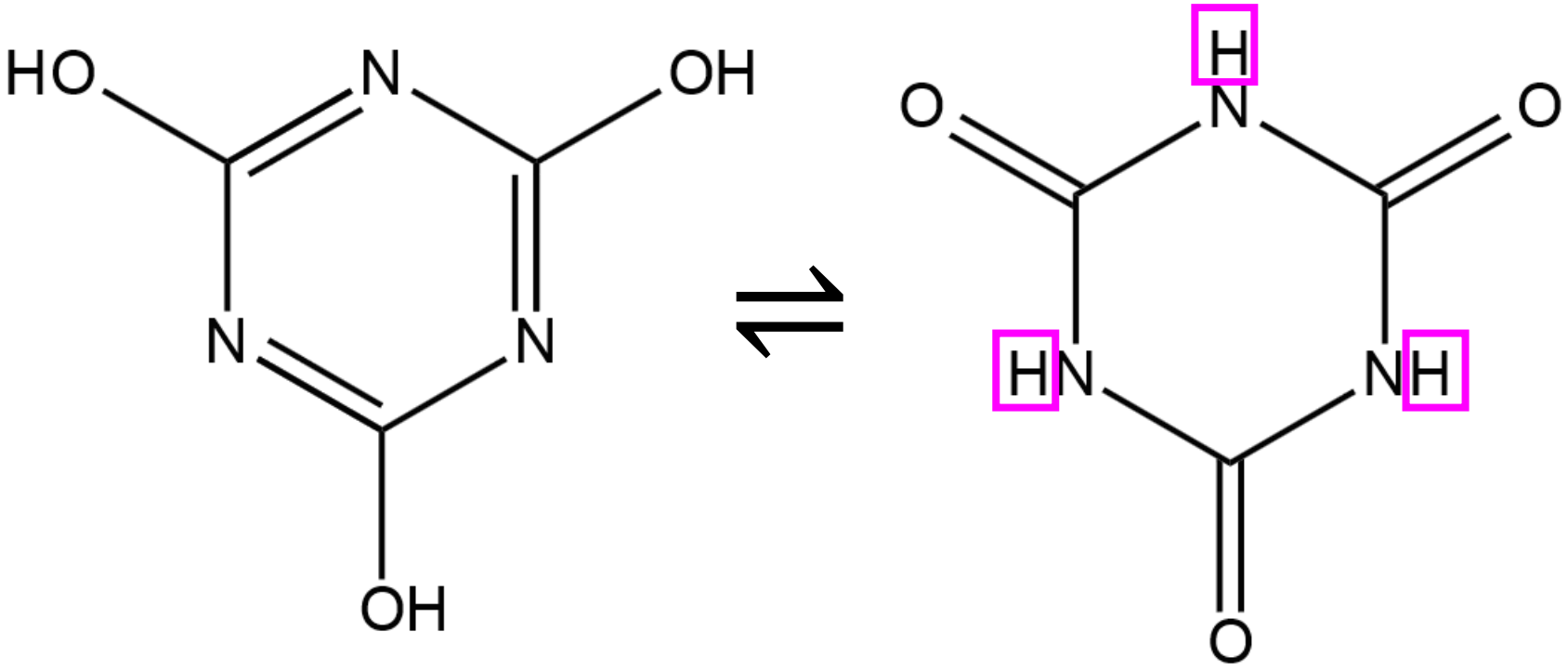
Free Chlorine, Sunlight, & CYA

- 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 (CYA) → 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)

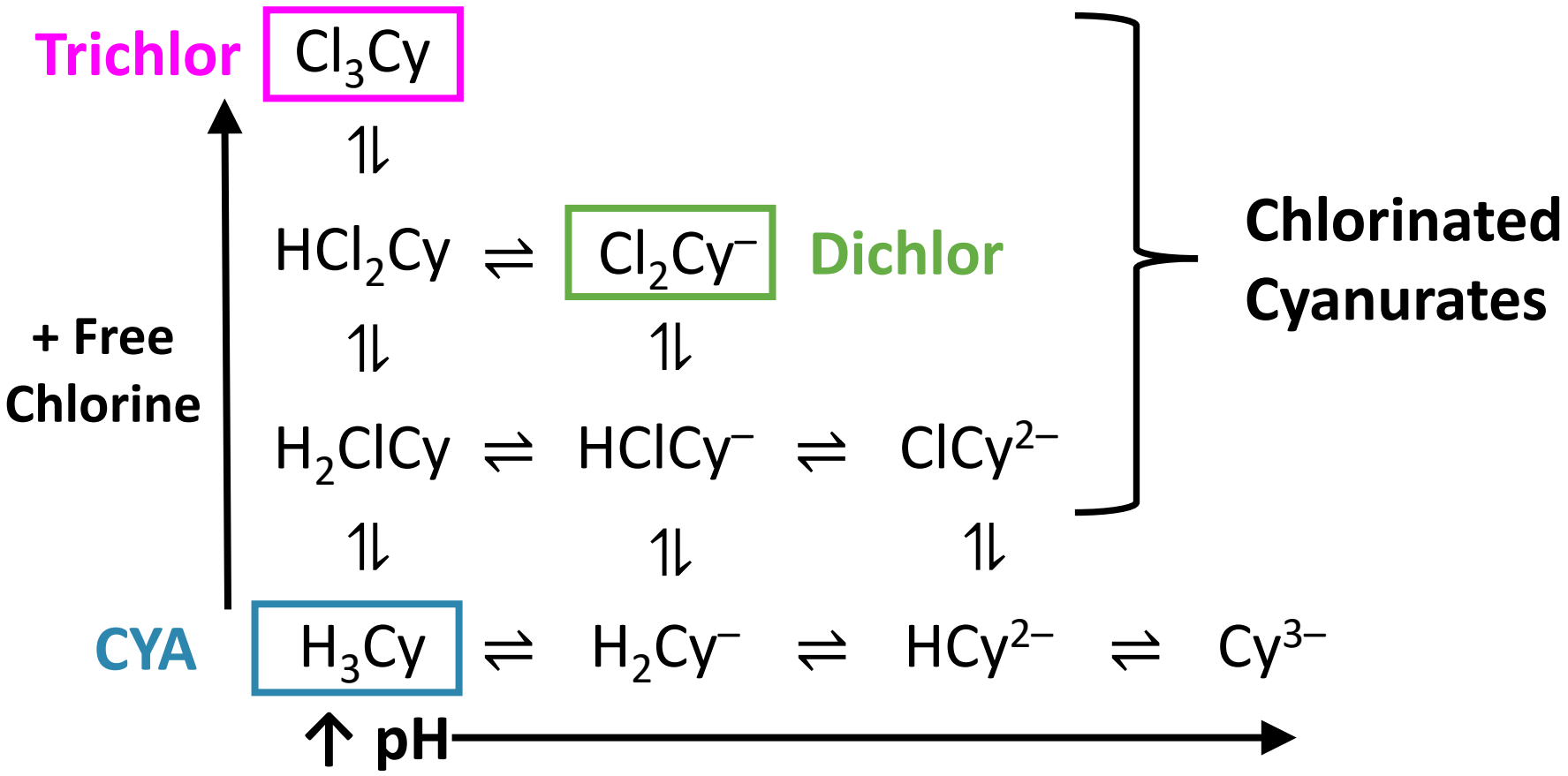


Cyanuric Acid
(enol form)

Isocyanuric Acid
(keto form)

- "Cy" = Cyanurate structure → H_3Cy

Chlorinated Cyanurates



- Free chlorine ⇌ chlorinated cyanurates
- Free chlorine is disinfectant

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
  - 30 mg/L max
  - 6 Dichlor[1] & 7 Trichlor[2]
- World Health Organization (WHO) guidelines
  - Sodium dichloroisocyanurate (Dichlor): 50 mg/L
  - Cyanuric acid: 40 mg/L
- 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

Reasons for Use

- Benefits (Kuechler 2009)
  - Tablet or granules
    - Safer than liquids or gases
    - Long storage life (i.e., years)
  - Concentrated chlorine
    - Trichlor → 90%
    - Dichlor → 55–65%

- 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
  - ↑CYA → ↓[HOCl] → ↓ reaction rate
  - ↑ stability (↓ DBPs)

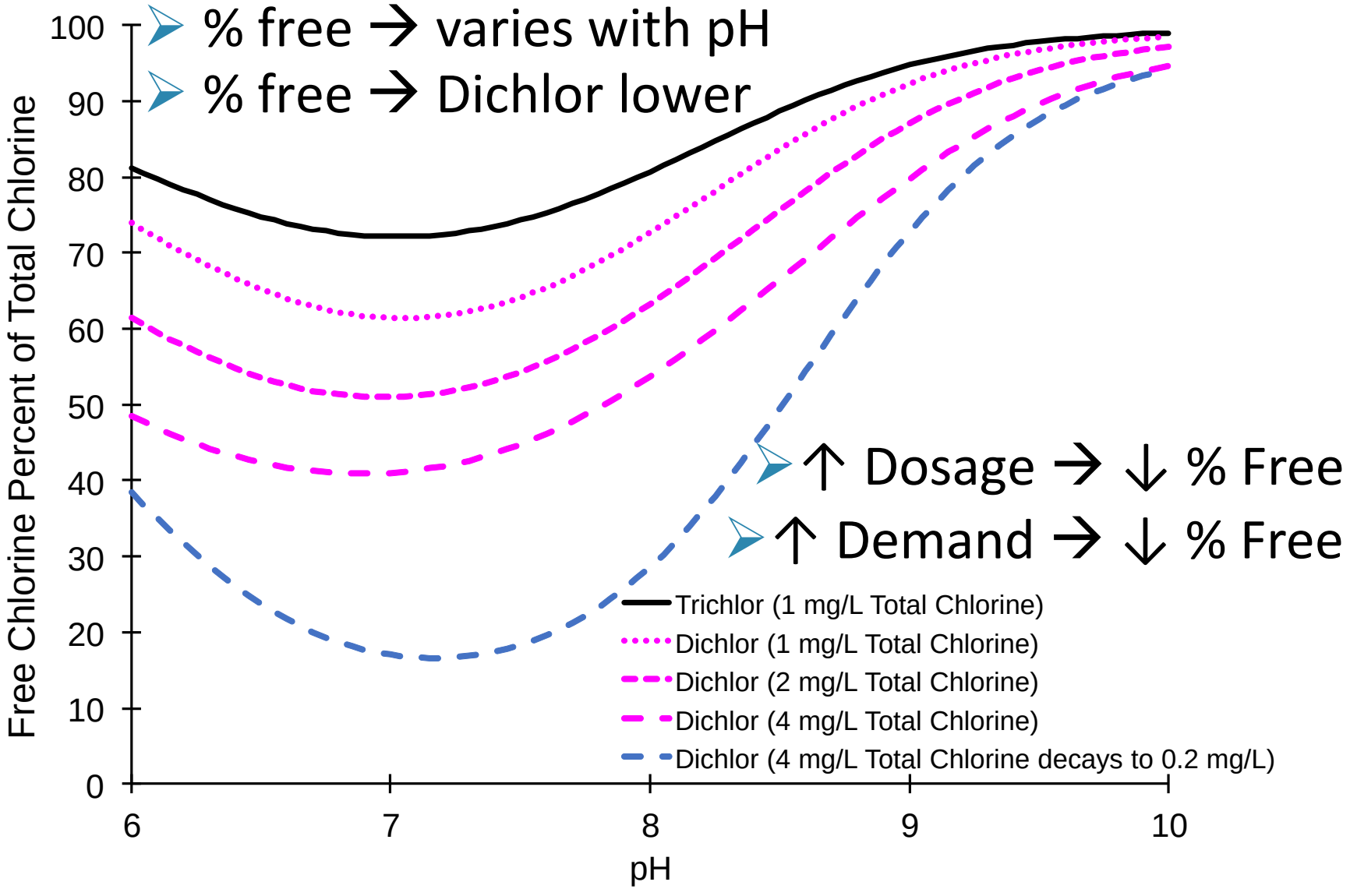
Water Chemistry

- Issue → free chlorine measurement interference
- 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
  - Total chlorine (TOTCl) mass balance
  - Total cyanurate (TOTCy) mass balance
  - Free chlorine equilibrium (temperature dependent)
  - 9 cyanurate equilibrium (temperature dependent)
- Unknowns = Equations → Solvable

Free Chlorine % Variation



Free Chlorine Measurement

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

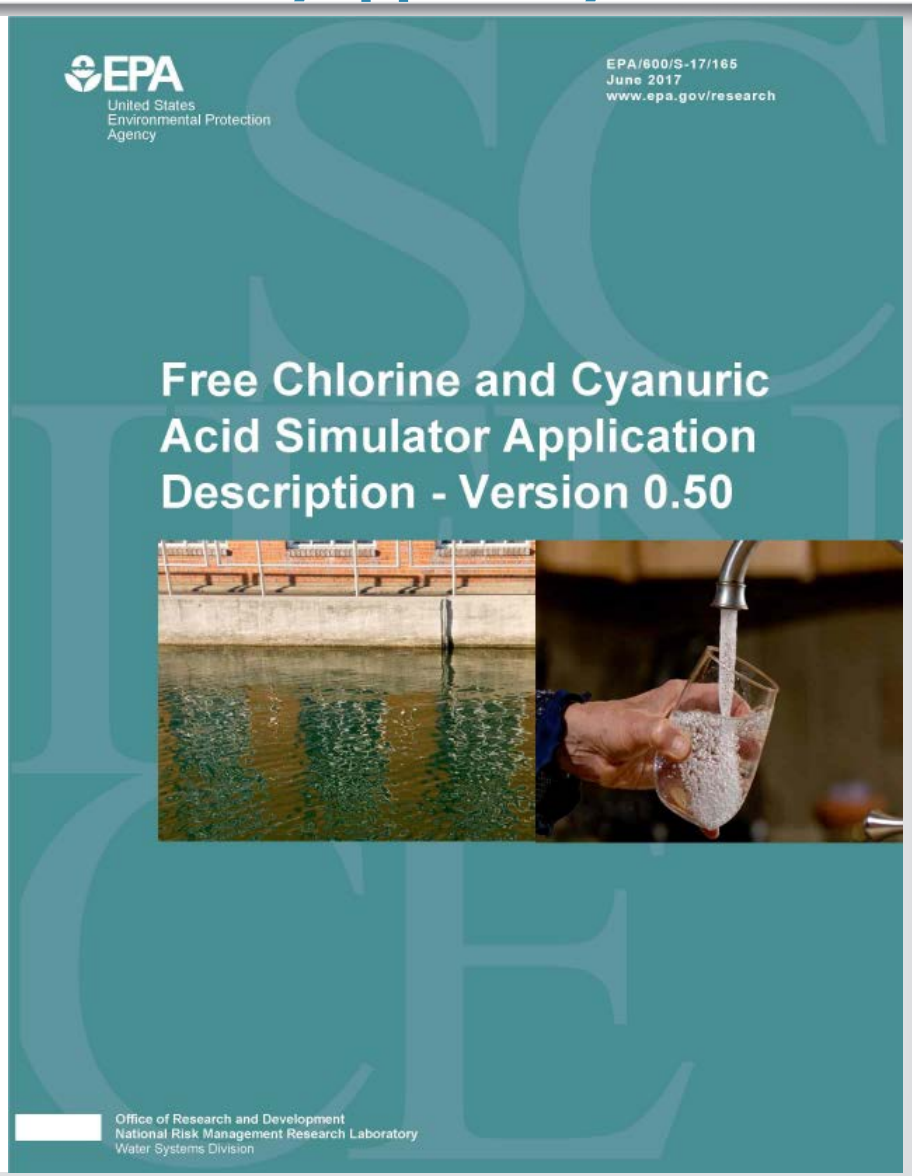
Free Chlorine Measurement

- 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 → free chlorine DPD
  - Total cyanurate
    - Current methods for pools (> 5 mg/L CYA)
    - Need drinking water field method (0.1–5 mg/L CYA)
    - Alternative → Estimate from chemical dosing
  - Temperature limitation
    - Only known for 25°C
    - 10 equilibrium constants

Free Chlorine & CYA App

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

- Assumptions
  - Full O'Brien model → 25°C
  - Know total chlorine
  - Know total cyanuric acid
  - 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



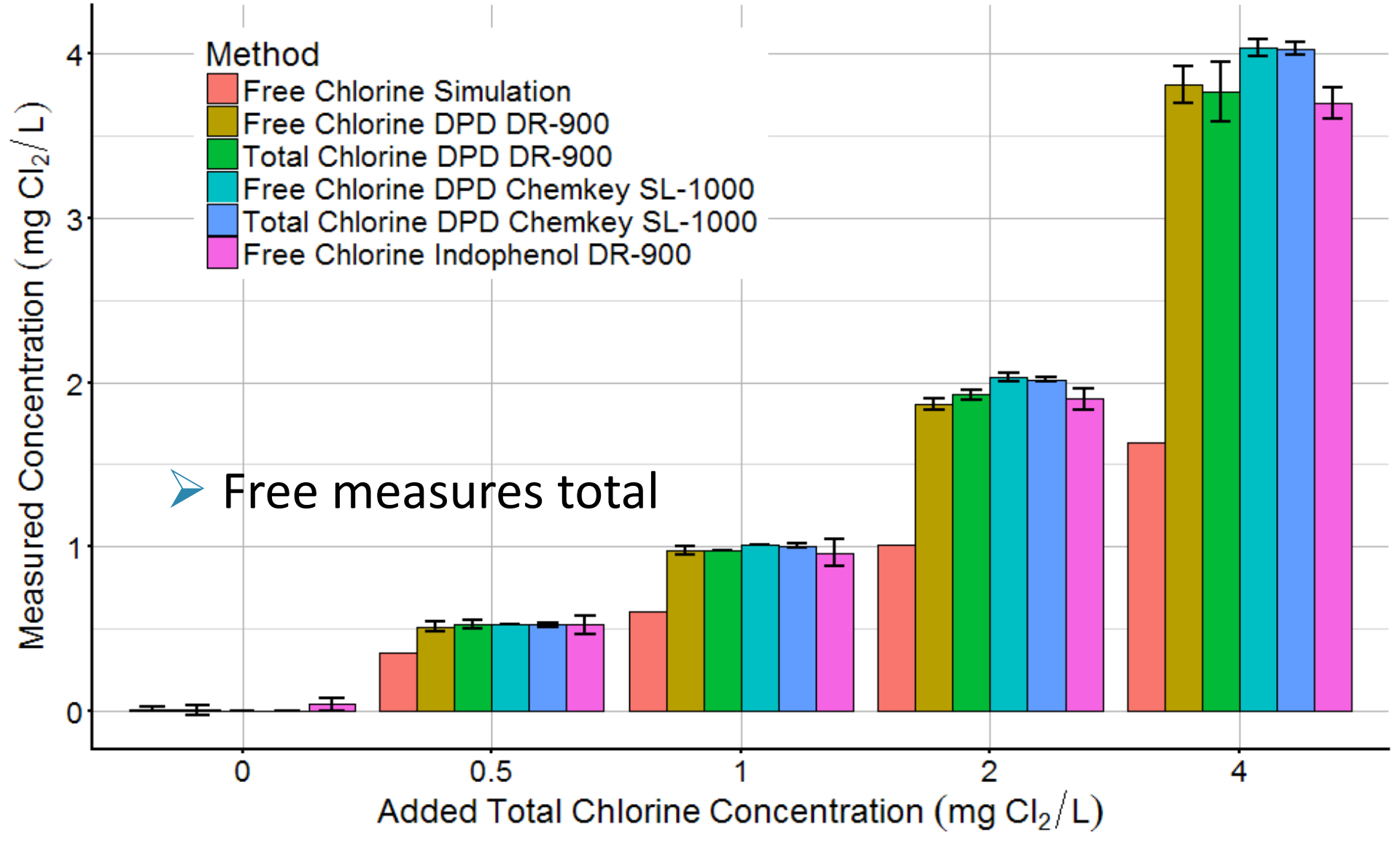
Research Objectives

1. Evaluate free chlorine method interferences (old and new)
2. Evaluate residual stability and regulated DBP formation
3. Update water chemistry model to include temperature dependence

Method Interference Study

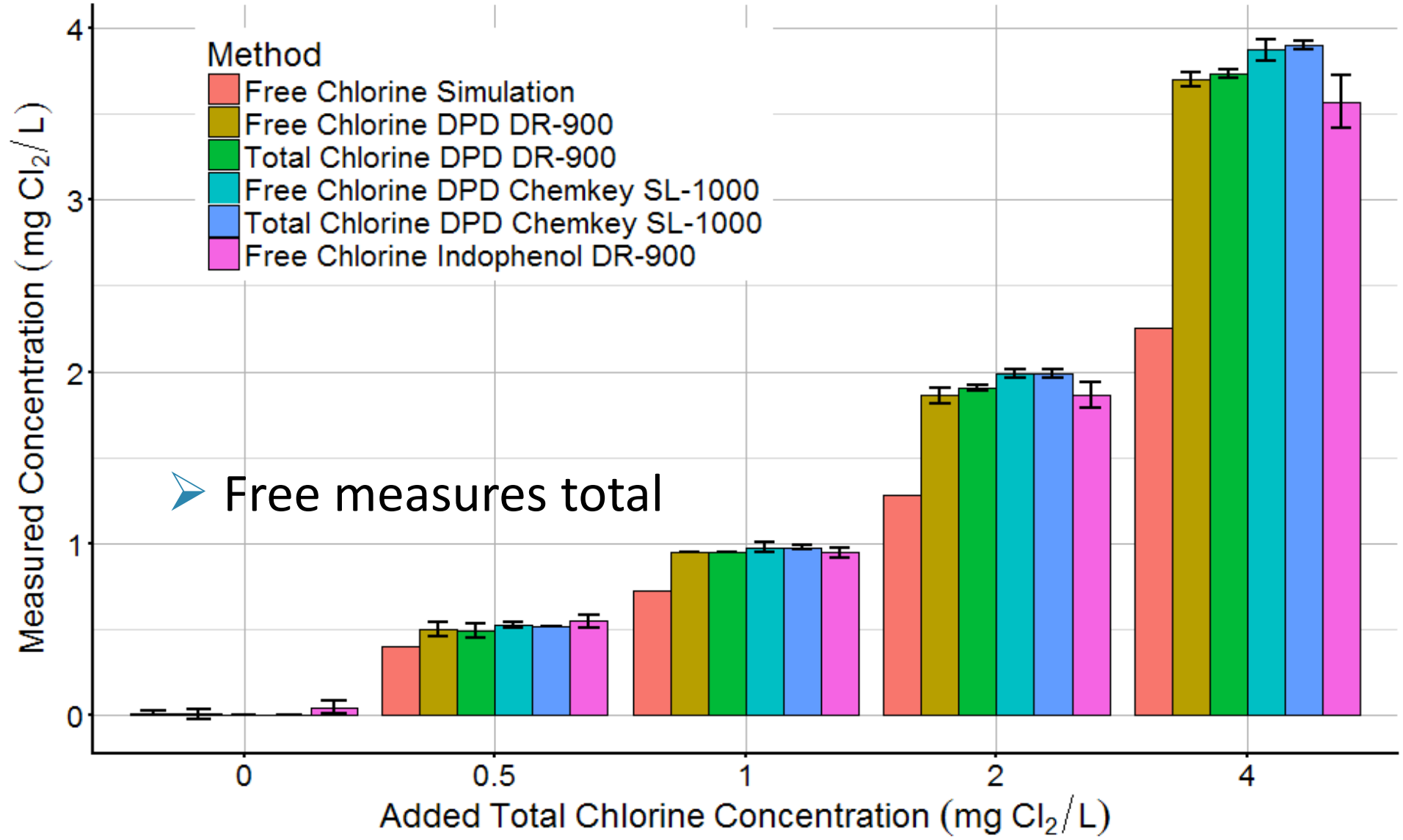
- Various solutions
  - Free chlorine & cyanuric acid, dichlor, & trichlor
  - pHs 7.0, 7.5, or 9.0
- Multiple methods
  - DPD based
    - Free chlorine & total chlorine
    - DR900 colorimeter & SL1000 portable parallel analyzer
  - Free chlorine indophenol (DR900)
  - Amperometric titration
- Compared results
  - Across methods
  - Versus simulated free chlorine → O'Brien model

Dichlor at pH 7



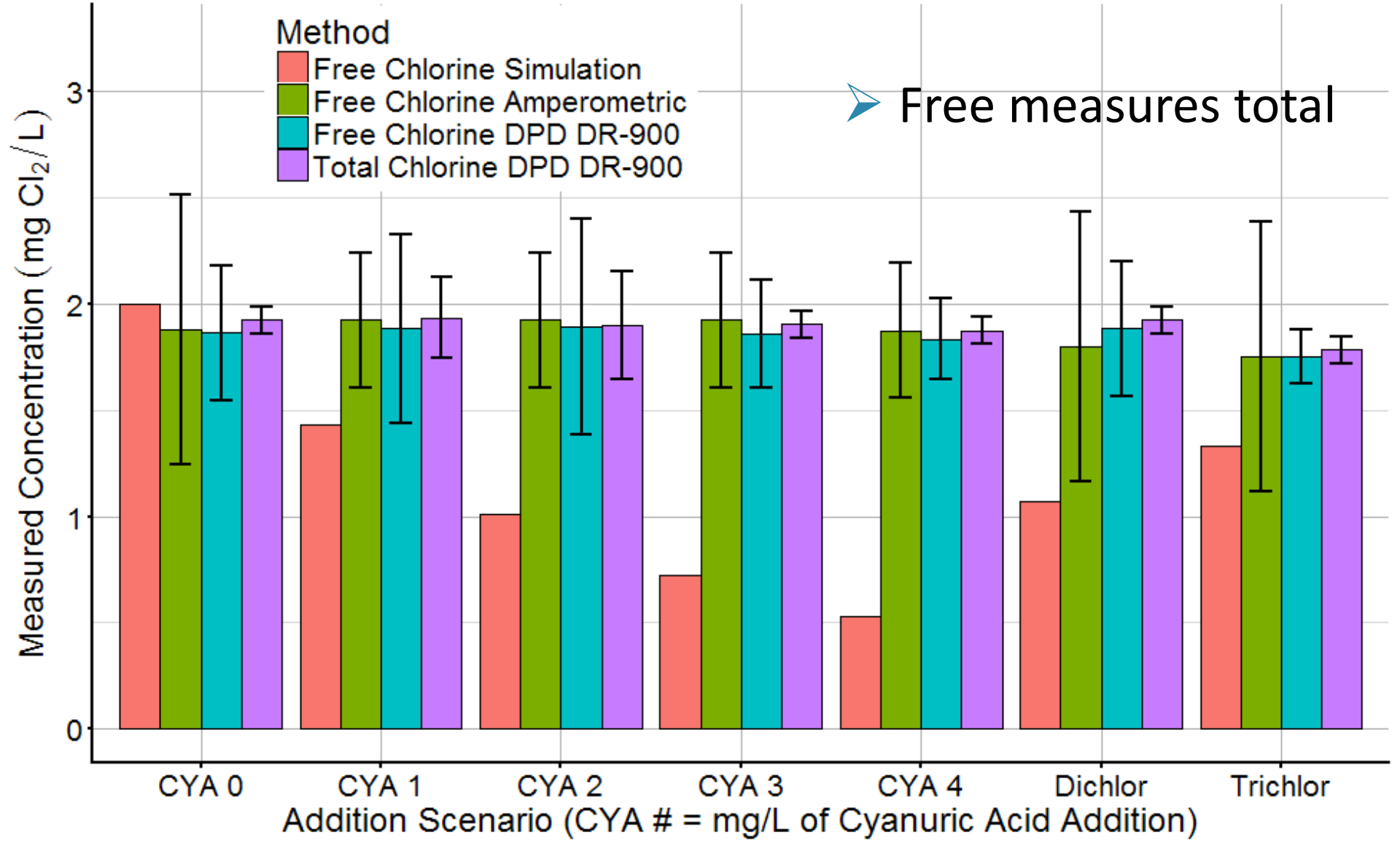
- Free measures total

Trichlor at pH 7



- Free measures total

2 mg Cl_2/L at pH 7.5



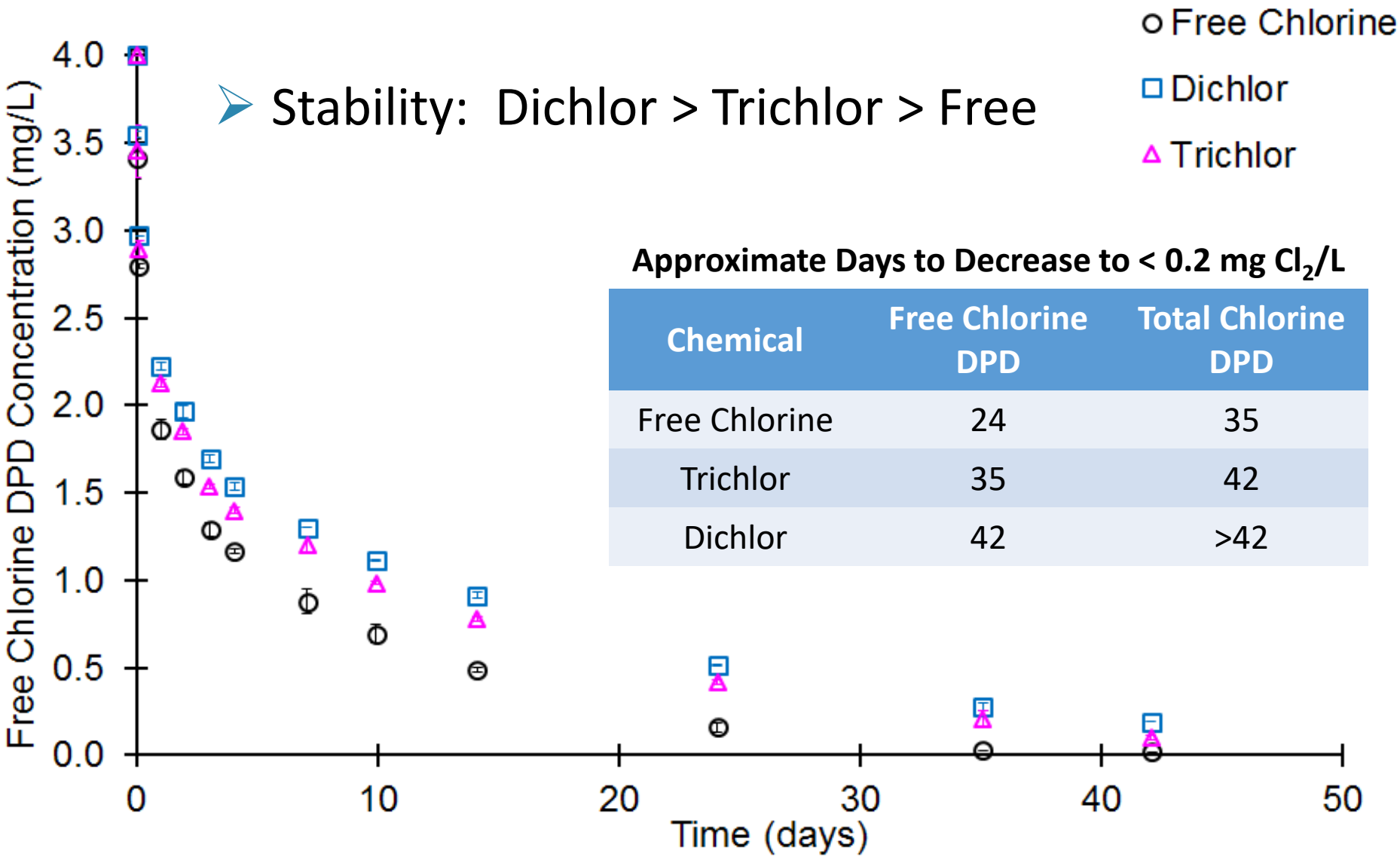
- Free measures total

Stability & DBPs – Hold Study

- Surface water → 3.8 mg C/L TOC
- Jar test water
  - 110 mg/L polyaluminum chloride
  - 0.75 mg/L potassium permanganate
  - Settled water → 2.3 mg C/L TOC
- Duplicate experiments
  - Free chlorine, dichlor, and trichlor
  - 4 mg Cl_2/L chlorine dose
  - 7.50 ± 0.18 pH & room temperature (22°C)
- Measurements
  - Free and total chlorine
  - THM4 and HAA5

Residual Stability Comparison

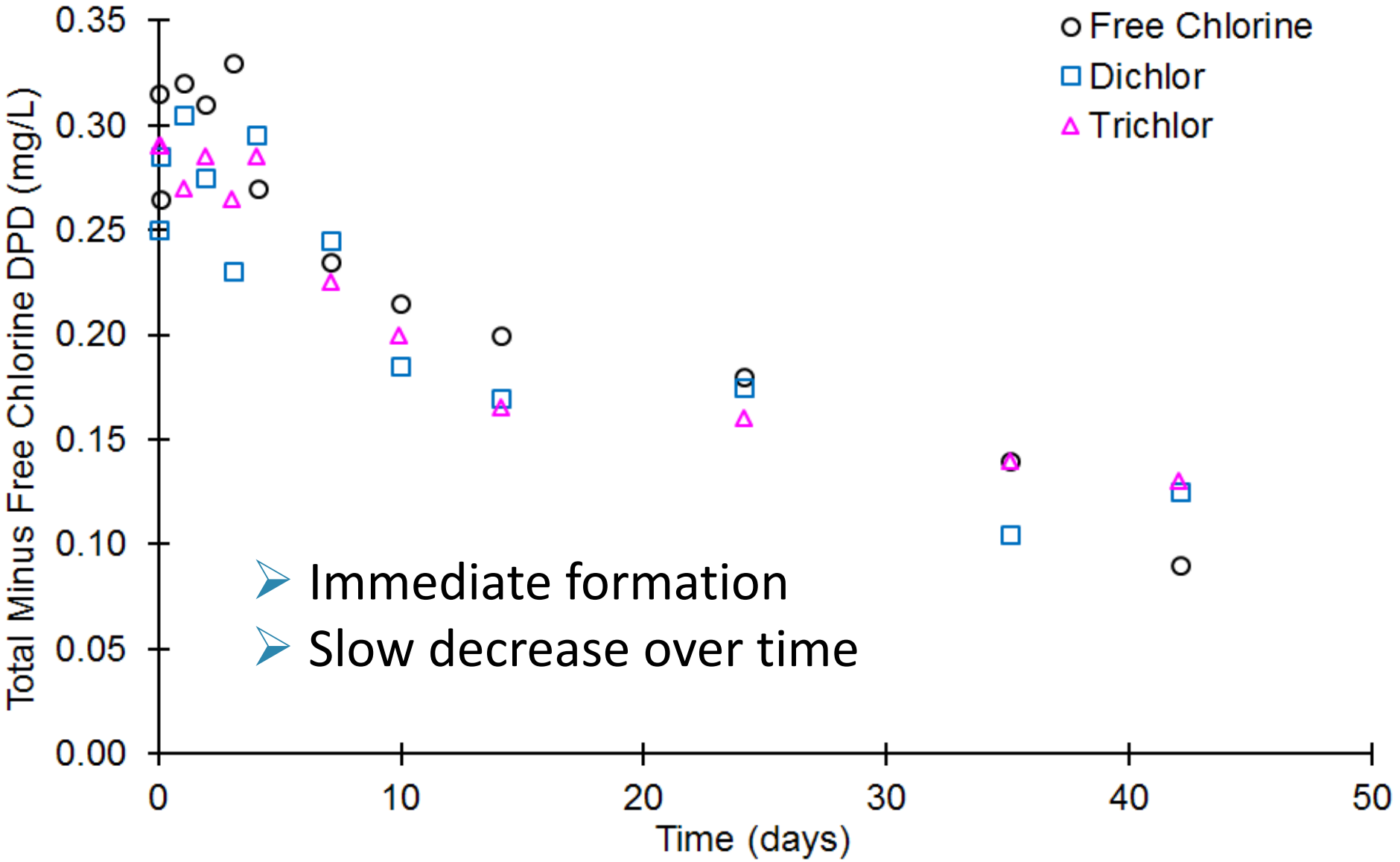
- Stability: Dichlor > Trichlor > Free



Approximate Days to Decrease to < 0.2 mg Cl_2/L

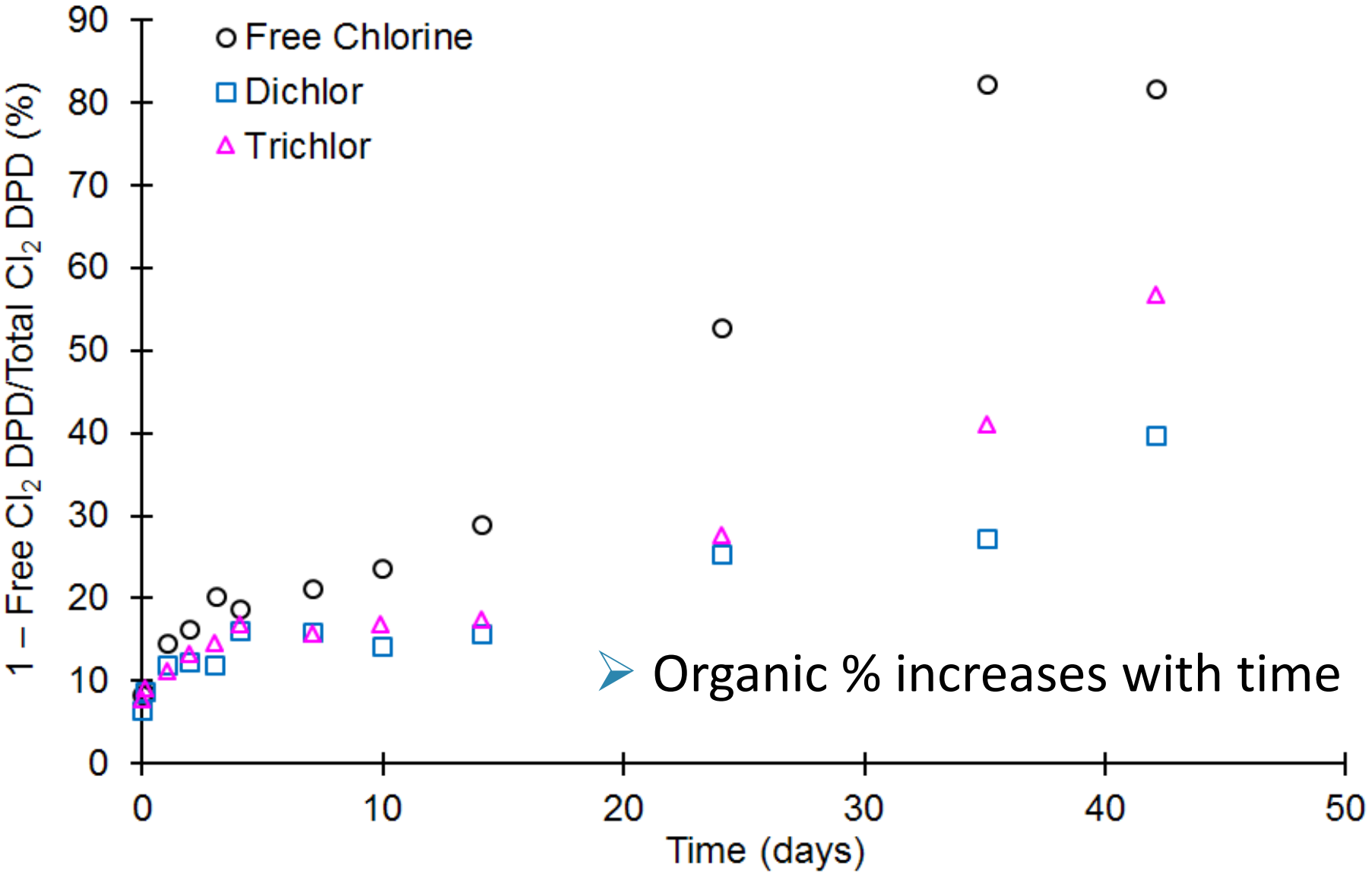
Chemical	Free Chlorine DPD	Total Chlorine DPD
Free Chlorine	24	35
Trichlor	35	42
Dichlor	42	>42

Organic Chloramine Formation



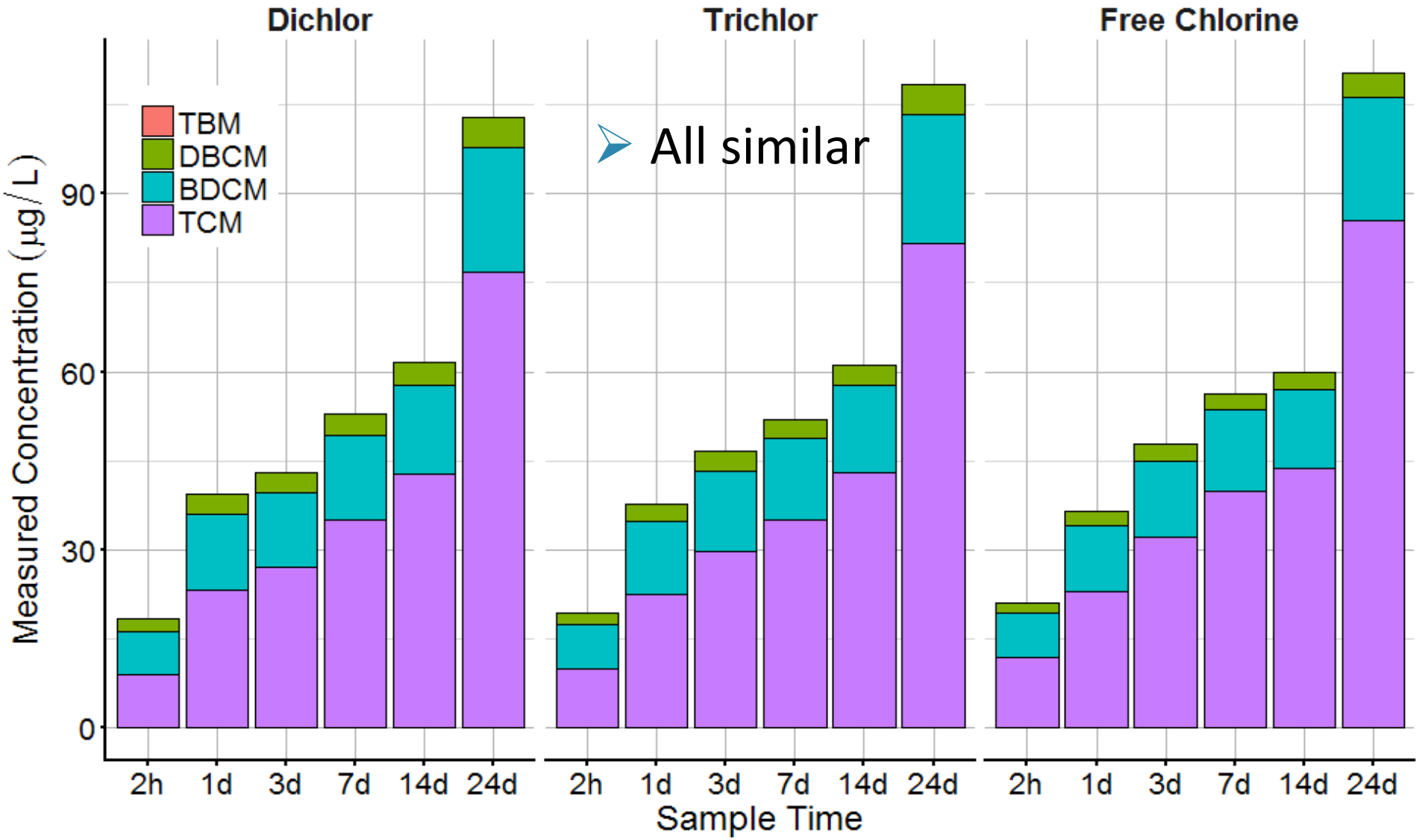
- Immediate formation
- Slow decrease over time

Percent Organic Chloramines



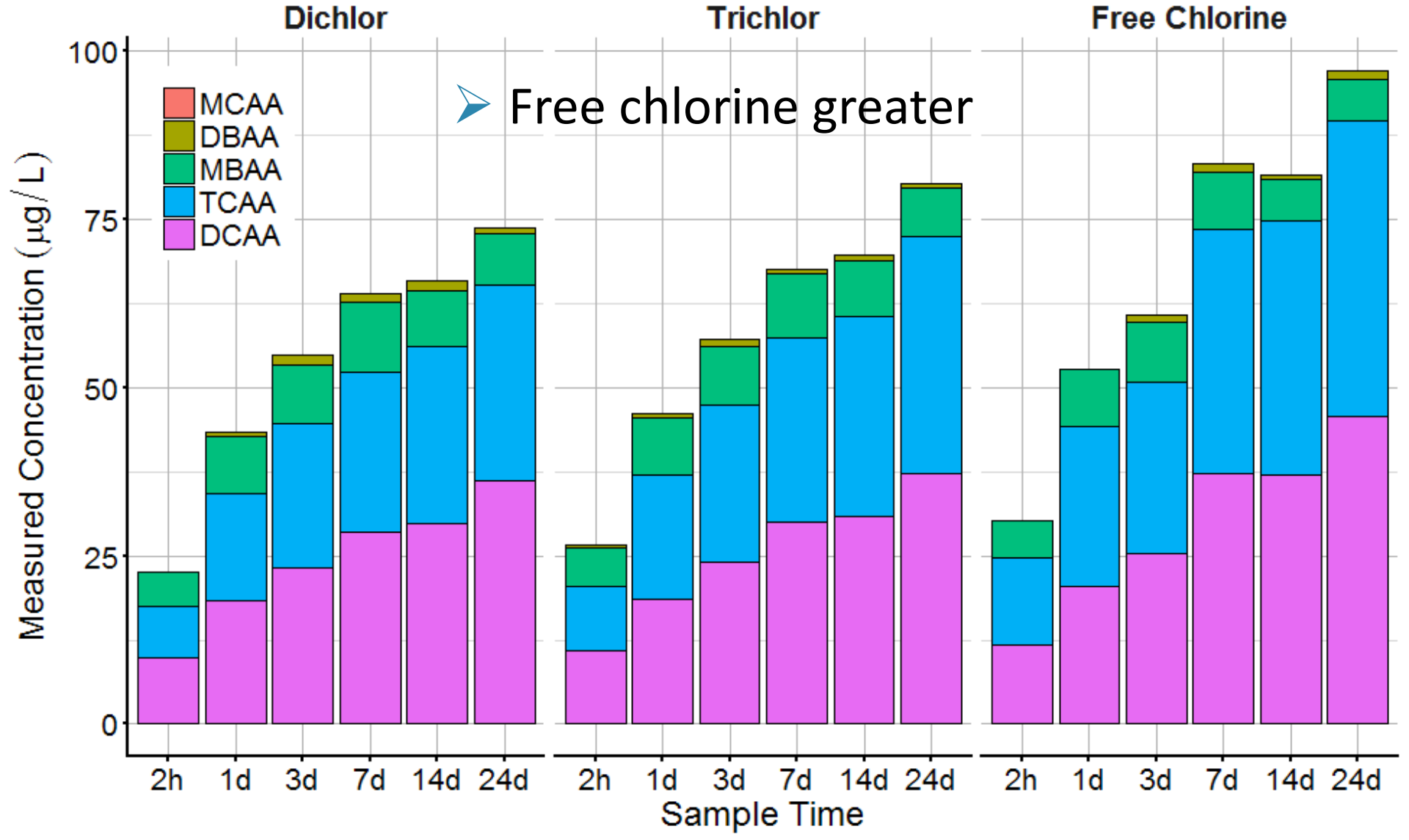
- Organic % increases with time

THM4 Formation & Speciation

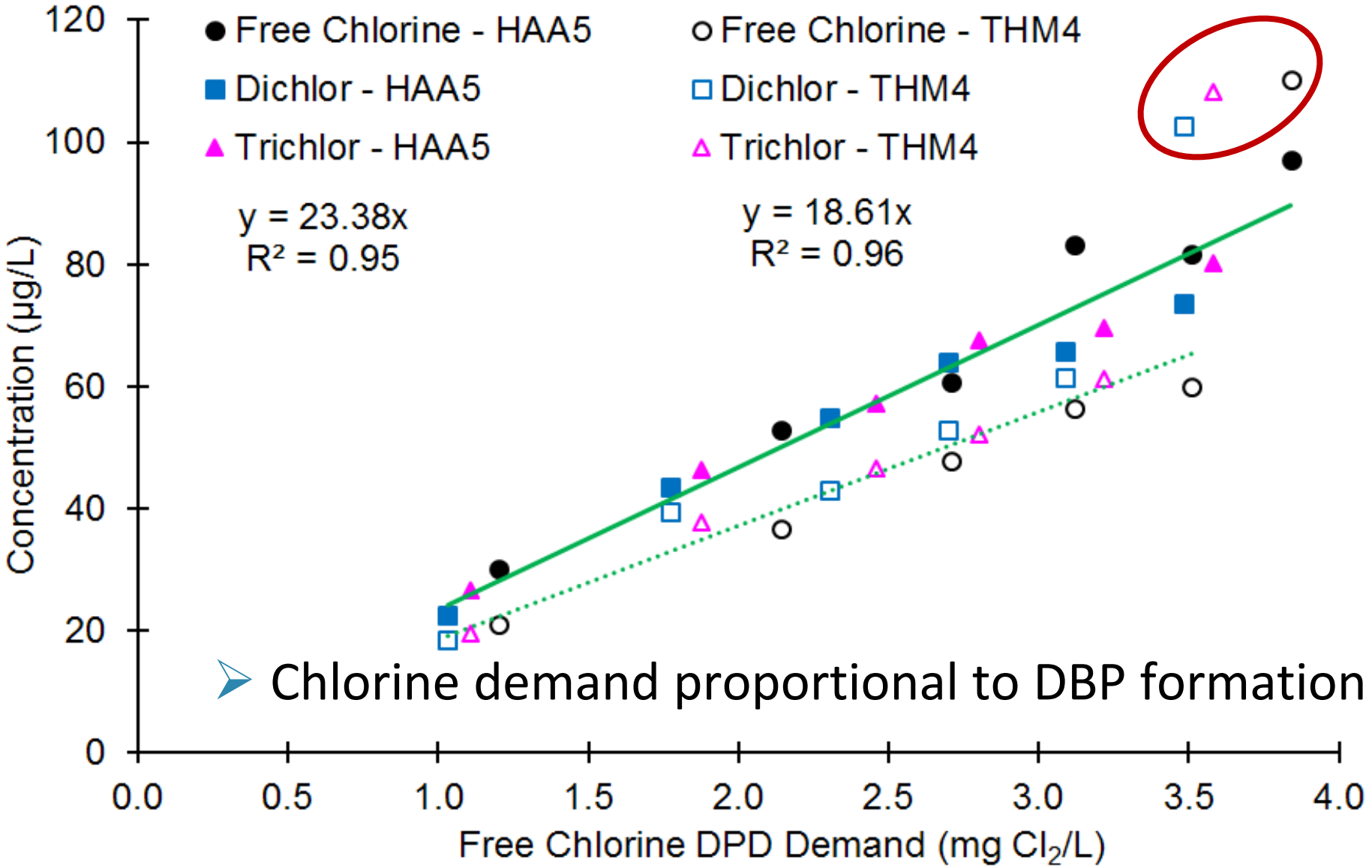


- All similar

HAA5 Formation & Speciation

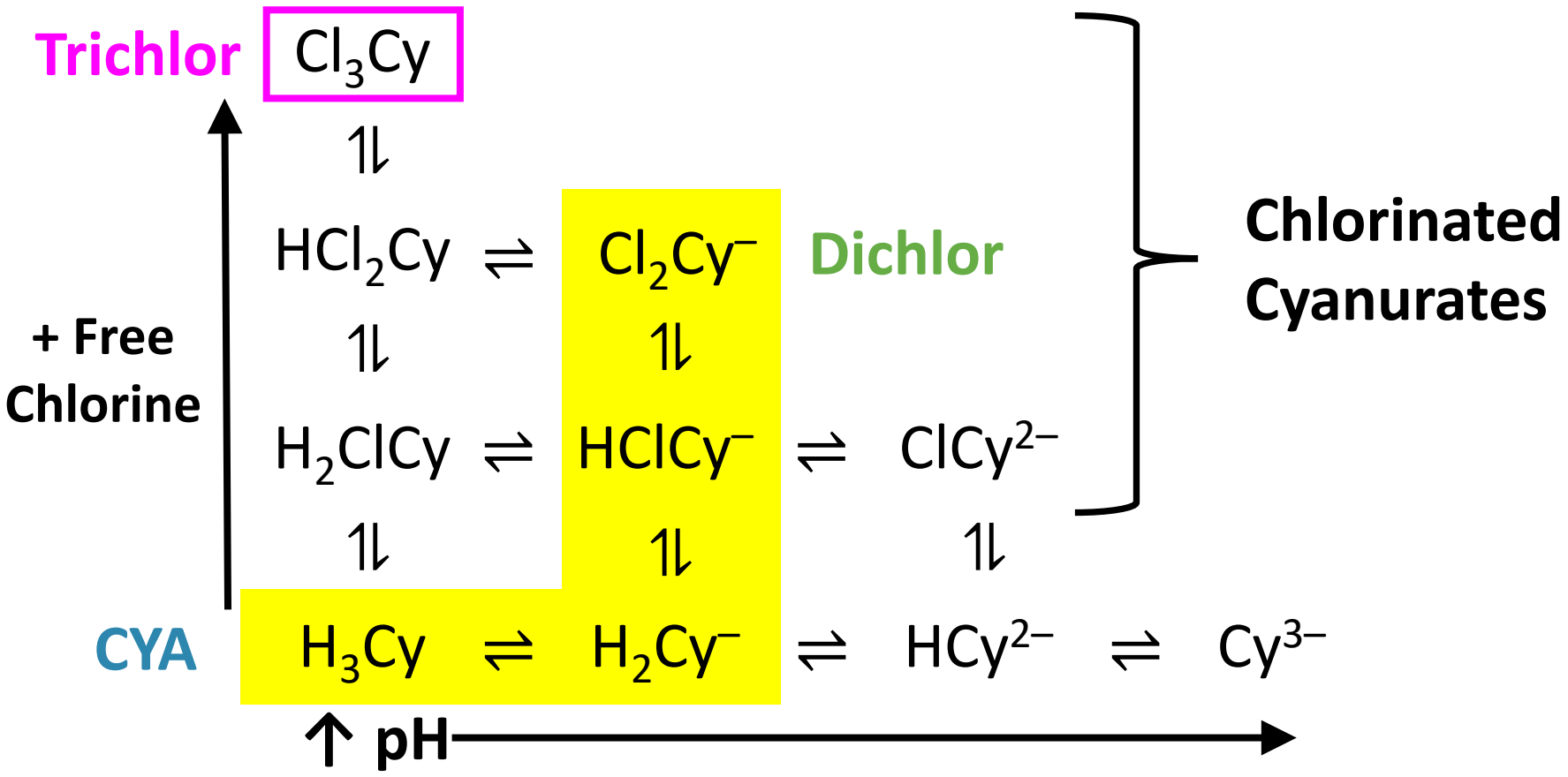


Formation vs. Chlorine Demand



- Chlorine demand proportional to DBP formation

Model Simplification?



- **Simplified model for drinking water?**

Simplified Model

$$HOCl \overset{K}{\rightleftharpoons} OCl^-$$

$$H_3Cy \overset{K_6}{\rightleftharpoons} H_2Cy^-$$

$$HClCy^- \overset{K_{9a}}{\rightleftharpoons} H_2Cy^- + HOCl$$

$$Cl_2Cy^- \overset{K_{7a}}{\rightleftharpoons} HClCy^- + HOCl$$

$$TOTCl = HOCl + OCl^- + HClCy^- + 2Cl_2Cy^-$$

$$TOTCy = H_3Cy + H_2Cy^- + HClCy^- + Cl_2Cy^-$$

- 6 chemical species
  - 2 free chlorine
  - 2 cyanuric acid
  - 2 chlorinated cyanurates
- 6 equations (4 equilibrium, 2 mass balance)

Simplified Model - Temperature

Morris (1966), T in Kelvin

$HOCl \rightleftharpoons OCl^- + H^+$ $\qquad K = 10^{-\left(\frac{3000}{T} - 10.0686 + 0.0253T\right)}$

Solastiouk (1989), T in Kelvin

$H_3Cy \rightleftharpoons H_2Cy^- + H^+$ $\qquad K_6 = 10^{-\left(31.08 - 0.154T + 2.44x10^{-4}T^2\right)}$

O'Brien (1972), 25°C

$HClCy^- + H_2O \rightleftharpoons HOCl + H_2Cy^-$ $\qquad K_{9a} = 10^{-5.62}$ at 25°C

$Cl_2Cy^- + H_2O \rightleftharpoons HOCl + HClCy^-$ $\qquad K_{7a} = 10^{-4.51}$ at 25°C

- **K_{7a} & K_{9a} temperature dependence?**

Temperature Study Experiments

- Various solutions
  - Added free chlorine → 2 or 4 mg Cl_2/L
  - Added cyanuric acid → 0, 1, 2, 3, or 4 mg/L
  - pHs → 7.5, 8.3, or 9.0
- Temperature controlled room
  - 5, 10, 15, 20, 25, 30, or 35°C
  - Duplicate experiments at 5, 20, and 35°C
- Free chlorine determination
  - % free chlorine = $Abs_{292nm,\ sample}$ / $Abs_{292nm,\ free\ only}$
  - Free chlorine = % free chlorine * free chlorine DPD

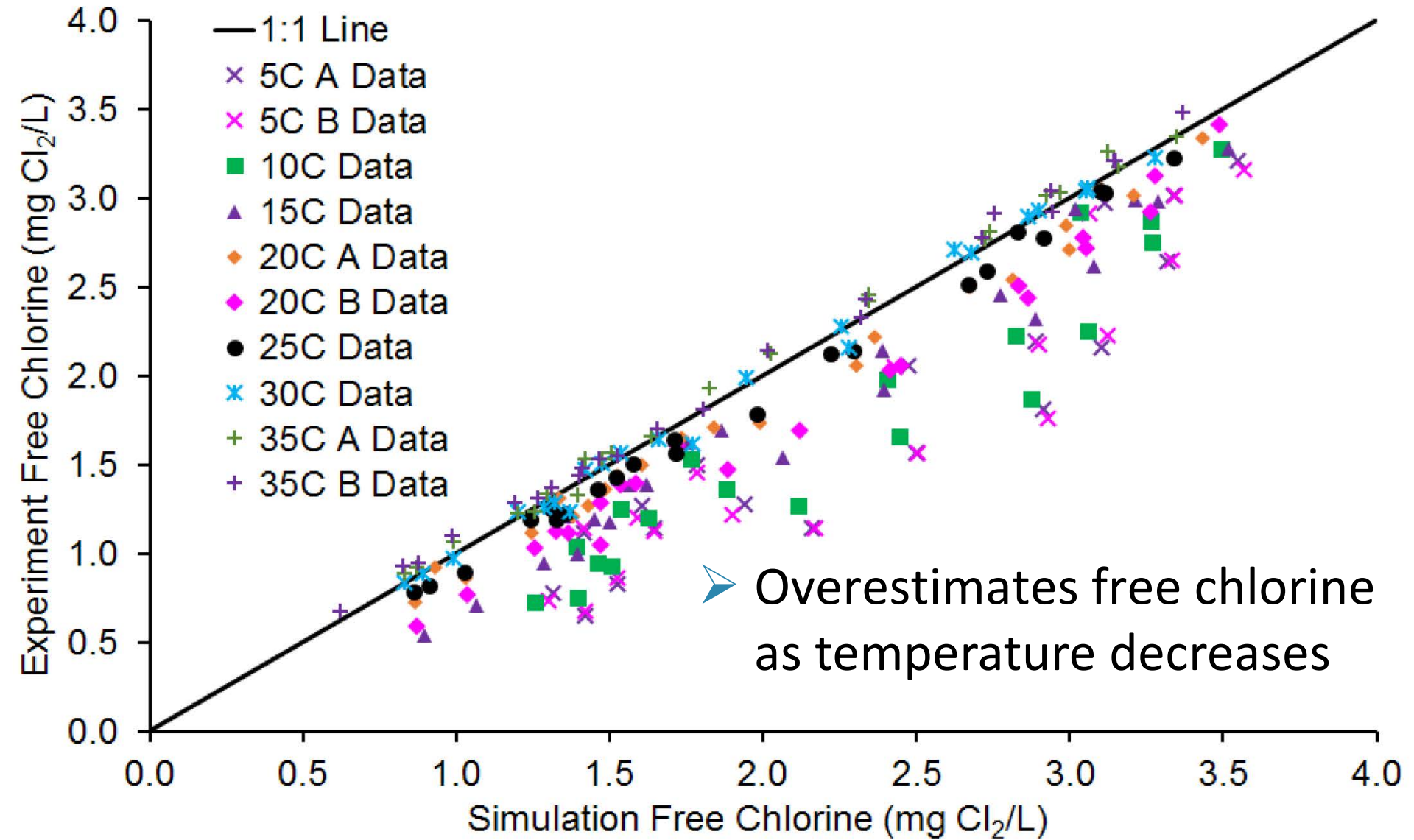
Temperature Study Analysis

$HClCy^- + H_2O \rightleftharpoons HOCl + H_2Cy^-$ $\quad K_{9a} = 10^{-5.62}$ at 25°C

$Cl_2Cy^- + H_2O \rightleftharpoons HOCl + HClCy^-$ $\quad K_{7a} = 10^{-4.51}$ at 25°C

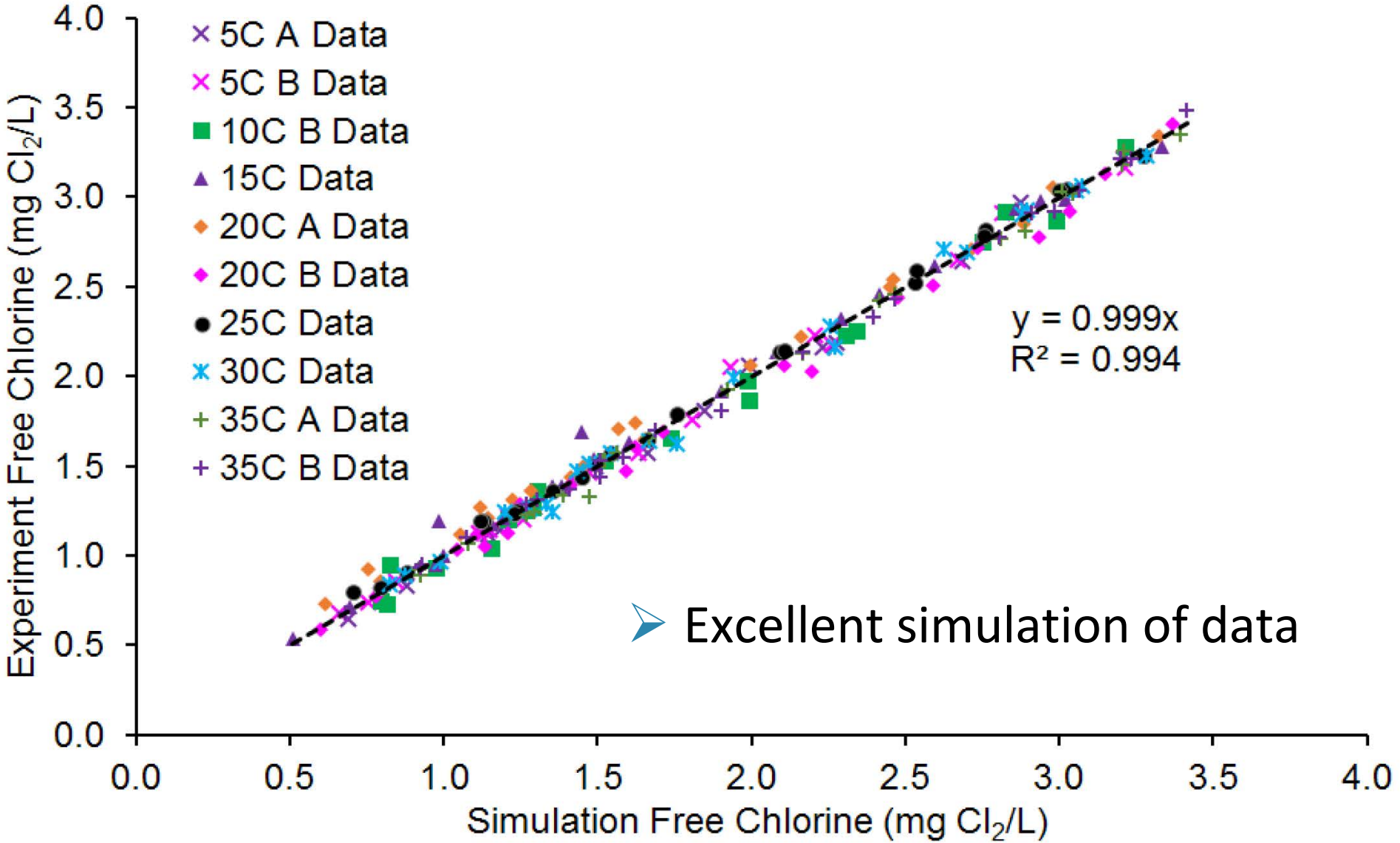
- Simplified model
  - y = free chlorine = [HOCl] + [OCl^-]
  - $ay^3 + by^2 + cy + d = 0$ and $y = f(pH, TOTCl, TOTCy, T, K_{eqs})$
- Parameters (K_{7a} & K_{9a})
  - Assume enthalpy change (ΔH^0) is temperature independent
  - $pK = A/T + B$ → T in Kelvin
  - Estimate → A_{7a}, A_{9a}, B_{7a}, B_{9a}
- Estimation → optim() & polynom() in R
  - 208 data points
  - Bootstrapping with replacement (n = 10,000)

O'Brien Simulations (25°C)



- Overestimates free chlorine as temperature decreases

Simplified Model with Temp.



- Excellent simulation of data

Parameter Estimate Summary

Parameter	Lower 95% CI	Estimate	Upper 95% CI
A_{7a}	1,538	1,920	2,305
B_{7a}	-3.12	-1.80	-0.50
A_{9a}	2,027	2,217	2,402
B_{9a}	-2.26	-1.64	-1.00
25°C pK_{7a}	4.58	4.64	4.70
25°C pK_{9a}	5.78	5.80	5.82
O'Brien pK_{7a}	4.46	4.51	4.56
O'Brien pK_{9a}	5.58	5.61	5.64

Results Summary

- All free chlorine methods measured total chlorine
- Residual stability → Dichlor > Trichlor > Free
- Organic chloramines
  - Initial formation
  - Increase in % of total chlorine with time
- Regulated DBPs
  - THM4 formation similar
  - HAA5 formation greater for free chlorine
  - Formation proportional to free chlorine DPD demand
- Model temperature dependence
  - K_{7a} & K_{9a} parameters estimated
  - Future implementation into web application

Questions?

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Contact Information

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