Preparation of Chloraminated Concentrated Drinking Water for Disinfection Byproduct Mixtures Research

Alison R. Kennicutt,
Paul Rossman,
Jacob Bollman,
Taylor Aho,
Gulizhaer Abulikemu,
Jonathan G. Pressman,
David G. Wahman

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Background

- Health effects research
  - Create DBP whole mixtures → known and unknown
  - No disinfectant residual
  - Concentrated natural organic matter (NOM)
- Concentration process (~140X)
- Developed in EPA Four Lab Project
- Free chlorine validated → representative DBP mixture
- Lyophilization (freeze-drying) process
  - Stable, transportable, and standardized
  - Reconstitute at greater NOM concentrations (~500X)
  - Free chlorine validated → representative DBP mixture
- Chloramination not studied/validated → Issues?

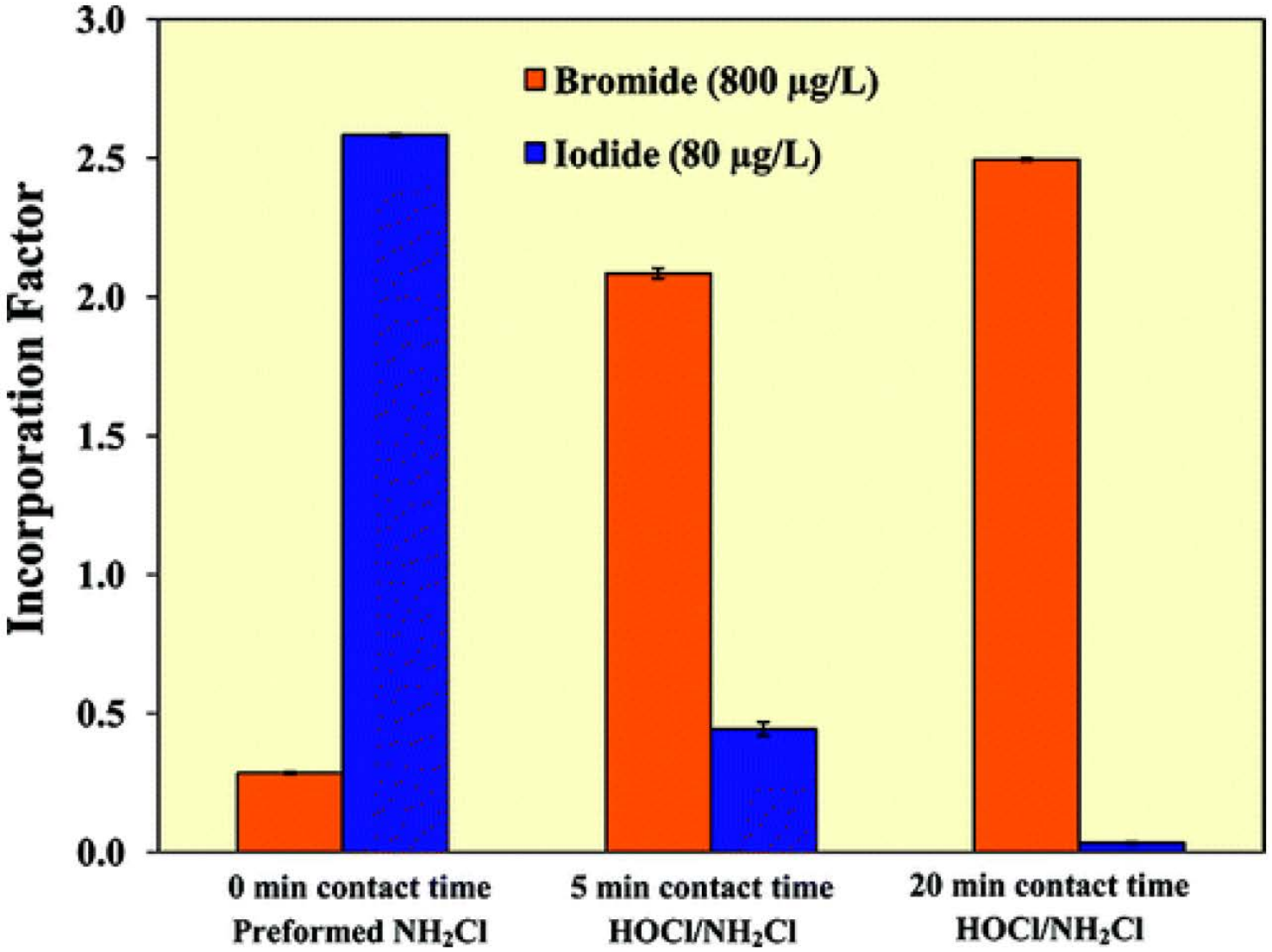
Issue #1 – Known DBP Speciation

$X_{Oxidant}$ + NOM → X_{DBPs} (X = Cl, Br, or I)

Toxicity → I_{DBPs} > Br_{DBPs} > Cl_{DBPs}

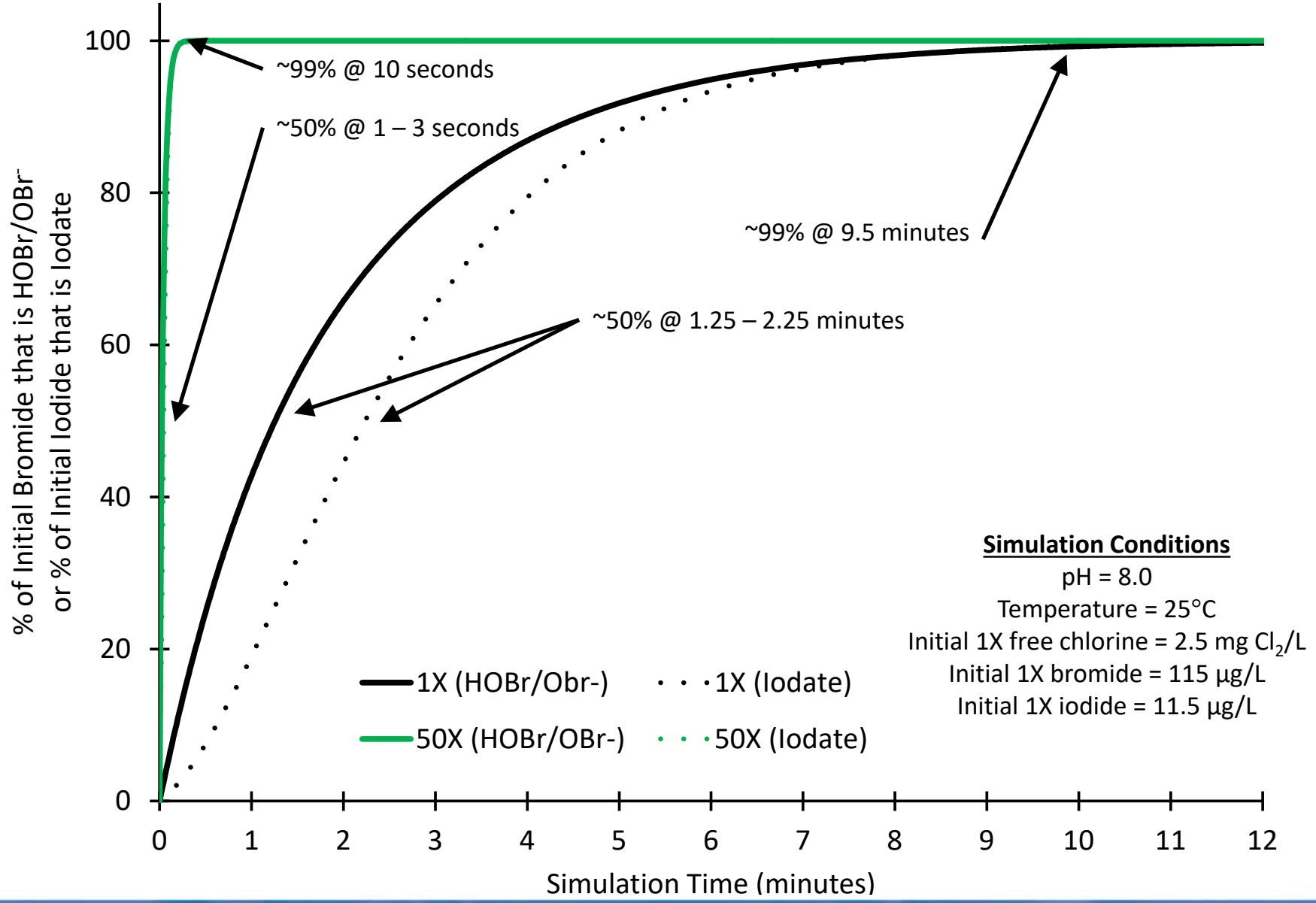
- Free chlorine only
  - HOCl/OCl^- (Cl_{DBPs})
  - Bromide → HOBr/OBr^- (Br_{DBPs})
  - Iodide → HOI/OI^- (I_{DBPs}) → Iodate (No I_{DBPs})
  - Favors Cl_{DBPs} & Br_{DBPs}
- Preformed chloramines
  - Chloramines (Cl_{DBPs})
  - Bromide → Bromamines/bromochloramines
  - Iodide → HOI/OI^- (I_{DBPs})
  - Favors Cl_{DBPs} & I_{DBPs} + nitrogenous DBPs (N_{DBPs})
- Free chlorine period + ammonia → chloramines
  - Short free chlorine period → Favors Cl_{DBPs}, Br_{DBPs}, & I_{DBPs} (>N_{DBPs})
  - Long free chlorine period → Favors Cl_{DBPs} & Br_{DBPs} (<N_{DBPs})

Issue #1 – Known DBP Speciation (con't)

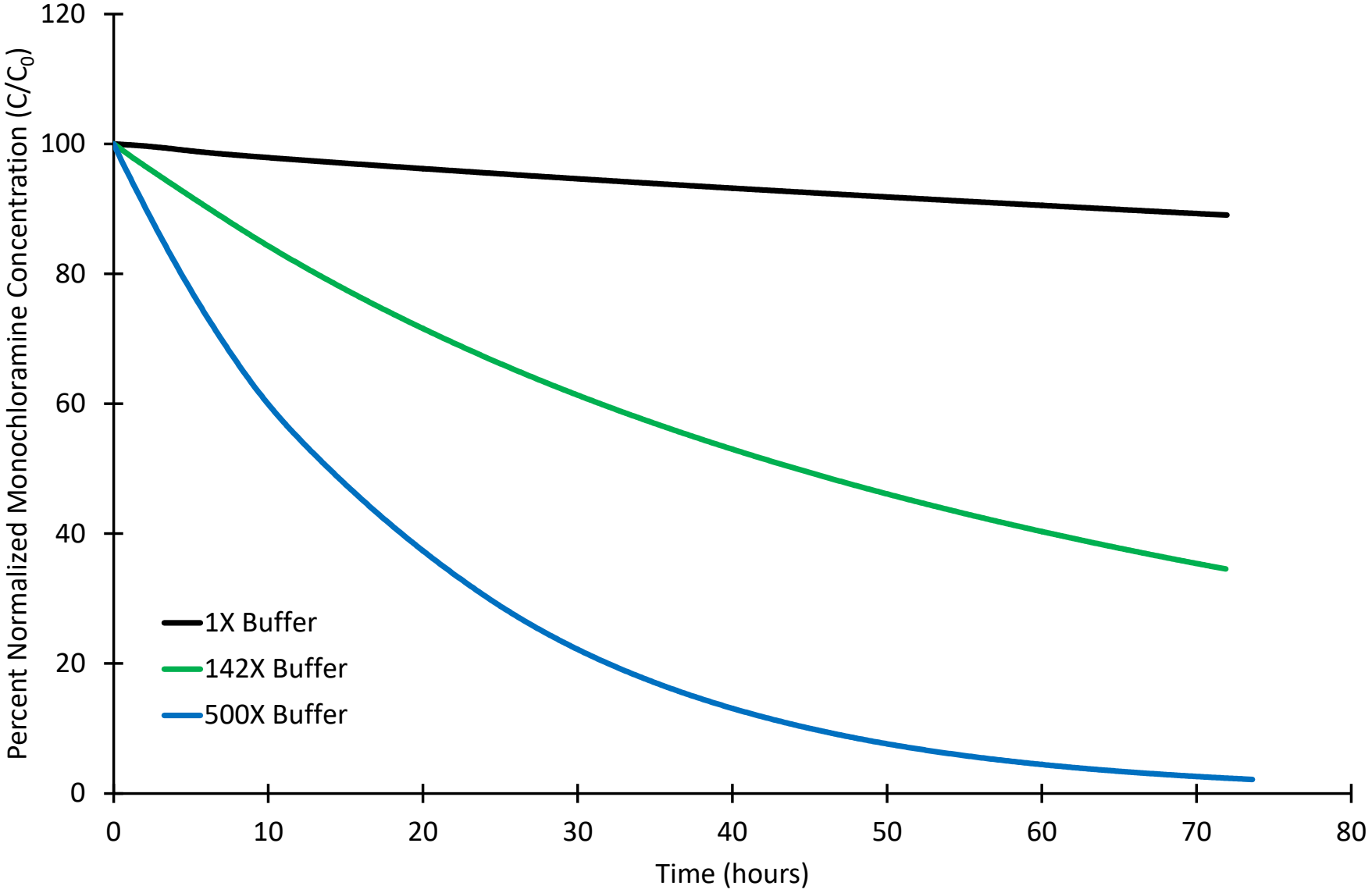


Source: Jones et al. (2011)

Issue #2 – Kinetic Scaling



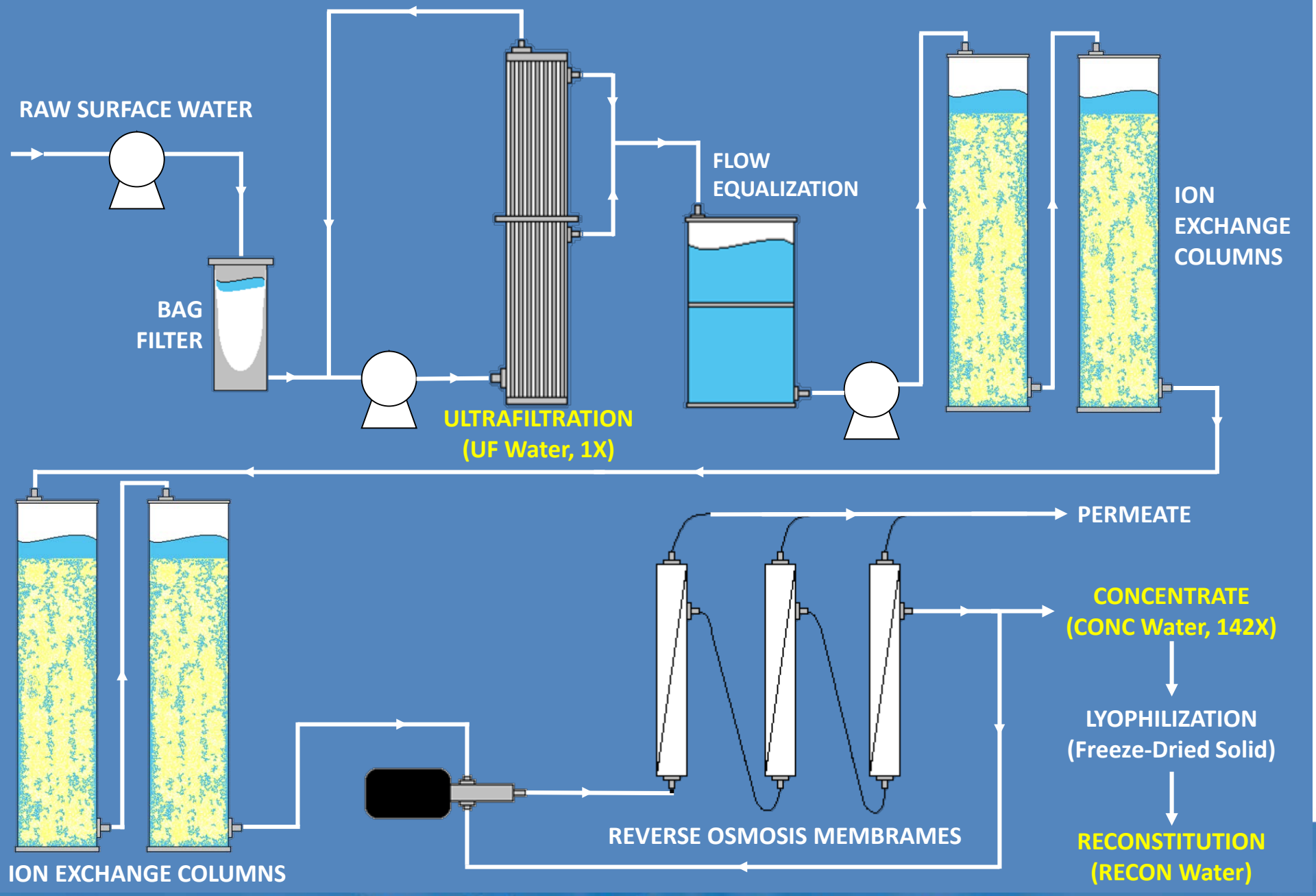
Issue #3 – Chloramine Stability



Objectives

- Develop a procedure to chloraminate concentrated/reconstituted NOM solutions
- Evaluate DBP mixture formation
  - Does the concentration and/or lyphilization processing change the DBP mixtures compared to source water?
  - What is the impact of the various chloramination methods?
  - How do the concentrated DBP mixtures scale relative to the unconcentrated waters?

Water Process Schematic



Experimental Waters

- Three water sources (via Ohio River)
  - UF = collected after ultrafiltration
  - CONC = reverse osmosis concentrate
  - RECON = reconstituted from lyophilized NOM
- Three concentration factors
  - 1X = UF1X, CONC1X, RECON1X
  - 142X = CONC142X, RECON142X
  - 500X = RECON500X
- General water conditions
  - pH 8.0
  - 1X bromide = 115 µg/L
  - 1X iodide = 11.5 µg/L
  - 1X total organic carbon = 2.0 mg C/L

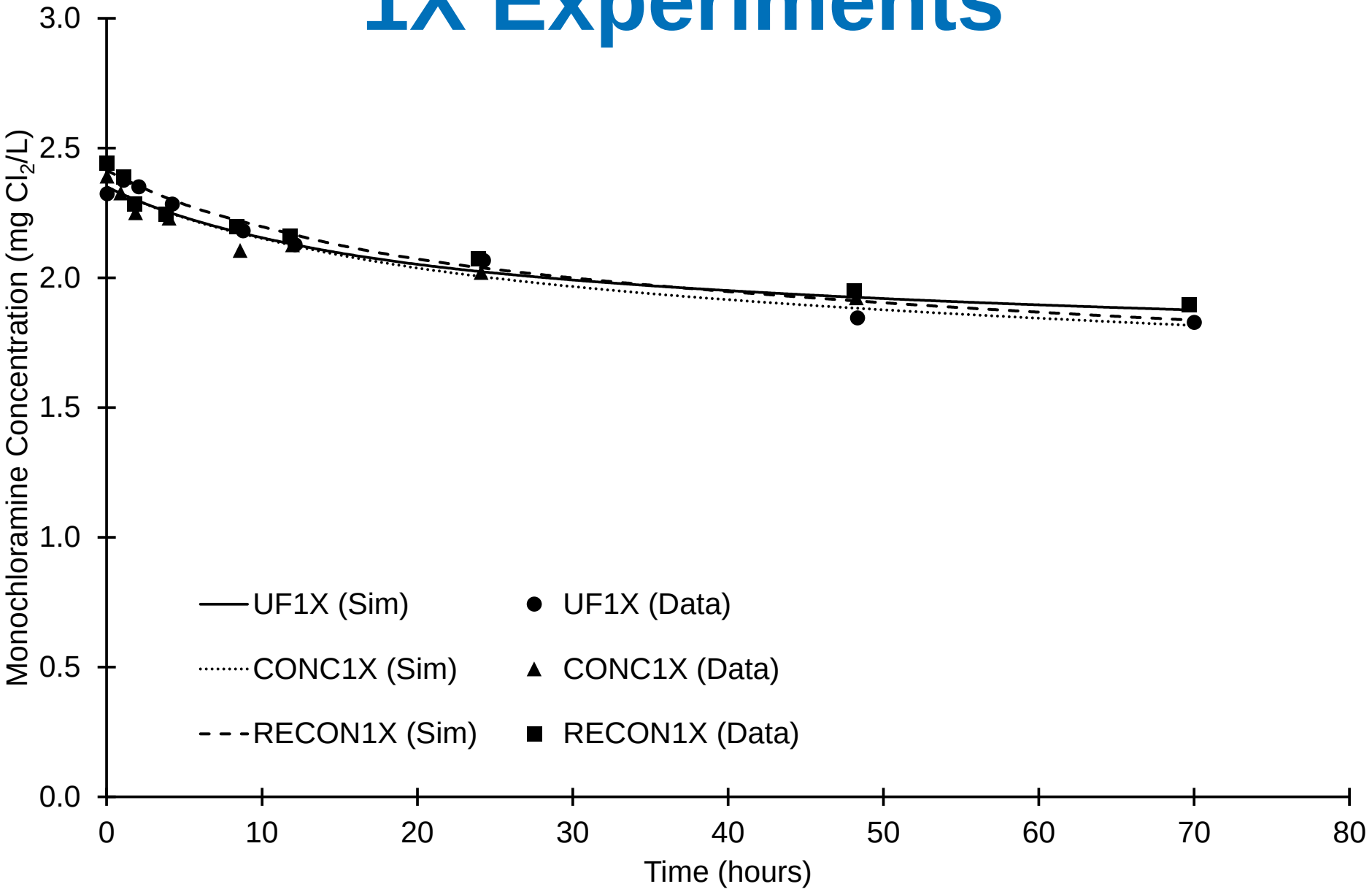
Experiment Types & Analysis

- Three experiment types
  - Preformed monochloramine
  - 3-min. free chlorine period → ammonia/monochloramine addition
  - 20-min. free chlorine period → ammonia/monochloramine addition
- 18 total experimental conditions (6 waters x 3 types)
- Analysis
  - 56 Individual DBPs
    - 10 THMs, 12 haloketones, 4 HANs, 1 HNMs, chloral hydrate
    - 12 HAAs, 9 haloamides
    - 7 nitrosamines
  - TOX, TOBr, TOI, total nitrosamines
  - Chlorate, bromate, iodate
  - Bromide and iodide

Research Approach (Preformed Chloramines)

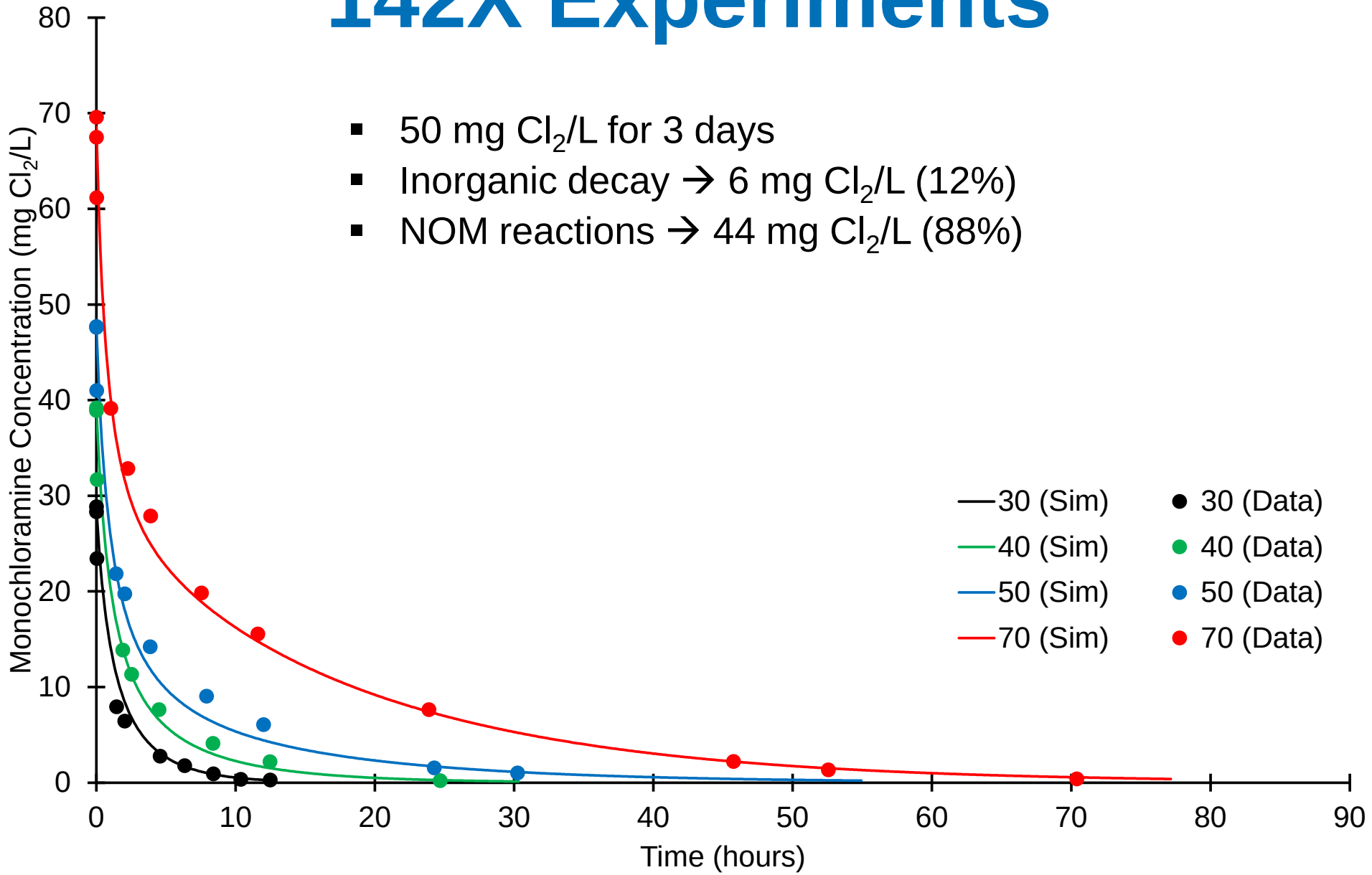
- Determine 1X chloramine consumption
  - Use NDMA formation potential test conditions
    - 2.5 mg Cl_2/L chloramines
    - 4.75:1 Cl_2:N ratio
    - 3 day reaction
  - Use kinetic model to analyze data
    - Apportion inorganic decay
    - Apportion reaction with NOM
    - Scale chloramine based on reaction with NOM
- Determine 142X & 500X conditions
  - Match scaled reaction with NOM
  - Zero residual at experiment end
  - Adjust initial chloramine and length as needed
- Conduct DBP experiments

1X Experiments



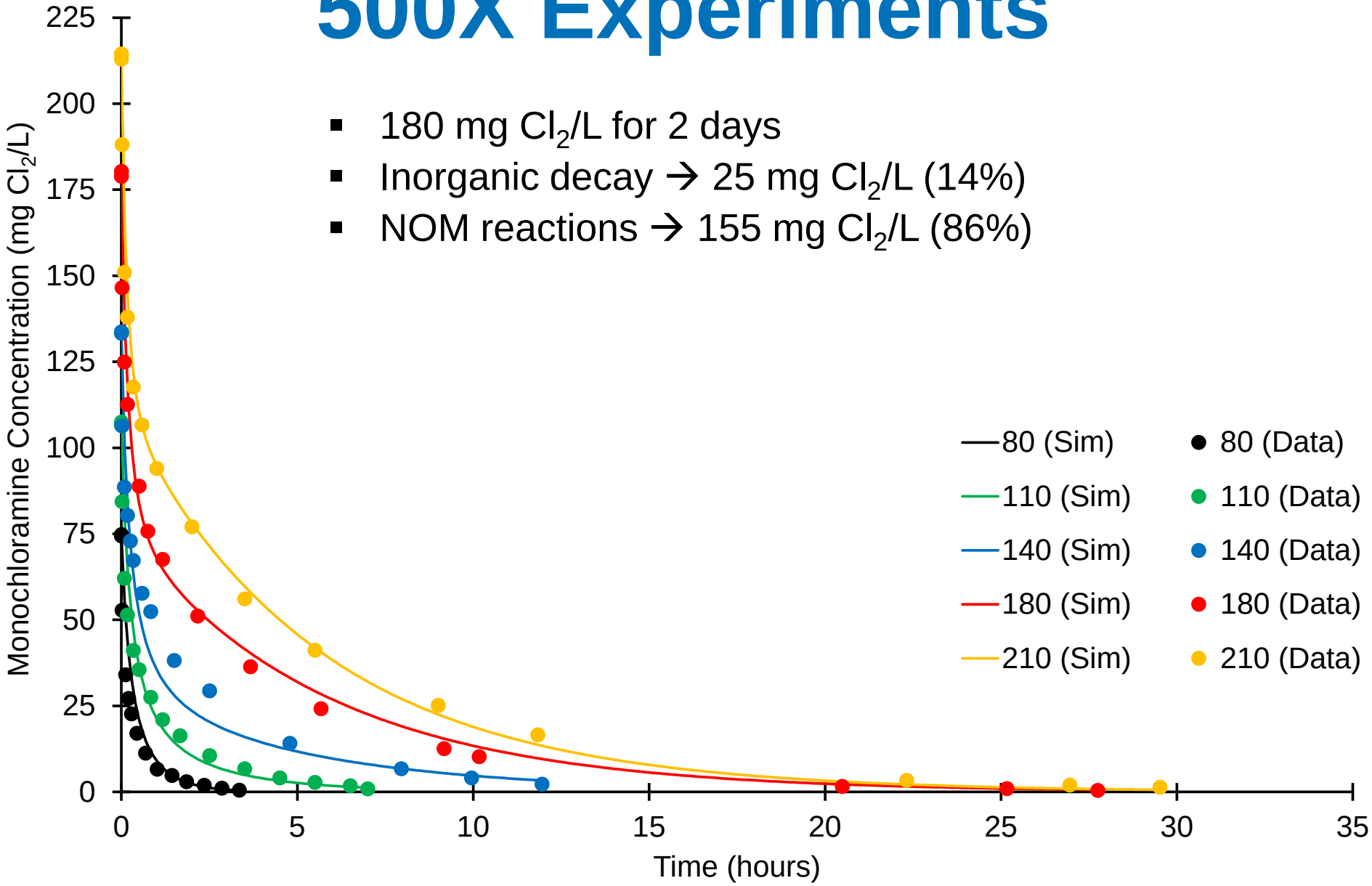
142X Experiments

- 50 mg Cl_2/L for 3 days
- Inorganic decay → 6 mg Cl_2/L (12%)
- NOM reactions → 44 mg Cl_2/L (88%)



500X Experiments

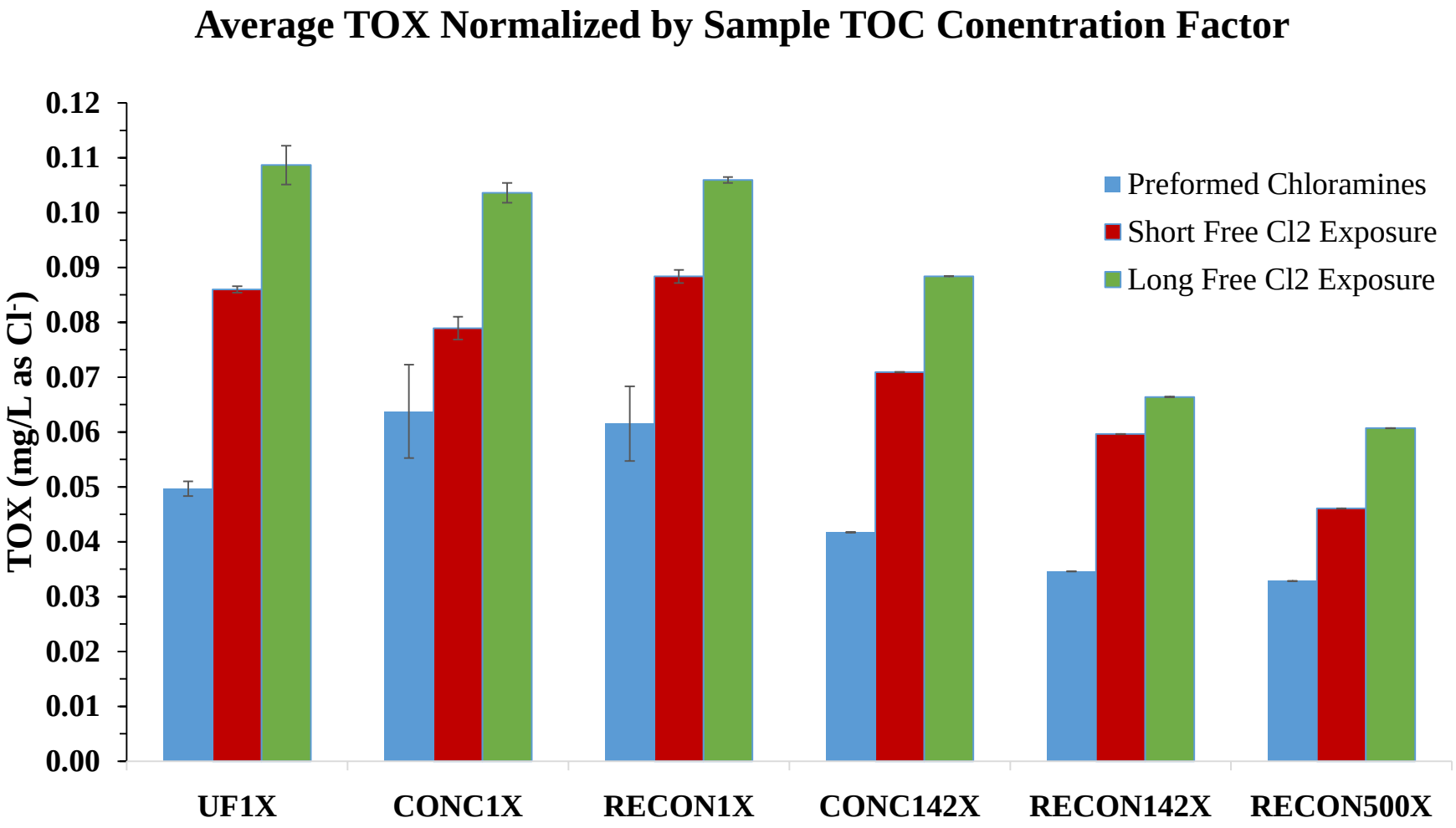
- 180 mg Cl_2/L for 2 days
- Inorganic decay → 25 mg Cl_2/L (14%)
- NOM reactions → 155 mg Cl_2/L (86%)



Data Analysis

- Evaluate NOM processing for chloramination
  - Comparing 1X DBPs (UF1X, CONC1X, RECON1X)
  - Comparing 142X DBPs (CONC142X, RECON142X)
- Evaluate impact of chloramine application method
- Assess scaling of DPB mixtures with regards to NOM concentration factors

Example: Total Organic Halogen (TOX)



Example: N-nitrosodi-n-butylamine (NDBA)