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Association

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AWWA WEBINAR AUGUST 5, 2020 | 11:00 A.M. - 12:30 P.M. MT

Disinfection By-Products:
Perspectives on Formation, Control and Mitigation

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WEBINAR MODERATOR



Chris Owen

**Director of Water and Reuse
Innovations**

Hazen and Sawyer

Chris is the Director of Water and Reuse Innovations for Hazen and Sawyer. She has 29 years of experience in water quality, research, treatment and regulatory compliance. Her utility roles have included regulatory compliance, research, laboratory management, source water assessment and protection, and distribution system issues. Research work included investigations of UF/MF/RO membranes, online monitoring, total coliform occurrence, enhanced coagulation, biofiltration, distribution system, corrosion, biostability, ion exchange, chloramine chemistry and stability, contaminants of emerging concern, and algal toxins. She is active in regulatory issues at the state and federal levels, promoting utility concerns and science-based decisions. She served on the USEPA SAB for Drinking Water and the USEPA NACEPT.

She is an active member of the American Water Works Association (AWWA), serving as a Trustee and the current Chair of the Water Science and Research Division. She is a Trustee for WateReuse FL and the President of the Board of Directors for the American Membrane Technology Association. She has been active in the Water Research Foundation (WRF) and the WateReuse Foundation for more than 20 years.

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PANEL OF EXPERTS



Susan Richardson
Arthur Sease Williams
Professor of Chemistry
University of South Carolina



Susan Teefy
Manager of Water Quality
East Bay Municipal Utility
District



Charlie (Qun) He
Vice President, Chief
Technologist – Decision Support
Carollo Engineers, Inc

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AGENDA

- | | |
|--|------------------|
| I. Identifying Key DBP Drivers of Toxicity | Susan Richardson |
| II. DBP Control Case Study | Susan Teefy |
| III. An Integrated Approach for DBP Mitigation | Charlie He |

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ASK THE EXPERT



Susan Richardson
University of South Carolina



Susan Teefy
East Bay Municipal Utility District



Charlie (Qun) He
Carollo Engineers, Inc

Enter your **question** into the **question pane** on the right-hand side of the screen.

Please specify to whom you are addressing the question.

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Identifying Key DBP Drivers of Toxicity

Susan D. Richardson
Department of Chemistry and Biochemistry
University of South Carolina

Uof SC South Carolina

Congaree National Park, SC

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Acknowledgements

From my group at USC:



Josh Allen



Hannah Liberatore

Our collaborators:



Michael Plewa
and Elizabeth Wagner
University of Illinois



Stuart Krasner
MWDSC
Also, Ai Jia, Tiffany Lee,
Carrie Guo, Raha Shirkhani
from Metropolitan

Funding:



And the many drinking water plants for
graciously providing us samples !

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Overview

- Background on DBPs
 - How they are formed, why they are important
- Methods and results of our study
- Which are toxicity drivers
- Potential strategies for DBP removal



Goal for audience:

A better understanding of priority unregulated DBPs and which are driving cytotoxicity in drinking water

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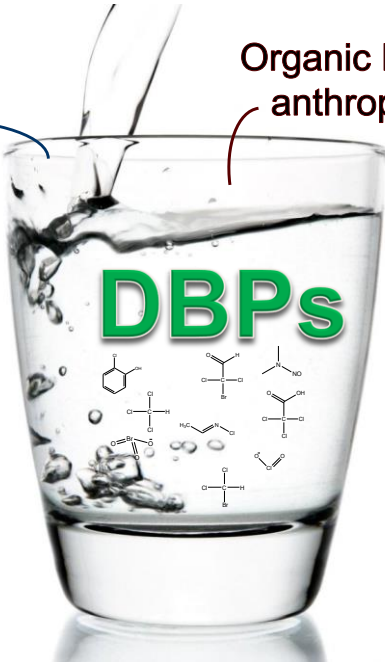
Disinfectants:
 Cl_2 , NH_2Cl
 O_3 , ClO_2

Organic Matter (natural or anthropogenic), Br^- , I^-

DBPs

Disinfection by-products are always in your drinking water (usually at ppb levels)

> 700 DBPs identified!



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Why this is important

DBPs linked to human health effects:
Bladder cancer, miscarriage, and birth defects



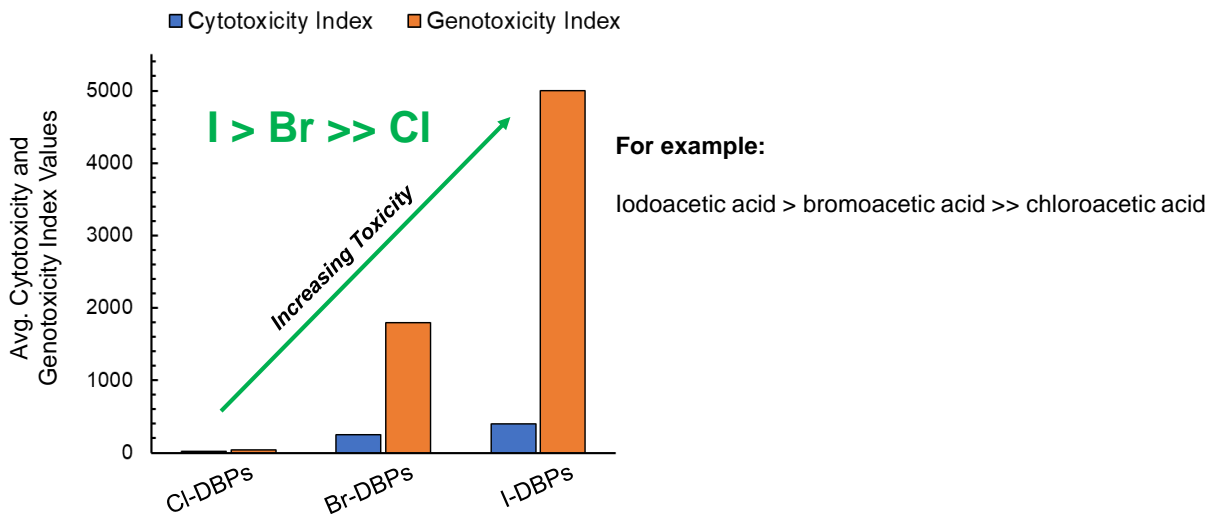
The Quest

- Determine the drivers of these effects
- Minimize toxicity drivers to make drinking water safer

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Cytotoxicity and Genotoxicity of Halogenated DBPs

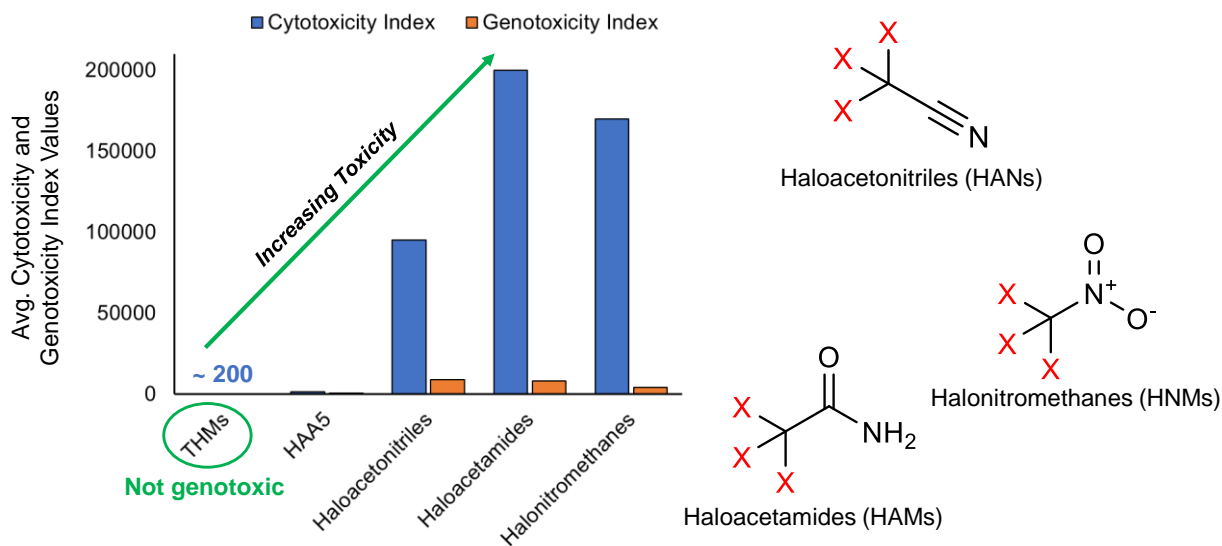


Yang, et al. *Environ. Sci. Technol.* **2014**, *48*, 12363-12369.

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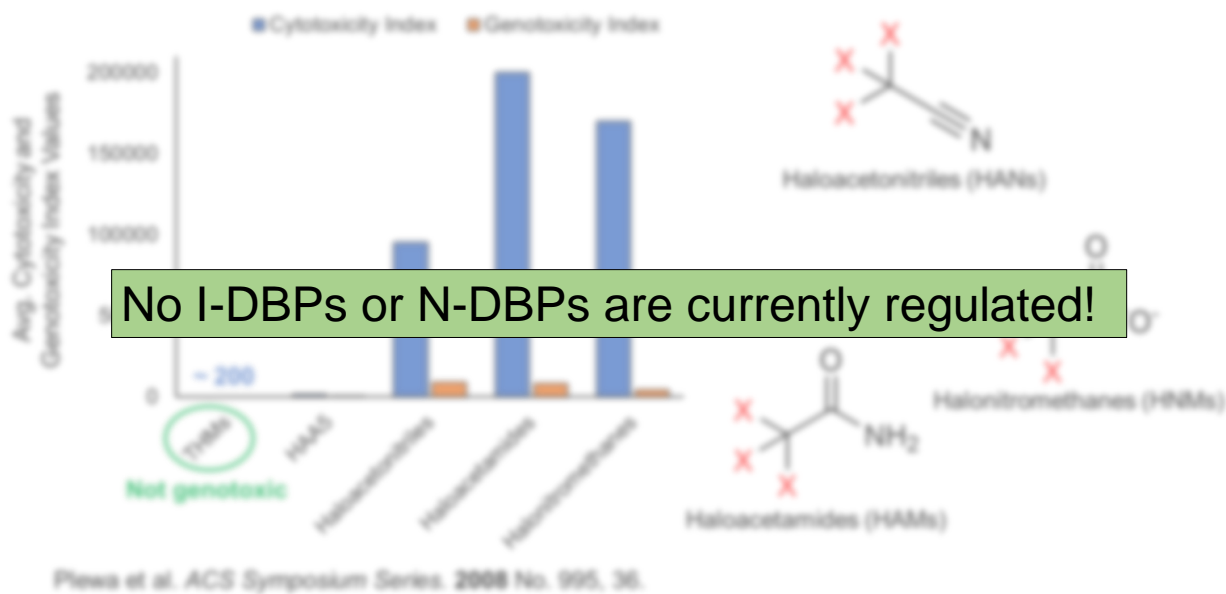
Cytotoxicity and Genotoxicity of Nitrogenous DBPs



Plewa et al. *ACS Symposium Series.* **2008** No. 995, 36.

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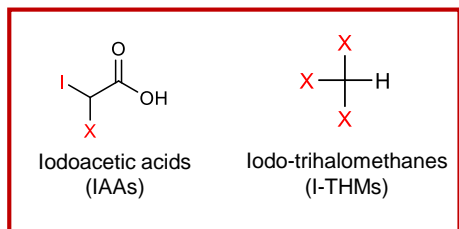
Goal of our study:
Identify the drivers of
cytotoxicity and genotoxicity
in drinking water



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>70 DBPs Quantified Using GC-MS

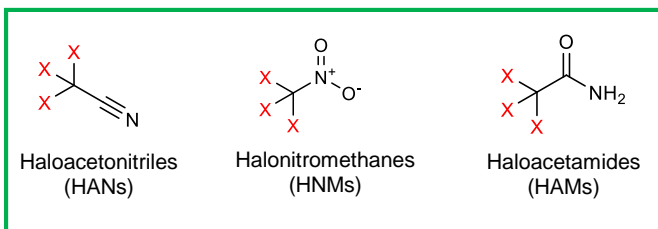
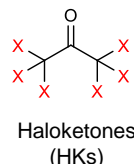
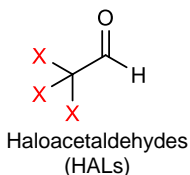


I-DBPs

X = H, Cl, Br, I

Also measured:

THM4 and HAA9
TOCl, TOBr, and TOI
Sucralose
TOC, SUVA, Br⁻, I⁻ of raw water
Mammalian cell cytotoxicity and genotoxicity



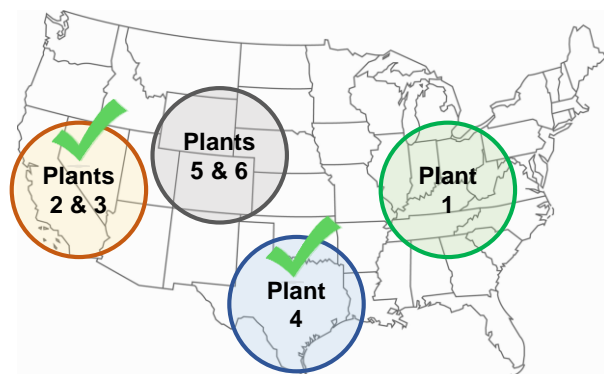
N-DBPs



Cuthbertson, et al. *Anal. Chem.* **2020**, 92, 3058-3068.

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Plants Sampled



Investigated:

- Disinfectant used (Cl₂, NH₂Cl, O₃)
 - Source water impacts
 - High Br⁻ and I⁻ (saltwater intrusion)
- Plant 2: Cl₂, GAC
Plant 3: O₃, NH₂Cl, biofiltration
Plant 4: NH₂Cl, conventional treatment

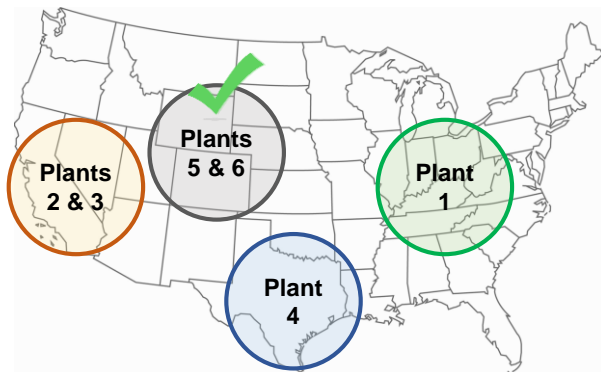
In Plants 2-4:

- Br⁻ ranged from 120 – 334 µg/L
- I⁻ was detected at least once in each plant, from 27 – 32 µg/L

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Plants Sampled



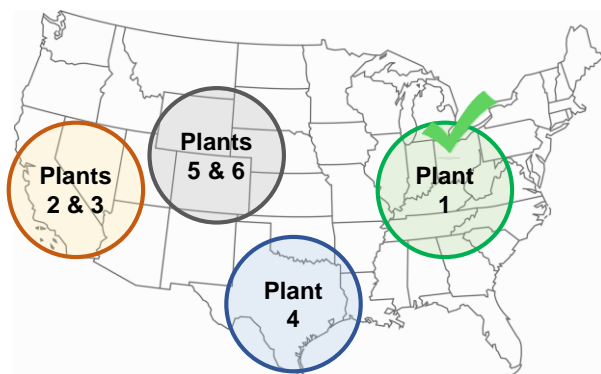
Investigated:

- Disinfectant used (Cl_2 , NH_2Cl , O_3)
- Source water impacts
 - High Br⁻ and I⁻ (saltwater intrusion)
- Plant 2: Cl_2 , GAC
- Plant 3: O_3 , NH_2Cl , biofiltration
- Plant 4: NH_2Cl , conventional treatment
- Plants 5 & 6: Wastewater-impacted sources
 - More DBP precursors
 - Also high in Br⁻ (92 – 143 $\mu\text{g/L}$)
 - Each use NH_2Cl with advanced treatment strategies (GAC, riverbank filtration, soil aquifer treatment for Plant 6, ultrafiltration for Plant 5)

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Plants Sampled



Investigated:

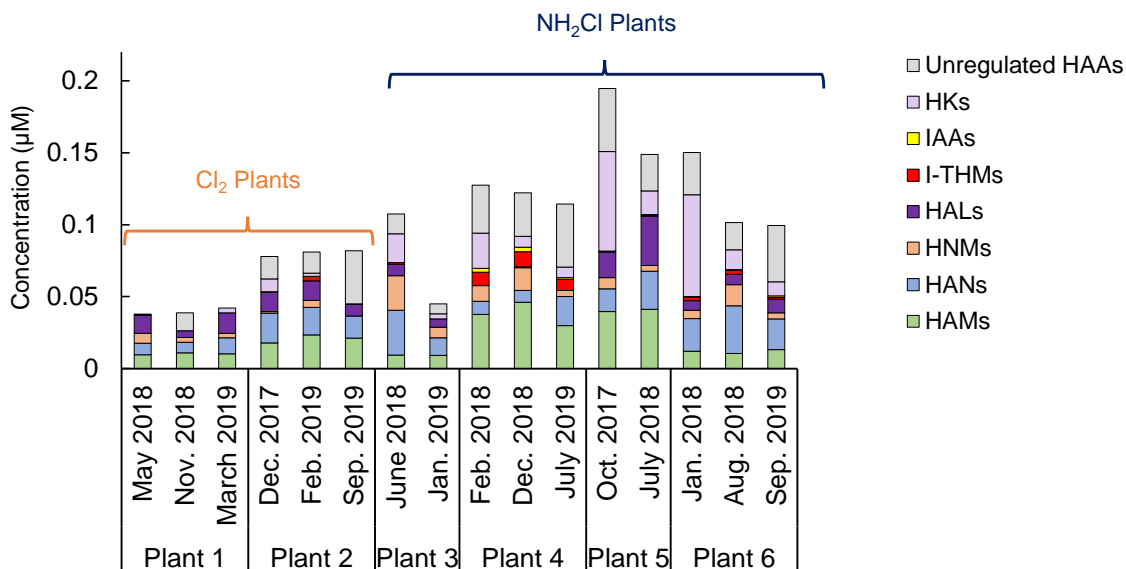
- Disinfectant used (Cl_2 , NH_2Cl , O_3)
- Source water impacts
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- Plant 2: Cl_2 , GAC
- Plant 3: O_3 , NH_2Cl , biofiltration
- Plant 4: NH_2Cl , conventional treatment
- Plants 5 & 6: Wastewater-impacted sources
 - More DBP precursors
 - Also high in Br⁻ (92 – 143 $\mu\text{g/L}$)
- Plant 1 – GAC/ Cl_2
 - Minimal wastewater or halide impacts (Br⁻: 20 – 44 $\mu\text{g/L}$; I⁻: < 10 $\mu\text{g/L}$)

2-3 Samplings each across different seasons

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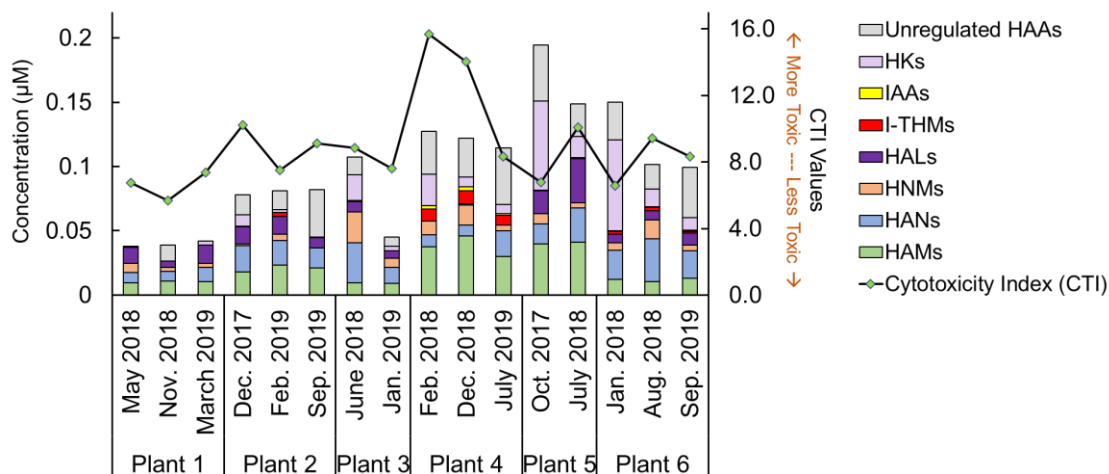
Unregulated DBP Formation



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Cytotoxicity and Unregulated DBPs

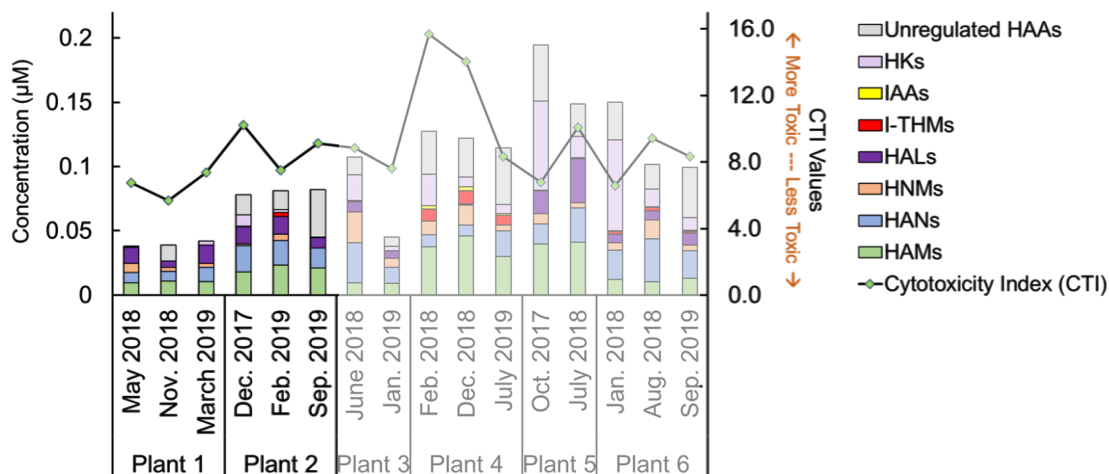


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GAC/Cl₂ Plants (1-2)

Plant 1: - Less DBP formation, likely from the use of GAC, and resulting cytotoxicity than most plants
 - Lower DBP formation than Plant 2, likely because of less halide impact

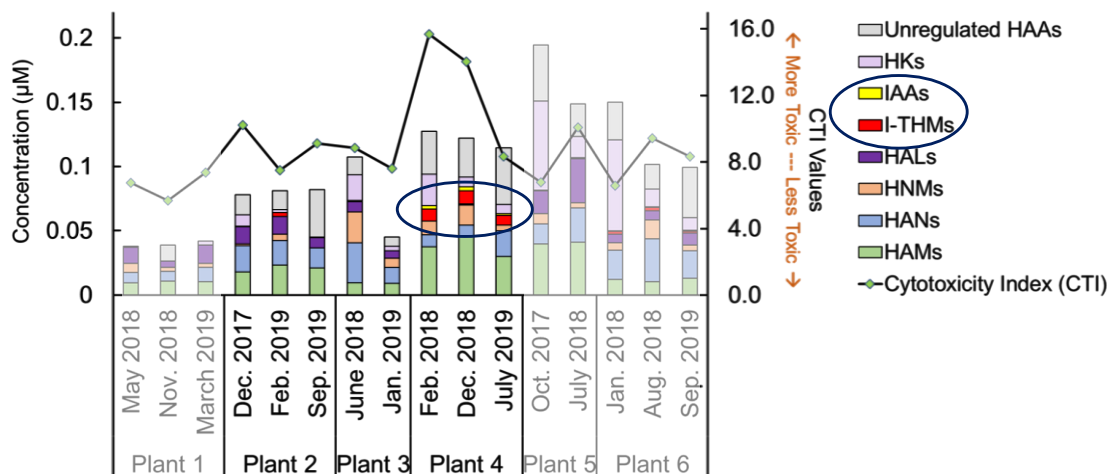


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High Halide, Low Wastewater-Impacted Plants (2-4)

Plant 4: - Higher [I-DBPs] in Plant 4, which uses NH₂Cl, where cytotoxicity was highest
 - Chloriodoacetamide and iodoacetoneitrile detected for the first time in U.S. drinking water

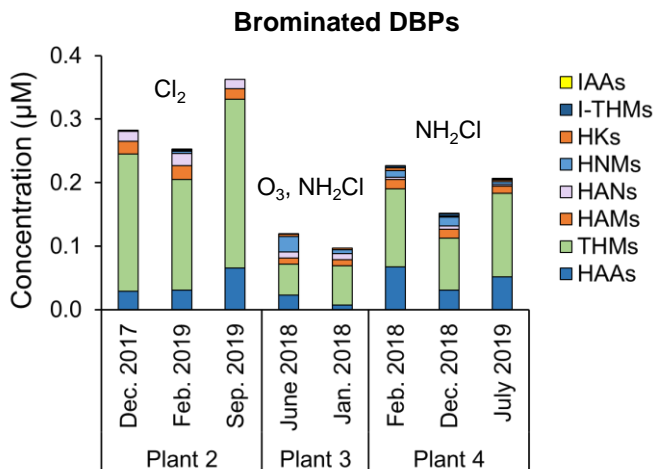


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Br-DBPs in Halide-Impacted Waters

- While Plant 2 had the most Br-DBP formation, only 27% of Br on average was converted into Br-DBPs based on TOBr data
 - Previous studies have reported up to 94% conversion in chlorinated waters¹
 - Removal of NOM by GAC is likely responsible for limiting Br-DBP formation
- Plants 3 and 4 each use NH₂Cl, but the additional use of O₃ by Plant 3 likely limited organic Br-DBP formation



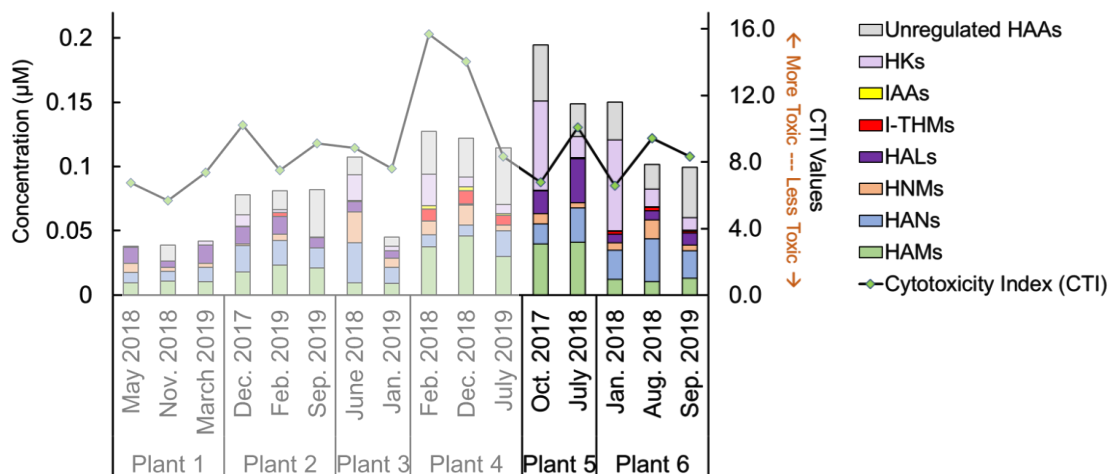
¹Tan et al. *Sci. Total Environ.* **2016**, 541, 1572-1580.

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Wastewater-Impacted Plants (5-6)

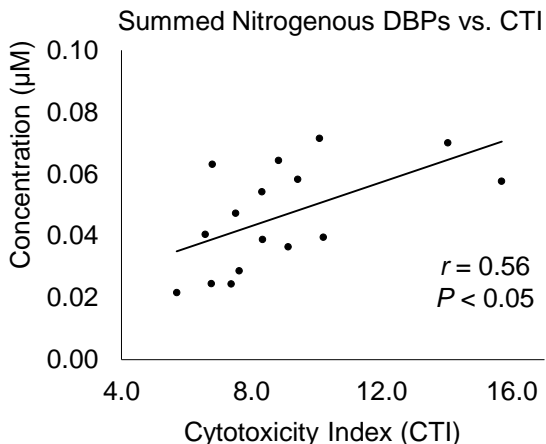
- Highest unregulated DBP formation on 3 occasions
- Higher [DBP] did not always result in higher cytotoxicity, but cytotoxicity trended well with N-DBPs



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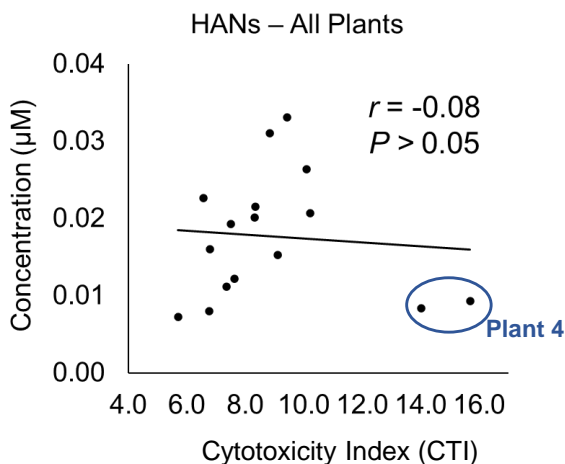
N-DBPs are Drivers of Drinking Water Cytotoxicity



- Nitrogenous DBPs (HANs, HAMs, HNMs) appear to be important drivers of cytotoxicity
- Supports the recent verification that DBP toxicity is additive¹

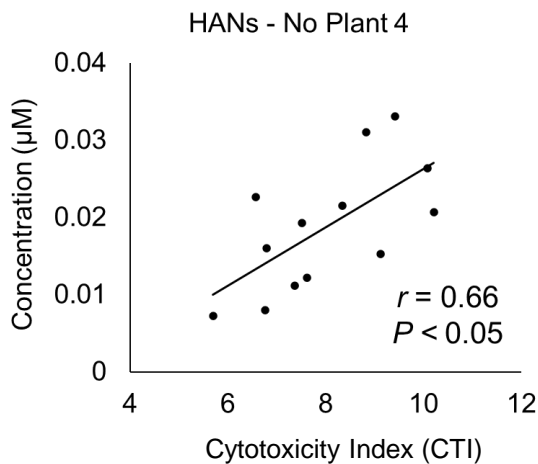
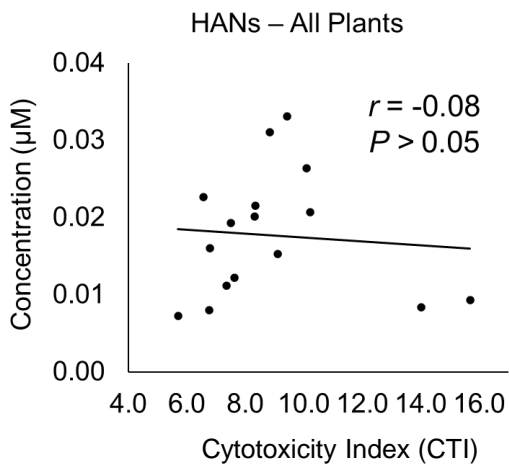
¹Lau, et al. *Environ. Sci. Technol.* **2020**, in press.

Haloacetonitrile (HAN)/Cytotoxicity Correlations



- While HANs were low, Plant 4 had two of the highest summed HAM concentrations. This was important in overall N-DBP correlation

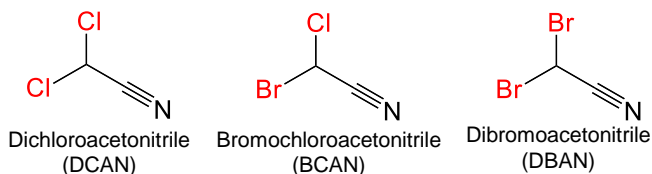
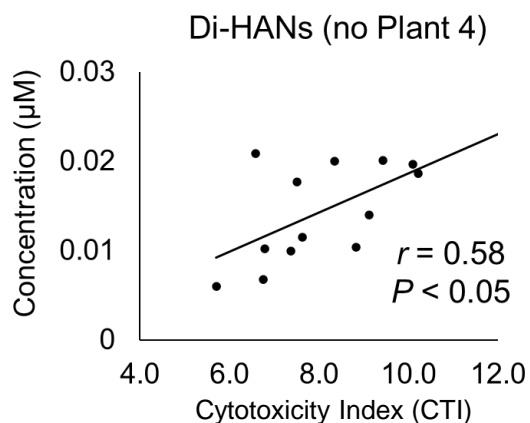
HAN/Cytotoxicity Correlations



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Di-HANs are Drivers of Drinking Water Cytotoxicity

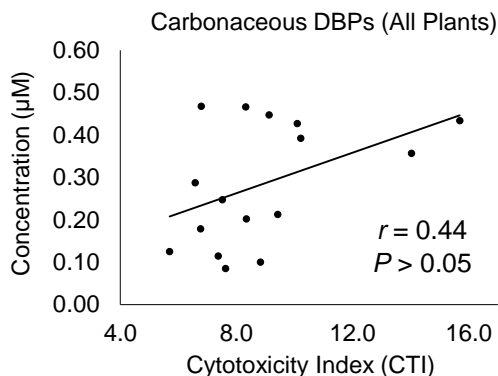


- Greatest influence on HAN cytotoxicity correlations
- **Ubiquitous** in disinfected water from all plants
- DBAN is 5th most cytotoxic DBP

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Carbonaceous DBPs and Cytotoxicity



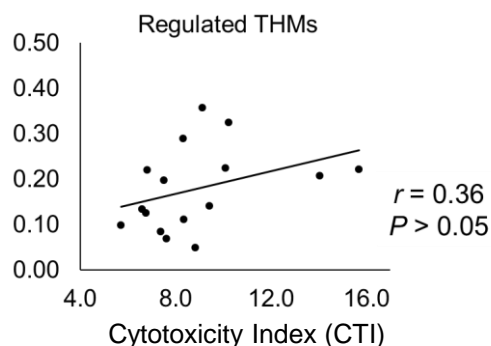
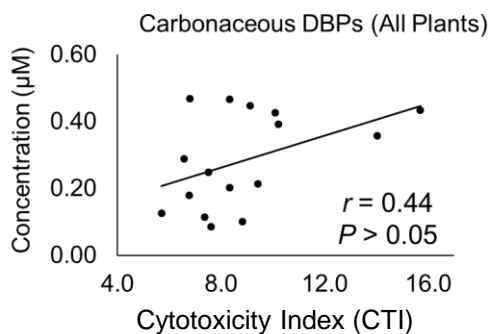
Carbonaceous DBPs: HAAs, THMs, HKs, HALs, I-THMs, IAAs

- Unlike N-DBPs, summed carbonaceous DBPs did not correlate with cytotoxicity

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Regulated THMs Do Not Correlate With Cytotoxicity in Drinking Water



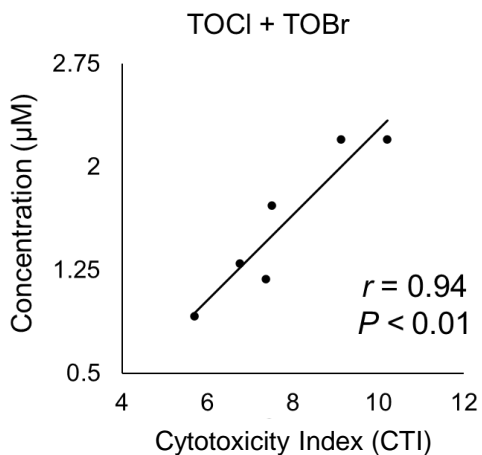
- Unlike N-DBPs, summed carbonaceous DBPs did not correlate with cytotoxicity
- Regulated THMs had no correlation with cytotoxicity and likely contribute little to the observed cytotoxicity

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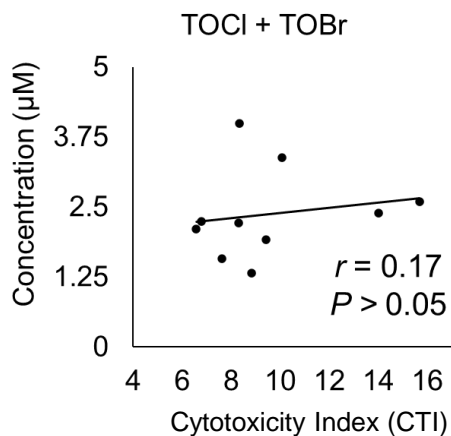
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TOCI and TOBr/Cytotoxicity Correlations

Cl₂ Plants



NH₂Cl Plants



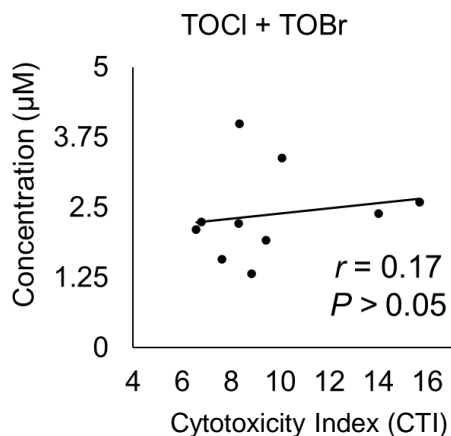
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TOCI and TOBr/Cytotoxicity Correlations

NH₂Cl Plants

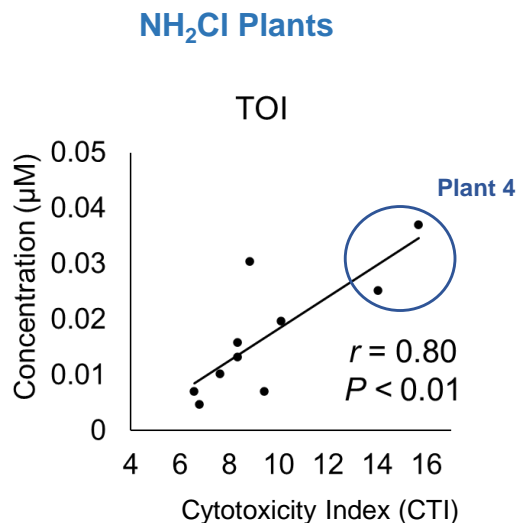
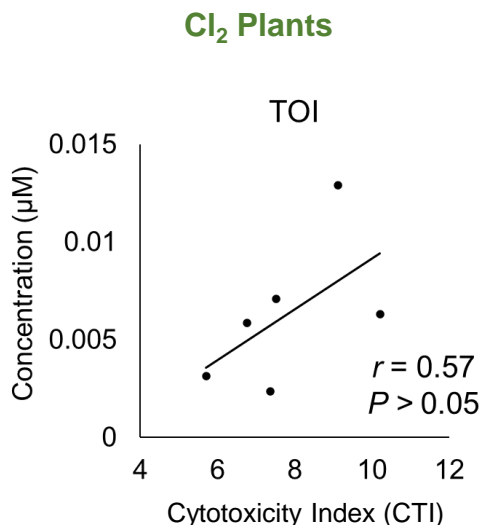
Other factors likely play an important role in NH₂Cl water cytotoxicity



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TOI/Cytotoxicity Correlations



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Summary and Strategies for Removal

- Drinking water is a complex mixture of hundreds of compounds
 - Difficult to attribute toxicity solely to any single chemical or chemical class
- N-DBPs are important drivers of cytotoxicity, particularly di-HANs
 - Di-HAN standards are inexpensive can be easily measured with existing EPA methods, so future regulation and monitoring would be feasible
- I-DBPs are drivers of cytotoxicity in iodide-impacted waters using NH₂Cl disinfection
 - GAC/Cl₂ or the use of O₃ could help mitigate I-DBP formation
- Halide removal strategies, such as ion-exchange resins, could help reduce Br-DBP and I-DBP formation, but can be expensive

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The goal: Clean and Safe Drinking Water



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Thank you!



My research group at USC



Special thanks to Michael & Elizabeth: 20 years of our labs working together!

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ASK THE EXPERT



Susan Richardson
University of South Carolina



Susan Teefy
East Bay Municipal Utility District



Charlie (Qun) He
Carollo Engineers, Inc

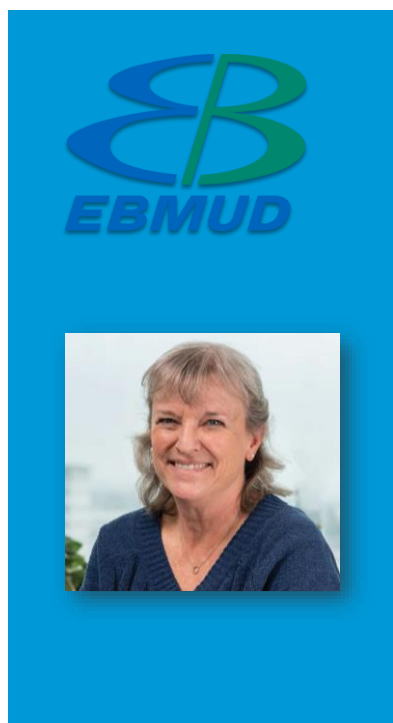
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DBP CONTROL CASE STUDY

Susan Teefy
Manager of Water Quality
East Bay Municipal Utility District
Oakland, California

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AGENDA

- Background/introduction
- Historical DBP control efforts
- Current and future DBP control strategies
- Modifying old facilities to meet new requirements

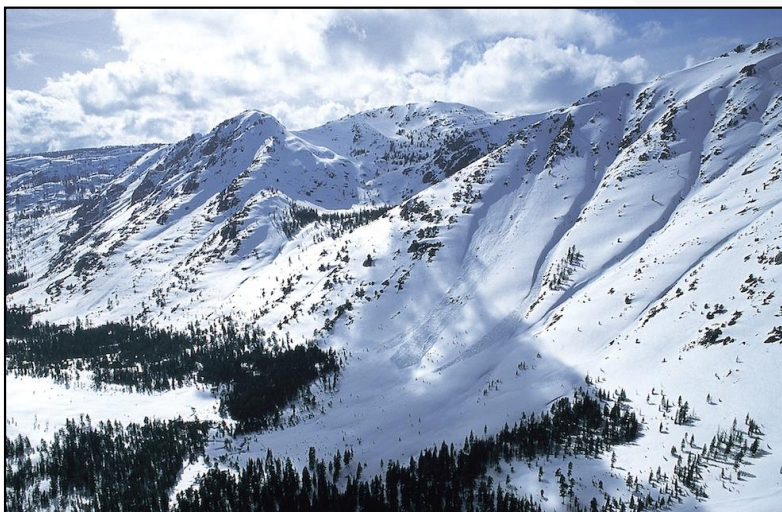
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WATER STORAGE

- Watershed in the Sierra Nevada mountains
- Snowmelt feeds Mokelumne River



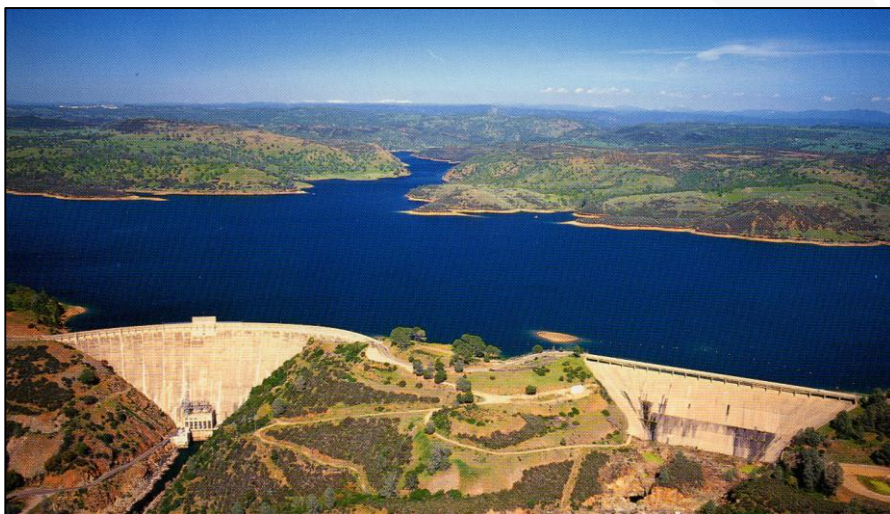
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PARDEE RESERVOIR

- Water is stored in Pardee Reservoir
- Gravity feed to the east bay



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MOKELUMNE AQUEDUCTS

- Convey water from Pardee Reservoir across Central Valley and Delta
- Mostly buried, some parts are above grade
- Lime is added at headworks for corrosion control
- 1929, 1949, 1963



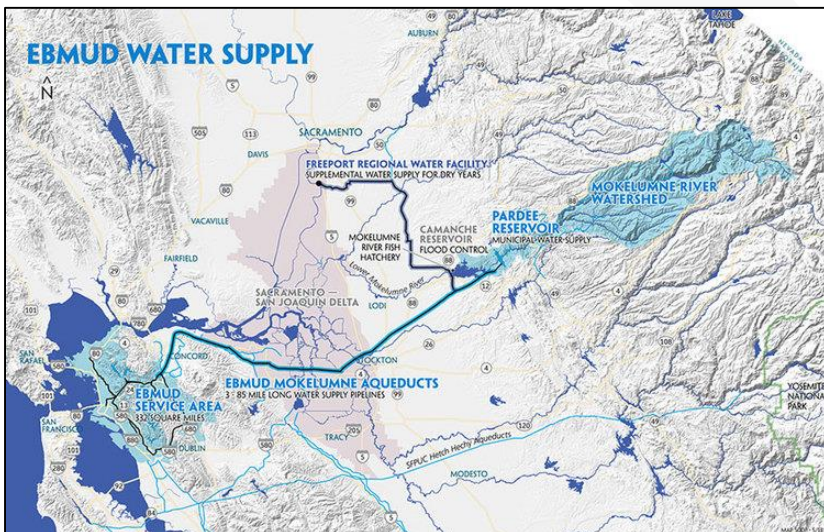
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TREATMENT AND DISTRIBUTION

- 1.4 million people
- Six treatment plants, all surface water
- 332 square miles
- 4,300 miles of pipes
- 165 storage reservoirs
- 124 pressure zones (0 – 1,500 ft)



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ORINDA WATER TREATMENT PLANT

- 200 mgd
- Low turbidity, low organic carbon source water
- Minimal treatment needed
 - Coagulation, filtration, disinfection
- Plant was not designed for today's regulations
- All of EBMUDs plants are older than USEPA)



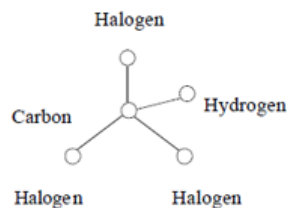
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SIMPLIFIED THM REGULATORY HISTORY

- 1979: 100 ppb
 - Four sites per treatment plant each quarter
 - Rolling annual average of all sites
 - Some sites can be very high
- 2002: Lower to 80 ppb
 - Continue rolling annual average of all sites
- 2012: 80 ppb at highest individual site
 - Number of sites based on population
 - Study DBP levels, select sites with highest values
 - No more averaging high sites with low sites

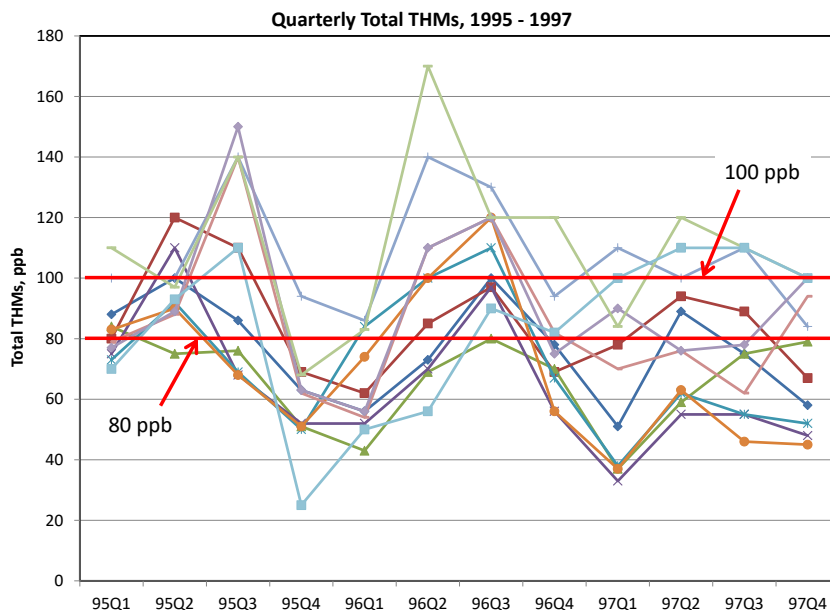


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- In compliance with regulations
- Some individual samples >100 ppb
- Rolling average below 100 ppb, generally <80 ppb
- Change was needed to ensure compliance



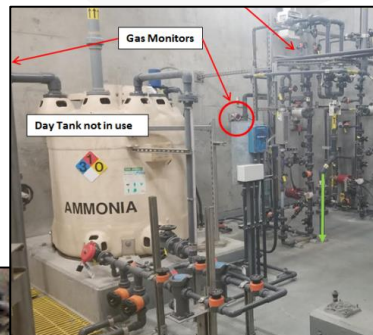
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CHLORAMINE CONVERSION

- Add ammonia to form chloramine
- Also, convert from gaseous chlorine to sodium hypochlorite (safer, RMP requirements)
- Improve chlorine residuals throughout distribution system
 - Help with total coliform rule compliance
 - Help with SWTR detectable residual compliance
- Fewer T&O complaints
- On line in 1998



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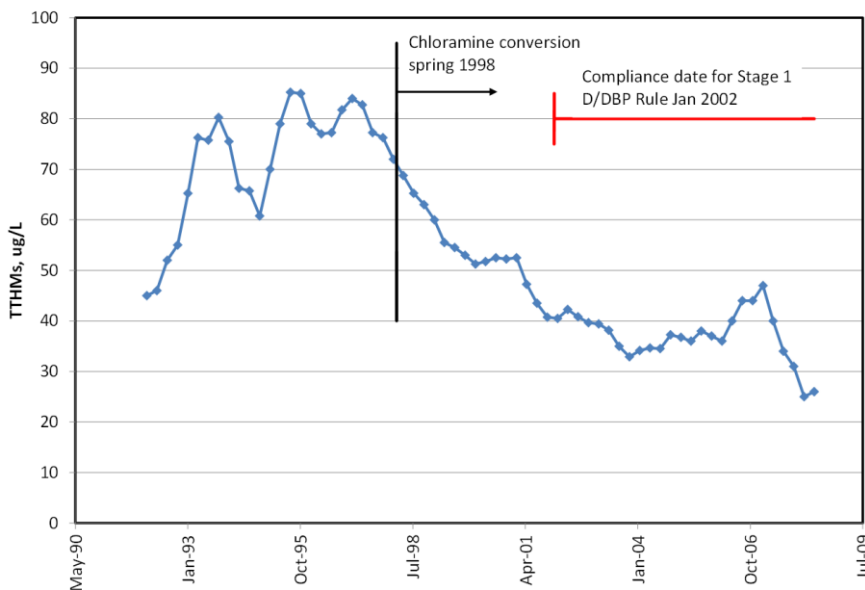


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LOWER THMS

- In compliance with regulations
- Significant decline in THM levels throughout system
- In general, all sites <<80 ppb

System-Wide Running Annual Average THMs, Before and After Chloramine Conversion



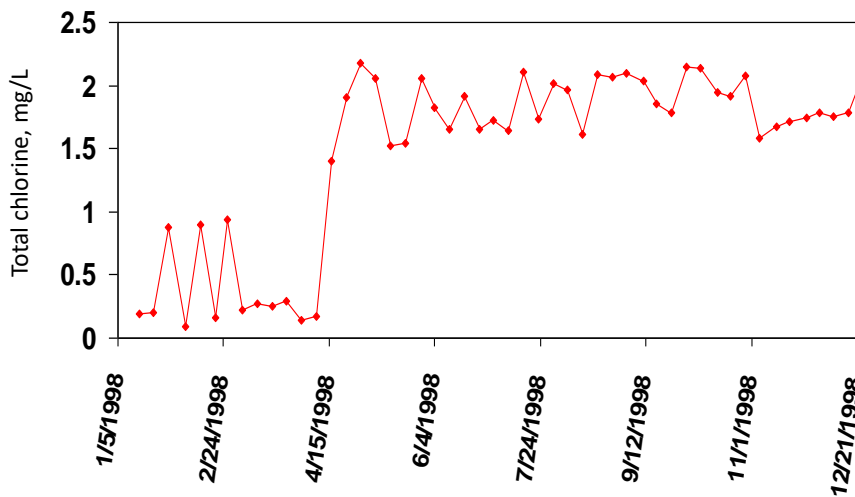
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HIGHER RESIDUALS IN DISTRIBUTION SYSTEM

- One representative sample tap (out of 125)
- In compliance with regulations
- Many locations that previous did not have a detectable chlorine residual improved



NITRIFICATION



NITRIFICATION CONTROL MEASURES

- Increase chloramine residual
- Additional monitoring
- Inspect and clean reservoirs
- Breakpoint chlorination of individual reservoirs
- Reduce storage
 - Approx. 40 reservoirs out of service
 - Replace large open-cut reservoirs with smaller tanks
- Minimize free ammonia



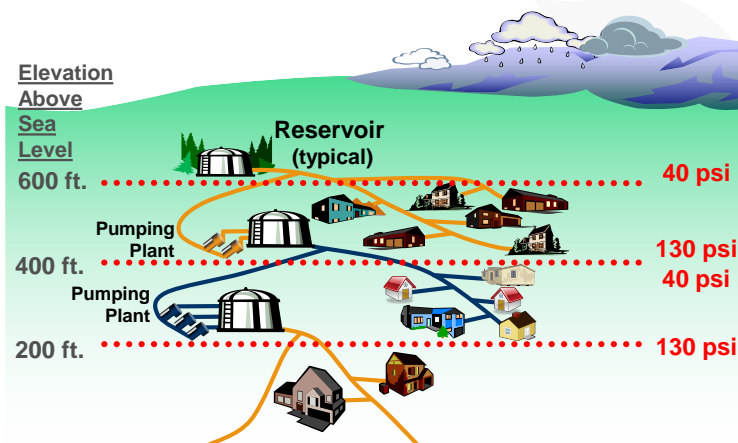
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HIGH WATER AGE

- Large distribution system, long residence times
- Customers using less water, longer residence times
- Wildland-urban interface, need to keep sufficient storage on hand for fire fighting



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CENTRAL RESERVOIR

- Constructed in 1909
- Intended to impound raw water behind dam
- 154 million gallon capacity
- Once water was delivered from Pardee Reservoir, used as finished water storage



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CENTRAL RESERVOIR

- Lining and roof added in 1960s
- Continued to be used as finished water reservoir



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CENTRAL RESERVOIR

- Freeway installed adjacent to reservoir site
- Surrounded by many homes and businesses
- Elevation too low to properly cycle



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CENTRAL RESERVOIR

- Dam needs to be upgraded to modern standards
- Capacity is too large, required storage is about 50 MG
- Mechanical mixers installed

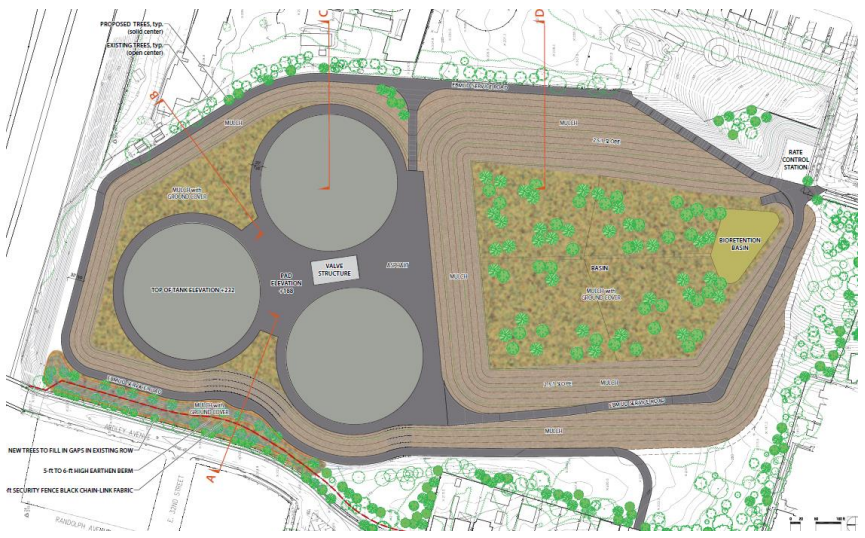


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CENTRAL RESERVOIR

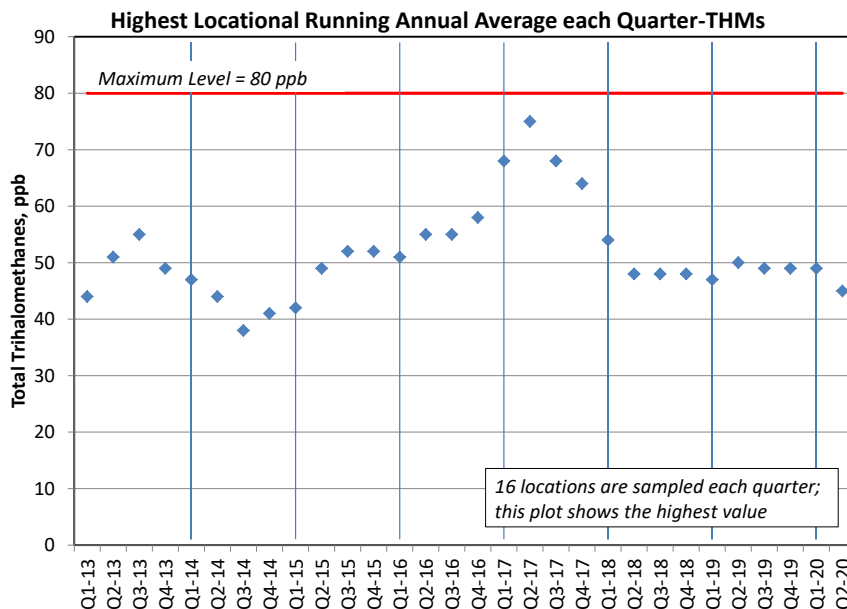
- Three concrete tanks, 17 MG each
- Increase elevation by >20 feet
- At least five year construction schedule
- At least \$120 M cost



CURRENT AND FUTURE DBP CONCERNS

SPRING 2017

- Highest LRAA reached 75 ppb
- Drought 2013-2017
- Winter 2017 had very high rainfall, heavy runoff with high organics
- Drought operations exacerbate nitrification control efforts



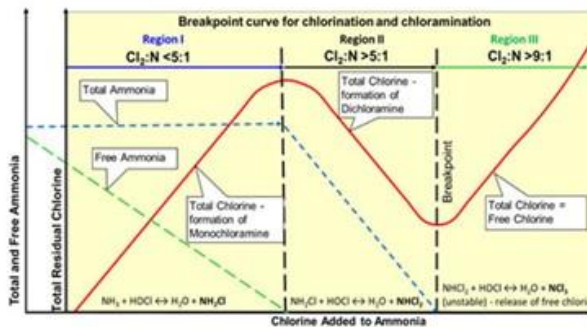
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CHLORINE – TO – NITROGEN RATIO

- Breakpoint curve: 5:1 is optimal
- Original target in 1998: 4.6:1
- Drought-associated increases in nitrification events
 - Various operational adjustments
 - Moved ratio closer to 5:1
- Began seeing increased THM formation in distribution system
 - <10 ppb was typical
 - Observed as high as 30 ppb increase in distribution system
- Investigated implications of >5:1 ratio



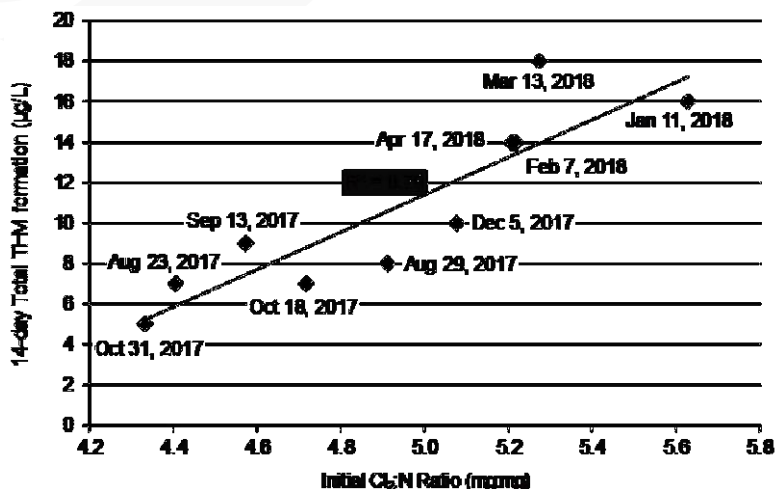
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“ADDITIONAL” THM FORMATION

- Ammonia added to chlorinated water
- Held for 14 days
- Varying initial Cl₂:N ratios (measured)



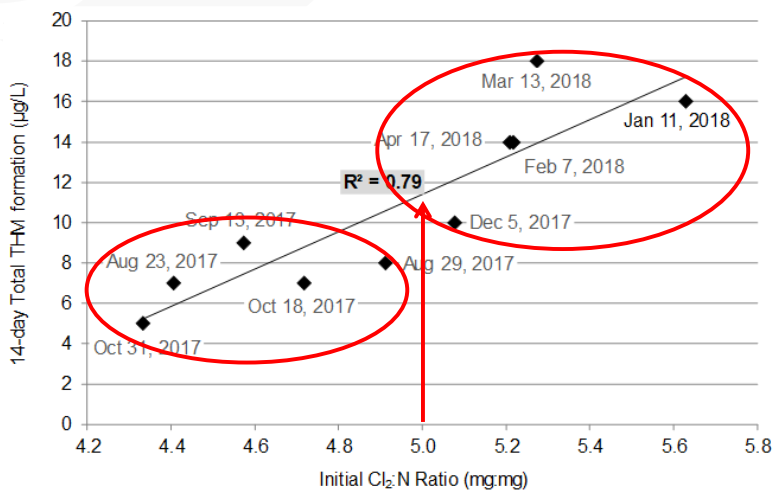
65



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“ADDITIONAL” THM FORMATION

- When Cl₂:N ratio exceeded 5:1, THM concentrations increased



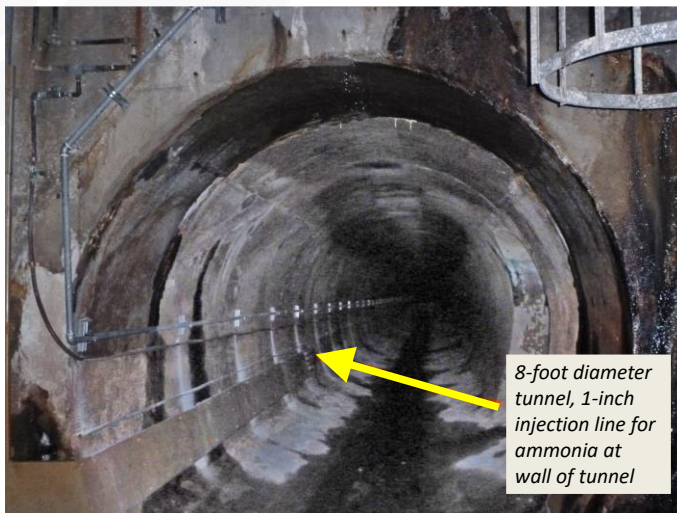
66



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AMMONIA INJECTION ISSUES

- Cannot collect proper plant effluent sample
- Plant flow rate changes frequently
- Although target is 5:1, periodically exceed this value
 - Increased formation of THMs
 - Accelerated degradation of chlorine residual
- Improvements needed to injection system
 - Operate at lower ratio until then
- Install analyzer at opposite end of tunnel, transmit signal back to operators



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UPCOMING PLANT MODIFICATIONS

- Minimal cost for treatment currently
- Plant effluent THM concentrations are still occasionally high
- Drought followed by high rainfall can result in high levels of DBP precursors
- No organic carbon removal capability
- Only minimally meeting disinfection requirements with free chlorine
- Wildfire in the watershed is inevitable, only a matter of time
- As climate warms, expect more severe and more variable weather
- Conclusion: need to invest in additional treatment processes



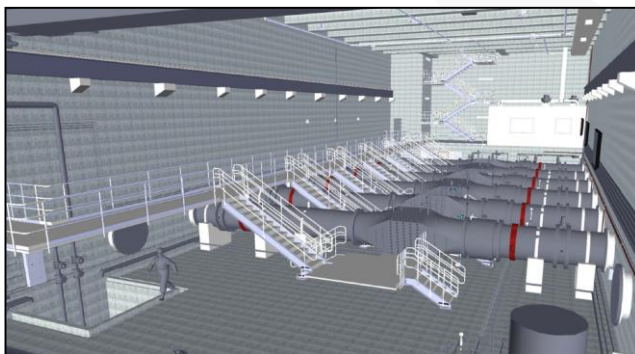
68



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CURRENTLY IN DESIGN

- Phase 1:
 - Add UV after filtration for *Giardia* inactivation
 - Add small chlorine contact chamber for virus inactivation
- Phase 2:
 - Add clarification process, most likely ballasted flocculation, for additional carbon and solids removal
 - Ability to bypass when raw water quality is good
 - Solids handling facilities



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SUMMARY

- Conversion from free chlorine to chloramine lowered THMs and increased stability of distribution system residuals
 - Caused nitrification issues
- Balance competing objectives
 - Disinfection vs. DBPs
 - DBP control vs. nitrification
 - High storage for emergencies and fire-fighting vs. high water age for nitrification
- Legacy systems can be modified to meet current standards
 - Takes a lot of time, costly



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ASK THE EXPERT



Susan Richardson
University of South Carolina



Susan Teefy
East Bay Municipal Utility District



Charlie (Qun) He
Carollo Engineers, Inc

Enter your **question** into the **question pane** on the right-hand side of the screen.

Please specify to whom you are addressing the question.

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The image shows a blue-bordered box containing the Carollo Engineers logo at the top and a portrait of Charlie He at the bottom. The logo includes the text 'carollo' in a stylized font and 'Engineers...Working Wonders With Water®' below it. The portrait shows Charlie He, a man with glasses wearing a white shirt and blue tie.

AN INTEGRATED APPROACH FOR DBP MITIGATION

Charlie He
Vice President, Chief
Technologist – Decision
Support
Carollo Engineers, Inc.

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LEARNING OBJECTIVES

1. Understand the chemical and environmental factors that drive DBP formation.
2. Will get a glimpse into ongoing research that is helping us understand current of emerging DBPs and their formation.
3. **Describe the variety of tools that a utility can use to manage DBPs in their distribution system.**
4. **Create an integrated and effective management approach to mitigate DBPs challenges in the distribution system.**

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AN INTEGRATED APPROACH FOR DBP MITIGATION

COMBINING WATER QUALITY MODEL
AND HYDRAULIC MODEL



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PRESENTATION OUTLINE

- Distribution System Water Quality Overview
- Conventional and Integrated Approach
- Conventional and Innovative Tools
- Conventional and Innovative Charts

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CURRENT DISINFECTION PRACTICES IN US

Type	No. of POE into Distribution system	Free Chlorine	Chloramine	Other Disinfectants				
				Ozone	Chlorine Dioxide	UV	Other	No Disinfection
Ground-water	8,846	81.3%	9.1%	0.5%	0.5%	0.2%	1.2%	6.8%
Surface Water	2,886	51.7%	27.9%	7.5%	8.1%	4.2%	1%	0%

Data Source: UCMR3 Exhibit 6.2

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FACTORS INFLUENCING DISTRIBUTION SYSTEM WATER STABILITY AND DBP

Chemical Factors:

- **DBP: pH, temperature, TOC, UV254, chlorine dose, bromide, Cl:N ratio**
- **Corrosion and Stability: pH, TDS, calcium, alkalinity, temperature, chloride, sulfate, etc.**

Biological Factors:

- Presence of biofilm, iron or sulfate-reducing bacteria and nitrification bacteria

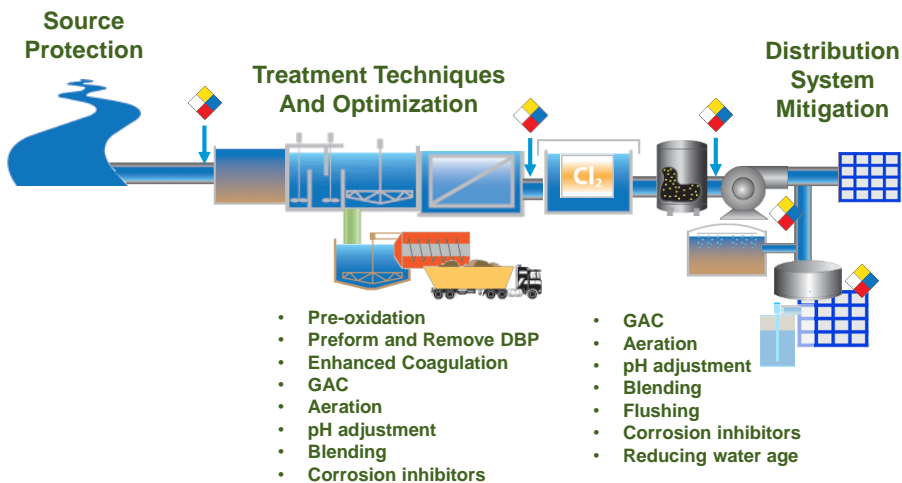
Physical Factors:

- Pressure, flow, blends of sources,
- Water Age
- Pipe materials and age of pipe
- Soil moisture, and presence of electric currents



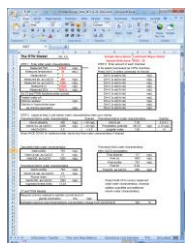
77

MANY FACTORS IMPACT DISTRIBUTION SYSTEM WATER QUALITY



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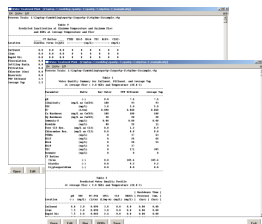
SEVERAL MODELING TOOLS ARE AVAILABLE FOR ANALYZING DISTRIBUTION SYSTEM WATER QUALITY



RTW Model



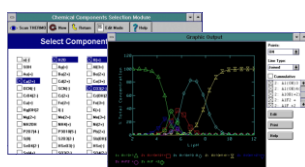
WaterPro Model



EPA WTP Model



Hydraulic Model
(e.g., Inflow MSX: Multi-Species eXtension)



MINEQL+

Table 43. Smith expression of the TTHM.

Chemical	Reaction	Rate Constant (k ₁)	Rate Constant (k ₂)	Reference
CHCl ₃	CHCl ₃ = k ₁ · (TOC) ^x · (Cl ₂ Dose / TOC) ^y · (ReactionTime) ^z	k ₁ = 0.00309 · (UV · TOC) ^{0.440} · (Cl ₂ Dose) ^{0.409} · (Br + 1) ^{0.0358} · (ReactionTime) ^{0.265} · (Temperature) ^{1.06} · (pH - 2.6) ^{0.715}	k ₂ = 10834 · ΔUV ₂₇₂	Amy, Chadik, and Chowdhury (1987)
THM	THM = k · (pH - 2.8) · (TOC) ^{0.25} · (ReactionTime) ^{0.36}	k = 3.5 × 10 ⁻³ · e ^(-4470 / TEMP)		Urano, Wada, and Takemasa (1983)
TTHM	TTHM = k _n · (Cl ₂) ^m · (TOC) ⁿ			Trussell and Umphres (1978)

Mechanistic DBP Models and Apps



Corrosion and Stability Indices

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EMPIRICAL D/DBP MODELS

$$Cl_2 = C_0 * (TOC^{C1}) * (pH^{C2}) * (time^{C3}) * (temp^{C4}) * (Br^{C5}) * (CLdose^{C6}) * (UVA^{C7})$$

$$TTHM = T_0 * (TOC^{T1}) * (pH^{T2}) * (time^{T3}) * (temp^{T4}) * (Br^{T5}) * (CLdose^{T6}) * (UVA^{T7})$$

Coefficients were provided for
 CASE I: All CAP raw and treated water
 CASE II: All Lake Houston raw and treated water
 CASE III: All Harwoods Mill Reservoir (VA) raw and treated water
 CASE IV: All Lake Manatee Water (FL) raw and treated water
 CASE V: All Water raw and treated combined

Reference: Arizona State University Thesis, He, 2001

Research Done By	Model Expression
Moore, Tuthnill, and Polakoff (1979)	$CHCl_3 \text{ (in mg/L)} = -11.24 + 22.23 \text{ Cl}_2 \text{ Dose (in mg/L)} \quad (1.5)$ <p>Which is based on applied chlorine dose, reflecting the fact that the extent of chloroform formation parallels that of chlorine consumption.</p>
Trussell and Umphres (1978)	$\frac{dTTHM}{dt} = k_n (Cl_2) (TOC)^m \quad (1.6)$ <p>Where m is the order of the reaction with respect to the concentration of TOC precursor, and k_n is the reaction rate constant.</p>
Kavanaugh et al. (1980)	$\frac{dTTHM}{dt} = k_n (TOC) (Cl_2 \text{ Dose} - \frac{3TTHM}{f})^m \quad (1.7)$ <p>Which included a THM yield parameters (f).</p>
Engerholm and Amy (1983)	$CHCl_3 = k_1 k_2 \cdot (TOC)^x \cdot (Cl_2 \text{ Dose} / TOC)^y \cdot (\text{ReactionTime})^z \quad (1.8)$ <p>Where k₁ and k₂ are experimentally derived reaction constant related to pH and temperature respectively.</p>
Urano, Wada, and Takemasa (1983)	$TTHM = k \cdot (pH - 2.8) \cdot (TOC)^{0.25} \cdot (\text{ReactionTime})^{0.36} \quad (1.9)$ <p>Where $k = 3.5 \times 10^{-3} \cdot e^{(-4470 / TEMP)}$</p>
Amy, Chadik, and Chowdhury (1987)	$TTHM = 0.00309 \cdot (UV \cdot TOC)^{0.440} \cdot (Cl_2 \text{ Dose})^{0.409} \cdot (Br + 1)^{0.0358} \cdot (\text{ReactionTime})^{0.265} \cdot (Temperature)^{1.06} \cdot (pH - 2.6)^{0.715} \quad (1.10)$
Korshin G. V., Li C., and Benjamin M. M. (1997)	$TOX = 10834 \Delta UV_{272} \quad (1.11)$ <p>Where TOX is in µg/L and ΔUV₂₇₂ is in cm⁻¹ and represents the change in UV₂₇₂ absorbance before and after chlorine addition.</p>

Reference: Arizona State University Thesis, He, 2001

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EPA WTP MODEL VERSION 1.5 (1992) – 2.0 (2001)

The screenshot displays the 'Edit Process Train' window of the EPA WTP Model. The 'Process Train' list includes: Influent, DBP Model Inputs, Alum, Rapid Mix, Flocculation, Settling Basin, Filtration, GAC, Chlorine (Gas), Contact Tank, Contact Tank, Contact Tank, Contact Tank, and WTP Effluent. The 'Available Selections' panel is divided into 'Unit Processes' (Rapid Mix, Flocculation, Settling Basin, Filtration, GAC, MF/UF, NF, Ozone Chamber, Contact Tank, Reservoir) and 'Chemical Feeds' (Alum, Ammon. Sulfate, Ammonia, Carbon Dioxide, Chlorine (Gas), Chlorine Dioxide, Iron, Lime, Ozone, Permanganate, Sod. Hypochlor., Soda Ash, Sodium Hypochlor.). 'Sample Points' include WTP Effluent, Average Tap, End of System, and Additional Point. Buttons for Move, Edit, Delete, Clear, Cancel, and OK are visible at the bottom.

EPA WTP Model Version 2.0 (Empirical Model)

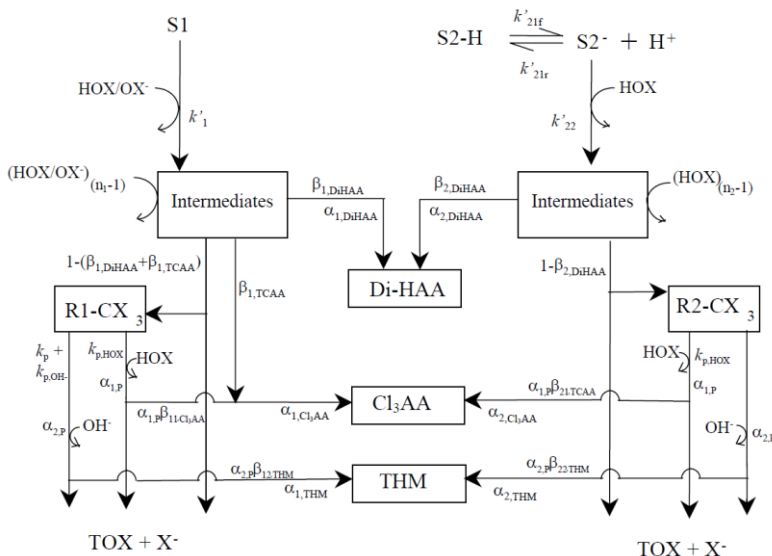
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MECHANISTIC-BASED DBP MODELS

(Adapted from McCellan, 2000)



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EPA WTP MODEL VERSION 2.1 (2002)

DBP Model Inputs Parameters

Mechanistic-based or Empirical DBP Model? **MECH** (MECH or EMP)

Input S1 and S2 or Calculate with TOC, UVA? **INPUT** (INPUT or CALC)

S1 Concentration (Initial) **1.05** (uM/L)

S2 Concentration (Initial) **5.59** (uM/L)

CHCl3 Concentration (Initial) **0.00** (ug/L)

BDCM Concentration (Initial) **0.00** (ug/L)

DBCM Concentration (Initial) **0.00** (ug/L)

CHBr3 Concentration (Initial) **0.00** (ug/L)

MCAA Concentration (Initial) **0.00** (ug/L)

MBAA Concentration (Initial) **0.00** (ug/L)

BCAA Concentration (Initial) **0.00** (ug/L)

DCAA Concentration (Initial) **0.00** (ug/L)

DBAA Concentration (Initial) **0.00** (ug/L)

TCAA Concentration (Initial) **0.00** (ug/L)

DBP Model Inputs Parameters (Continued)

Input Cl2 Demand as % of Dose or as MG/L? **DOSE%** (MG/L or DOSE%)

Cl2 Demand: fraction of Cl2 Dose **10.00** (%)

Cl2 Demand: specified value **0.00** (mg/L as Cl2)

k_11 **2.00** [10^-2/uM/hr]

k_12 **6.66** [10^-4/uM/hr]

k_21f **11.25** [10^-3/hr]

k_21r **1.44** [10^-7/M/hr]

k_22 **4.53** [10^-1/uM/hr]

k_TOBr **0.00** [1/hr]

alpha_TOBr **0.00**

Theta_1 **1.014**

Theta_21f **1.032**

Theta_21r **1.000**

Theta_22 **1.000**

EPA WTP Model V 2.1 (Mechanistic Based)

This version of the WTP Model has the option to model DBP formation, chlorine and bromine consumption using mechanistic based algorithms developed by researchers at the University of Massachusetts Lowell, Arizona State University and University of Colorado at Boulder. Programming and testing was performed by Malcolm Pirnie, Inc.

Logos for Colorado State University, UMMASS, ASU, and MALCOLM PIRNIE.

EPA WTP MODEL VERSION 3.0 (2016)

• 2-in-1

- **WTP2.2:** Mechanistic models for conventional treatment and GAC processes, with some updates for regulatory analysis
- **WTP-ccam:** Scenario Analysis, Monte Carlo analysis, cost curve analysis.

Number	Q1n MGD	Alk mg/L	Bro mg/L	Ca-H mg/L	Tt-H mg/L	NH3 mg/L	Turb mg/L	PH	Temp C	TOC mg/L	UVA 1/cm
1	120.6	55.32	0.035	44.4	100.8	0.061	12.0	7.60	18.6	3.06	0.061
2	120.6	63.23	0.033	44.4	107.3	0.124	12.5	7.60	18.6	3.76	0.109
3	120.6	61.30	0.033	74.0	104.9	0.191	26.5	7.57	18.6	4.74	0.130
4	120.6	30.96	0.027	62.6	83.5	0.141	26.8	7.52	18.6	1.98	0.093
5	120.6	82.32	0.035	54.8	117.9	0.171	21.1	7.77	18.6	4.99	0.147
6	120.6	59.42	0.031	95.9	108.1	0.263	15.9	7.93	18.6	2.77	0.061
7	120.6	100.32	0.026	89.0	120.5	0.268	281.7	7.87	18.6	5.81	0.406
8	120.6	45.33	0.036	45.6	94.3	0.291	32.3	7.39	18.6	3.14	0.100
~											
995	120.6	47.58	0.028	44.5	90.5	0.236	11.9	7.71	18.6	2.85	0.042
997	120.6	51.37	0.031	56.6	93.3	0.246	44.9	7.57	18.6	3.98	0.106
998	120.6	41.82	0.030	89.7	90.9	0.219	12.5	7.44	18.6	3.17	0.038
999	120.6	38.67	0.027	82.0	101.6	1.538	146.5	7.80	18.6	5.09	0.147
1000	120.6	40.39	0.031	72.4	94.3	0.351	18.1	7.60	18.6	2.14	0.041
Samp Tes	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Mean	220.6	58.18	0.030	62.6	98.5	0.359	42.7	7.71	18.6	3.83	0.113
St. dev	0.0	22.38	0.006	23.2	18.0	0.446	40.5	0.16	0.0	1.11	0.036
Min	220.6	15.48	0.014	23.8	49.5	0.203	1.1	7.14	18.6	1.36	0.024
Max	120.6	232.32	0.053	183.3	219.6	4.178	506.9	8.13	18.6	8.82	0.406

Monte Carlo Setting

Options:

Preserve Correlation

Quarterly Running Average

Correlation Control

Controlled Contaminant: TOC

Controlled Processing Unit: GAC

Raw WQ Probability Data: LogNormal

Control Parameters:

Number of Runs: >1

Seed for Random Number, 1-10000

Regulation Standard, mg/L

Margin of Safety, mg/L

Source of Influent WQ Statistics:

Computed by Available Data File(s), Please Click Here

Or input manually, Please Click Here

Correlation Matrix:

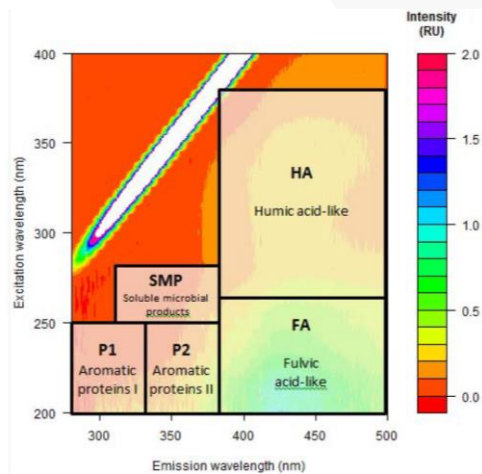
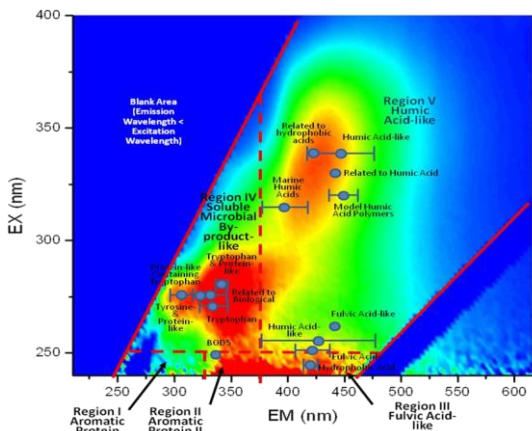
Please Provide Data File(s) Here if Preserve Correlation is Checked

Raw Water Quality Statistics Input Window

Time Horizon: Spring

Parameter	Average	Standard Deviation
pH	7.7	0.17
Alkalinity, mg/L	55.5	18.2
Turbidity, NTU	43.4	38.0
Calcium Hardness, mg/L	63.5	23.3
Total Hardness, mg/L	110.4	18.4
TOC, mg/L	2.3	0.6
UVA, 1/cm	0.12	0.06
Bromide, mg/L	0.03	0.01
Ammonia, mg/L	0.29	0.41
Temperature, Celsius	12.4	0
Flow Rate, MGD	108.4	0

FLORESCENT EMISSION EXCITATION MATRIX BASED DBP MODELS



	TOC	TON	HOCl demand	UV ₂₅₄	ΦP1 _n	ΦP2 _n	ΦFA _n	ΦSMP _n	ΦHA _n
THM4*	0.88 (3.5×10 ⁻¹²)	0.70 (1.9×10 ⁻⁷)	0.91 (1.5×10 ⁻¹³)	0.76 (1.3×10 ⁻⁸)	0.15 (0.057)	0.32 (0.003)	0.85 (8.1×10 ⁻¹¹)	0.46 (2.2×10 ⁻⁴)	0.72 (7.8×10 ⁻⁸)

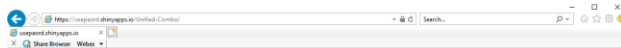
Lyon, et. al, 2013

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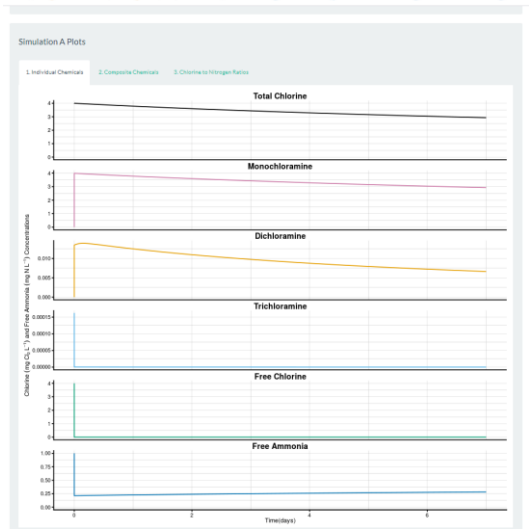
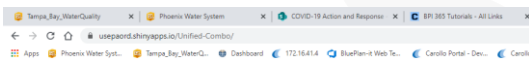
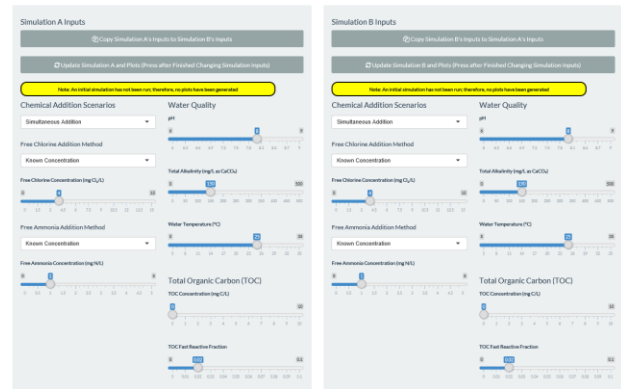


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EPA CHLORINE AND CHLORAMINE WEB APP(2016)



Batch (Plug Flow) Reactor Simulation of Drinking Water Chlorine Formation and Decay (Version 0.52, Updated 02/16/2016)
 Created by David G. Wahman, United States Environmental Protection Agency, Office of Research & Development.
 Chloramine kinetic model implementation from Jahnert & Valentine (Environ. Sci. Technol., 1992, 26 (3), pp 577-586) and Vibastrand et al. (Water Res., 2005, 39 (7), pp 1766-1776).
 Natural organic matter reaction implementation from Durk et al. (Water Res., 2003, 39 (14), pp 3432-3435) using their average fast and slow organic reaction rate constants.
 The provided application provides two side-by-side simulations (A and B) and associated graphs to allow comparison of input choices on chloramine formation and decay.
 The application was developed by the United States Environmental Protection Agency (EPA). No warranty expressed or implied is made regarding the accuracy or utility of the system, nor shall the act of distribution constitute any such warranty. EPA has relinquished control of the information and no longer has responsibility to protect the integrity, confidentiality or availability of the information. Any reference to specific commercial products, processes, or services by service mark, trademark, manufacturer, or otherwise, does not constitute or imply their endorsement, recommendation or favor by EPA. The EPA seal and logo shall not be used in any manner to imply endorsement of any commercial product or activity by EPA or the United States Government. This application has been reviewed in accordance with EPA policy and has been approved for external and free use. The views expressed in this application do not necessarily represent the views or policies of the agency, although reasonable effort has been made to assure that the results obtained are correct. This application is experimental. Therefore, the author and the EPA are not responsible and assume no liability whatsoever for any results or any use made of the results obtained from this application, nor for any damages or litigation that result from the use of the application for any purpose.



<https://usepaord.shinyapps.io/Unified-Combo/>



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EPA CHLORINE BREAKPOINT CURVE WEB APP(2017)

Chlorine Breakpoint Curve Simulator (Version 0.25, Updated 12/18/2017)
 Created by David G. Wahman, United States Environmental Protection Agency, Office of Research & Development Implementation from Jalvert & Valentine (Environ. Sci. Technol., 1992, 26 (3), pp 577-586) and Vikesland et al. (Water Res., 1992, 26 (3), pp 577-586)

The provided application generates two side-by-side breakpoint curves (A and B) for comparison purposes with user defined condition to complete.

The application was developed by the United States Environmental Protection Agency (EPA). No warranty expressed or implied is a relinquished control of the information and no longer has responsibility to protect the integrity, confidentiality or availability of the otherwise, does not constitute or imply their endorsement, recommendation or favoring by EPA. The EPA seal and logo shall not be application has been reviewed in accordance with EPA policy and has been approved for external and free use. The views expressed assure that the results obtained are correct, this application is experimental. Therefore, the author and the EPA are not responsible or litigation that result from the use of the application for any purpose.

Simulation A Inputs

Note: An initial simulation has not been run; therefore, no plot has been generated.

Initial Conditions

Select Chemical with Initial Fluid Concentration

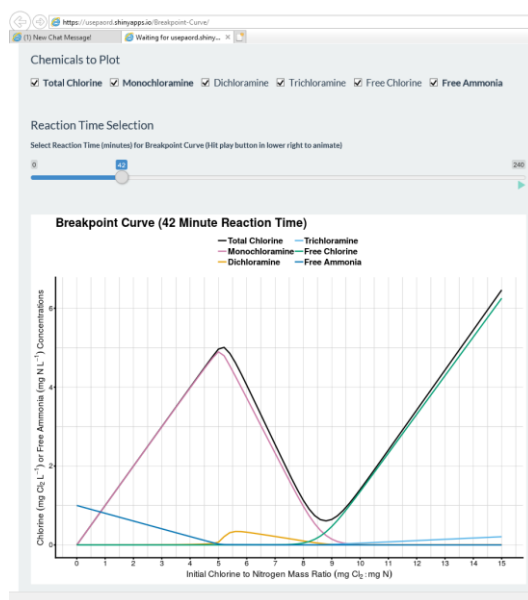
Free Ammonia

Initial Free Ammonia Concentration (mg N/L) [0 to 100]

Total Alkalinity (mg/L as CaCO₃) [0 to 500]

pH [6.5 to 9]

Water Temperature (°C) [5 to 35]



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EPANET MULTI-SPECIES EXTENSION FOR HYDRAULIC MODEL

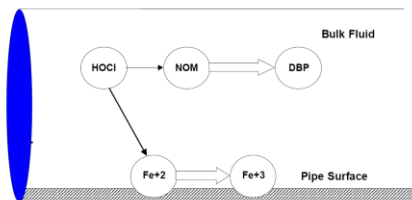


Figure 2-1 Example of reactions in the mobile bulk phase and at the fixed pipe surface phase.

Table 5-1 Monochloramine decay model based on Vikesland et al. (2001) and Duirk et al. (2005)

Reaction Stoichiometry	Rate Coefficient/ Equilibrium Constant ^a
R.1 HOCl + NH ₃ → NH ₂ Cl + H ₂ O	k ₁ = 1.5 × 10 ¹⁰ M ⁻¹ h ⁻¹
R.2 NH ₂ Cl + H ₂ O → HOCl + NH ₃	k ₂ = 7.6 × 10 ⁻² h ⁻¹
R.3 HOCl + NH ₂ Cl → NHC ₂ + H ₂ O	k ₃ = 1.0 × 10 ⁶ M ⁻¹ h ⁻¹
R.4 NHC ₂ + H ₂ O → HOCl + NH ₂ Cl	k ₄ = 2.3 × 10 ³ h ⁻¹
R.5 NH ₂ Cl + NH ₂ Cl → NHCl ₂ + NH ₃	k ₅ = 2.5 × 10 ⁷ [H ⁺] + 4.0 × 10 ⁴ [H ₂ CO ₃] + 800 [HCO ₃ ⁻] M ⁻² h ⁻¹
R.6 NHCl ₂ + NH ₃ → NH ₂ Cl + NH ₂ Cl	k ₆ = 2.2 × 10 ⁸ M ⁻² h ⁻¹
R.7 NHC ₂ + H ₂ O → I	k ₇ = 4.0 × 10 ⁵ M ⁻¹ h ⁻¹
R.8 I + NHC ₂ → HOCl + products	k ₈ = 1.0 × 10 ⁵ M ⁻¹ h ⁻¹
R.9 I + NH ₂ Cl → products	k ₉ = 3.0 × 10 ⁷ M ⁻¹ h ⁻¹
R.10 NH ₂ Cl + NHC ₂ → products	k ₁₀ = 55.0 M ⁻¹ h ⁻¹
R.11 NH ₂ Cl + S ₁ × TOC → products ^b	k ₁₁ = 3.0 × 10 ⁴ M ⁻¹ h ⁻¹
R.12 HOCl + S ₂ × TOC → products ^c	S ₁ = 0.02 k ₁₂ = 6.5 × 10 ⁵ M ⁻¹ h ⁻¹ S ₂ = 0.5
E.1 HOCl ↔ H ⁺ + OCl ⁻	pK _a = 7.5
E.2 NH ₄ ⁺ ↔ NH ₃ + H ⁺	pK _a = 9.3
E.3 H ₂ CO ₃ ↔ HCO ₃ ⁻ + H ⁺	pK _a = 6.3
E.4 HCO ₃ ⁻ ↔ CO ₃ ²⁻ + H ⁺	pK _a = 10.3

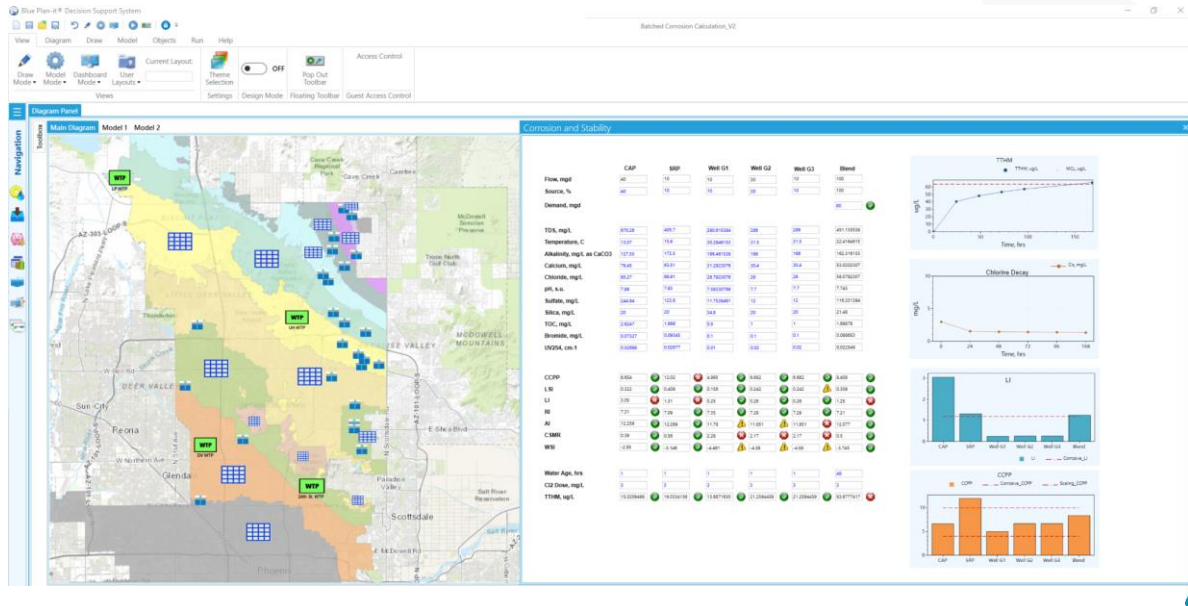
Notes:

- All rate coefficients and equilibrium constants are for 25 degrees C.
- S₁ is the fast reactive fraction of TOC.
- S₂ is the slow reactive fraction of TOC.

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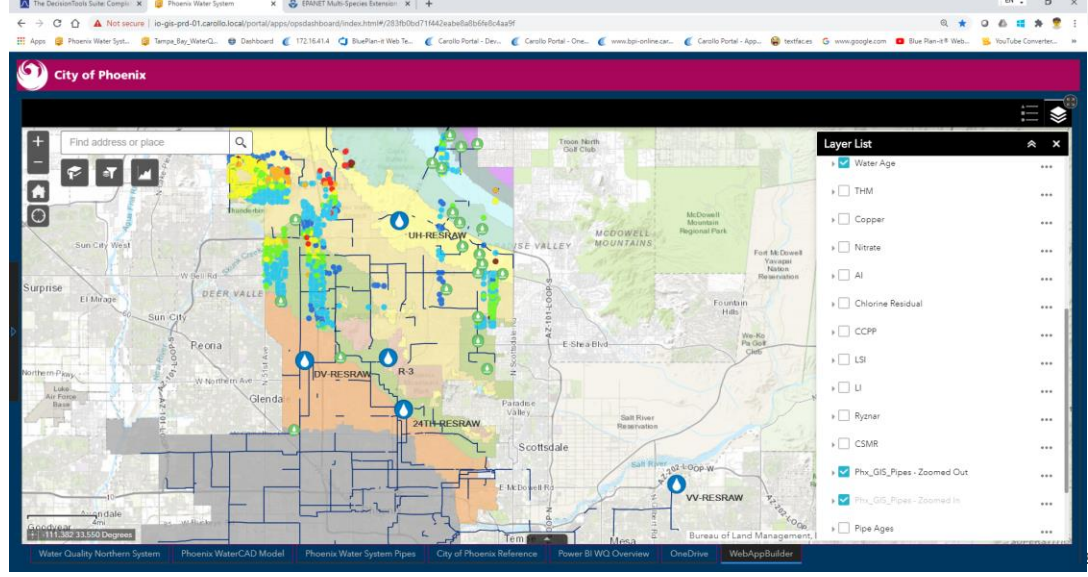
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BLUE PLAN-IT® 365 FOR WATER QUALITY MODELING



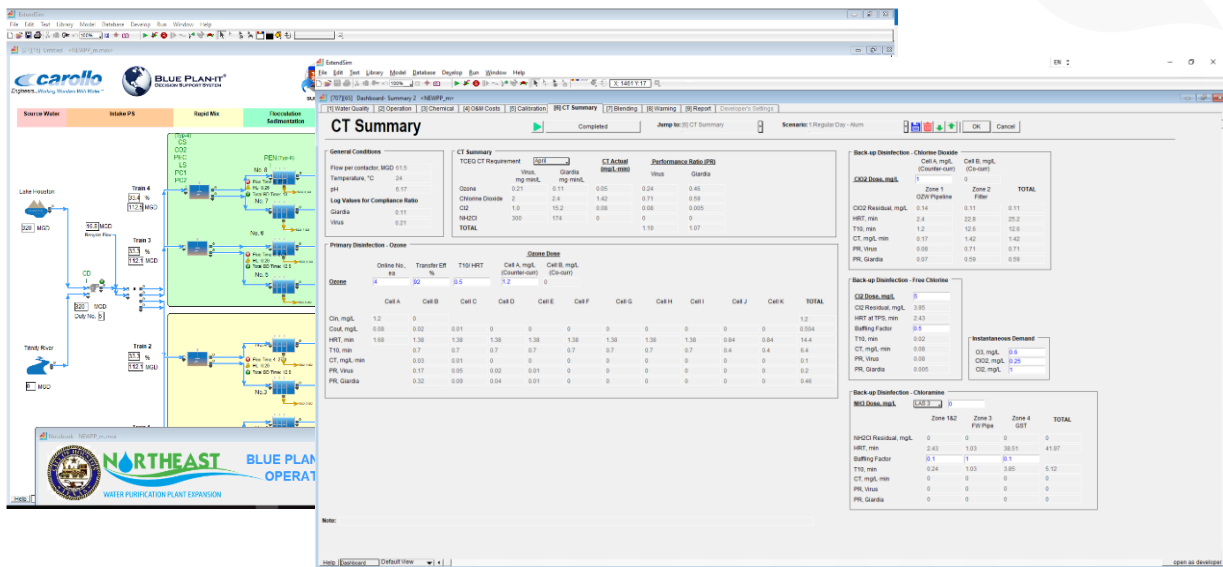
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INTEGRATED BPI AND GIS WEB APP DISPLAY MODELING RESULTS GEOGRAPHICALLY



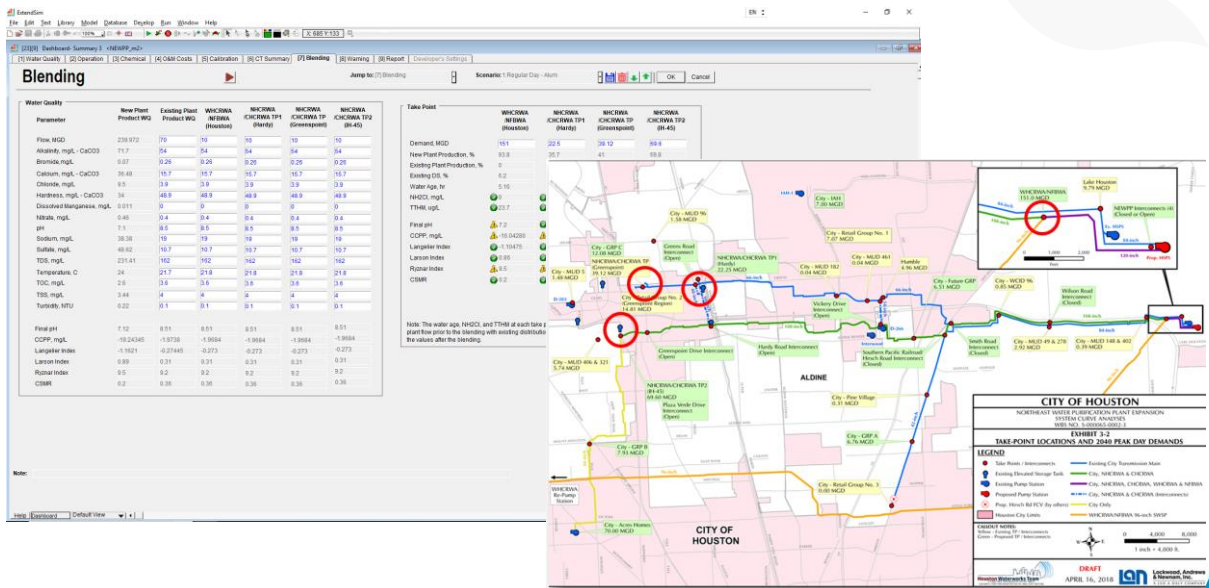
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INTEGRATED TREATMENT PLANT MODEL FOR OZONE, CLO₂, CHLORINE AND CHLORAMINE



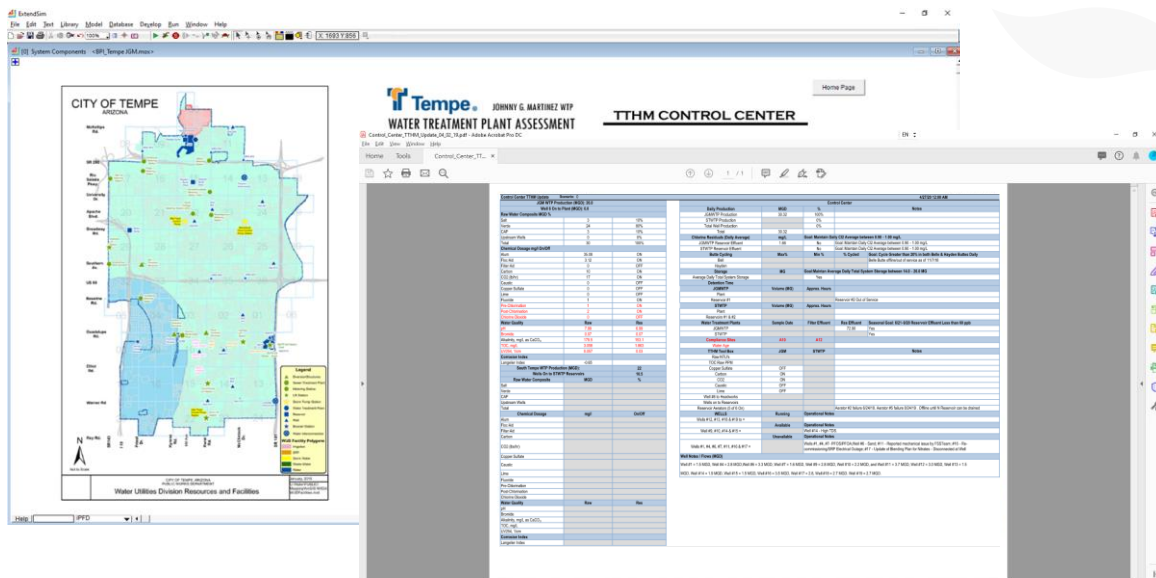
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PREDICT FINISHED WATER QUALITY AT EACH AUTHORITY TAKE-POINTS



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MODEL GENERATES PROCESS CONTROL REPORTS

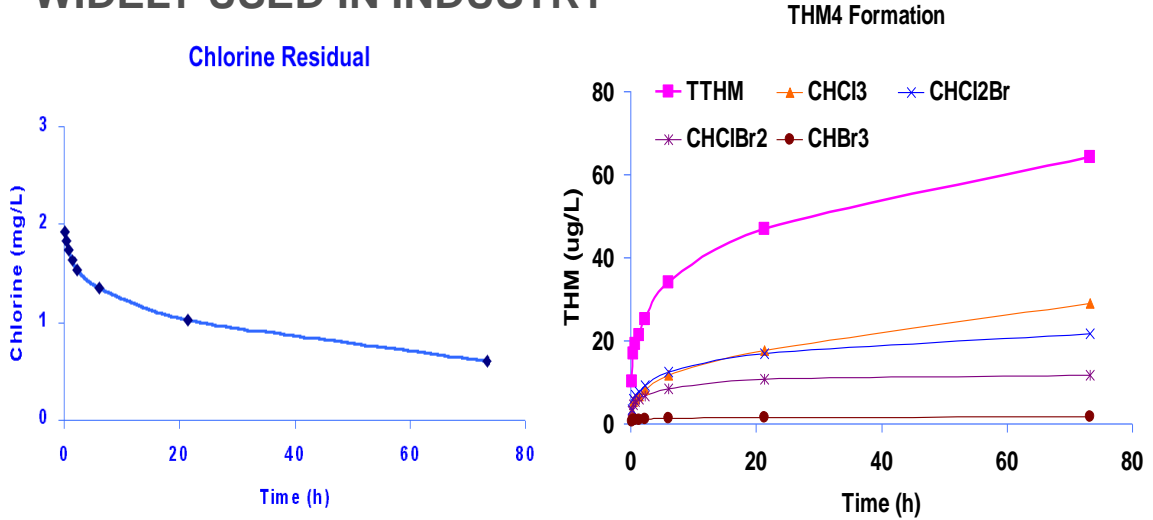


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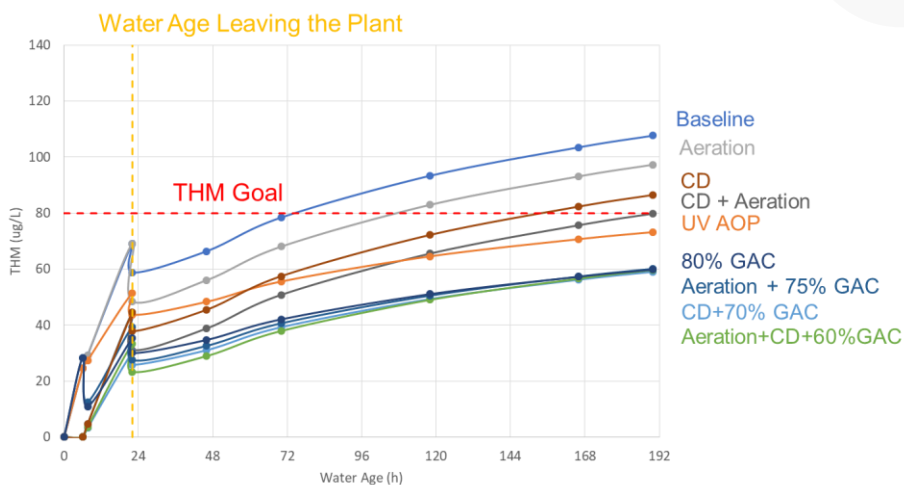
95

CHLORINATION AND TTHM FORMATION CURVES ARE WIDELY USED IN INDUSTRY



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MODELING IMPACT OF TREATMENT ALTERNATIVES AND FLOW FLUCTUATIONS ON TTHMS

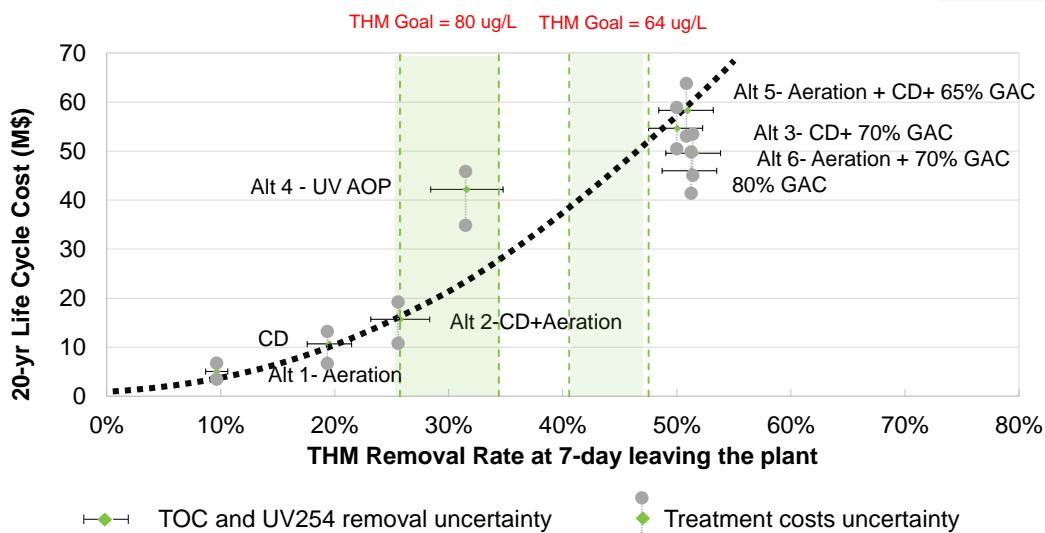


80% GAC means 80% of the filtered flow is treated by GAC



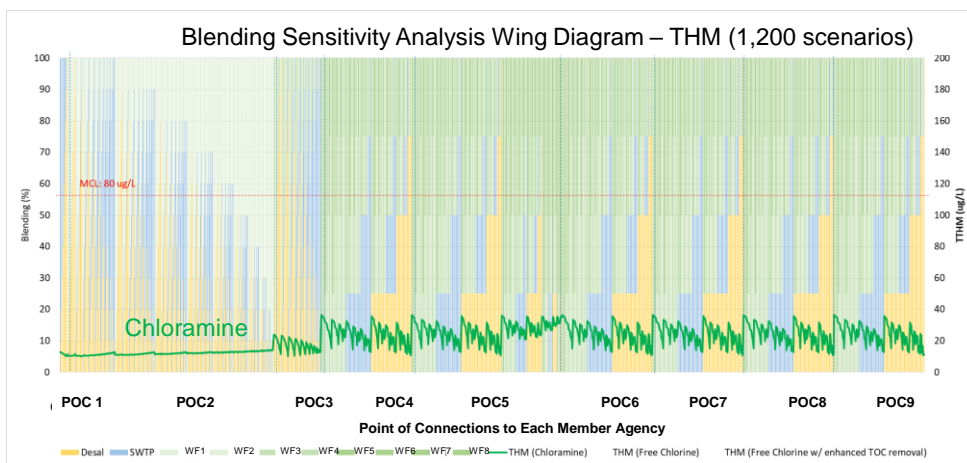
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MODELING COST BENEFIT CURVES TO SUPPORT DECISION MAKING ON PROPOSED TREATMENT



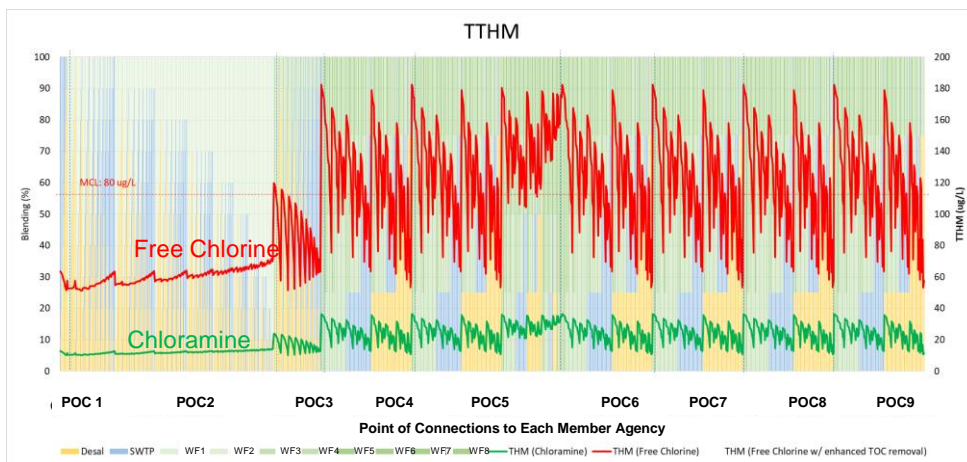
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MODELING IMPACT OF TREATMENT ON THM AT EACH POINT OF CONNECTION (1200 SCENARIOS)



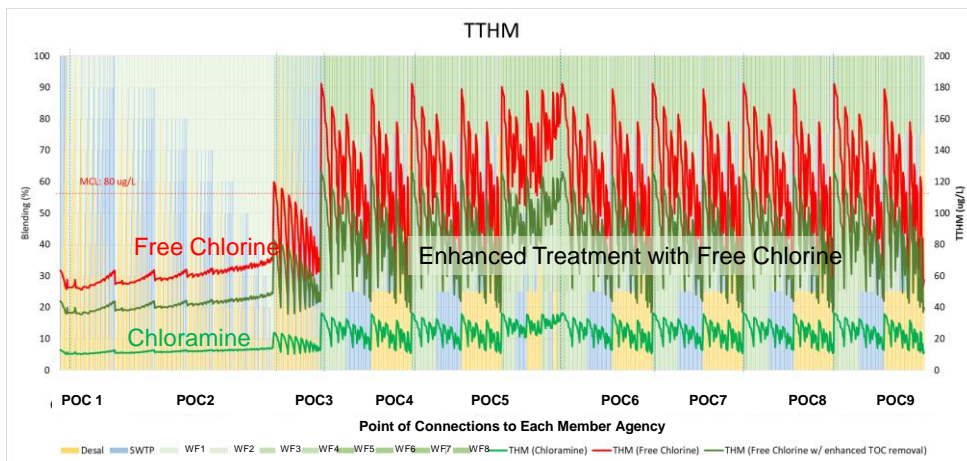
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MODELING IMPACT OF TREATMENT ON THM AT EACH POINT OF CONNECTION (1200 SCENARIOS)



100

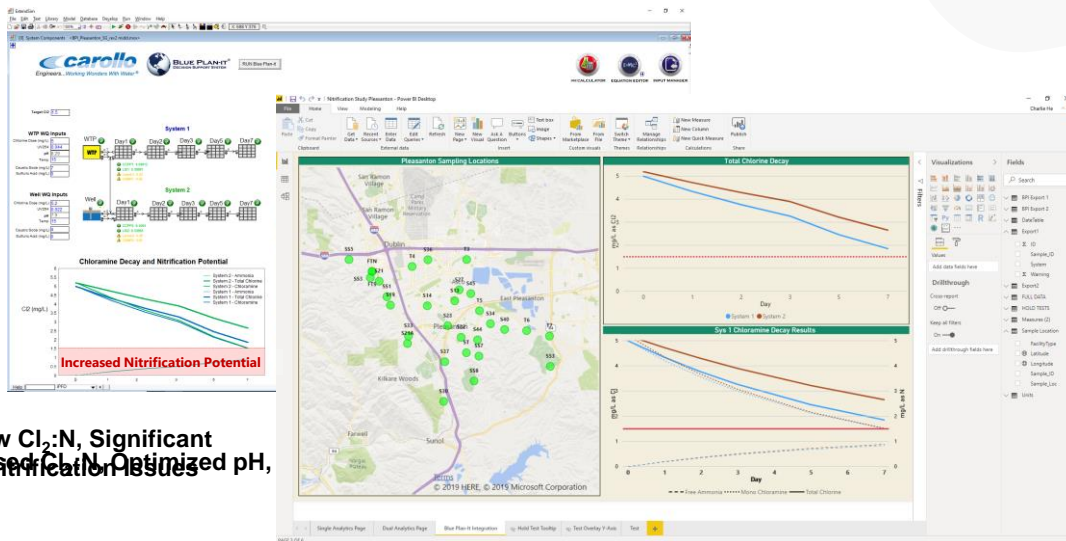
MODELING IMPACT OF TREATMENT ON THM AT EACH POINT OF CONNECTION (1200 SCENARIOS)



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MODELING CHLORAMINE SYSTEM TO CONTROL NITRIFICATION

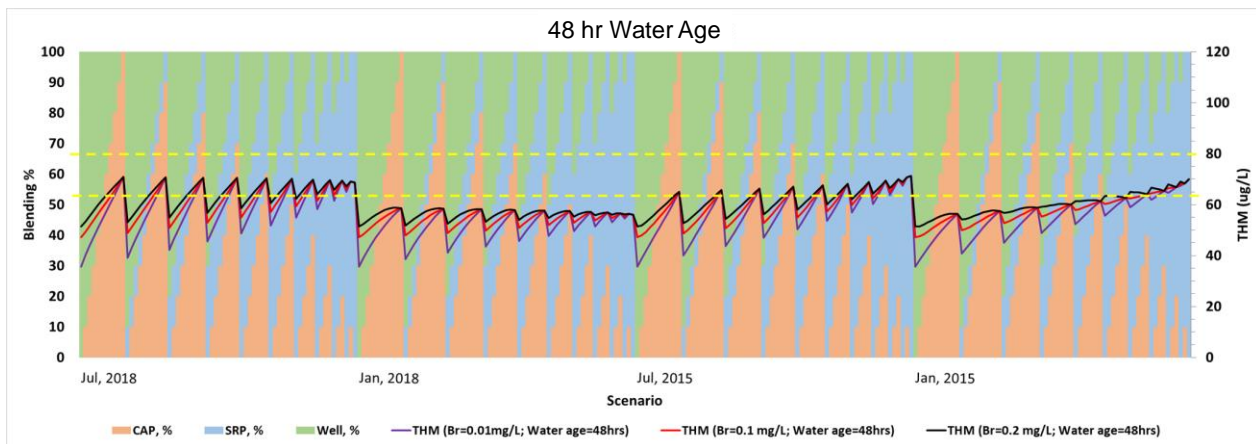


Low Cl₂:N, Significant Increased Cl₂:N, Optimized pH, Nitrification Issues

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MODELING IMPACT OF BLENDING OF GROUNDWATER AND BROMIDE ON TTHMS (4000 SCENARIOS)

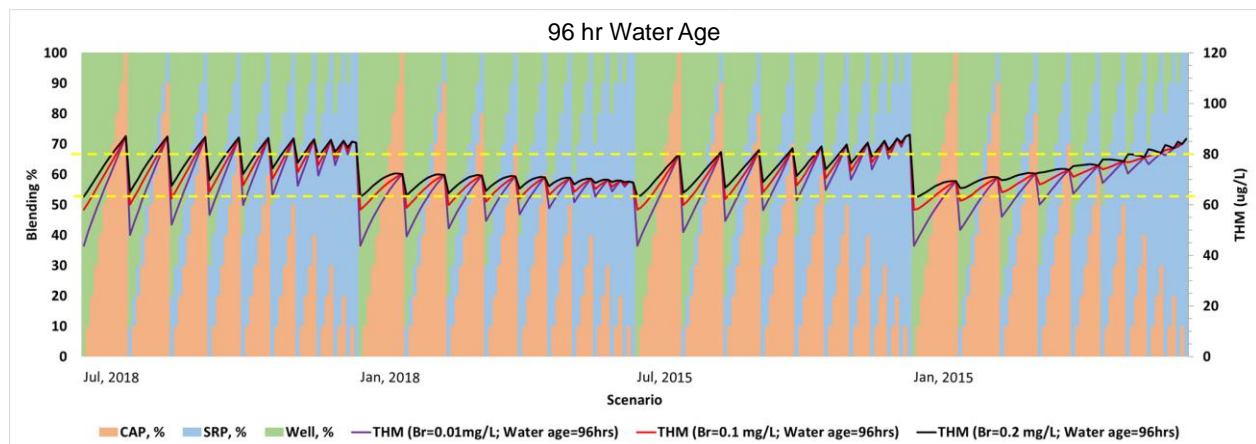


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MODELING IMPACT OF BLENDING OF GROUNDWATER AND BROMIDE ON TTHMS

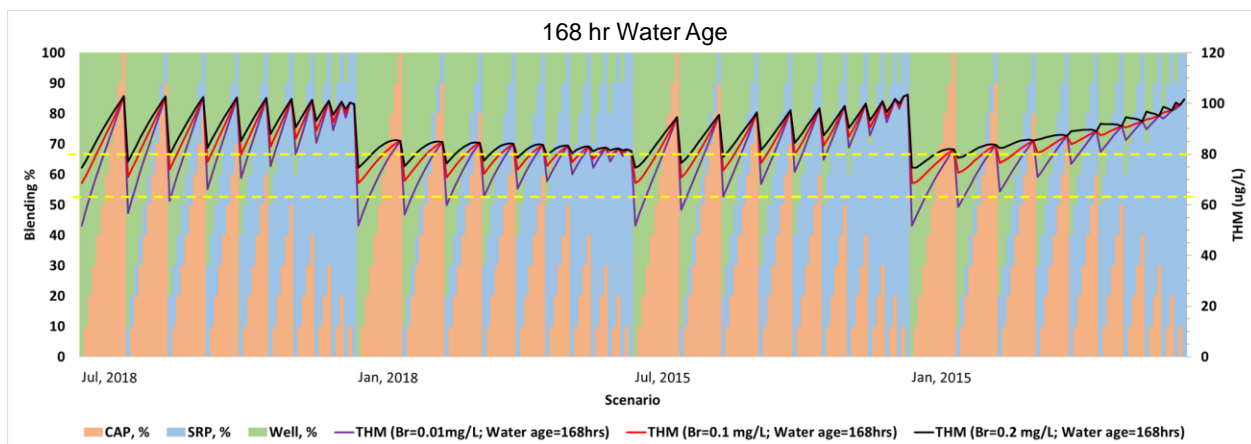


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MODELING IMPACT OF BLENDING OF GROUNDWATER AND BROMIDE ON TTHMS



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CONCLUSIONS

- Assessing distribution water quality requires combining several modeling tools
- Integrated approach to DBP mitigation offers several benefits:
 - Combine water treatment plant operations model and distribution system model for better water quality controls
 - Combine water quality modeling and hydraulic modeling for more accurate and geographical presentation
 - Combine steady state modeling and advanced computation techniques to better address WQ variations
 - Combine water quality modeling and cost estimates for more productive decision support

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ASK THE EXPERT



Susan Richardson
University of South Carolina



Susan Teefy
East Bay Municipal Utility District



Charlie (Qun) He
Carollo Engineers, Inc

Enter your **question** into the **question pane** on the right-hand side of the screen.

Please specify to whom you are addressing the question.

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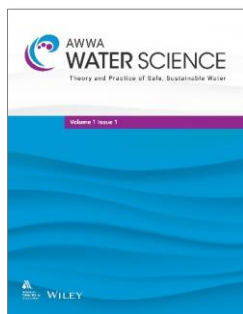


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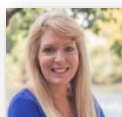
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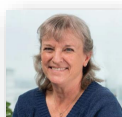


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PRESENTER BIOGRAPHY INFORMATION



Susan D. Richardson is the Arthur Sease Williams Professor of Chemistry in the Department of Chemistry and Biochemistry at the University of South Carolina; prior to coming to USC, she was a Research Chemist for several years at the U.S. EPA's National Exposure Research Laboratory. Susan is the recipient of the 2008 American Chemical Society Award for Creative Advancements in Environmental Science & Technology, has received an honorary doctorate from Cape Breton University in Canada, was recognized as an American Association for the Advancement of Science (AAAS) Fellow and an ACS Fellow, and is currently the President of the American Society for Mass Spectrometry and an Associate Editor for Environmental Science & Technology. Susan has a Ph.D. in Chemistry from Emory University and a B.S. in Chemistry & Mathematics from Georgia College & State University.



Susan Teefy is the Water Quality Manager for the East Bay Utility District in Oakland, California. She has 30 years of experience in drinking water treatment, distribution, water quality and regulatory compliance issues. She has a bachelor's degree in Civil Engineering from University of California, Berkeley, and a master's degree in Environmental Engineering from University of North Carolina, Chapel Hill. She is also a licensed water treatment and water distribution operator in California. East Bay MUD's treatment plants use free chlorine, ozone, and chloramine, and thus Susan has experience with several disinfection byproduct monitoring and control issues.



Charlie (Qun) He, a vice president and chief technologist with Carollo, has more than 19 years of experience in water and wastewater treatment, water quality, and water resources. Mr. He has extensive experience in water and wastewater treatment, with an expertise in developing and optimizing treatment strategies for complex industrial wastewater treatment. He has gained experienced working with semiconductor, data center, mining, chemical, power, textile, food and beverage, and manufacturing industries. He leads the company's integrated decision support system team and is leading the research and development of Blue Plan-it® Decision Support System, an advanced water and wastewater system simulation and optimization tool. He is Carollo's membrane desalination and concentrate management expert for the southwest region and one of the R&D Innovation Lead for the Carollo's Research Group. He is the chair of AWWA Manual of Practice 69 – Inland Desalination and Concentrate Management and the vice chair of the AWWA Joint Research Committee. He is the ex-chair of AZ Water Association Research Committee and the ex-chair of the AWWA Joint Research Committee. In addition, Mr. He is a LEED AP and has gained extensive exposure to the field of sustainability.

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