THE Water Research FOUNDATION **Webcast**

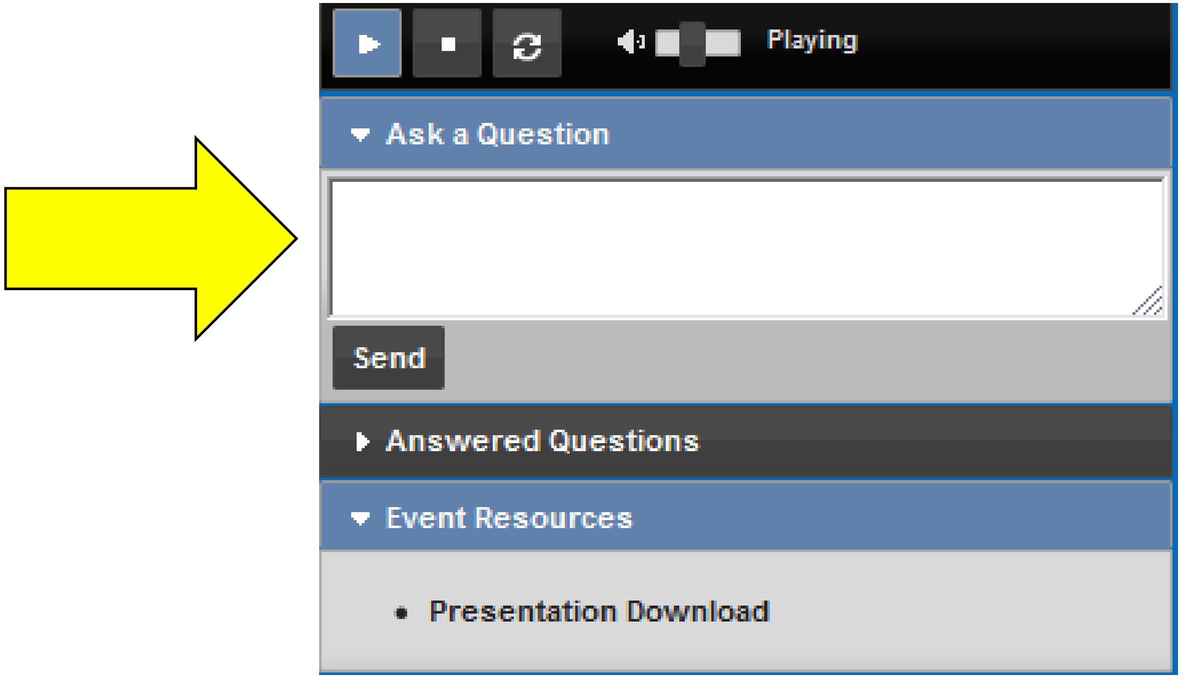
Characterizing and Controlling Organics in Direct Potable Reuse Projects

November 19, 2019

Housekeeping Items

- Submit questions through the question box at any time! We will do a Q&A near the end of the webcast.
- Slides and a recording of the webcast will be available at www.waterrf.org.
- Send an email to Michelle Suazo at msuazo@waterrf.org for a PDH certificate.
- Survey at the end of the webcast.

Input your webinar questions here



Q&A at end of webinar

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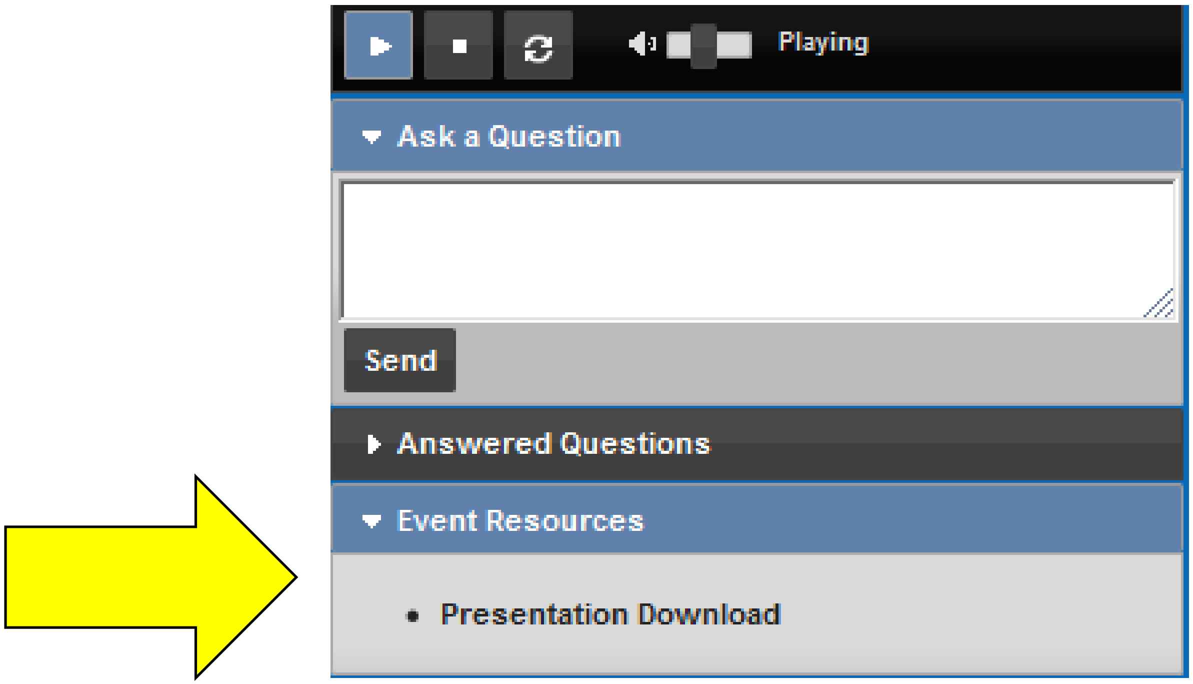


Slides and recording will be available to WRF subscribers WITHIN 24 hours after the webcast

Webcast Agenda

- Background and Participating Utilities
- Summary of Analytical Testing
- Framework Description and TOC Monitoring
- DBPs and Toxicity Index
- CECs and Bioassays
- Testing the Framework
- Summary
- Q&A

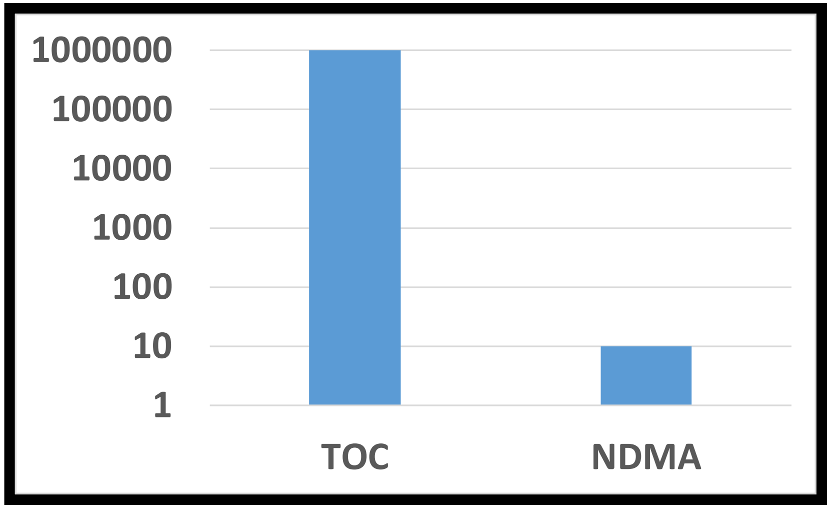
Wide Variety of How Organics are Regulated for Potable Reuse

- TOC + MCLs (e.g., SOCs, VOCs, THMs, HAAs)

Location	Organics Limit
California[1]	TOC < 0.5 mg/L
HRSD SWIFT Project	TOC < 4 mg/L
Virginia (Occoquan and Dulles Policies)	COD < 10 mg/L
Georgia (Gwinnett County)	COD < 18 mg/L
Texas (El Paso; Big Spring)	None
Florida	TOC < 3 mg/L; TOX ≤ 0.2 mg/L
EPA Guidelines (2012)	TOC < 2 mg/L; TOX ≤ 0.2 mg/L
De Facto Reuse[2]	None
1. Requirements are for 100% groundwater injection 2. Regulated by CWA and SDWA	

Organics Dilemma for Potable Reuse

- Bulk organic measurements (e.g., TOC, COD) may be too broad to accurately reflect exposure to the small fraction of organics that may be harmful or toxic



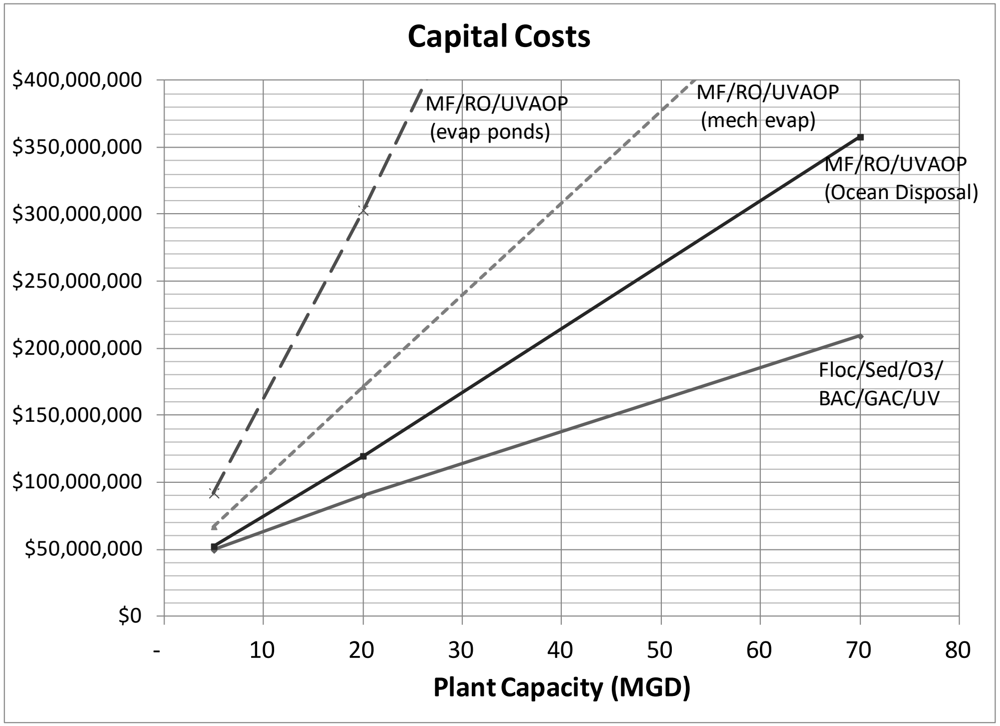
- Therefore, use of bulk organic limits (e.g., TOC < 2 mg/L) may not protective of public health and not universally applicable

Research Goals

- Develop a site-specific framework for utilities pursuing direct potable reuse to demonstrate that their DPR water is "safe" from an organics perspective
  - Compare "safety" of potable reuse water to "safety" of local potable water from which DPR water was sourced
  - Compare organics profile at various locations in the domestic water cycle

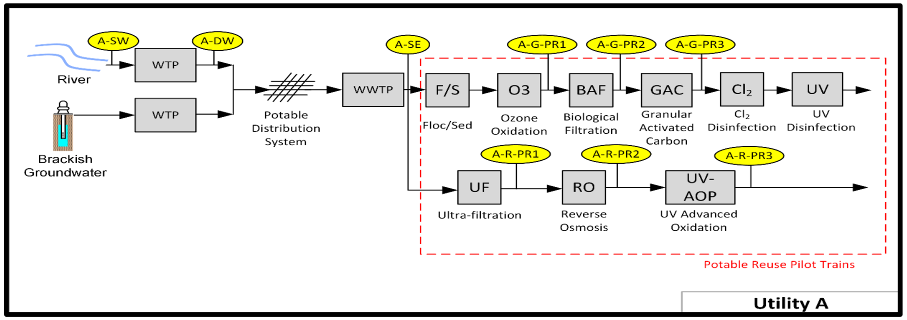
Utility Selection

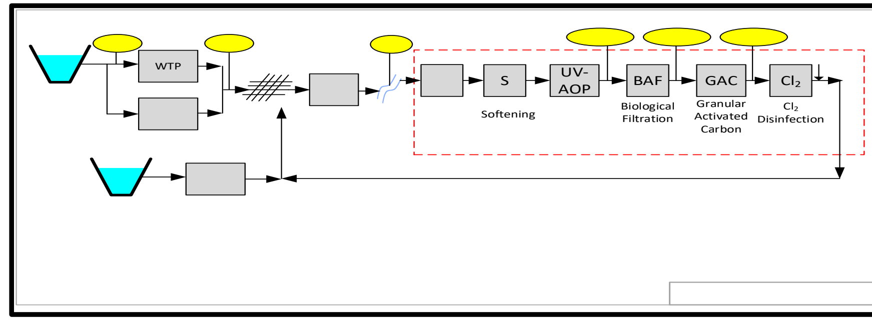
- Six potable reuse utilities selected (5 IPR facilities and 1 DPR facility)
- Geographically diverse: four in U.S., two international
- Focused on utilities not using reverse osmosis (RO) based treatment:
  - TOC limit not really necessary for RO (TOC <0.1 mg/L)
  - Implementation is prohibitively expensive at in-land locations

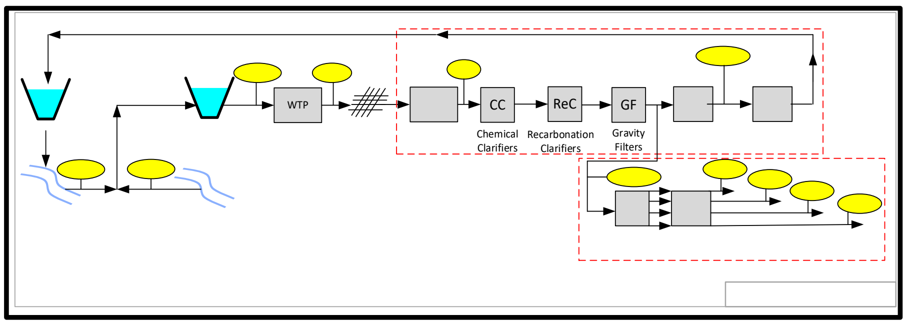


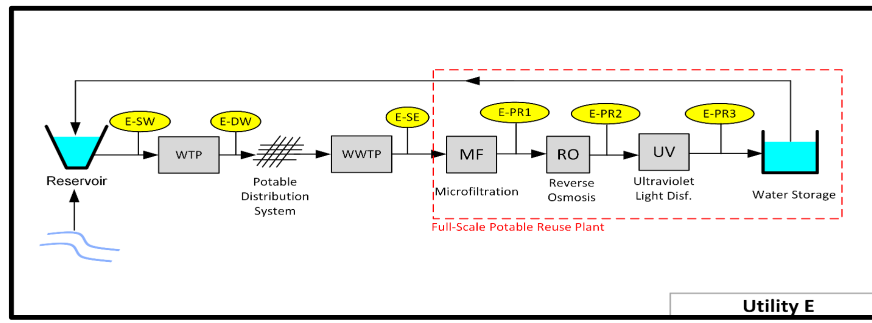
Schimmoller and Kealey, 2014

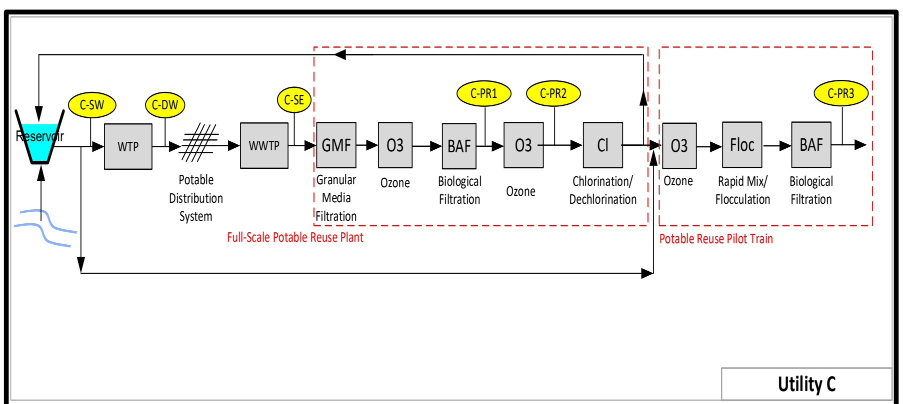
Participating Utilities – Potable Reuse Schemes

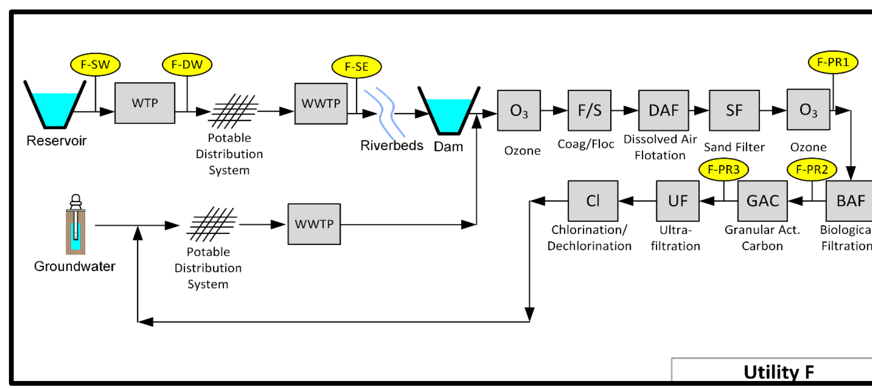






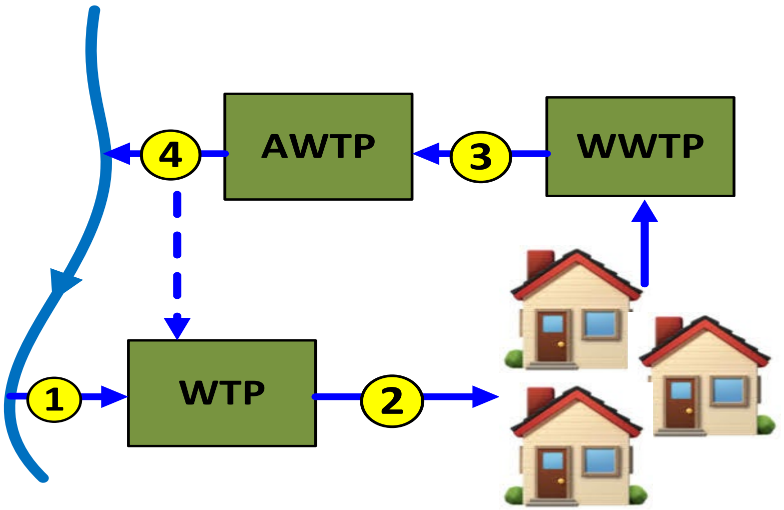






Analytical Testing

- Four samples collected over 1-year at multiple points within the domestic water cycle
  - Bulk organics (**TOC**, COD, UVA)
  - EEM
  - **DBPs (regulated and non-regulated)**
  - **CECs (or TOrCs)**
  - SEC-OCD
  - **Bioassays**
  - Other (e.g., non-targeted analysis)



Sampling in the Domestic Water Cycle

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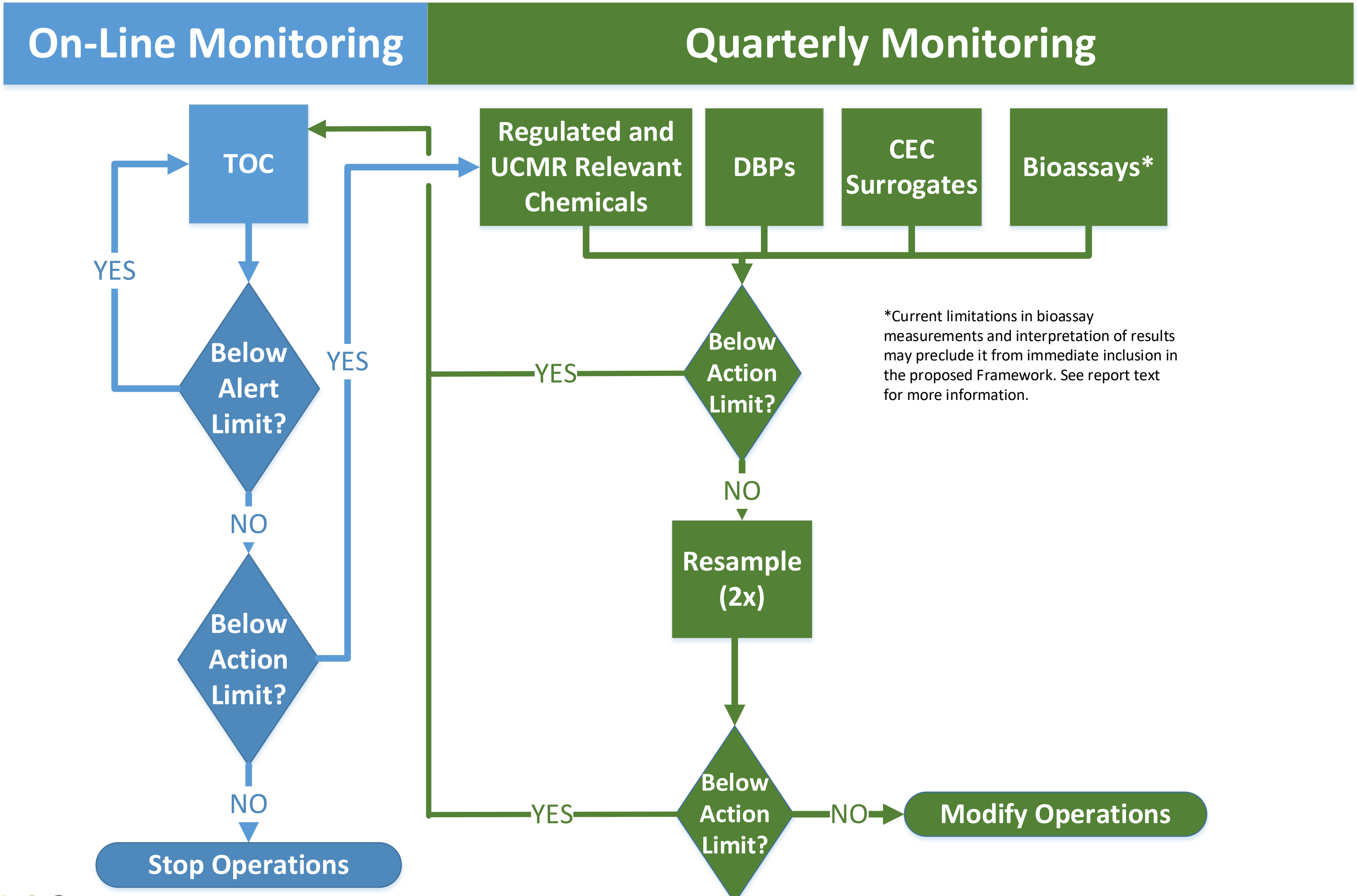
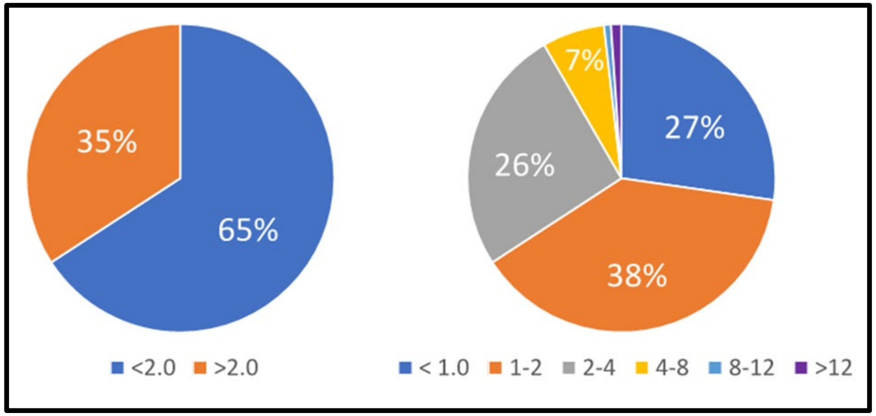
Proposed Framework for Controlling Organics in DPR Projects



*Current limitations in bioassay measurements and interpretation of results may preclude it from immediate inclusion in the proposed Framework. See report text for more information.

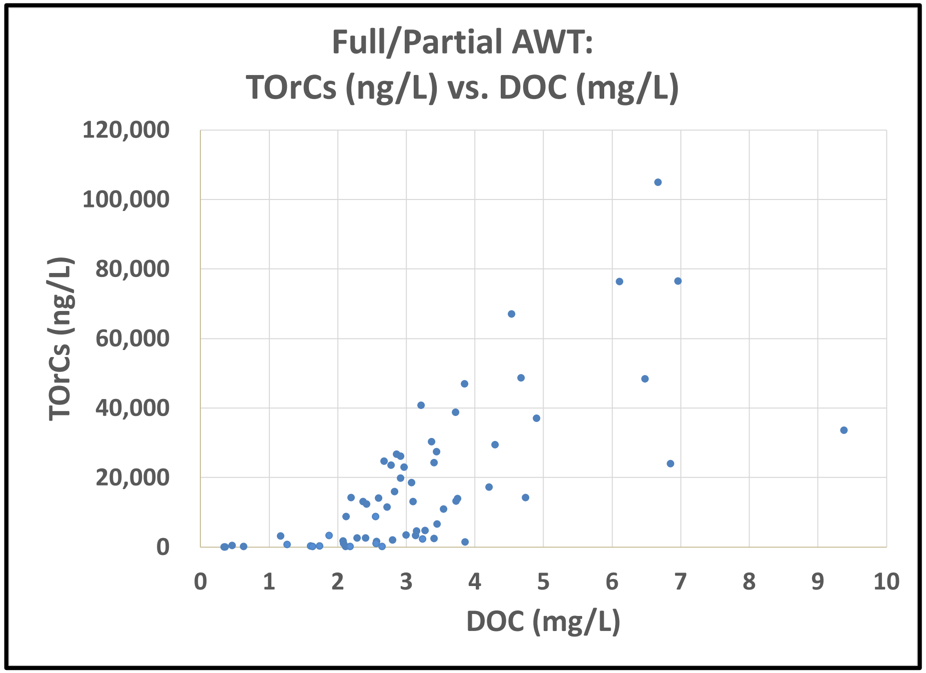
Setting Action and Alert Limits for TOC

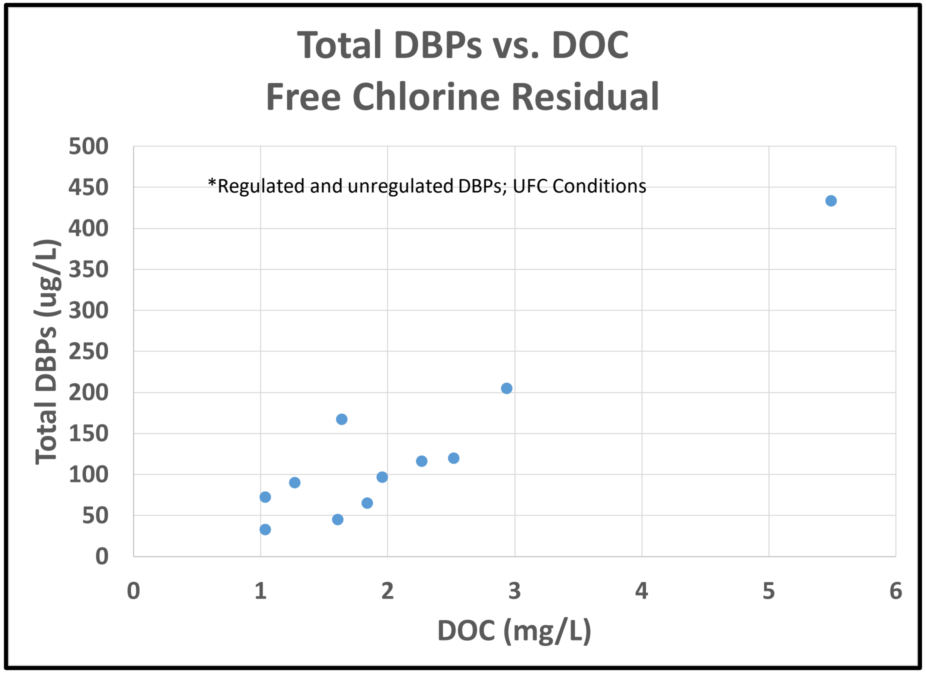
- Ideally, prevent the potential for elevated hazardous organic chemicals to occur in DPR water
- Selection of limits that are too low can result in unreasonable construction and operating costs
- Numerous drinking water systems provide safe drinking water to their customers at TOC concentrations ranging from below 1 mg/L to above 4 mg/L



TOC in U.S. Potable Water (n=276); AWWA 2017

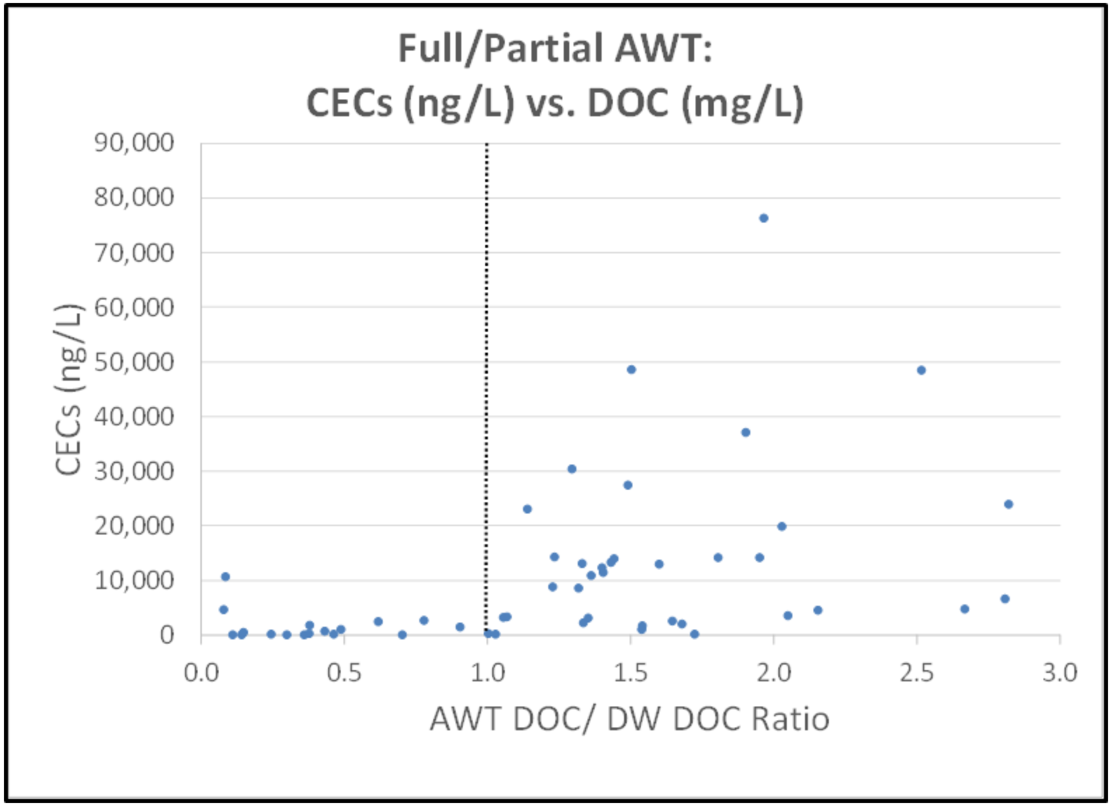
TOC Provides Some Correlation to Potential Health Relevance



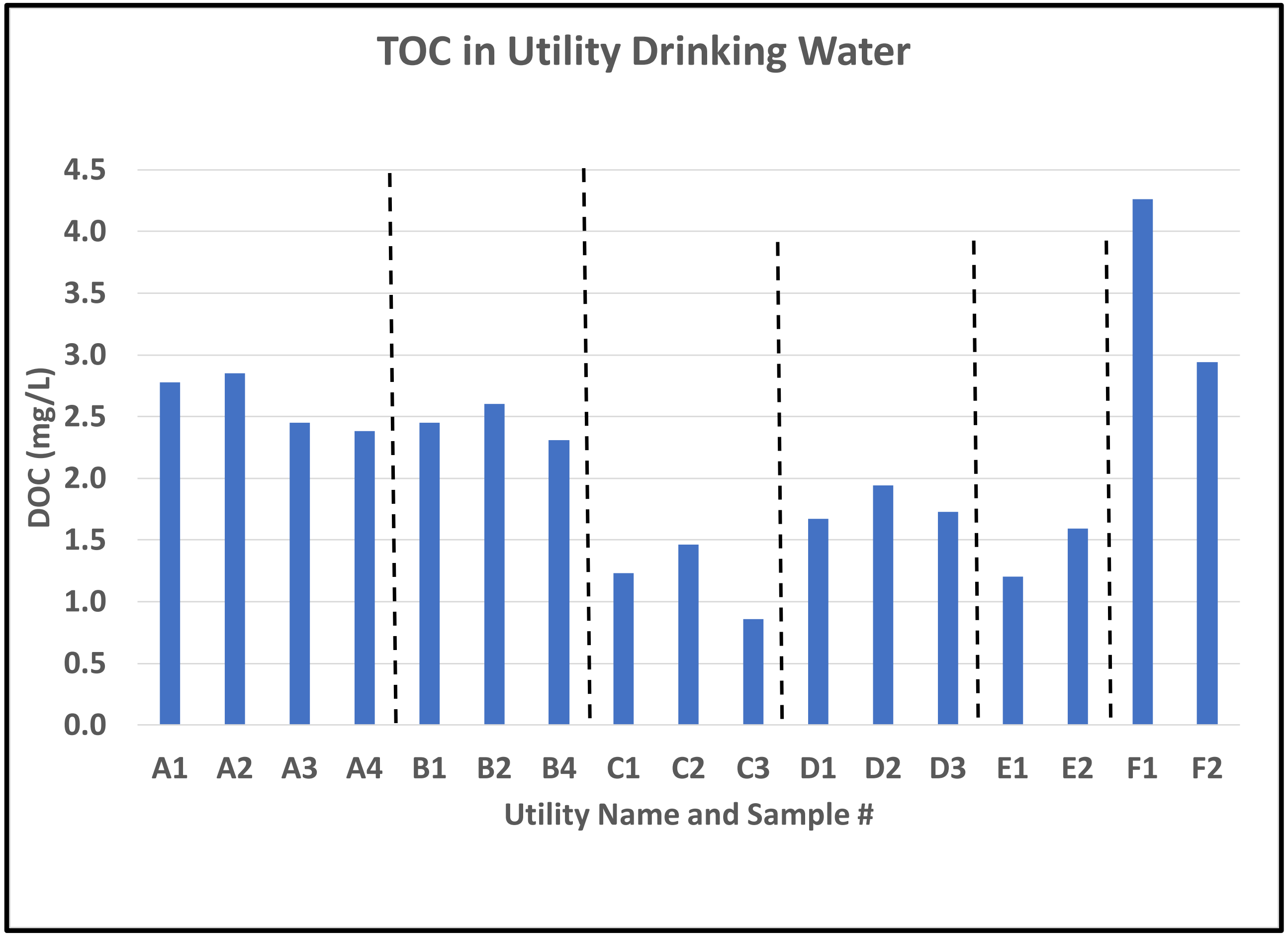


Comparison to TOC in Local Drinking Water

- When DOC in DPR water exceeds DOC in local drinking water, concentration of chemicals increase
- DPR treatment goal: return water's bulk organic characteristics back to approximately that of the local drinking water



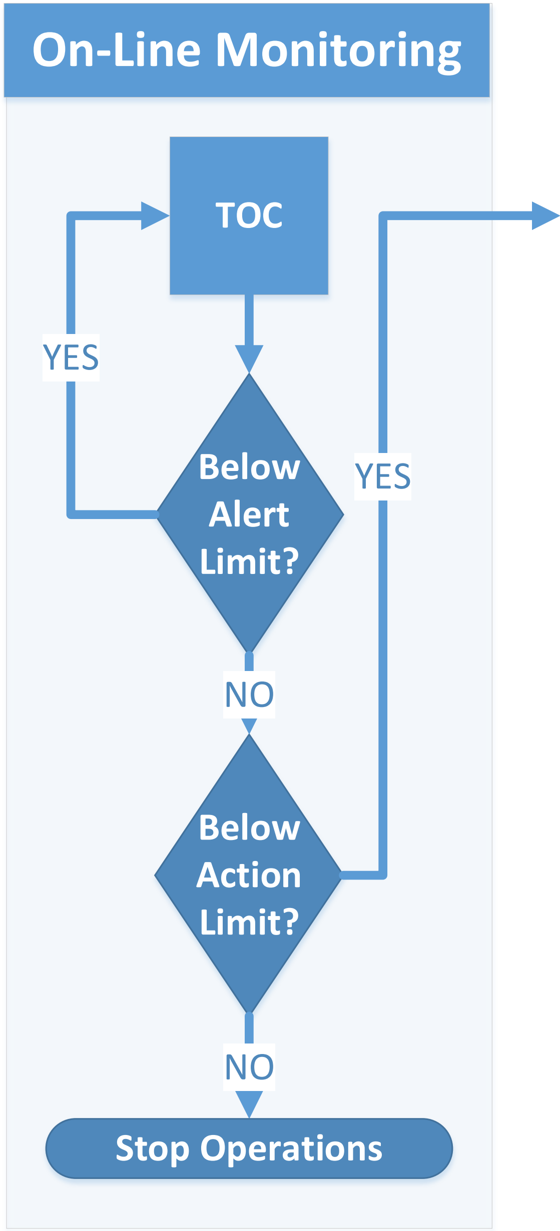
Drinking Water TOC in this Study



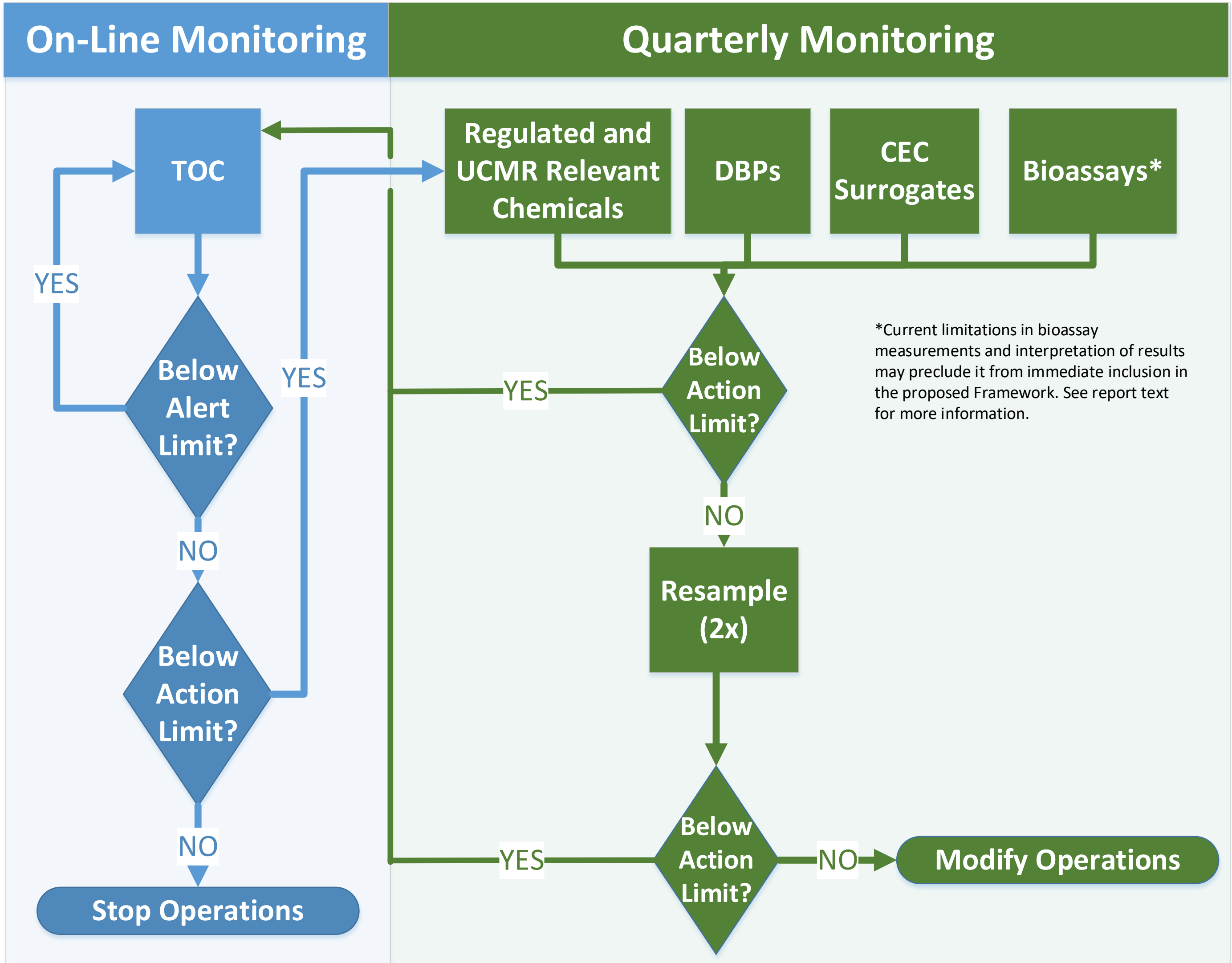
- TOC ranged from 1- 4 mg/L

What are appropriate TOC Limits for DPR Water?

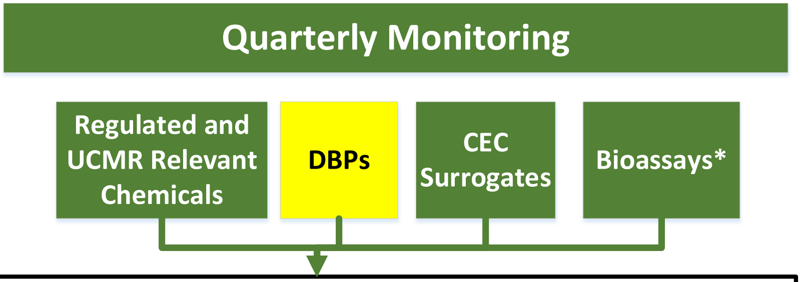
- **Alert Limit**: 50th percentile of drinking water TOC
  - When DPR water's 30-day running average for TOC exceeds Alert Limit, more analysis required (CECs, DBPs, Bioassays, MCLs)
- **Action Limit**: 1.5 x 95th percentile of drinking water TOC
  - When DPR water's on-line TOC exceeds Action Limit, stop operations



Quarterly Monitoring



Benefits of Including DBPs in Framework



- Margins of safety in potable reuse are lowest for DBPs

TABLE 7-1 Summary of Margin of Safety (MOS) Estimates for the Three Scenarios Analyzed by the Committee

Chemical	Risk-Based Action Level[a]	MOS Scenario 1, de Facto Reuse	MOS Scenario 2, SAT, No Disinfection	MOS Scenario 3 MF/RO/UV
Nitrosamines				
NDMA	0.7 ng/L	>0.4	>0.4	>0.4
Disinfection byproducts				
Bromate	10 μg/L	N/A	N/A	> 2
Bromoform	80 μg/L	27	160	>160
Chloroform	80 μg/L	16	80	16
DBCA	60 μg/L	>60	>60	>60
DBAN	70 μg/L	>54	>140	N/A
DBCM	80 μg/L	>80	N/A	>160
DCAA	60 μg/L	12	>60	>60
DCAN	20 μg/L	>20	>20	N/A
HAA5	60 μg/L	6	12	12
THM	80 μg/L	2.7	16	8
Pharmaceuticals				
Acetaminophen	350,000,000 ng/L	>350,000,000	>350,000,000	>35,000,000
Ibuprofen	120,000,000 ng/L	>120,000,000	56,000,000	>280,000,000
Carbamazepine	186,900,000 ng/L	10,000,000	1,200,000	>190,000,000
Gemfibrozil	140,000,000 ng/L	8,600,000	2,300,000	>140,000,000
Sulfamethoxazole	160,000,000 ng/L	>80,000,000	720,000	>160,000,000
Meprobamate	280,000,000 ng/L	17,000,000	8,800,000	>930,000,000
Primidone	58,100,000 ng/L	10,000,000	450,000	>58,000,000
Others				
Caffeine	70,000,000 ng/L	3,500,000	>70,000,000	>23,000,000
17-β Estradiol	3,500,000 ng/L	>35,000,000	>35,000,000	>35,000,000
Triclosan	2,100,000 ng/L	>3,500,000	840,000	>2,100,000
TCEP	2,100,000 ng/L	>84,000	5,800	>210,000
PFOS	200 ng/L	17	4	>200
PFOA	400 ng/L	36	19	>80

NOTES: > indicates that the assumed concentration was below detection, and only an upper limit on the risk calculation was determined. See Appendix A for further detail. [a]Sources of the risk-based action limits are provided in Table A-11 of Appendix 11.

Water Reuse, National Academies of Science, 2011

Toxicity Index vs. Current Regulatory Approach

- Mix of
  - Bulk parameter surrogates
    - TOC < 0.5 mg/L in CA
  - Limits on specific chemicals (e.g., MCLs)
    - THM4 < 80 μg/L
    - NDMA < 10 ng/L

Challenges with the Current Approach

1. Bulk parameter surrogates – TOC < 0.5 mg/L
   - Does TOC reflect anthropogenic contaminants?
     - TOC likely reflects high molecular weight, non-toxic biopolymers
     - Not the low molecular weight contaminants at ng/L – μg/L
   - Drives process selections (RO) with drawbacks
     - High energy/brine disposal
   - Interest in alternatives (O_3/BAC)
     - But how to validate effluent chemical quality?

Challenges with the Current Approach

2. Are specific targets (THMs, NDMA) the most important?

- Choice of target drives treatment train design
  - Each disinfectant produces different carcinogens
    - Chloramines → NDMA
    - Chlorine → THMs, etc
  - Which are the toxicity drivers?

Challenges with the Current Approach

3. Regulations target different risk levels
   - NDMA at 10^{-5} lifetime cancer risk (10 ng/L)
   - Bromate at 10^{-4} lifetime cancer risk (10 μg/L)
   - Does this bias treatment towards NDMA control?

Challenges with the Current Approach

4. Focus on individual chemicals
   - No explicit consideration of mixtures
   - Water with 10 contaminants each just below MCLs “safer” than water with 1 contaminant at MCL

Challenges with the Current Approach

5. No solid basis for comparison
   - 1000s of chemicals in wastewater
     - Each detection in reuse water → "the sky is falling"
     - Do they really matter?
   - Contaminants occur in conventional drinking waters too (DBPs)
   - When are reuse waters "safe enough"?

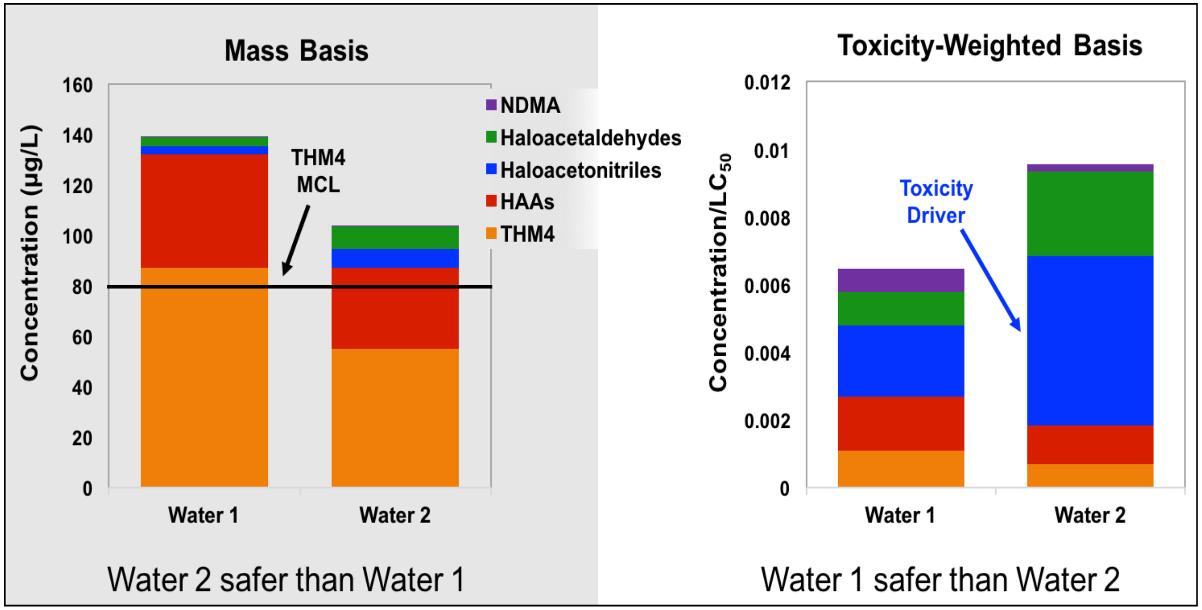
Proposed Approach

- **Contribution to toxicity = Concentration x Toxic Potency**
  - **Weight measured concentrations by toxic potency**
    - On a common risk basis (50%):
      - 50% risk for cytotoxicity (LC_{50}) in CHO cells
        - Broad toxicity metric
        - Quantitative data is available
        - $[DBP]/LC_{50}$
  - **Sum toxicity-weighted contaminant concentrations**
    - Assumes risk is additive
  - **Compare these values between reuse and conventional drinking water**
    - Considered safe by regulators and the public

Proposed Framework

- Comparing potable reuse to local conventional DW
- Compare toxicity-weighted stacked bars
  - If potable reuse stacked bar ≤ conventional ➔ "safe"
  - If potable reuse > conventional ➔ improve treatment until lower
    - Choose a treatment that targets the "toxicity driver"

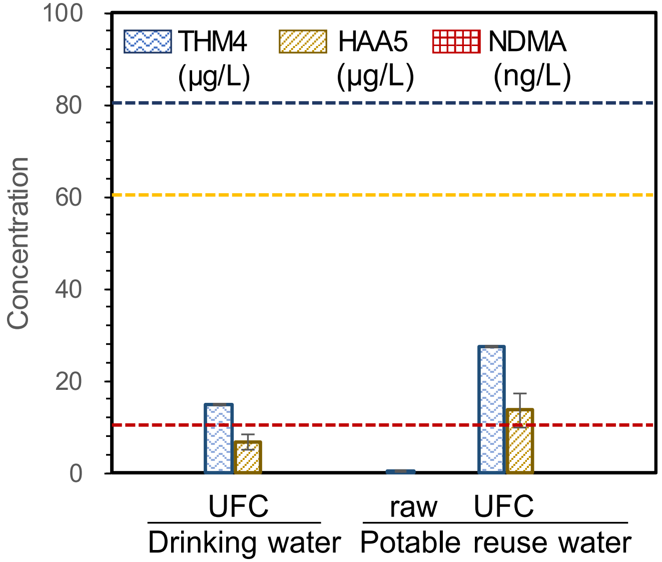
Current **Proposed**



Li, X.-F.; Mitch, W.A. *Environ. Sci. Technol.*, **2018**, 52, 1681-1689..

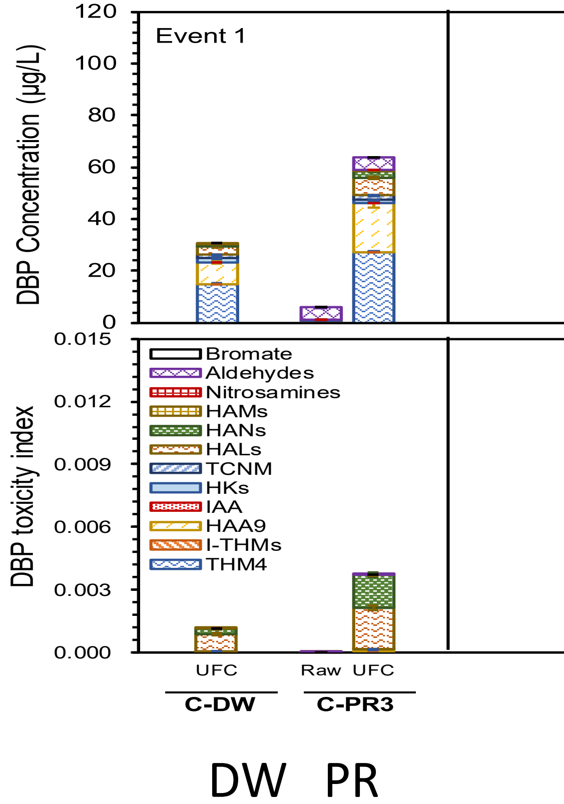
Example 1: Chlorine

- Non-RO-based advanced train vs. conventional DW
  - Advanced train: **Secondary** ➔ UF ➔ **O_3/BAC** ➔ **O_3** ➔ BAC ➔ **chlorinate**
  - Conventional DW: Sample upstream of disinfection ➔ **chlorinate**
  - Chlorination: 1 mg/L residual after 24 h at pH 8 (Uniform Formation Conditions (UFC))
  - 4 sample events over a year
- DOC
  - Conventional: 0.86-1.46 mg/L
  - Potable reuse: 1.17-2.60 mg/L
- Regulated DBPs (existing regs unlikely to disappear)
  - Both meet limits



Example 1: Chlorine

- Chlorinated potable reuse (PR) higher than chlorinated DW
  - Mass basis: THMs/HAAs important (not nitrosamines)
  - Toxicity-weighted: halogenated aldehydes, haloacetonitriles dominate
    - THMs/HAAs/nitrosamines not so important



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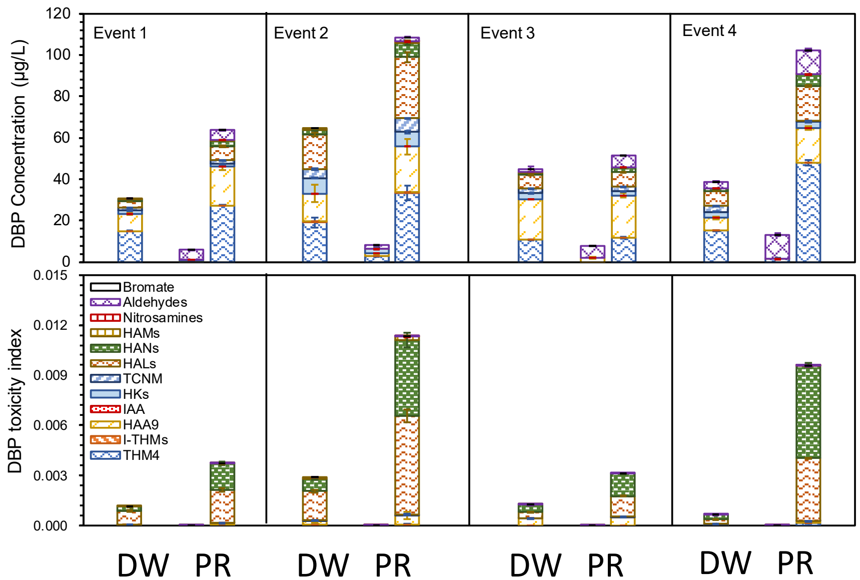
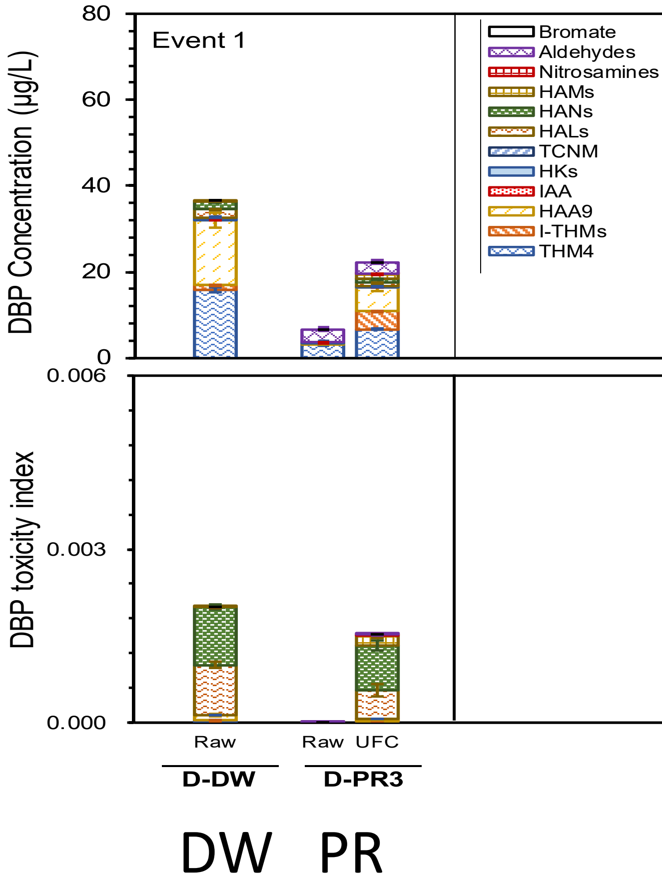


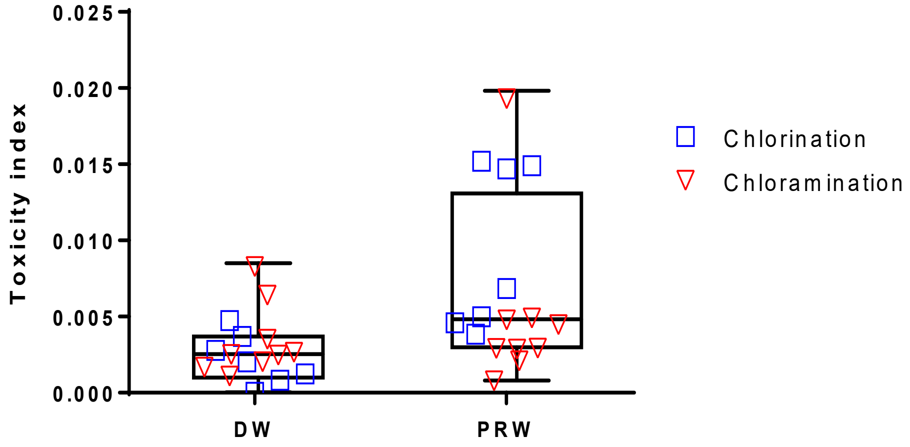
Example 2: Chloramines

- **Non-RO-based advanced train vs. conventional DW**
  - Advanced train: **Secondary** ➔ Softening ➔ UV/AOP ➔ **BAC** ➔ **GAC** ➔ **chloramines**
  - Conventional DW: Sample upstream of disinfection ➔ **chloramines**
  - Chlorination: 5 mg/L residual for 3 days at pH 8 (Uniform Formation Conditions (UFC))
  - 4 sample events over a year
- **Reuse lower than DW**
  - Mass basis: THM4, HAA9
  - Toxicity basis: HANs and HALs



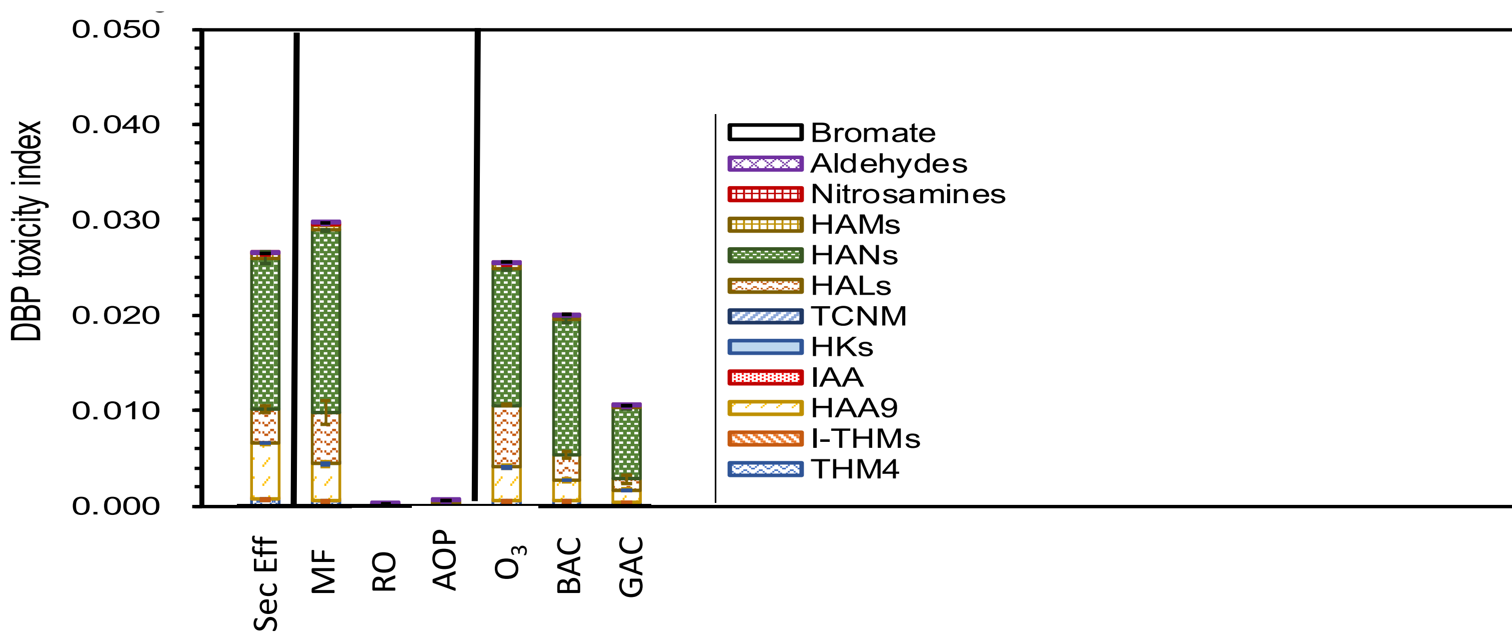
Overall Chlorine vs. Chloramines

- 5 non-RO reuse facilities: DW vs. Potable reuse effluents
  - Sorted by chlorine or chloramines
- Chlorinated potable reuse effluents often higher
  - Chloraminated potable reuse effluent often comparable



O_3/BAC/GAC vs. MF/RO/AOP

- Parallel pilot trains
  - Chlorine UFC-treated effluents
  - MF/RO/AOP delivers a high quality water
  - GAC can help reduce calculated toxicity after O_3/BAC

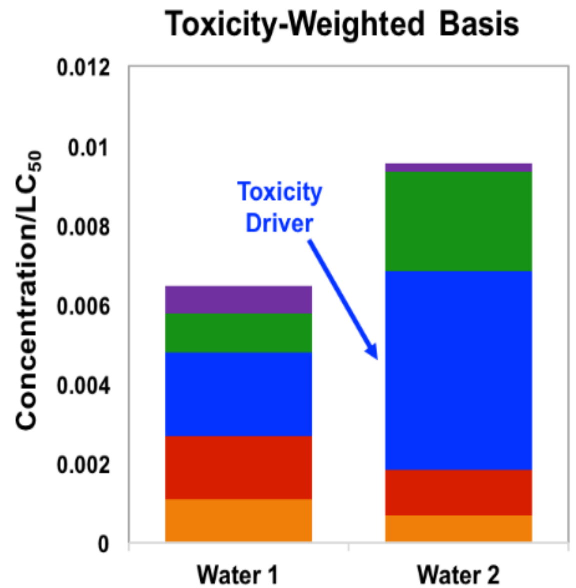


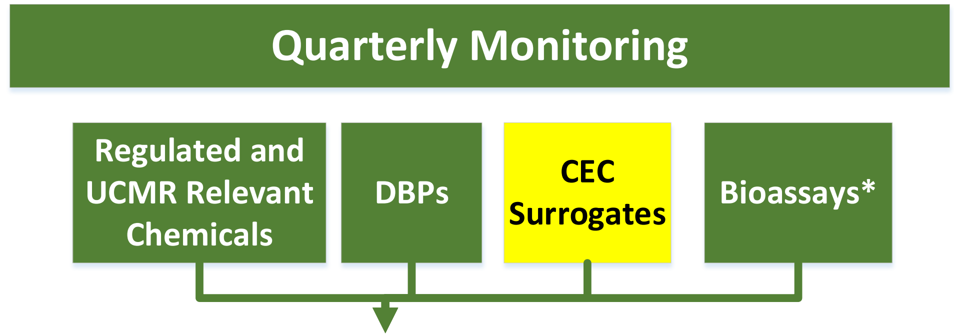
Overall

- Potable reuse can deliver comparable or higher DBP-associated water quality to conventional drinking water
  - MF/RO/AOP higher quality even with chlorine
  - O_3/BAC/GAC ≈ conventional drinking water if use chloramines

Benefits

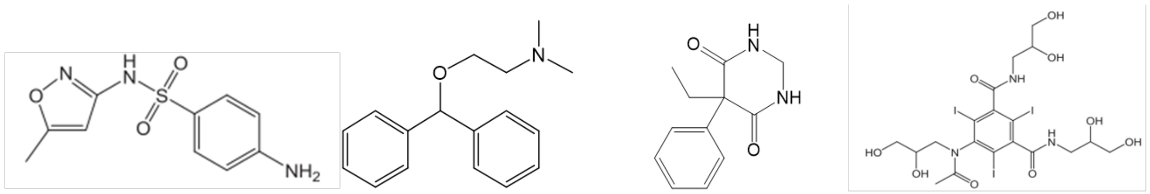
- Considers toxins
  - Not bulk parameters of unclear meaning
- Evaluates on a common risk basis
  - MCLs don't ➔ unfairly weight certain chemicals (NDMA over bromate)
- Considers mixtures ➔ estimate whole exposure
- Helps to prioritize potential toxicity drivers
  - Flexibility to utilities
  - Goal is to reduce overall toxic exposure, not individual MCLs
- Comparison to current tap water as accepted level of safety
  - Otherwise a moving goalpost – every detection a problem



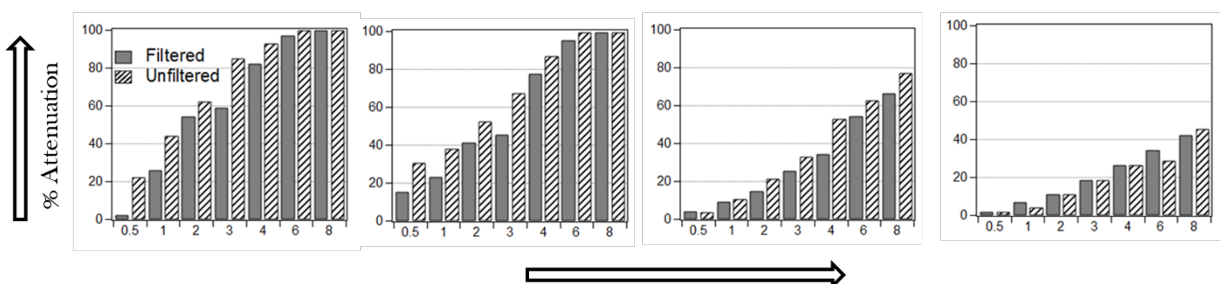


CECs

- Good removal of CECs in DPR trains is important to ensure removal of unknown hazardous compounds or known compounds where human health risk data is lacking (e.g, PFAS)

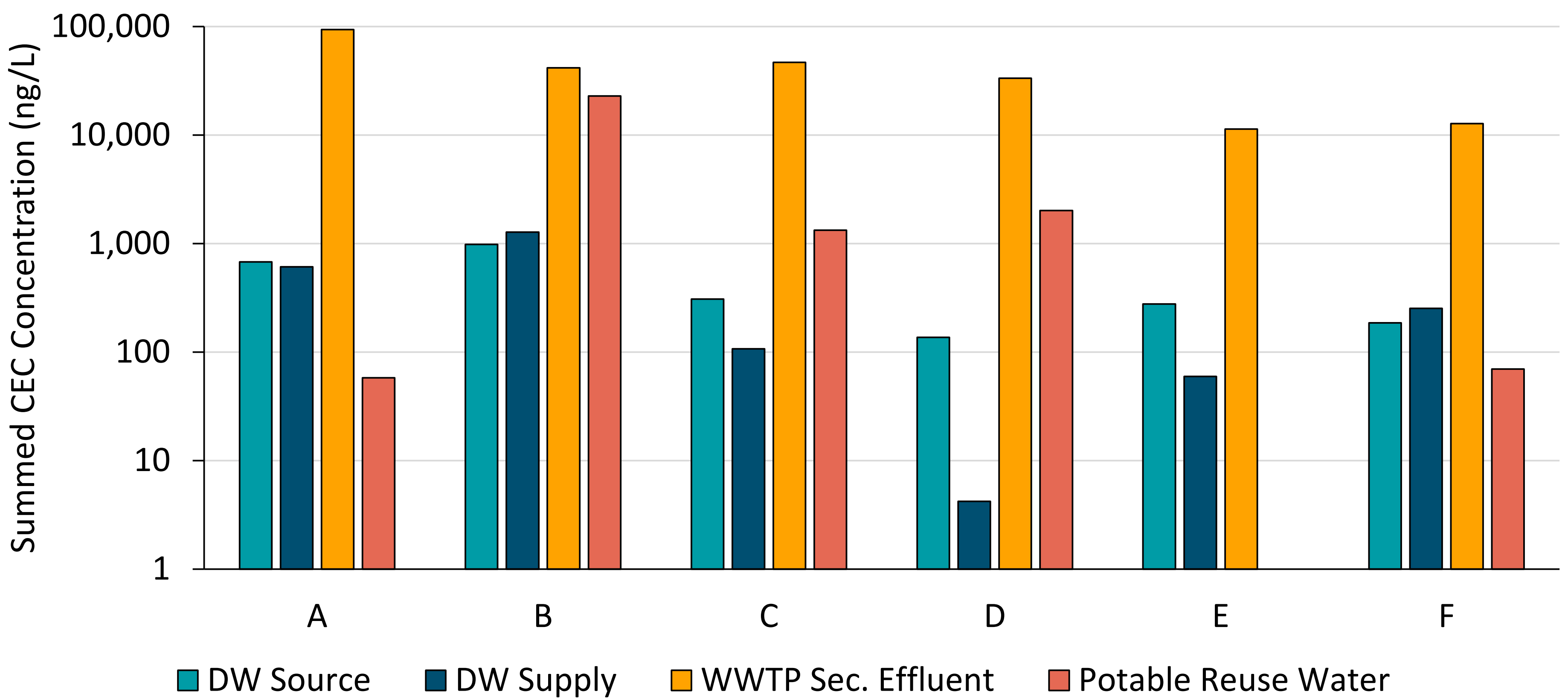


Group I: Sulfamethoxazole | Group II: Diphenhydramine | Group III: Primidone | Group IV: Iohexol

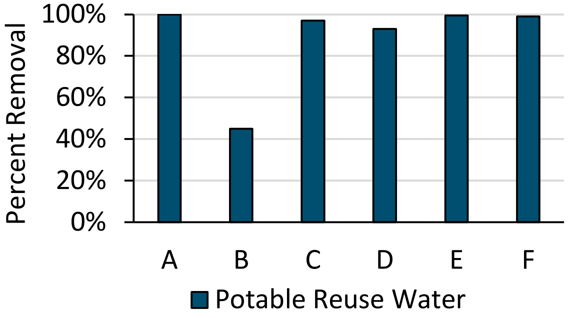


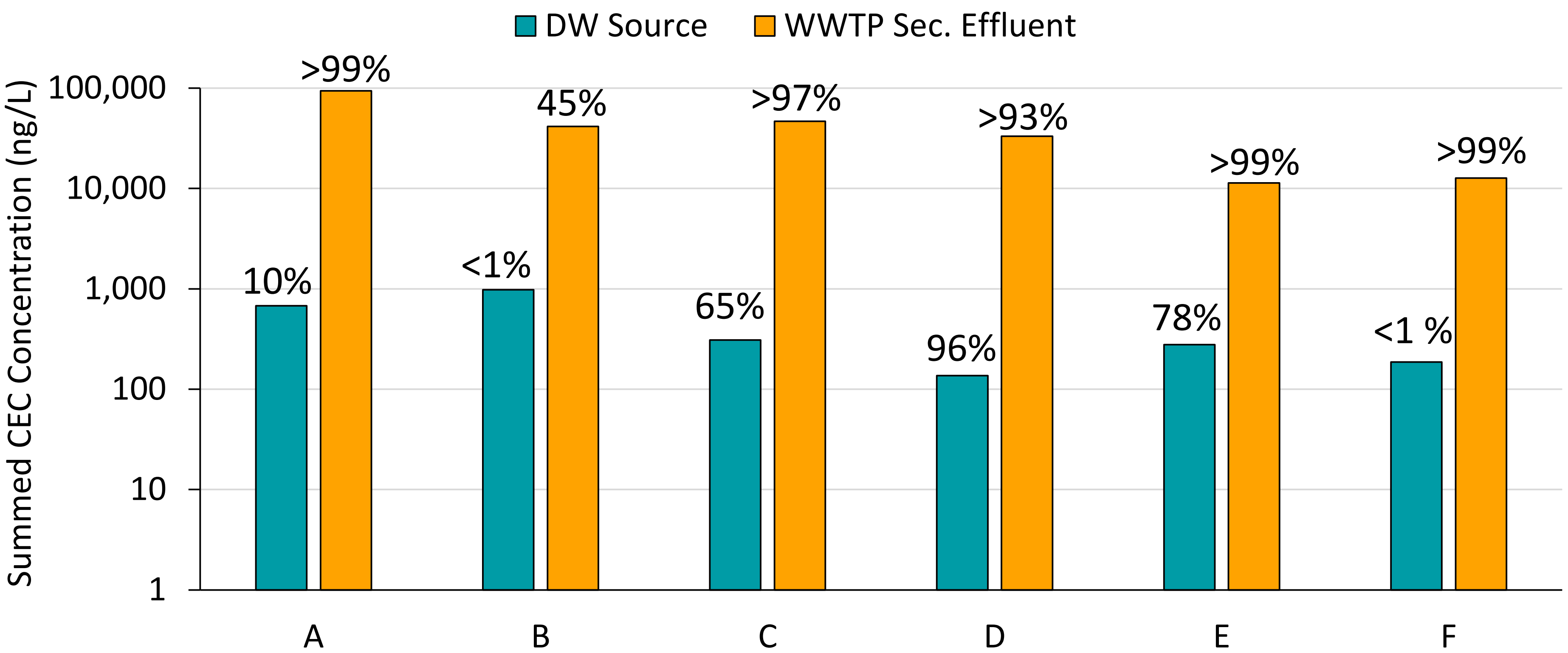
Park, M., Anumol, T., Daniels, K.D., Wu, S., Ziska, A.D., Snyder, S.A., 2017. **Water Res.** 119, 21–32

CEC Occurrence



CEC Removal

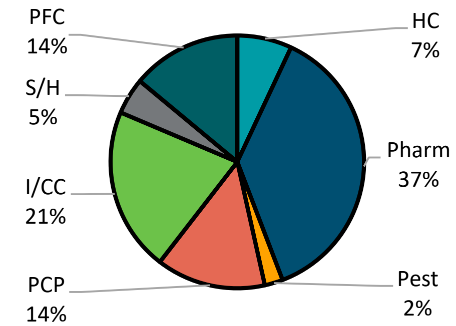


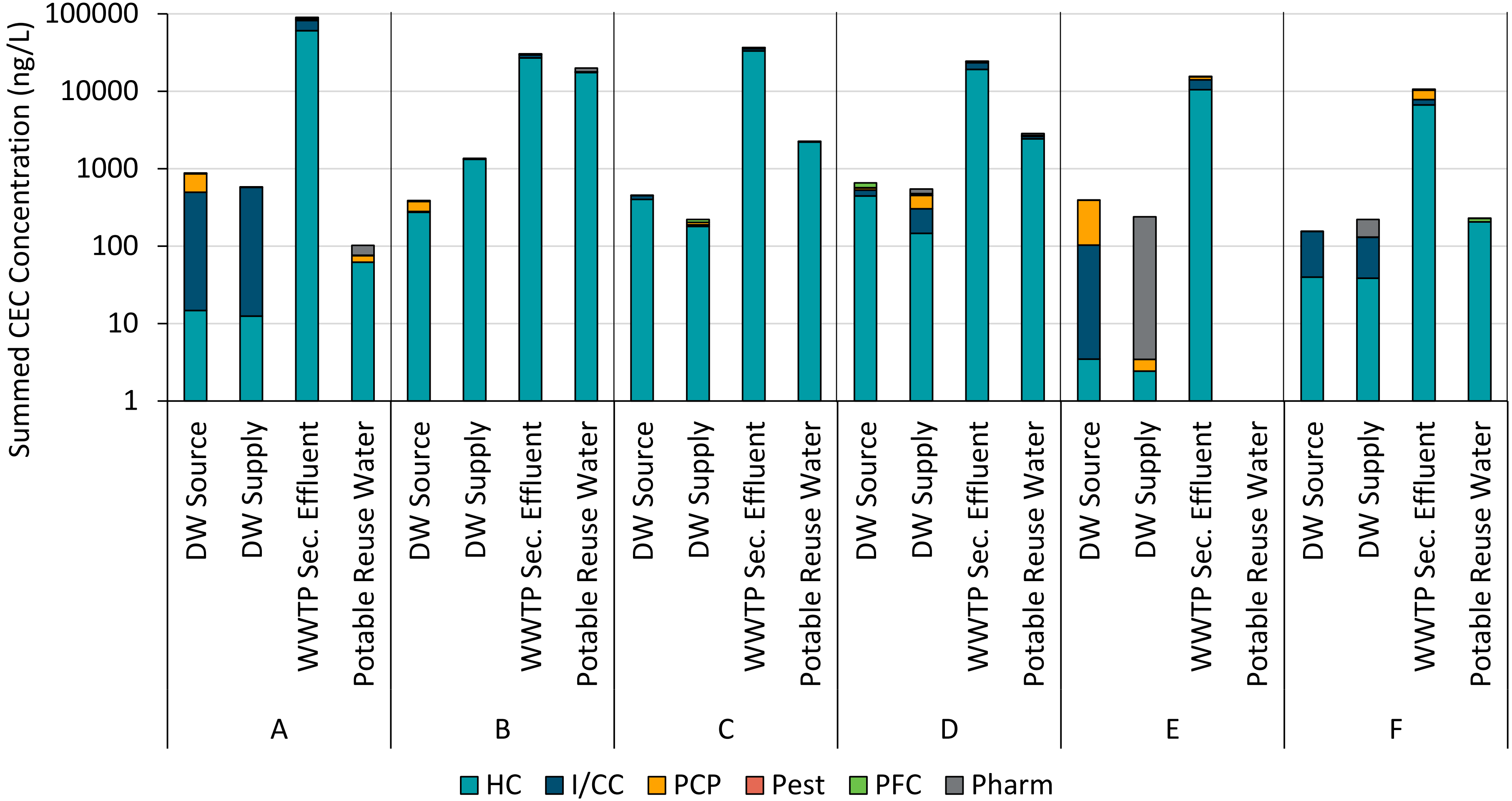


Average DW Source Removal = 42%

Average Potable Reuse Removal = 89%

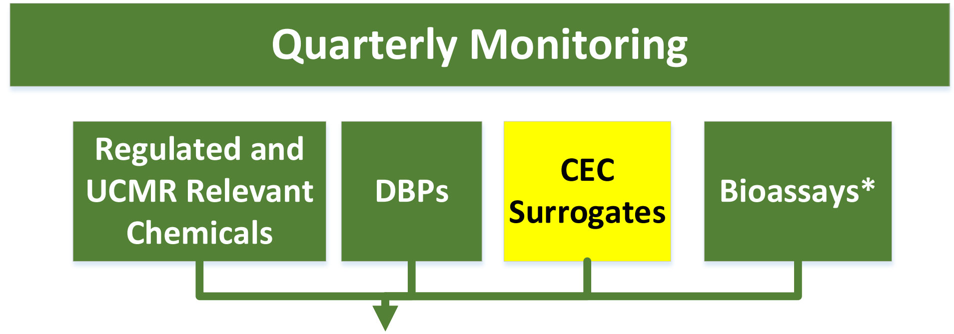
CEC Breakdown





HC: Household chemical; I/CC: Industrial/commercial chemical; PCP: Personal-care product; Pest.: Pesticide; PFC: Perfluorinated compound; Pharm.: Pharmaceutical; S/H: Steroid/Hormone

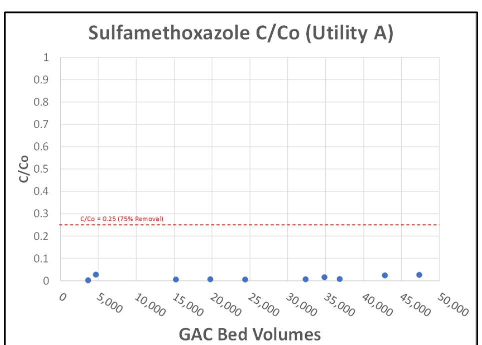
CEC Performance Indicators

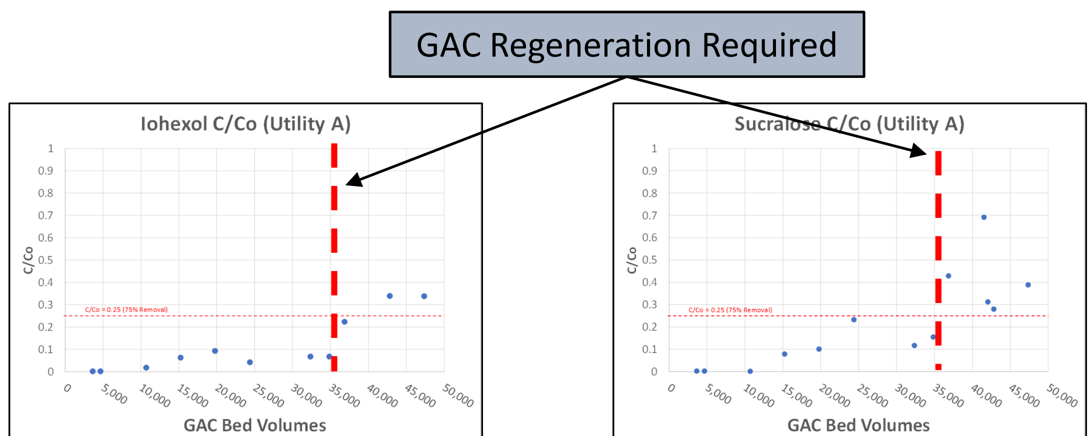


- Framework proposes that select CECs be used as treatment performance indicators to ensure proper operation of AWT for removal of chemicals with similar properties
- Selection of CEC performance indicators:
  - Prevalent in secondary effluent at significant concentrations
  - Physical/chemical properties prove good removal of AWT treatment processes
- Proposed Limit: > 75% removal across treatment train

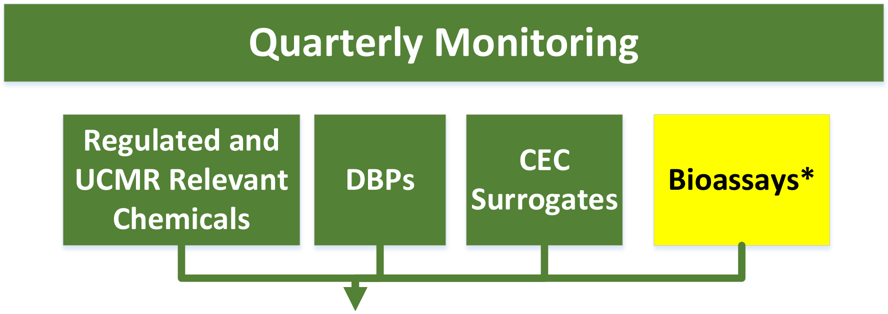
CEC Performance Indicators

CEC	Prevalence In Secondary Effluent Samples	Concentration (ng/L)	AWT Processes Verified
Sulfamethoxazole	100% present	Range: 44 – 3,671 50th perc = 577	Oxidation
Iohexol	80% present	Range: BDL – 32,000 50th perc = 2,357	Oxidation, Biofiltration, Adsorption
Sucralose	95% present	Range: BDL – 110,000 50th perc = 20,590	Adsorption

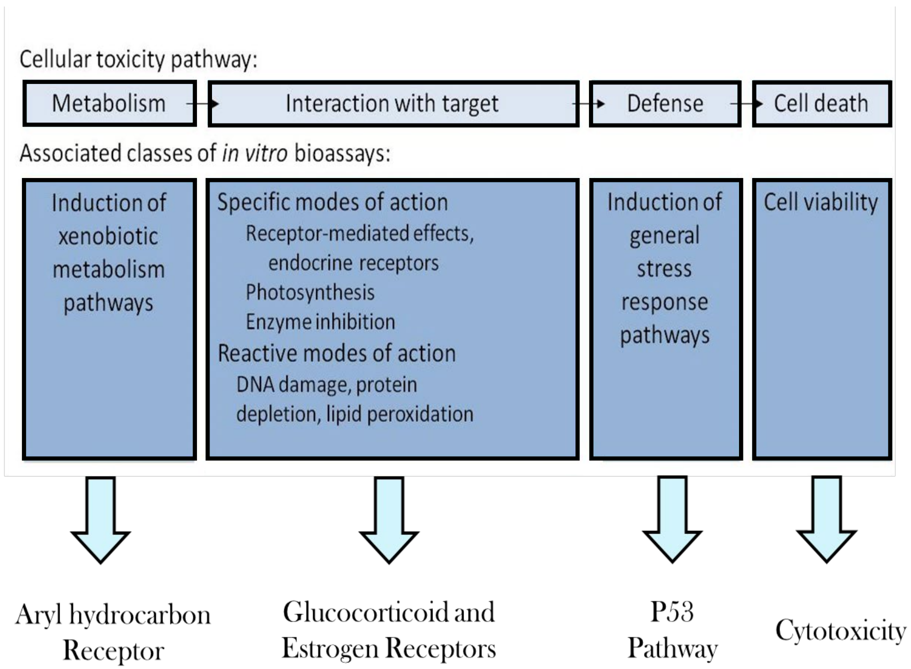




Bioassays

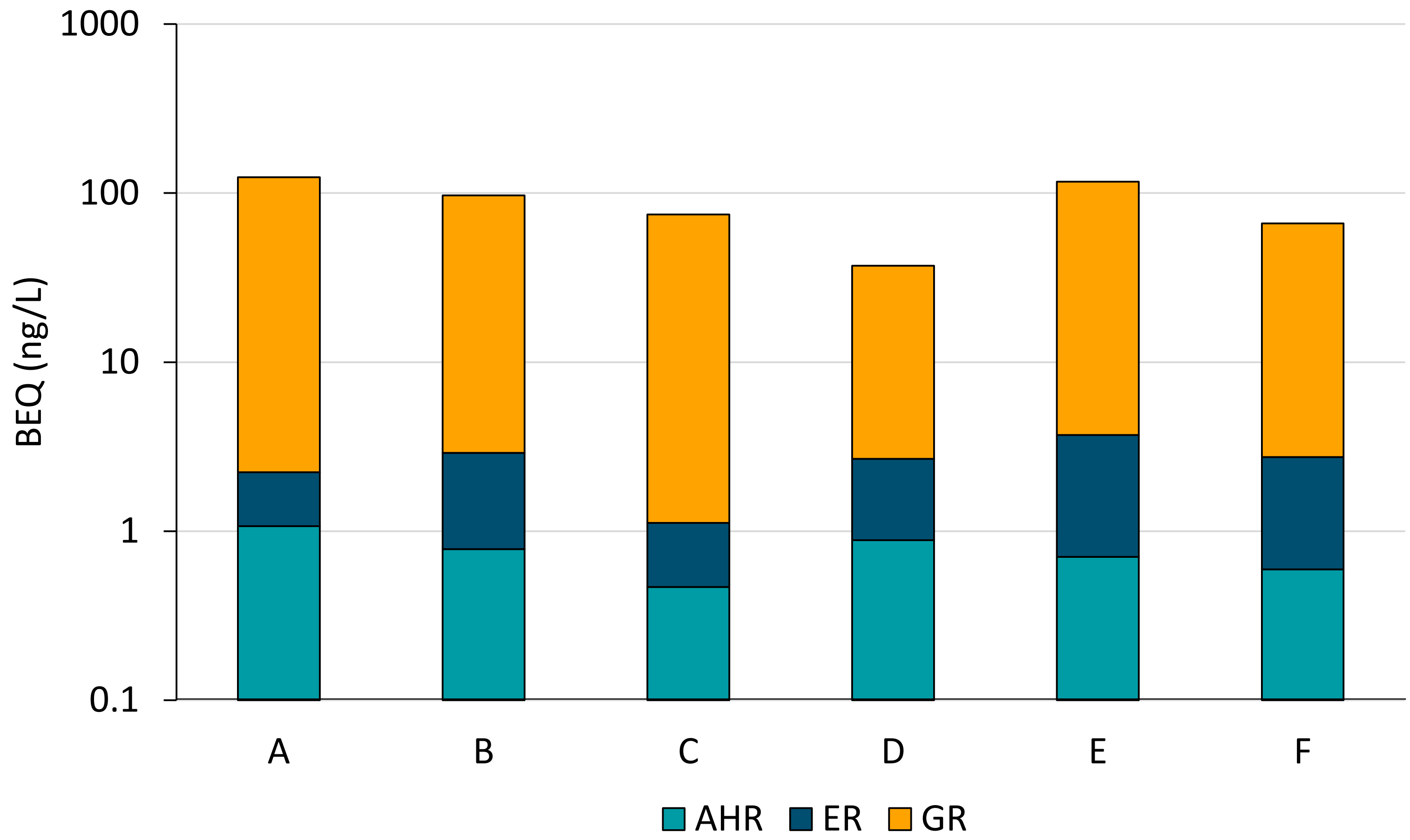


- Used to identify the overall toxicity of known and unknown contaminants in a mixture with the use of a biological system
- Samples concentrated 12.5x
- 5 *in vitro* bioassays tested:
  - Estrogen Receptor (ER)
  - Glucocorticoid Receptor (GR)
  - Aryl hydrocarbon Receptor (AhR)
  - p53 pathway
  - HepG2 (Cytotoxicity)



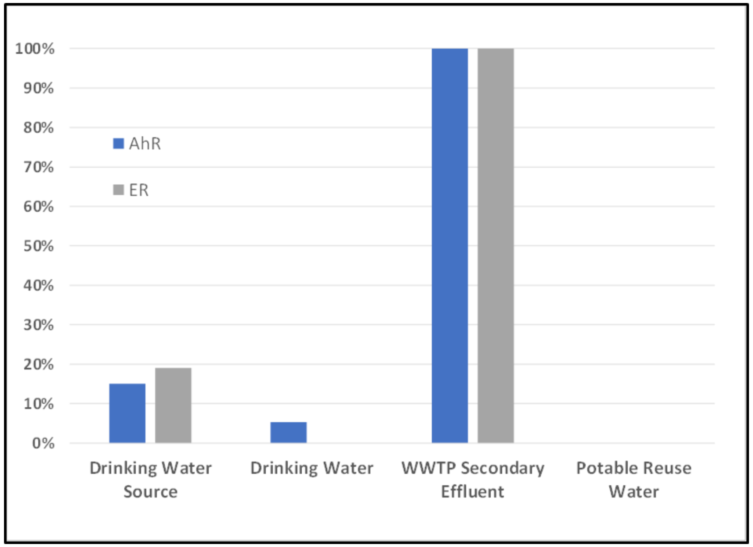
Escher, B. I., et al. (2014). ***Environ. Sci. Technol***, *48*(3), 1940–1956

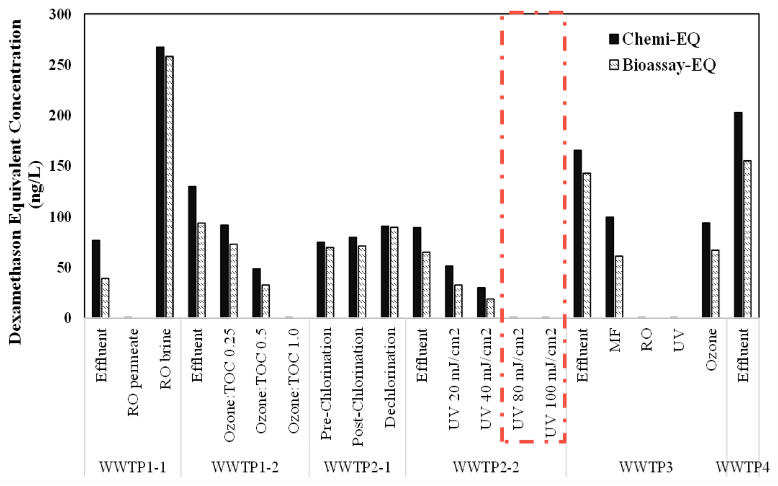
Observed Bioactivity in WWTPs Sec. Effluent



Bioassay Results (AhR and ER)

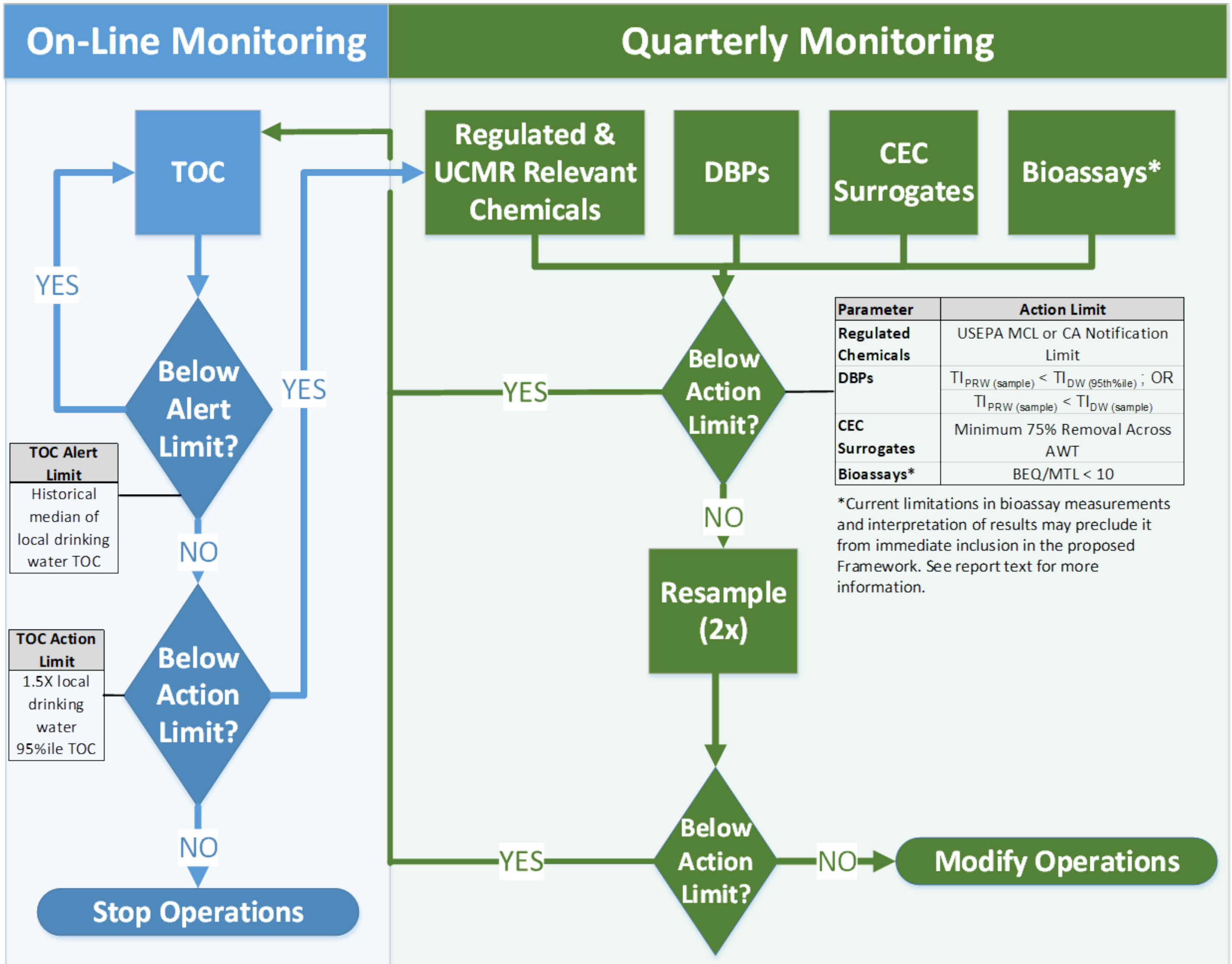
- About 20 samples analyzed for each type of water across the six utilities
- Proposed Limit for Framework:
  - BEQ/MTL < 10
  - BEQ = bioanalytical equivalent concentration
  - MTL = monitoring trigger level
- More work required on bioassays:
  - Development of standard measurement methods
  - Interpretation of results



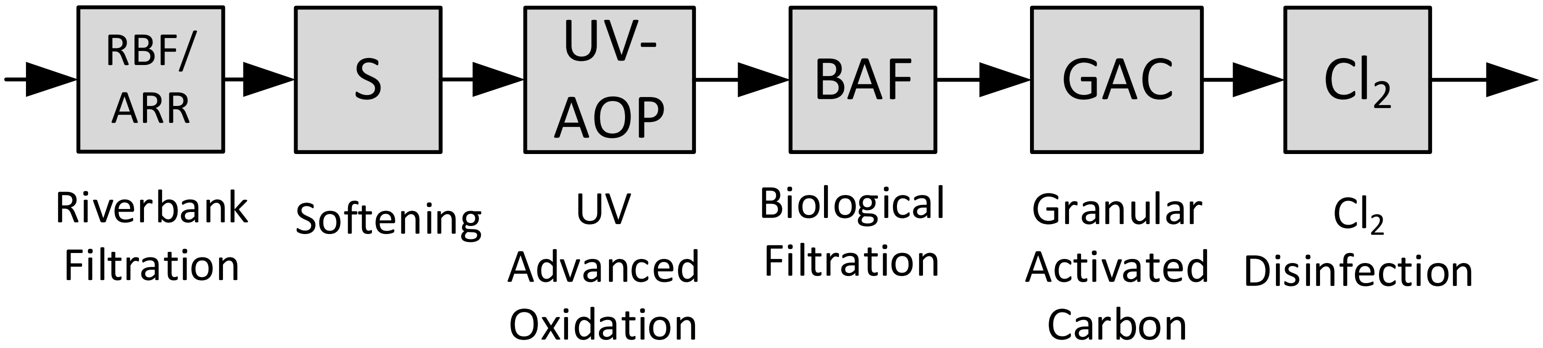


Jia, A., Wu, S., Daniels, K.D., Snyder, S.A., 2016. **Environ. Sci. Technol.** 50, 2870–2880.

Testing the Framework



Testing the Framework – Utility D

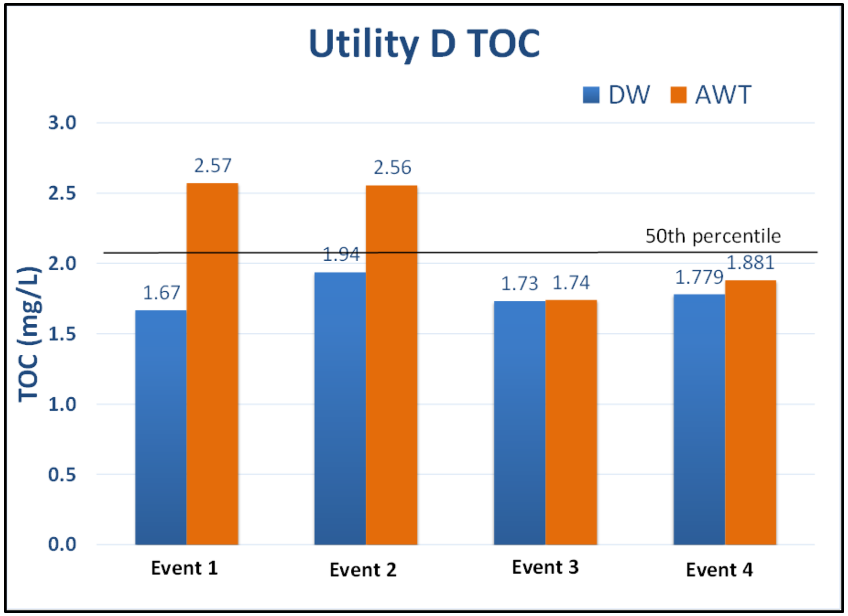


Testing the Framework - TOC

Parameter	Event 1	Event 2	Event 3	Event 4
TOC				
DBP Toxicity Index				
CEC Surrogates				
Bioassays				

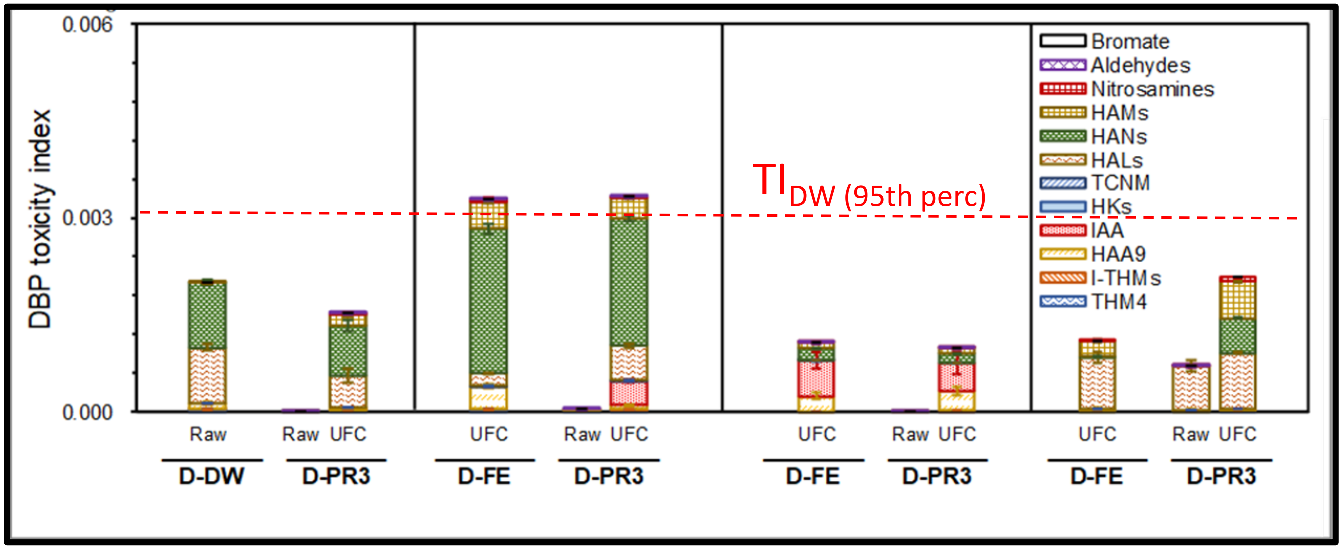
Testing the Framework - TOC

Parameter	Event 1	Event 2	Event 3	Event 4
TOC	> Alert Limit	> Alert Limit	< Alert Limit	< Alert Limit
DBP Toxicity Index				
CEC Surrogates				
Bioassays				



Testing the Framework - TOC

Parameter	Event 1	Event 2	Event 3	Event 4
TOC	> Alert Limit	> Alert Limit	< Alert Limit	< Alert Limit
DBP Toxicity Index	< DW TI_{annavg}	< DW TI_{sample}	< DW TI_{annavg}	< DW TI_{annavg}
CEC Surrogates				
Bioassays				



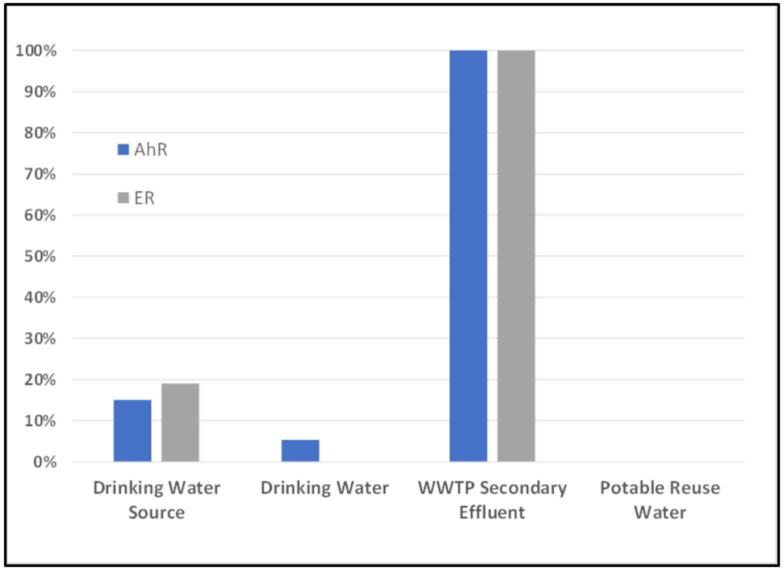
Testing the Framework - TOC

Parameter	Event 1	Event 2	Event 3	Event 4
TOC	> Alert Limit	> Alert Limit	< Alert Limit	< Alert Limit
DBP Toxicity Index	$< DW\ TI_{annavg}$	$< DW\ TI_{sample}$	$< DW\ TI_{annavg}$	$< DW\ TI_{annavg}$
CEC Surrogates	>75% removal	>75% removal	>75% removal	>75% removal
Bioassays				

Sample Event	Sulfamethoxazole	Iohexol	Sucralose
1	>97%	>98%	93%
2	>96%	>98%	**75.2%**
3	>99%	>96%	>96%
4	>96%	>91%	89%

Testing the Framework - TOC

Parameter	Event 1	Event 2	Event 3	Event 4
TOC	> Alert Limit	> Alert Limit	< Alert Limit	< Alert Limit
DBP Toxicity Index	< DW TI_{annavg}	< DW TI_{sample}	< DW TI_{annavg}	< DW TI_{annavg}
CEC Surrogates	>75% removal	>75% removal	>75% removal	>75% removal
Bioassays	BEQ/MTL < 10	BEQ/MTL < 10	BEQ/MTL < 10	BEQ/MTL < 10



✓-Pass

Conclusions

- Domestic water cycle adds significant refractory organics
- TOC provides some correlation to potential health relevance (e.g., chemicals, DBPs) – include in framework as an indicator
  - Absolute value that is universally applied across geographies is not appropriate nor necessarily protective of public health – set local TOC limit based on drinking water TOC
- Measurement of TOC, DBPs, CECs, and bioassays provide good assurance that water is of similar quality to local drinking water
- A GAC adsorption process (with periodic regeneration) is critical for non-RO based treatment in DPR applications
  - Oxidation and biological filtration alone likely not sufficient

Questions?

Thank You

Comments or questions, please contact:

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For more information, visit

www.waterrf.org