



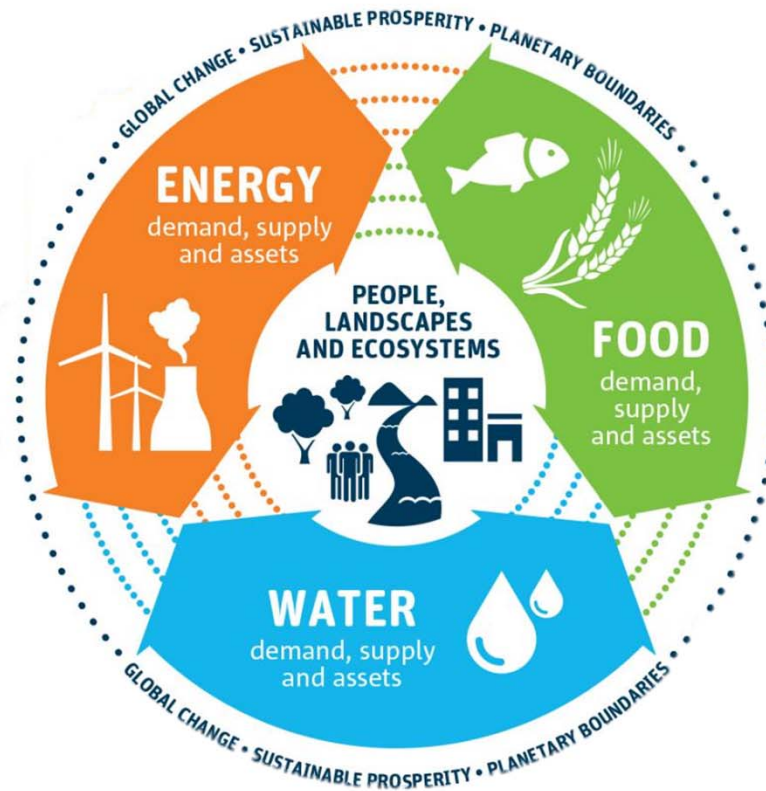
Advanced LC-MS/MS Methods for the Detection
of Trace Organic Compounds throughout
Advanced Water Treatment

Kevin D. Daniels, Christiane Hoppe-Jones,
Guillermo S. Flores, Alec B. Nienhauser,
Juliana S. Ordine, and Shane A. Snyder





Why Water is Important



“We forget that the water cycle and the life cycle are one.”

Jacques Cousteau 1910 - 1997

Cape Town drought declared a 'national disaster'

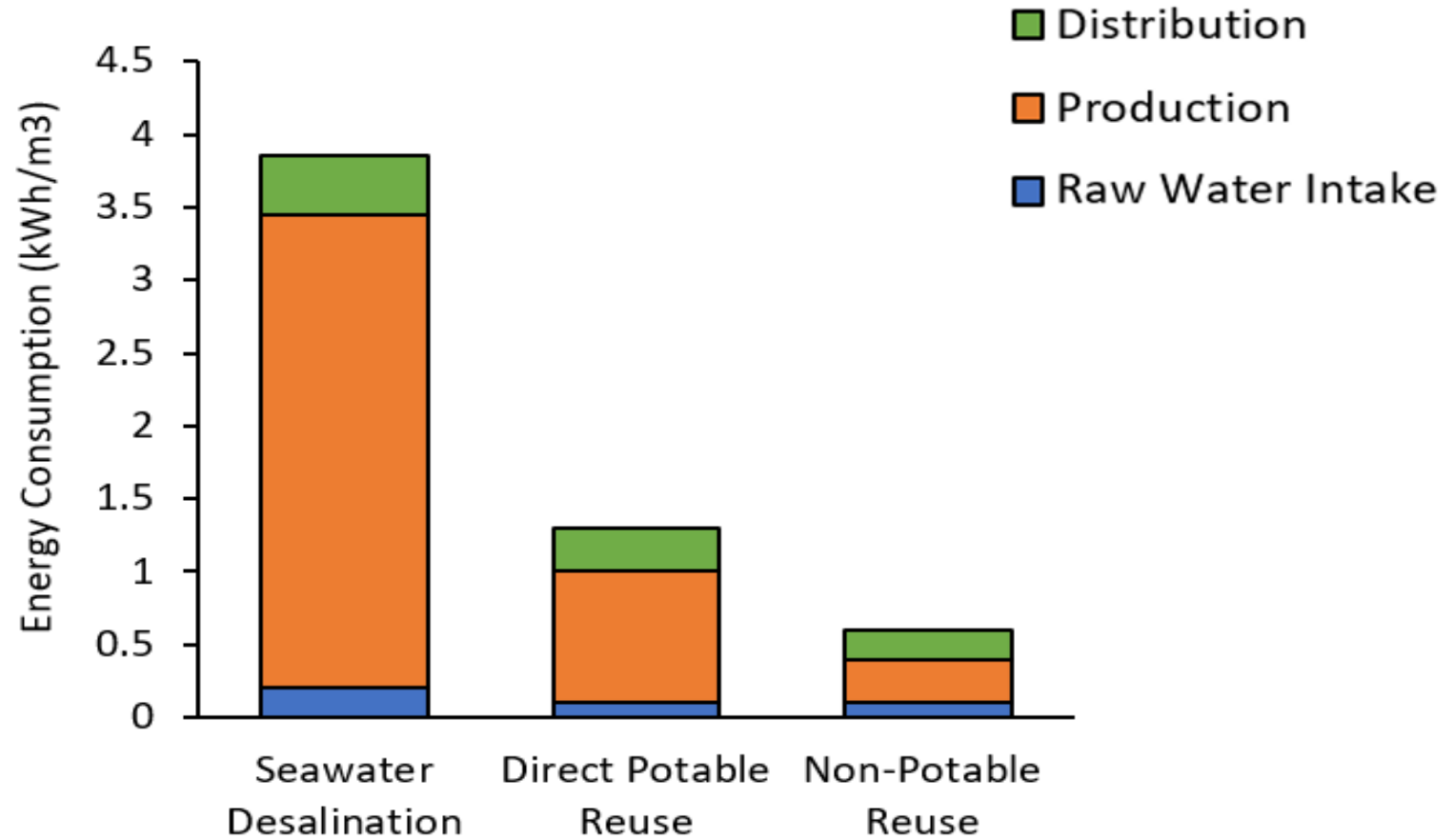
13 February 2018



South Africa has declared the drought which has seen Cape Town hurtling towards "Day Zero" a national disaster.



Energy Requirements



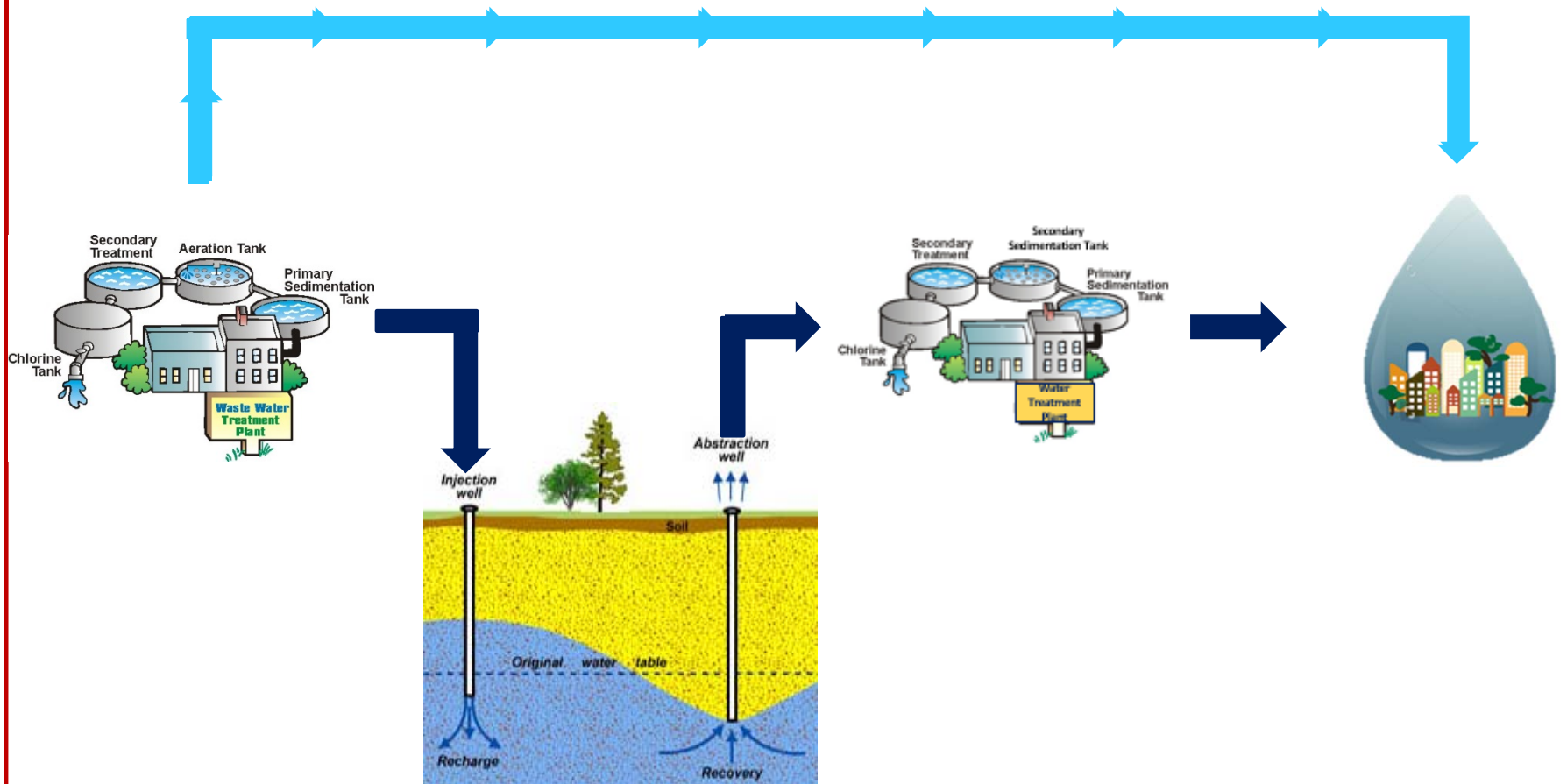
Schaum, C., Lensch, D., Cornel, P., 2015. *J. Water Reuse Desalin.* 5, 83-94.



Water Reuse

Indirect Potable Reuse

Direct Potable Reuse

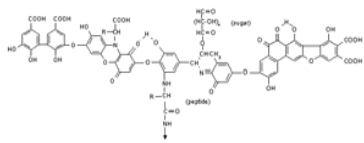
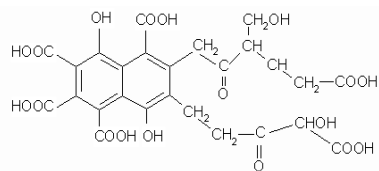




How do we Monitor DPR



Fulvic Acids



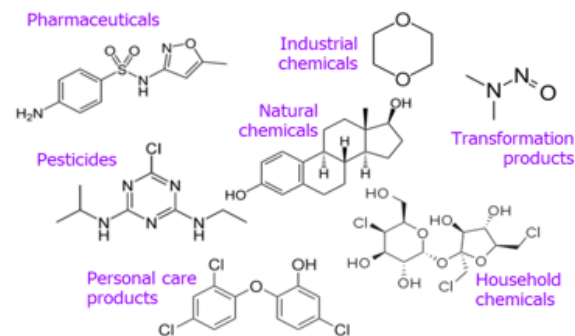
Humic Acids



Chlorine

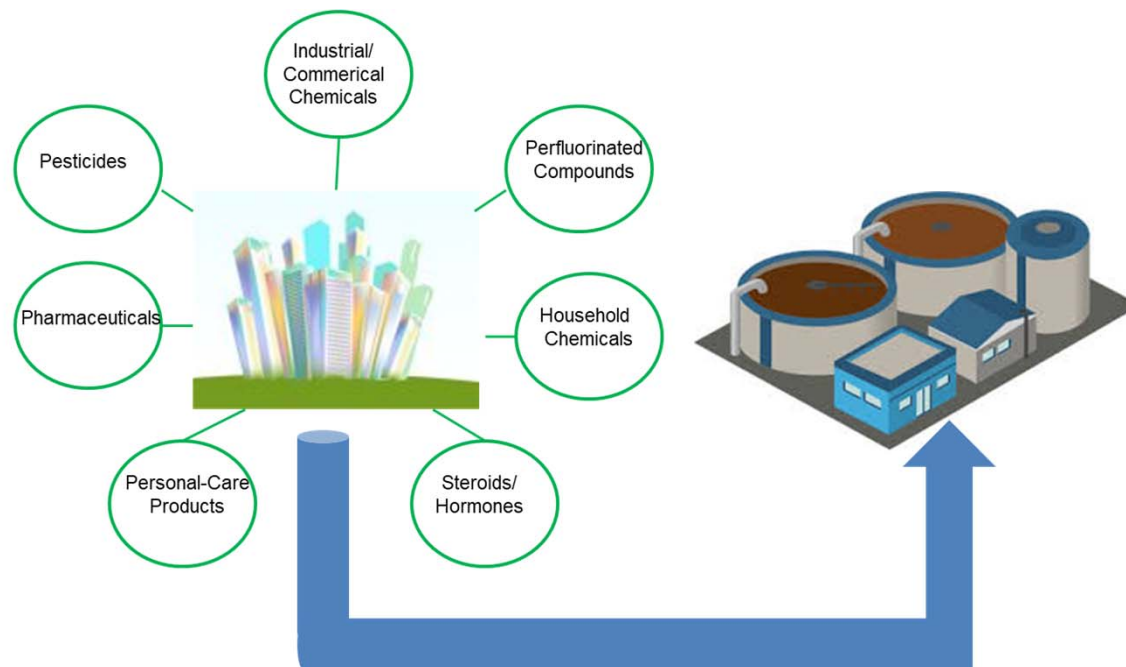


Sodium





Wastewater



CONTAMINANTS OF EMERGING CONCERN IN MUNICIPAL WASTEWATER EFFLUENTS AND MARINE RECEIVING WATER

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Trace Organic Compounds

Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999–2000: A National Reconnaissance

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Pharmaceuticals in groundwaters Analytical methods and results of a monitoring program in Baden-Württemberg, Germany

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Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water

MARK J. BENOTTI,
REBECCA A. TRENHOLM,
BRETT J. VANDERFORD,
JANIE C. HOLADY,
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Pharmaceuticals, Personal Care Products, and Endocrine Disruptors in Water: Implications for the Water Industry

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Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant

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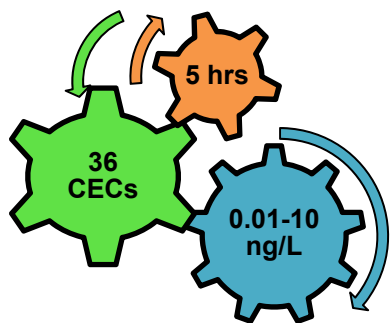
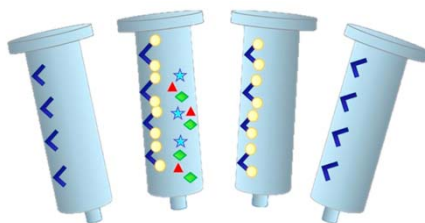


Extraction Methods

Conventional SPE



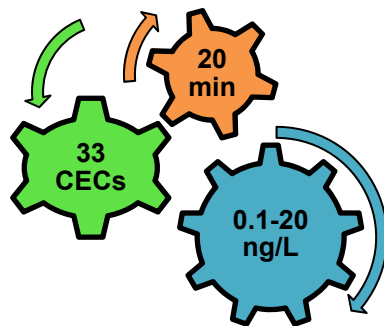
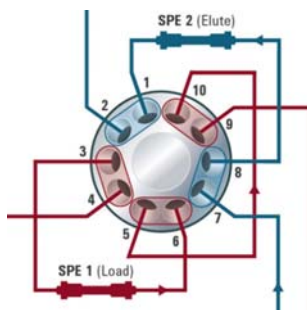
1 L



Online SPE



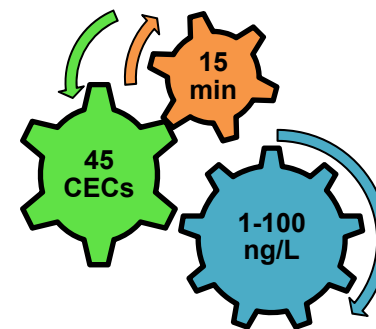
5 mL



No Extraction



1 mL





Purpose

Overall Goal: Evaluate the performances of advanced LC-
QQQ methods for trace organic compounds during advanced
water treatment

Objectives:

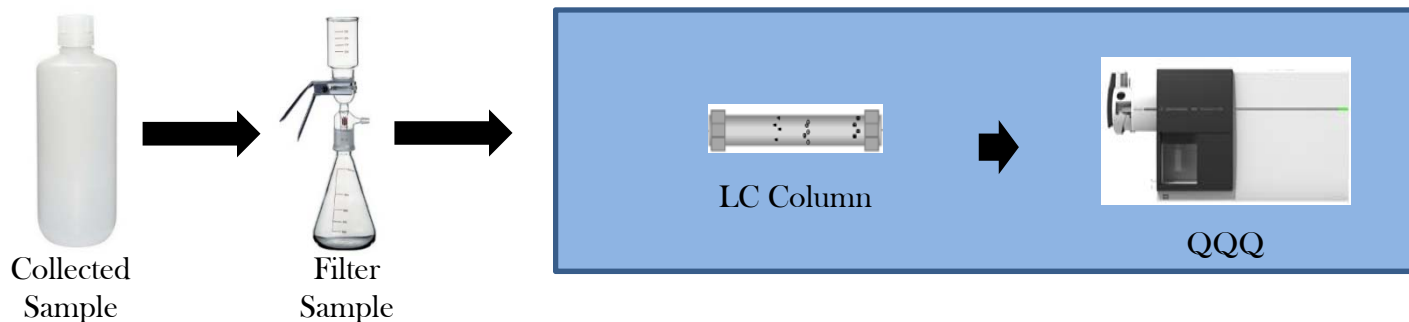
- Labor and time requirements
- Selectivity
- Accuracy
- Sensitivity



Direct Water Injection

Sample is directly injected onto the analytical column

- 80 uL injection volume
- 3 samples per hour
- Column: ZORBAX Eclipse Plus 95Å C-8 (2.1 x 100 mm, 1.8 μm)
- Mobile Phases: H₂O + 0.1% Acetic Acid and Acetonitrile

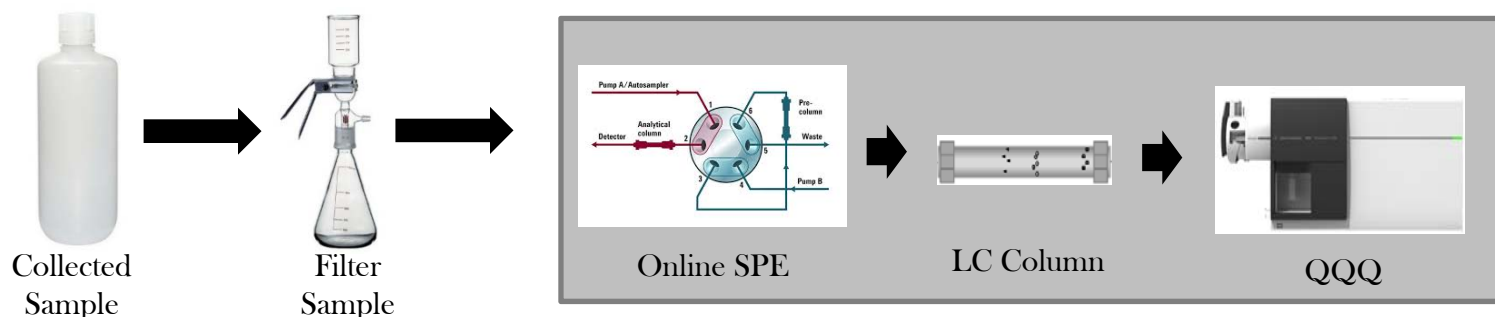




Online-SPE

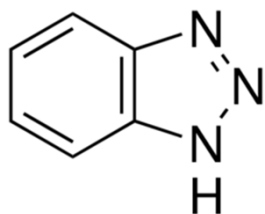
Sample gets extracted using a cartridge incorporated before separation

- 1.7 mL injection volume
- 3 samples per hour
- Column: Poroshell 120 EC C-18 (2.1 x 50 mm, 2.7 μm)
- Mobile Phases: H_2O + 0.1% Acetic Acid and Acetonitrile





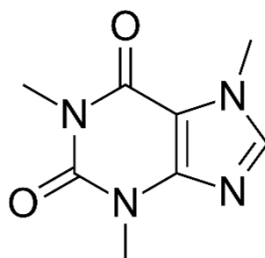
Targeted Compounds



Benzotriazole

I/CC

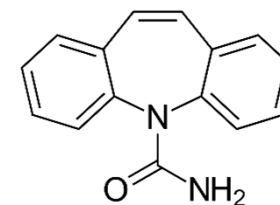
Restrainer in photographic emulsions



Caffeine

HC

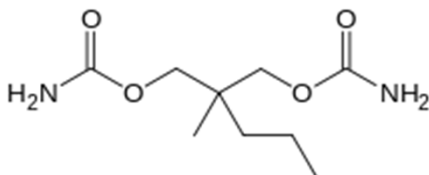
Stimulant



Carbamazepine

Pharm

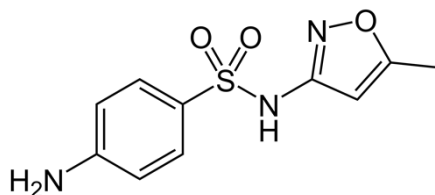
Antiepileptic, analgesic



Meprobamate

Pharm

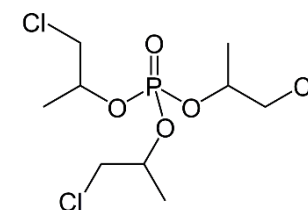
Anxiolytic drug, tranquilizer



Sulfamethoxazole

Pharm

Antibiotic



TCPP

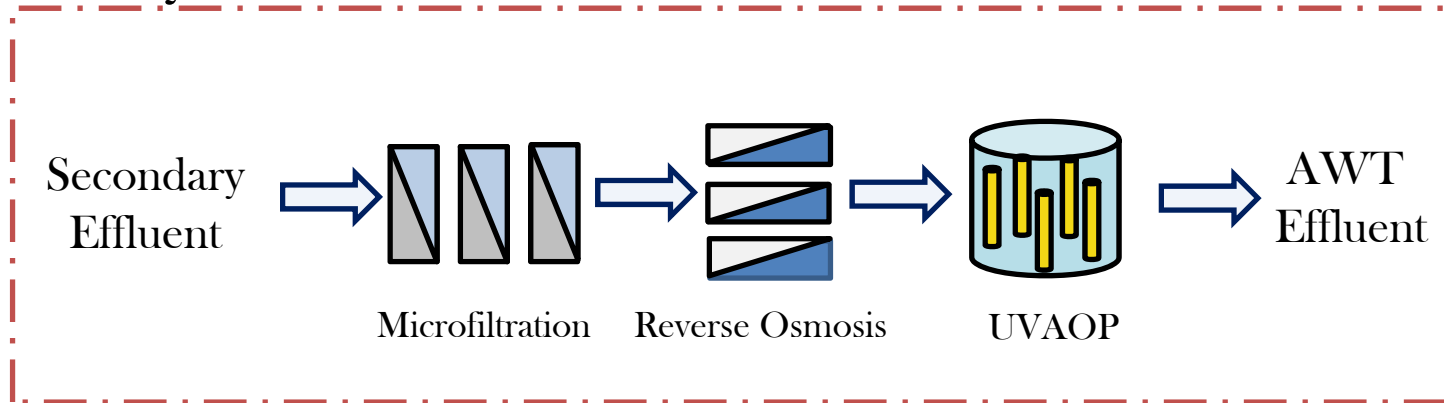
PCP

Fire retardant

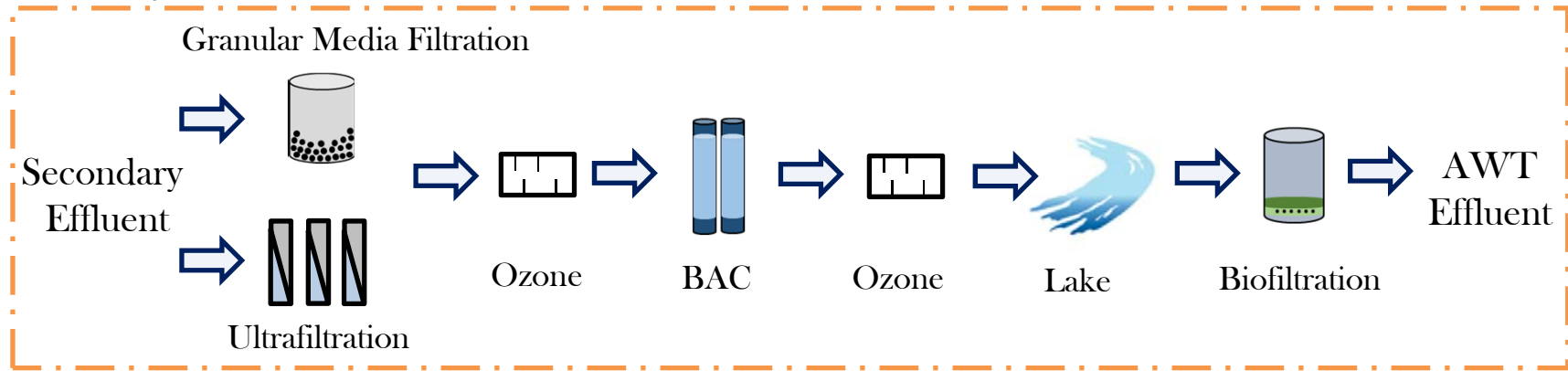


Experimental

Utility 1



Utility 2



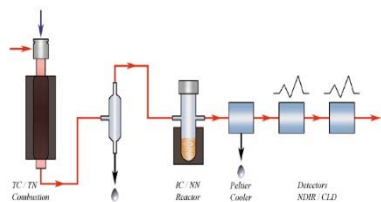


DOC Results

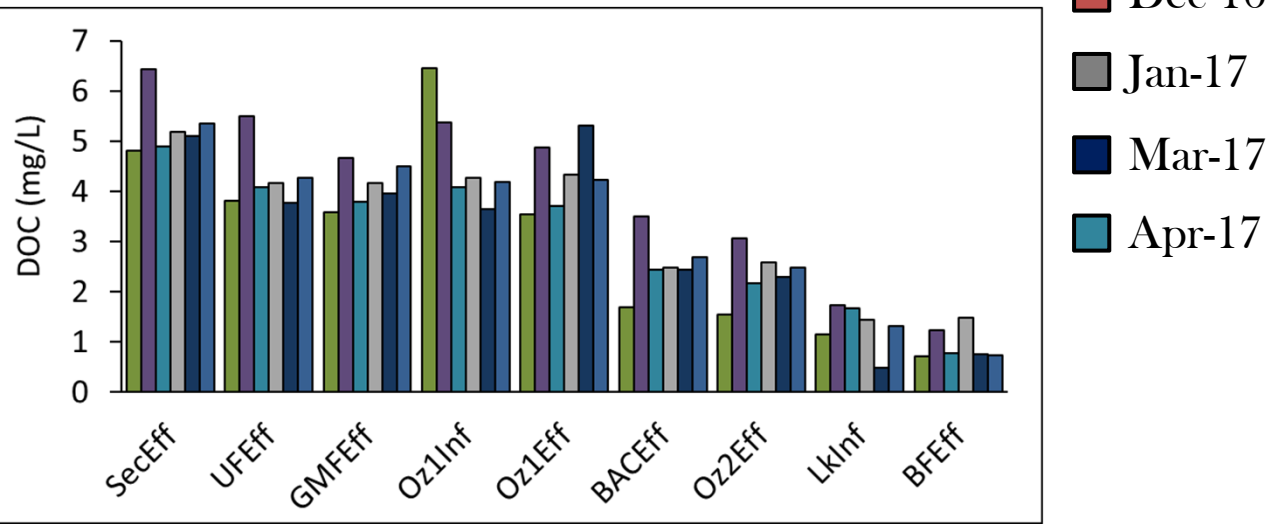
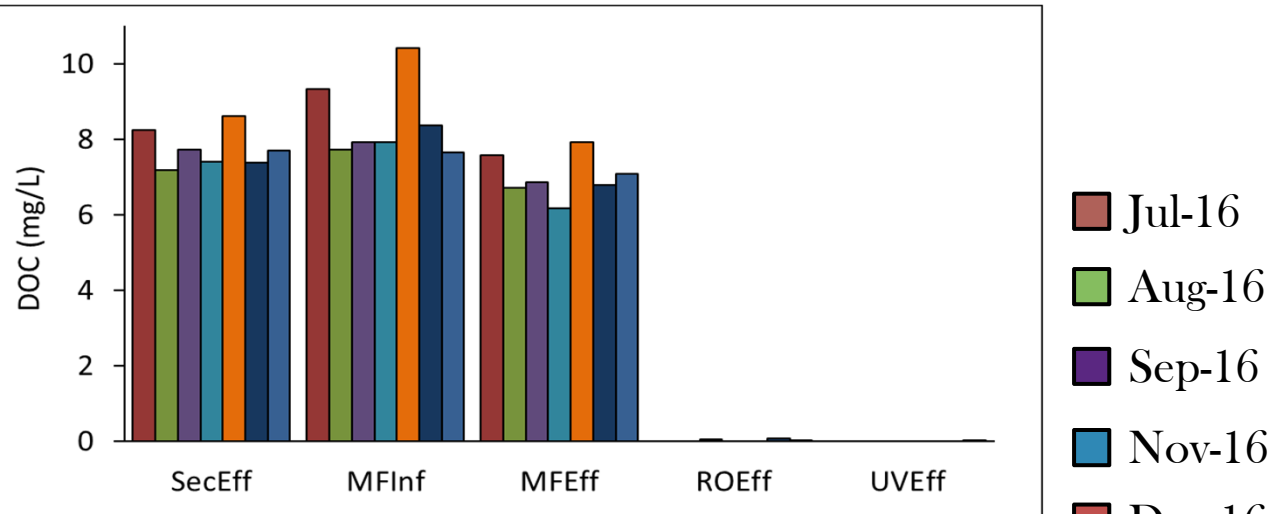
Dissolved Organic Carbon



Shimadzu TOC Analyzer

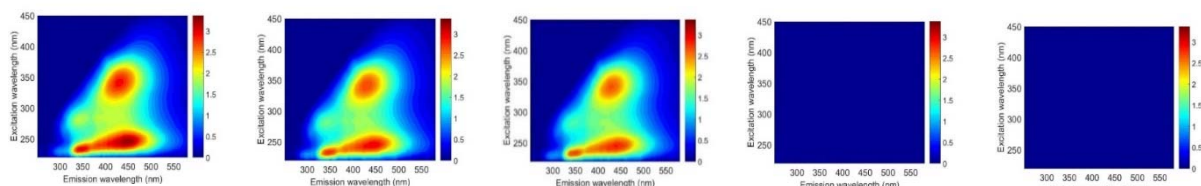


Standard Method:
5310 B





EEM Results



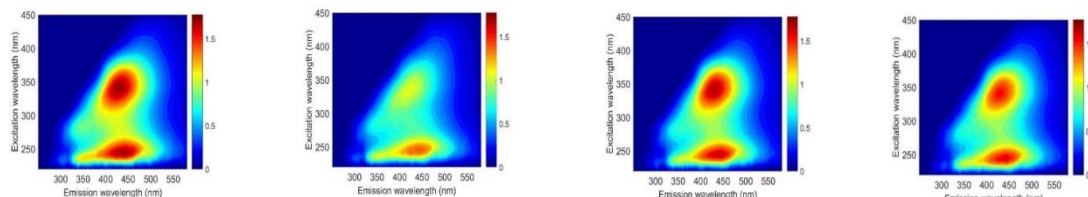
Sec-Eff

MF-Inf

MF-Eff

RO-Eff

UV-Eff

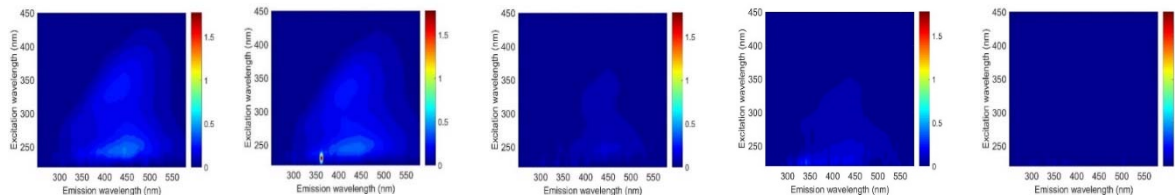


Sec-Eff

UF-Eff

GMF-Eff

Oz1-Inf



Oz1-Eff

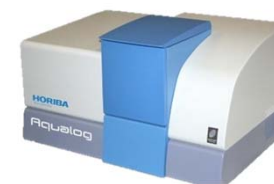
BAC-Eff

Oz2-Eff

Lk-Inf

BF-Eff

Ex/Em Matrix



Horiba
Aqualog

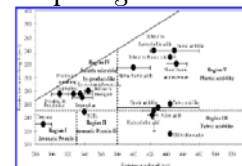


FIGURE 1. Scatter plot of 1000 points (colored) based on Horiba reports and separately entered excitation and emission wavelengths. Water was tested first for the UV region.

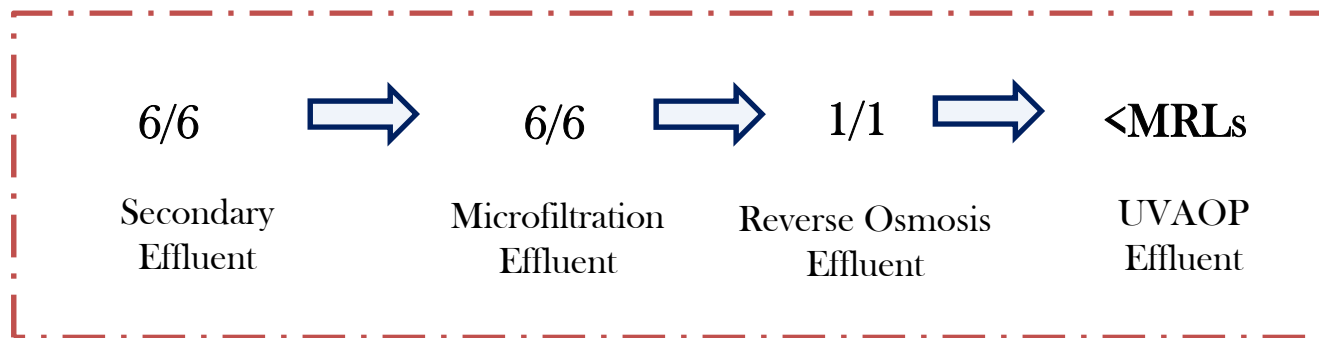
Published Method:
Lakowicz, 2006



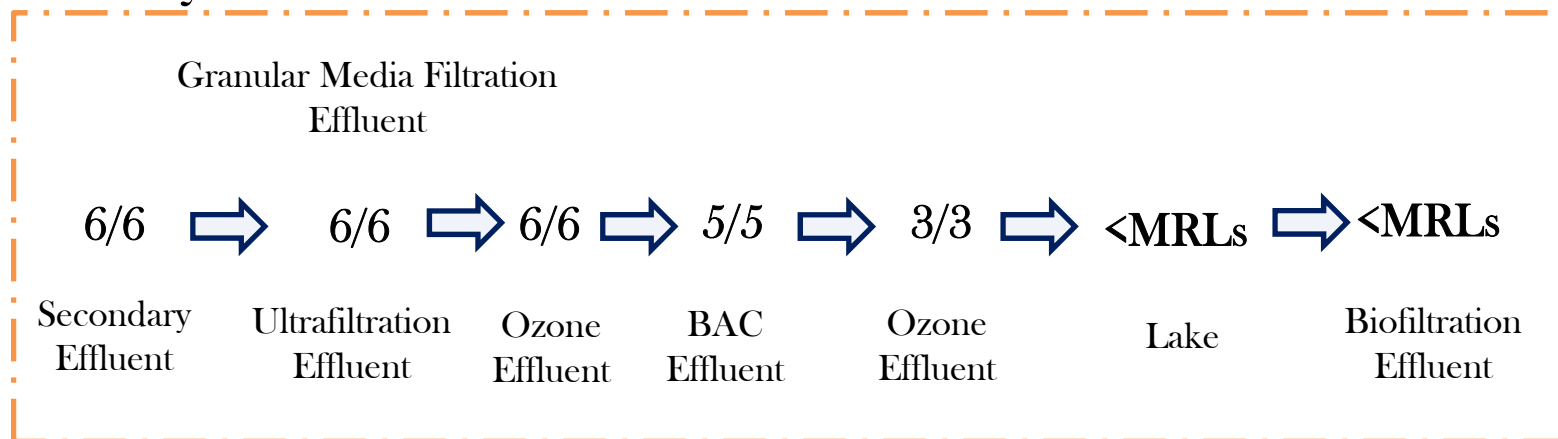
CEC Overview

OSPE/DWI

Utility 1



Utility 2





Secondary Effluent Concentrations

OSPE/DWI

>1,000 ppt

Benzotriazole

10,040/9,280

1152/1800

Sulfamethoxazole

1,840/1,600

1,217/1,057

TCPP

2,100/2,200

1,533/2,325

< 1,000 ppt

Caffeine

472/434

55/197

Carbamazepine

212/240

146/139

Meprobamate

342/433

167/150



Secondary Effluent Concentrations

OSPE/DWI

>1,000 ppt

< 1,000 ppt

7%



35%

Benzotriazole

10,040/9,280

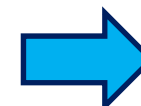
1152/1800

Caffeine

472/434

55/197

8%



72%

Sulfamethoxazole

1,840/1,600

1,217/1,057

Carbamazepine

212/240

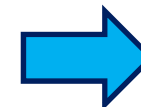
146/139

13%



13%

11%



5%

TCPP

2,100/2,200

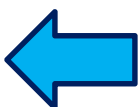
1,533/2,325

Meprobamate

342/433

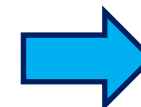
167/150

4%



34%

21%



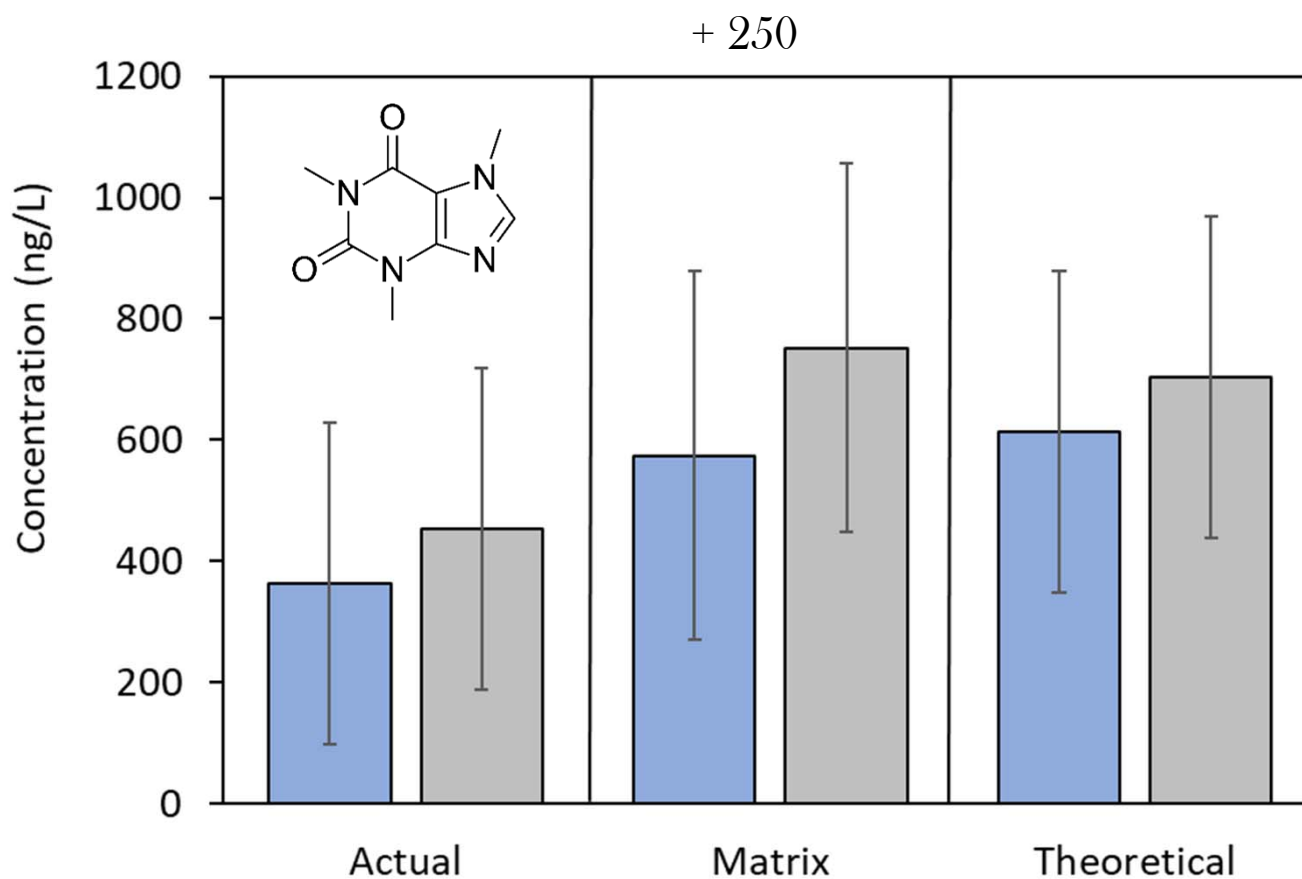
10%



Caffeine Results

Utility 1 - Microfiltration Effluent

■ DWI ■ O-SPE

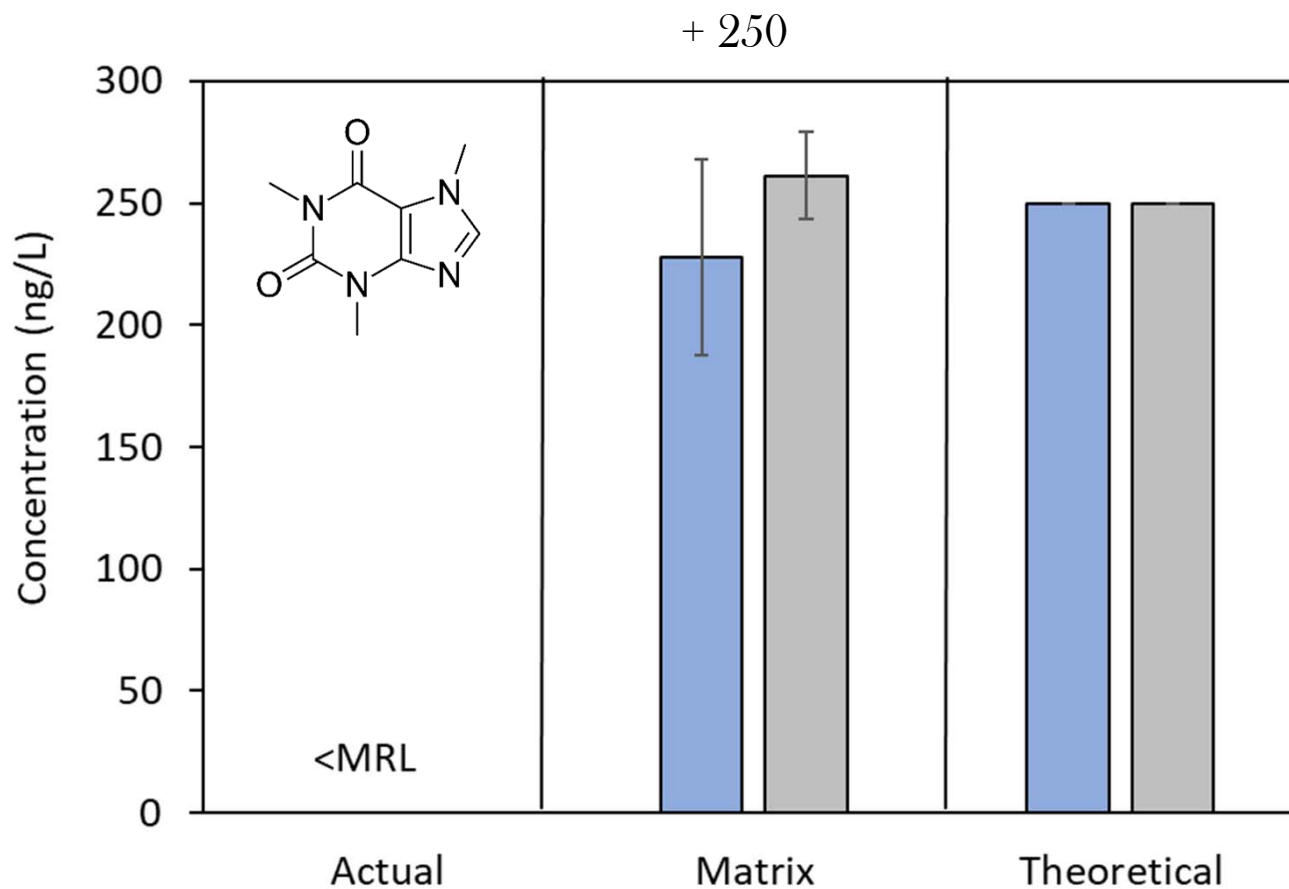




Caffeine Results

Utility 2 - Ozone Effluent

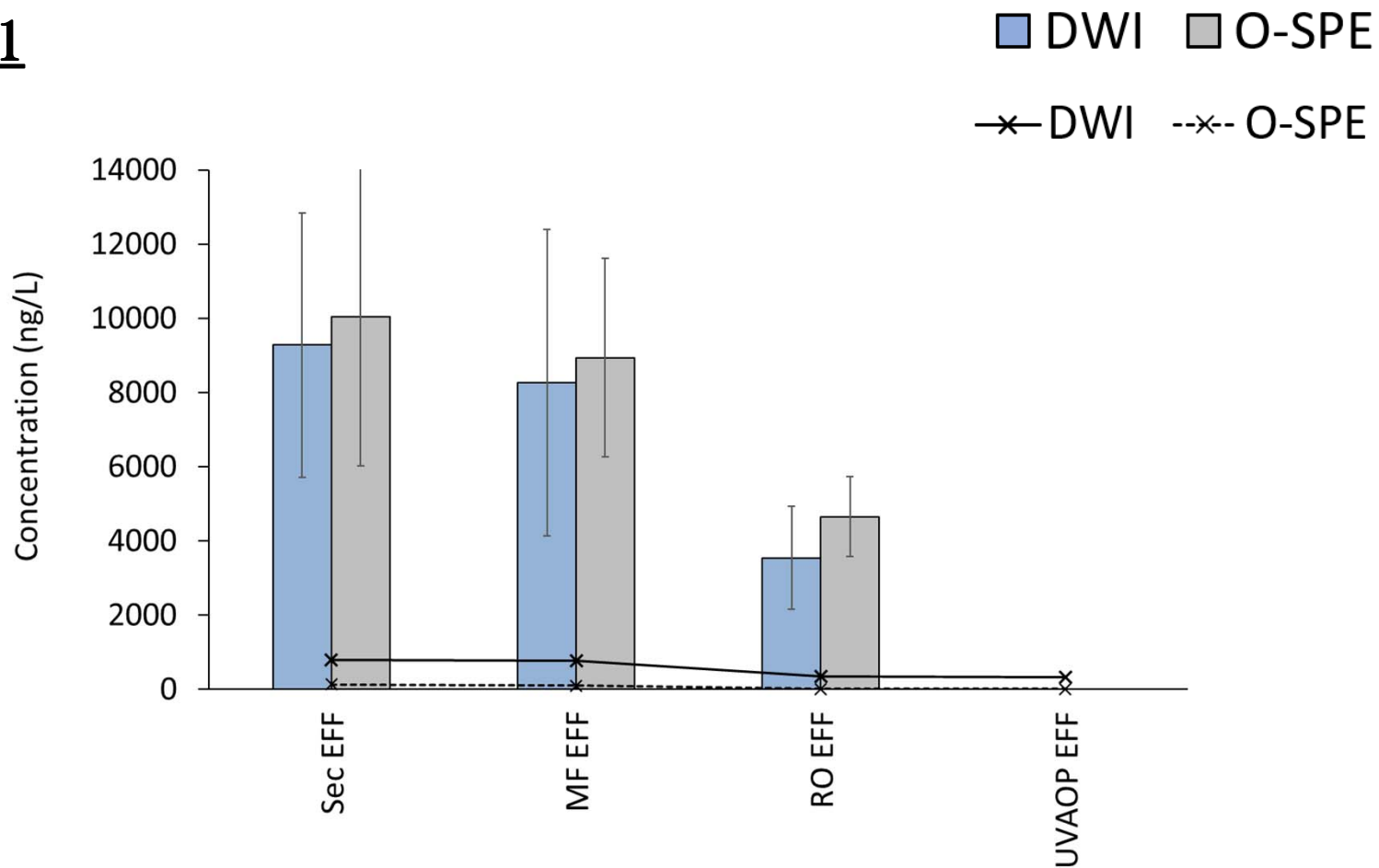
■ DWI ■ O-SPE





Benzotriazole Results

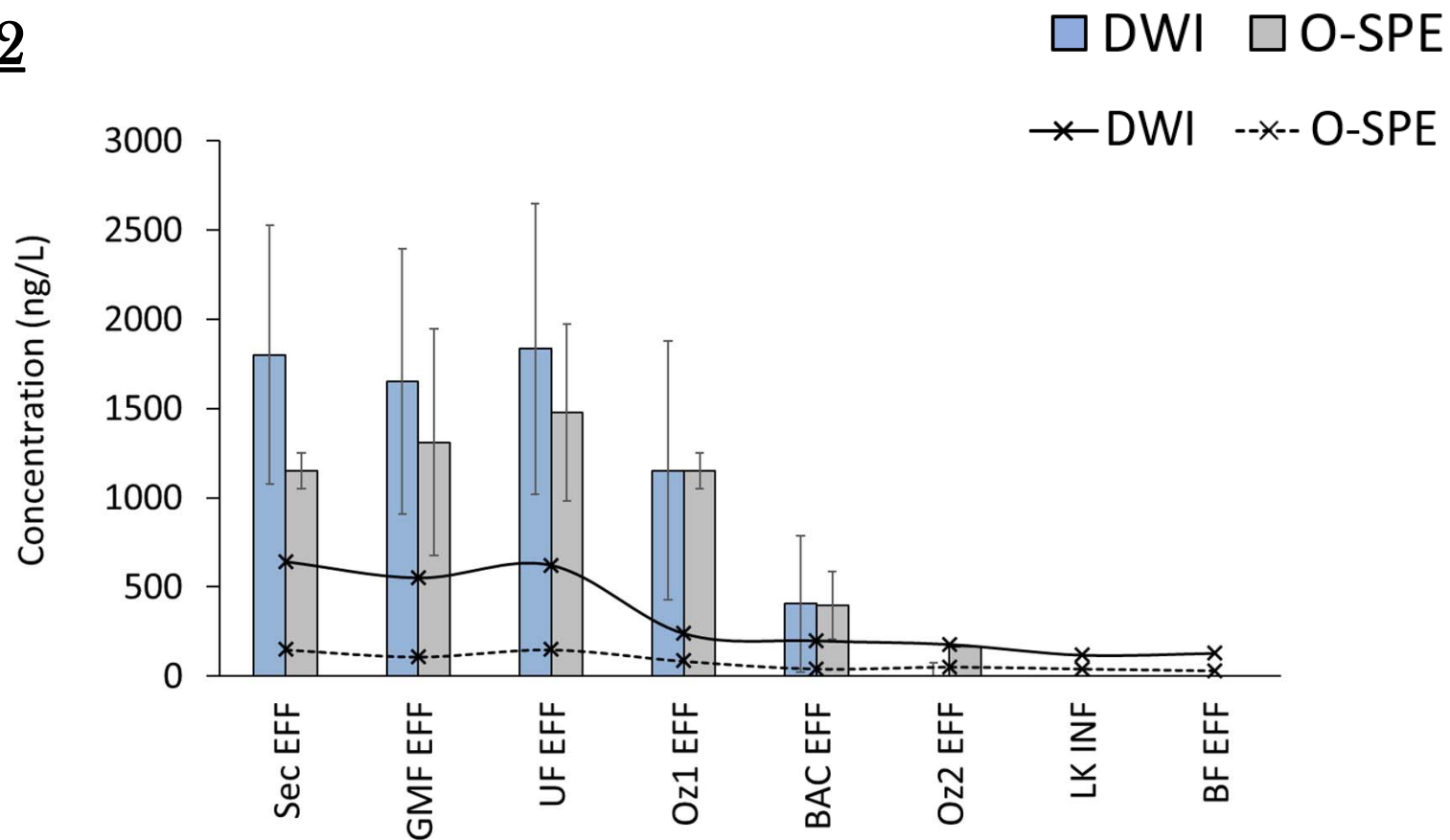
Utility 1





Benzotriazole Results

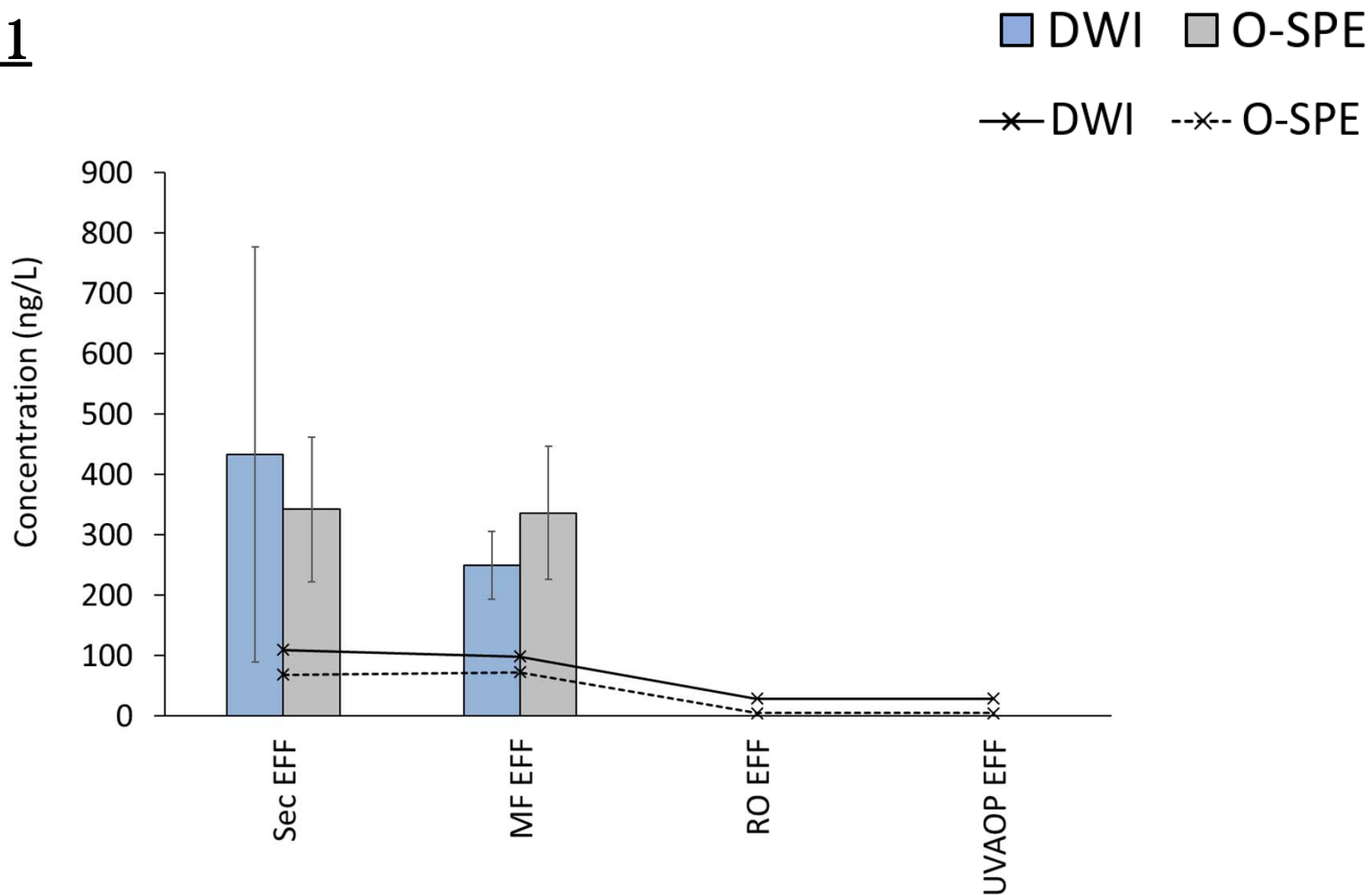
Utility 2





Meprobamate Results

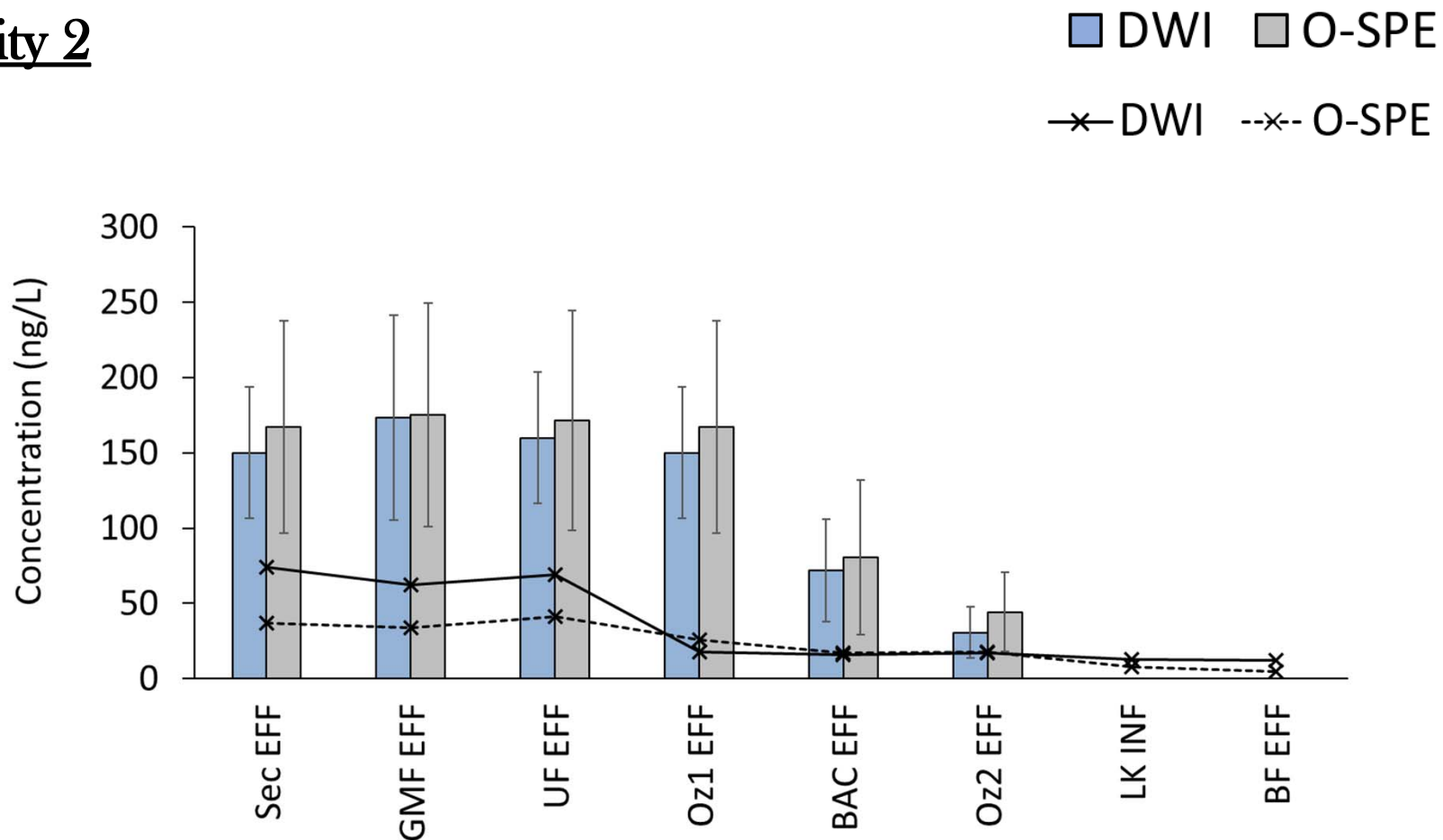
Utility 1





Meprobamate Results

Utility 2





MRLs at Utility 1

	Secondary Eff		MF Eff		RO Eff		UVAOP EFF	
	DWI	O-SPE	DWI	O-SPE	DWI	O-SPE	DWI	O-SPE
Benzotriazole	800	130	760	100	340	8	320	8
Caffeine	60	44	51	41	17	5	18	6
Carbamazepine	120	31	130	32	26	4	27	4
Meprobamate	110	69	99	73	29	5	29	5
Sulfamethoxazole	51	54	44	42	15	5	16	5
TCPP	290	720	260	600	200	57	200	71



MRLs at Utility 2

	Sec EFF		Oz1 EFF		BAC EFF		Oz2 EFF		LK INF		BF EFF	
	DWI	OSPE	DWI	OSPE	DWI	OSPE	DWI	OSPE	DWI	OSPE	DWI	OSPE
Benzotriazole	640	150	240	86	200	43	180	54	120	53	130	33
Caffeine	27	63	14	26	12	17	13	22	11	13	11	6
Carbamazepine	110	20	89	22	24	12	22	10	23	3	21	3
Meprobamate	74	37	18	26	16	17	17	18	13	8	12	5
Sulfamethoxazole	38	51	11	28	10	18	10	18	9	11	9	8
TCPP	150	610	35	400	31	190	30	180	29	180	29	120



Conclusion

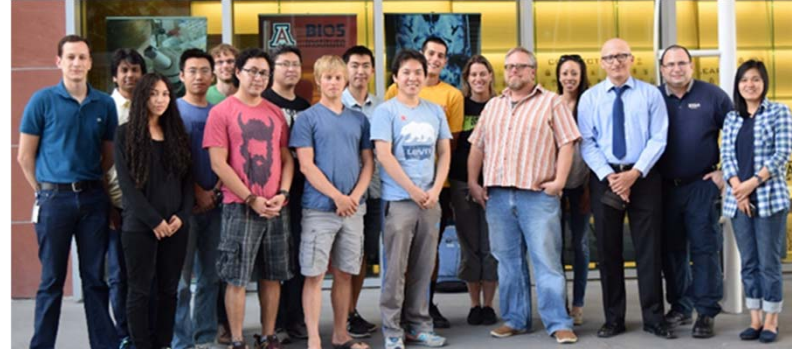


- Various TOrCs were present in the secondary effluent and throughout the treatment trains
- All TOrCs were reduced to below detection limits in the final advanced water treatment effluents
- Both analytical methods displayed similar concentrations for the different effluents
- O-SPE demonstrated lower MRLs for most of the indicator compounds analyzed
- Both methods offer similar labor intensity and run times, as well as comparable costs



Acknowledgments

Project Members:
Dr. Christiane Hoppe-Jones
Israel Lopez



Guillermo Flores
Alec Nienhauser
Juliana Ordine
Erica Clevenger



Agilent Technologies



BioDetection Systems

Many thanks to Dr. Armando Durazo for instrument assistance



Questions





Thank You





