Attenuation of emerging contaminants in recycled water using physical and oxidative processes

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July 27, 2015

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Water Reuse

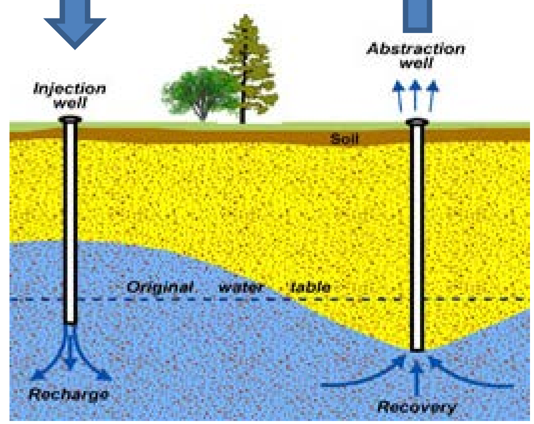
Alternate Sources of Water to Augment Supplies

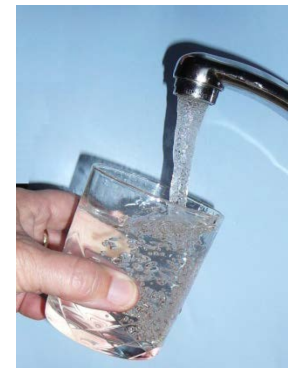
“Drought-Proof Resource”

Scientific Perception

Direct water reuse

Indirect water reuse





Public Perception

NRC Report on Reuse (2012)

USA TODAY

THE NATIONAL ACADEMIES

Advisers to the Nation on Science, Engineering, and Medicine

Report: Drinking wastewater preferable to wasting it

Council touts it as potable after treatment

By Wendy Koch
USA TODAY

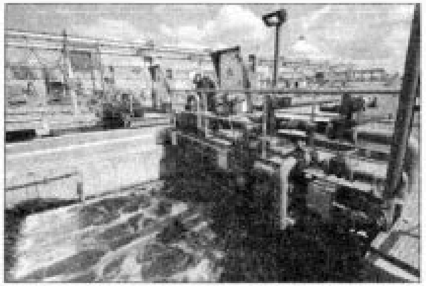
Drinking wastewater? The idea may sound distasteful, but new federally funded research says more Americans are doing so — whether they know it or not — and this reuse will be increasingly necessary as the U.S. population expands.

Treated wastewater poses no greater health risks than existing water supplies and, in some cases, may be even safer to drink, according to a report released Tuesday by the National Research Council, a science advisory group chartered by Congress. "We believe water reuse is a viable option" to deal with growing water scarcity, especially in coastal areas, says Jörg Drewes, an engineering professor at the Colorado School of Mines who contributed to the report.

"This can be done reliably without putting the public at risk," he says, citing technological advances. He says it's a waste not to reuse the nation's wastewater, because almost all of it is treated before discharge. This water includes storm runoff as well as used water from homes, businesses and factories.

Of the 32 billion gallons of wastewater discharged every day in the USA, the report says 12 billion — equal to 6% of total U.S. water use — is sent to an ocean or estuary and is thus a lost resource.

Many communities reuse wastewater for irrigation and industrial purposes. Some — notably Cloudcroft, N.M., and California's Orange County — have treatment facilities to reuse it as drinking water.



By Mark Greenberg for USA TODAY

Wastewater treatment: Mechanic Phillip Castro does a routine inspection of the systems at a plant in San Antonio.

In many places, the report says, the public does not realize it is drinking water that was treated after being discharged as wastewater somewhere upstream. For example, wastewater discharged into the Trinity River from Dallas/Fort Worth flows south into Lake Livingston, the source for Houston's drinking water.

Despite the growing importance of this "de facto reuse," the report says there has been no systemic analysis of its extent nationwide since a 1980 study by the Environmental Protection Agency.

"There's always someone downstream," says Alan Roberson of the American Water Works Association, a non-profit group dedicated to clean water. He says wastewater reuse is common, so the council's report is important but not surprising.

Roberson says he expects this recycling will continue to increase, especially for irrigation and industrial needs.

He says it will take longer to establish potable uses because of public skittishness about drinking wastewater, however treated.

"We have to do something" to address water scarcity, says Olga Naidenko, a senior scientist at the non-profit Environmental Working Group. She says less than 10% of potable water is used for drinking, cooking, showering or dishwashing.

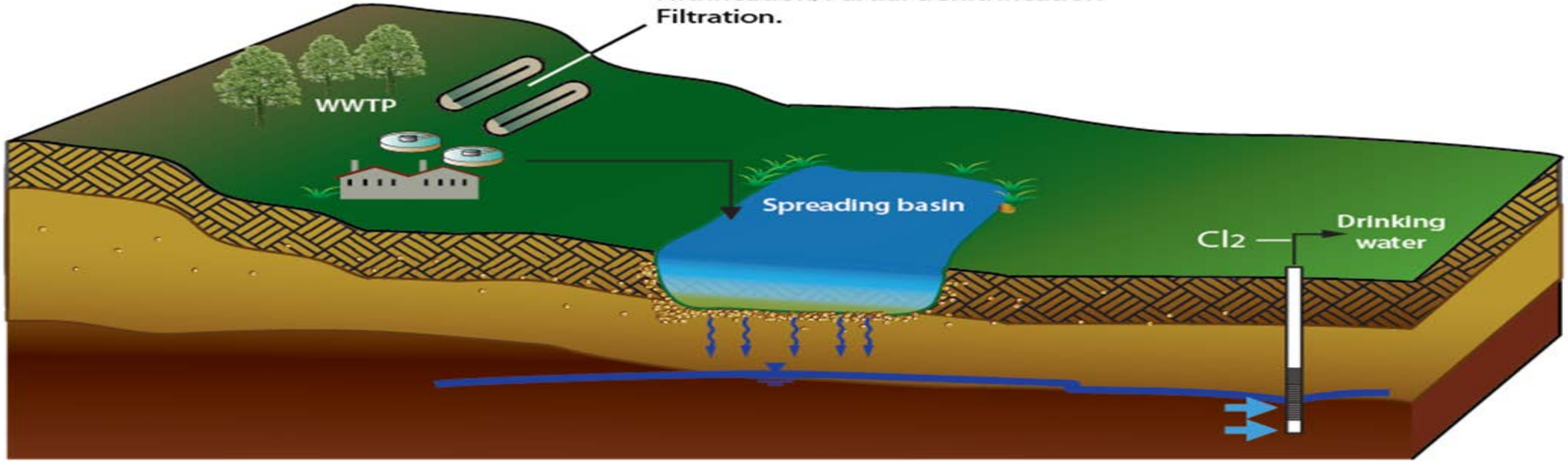
"We flush it down the toilet, literally," she says. Technologies exist to safely treat the water, she says, although some are expensive.

The report says water reuse projects tend to cost more than most water conservation options but less than seawater desalination and other supply alternatives. It calls on the EPA, a co-sponsor of the report, to develop rules that set safe national standards.

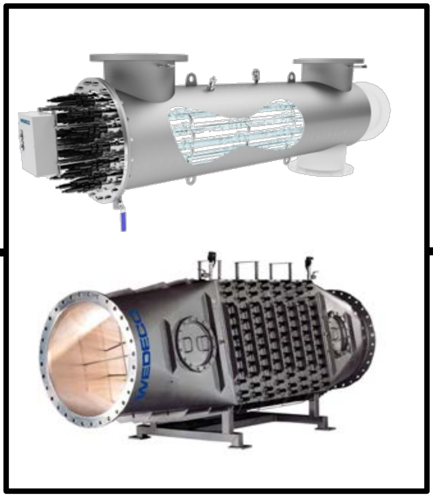
"…distinction between *indirect* and *direct* potable reuse is not scientifically meaningful…"

Water Reuse – Natural Systems

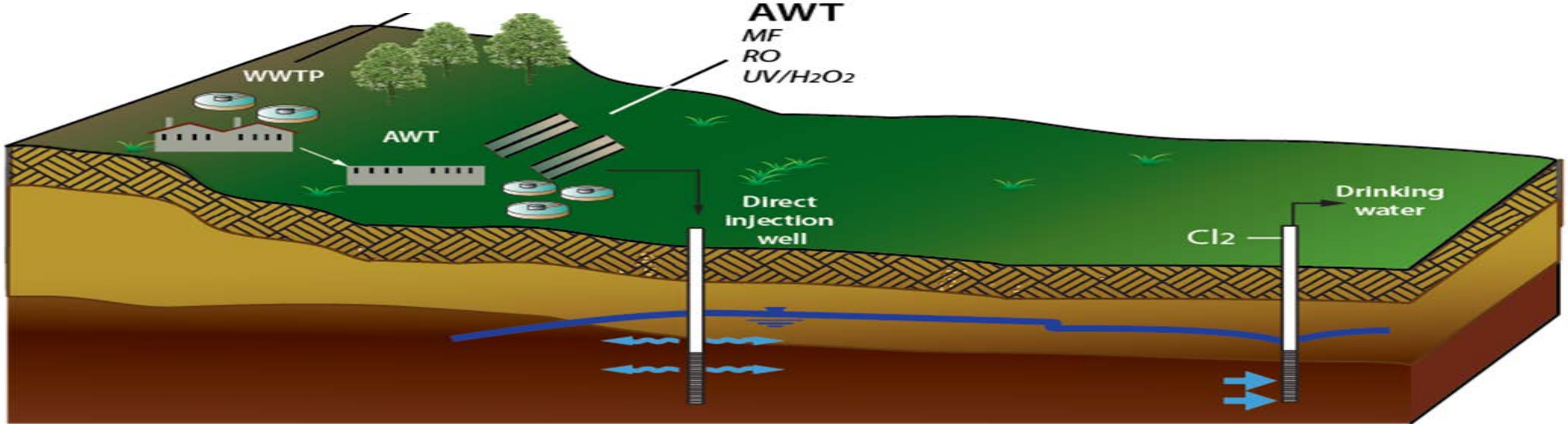
WWTP
Nitrification/Partial denitrification
Filtration.



Water Reuse – Advanced Treat.



WWTP



Water Reuse – Direct Potable

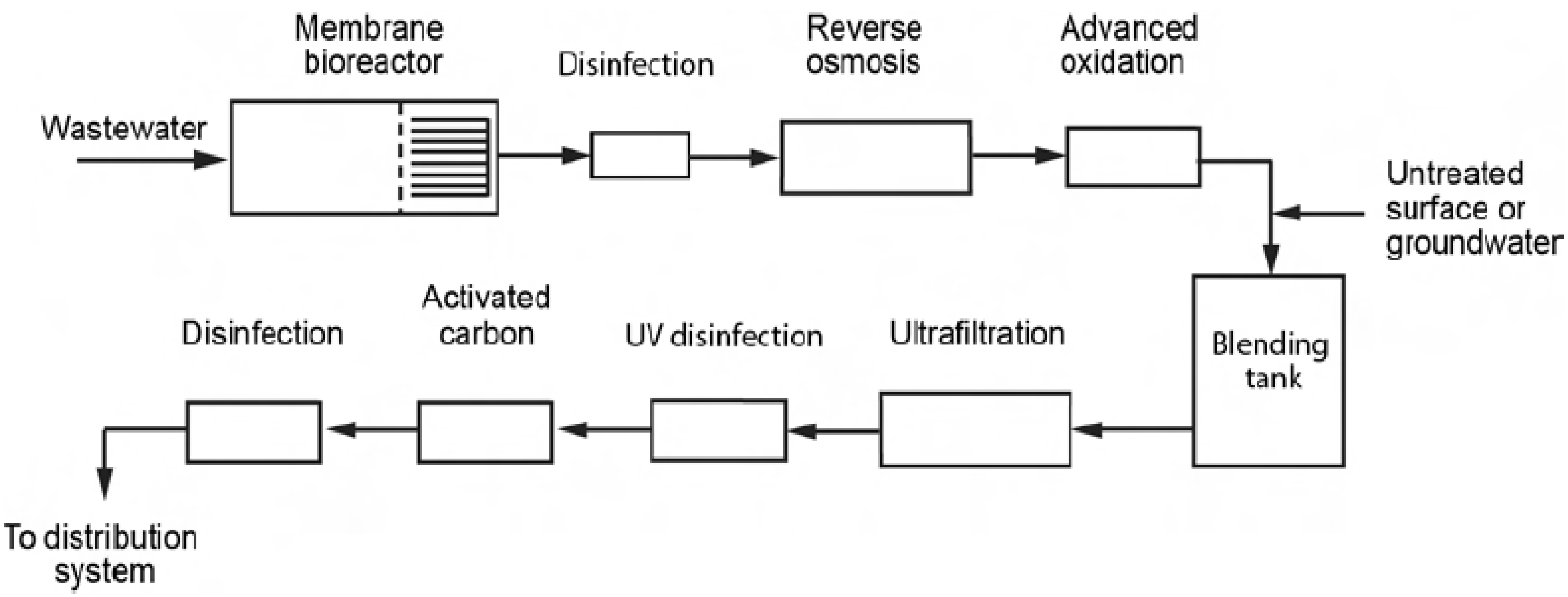
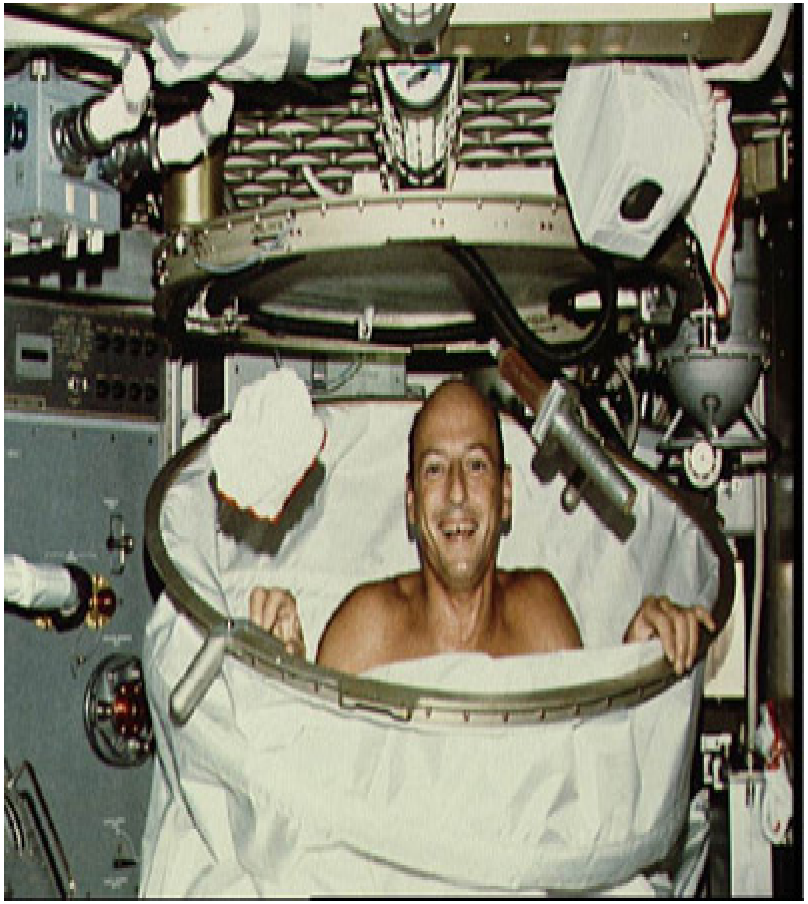


Figure 3-7

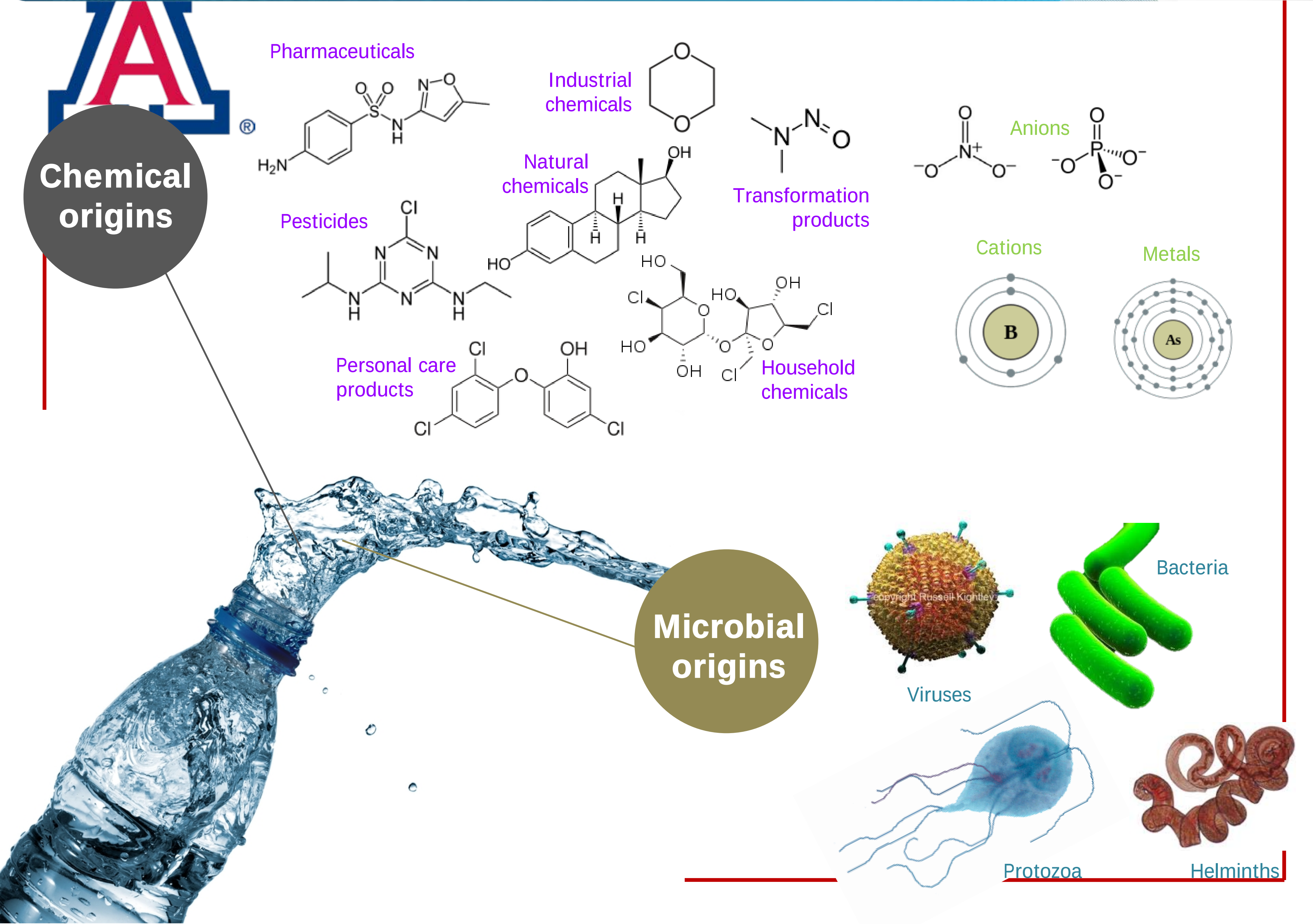
Schematic of Cloudcroft, NM DPR treatment process flow diagram (Adapted from Livingston, 2008).

Any Aqueous Liquid Can Be Made Drinkable

Simply a matter of safety, cost, and reliability…



Contaminants potentially detectable in reclaimed water



Indicator Example – Secondary WWTP

Faster transformation during secondary treatment

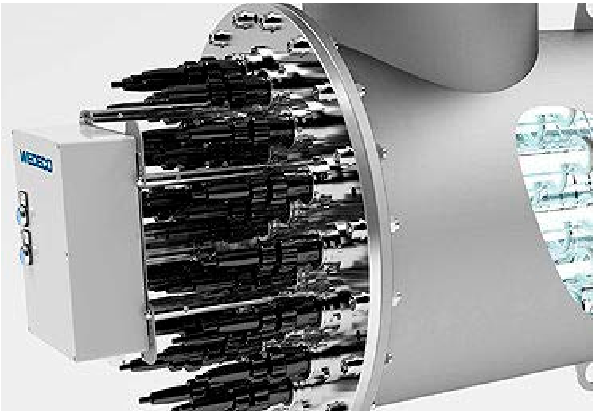
Higher sorption during secondary treatment

		Biotransformation (K_b, L/g-d)		
		Recalcitrant <0.1	**Moderate Slow 0.1-10**	**Rapid >10**
Sorption (log K_d)	**Low <2.5**	Carbamazepine Meprobamate Primidone TCEP Sucralose	DEET Sulfamethoxazole Gemfibrozil Iopromide	Acetaminophen Caffeine Naproxen Ibuprofen Atenolol
	Sorptive 2.5-3	TCPP	Cimetidine Trimethoprim	Benzophenone Diphenhydramine Bisphenol A
	Effective >3	Triclocarban		Triclosan Fluoxetine

WERF CEC4R08 – Tanja Rauch-Williams *et al.* 2013

Basic Categories of Treatment

Biological ***Physical*** ***Oxidation***



Objectives

- To show various physical and oxidative treatment processes for CEC attenuation in water reuse applications
- To demonstrate multi-barrier approaches for the attenuation of CECs
- To explore various monitoring tools including bioassay and surrogate indicator approach to ensure treated water qualities

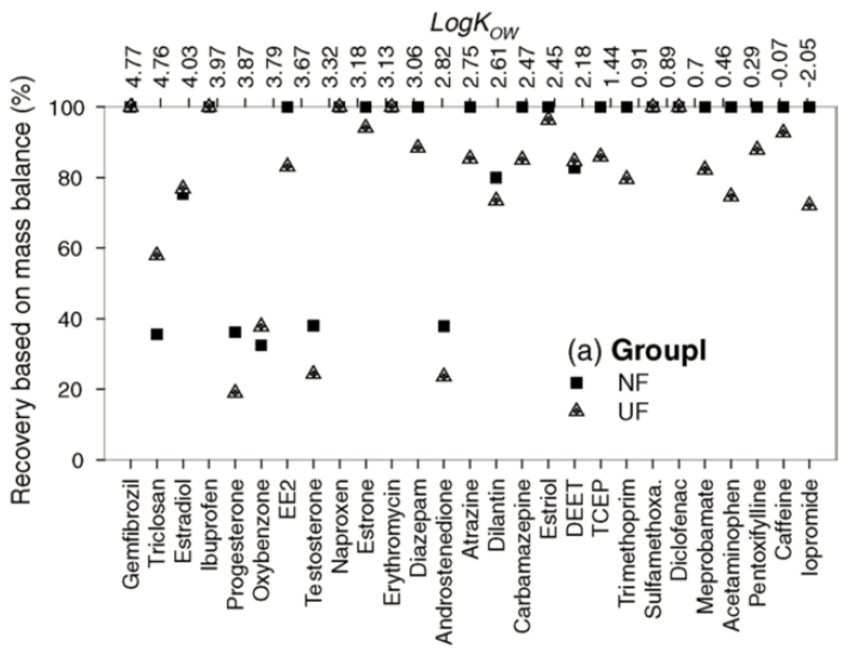
PHYSICAL PROCESSES

Physical processes

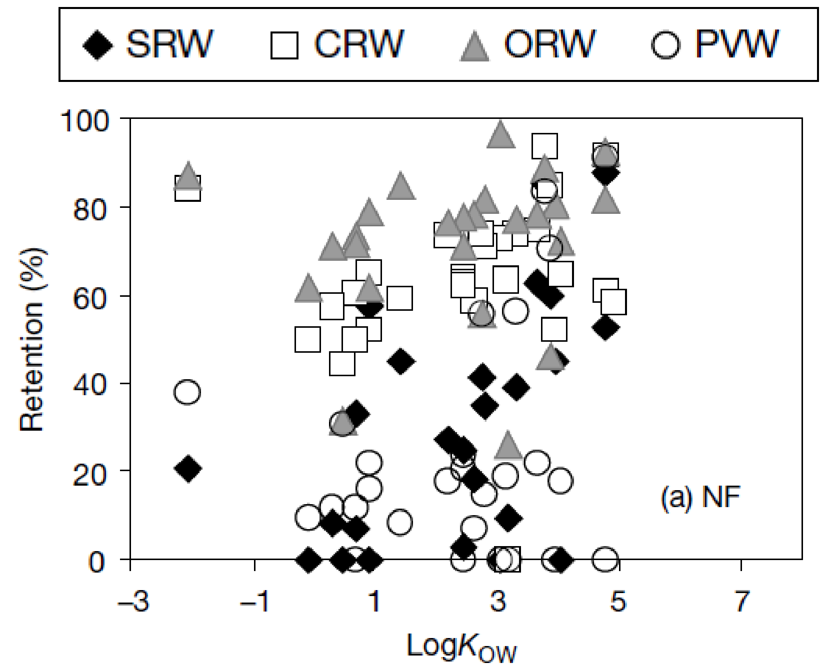
Membrane separation

Activated carbon adsorption

CEC removal by NF



Recovery of EDC/PPCPs based on mass balance with feed, permeate, and retentate for NF and UF

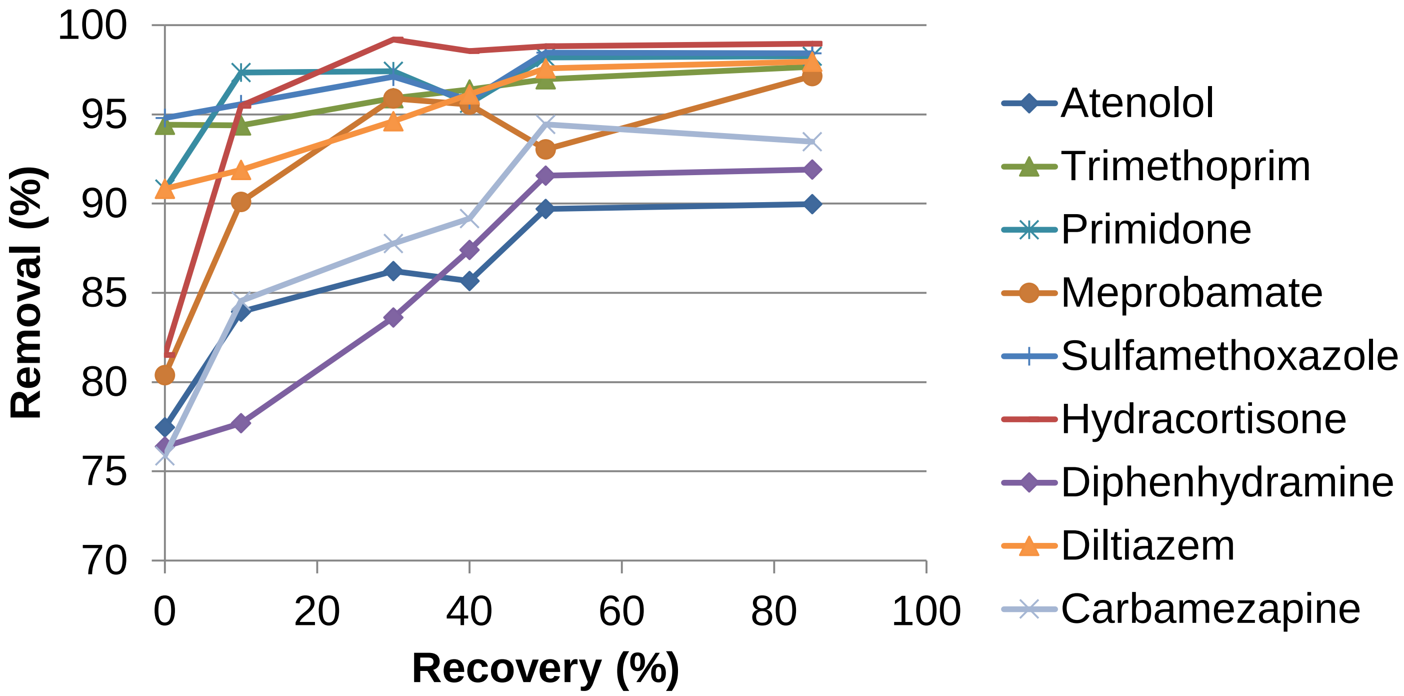


Retention of EDC/PPCPs as a function of Log *K*ow for the NF and UF membranes in various source waters in NF membrane

Yoon, Y., Westerhoff, P., Snyder, S.A., Wert, E.C. and Yoon, J. (2007) Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes. Desalination 202(1–3), 16-23.

NF membrane filtration

- Dow NF270-4040: CECs spiked in CRW



Granular Activated Carbon

Breakthrough curves

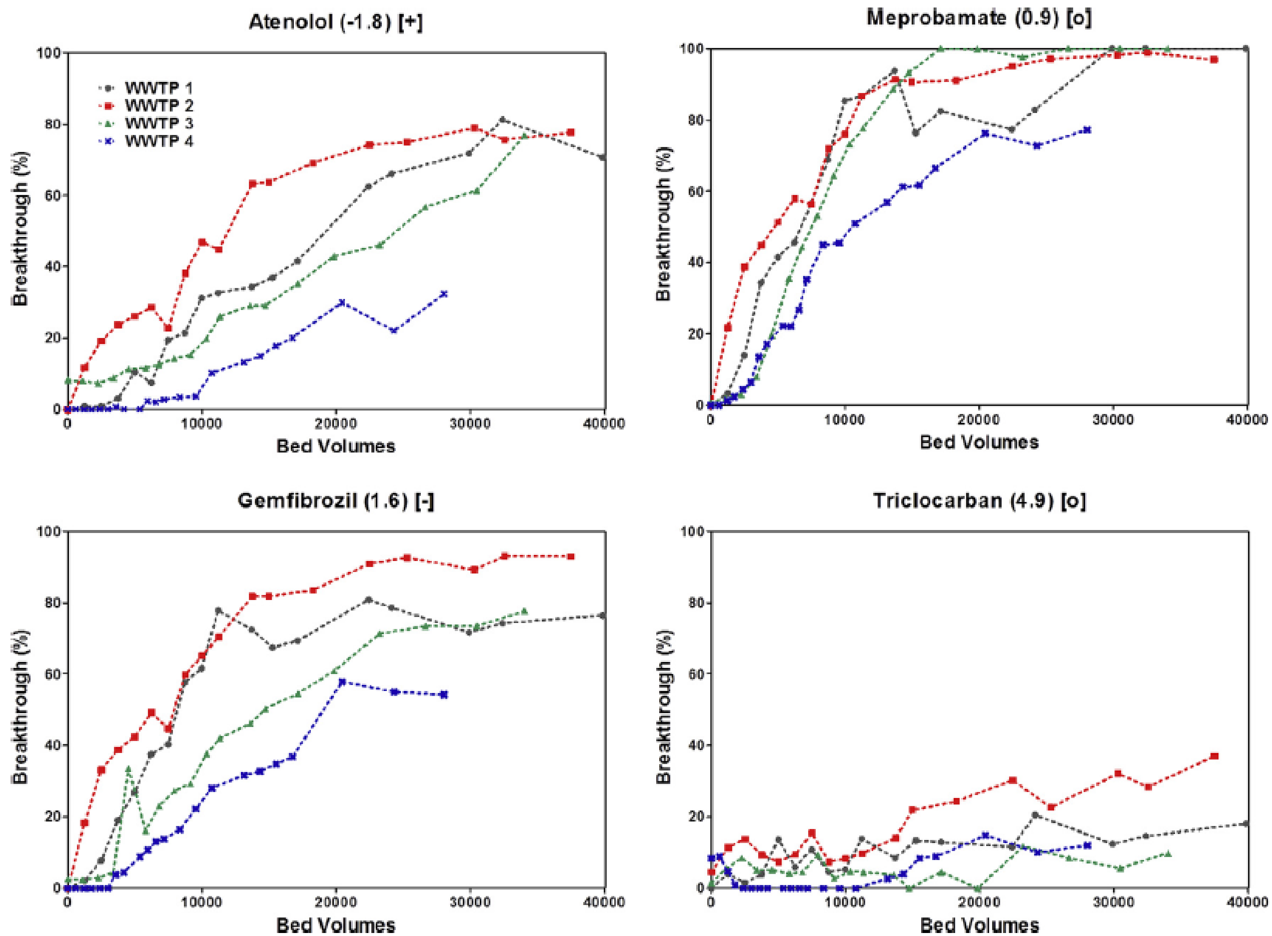
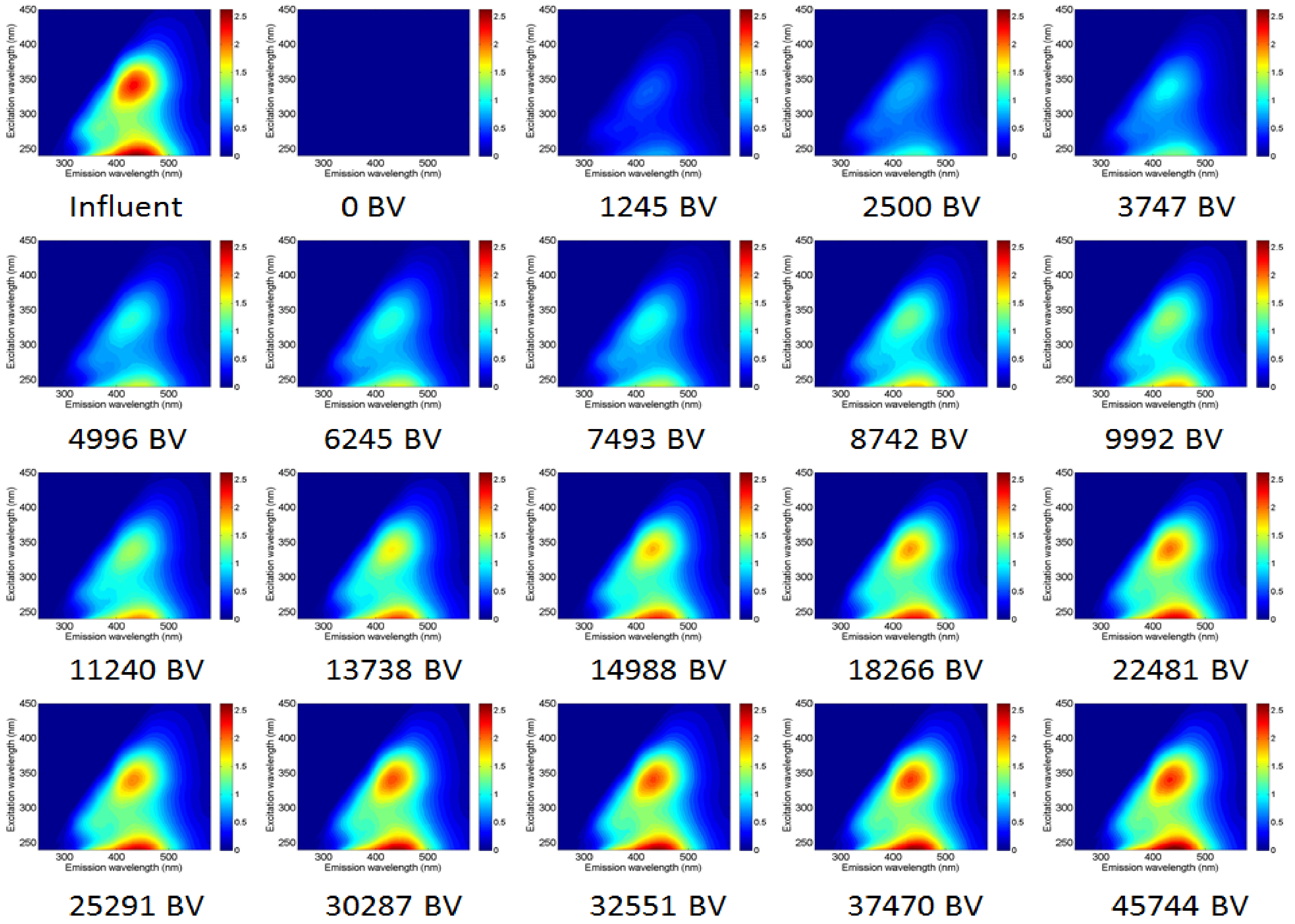


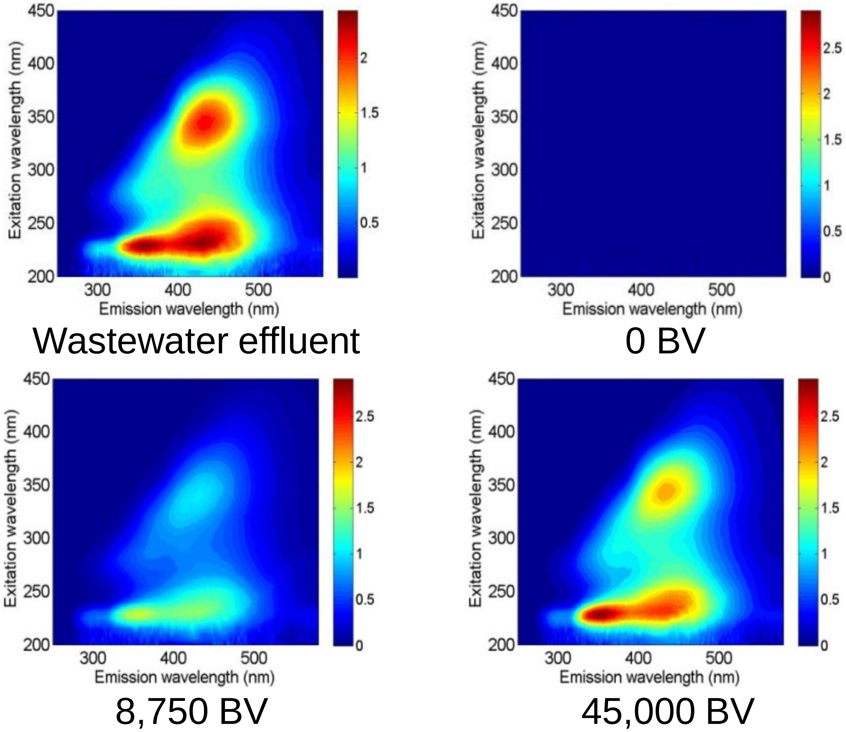
Fig. 2 – Breakthrough curves for representative TOrCs in four wastewaters tested with the Log D_{ow} and charge indicated in () and [] respectively at pH: 7.5. +, Positive; −, Negative; o, Neutral.

Anumol, T., Sgroi, M., Park, M., Roccaro, P. and Snyder, S.A. (2015) Predicting trace organic compound breakthrough in granular activated carbon using fluorescence and UV absorbance as surrogates. Water Research 76(0), 76-87.

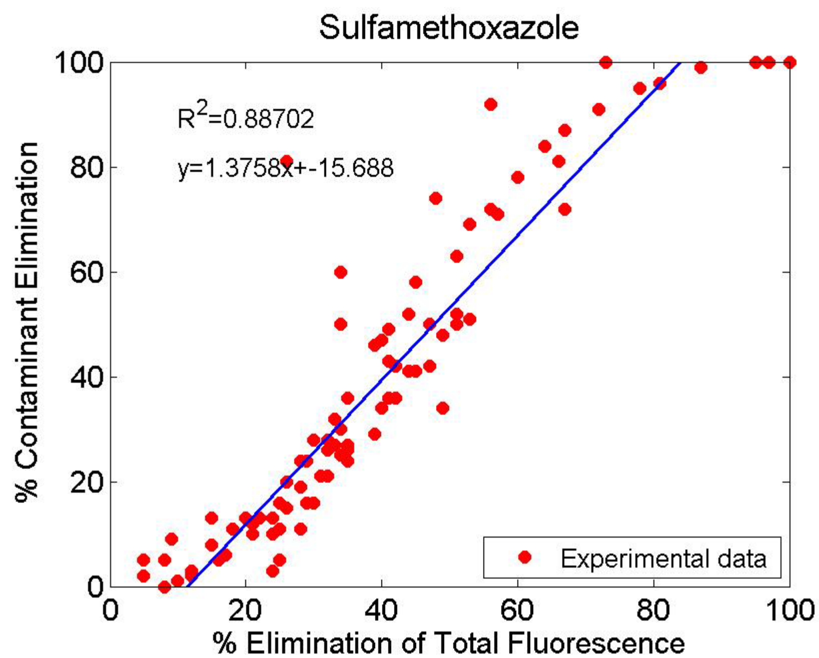
Application of fluorescence as surrogate for water quality



Surrogates for Water Quality



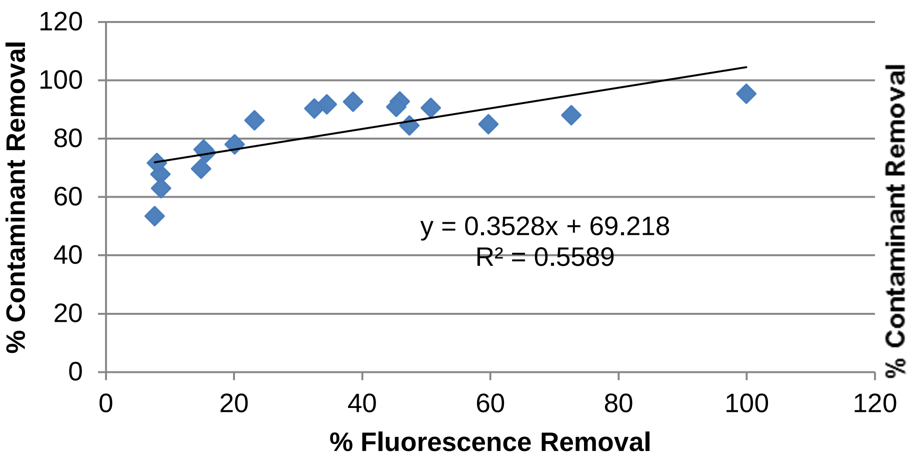
< Excitation-emission matrices of wastewater effluent on GAC >



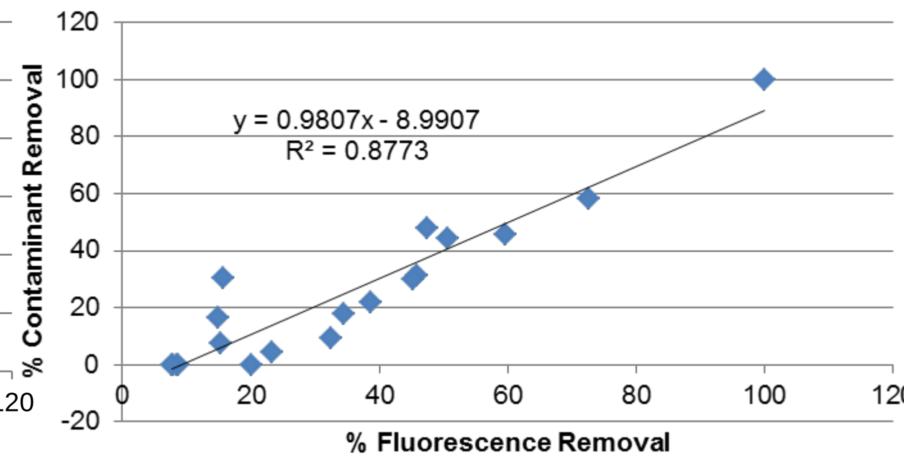
< Correlation of sulfamethoxazole with fluorescence by GAC>

Fluorescence Surrogate Correlation to LC-MS/MS

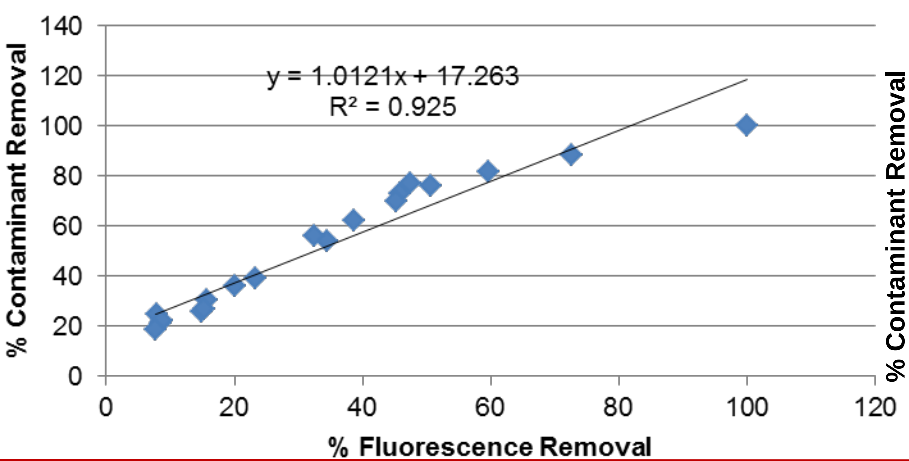
Group 1: Triclocarban



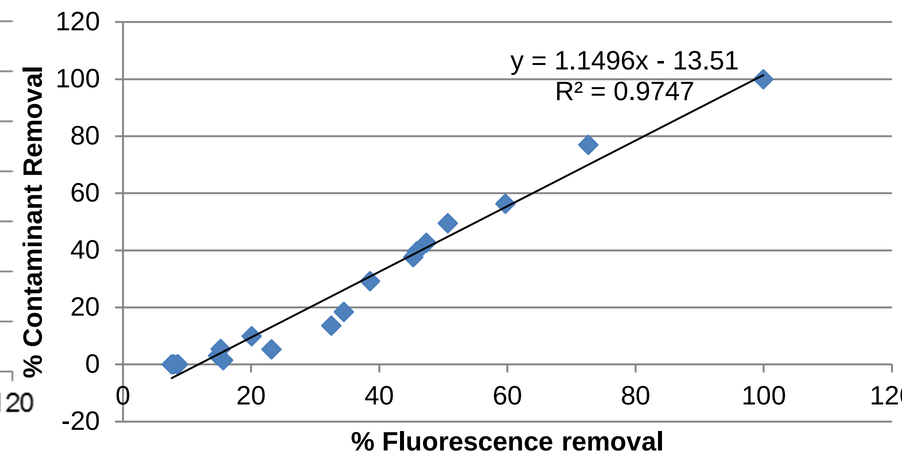
Group 2: PFOA



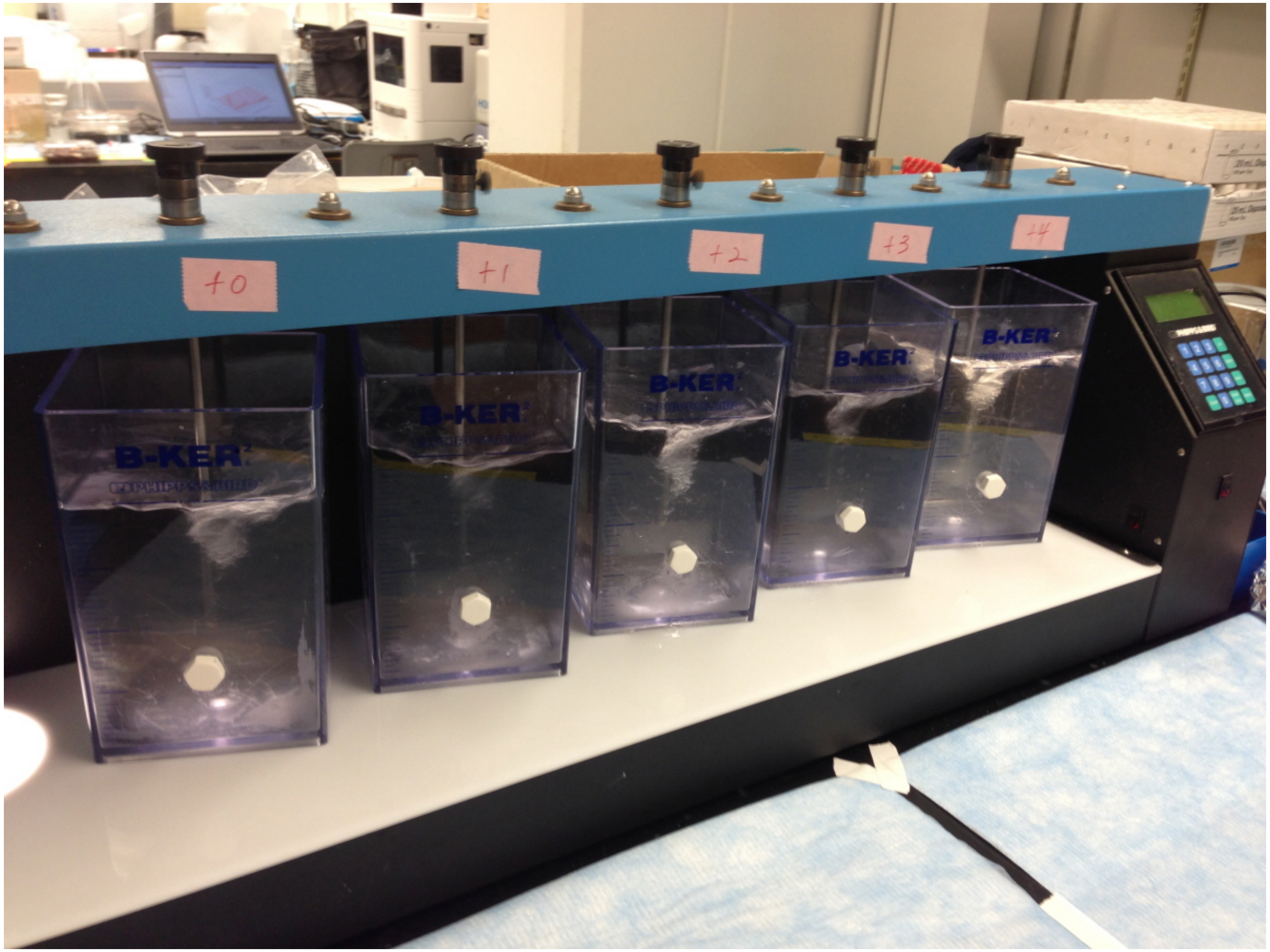
Group 3: Atenolol



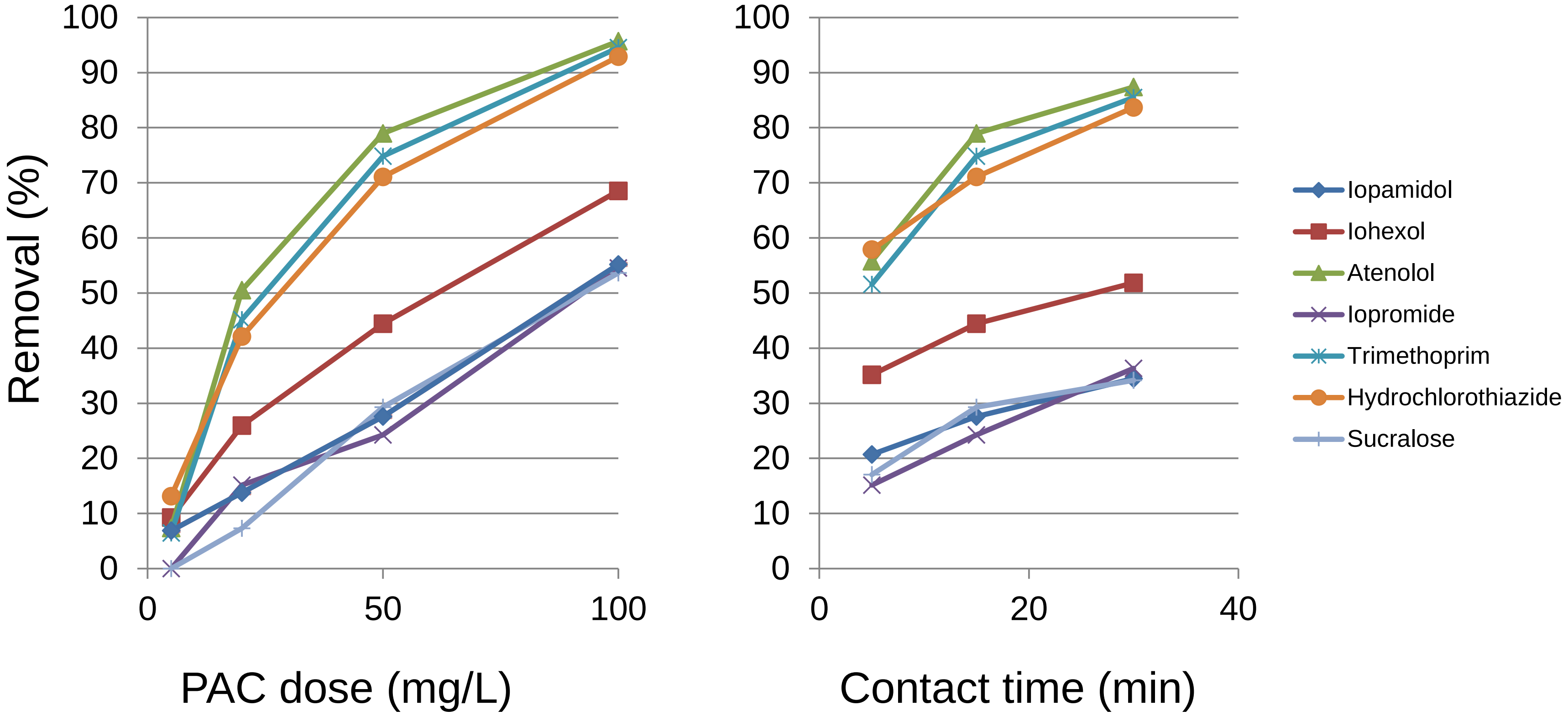
Group 4: Primidone



Powdered activated carbon

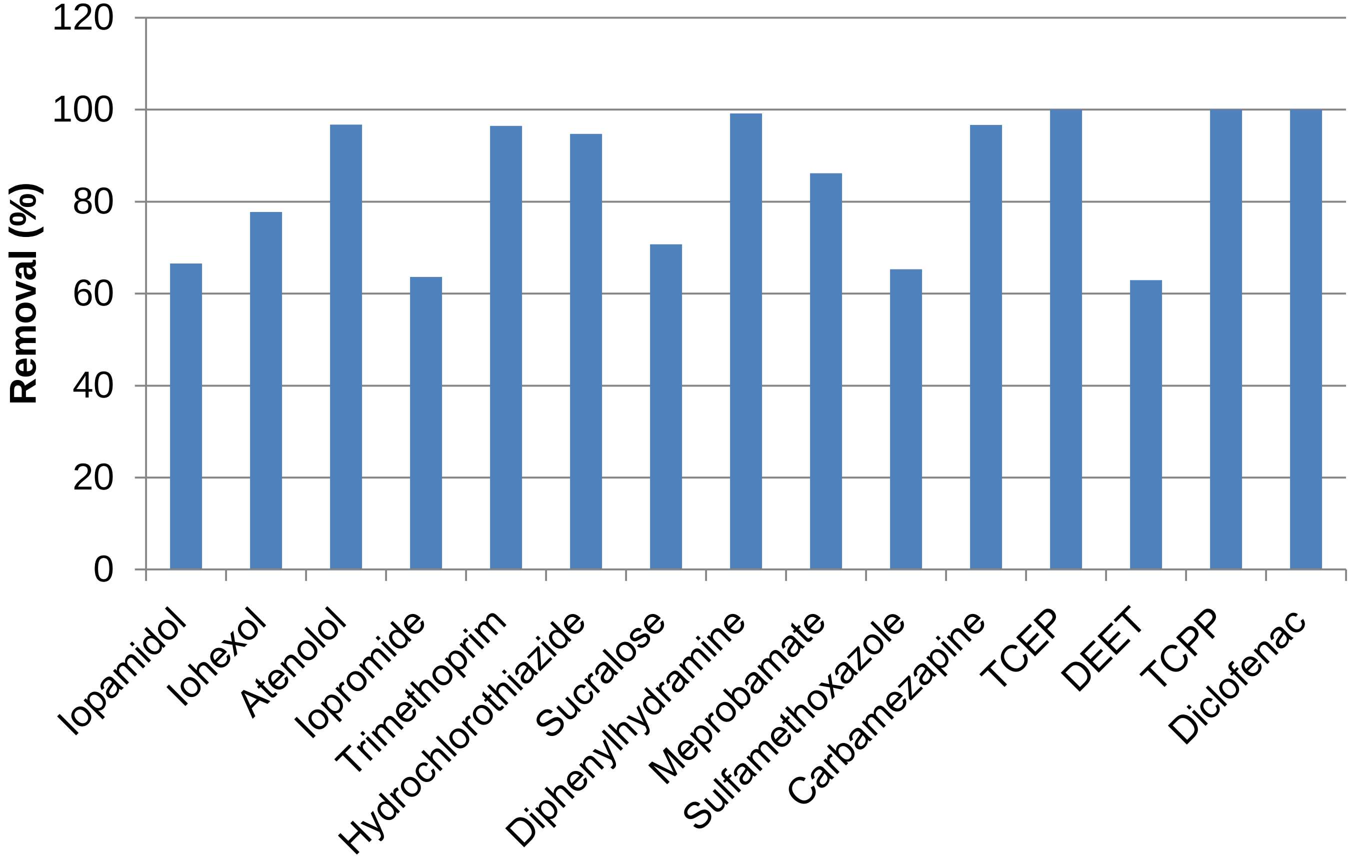


Effects of PAC dose and contact time



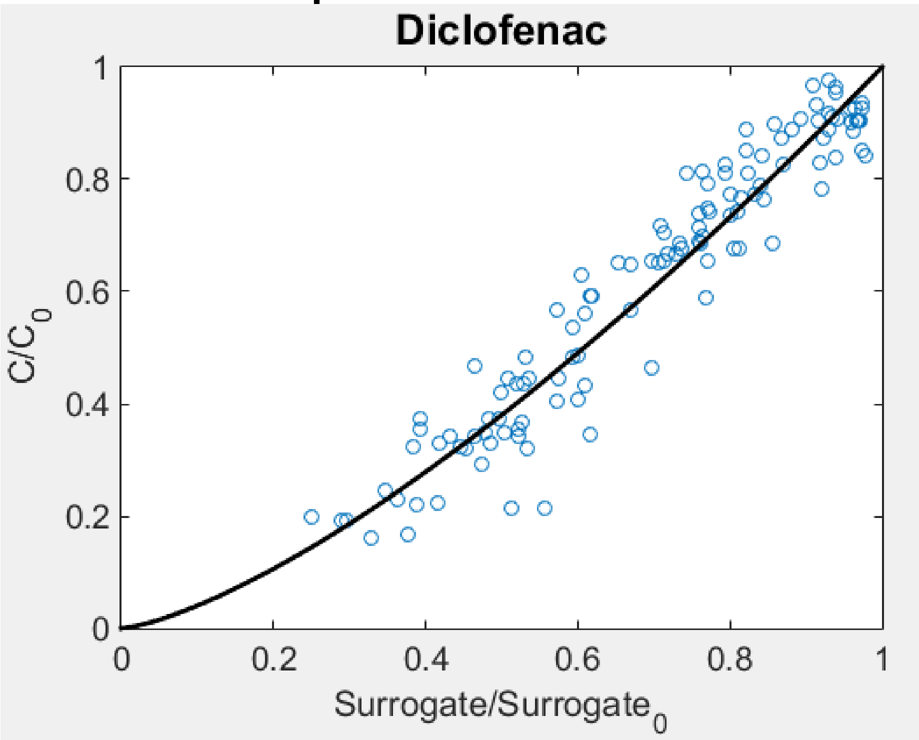
CECs removal by PAC

Calgon PWA 100mg/L (Contact time: 30 min)



Surrogates for water quality

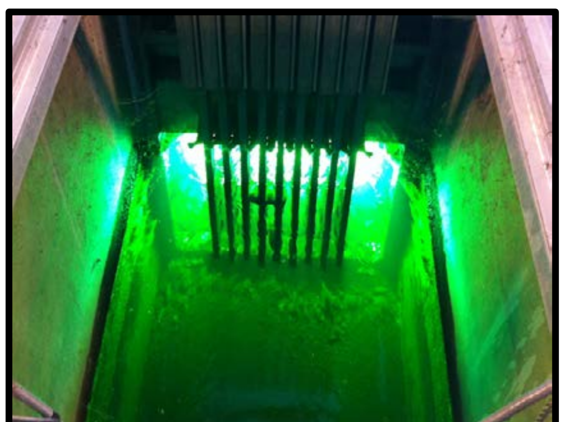
- Total fluorescence (TF) as a surrogate indicator of CEC removal in PAC adsorption



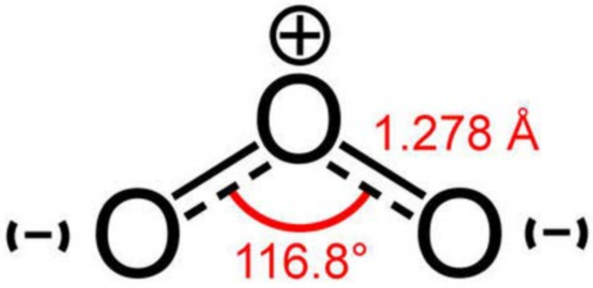
OXIDATIVE PROCESSES

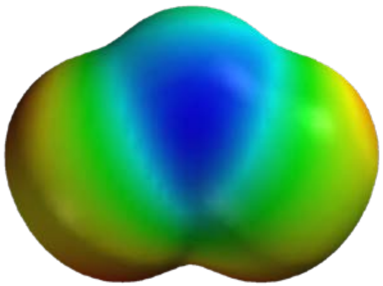
The Multi-Barrier Approach

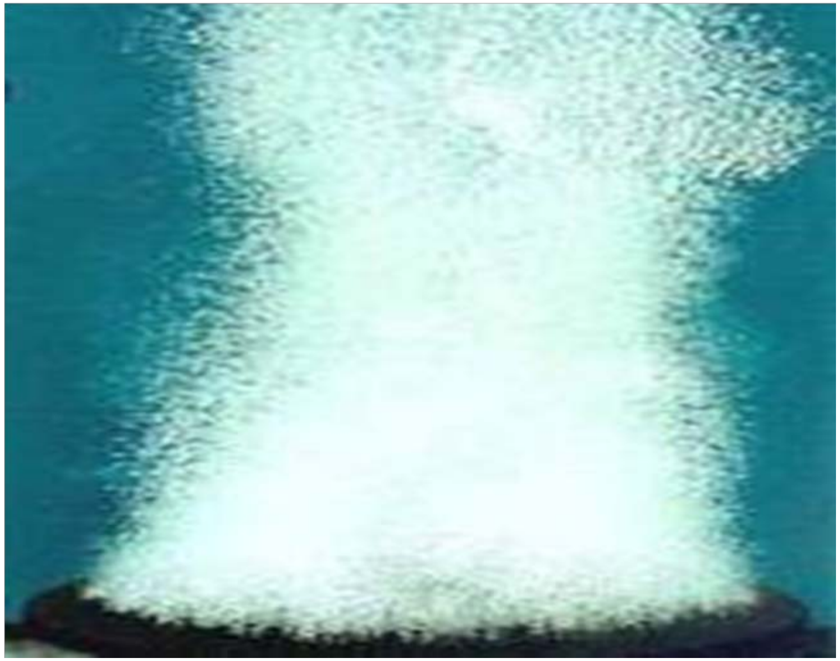
Disinfectant	Bacteria	Viruses	Parasites	DBPs
Free Chlorine	✓	✓	✗	THMs, HAAs
Chloramines	—	✗	✗	NDMA
UV	✓	—	✓	None???
Ozone	✓	✓	—	Bromate, NDMA



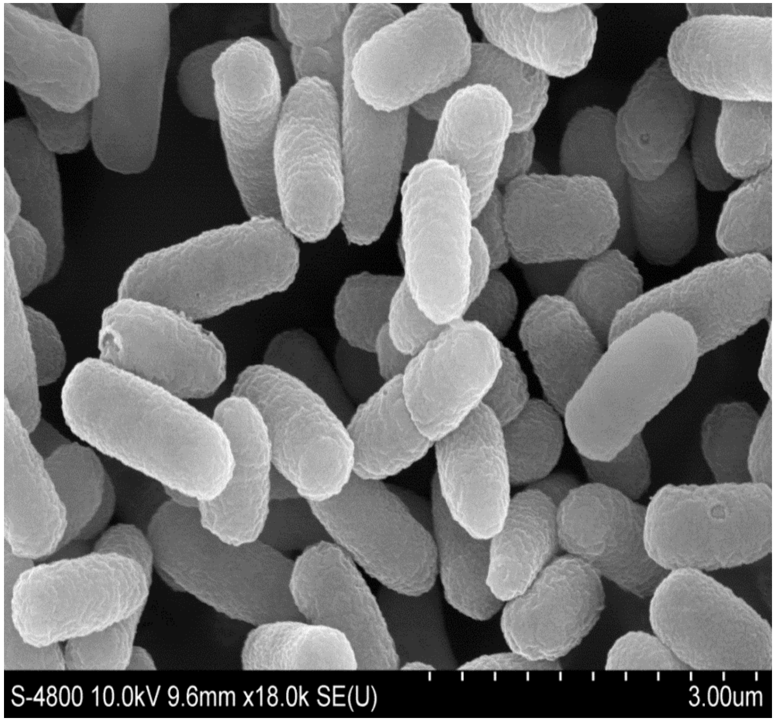
Oxidation of Trace Contaminants: Ozone



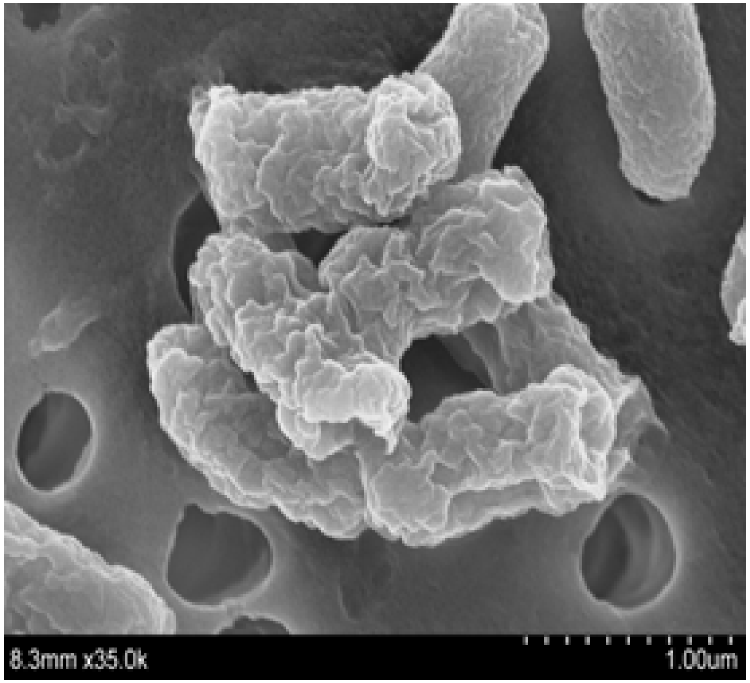




Disinfection



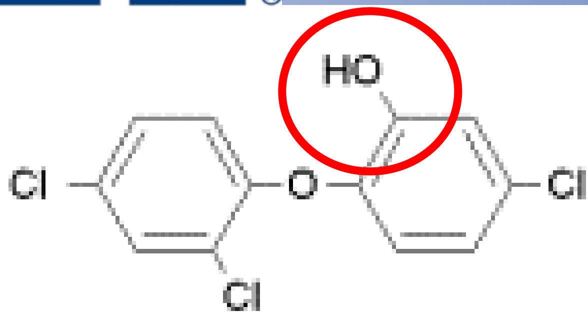
E. Coli - Healthy



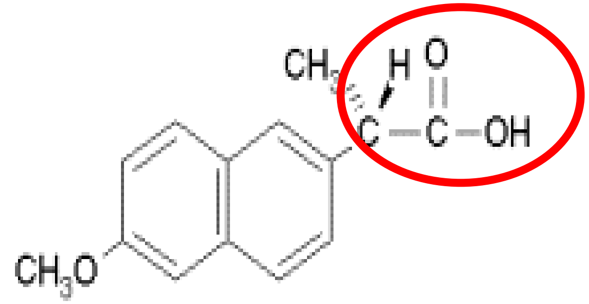
Post-AOP

Sherchan, S. P.; Snyder, S. A.; Gerba, C. P.; Pepper, I. L. *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.* **2014,** *49* (4), 397-403.

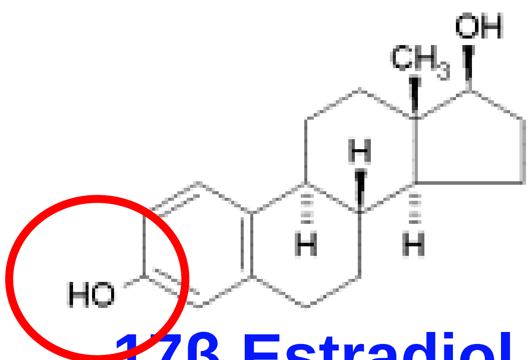
Easy to oxidize



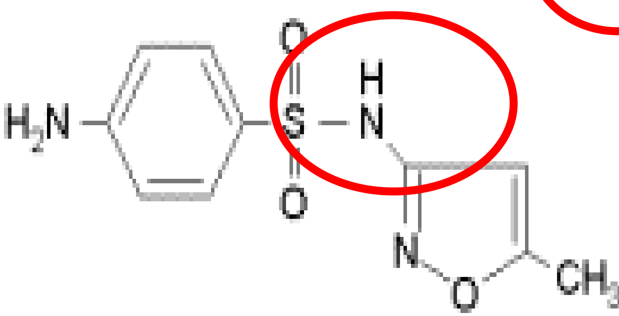
Triclosan



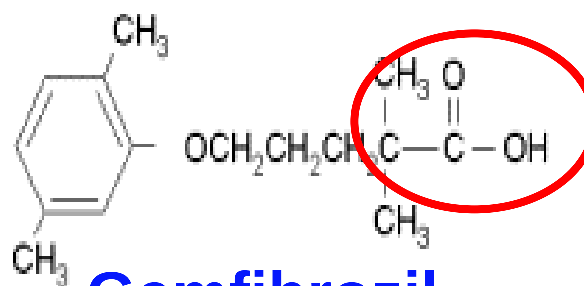
Naproxen



17β Estradiol

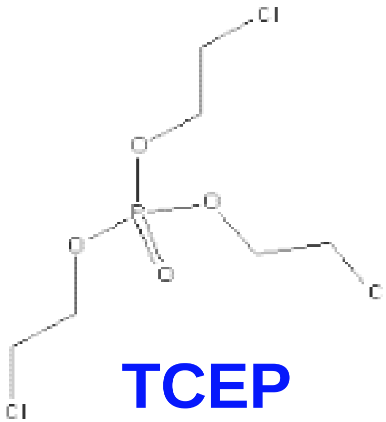


Sulfamethoxazole

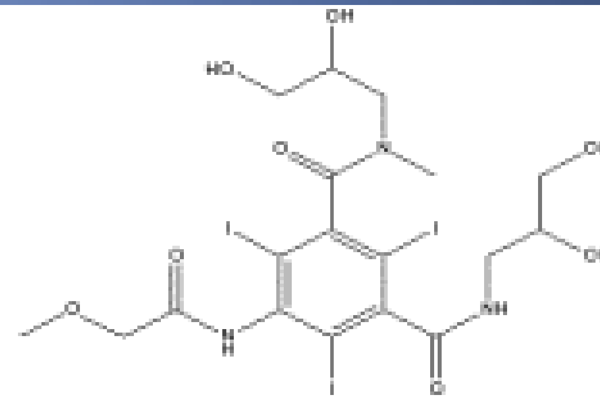


Gemfibrozil

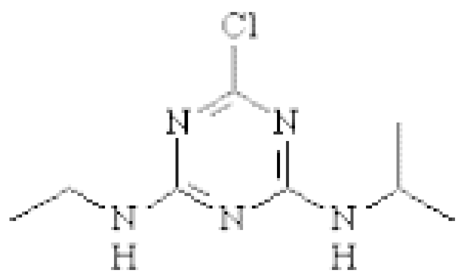
Difficult to oxidize



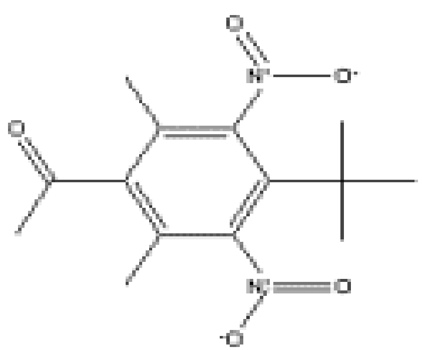
TCEP



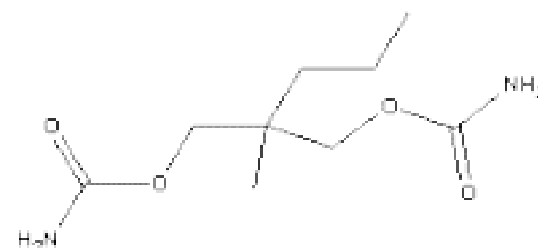
Iopromide



Atrazine

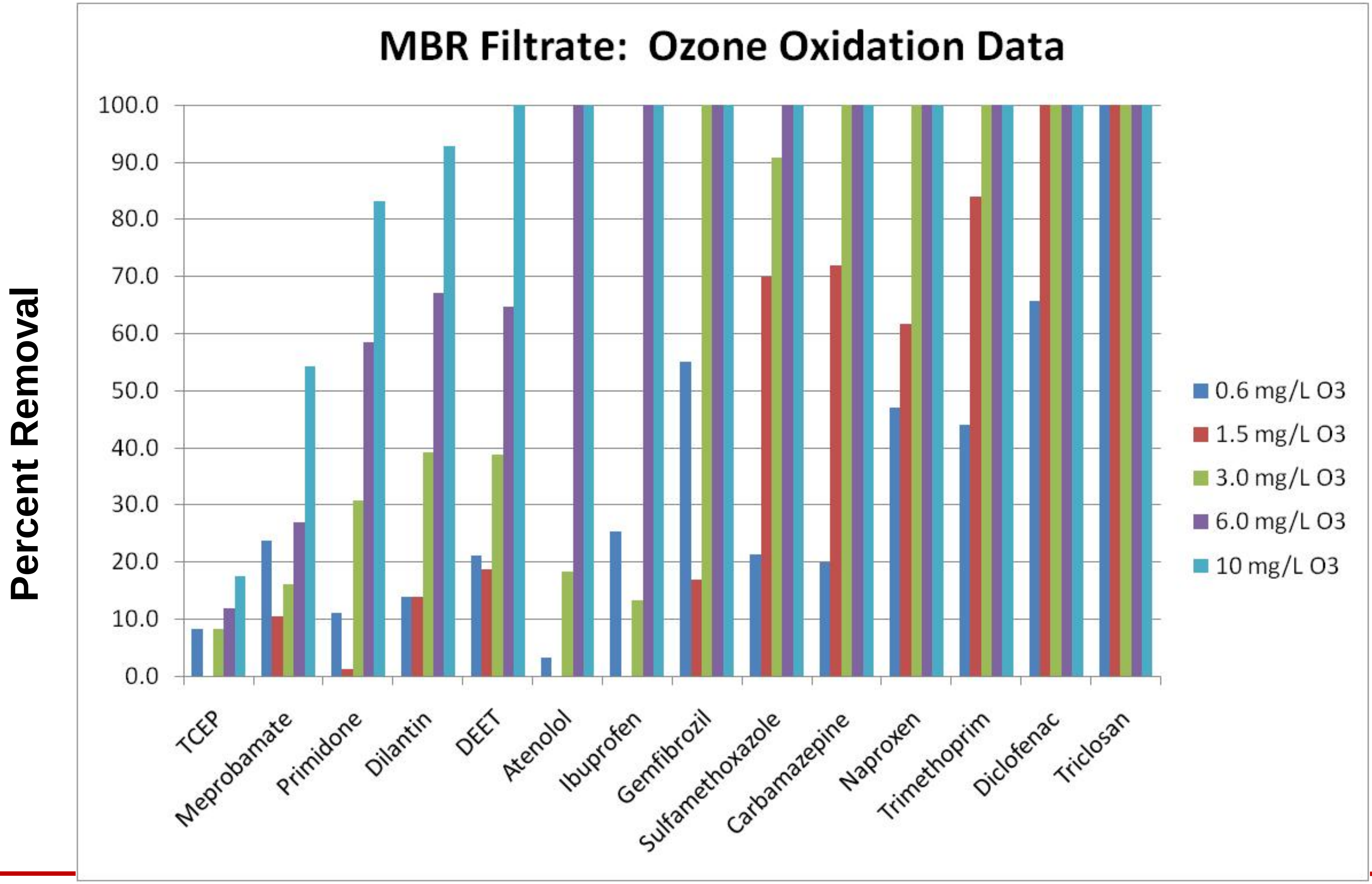


Musk Ketone



Meprobamate

Ozone

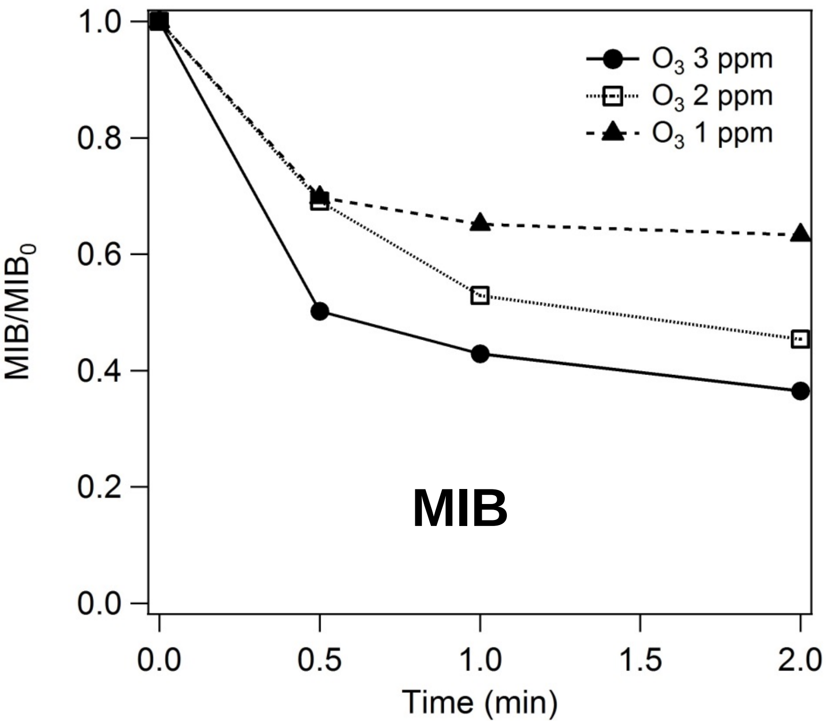


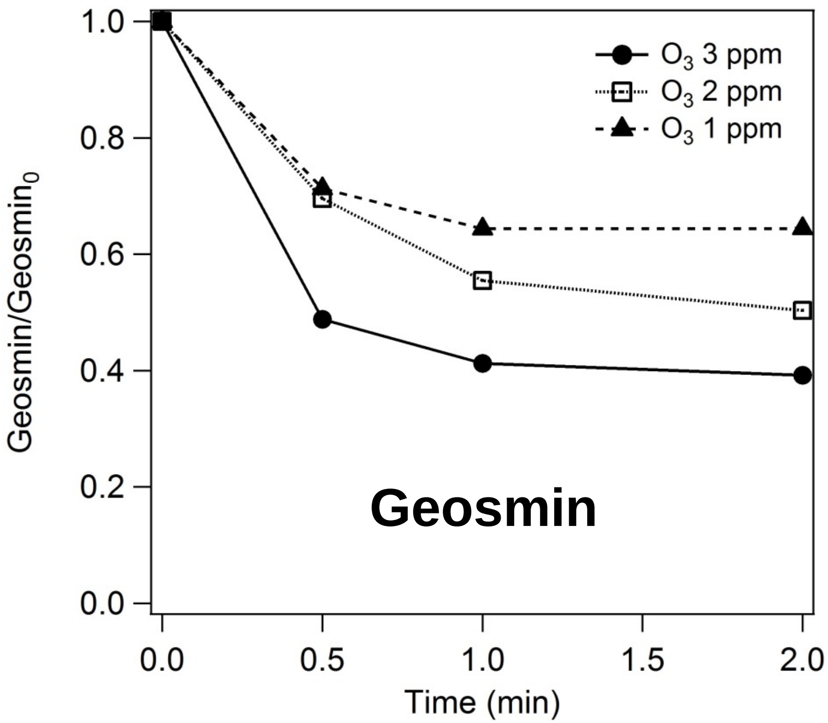
MBR Filtrate: Ozone Oxidation Data
Percent Removal
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
TCEP
Meprobamate
Primidone
Dilantin
DEET
Atenolol
Ibuprofen
Gemfibrozil
Sulfamethoxazole
Carbamazepine
Naproxen
Trimethoprim
Diclofenac
Triclosan
0.6 mg/L O3
1.5 mg/L O3
3.0 mg/L O3
6.0 mg/L O3
10 mg/L O3

Oxidation Kinetics of MIB/Geosmin

Removal of MIB/Geosmin by ozone oxidation

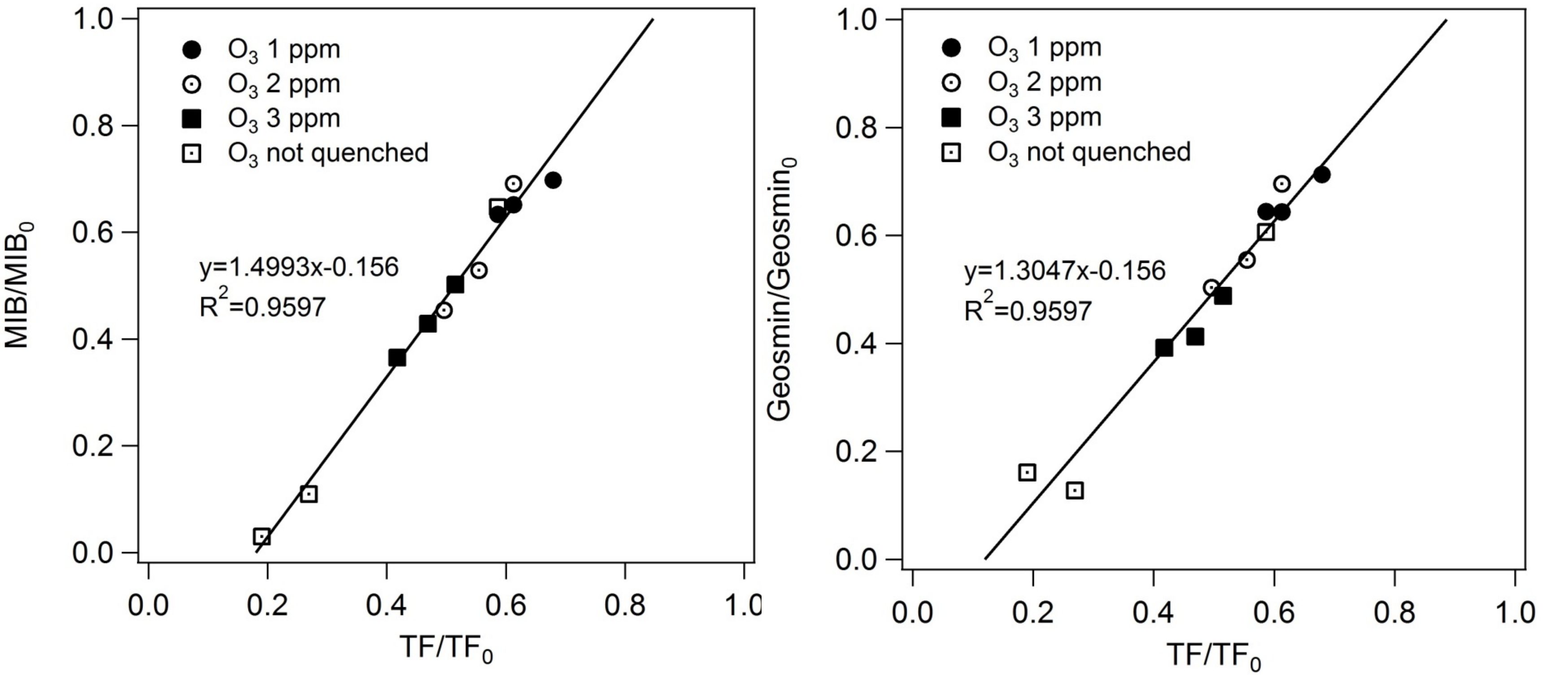
- MIB/Geosmin has similar removal rate at corresponding applied ozone dose and contact time.





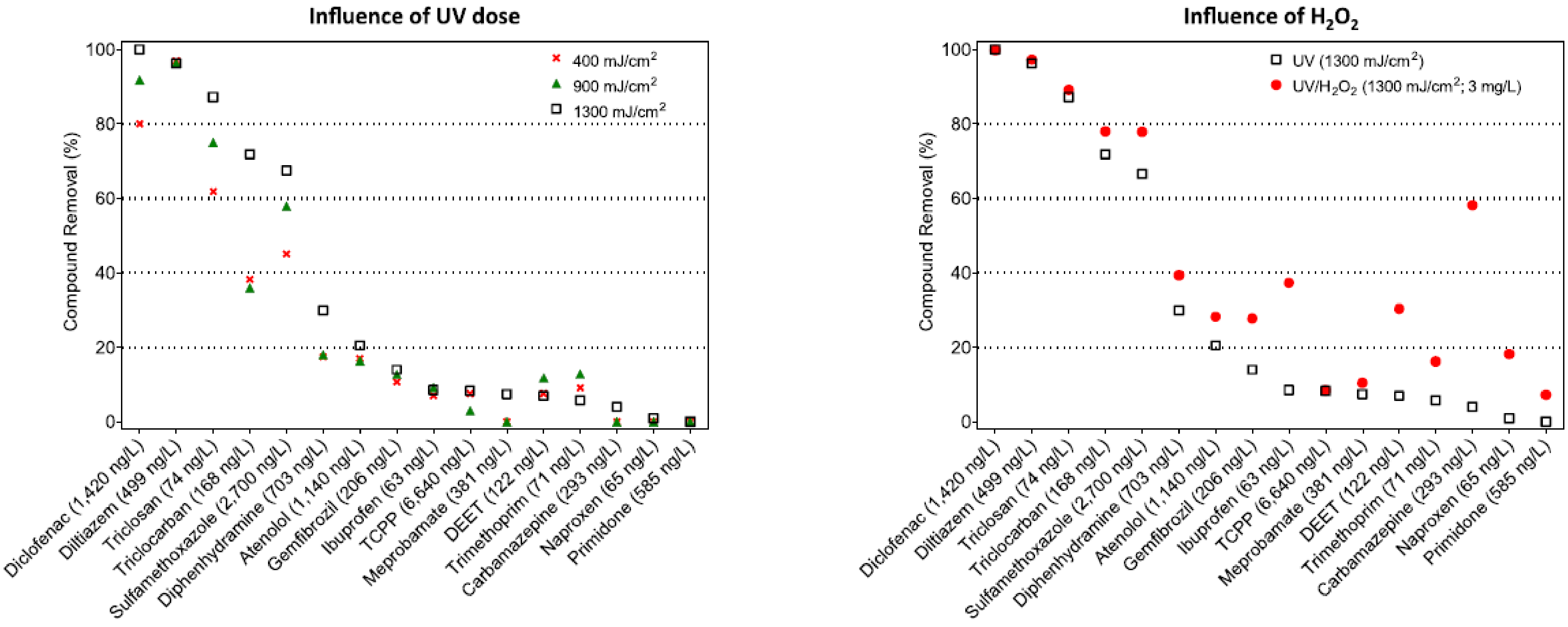
Oxidation Kinetics of MIB/Geomin

EEM as surrogate indicator for T&O Oxidation



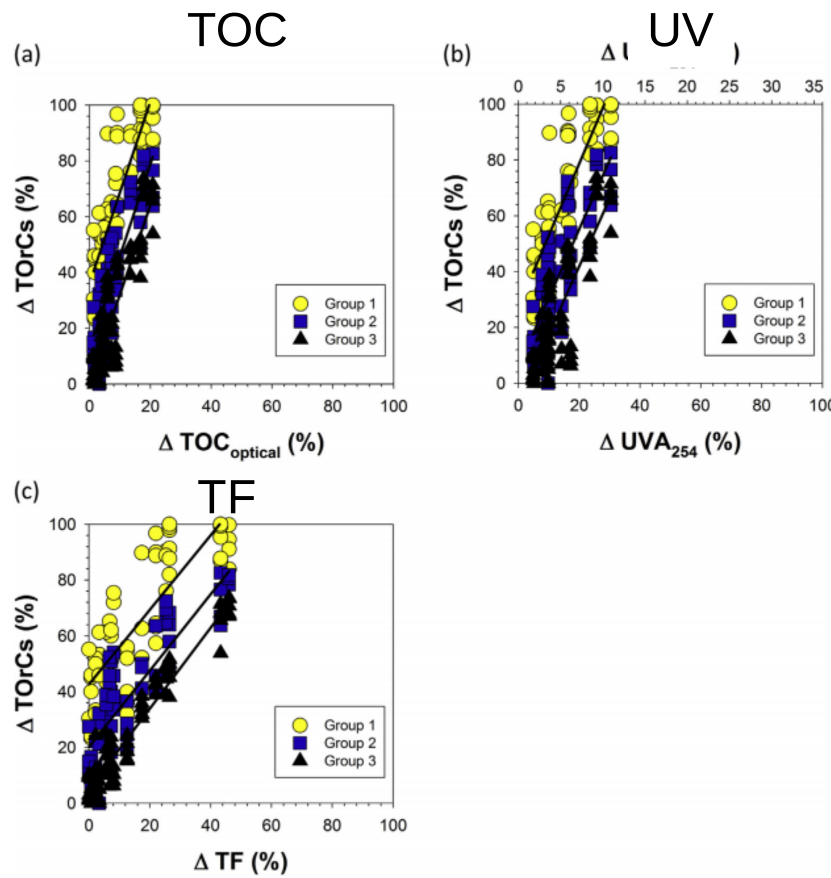
UV AOP

Assessment of UV-AOP Performance on Selected TOrCs in Secondary Wastewater Effluent



Merel, S., Anumol, T., Park, M. and Snyder, S.A. (2015) Application of surrogates, indicators, and high-resolution mass spectrometry to evaluate the efficacy of UV processes for attenuation of emerging contaminants in water. Journal of Hazardous Materials 282(0), 75-85.

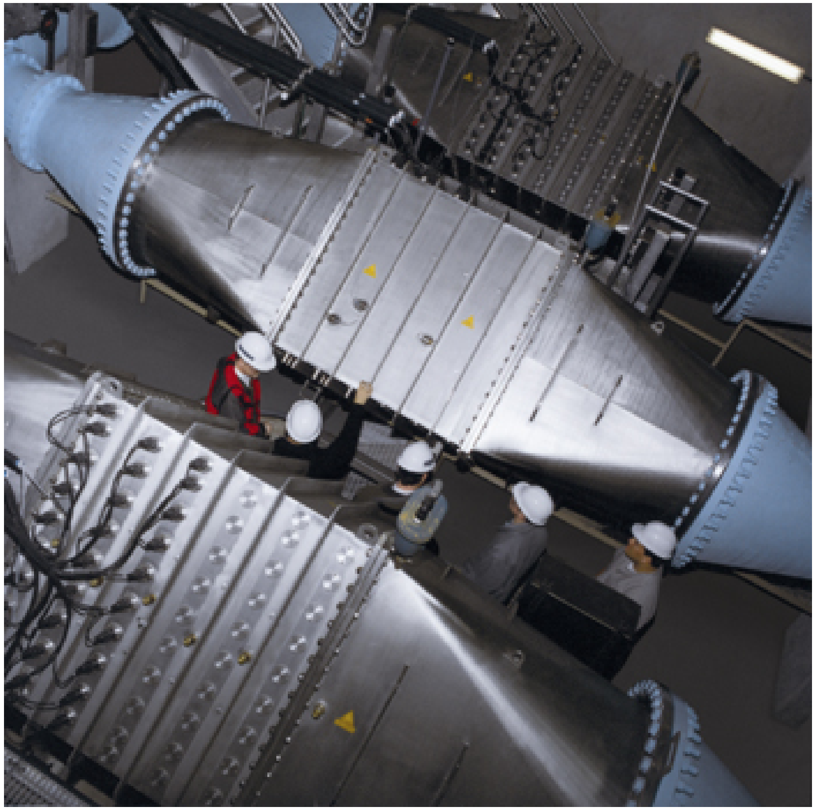
Online sensor in UV AOP



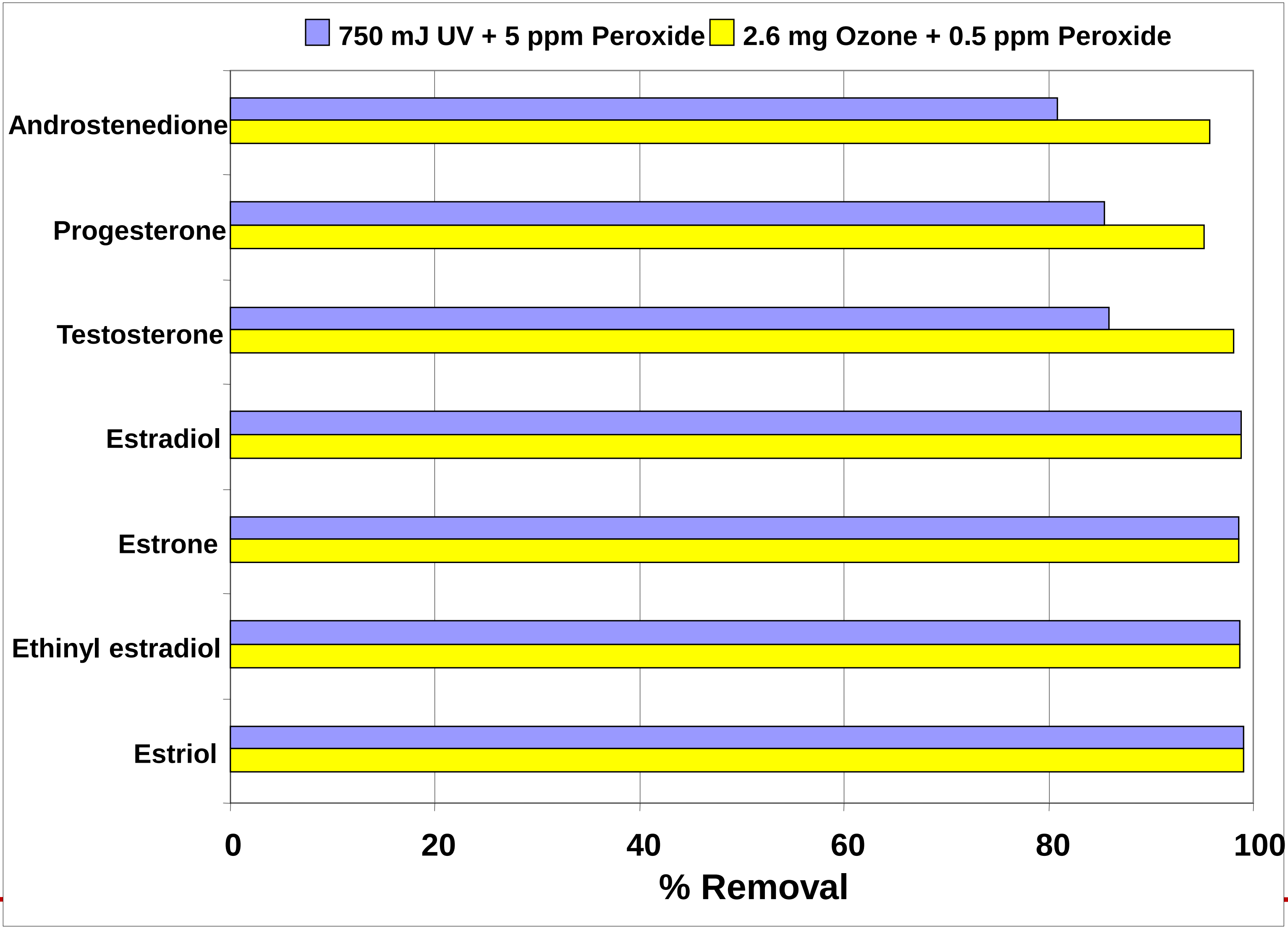
Yu, H.W., Anumol, T., Park, M., Pepper, I., Scheideler, J. and Snyder, S.A. (2015) On-line sensor monitoring for chemical contaminant attenuation during UV/HO advanced oxidation process. Water Res 81, 250-260.

UV AOP vs. Ozone AOP

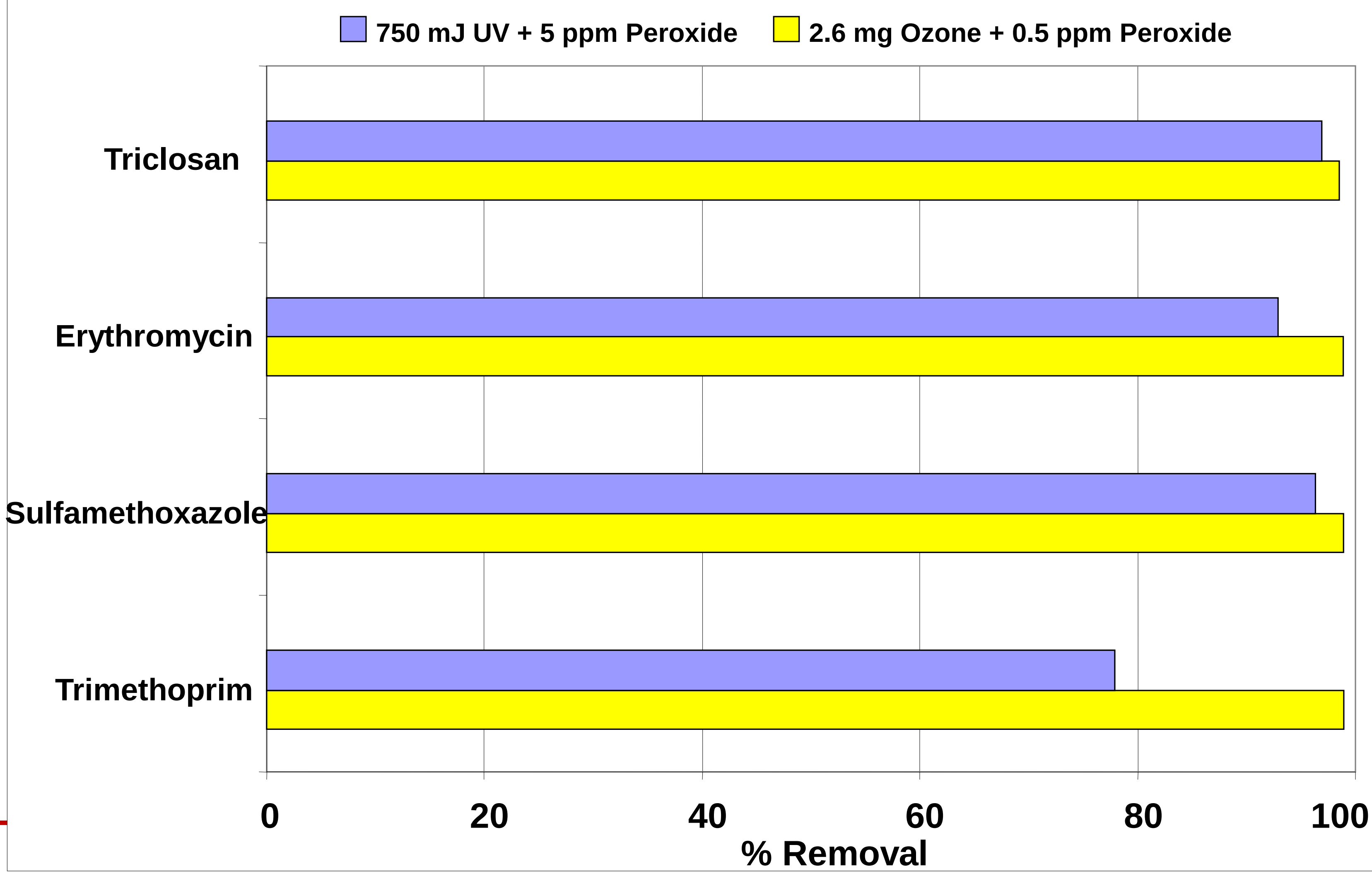
UV AOP vs. Ozone AOP



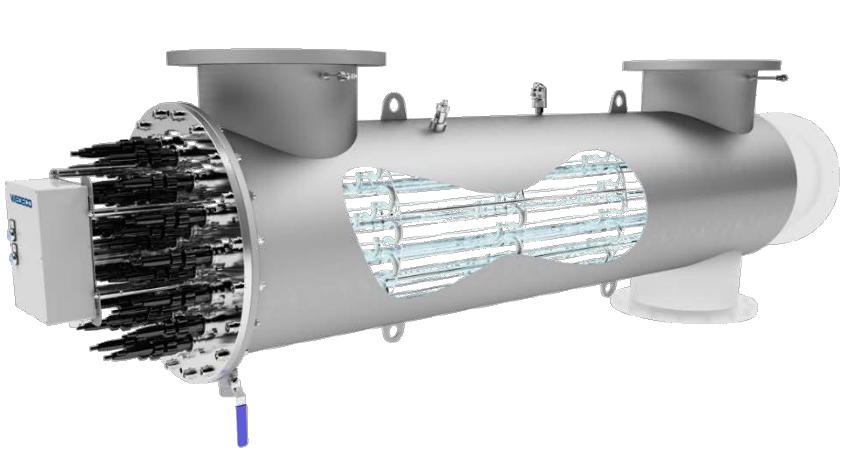
UV AOP vs. Ozone AOP



UV AOP vs. Ozone AOP



UV Hypo system



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Benefits (LP UV + NaOCl)

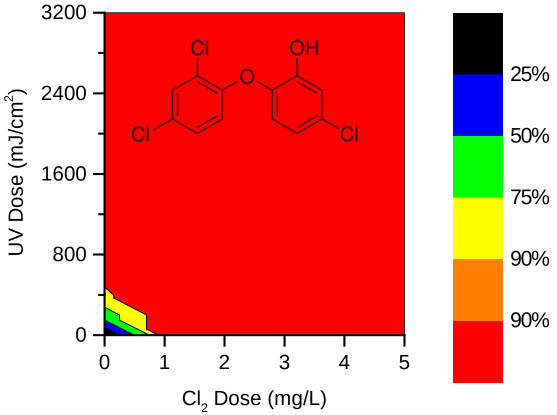
- Implementation does not require additional dosing equipment, chemical storage or quenching
- The pH of RO effluent <6.5 is beneficial for the UV Hypo process
- Low pressure UV provides low OPEX

Application of UV Hypo in IPR

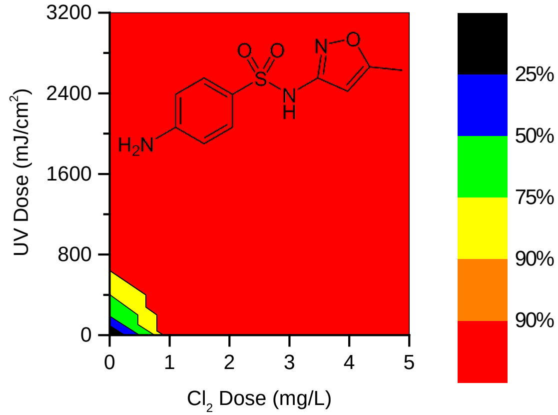
Terminal Island in LA

Removal of CECs by UV/Cl_2

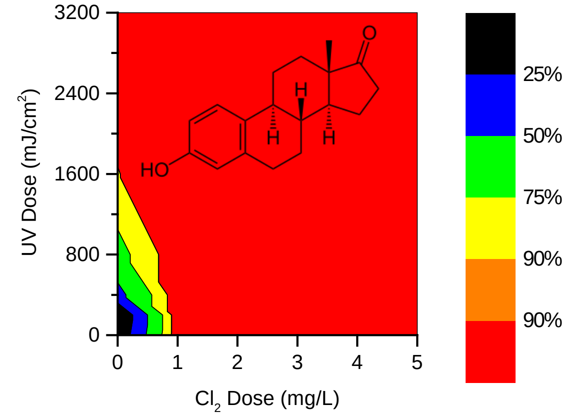
Triclosan



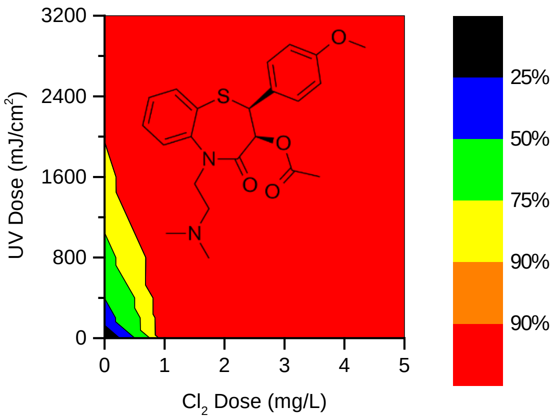
Sulfamethoxazole



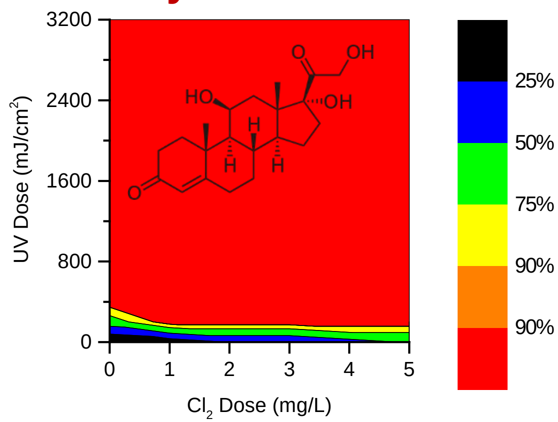
Estrone



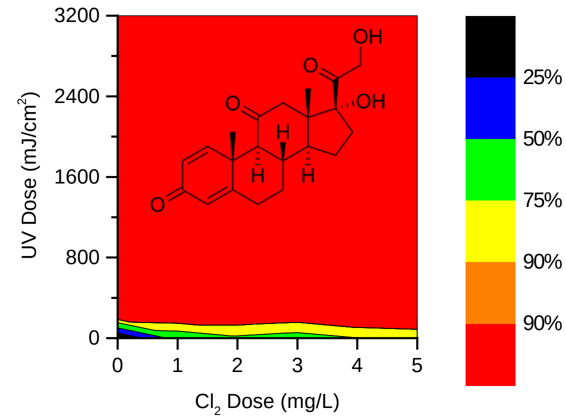
Ditiazem



Hydrocortisone



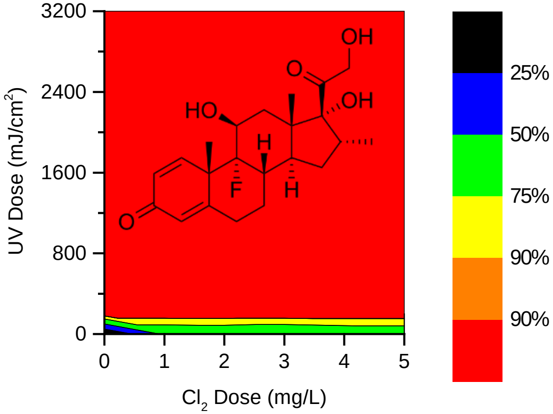
Prednisone



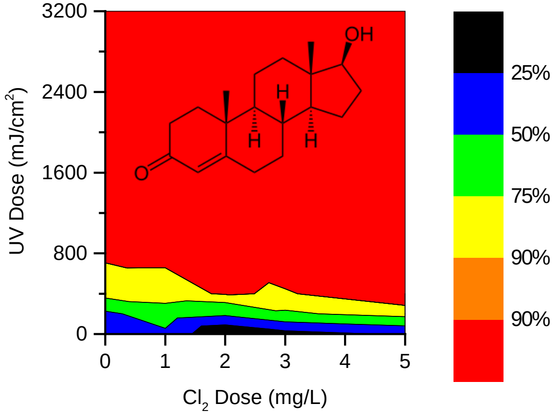
- Removal: Good (>90%); Intermediate (90-50%; 50-25%); Poor (<25%)

Removal of CECs by UV/Cl_2

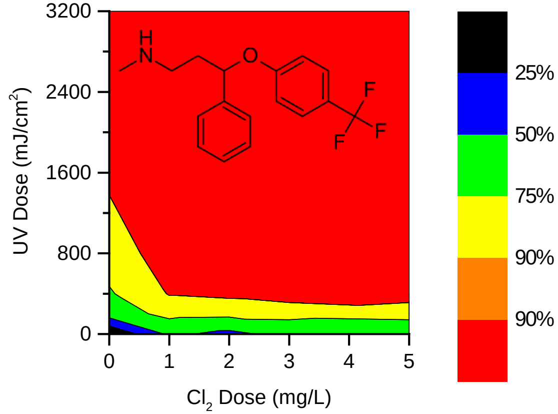
Dexamethasone



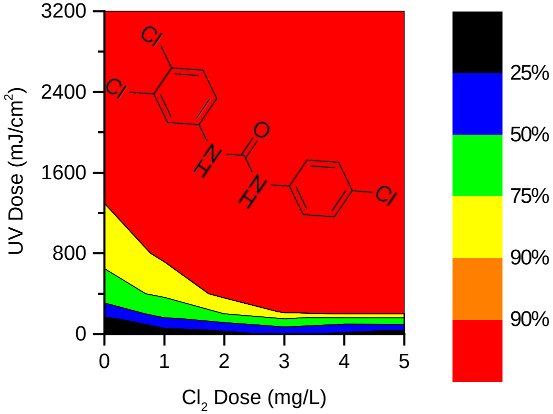
Testosterone



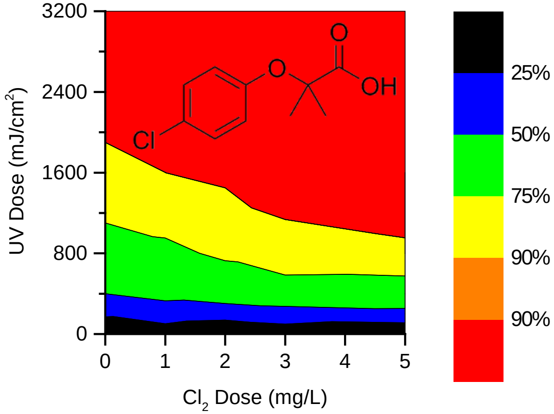
Fluoxetine



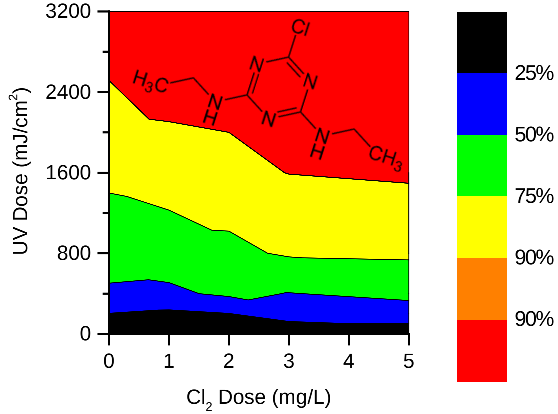
Triclocarban



Clofibric Acid

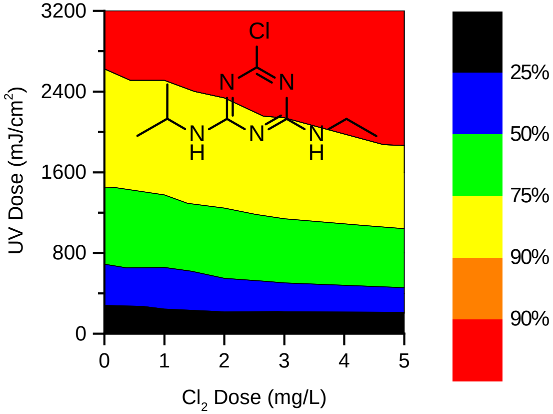


Simazine

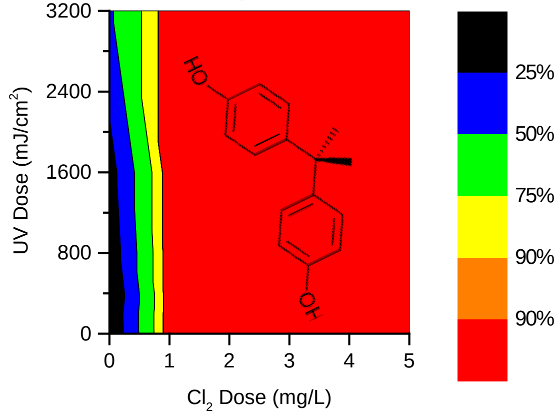


Removal of CECs by UV/Cl_2

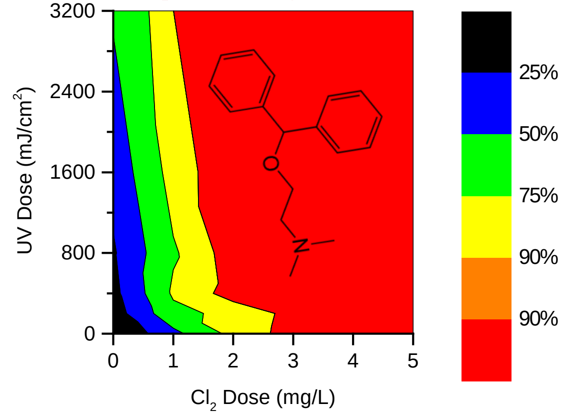
Atrazine



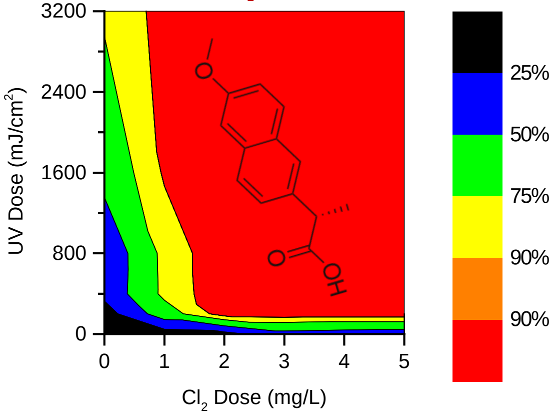
Bisphenol A



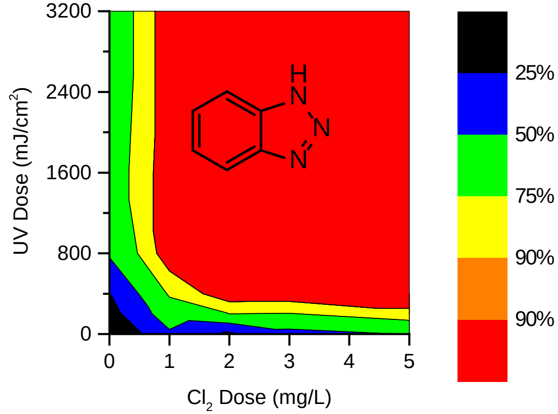
Diphenhydramine



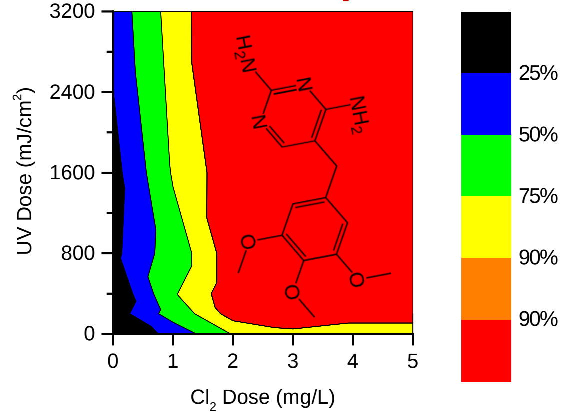
Naproxen



Benzotriazole

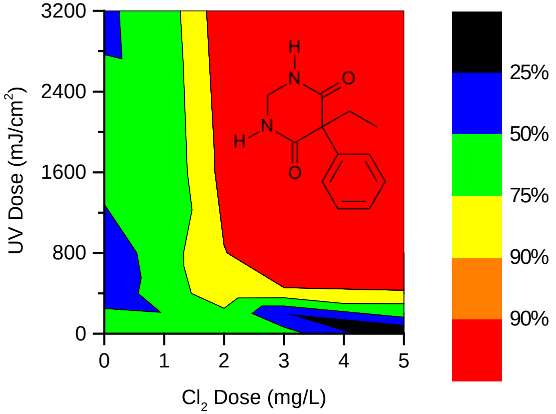


Trimethoprim

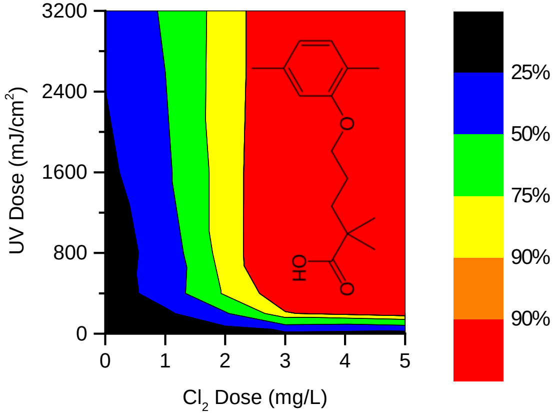


Removal of CECs by UV/Cl_2

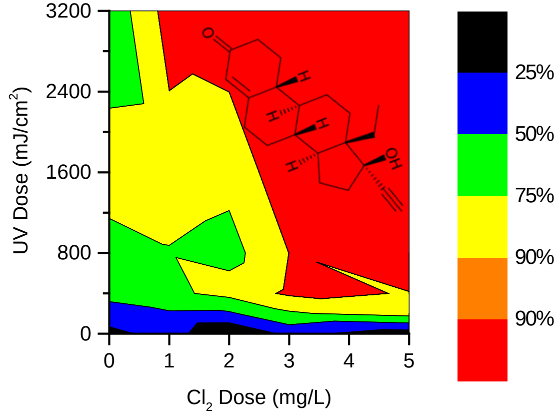
Primidone



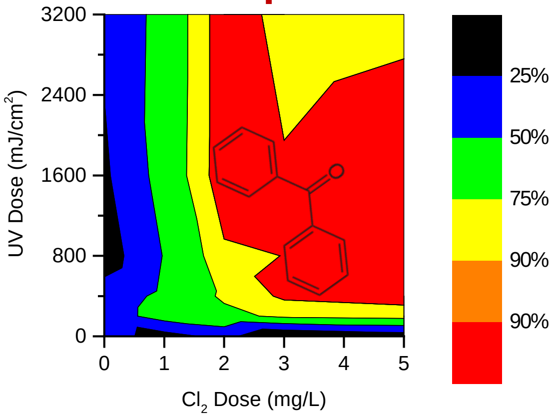
Gemfibrozil



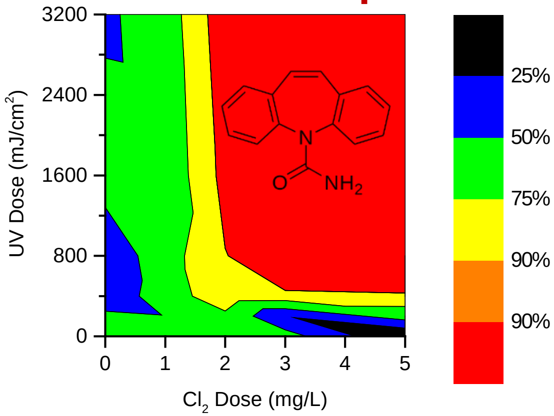
Norgestrel



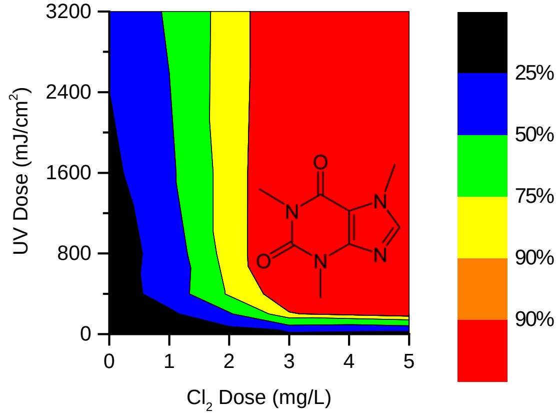
Benzophenone



Carbamezapine

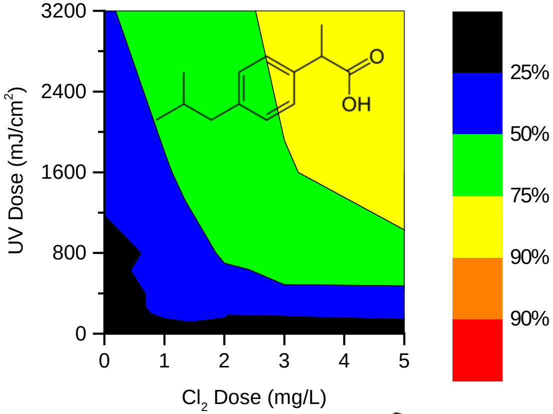


Caffeine

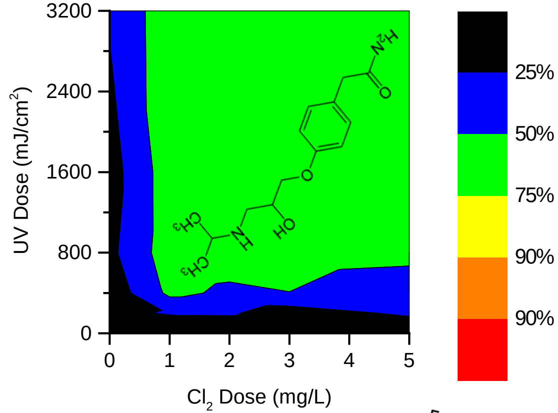


Removal of CECs by UV/Cl_2

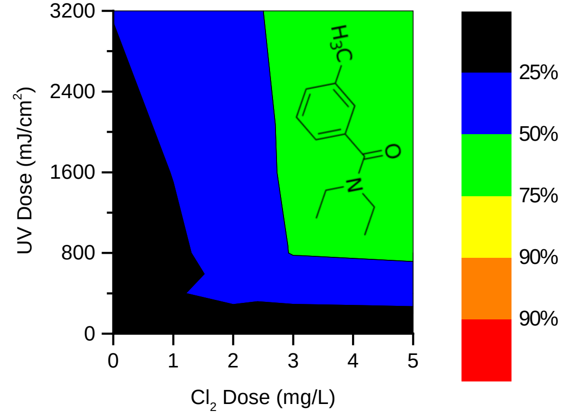
Ibuprofen

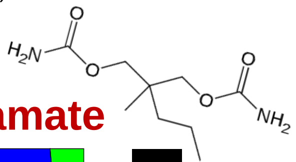


Atenolol

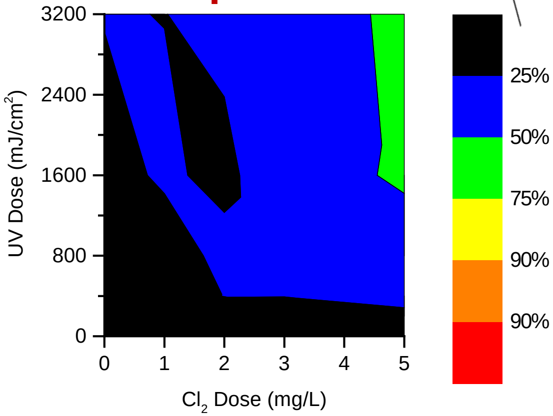


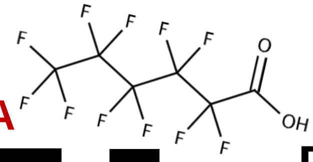
DEET



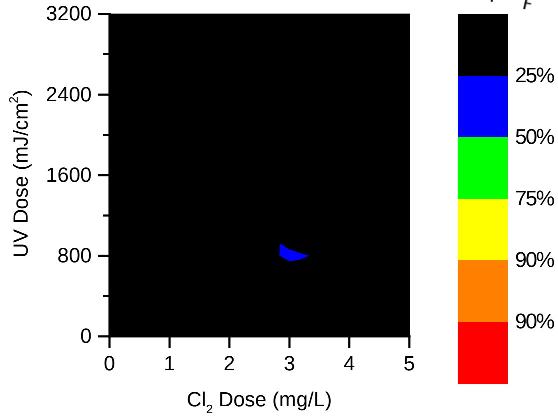


Meprobamate





PFHxA

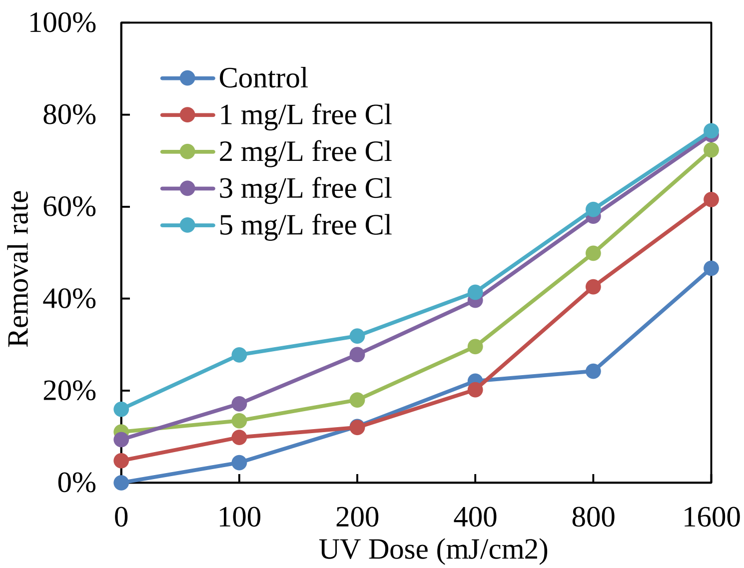


Poor Removal by UV/Cl_2:

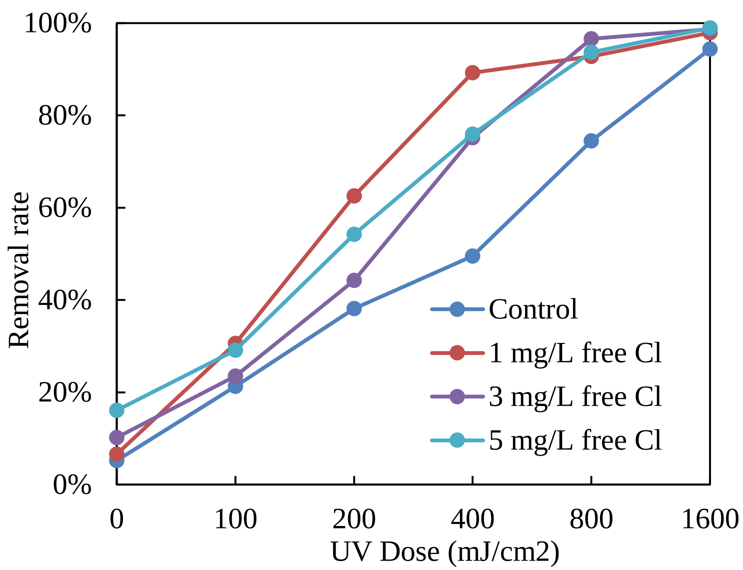
- ❑ PFHxA (→PFCs)
- ❑ Meprobamate
- ❑ DEET
- ❑ Atenolol (<70%)

Removal of MIB in UV/Cl_2

LPUV/Cl2



MPUV/Cl2

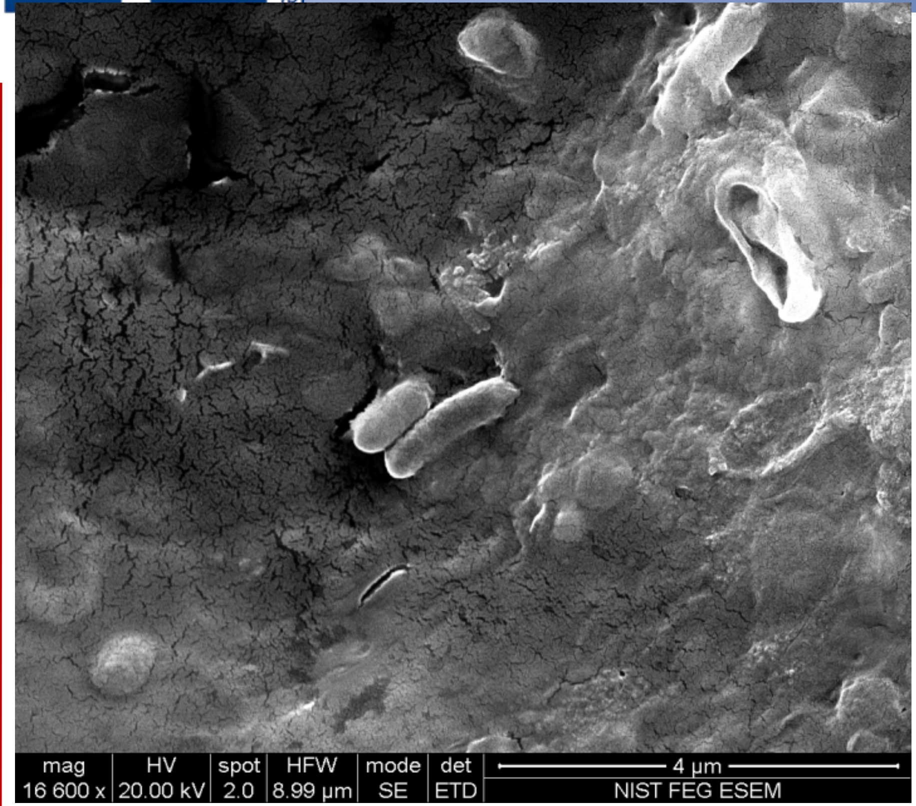


- ❑ With LPUV irradiation of 1600 mJ·m^{-2} alone, the removal of MIB was 47%. Removal rate can be as high as 80%.
- ❑ With MPUV irradiation of 1600 mJ·m^{-2} alone, the removal of MIB was 98%.

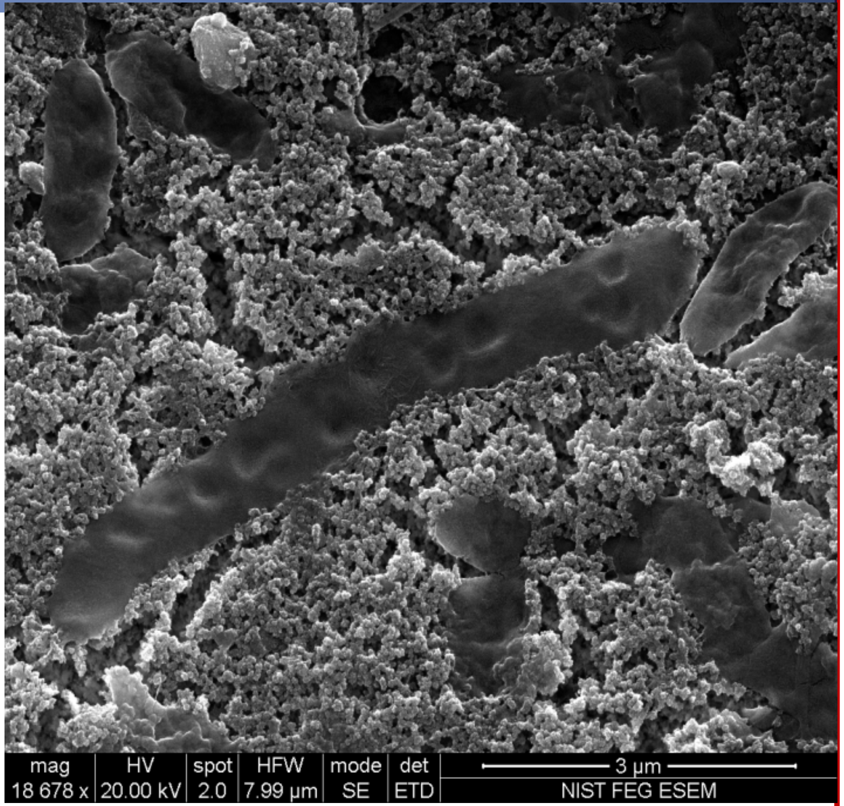
❑ Both LPUV/MPUV-Cl_2 are capable of MIB removal.

COMBINATION OF PHYSICAL AND OXIDATIVE PROCESSES

Ozone Reduces Membrane Fouling



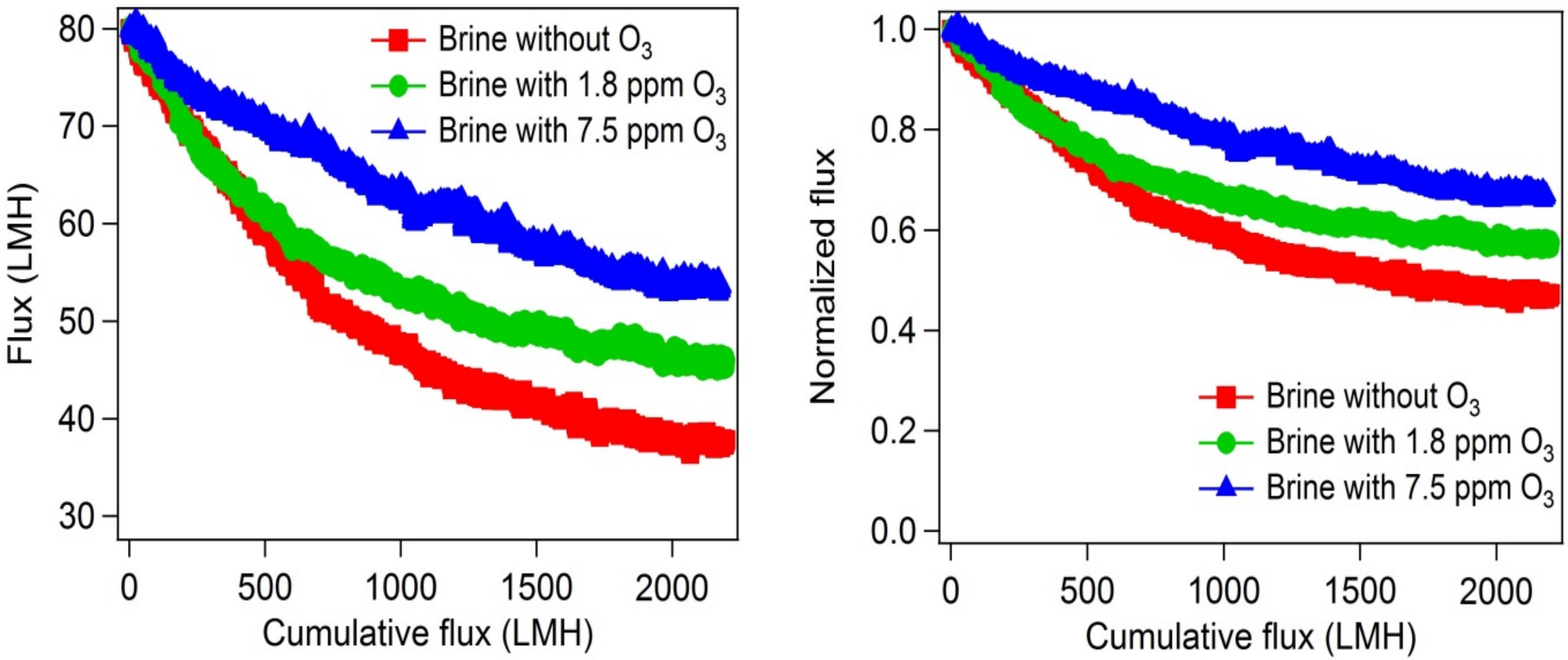
MBR-RO control



MBR-Ozone-RO (3 mg/L)

Stanford, B. D.; Pisarenko, A. N.; Holbrook, R. D.; Snyder, S. A., Preozonation Effects on the Reduction of Reverse Osmosis Membrane Fouling in Water Reuse. *Ozone-Sci. Eng.* **2011,** *33* (5), 379-388.

Decreased Fouling by Pre-Ozone

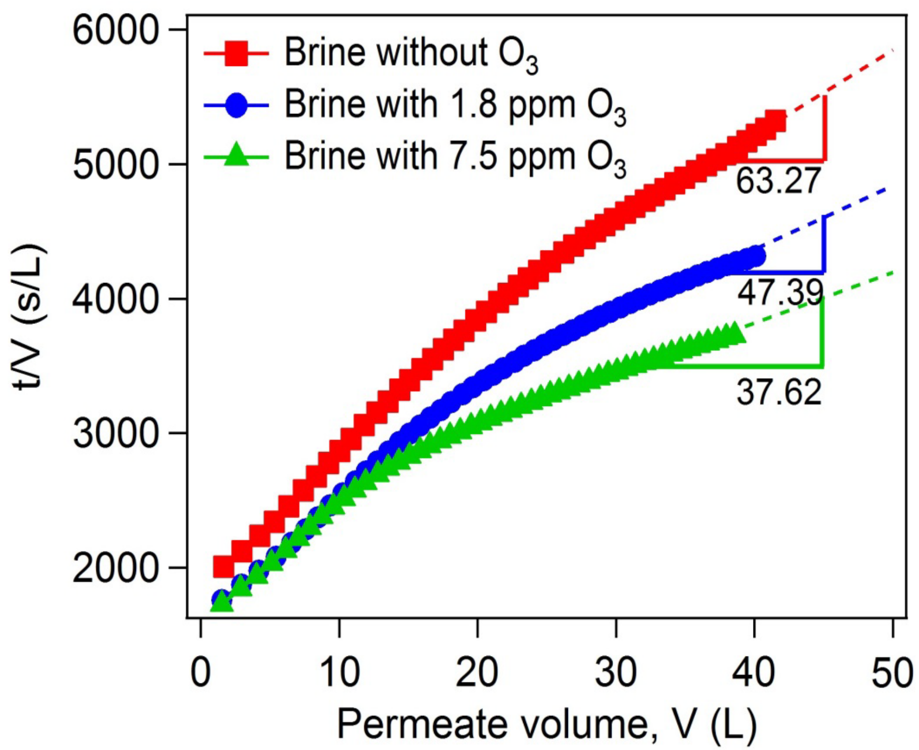


Modified Fouling Index (MFI)

Ozone reduced MFI value about 1.7 fold

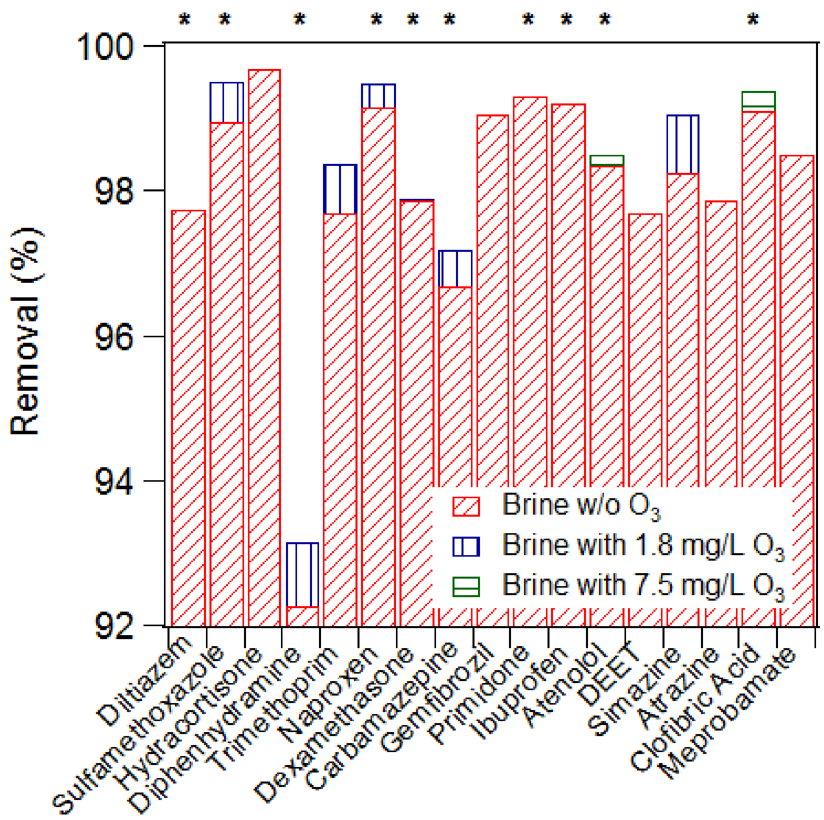
$$\frac{t}{V} = \frac{\eta R_m}{A \Delta P} + \underbrace{\frac{\eta I}{2 \Delta P A^2}}_{MFI} V$$

Matrix	MFI (s/L^2)
Brine w/o O_3	63.27
Brine w/ 1.8 ppm O_3	47.39
Brine w/ 7.5 ppm O_3	37.62



Additive removal

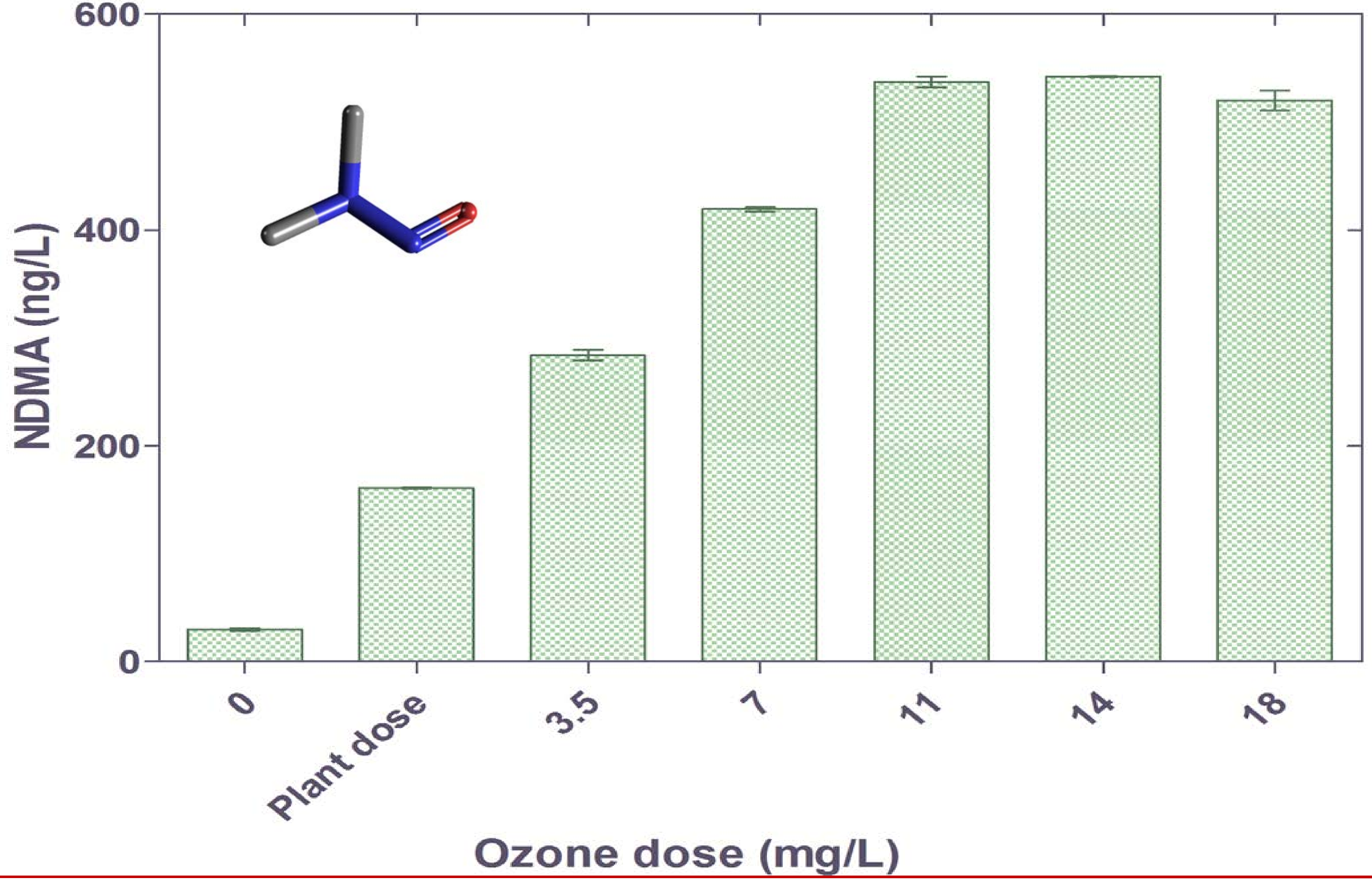
Pre-ozonation + NF membrane



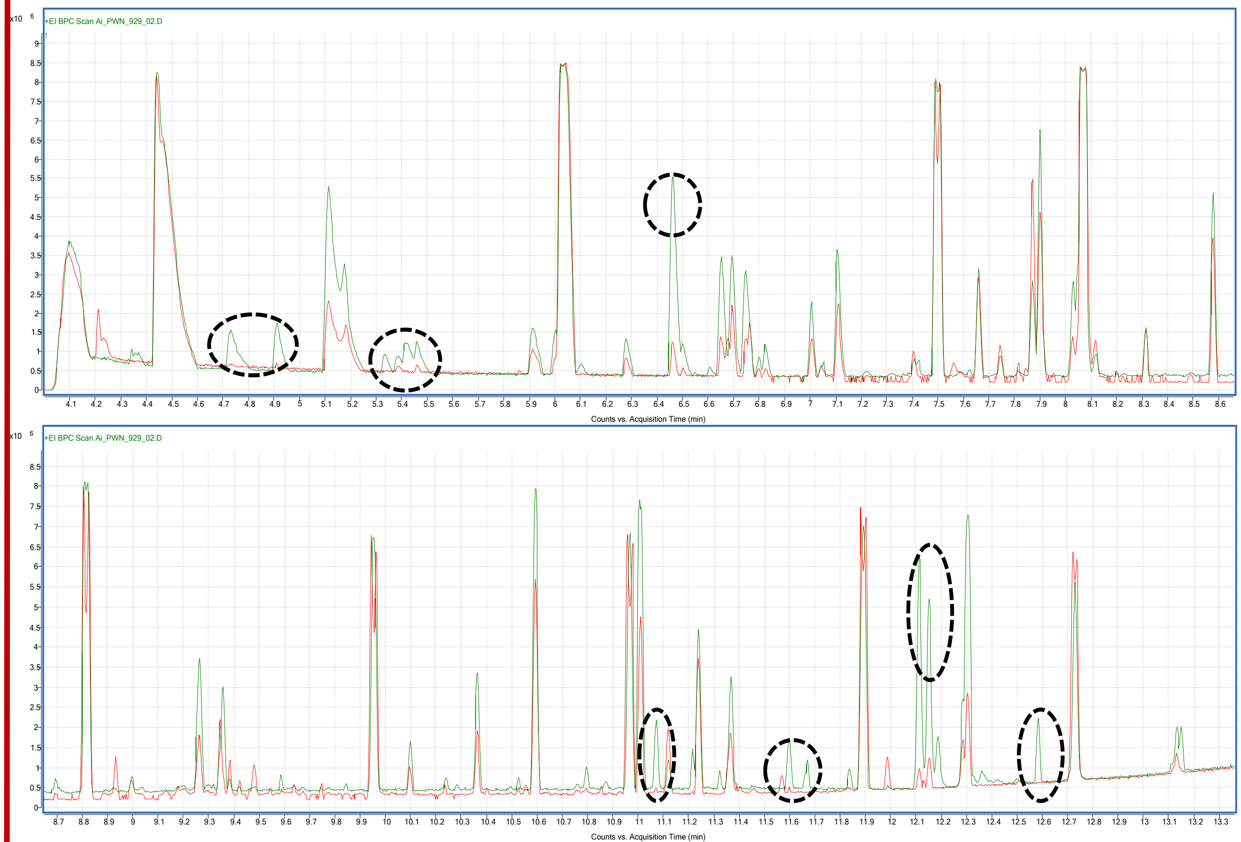
*: Compounds below method detection limit

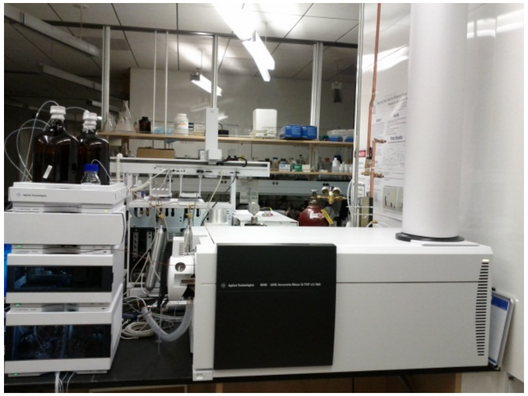
BYPRODUCTS FORMATION

NDMA-FP with Ozone (West Basin)

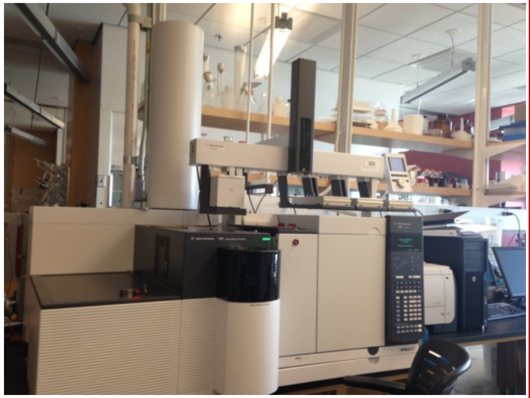


Discovery of New DBPs





LC-QTOF



GC-QTOF

Monitoring Ozonation Through LC-QTOF Analysis

Impact of Ozone on Water Quality

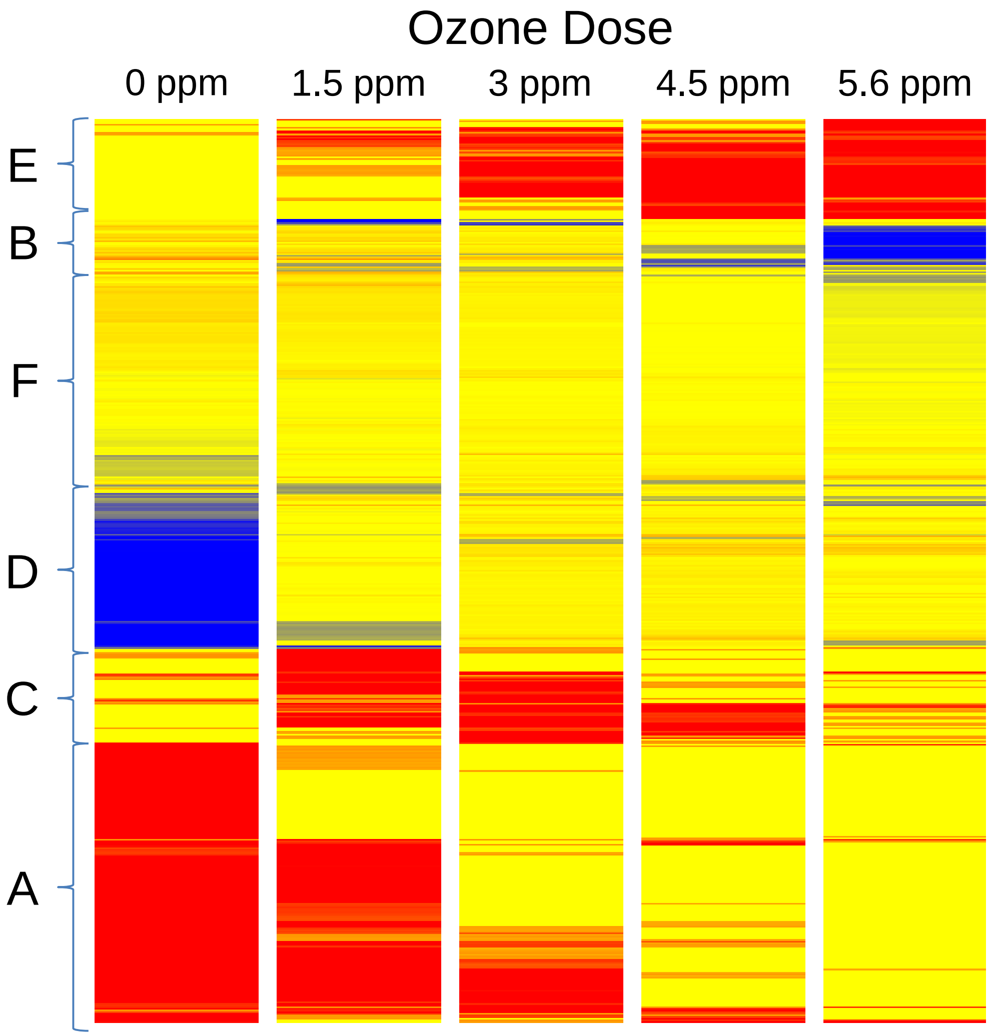
2155 Molecular features (compounds) across 5 samples

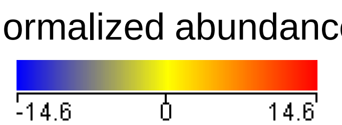
Compounds attenuated
A & B

Intermediates
C

By-products
D & E

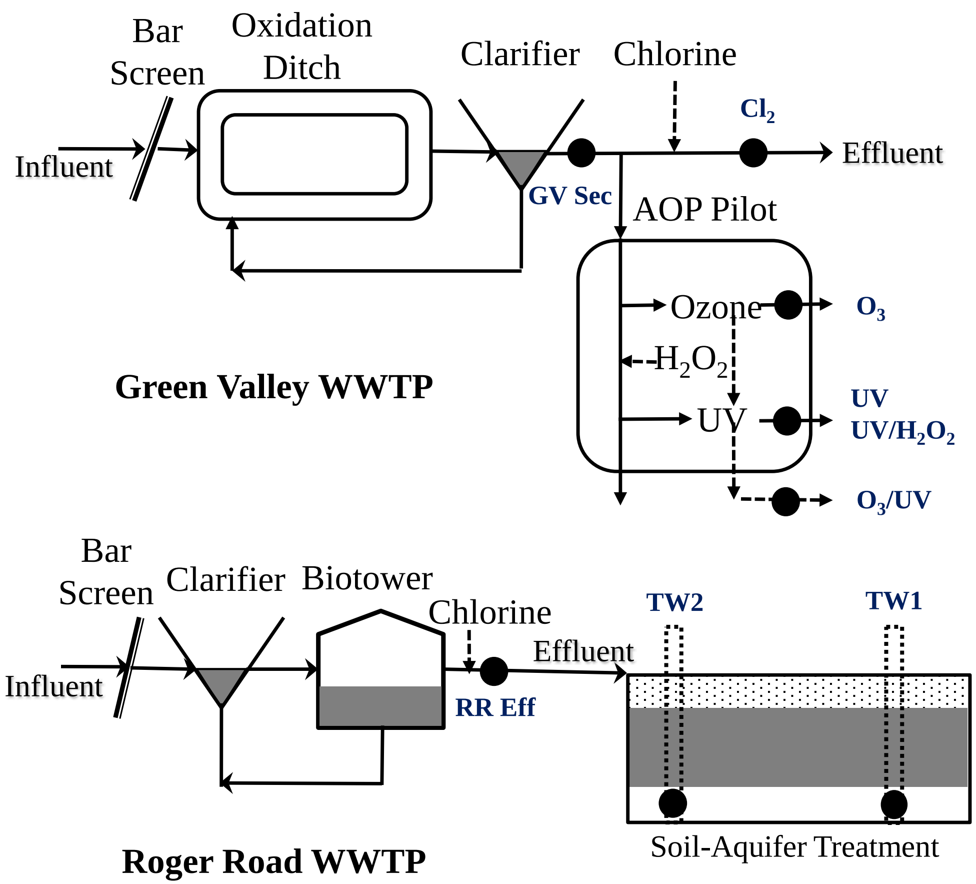
Recalcitrant compounds
F





Pilot plant test: various AOPs

Sample collection



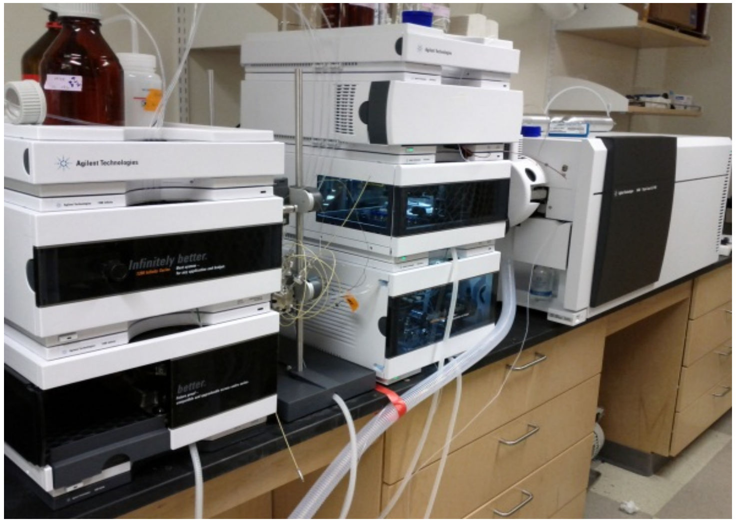
Xylem Wedeco pilot AOP system

● Sampling Point

Analytical Chemistry VS Bioassay

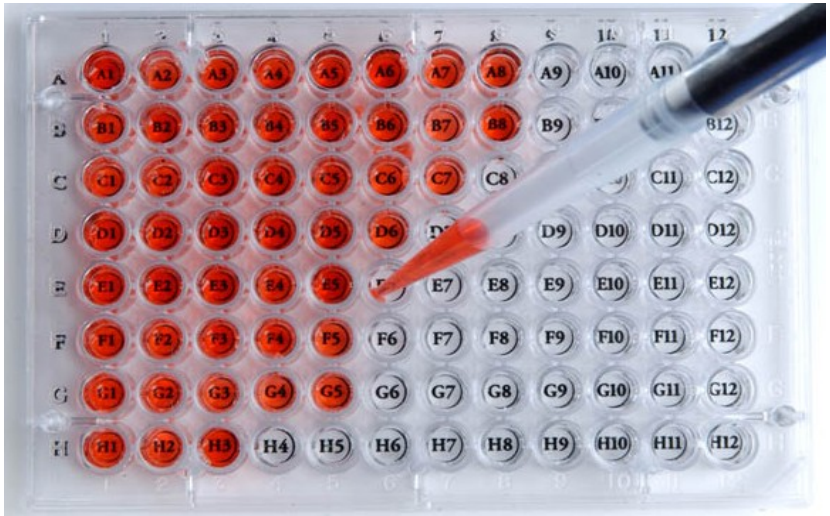
Targeted Analytical

Known compounds
Quantitative
Individual compounds



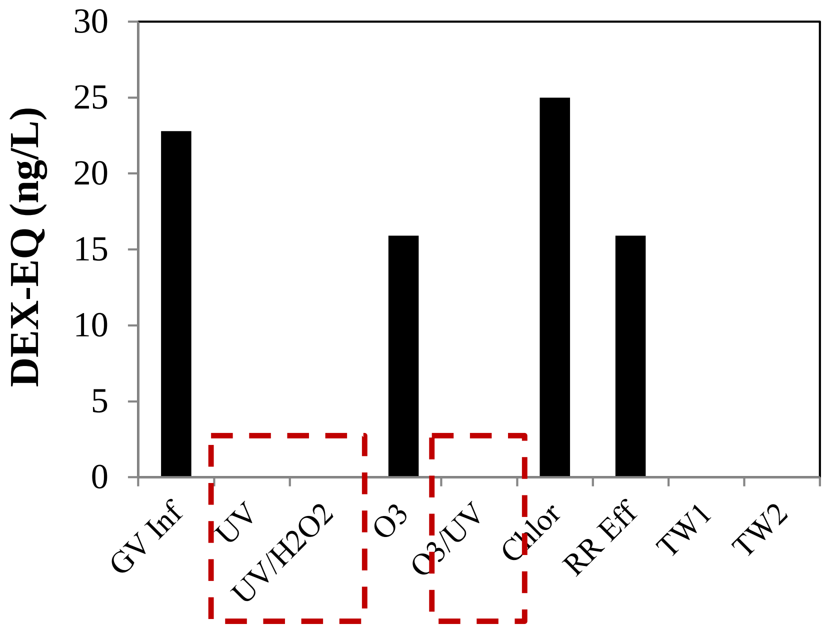
Mechanistic Bioassay

Knowns/unknowns
Semi-quantitative
Synergism/Antagonism

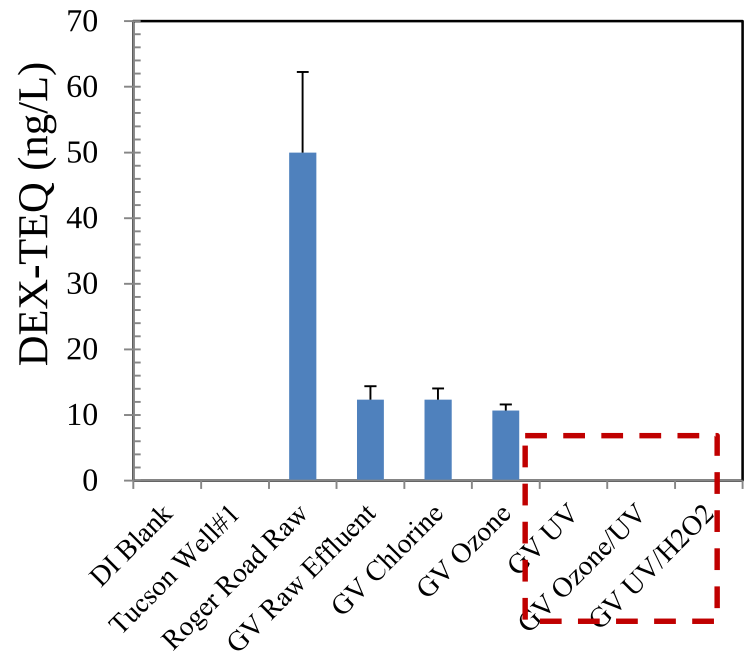


Removal of GR Activity in Various Treatments: Results

Results



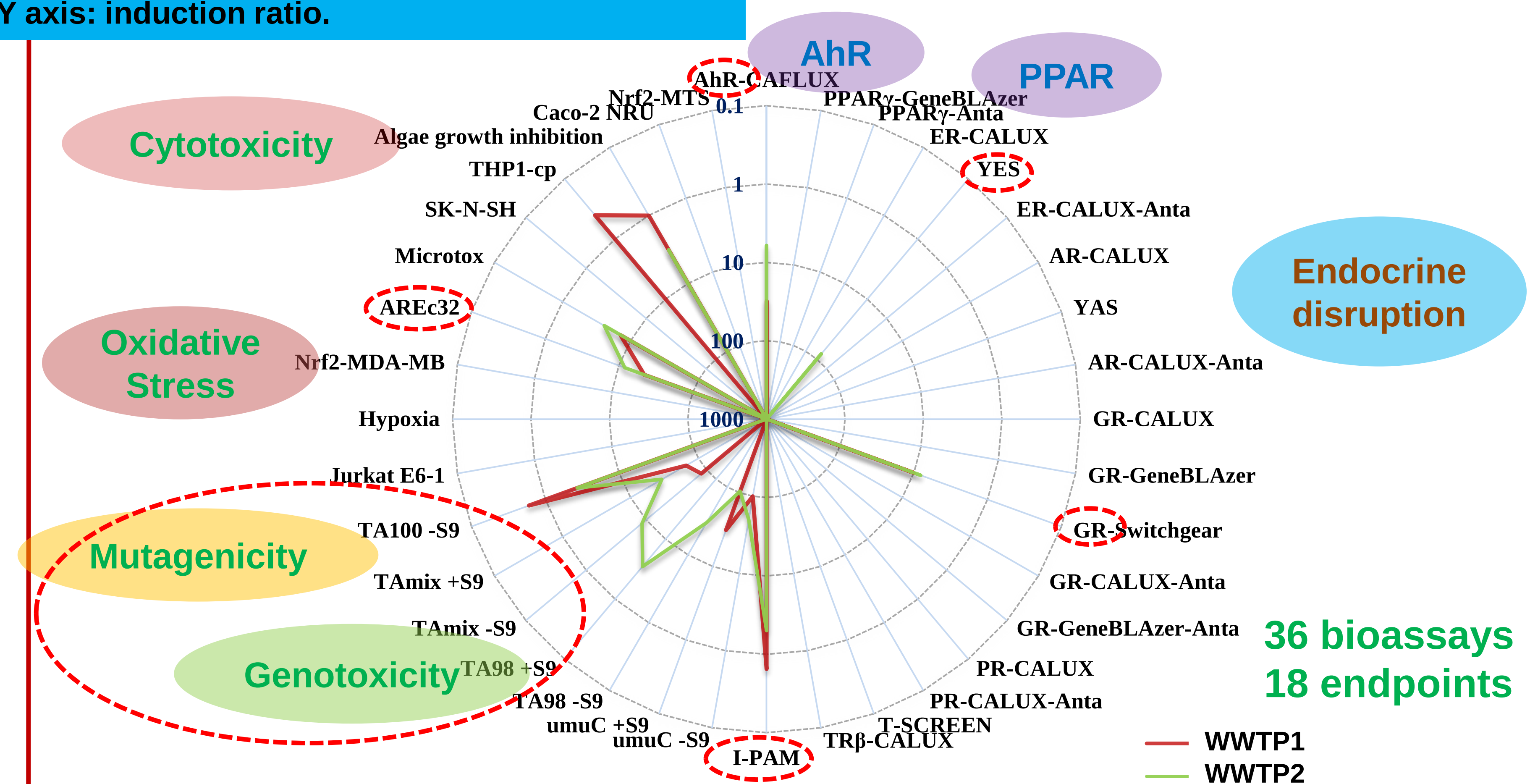
Repeat Sampling



- GR activity was detected in the WWTP effluent as well as AOP treated samples. UV treatment appeared to be the most efficacious AOP at GR activity attenuation, while ozone and chlorine cannot. Infiltration is a great process to prevent GR coming into the ground water system.

Bioassay battery

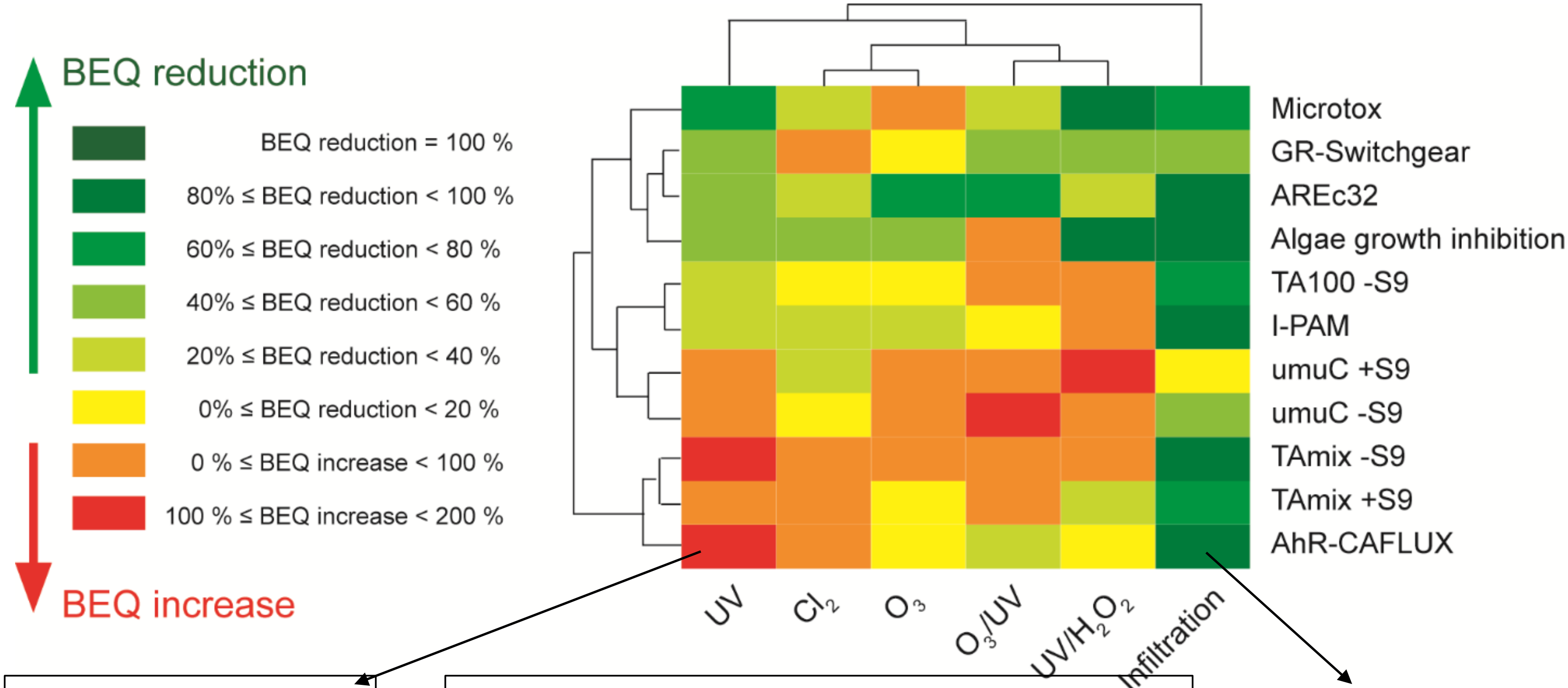
Bioassay battery on two AZ WWTP 2nd effluents.
Y axis: induction ratio.



36 bioassays
18 endpoints

Water Research, **2015**, 80, 1-11.

Toxicity attenuation during different water reuse treatment techniques



new DBPs may generated in AhR and mutagenicity under UV

UV based treatment is good for GR removal;
Ozone: efficient for oxidative stress;
Chlorinatin could partially eliminate genotoxicity

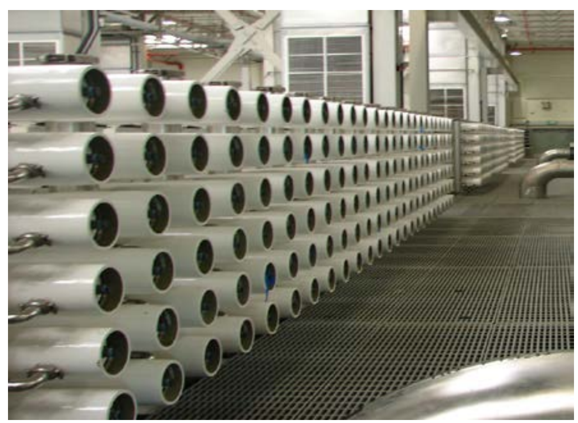
Efficient for most activities

Water Research, **2015**, 80, 1-11.

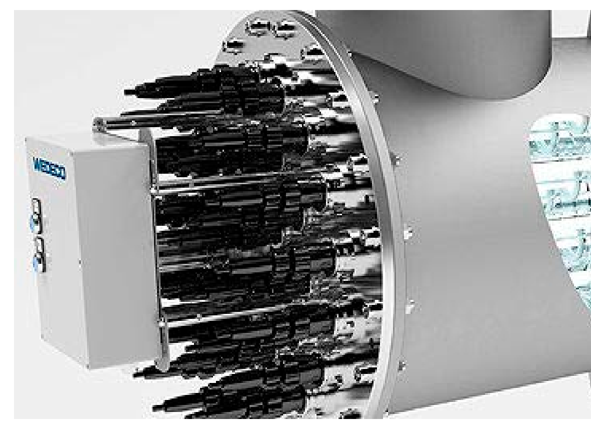
Multi-barrier approach

Biological

Physical



Oxidation



CONCLUSIONS

Concluding remarks

- The extent of CECs attenuation depends on physico-chemical natures of individual CEC as well as the characteristics of treatment processes.
- Multi-barrier approach is required to secure water quality of treated water against CEC.
- Real-time online sensor for infallible treatment verification can be achieved using surrogate indicators.
- Bioassay screening would help to evaluate the integrated biological effects.

Acknowledgement

- Snyder Research group (University of Arizona)
  - Dr. Ai Jia
  - Dr. Hye-weon Yu
  - Dr. Tarun Anumol (in Agilent Technologies now)
  - Shimin Wu (PhD student)

WEDECO a xylem brand

Agilent Technologies

TUCSON WATER

Q&A

Thank you!!!!
Any question???