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October 29, 2014

Looking Beyond the Parents – The Presence and Toxicity of Transformation Products

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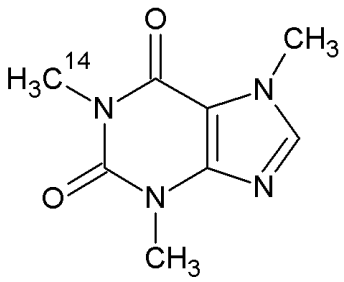
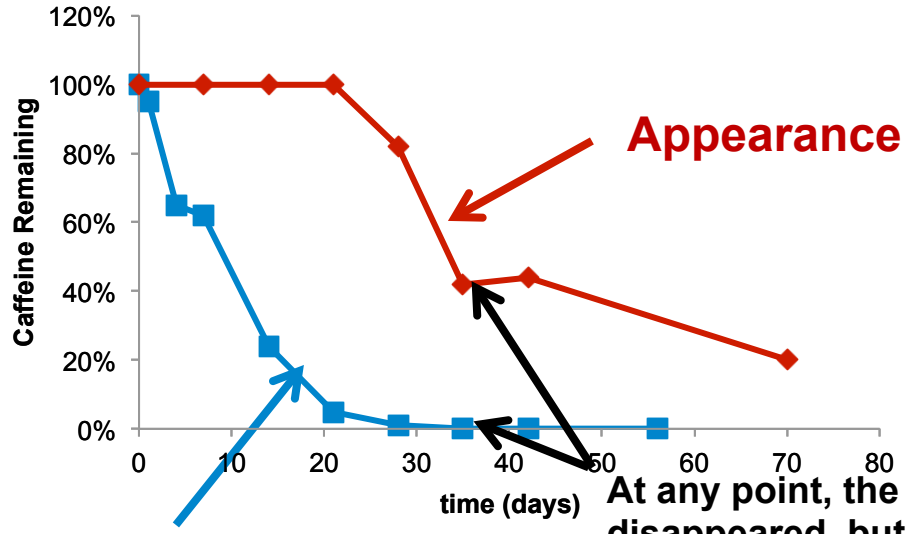
Removal vs. Transformation

- Removal infers disappearance of a target compound… is this appropriate?
- During water treatment, a common removal mechanism is via chemical oxidation





Appearance of $^{14}CO_2$

Loss of Caffeine

At any point, the parent molecule has disappeared, but the carbon has not yet been oxidized to CO_2

Benotti and Brownawell, Environmental Pollution 157 (2009) 994-1002

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Pharmaceuticals and Endocrine Disrupting Compounds (EDCs)

- Prescription and non-prescription pharmaceuticals (e.g. fluoxetine, ibuprofen)
- Naturally occurring chemicals (e.g. caffeine)
- Human-Health Compounds (e.g. DEET)
- Industrial chemicals (e.g. bisphenol A)
- Endocrine disrupting compounds (EDCs: e.g. 17α-ethynylestradiol, 17β-estradiol)
- *There is no single "list", but they are generally polar organic compounds and* usually *wastewater-derived*

Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) generate species with very high oxidation potentials, particularly hydroxyl radicals

Compound	Oxidation Potential (Volts)	Relative Oxidizing Power to Chlorine
Hydroxyl Radical (•OH)	2.8	2.1
Ozone (O_3)	2.1	1.5
Hydrogen Peroxide (H_2O_2)	1.8	1.3
Permanganate (MnO_4^-)	1.7	1.2
Chlorine Dioxide (ClO_2)	1.5	1.1
Chlorine (Cl_2)	1.4	1.0
Oxygen (O_2)	1.2	0.9
Bromine (Br_2)	1.1	0.8

Outline of Talk

1. Evaluation of a pilot-scale photocatalytic membrane reactor
2. Mass spectrometry for measuring transformation products following UV and UV/H_2O_2 treatment
3. Ongoing work with the EPA National Homeland Security Research Center to assess toxicity of AOP-treated water

Part 1: Evaluation of a pilot-scale photocatalytic membrane reactor

SOUTHERN NEVADA WATER AUTHORITY

UV/TiO_2 photocatalysis

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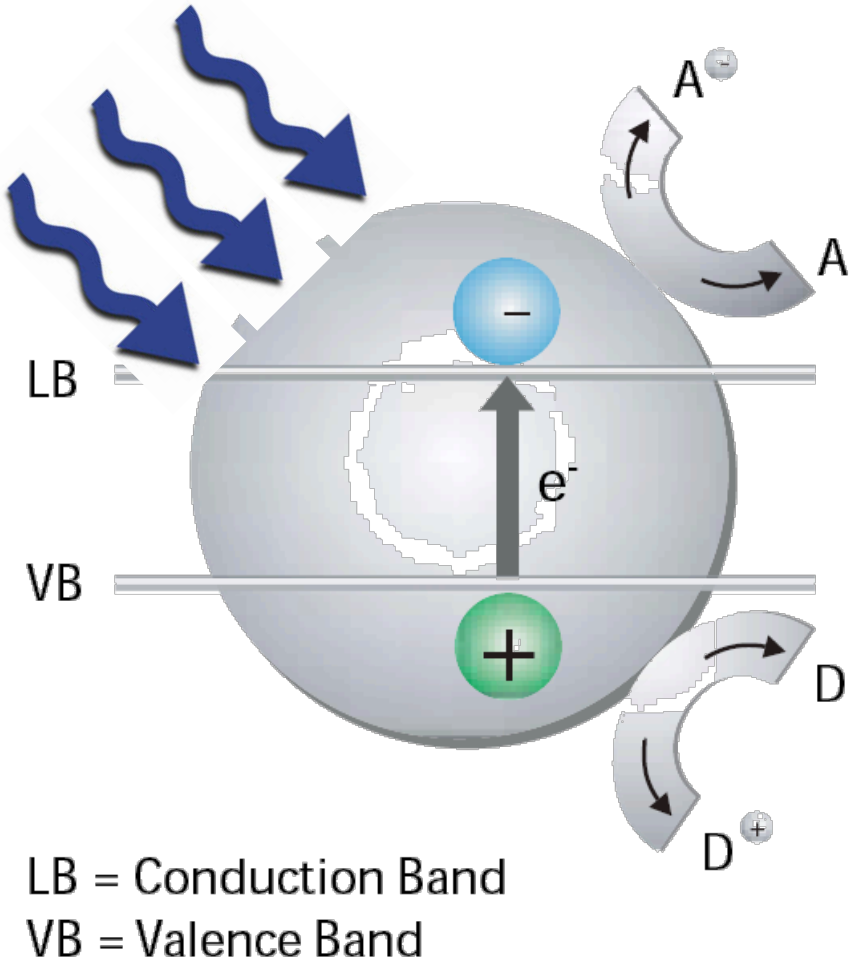
UV-TiO_2 Photocatalysis

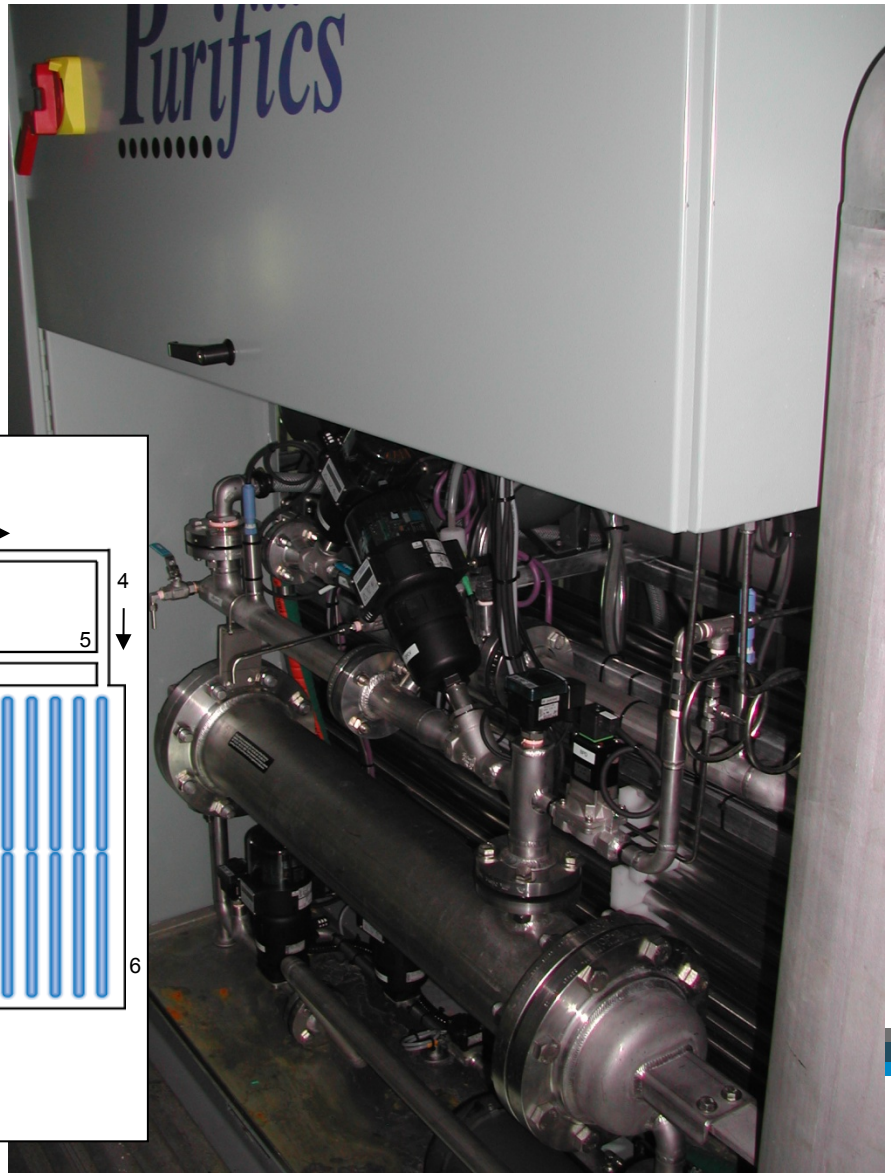


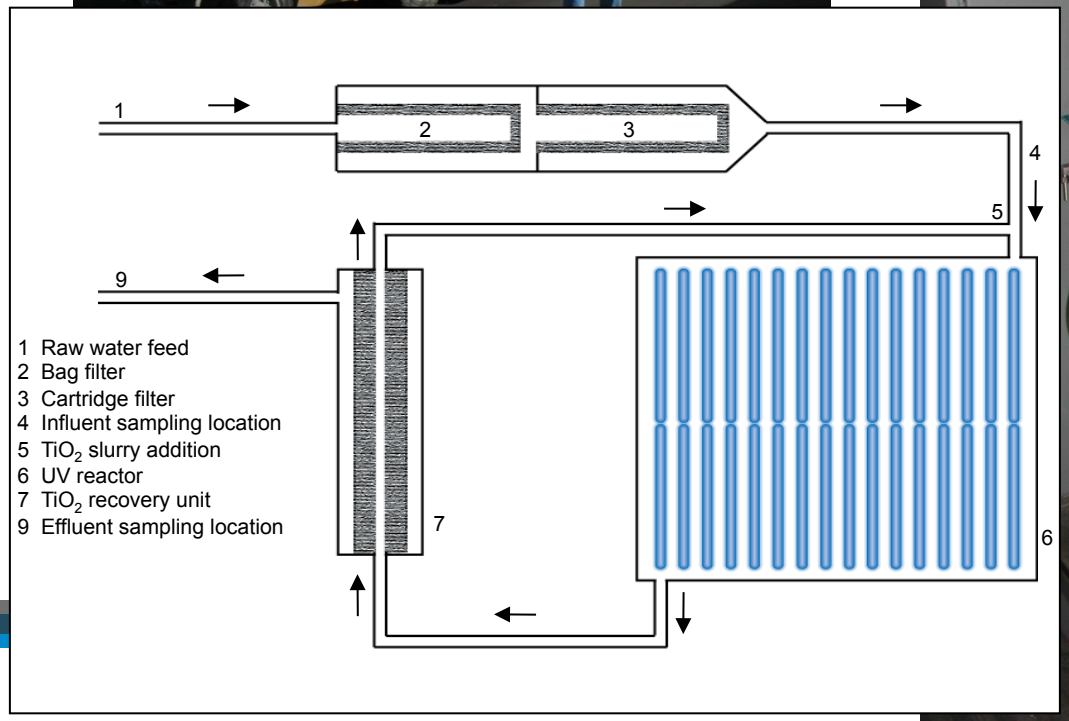
Formation of O_2^-

For TiO_2, this band gap energy is 3.2 eV

Formation of •**OH** or **direct oxidation** of organic compounds

Photocatalytic Membrane Reactor



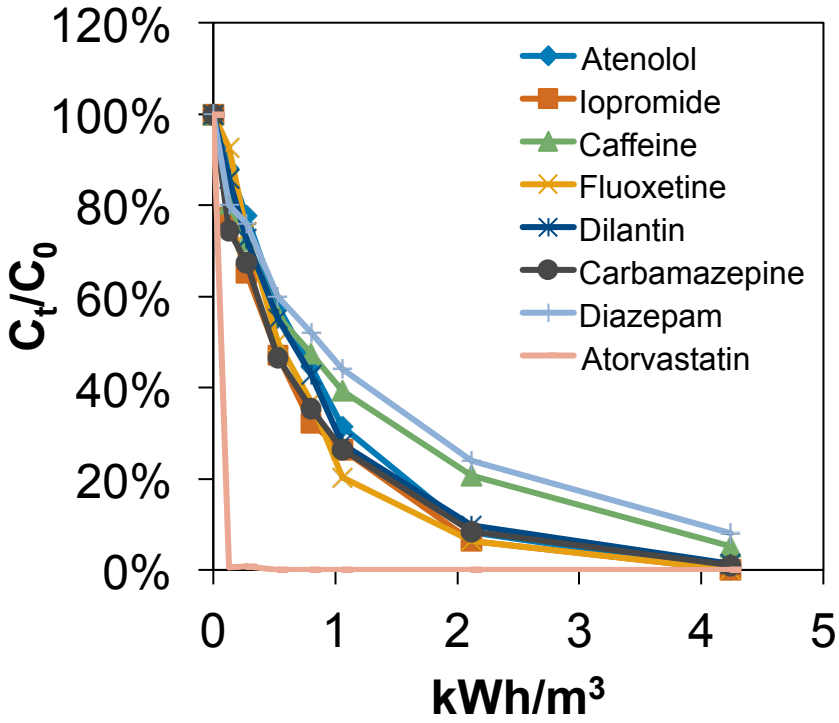


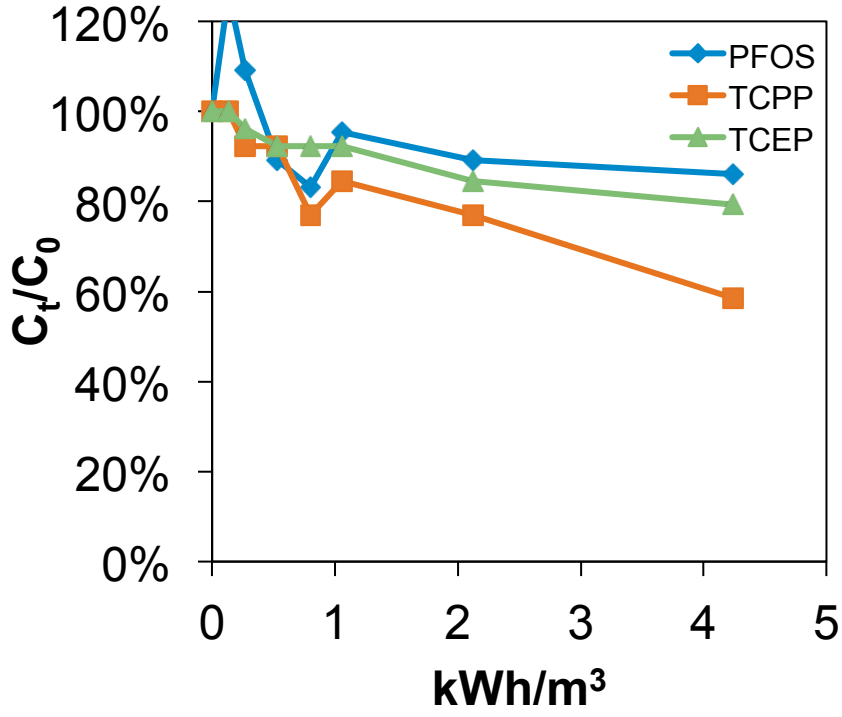
Pilot-Scale Testing

- 32 compounds spiked into 3000 gallon tank containing Colorado River Water at ng/L concentrations
- Photocatalytic Reactor Membrane parameters…
  - ~50 mg/L TiO_2 nanoparticles (Degussa)
  - Unit operated at 24 lpm and with 0-32 UV lamps (medium pressure, high output)
  - pH was ~8 (pH of Colorado River Water)
  - Measured pre-treatment concentrations at start and end of experiment to ensure homogenization, and following each treatment
  - Also used yeast estrogen screen assay (YES) to measure total estrogenic activity of the water

Removal of Pharmaceuticals and EDCs by UV-TiO_2 Photocatalysis

Most pharmaceuticals/EDCs were well removed…





…except for those compounds designed not to oxidize

Benotti et al., Water Research 43 (2009): 1513-1522

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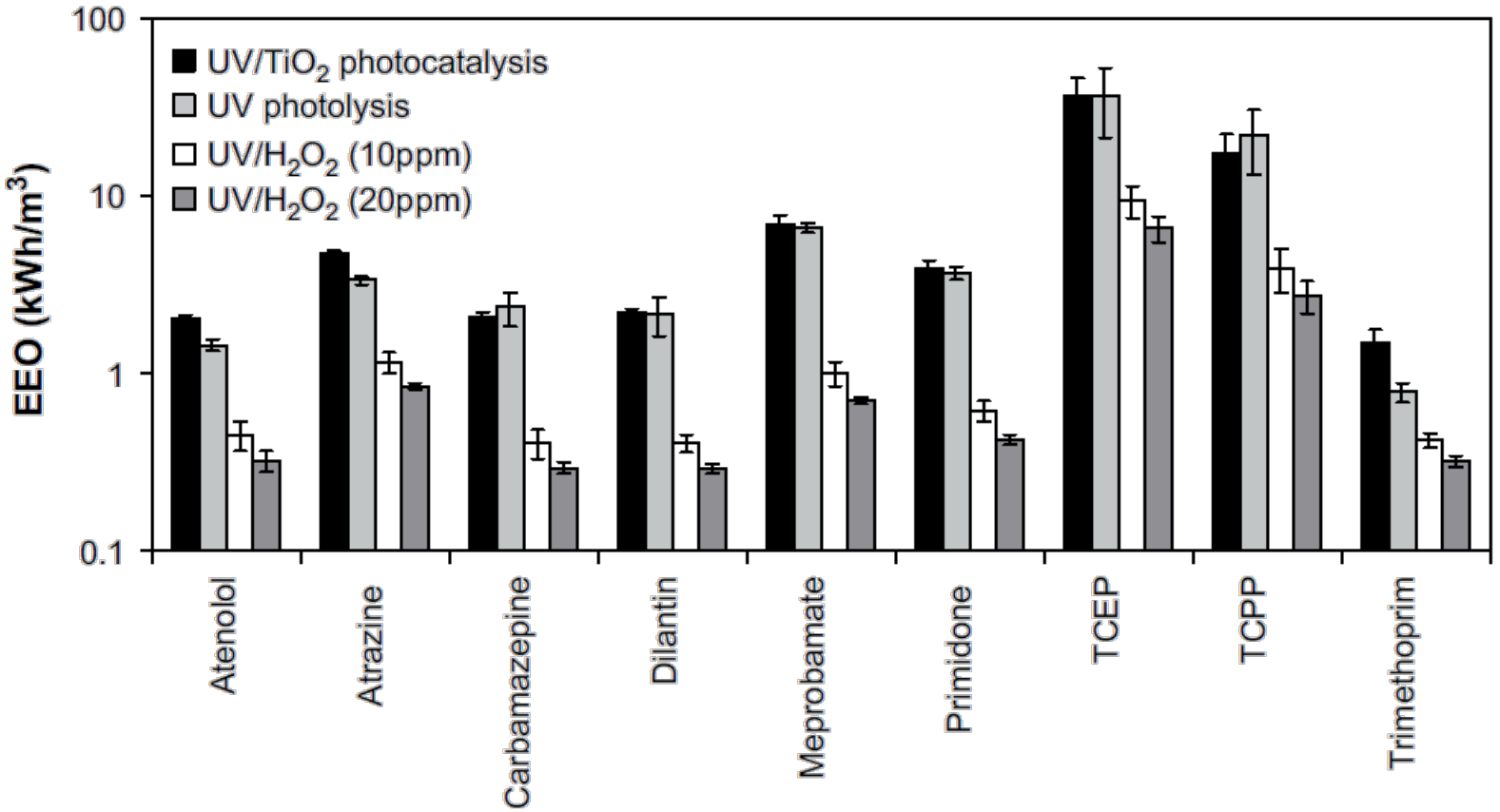
AOP Energy Requirements

EEO = Electrical Energy per order of removal



Benotti et al., Water Research 43 (2009): 1513-1522

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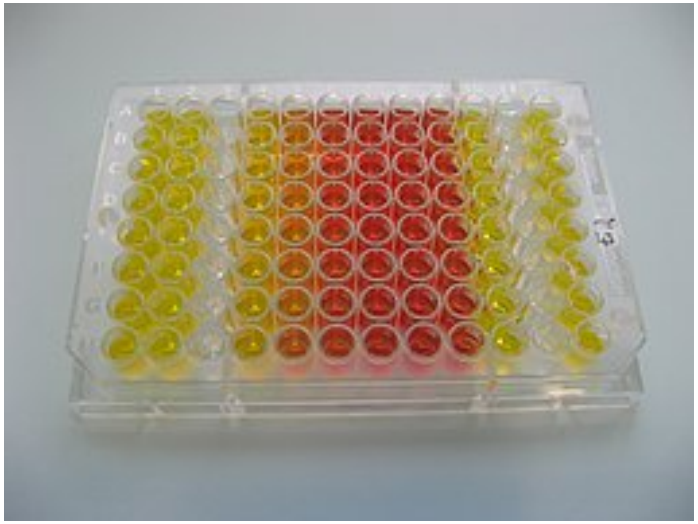
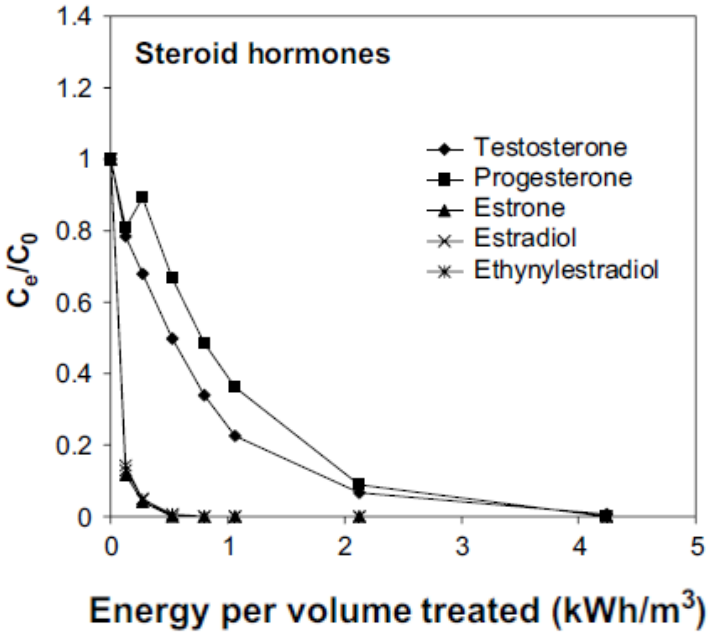
Yeast Estrogen Screen

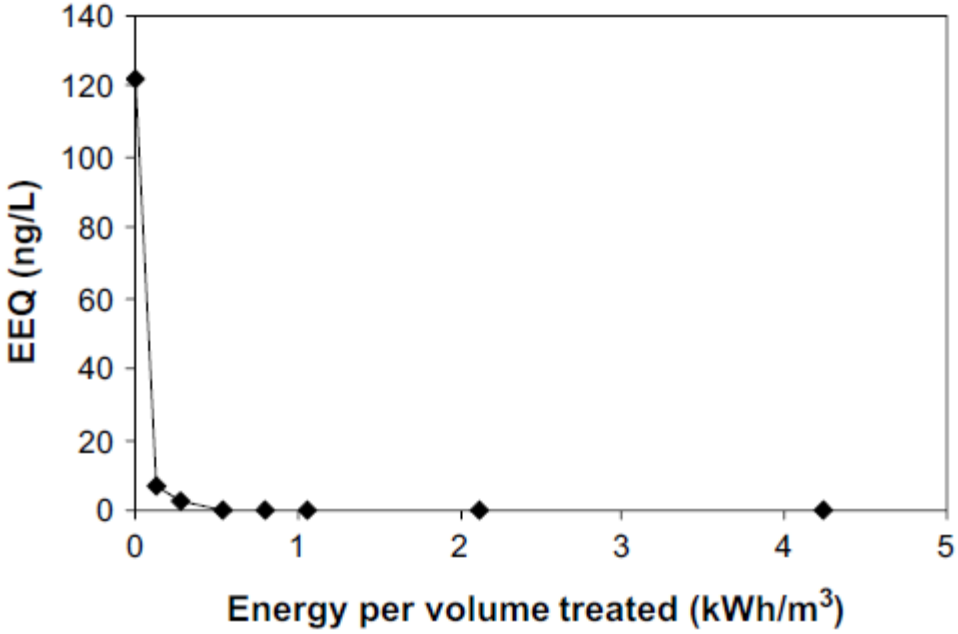
- Yeast cells containing the human estrogen receptor (hER) are exposed to process water
- Color change indicates amount of estrogenic activity of the water



Benotti et al., Water Research 43 (2009): 1513-1522

Removal of Steroid Hormones and Estrogenic Activity





The rate of removal of estrogenic activity was similar to the rate of removal of estrogenic hormones – any transformation products did not bear estrogenic activity

Benotti et al., Water Research 43 (2009): 1513-1522

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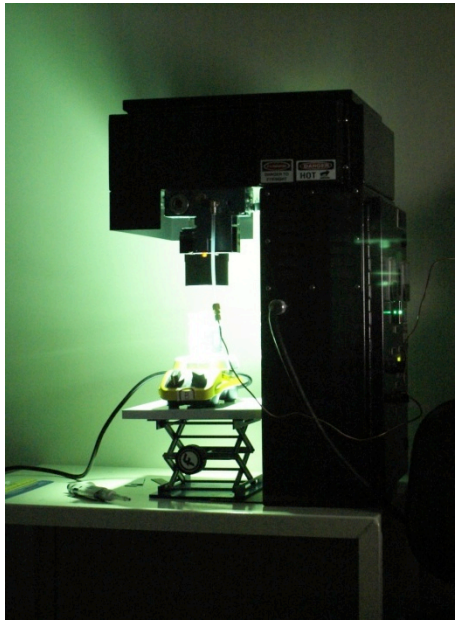
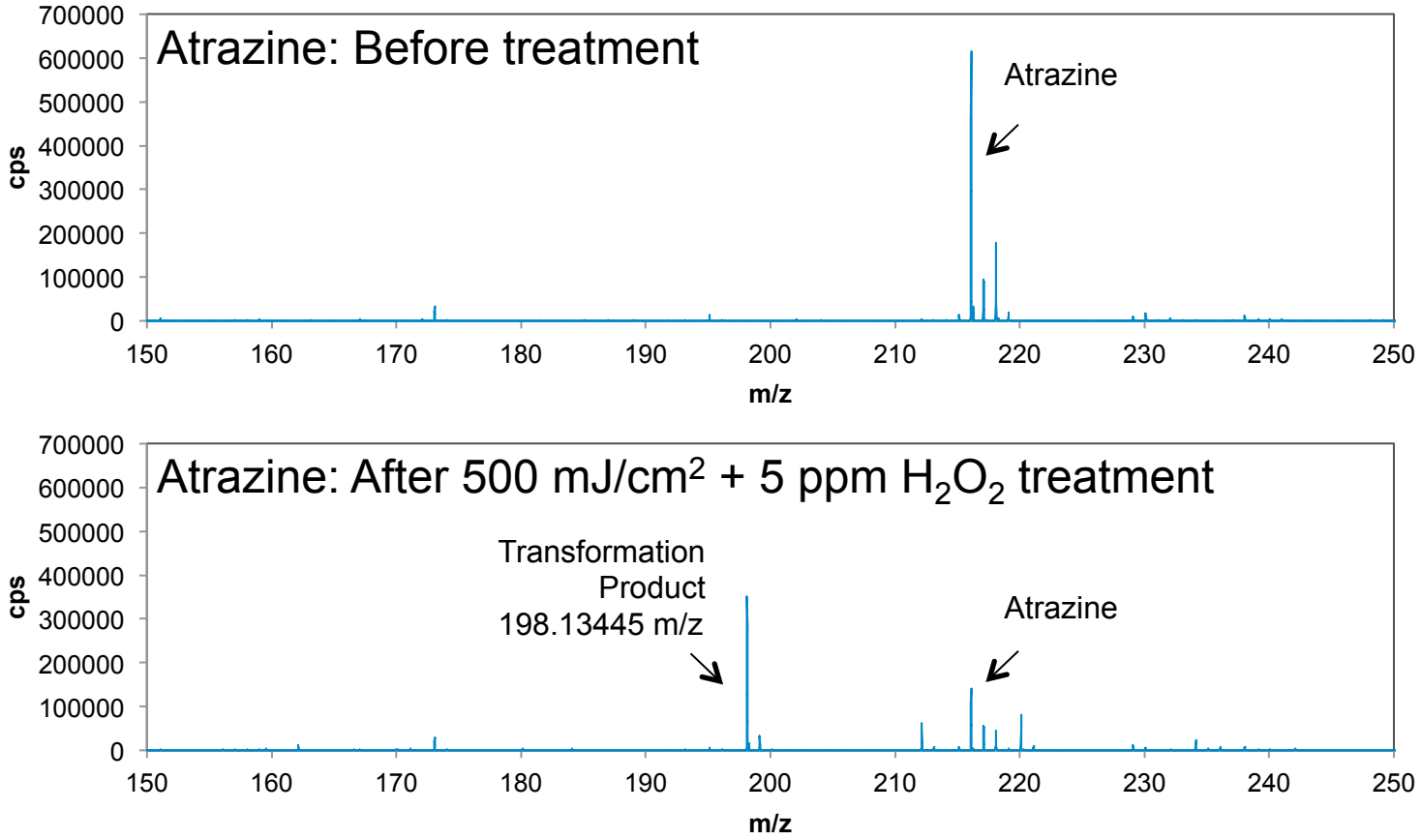
Part II: Screening for Transformation Products

- transformation of sulfamethoxazole, carbamazepine, atrazine and pharmaceuticals UV/H_2O_2 using a collimated beam apparatus



Parameters Investigated	
UV dose	0, 300, 500 and 700 mJ/cm^2
H_2O_2 dose	0, 5, and 10 mg/L
lamps	Low pressure and medium pressure

QToF-MS


Atrazine: Before treatment
Atrazine
cps
m/z
Atrazine: After 500 mJ/cm2 + 5 ppm H2O2 treatment
Transformation Product 198.13445 m/z
Atrazine
cps
m/z

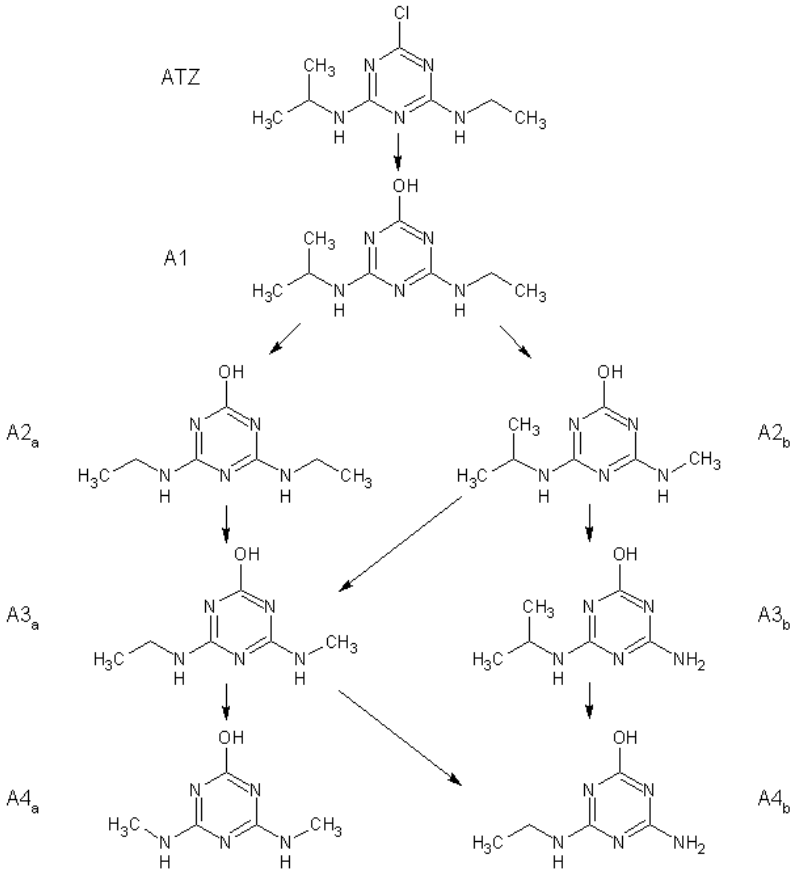
Accurate Mass and Molecular Formula of Transformation Products

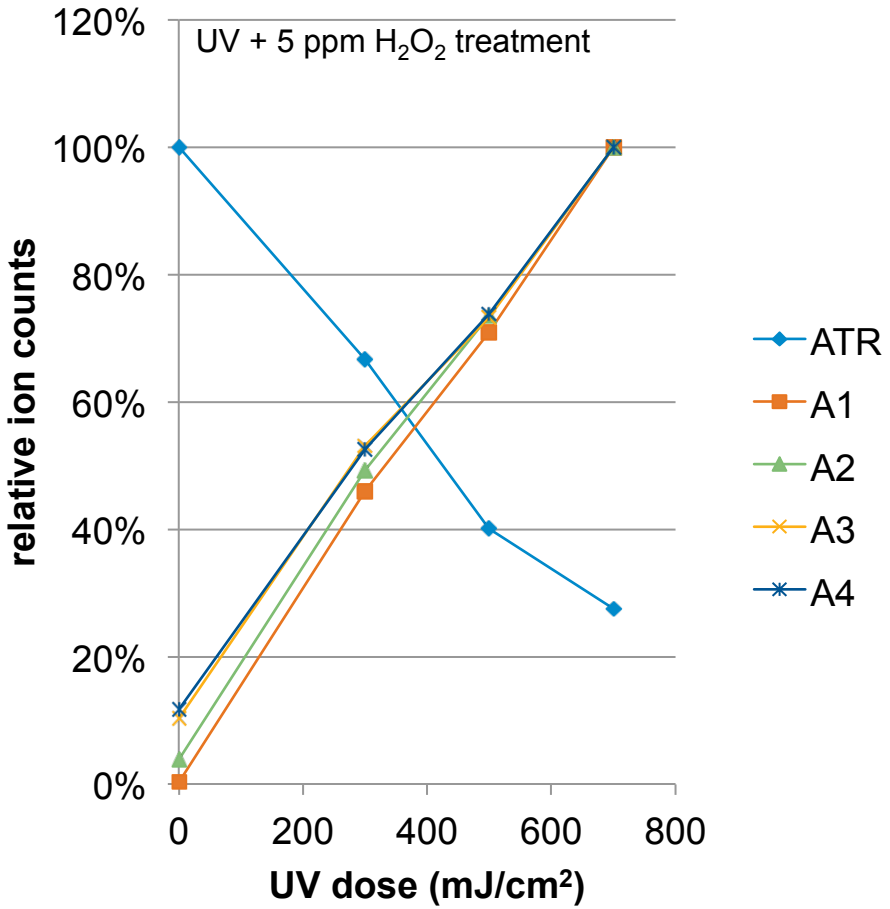
From the estimation of accurate mass, we can calculate molecular formulas

	Formula	Experimental (m/z)*	Calculated (m/z)*	Mass error (ppm)
Atrazine (ATZ)	$C_8H_{14}ClN_5$	216.10121	216.10105	0.74
A1	$C_8H_{15}N_5O$	198.13445	198.13494	2.5
A2	$C_7H_{13}N_5O$	184.11876	184.11929	2.9
A3	$C_6H_{11}N_5O$	170.10307	170.10364	3.4
A4	$C_5H_9N_5O$	156.08716	156.08799	5.3

Lekkerkerker-Teunissen et al., Separation and Purification Technology 96 (2012) 33–43

Atrazine Transformation by UV/ H_2O_2





Lekkerkerker-Teunissen et al., Separation and Purification Technology 96 (2012) 33–43

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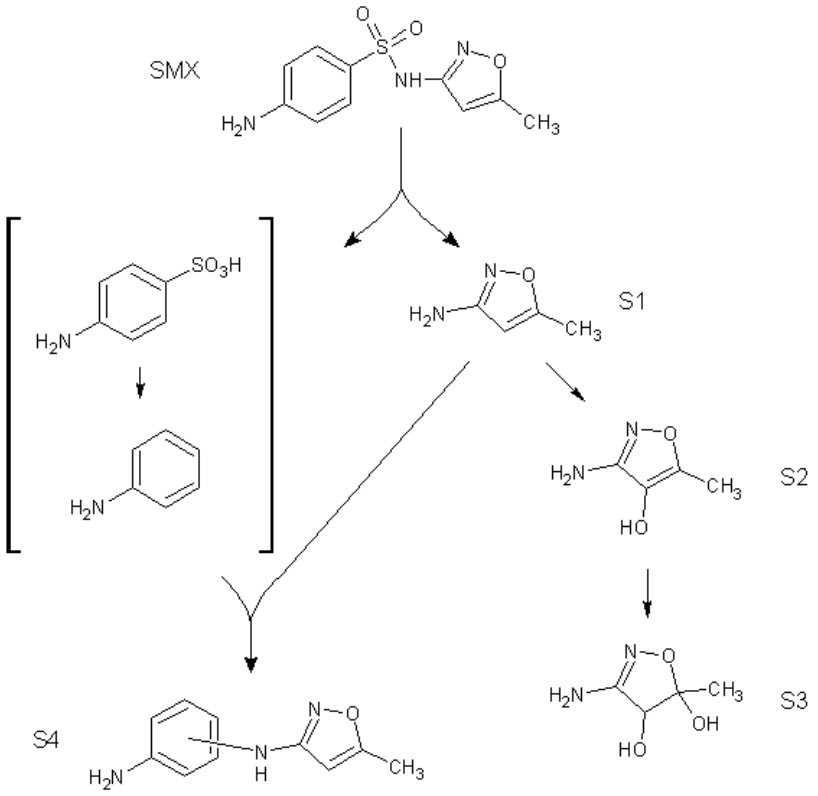
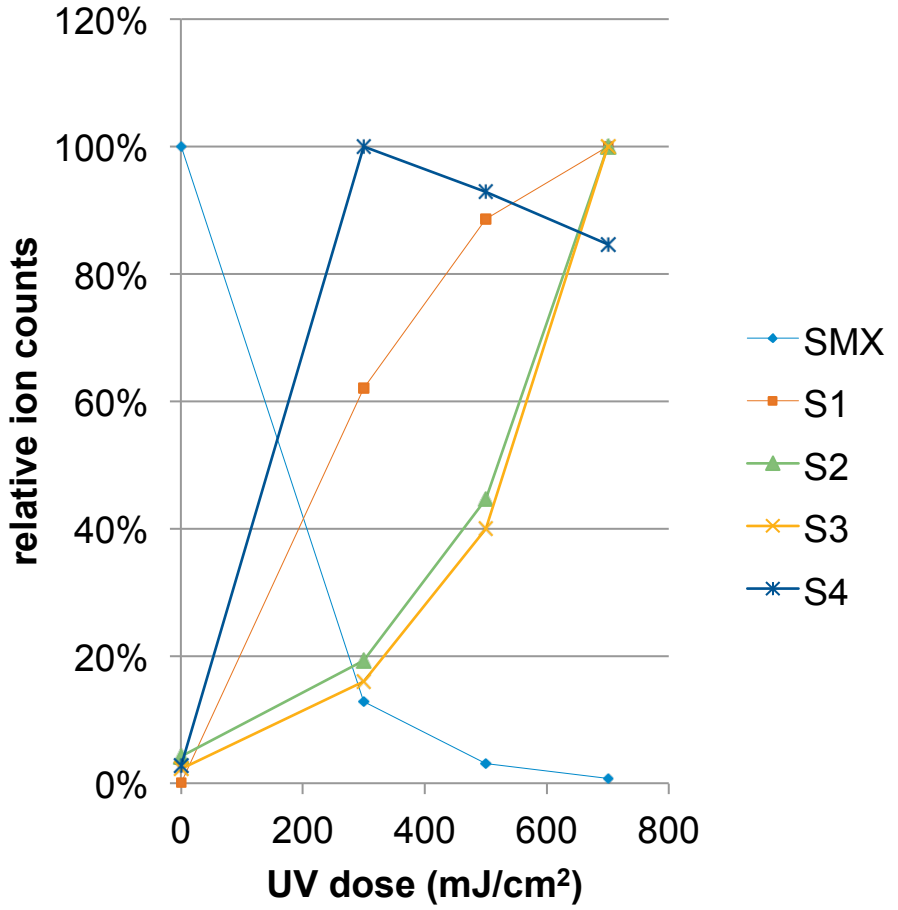
Carbamazepine Transformation by UV/H_2O_2





Lekkerkerker-Teunissen et al., Separation and Purification Technology 96 (2012) 33–43

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Part III: Treating Contaminated Water and How to Deal with Treated Water?

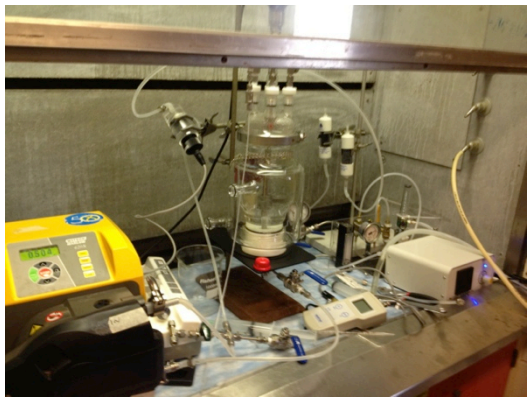
- How to deal with large volumes of decontaminated washwater and contaminated water and wastewater?
  - Incinerate water?
  - Haul thousands/millions/billions of gallons long distances to specialty facility?
  - Drain disposal to local wastewater plant?
- Drain disposal requires appropriate pre-treatment and assurance that pre-treated water will not impact wastewater operations and results in dischargeable effluent.

Technical Approach

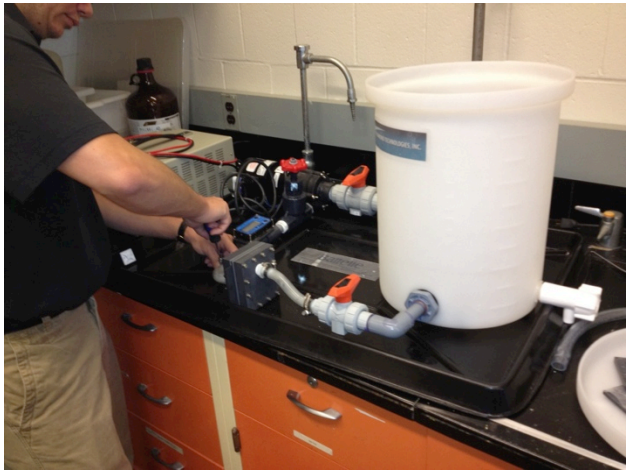
- Investigate different AOP technologies for the treatment and disposal of drinking water contaminated with chemicals into public sewer (collection) systems
  - Assess ~12 pharmaceuticals, EDCs and current-use pesticides
  - ppm concentrations of each compound
- Perform toxicity tests to assess whether or not treated water will interfere with wastewater treatment plant operation or be toxic to the environment

Target AOP Technologies

- Ozone/peroxide
  ($2O_3 + H_2O_2 \rightarrow 2OH\bullet + 3O_2$)



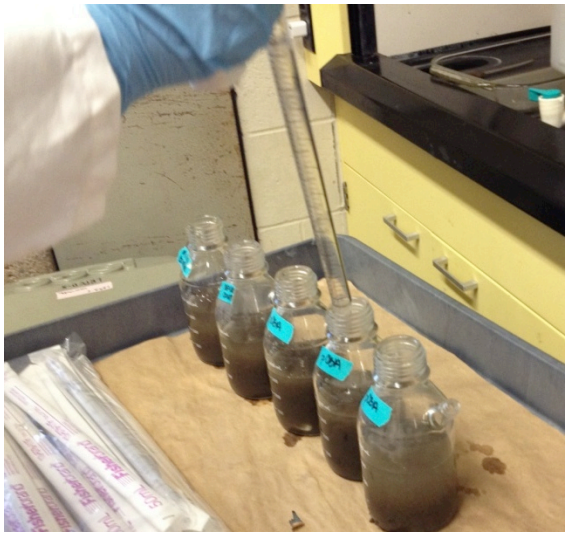
- Boron-doped diamond electrode
  (produces many free radicals, including OH•)

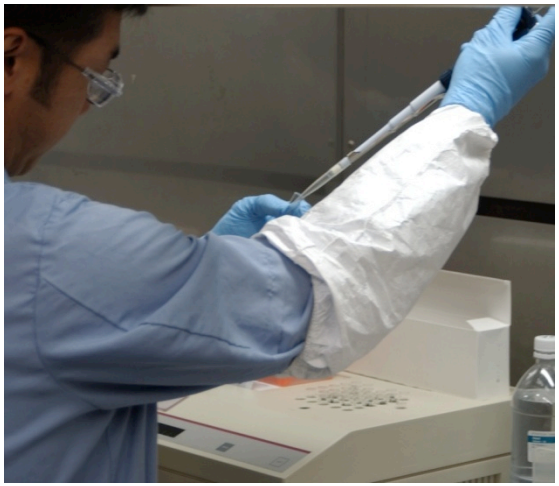


- UV/Peroxide ($H_2O_2 \rightarrow 2OH\bullet$)

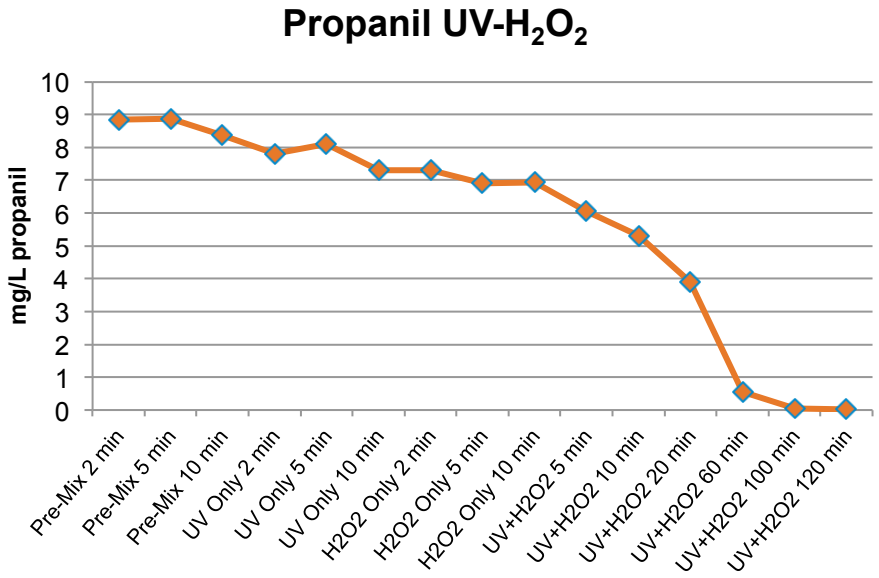
Toxicity Testing

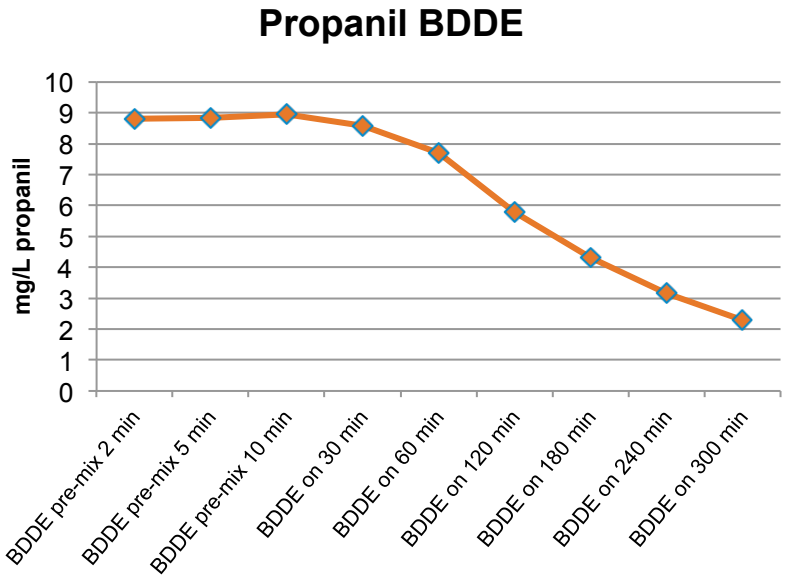
- Nitrification Inhibition testing
  - Nitrifying bacteria in mixed liquor sample exposed to test samples
  - Rate of decrease of ammonia measured
  - An inhibition is an indication that the process water is toxic to the microbial community
- Microtox Toxicity Test
  - Luminescent marine bacteria
  - Indicator of eco-toxicity for environmental discharge

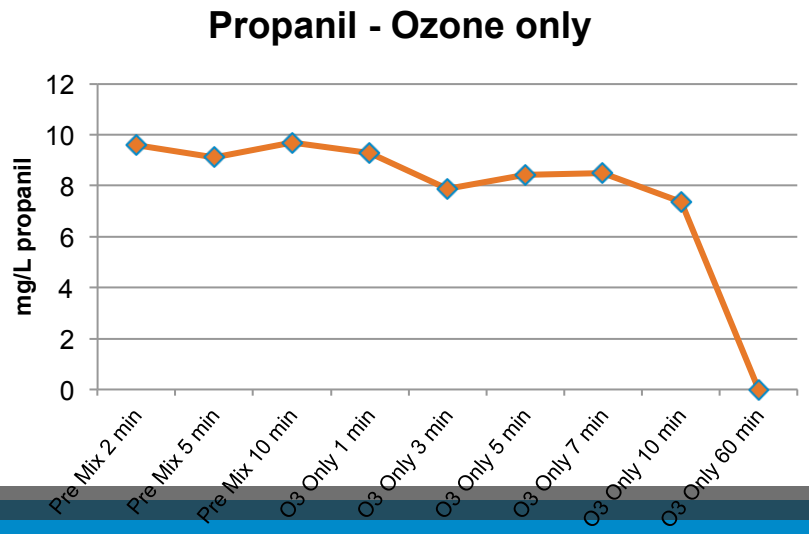


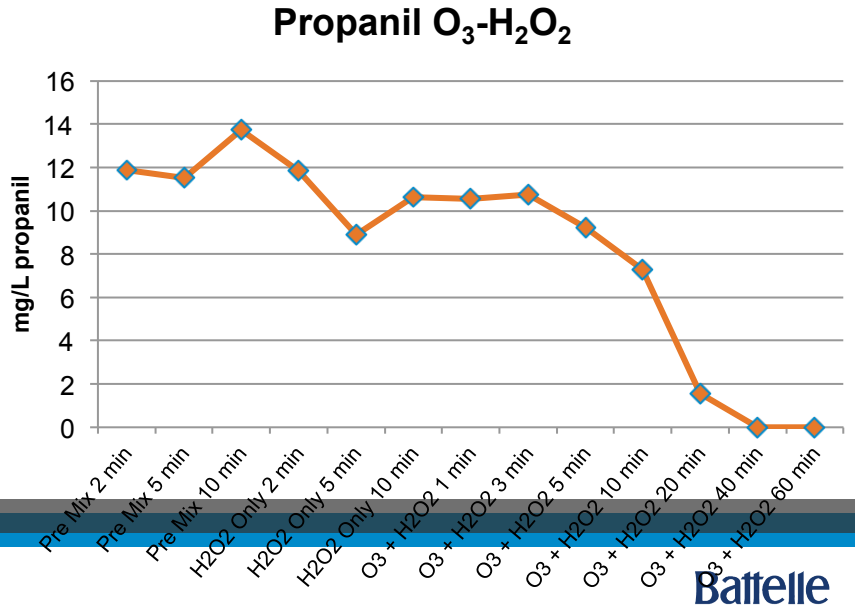


AOP Results - Propanil

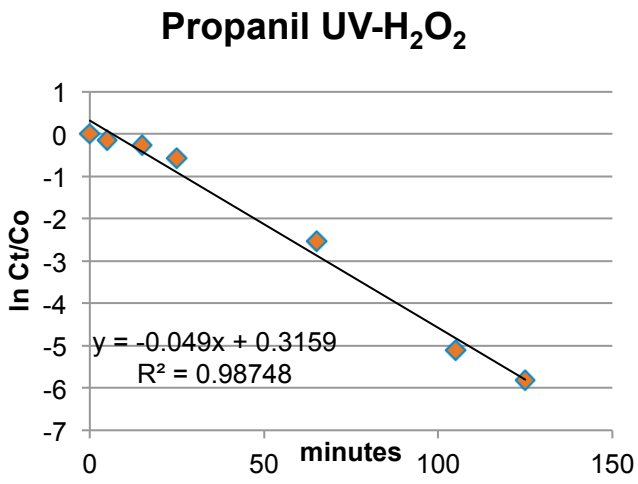


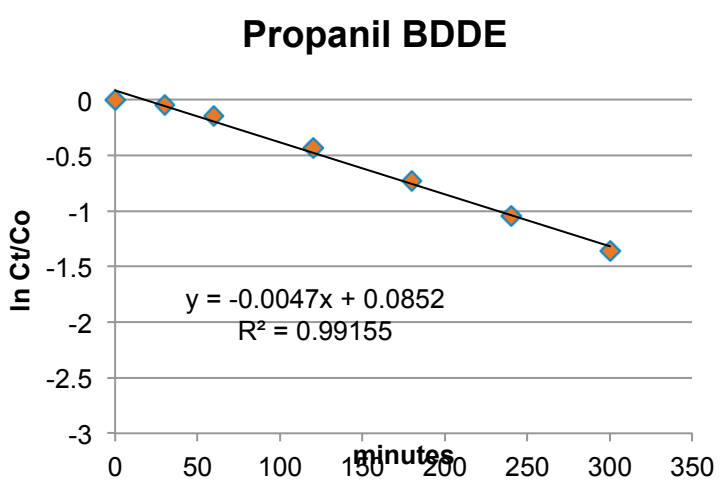


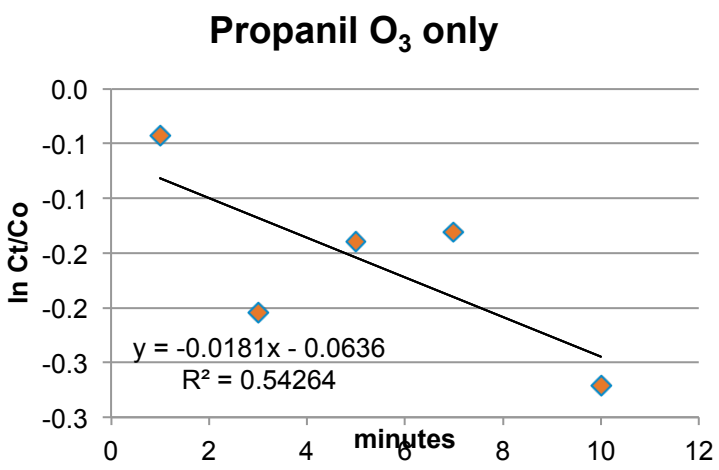


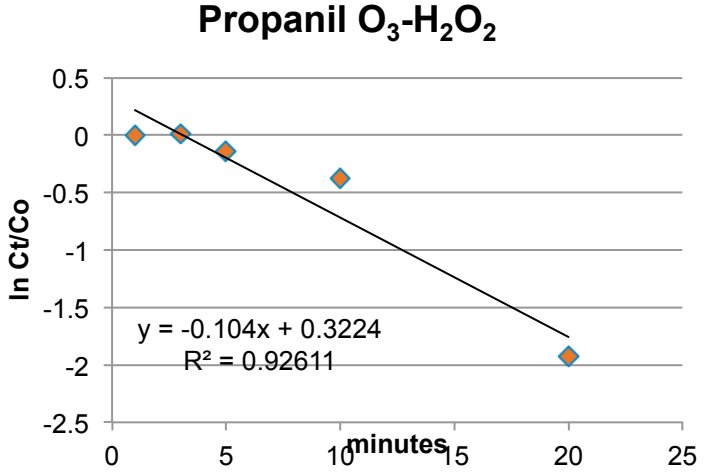


AOP Results - Propanil









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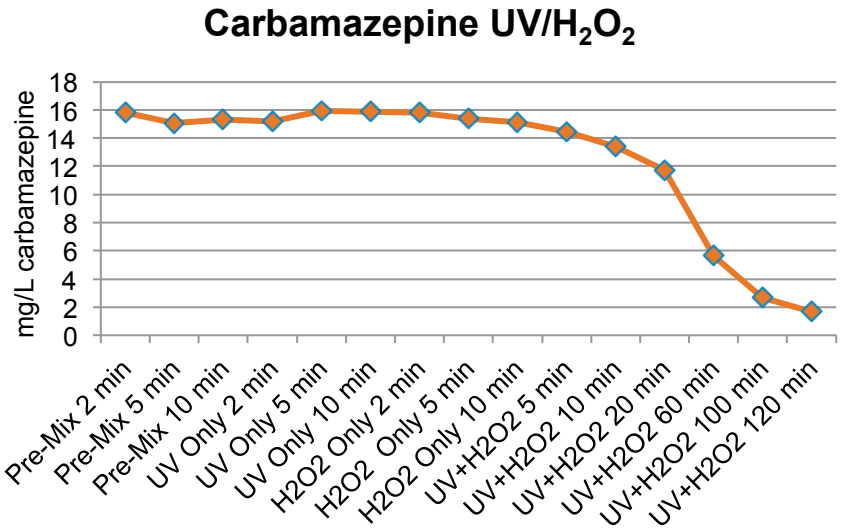
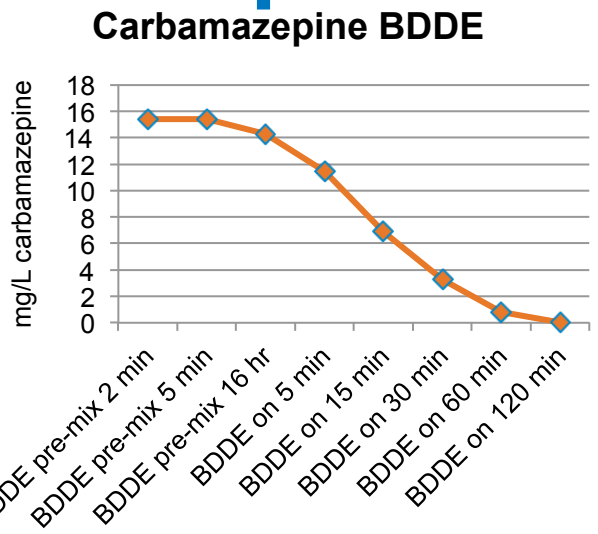
Toxicity Results - Propanil

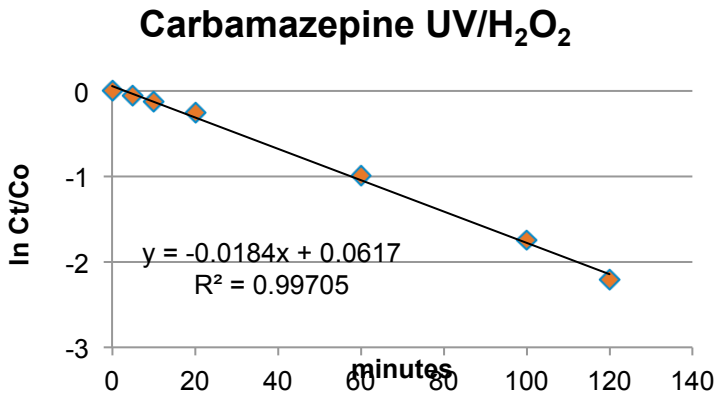
	UV-H_2O_2		BDDE		O_3-H_2O_2	O_3 only
	NI (% N reduction)	Microtox (%Inhib)	NI (% N reduction)	Microtox (%Inhib)	Microtox (%Inhib)	Microtox (%Inhib)
DW control	0 ± 13	0 ± 2	0 ± 11	0 ± 1	0 ± 4	0 ± 2
pre-treatment	63 ± 29	47 ± 1	32 ± 1	26 ± 0	26 ± 1	39 ± 1
post-treatment	10 ± 6	19 ± 1	153 ± 48	100 ± 0	100 ± 0	86 ± 0

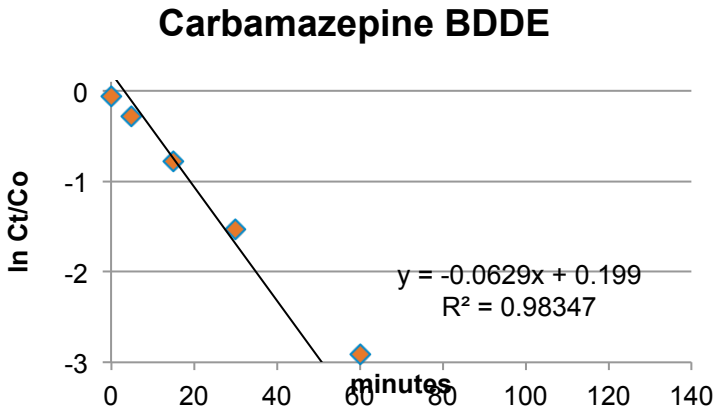
- The UV/H_2O_2 system produces a less toxic process water (for both the nitrification inhibition tests and for the microtox tests)
- The BDDE, ozone, and ozone/H_2O_2 produce a more toxic process water

AOP Results - Carbamazepine









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Toxicity Results - Carbamazepine

	UV-Peroxide		BDDE	
	NI (% N reduction)	Microtox (%Inhib)	NI (% N reduction)	Microtox (%Inhib)
DW control	0 ± 8	0 ± 4	0 ± 7	0 ± 2
pre-treatment	19 ± 20	48 ± 2	8 ± 8	20 ± 3
post-treatment	15 ± 4	8 ± 2	71 ± 7	100 ± 0

- The UV/H_2O_2 system produces a less toxic process water (for both the nitrification inhibition tests and for the microtox tests)
- The BDDE produces a more toxic process water

Conclusions

- During water treatment, chemical oxidation alters structure of target compounds
  - It is not enough to say that compounds are “removed”
- Understanding what these transformation products are is very challenging
  - When toxicological endpoints are being considered, toxicological information (estrogenic activity, mictrotox, nitrification inhibition) may be combined with chemical information (i.e. removal of target analytes) to infer whether or not transformation products are toxic
  - Mass spectrometric techniques can generate structural information, but equipment is expensive and process is not streamlined

Acknowledgements

- Part 1: Ben Stanford (SNWA, now Hazen and Sawyer), Eric Wert (SNWA) and Shane Snyder (SNWA, now U. of Ariz.)
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- Part 3: Ryan James (Battelle); Matthew Magnuson & Rebecca Phillips (EPA NHSRC); Andrea Burkes, Raghu Venkatapathy, and Wayne Brashear (Pegasus)

QUESTIONS?