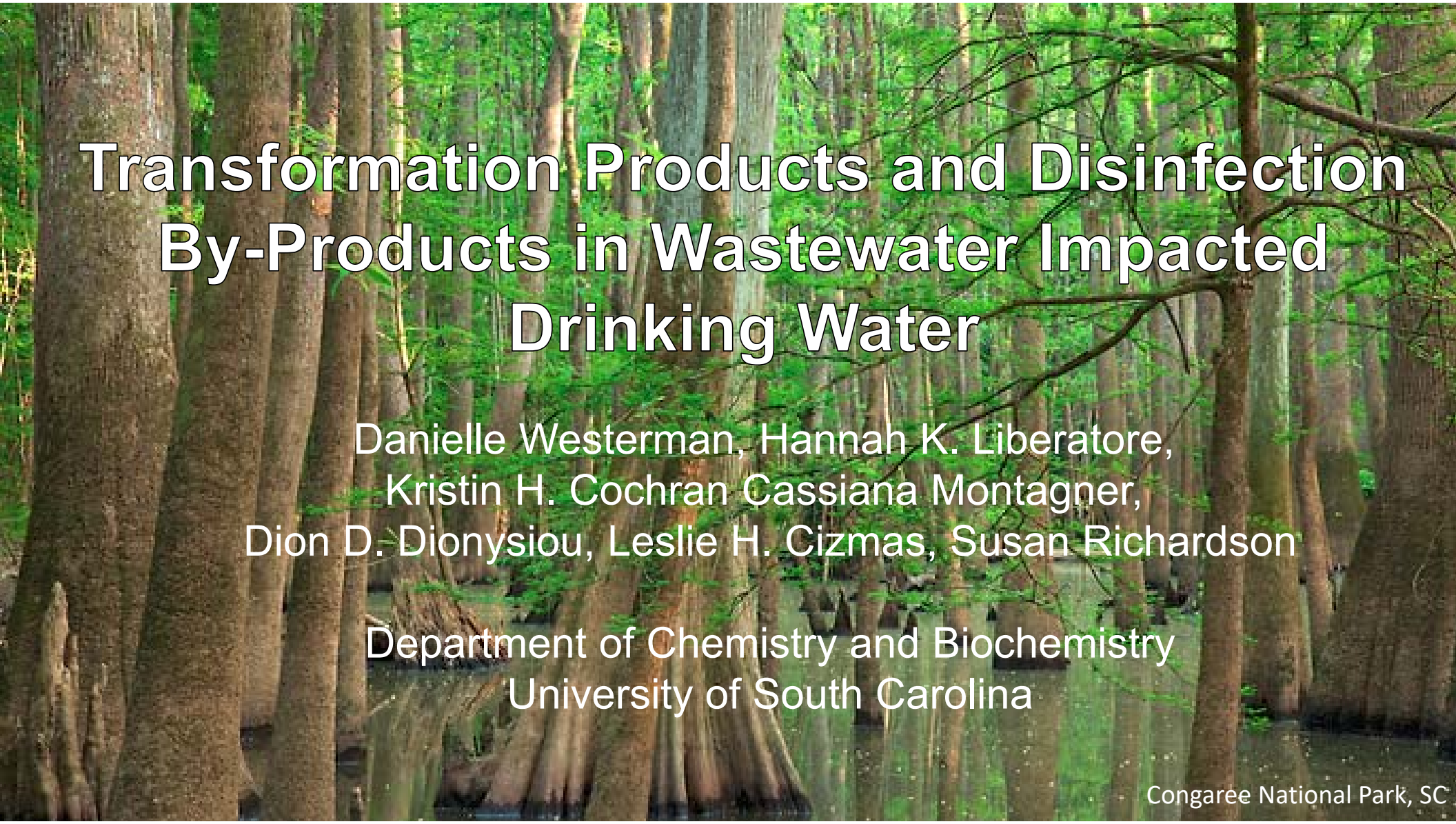


Transformation Products and Disinfection By-Products in Wastewater Impacted Drinking Water

Danielle Westerman, Hannah K. Liberatore,
Kristin H. Cochran Cassiana Montagner,
Dion D. Dionysiou, Leslie H. Cizmas, Susan Richardson

Department of Chemistry and Biochemistry
University of South Carolina

Congaree National Park, SC

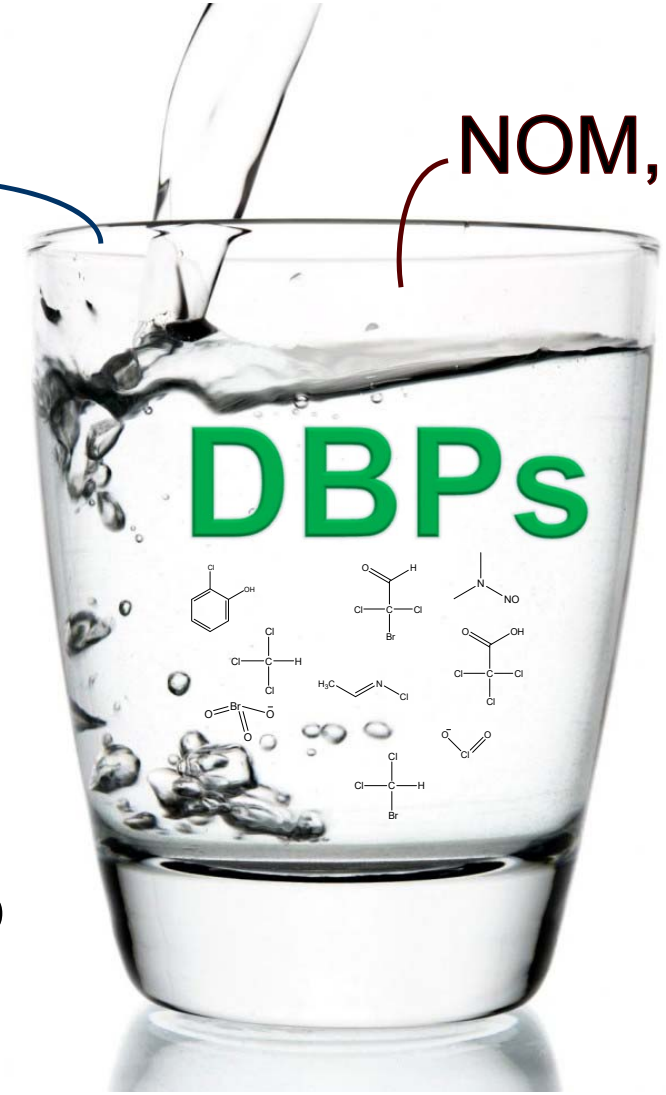
What's in my water?

These chemicals may or may not be in your drinking water…

But there is always something that is in your water…

Disinfectants:
Cl_2, NH_2Cl
O_3, ClO_2

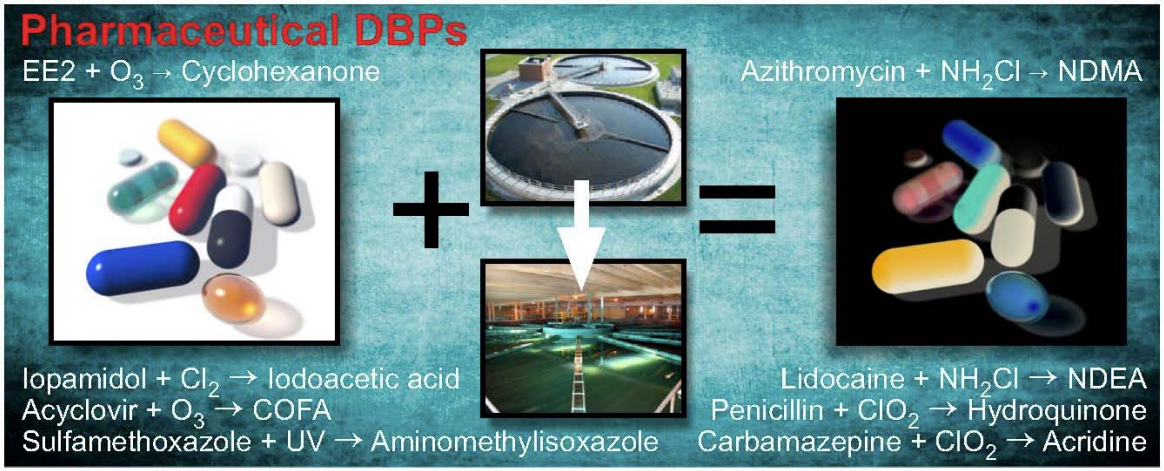
NOM, Br^-, I^-



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

DBPs can also form from pollutants…

- Pesticides
- Pharmaceuticals
- Antibacterial agents
- Estrogens
- Textile dyes
- Bisphenol A
- Parabens (swimming pools)
- Alkylphenol ethoxylate surfactants
- Algal toxins
- Musks



Postigo and Richardson, *J. Hazardous Materials* 2014, 279, 461-475.

Drinking Water DBPs—What are the Issues?

Concern over possible human health risk:

- Epidemiologic studies: risk of bladder cancer, miscarriage, and birth defects

New: Cardiac birth defects (Wright et al. 2016)

Only 11 DBPs Regulated in U.S.

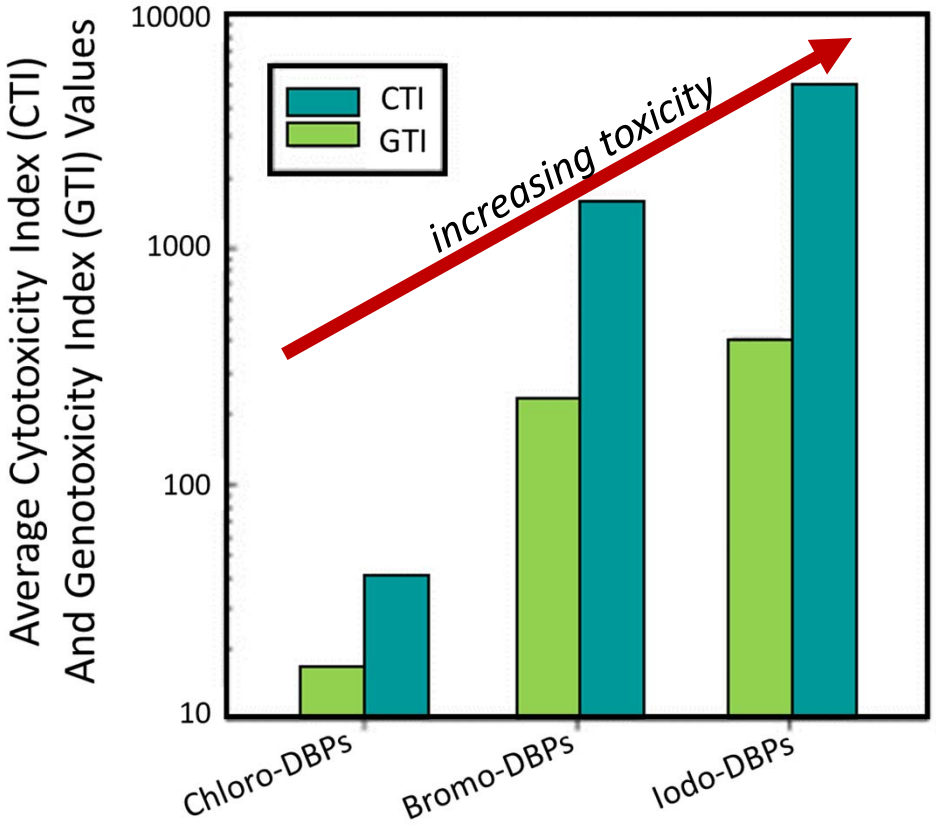
DBP	MCL (µg/L)
Total THMs	**80**
5 Haloacetic acids	**60**
Bromate	**10**
Chlorite	**1000**

But >700 DBPs now known

Little known about occurrence, toxicity of unregulated DBPs

Regulated DBPs do not cause bladder cancer in animals!

Bromo- and Iodo-DBPs are important



Halogenated DBP
Relative Toxicity:

I > Br >> Cl

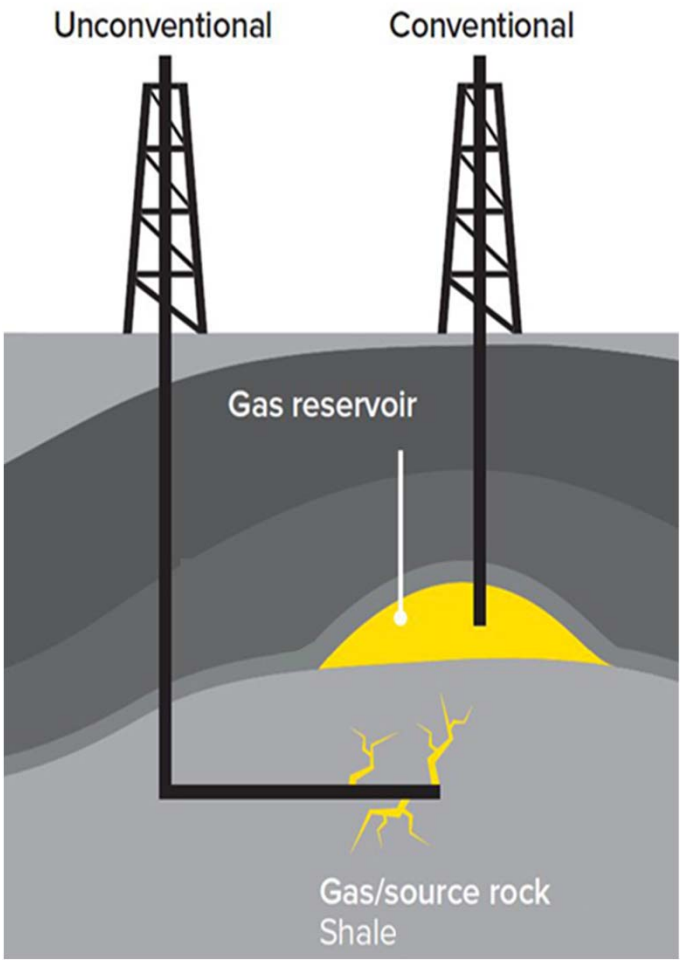
Iodoacetic acid is the most genotoxic DBP and is tumorigenic in mice

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

New Issues

- New impacts (hydrofracking, coal fired power plants)
- Climate Change -> drought
- Growing populations, water scarcity
- New water resources:
  - Wastewater reuse

Part 1: Hydraulic Fracturing



Lots going on in the U.S.! (and in other countries!)

High pressure water, sand, surfactants, biocides,
injected deep into the ground to enhance extraction of oil and natural gas

Source: U.S. Energy Information Administration based on data from various published studies. Canada and Mexico plays from ARI.
Updated: May 9, 2011

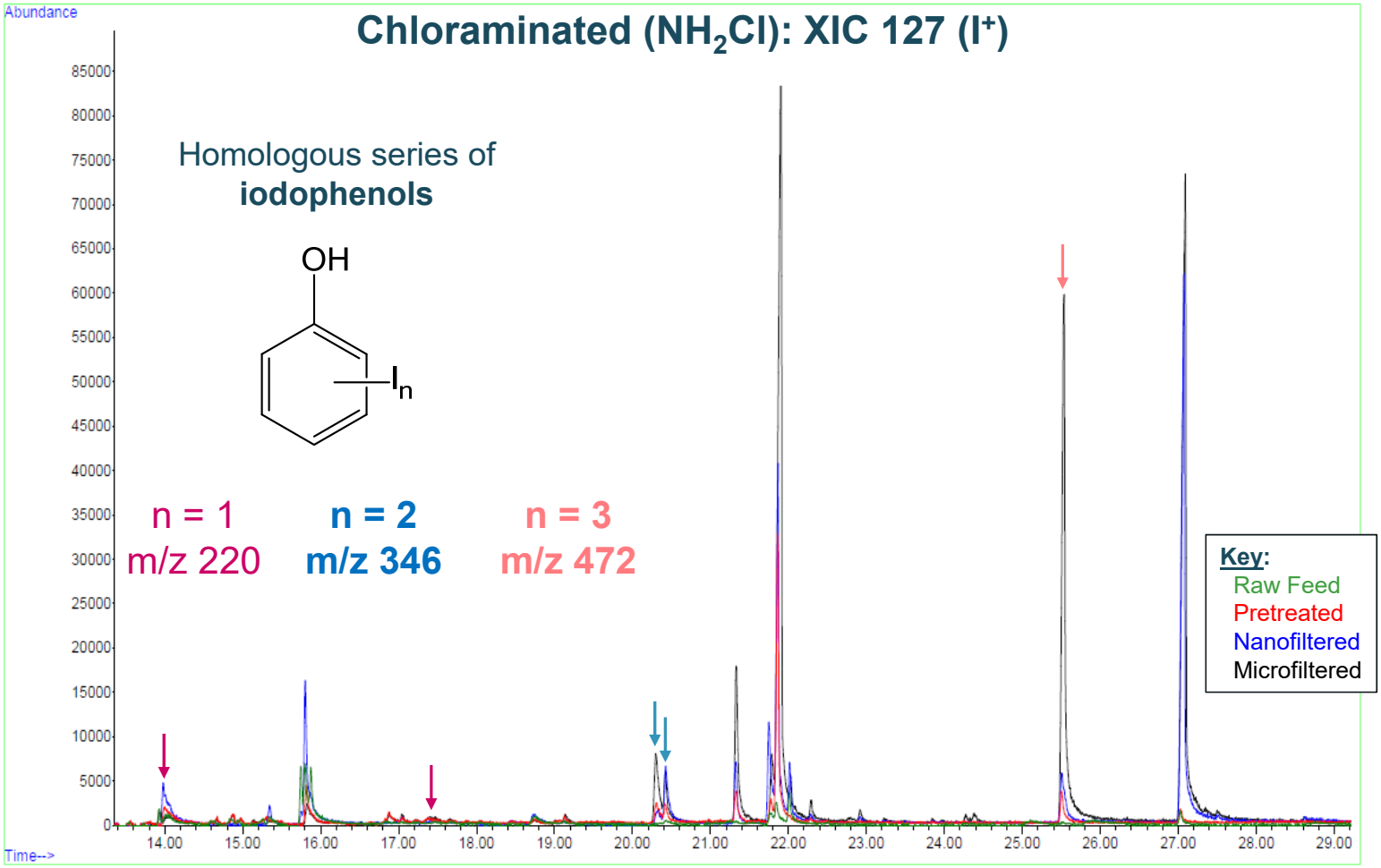
Hydraulic Fracturing

Hannah Liberatore

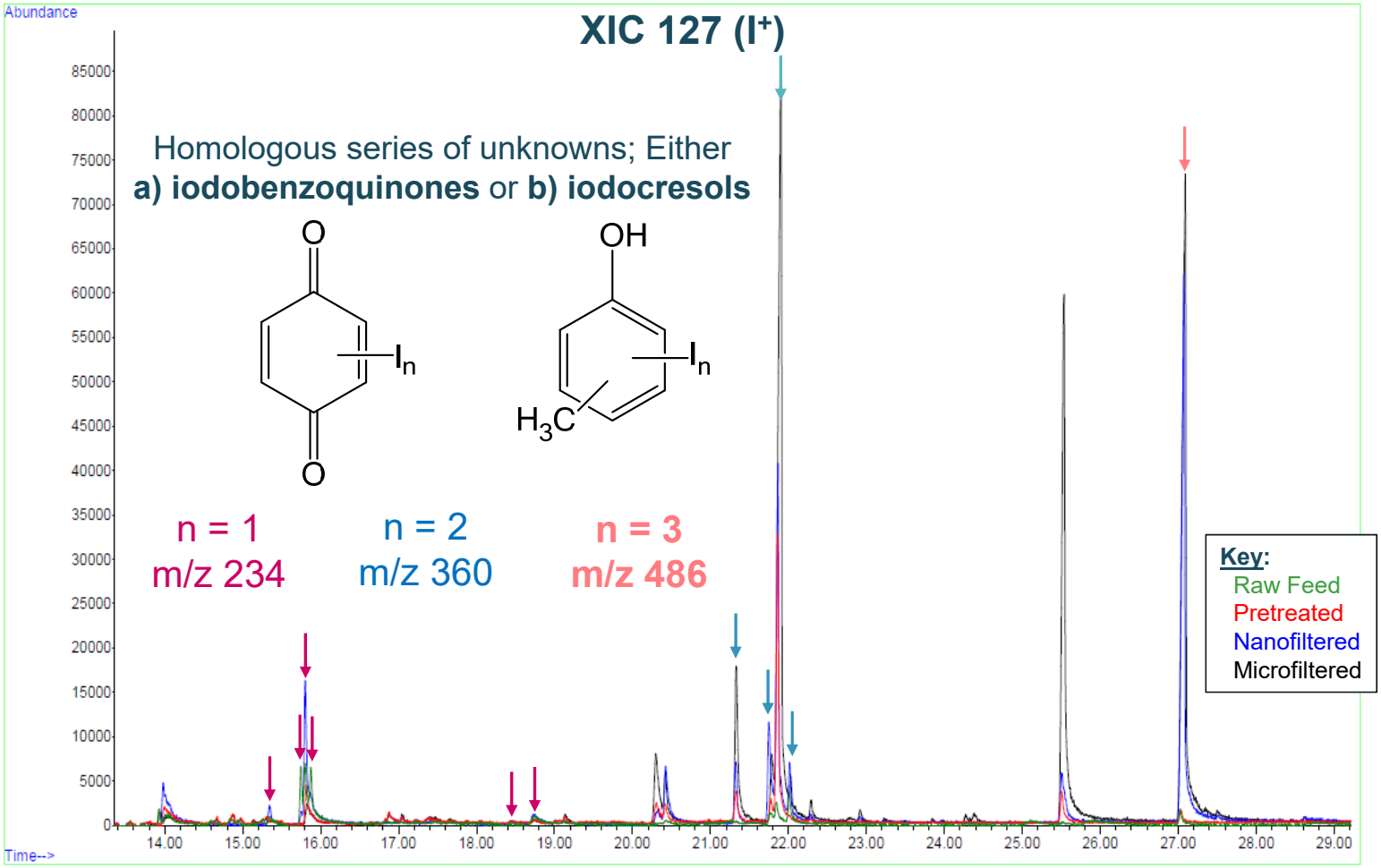
What would happen if HF waters entered our drinking water supplies?

$$\xrightarrow[NH_2Cl]{HOCl} \text{DBPs}$$

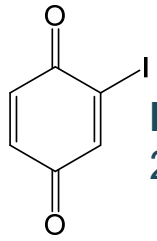
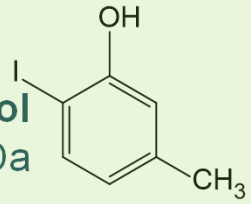
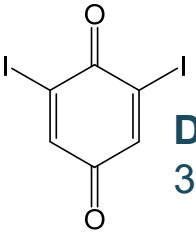
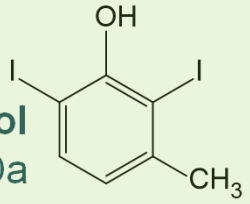
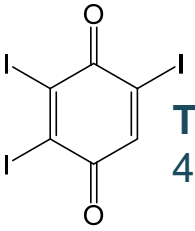
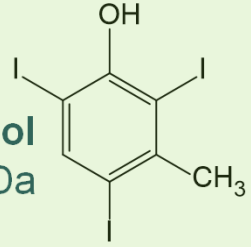
Results: New Iodo-DBPs



New Iodo-DBPs: Chloraminated Water



High Resolution Accurate Mass MS

			Observed m/z
 **Iodobenzoquinone** 233.9173 Da	**VS.**	**Iodocresol** 233.9537 Da 	233.9536 Da
 **Diiodobenzoquinone** 359.8139 Da	**VS.**	**Diiodocresol** 359.8503 Da 	359.8505 Da
 **Triiodobenzoquinone** 485.7100 Da	**VS.**	**Triiodocresol** 485.7469 Da 	485.7490 Da

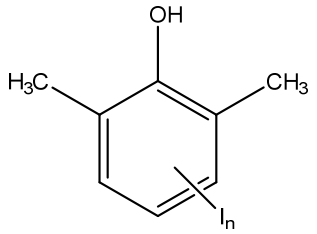
High Resolution Accurate Mass MS

Compound	Formula	Observed Mass	Theoretical Mass
Iodophenol	C_6H_5IO	219.9381	219.9375
Diiodophenol	$C_6H_4I_2O$	345.8352	345.8347
Triiodophenol	$C_6H_3I_3O$	471.7315	471.7310
Iodocresol	C_7H_7IO	233.9536	233.9537
Diiodocresol	$C_7H_6I_2O$	359.8505	359.8503
Triiodocresol	$C_7H_5I_3O$	485.7490	485.7469
Iodoxylenol	C_8H_9IO	247.9693	247.9693
Diiodoxylenol	$C_8H_8I_2O$	373.8659	373.8660
Triiodoxylenol	$C_8H_7I_3O$	499.7626	499.7626

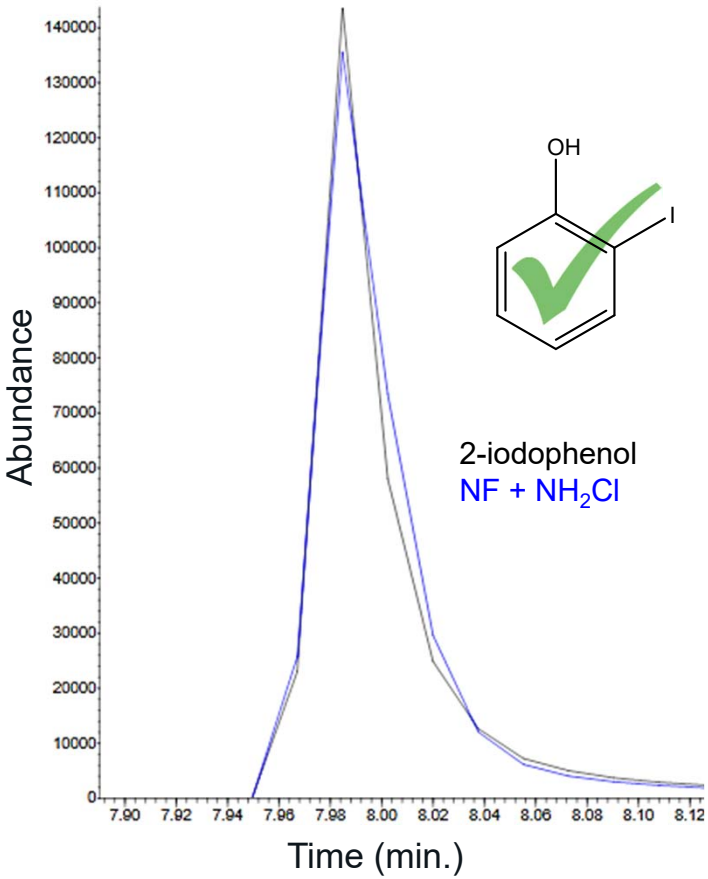
LECO Pegasus GC-HRT

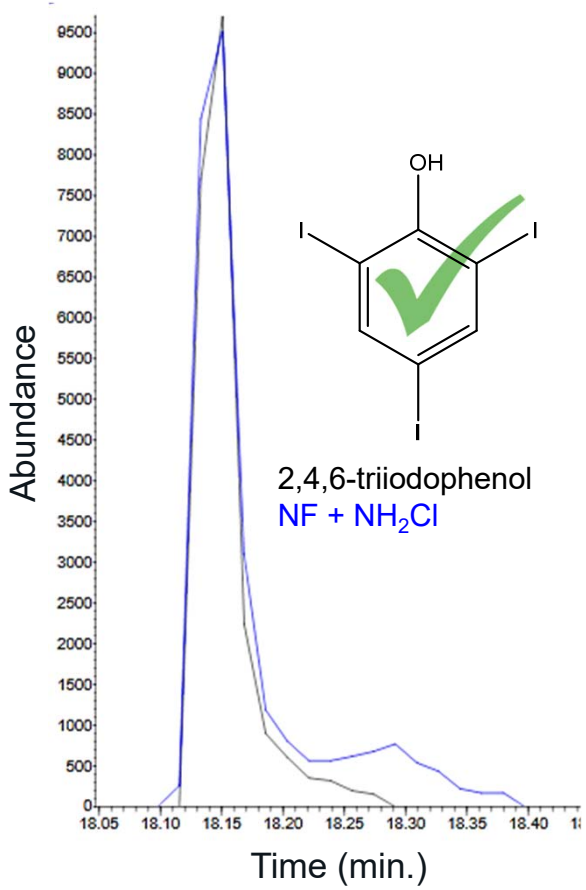
50,000 resolution

Another class identified: ***iodoxylenols***

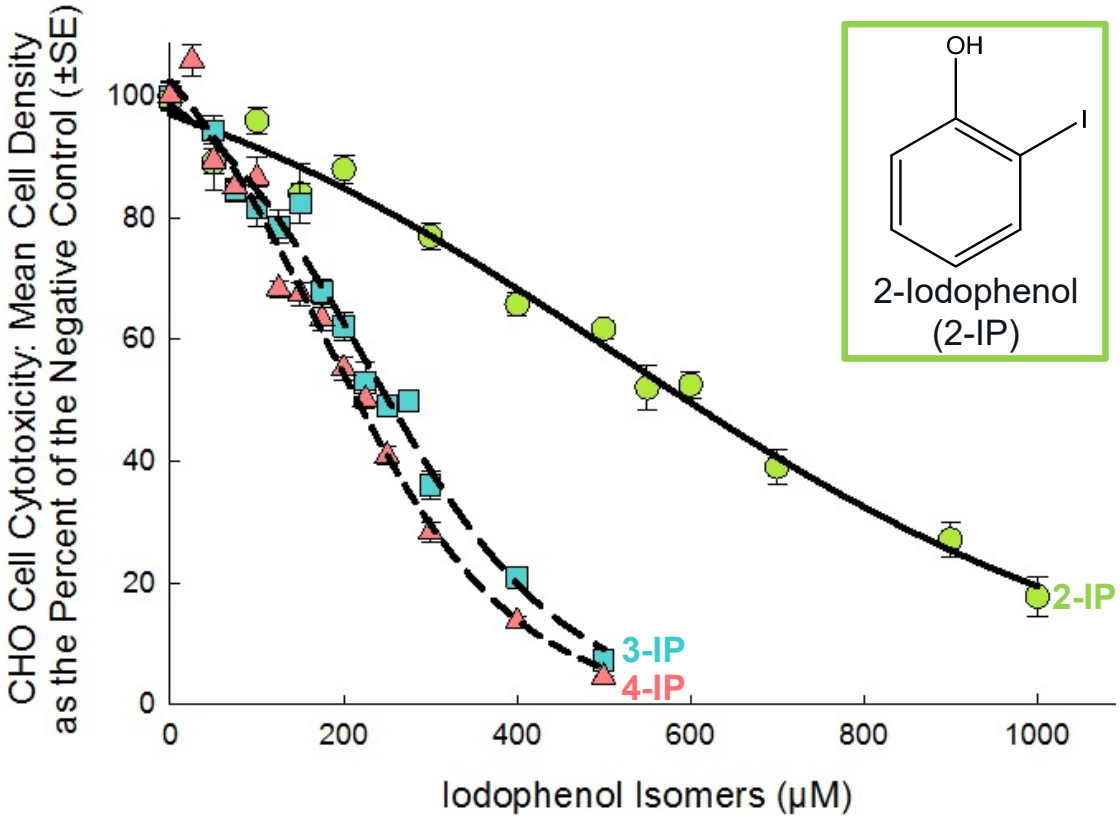


Isomer Identification: Retention Time Confirmation

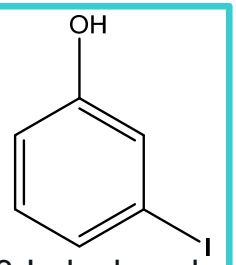




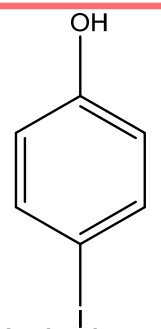
Mammalian Cell Cytotoxicity of Iodophenols



2-Iodophenol
(2-IP)



3-Iodophenol
(3-IP)



4-Iodophenol
(4-IP)

Lethal Concentration, 50% (LC_{50})

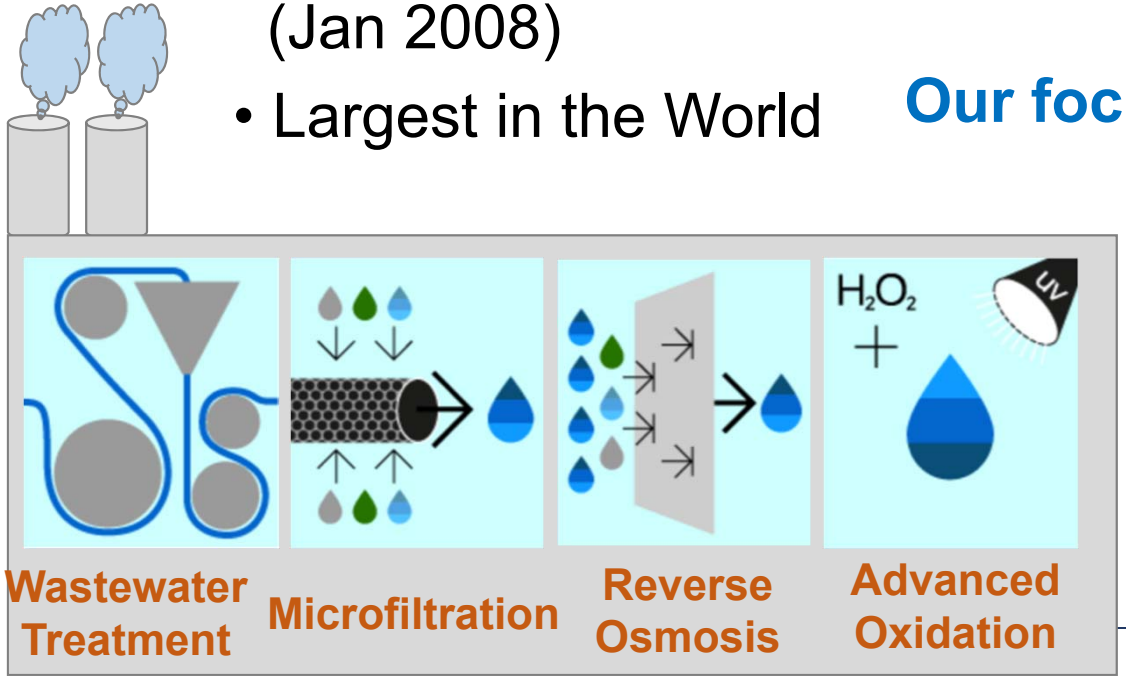
Concentration required to kill half of the population

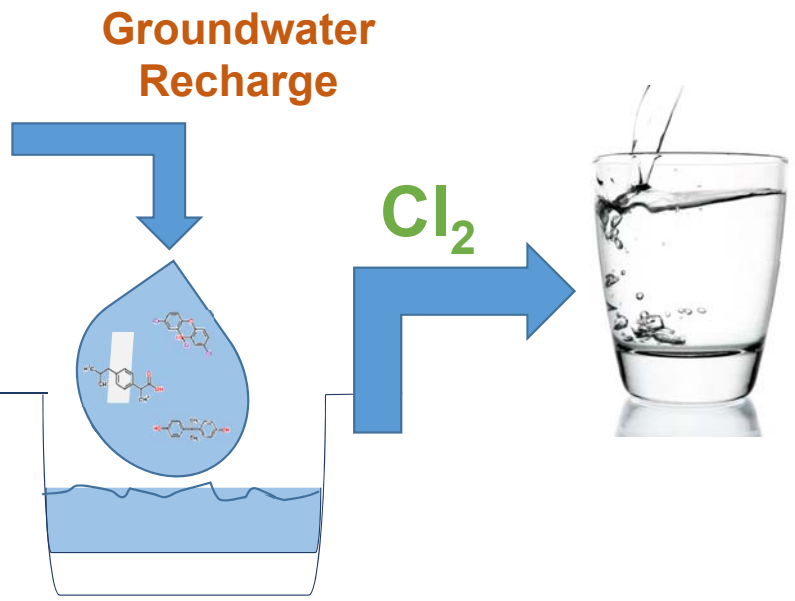
Measured as cell density, in relation to that of the negative control

Part 2: Wastewater Reuse

- Orange County, CA: Indirect Potable Water Reuse (Jan 2008)
- Largest in the World

Our focus: 21 Priority ECs





El Paso, TX is building the largest direct WW reuse plant in the world

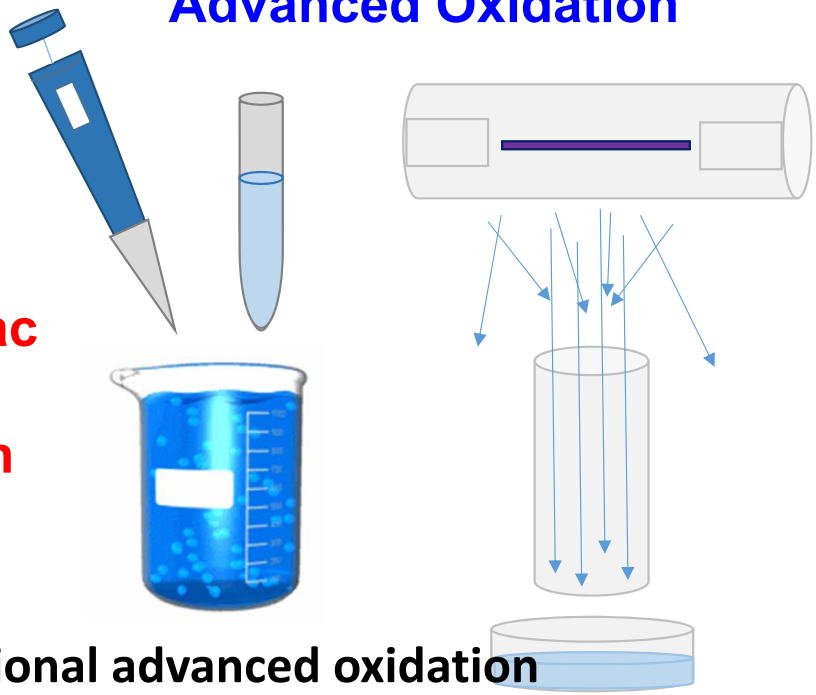
21 Emerging Contaminants

- **PFOA, PFOS**
- **Pharmaceuticals**
- **Hormones**
- **Flame retardants**
- **Pesticides**
- **DBP (NDMA)**
- **Antimicrobial (Triclosan)**
- **Plastics (BPA, phthalates)**

Advanced Oxidation for Removing 21 Priority Emerging Contaminants

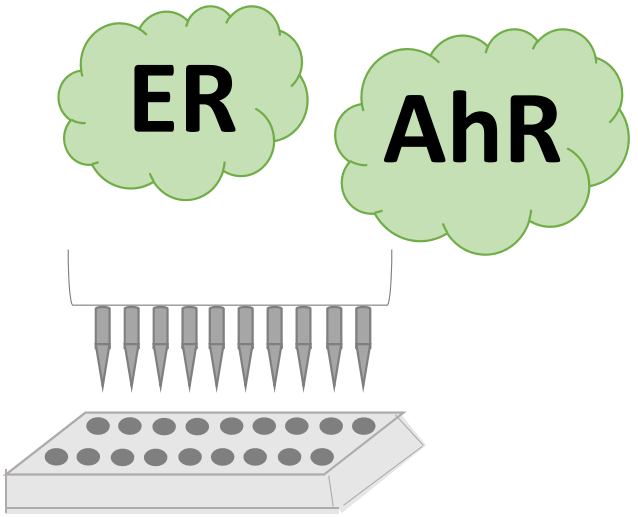
Advanced Oxidation

Triclosan
Diclofenac
BPA
Ibuprofen
Estrone



Unconventional advanced oxidation of EC spiked OC treated waters (carbonate radicals, TiO_2/UV)

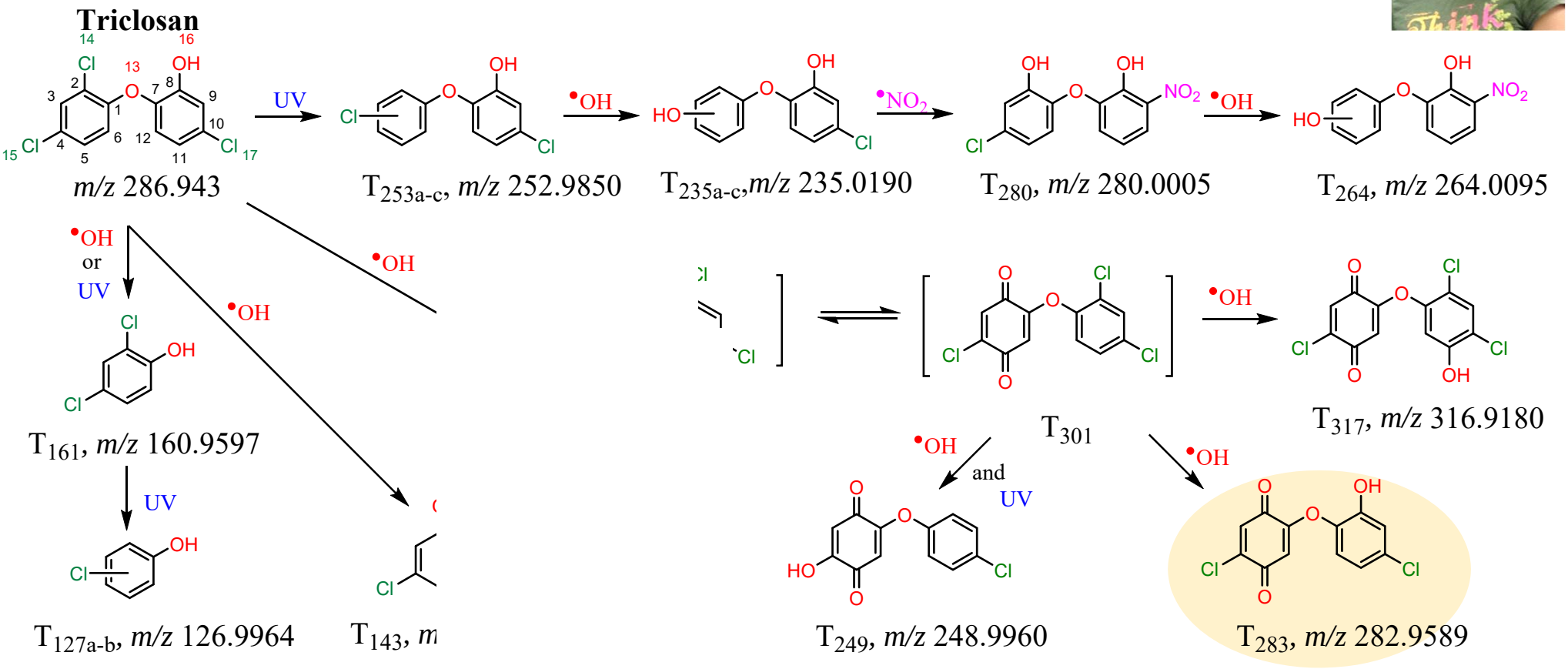
Cytotoxicity



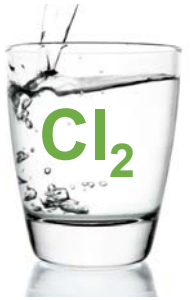
Cytotoxicity and estrogen activity analyzed using estrogen receptor and aryl hydrocarbon receptor assays

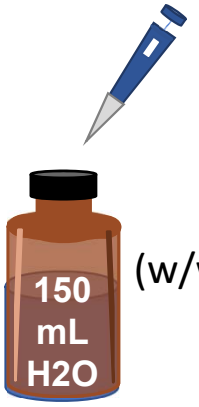
Using LC-MS/MS to determine reaction pathways

Kristin Cochran



Chlorination:
Simulating further drinking water treatment



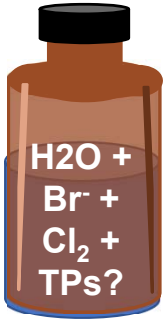


NaOCl
(w/without Br-)

Sample Rxn

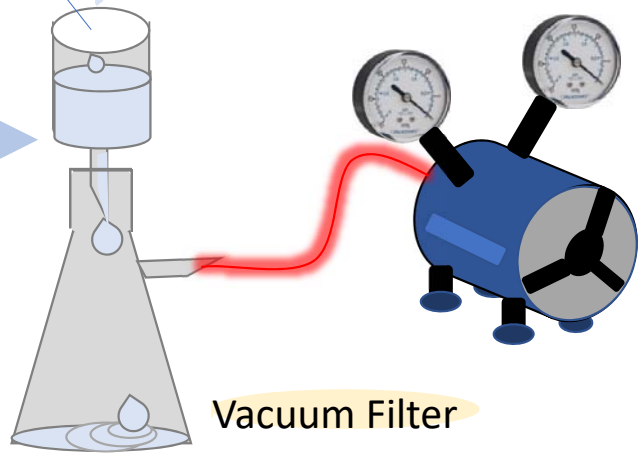
48 Hr
Room Temp

H_2SO_4

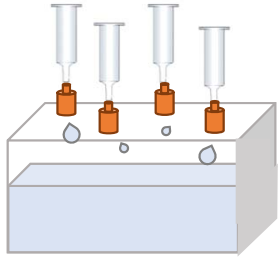


Acidify

Glass
Filter

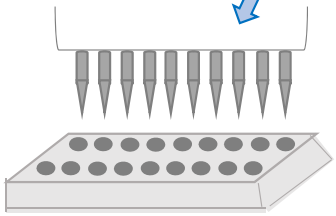


Vacuum Filter



Solid Phase Extraction

1. Condition
2. Load
3. Wash
4. Dry (N_2)



Cytotoxicity and
Estrogen
Activity

and LC-MS/MS

The goal:
Clean and Safe Drinking Water

Thank you!

Funding:

NSF

NIWR
THE NATIONAL INSTITUTES FOR WATER RESOURCES

USGS
science for a changing world

Thanks to Waters, Agilent, and LECO

My research group at USC

Dion Dionysiou

Dan Schlenk

Michael Plewa