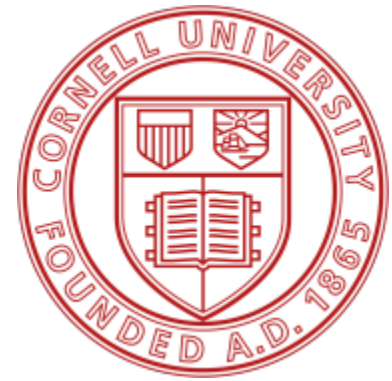


**CornellEngineering**

Civil and Environmental Engineering



**CEE 4540**

**Sustainable municipal drinking water treatment**

**Topic: Advanced Oxidation Processes (AOP)**

Instructor: YuJung Chang

YuJung.Chang@aecom.com

**Class #23 11/19/2018 2:55 – 4:10pm**

# A Few Announcements

- 2<sup>nd</sup> Team Report Comments have been released
- Participation on Independent Study is optional, but need to sign up before 12/13 (last day of school) with selected topic

# Homework & Reading Assignment

- Chapter 8 & 18
- Homework (Due 11/26) Washington Aqueduct is experiencing seasonal Taste & Odor problems and would like to implement an Advanced Oxidation Process to mitigate the impact from T&O events. As a process design engineer, please select and design an AOP process with the following information:
  - Name of the Technology
  - Justification of the selection with Pros & Cons analysis
  - Assumptions
  - Potential challenges and proposed resolutions
  - How do you monitor and assess the performance of your T&O treatment process?

# Advanced Oxidation Process (AOP)

- What is AOP?
  - A treatment process that utilize physical or chemical process to destruct C-C bond
- Purpose of Advanced Oxidation Process
  - Destroy regulated synthetic organic contaminants (e.g., 1,2,3 TCP, 1,4 Dioxane, non-aqueous phase liquid, or NAPL)
  - Destroy Taste & Odor (T&O) causing chemicals secreted by Cyanobacteria (, e.g., MIB & Geosmin, produced by algae) in water supply



Rio St Lucie River, Jeff Tucker 6-24-16



# Challenges of Cyanobacteria Induced Contaminants

- Cyanobacteria is also known as Blue Green Algae
- It is not a bacteria, and not true algae neither
- Most Cyanobacteria will release contaminants due to cell damage and natural decay process
  - MIB/Geosmin (causing bad taste & odor problem)
    - Secondary MCL for T&O is 3



**Cyanobacteria**

40 μm



# Cyanotoxin is Toxic to both Animals and Human

- Cyanotoxin
  - Anatoxins
  - Microcystins
  - Saxitoxins
- Not regulated by USEPA yet
- On EPA's Draft CCL4



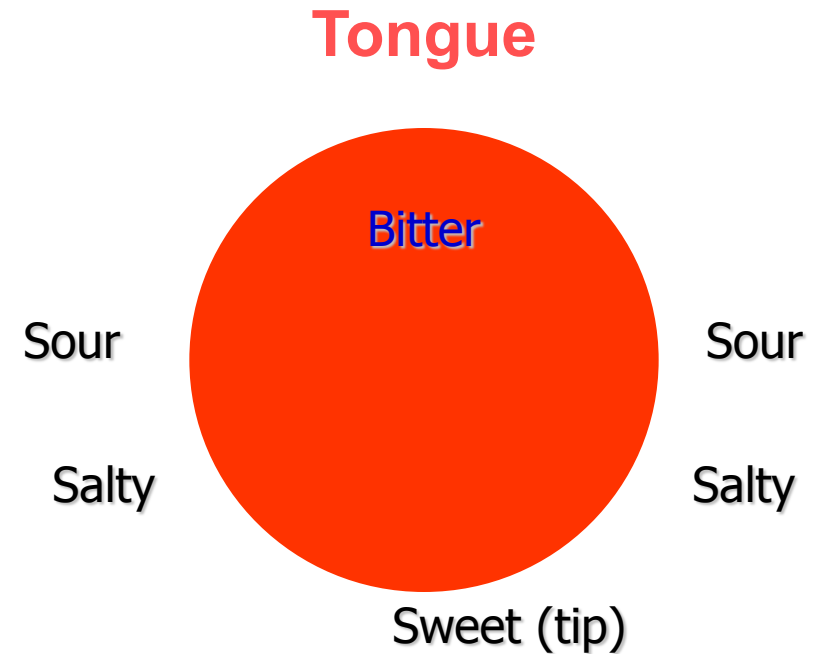
# Basics of Taste & Odor (T&O) in Drinking Water

## ***What is Off-Flavor?***

An off-flavor is an observation by consumers or experts that a flavor (a taste, odor or mouth feel sensation) exists in a water sample that is not normally present and that this quality is perceived as offensive.

# A Sip of Tap Water, and.....

- 💧 **Four basic tastes**
- 💧 **Plus millions of odors**
- 💧 **Plus mouth “feelings”**
- 💧 **Plus aftertastes**

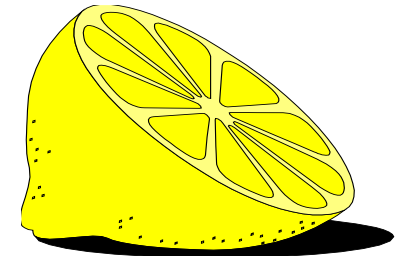
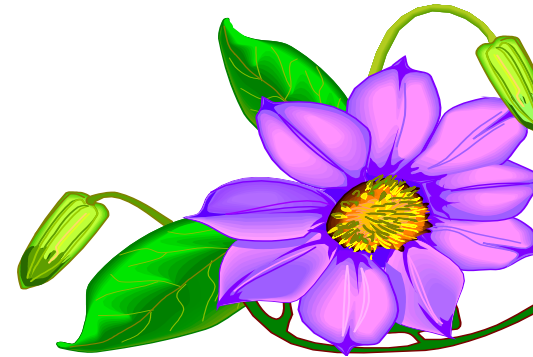
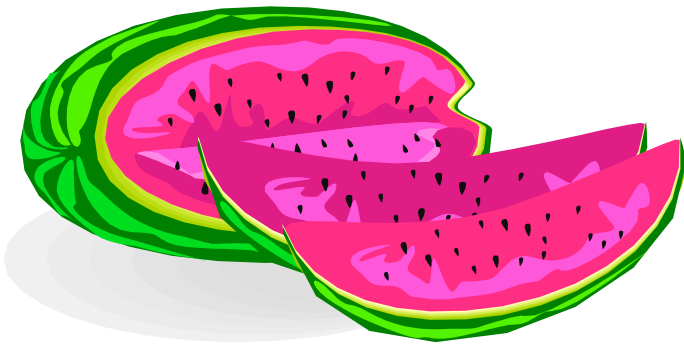


Optimum at 20-40°C, relative to saliva



# Communicating & Controlling T&O Problems

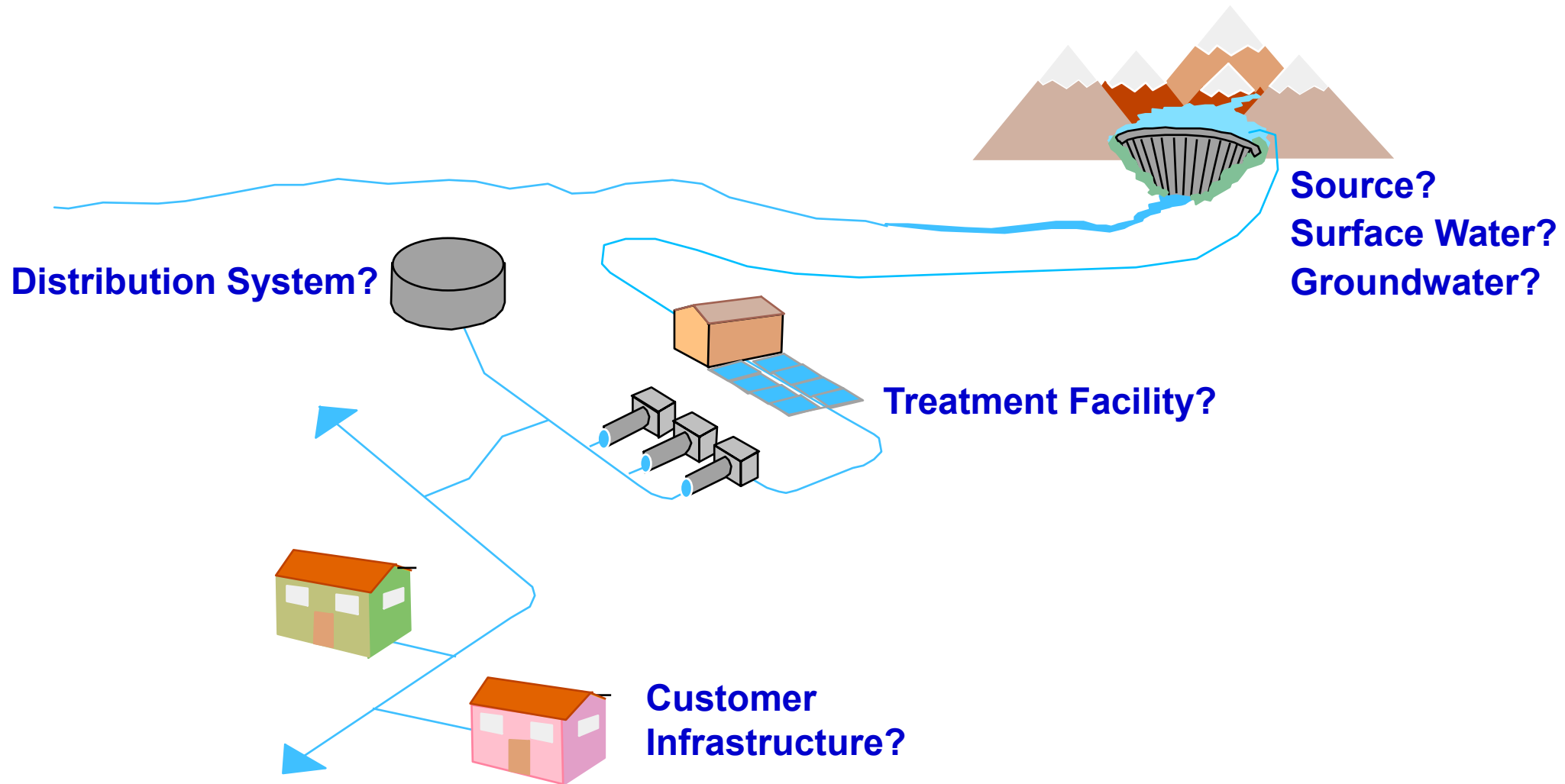
- T&O is not a health issue, but an important factor for customers' perspectives on whether the water is “safe” to drink!
- Taste & Odor issue is very subjective
- It could be more a “change in T&O” rather than having a new T&O compounds in the water
- Using consistent descriptors for T&O is key to an effective communication and control program



# T&O Wheel for Drinking Water



# Where do T&O Problems Come From?



# A Snap Shot of T&O Episodes

## Days with an episode:

💧 0-5:	18%
💧 6-10	20%
💧 11-15:	12%
💧 26-30:	10%

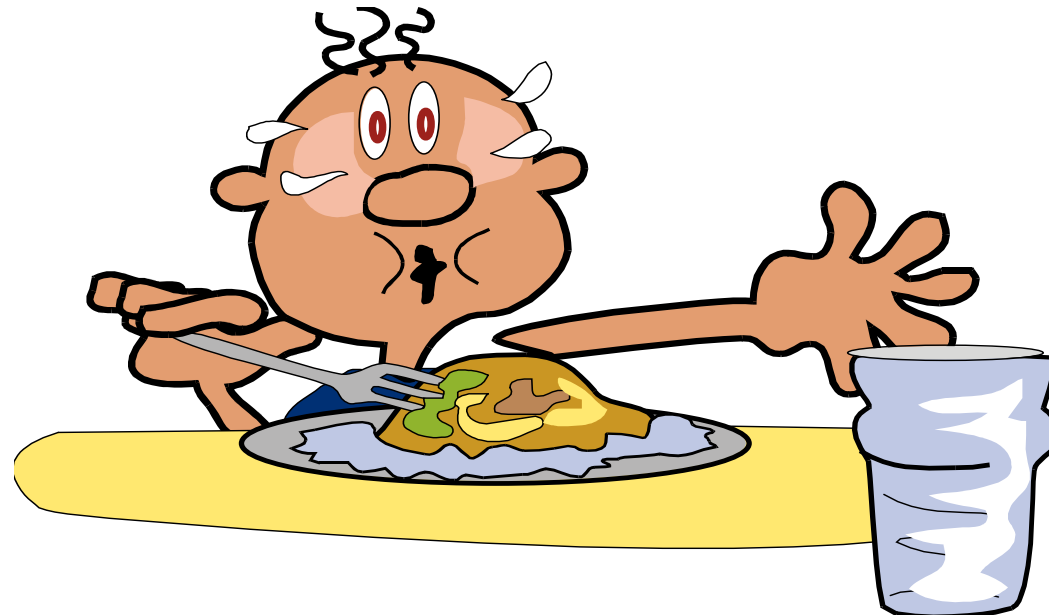
## Months of episode:

💧 September	49%
💧 August	45%
💧 July	42%
💧 October	36%
💧 June	34%
💧 April/Nov.	26%
💧 May	23%
💧 March	18%
💧 December	14%
💧 Jan./Feb.	8%

*Fall turnover seems to be the prime time for T&O events*

# A Survey on Types of Taste Complaints

1. Sour
2. Miscellaneous
3. Metallic
4. Bitter
5. Salty
6. Sweet



# A Survey on Types of Odor Complaints

1. Chlorinous
2. Earthy
3. Fishy
4. Medicinal
5. Chemical
6. Swampy
7. Grassy
8. Petroleum
9. Sulfidy
10. Septic





# Causation for T&O Complaints

## *In order of importance:*

1. **Distribution system**
2. **Disinfection process**
3. **Planktonic algae blooms**
4. **Reservoir turnover**
5. **Decaying vegetation**
6. **Bacterial growth**
7. **High mineral content**
8. **Benthic algae bloom**
9. **Synthetic organic chemicals**
10. **Industrial wastes**



# Detection of T&O Event

- Analytical Methods
  - *CLSA: Close Loop Stripping Analysis*
  - \$500 per sample
  - Takes 2 – 4 weeks to receive testing results
- People – sensory analysts
  - Although human senses are very sensitive, humans are more costly and difficult to control
  - Immediate testing results

# Selecting Right People for Sensory Testing

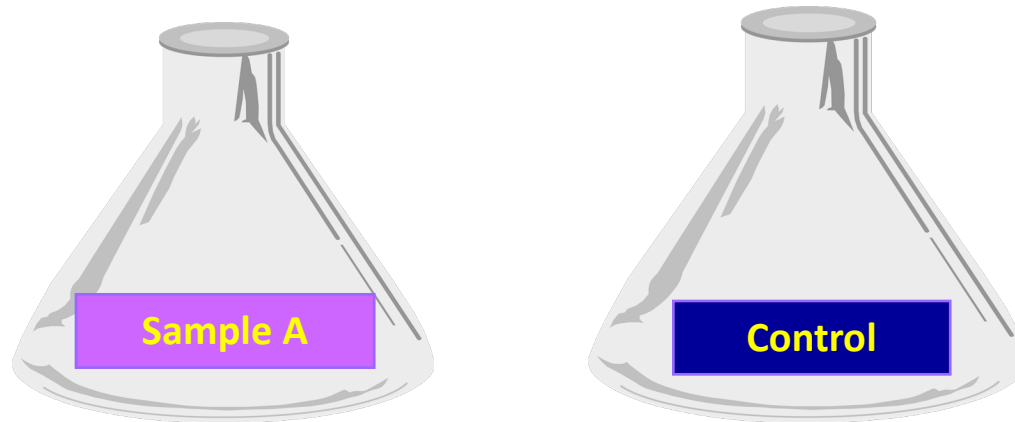
- Initially, all interested persons are qualified
- Orientation
- Test of overall smell ability
- Test for specific odor recognition and detection abilities
- Assessment and final selection
- Training
- In most cases the selected “Sensor” is selected from WTP Staff

# Sensory Methods for Drinking Water T&O Identification

- 💧 **TON** (Threshold Odor Number) --- Most commonly used
- 💧 **FPA** (Flavor Panel Assessment)
- 💧 **Attribute Rating**
- 💧 **Rating System for Distribution System**
- 💧 **2-out-of 5**

# Preparation for T&O Panel Testing & Selection

- Odor reference standards
- Taste/odor-free water
- Dedicated glassware for testing and sampling
- Clean testing room



# Threshold Odor Number (TON) Procedure: Label Flasks





# Identification Procedure

The analyst determines whether the test water and control water are different.



Swirl flasks before sniffing.



Sniff!

# Determine TON

$$\text{TON} = \frac{(\text{Sample Volume} + \text{Dilution Water Volume})}{\text{Sample Volume}}$$

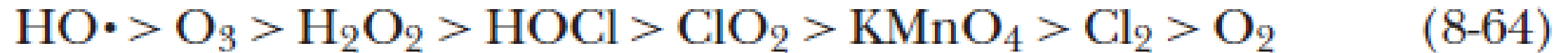
- **TON is a dilution number**
- Usually only one analyst performs the test
- EPA Secondary Standard TON = 3
- Current version published in 1965, 12<sup>th</sup> ed. *Standard Methods*

# Limitations of the Threshold Odor Number Method

- It IS NOT a measure of absolute odor strength.
- It IS a measure of odor persistence in a diluted sample.
- It does not focus on characterizing the odors.
- But, it is fast and inexpensive

# Typical Oxidation Process in Water Treatment

- Hydroxyl radical is the most powerful oxidant in common water treatment
- While  $\text{ClO}_2$  is a strong oxidant, its application is limited to chlorite concentration limit in the finished water (1 ppm)



# Commonly Seen AOP Processes (in the order of commonality)

- UV + H<sub>2</sub>O<sub>2</sub> (UV-Peroxide)
- Ozonation
- Ozone + Peroxide (PerOzone)
- UV + TiO<sub>2</sub> Catalytic Oxidation
- Fenton's Reactions
- UV/Chlorine AOP (fairly new)
- Electrode Oxidation (new to water treatment)

Note: While conventional disinfectant such as chlorine and chloramine are also oxidants, their oxidation power is not enough to oxidize organic synthetic chemicals

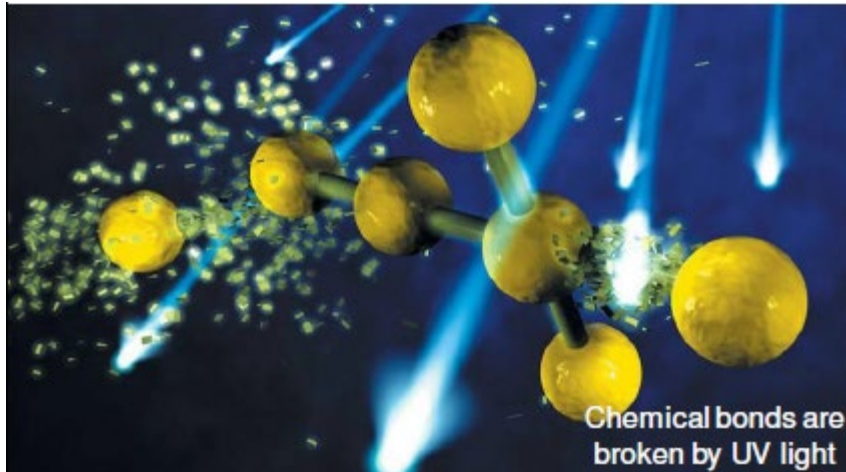


Liquid Oxygen (LOX) Tank  
for Ozone Generator

# Direct Oxidation v.s. Radical Oxidation

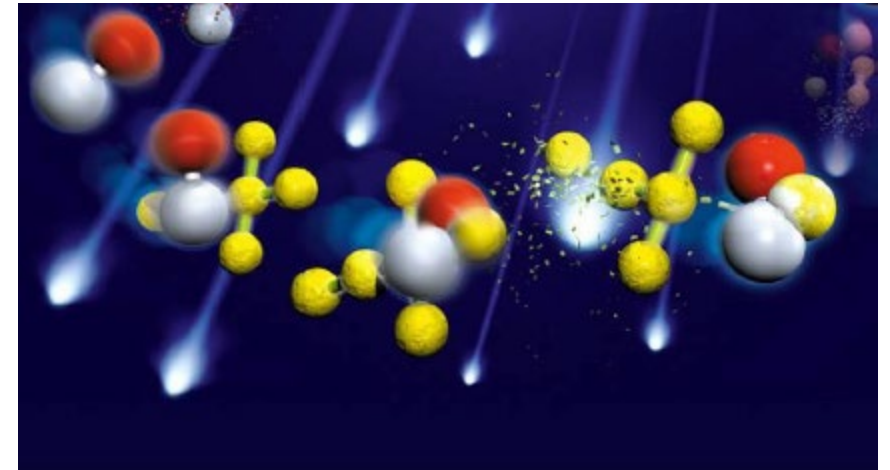
Destruction = Photolysis + Oxidation

Depends on  
Contaminant  
Characteristics



Weaker Oxidation

Oxidation occurs  
when peroxide or  
chlorine is added

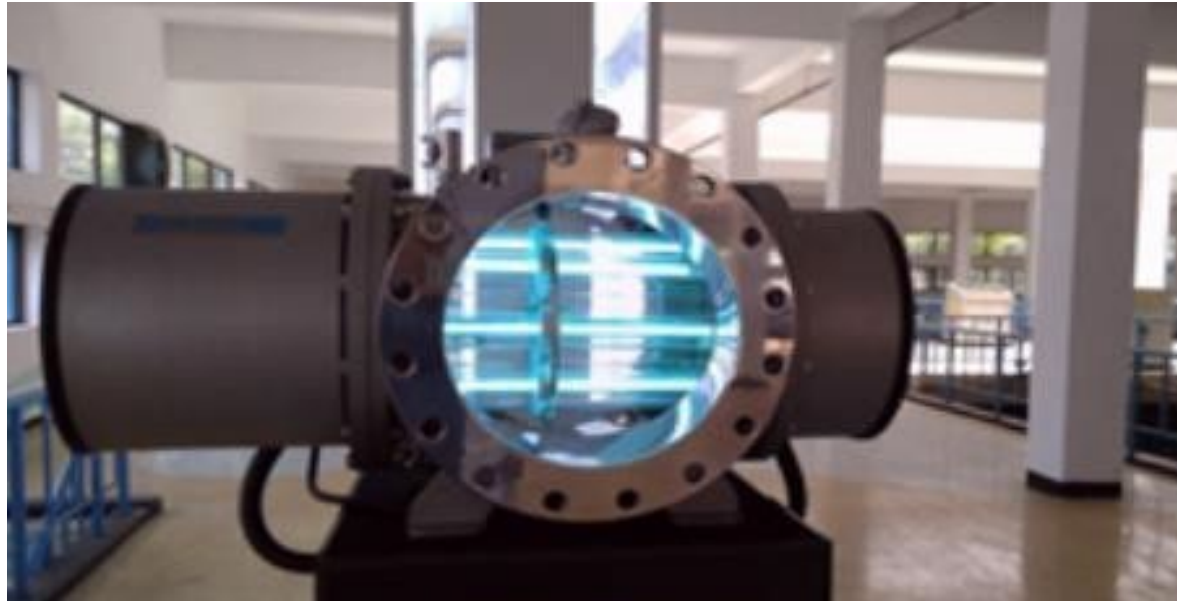


Stronger Oxidation



# Mechanisms of AOP

- Primary Mechanism: Hydroxyl Radicals  $\text{OH}^\bullet$
- Hydroxyl Radicals are very short lived ( $\sim 10 \mu\text{S}$ )
- It is NOT selective in terms of oxidation target



Orange County WD

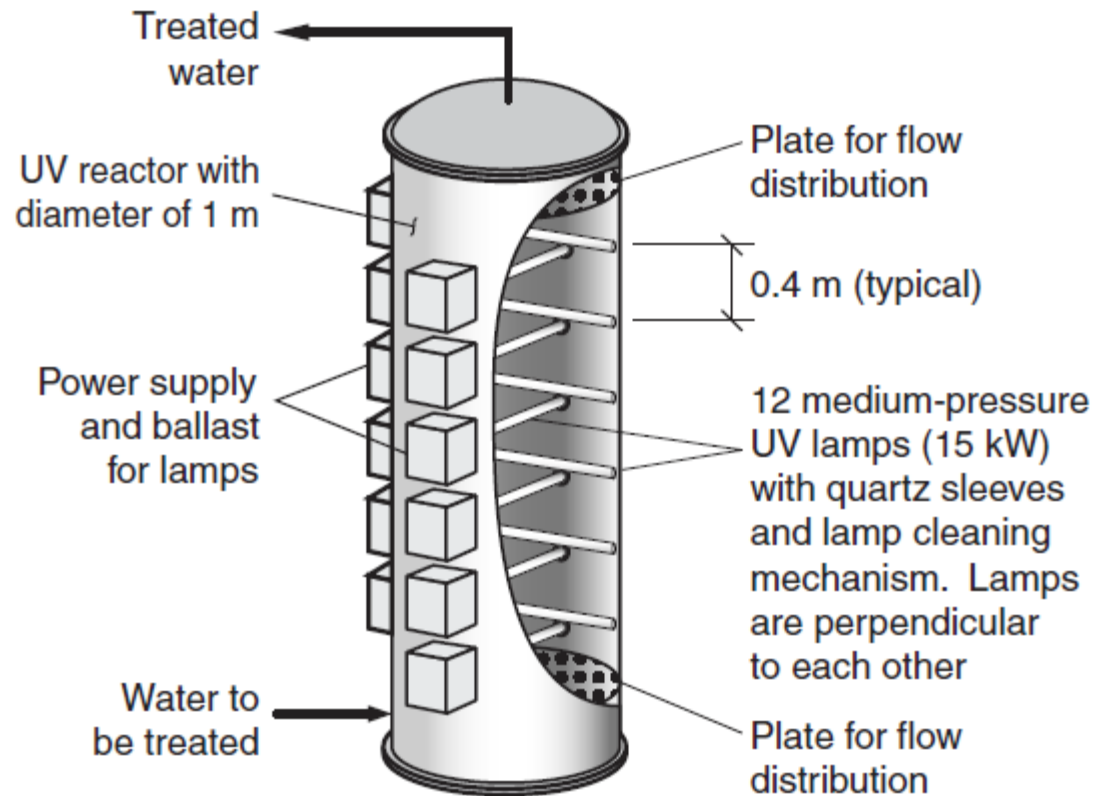
# Comparison of Oxidation Power for Various AOP Processes

Oxidizing Species	Relative Oxidation Power
Chlorine	1.00
Hypochlorous Acid	1.10
Permanganate	1.24
Hydrogen Peroxide	1.31
Ozone	1.52
Hydroxyl Radical	2.05

(Munter, 2001)

# UV/H<sub>2</sub>O<sub>2</sub> AOP Process

- UV/Peroxide process has been used in drinking water applications (100 mgd WTP at Lorne Park, Ontario, Canada)



# Calculations for UV/H<sub>2</sub>O<sub>2</sub> AOP Processes

- There are various “models” developed for UV/H<sub>2</sub>O<sub>2</sub> processes
- Required “UV Dose” depends on many factors, such as
  - Water pH and alkalinity
  - Presence of other “radical scavengers”, such as Fe, Mn, NOM, etc.
  - UV reactor design (proprietary information per UV system manufactures)
    - Lamp position
    - Number of lamps
    - Type of Lamps
    - Location of UV dosage monitor
- In reality, UV dosage is determined by UV manufacturers based on “Log Reduction Desired” for specific contaminants

# Concept of EE/O; Electrical Efficiency per Log Order Reduction

- 1 EE/O = 90% Reduction; 2 EE/O = 99% Reduction
- EE/O describe the required energy (in kWh) for 1-log reduction of contaminant for 1,000 US Gallon (3,785 L)

$$\text{EE/O} = \frac{P \times t}{V \times \log(C_i/C_f)} \quad (8-129)$$

$$\text{EE/O} = \frac{P}{Q \times \log(C_i/C_f)} \quad (8-130)$$

where EE/O = electrical efficiency per log order reduction,  
kWh/m<sup>3</sup> = 3.785 kWh/10<sup>3</sup> gal

$P$  = lamp power output, kW

$t$  = irradiation time, h

$V$  = reactor volume, m<sup>3</sup>

$C_i$  = initial concentration, mg/L

$C_f$  = final concentration, mg/L

$Q$  = water flow rate, m<sup>3</sup>/h

UV Lamp Output will  
reduce over time

# Potential Problems Associated with AOP

- Only 10 – 15% of  $\text{H}_2\text{O}_2$  is consumed in the UV/Peroxide reaction
  - Will require additional process to remove residual peroxide from the finished water
- Using chlorine to quench peroxide is a common practice, but costly
- Using proprietary catalytic GAC (from Calgon) is another viable option
  - Region of Peel 100 mgd membrane filtration plant
- Potential solution: using unintentional Biologically Active Filter (BAF) for peroxide quenching is possible

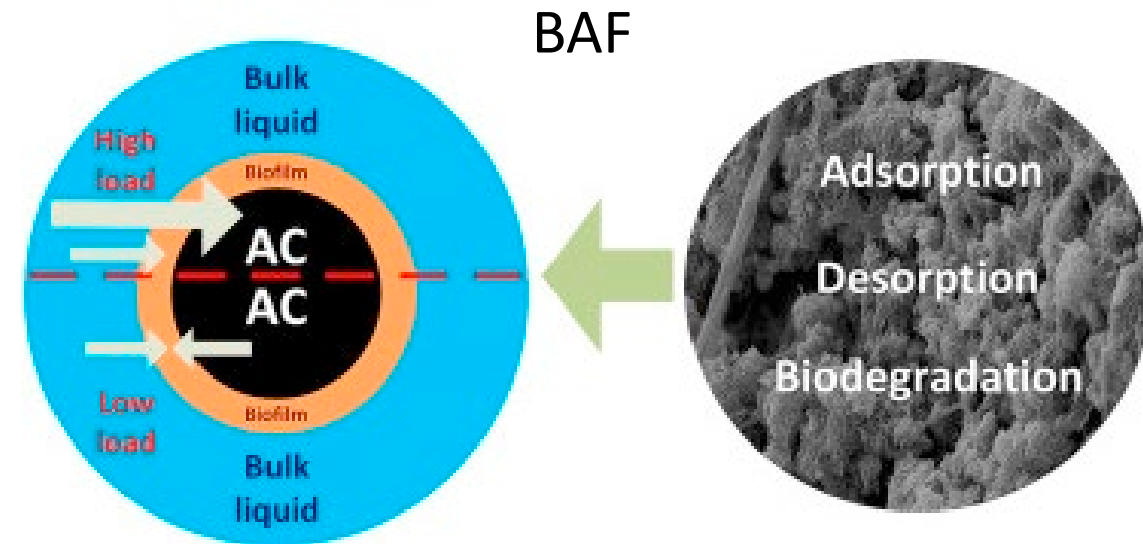


# AOP Will Generate “Food” for Biological Growth

- Produce oxidation by-products that can be assimilated by microbes
  - Assailable Organic Carbon (AOC) or Bio-Degradable Organic Carbon (BDOC)
    - Present in micrograms per liter ( $\mu\text{g/L}$ )
    - Causing excessive biological growth in the distribution system
- Usually require additional treatment processes to remove these small organic molecules
  - Using Biologically Active Filters (BAF) downstream is a common practice, which requires substantial experience in design and operation to maintain a healthy BAF

# Biologically Active Filter (BAF)

- Use GAC or Anthracite to serve as breeding ground for biofilms
- GAC can adsorb contaminants and incur a high surface concentration of contaminants
- Bacteria grow on the surface of substrates and utilize adsorbed contaminants as food source
- BAF requires special system design and operation/maintenance in order to maintain proper performance

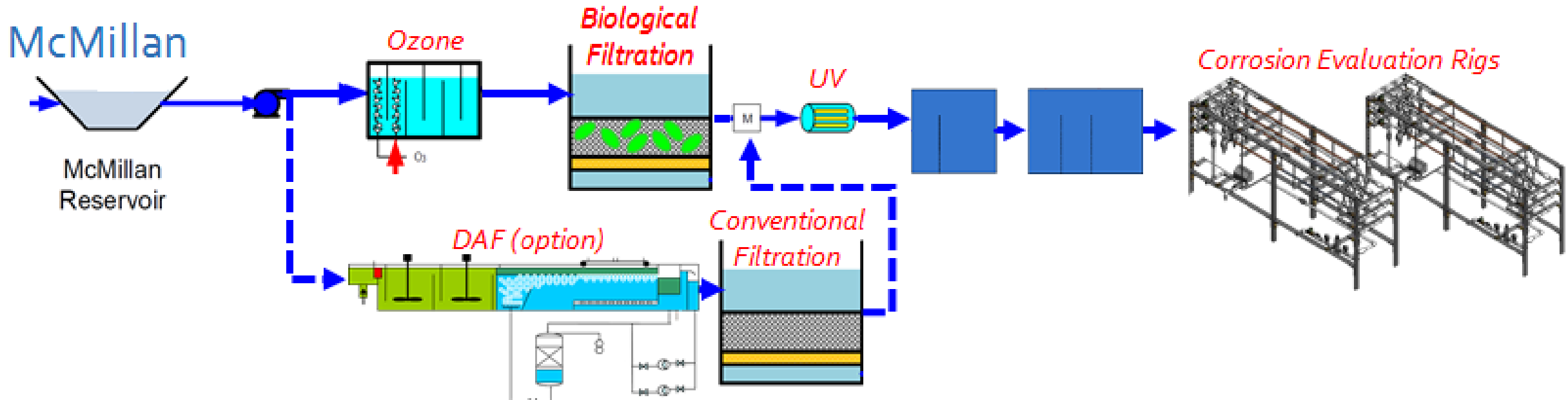


# Design Considerations for a Biological Filter

- Select proper filter media, either GAC or Anthracite (maximizing surface area for biological growth)
- Potential nutrient feeding system (e.g., acetic acid) for low organic season to maintain biological activity
- Occasional backwashing with low-Cl concentration to control excessive bio growth
- Proper underdrain design to avoid clogging by sloughed-off biomass
- Filter media sampling for occasional microbial speciation

# Example of Ozone/BAF Application

- Washington Aqueduct Ozone/BAF Pilot Project
- Convert from conventional to Ozone/BAF due to T&O Control
- Need to consider Distribution System Corrosion Control



# PFAS is A Class of Emerging Contaminants

## Per- and Polyfluoroalkyl Substances

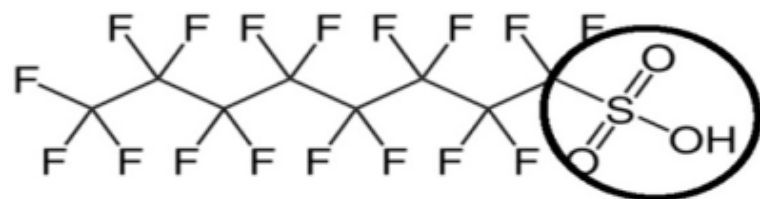
- **Per**fluoroalkyl Acids (**PFAAs**) , perfluorinated chemicals (**PFCs**)  
= all carbon atoms fully fluorinated (no hydrogen atoms)



**PFOA** (perfluorooctanoic acid )

A member of Perfluoroalkyl Carboxylates (**PFCAs**)

*Soluble and Persistent!*

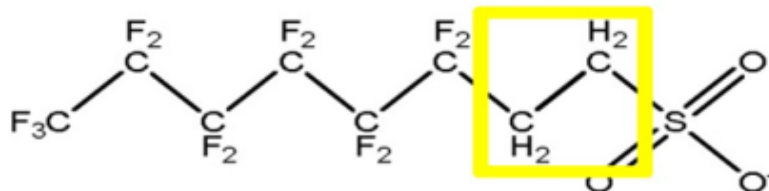


**PFOS** (perfluorooctane sulfonate)

A member of Perfluoroalkyl Sulfonates (**PFSAs**)

**DO NOT BIODEGRADE**

- **Poly**fluorinated = some carbons are not fully fluorinated (have H)



6:2 Fluorotelomer Sulfonate (**FtS**)

*May Transform into PFAAs*

- **Precursors** are those which can be transformed to PFCAs and PFSAs as terminal products

More than 3000 PFAS are, or have been, on the global market, < 35 detected

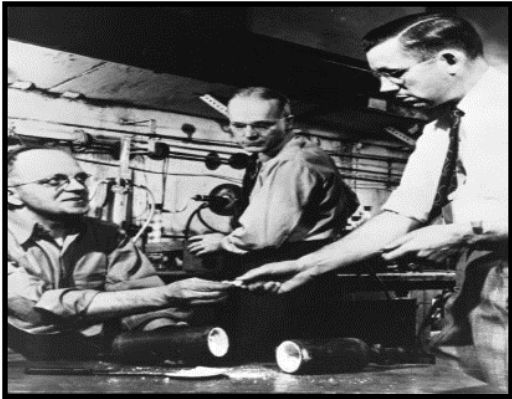
# PFAS History

1930's

1940's

1950's

1960's



**Teflon accidentally discovered in 1938, and introduced by DuPont in 1949**



**Teflon used in the Manhattan Project for the development of the atomic bomb**



**Consumer and industrial products (e.g., Teflon)**



**Aqueous Film Forming Foam (AFFF) is developed**

# PFAS History

1970's



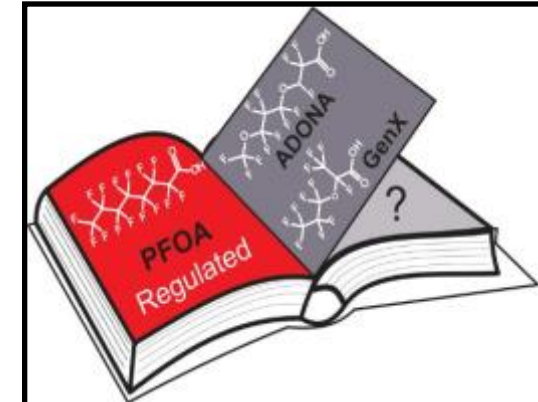
**Use of PFAS  
significantly expands  
in different industries**

2000's



**Global distribution of certain  
PFAS in biota**  
**Voluntary phase out of products**

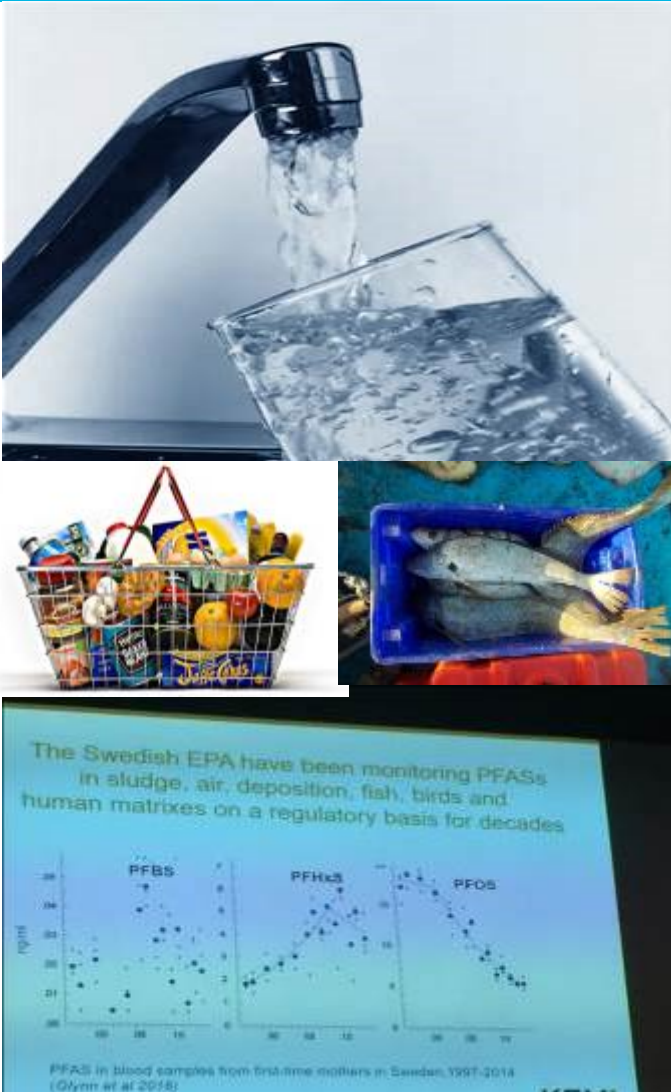
Current



**Increase public scrutiny  
Changing regulatory climate  
Lawsuit settlements  
Development and use of new PFAS**



# Potential PFOS and PFOA Health Effects



- Cancer effects
  - Suggestive evidence for kidney and testicular cancer (USEPA)
- Non-cancer effects
  - Increased serum cholesterol levels
  - Increased liver enzymes
  - Increased liver weight
  - Endocrine/thyroid effects
  - Decreased birth weights
- Adult – 60-80% of PFAS is from food + water\*
- Children – 40-60% from hand-to-mouth transfer from treated products\*
- Accumulates in serum protein, kidney and liver

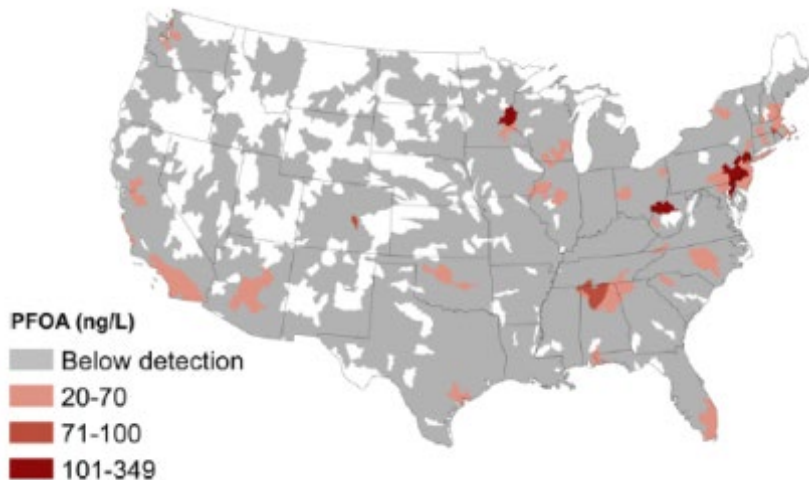
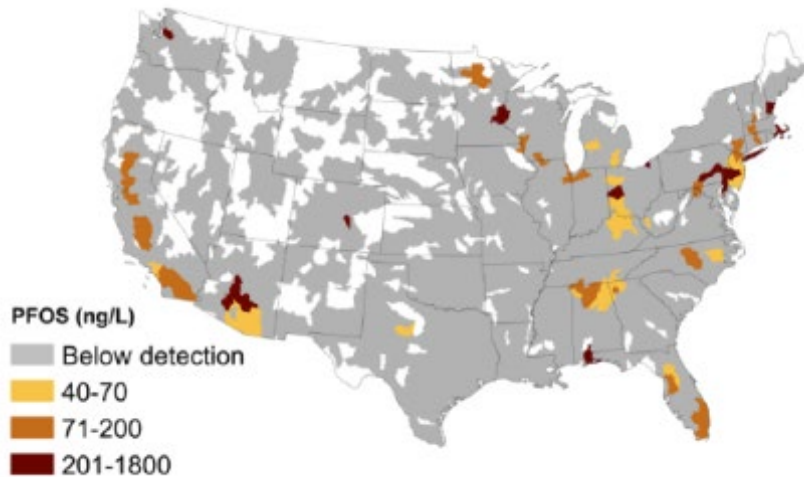
\* ATSDR Draft Toxicological Profile for PFAS Chapter 5 (2015)

# Where Do We Find PFAS?

- Uses
  - Surface treatments: Scotchgard™, non-stick cookware (Teflon®) and all weather clothing (Gore-tex®)
  - Mining & oil surfactant, vapor suppression additives for metal plating baths
  - Aqueous film forming foams (AFFF) used for firefighting
- Potential sources
  - Fire training facilities
  - Major airports
  - Metal plating
  - Landfills
  - **Untreated groundwater and wastewater discharges**
- DOD stated that it will no longer use PFAS in training, and will declare the use of a Hazardous Material when it needs to be used in emergency



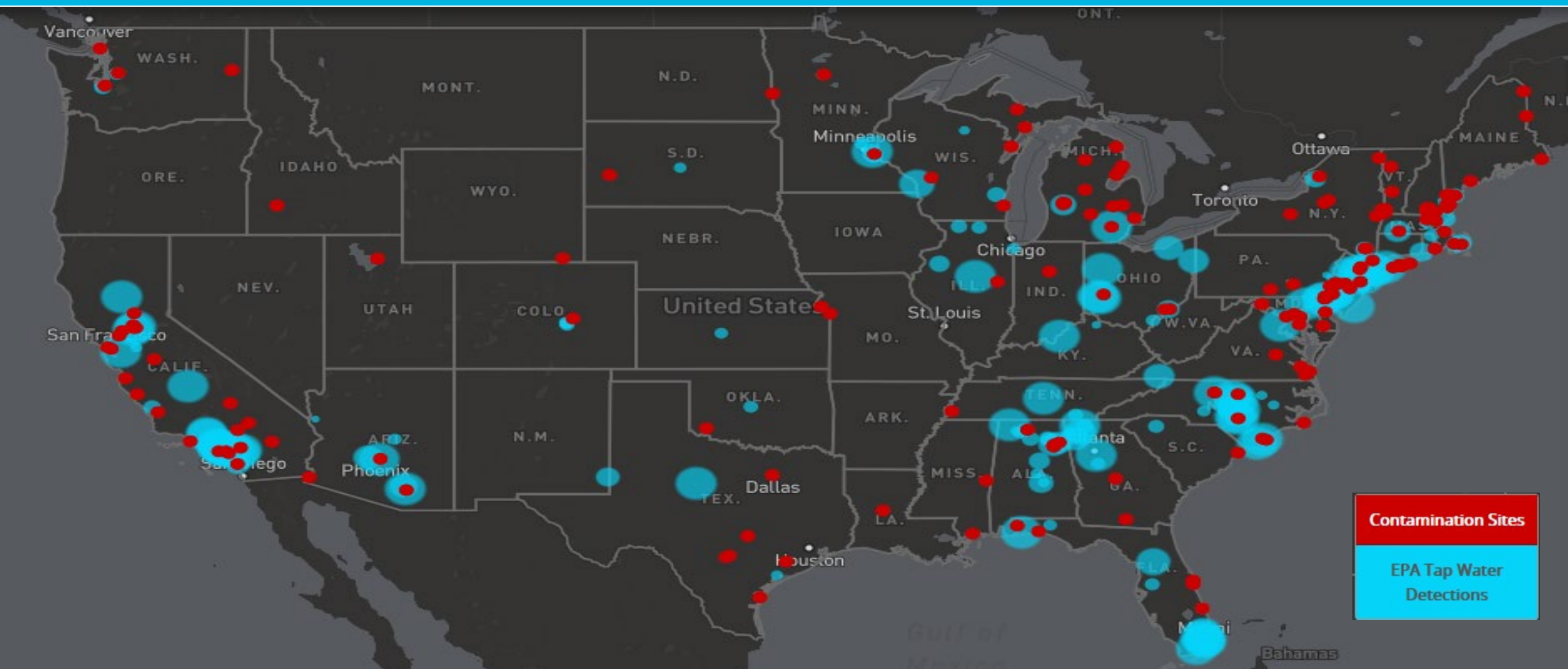
# PFAS Occurrence in US (EPA UCMR3)



## Point Sources Included:

- 16 industrial sites listed in EPA's PFOA Stewardship Program
- 8,572 WWTP
- 664 military fire training sites
- 533 civilian airports
- 6 M. US residents receive PWS exceeds 70 ng/L (Current USEPA Health Guidance)
- ~1,500 drinking water systems in 40 States

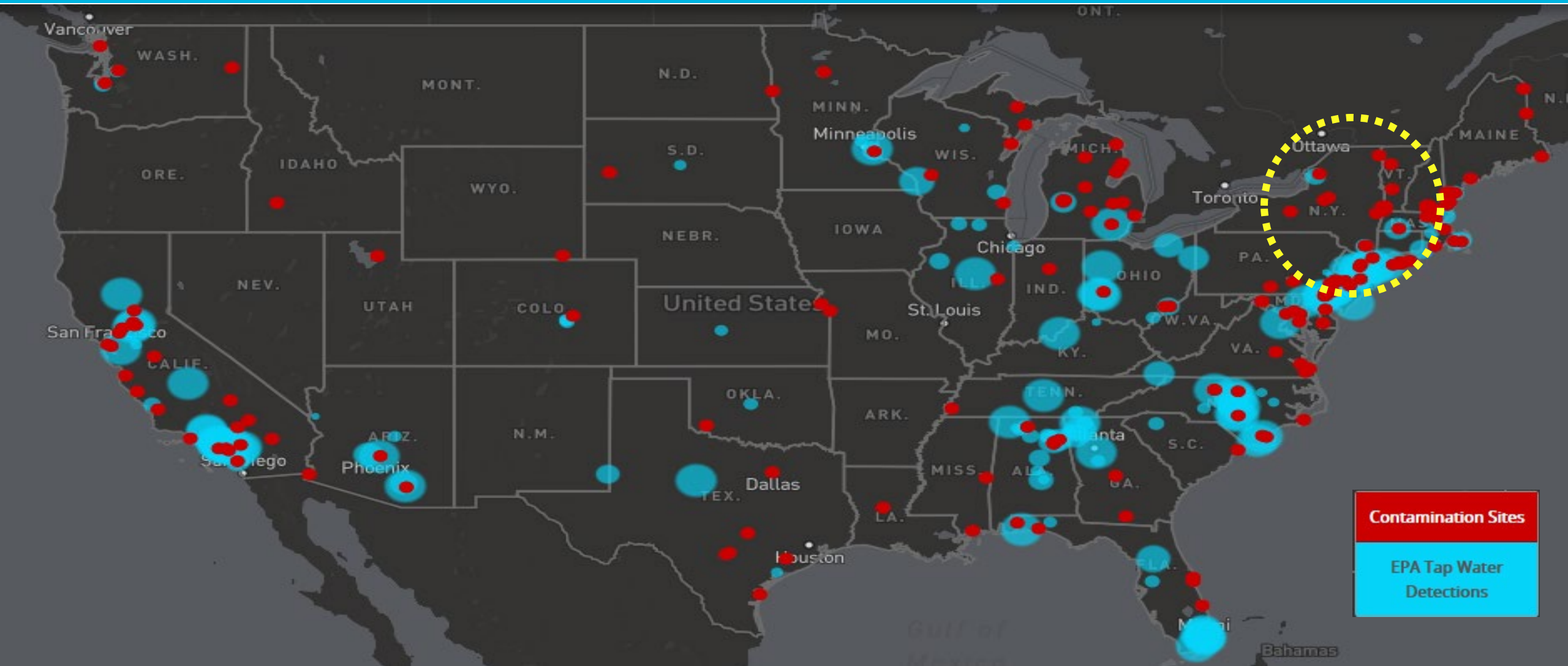
# Updated PFAS Impact Map in July 2018



*Courtesy of the Environmental Working Group 2018*

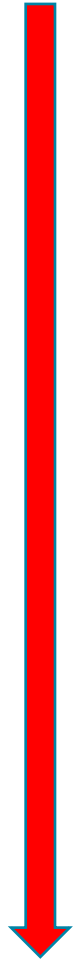


# Updated PFAS Impact Map in July 2018



*Courtesy of the Environmental Working Group 2018*

# Evolving Regulatory Guidance/Standards

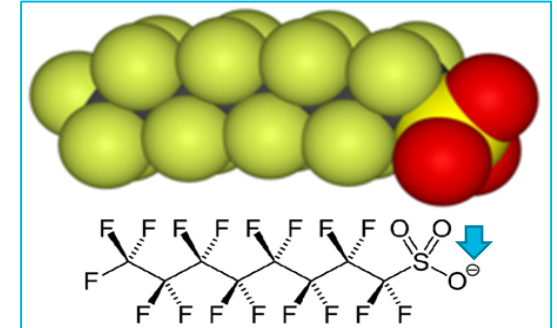


Authority	Guidance or MCL
USEPA	Guidance: 70 ppt PFOA, PFOS, PFOA+PFOS
Michigan	Cleanup Level: 70 ppt PFOA, PFOS, PFOA+PFOS
Colorado	Site Specific Groundwater Standard: 70 ppt for PFOA/PFOS
Connecticut	70 ppt total of PFHxA + PFHpA + PFOA + PFNA
Minnesota	Action Level: 35 ppt, 27 ppt PFOS
Vermont	MCL: 20 ppt PFOA+PFOS
New Jersey	MCL: 14 ppt PFOA; Draft MCL 13 ppt PFOS Proposed MCL:13 ppt PFNA (accepted)
California	07/13/2018 CA's DDW issued Drinking water NL of 14 ppt for PFOA and 13 ppt for PFOS.

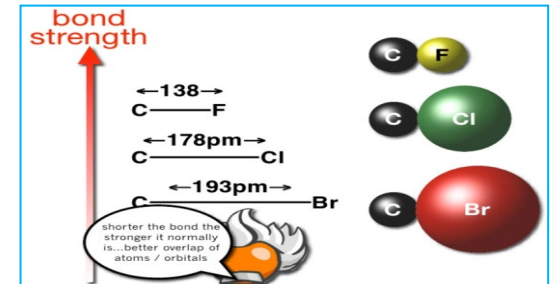
# C-F bond is the shortest and strongest bond in chemistry

- C-F bond is extremely strong; the strongest bonding in chemistry
- Molecule is stable in acids, bases, oxidants, and heat
- Relatively high solubility and low volatility
- PFAAs are not biodegradable

Negatively charged under most environmental conditions



Strong C-F Bond



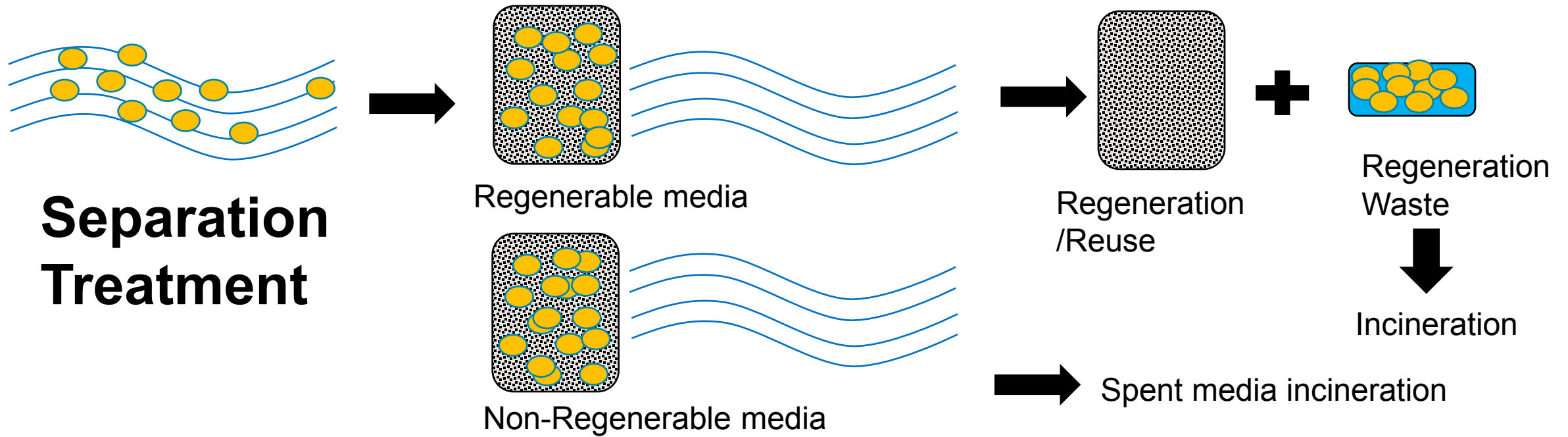
High C-F Bond Energy

Single Bond Energies (kJ/mol of bonds)										
	H	C	N	O	S	F	Cl	Br	I	
H	436									
C	413	346								
N	391	305	163							
O	463	358	201	146						
S	347	272	—	—	226					
F	565	485	283	190	284	155				
Cl	432	339	192	218	255	253	242			
Br	366	285	—	201	217	249	216	193		
I	299	213	—	201	—	278	208	175	151	

Chemical Properties	PFOA	PFOS	TCE	Benzene
Solubility (mg/L) (20-25°C)	3,400-9,500	519	1,100	1,780
Vapor Pressure (25°C) mmHg	0.5-10	2.48x10 <sup>-6</sup>	77.5	97



# Separation & Destruction Technologies



## Destruction Treatment



# GAC Treatment for PFOA at WV.

- Lead/lag treating PFOA to treat PFAS from  $< 1 \mu\text{g/L}$  to  $22 \mu\text{g/L}$
- GAC changeout criteria: **15 ng/L (lag beds)**
- Annual O&M of \$1.4MM for 8 PSDs (total  $\sim 0.4 \text{ mgd}$ )

Treatment Location	Influent PFOA Concentration ( $\mu\text{g/L}$ )		Operating Time Between Changeout (Months)			Total Volume Treated (million gallons)
	min	max	min	max	average	
PWS-1	0.138	0.49	4	11	8	2,948
PSW-2	0.19	1.2	2	6	4	420
PWS-3	1.8	14	2	4	3	2,150
PWS-4	0.24	1.3	2	10	5	2,121
PWS-5	0.0119	0.107	4	22	7	3,454
PWS-6	$<0.001$	0.021	6	17	12	627
PWS-7	$<0.0032$	0.041	6	18	11	395
PWS-8	0.0035	$<0.021$	10	13	12	660
<b>Total Volume Treated*</b>						<b>12,775</b>

# Challenge for Existing Treatment Technologies: Residual

- Convert PFAS from liquid phase to solid phase
  - WTP sludge (ferric & aluminum sludge)
  - Spent GAC
  - Spent IXR
- Convert PFAS from liquid phase to gas phase
  - Incineration of spent GAC & IXR
- PFAS still resides in the environment



# Effectiveness of Current Technologies

Which criteria do they currently meet?

## *Criteria*

1. meeting current low ppt treatment goals
2. life cycle management experience
3. potential to treat more PFAS compounds than currently regulated
4. potential to achieve lower criteria than current criteria
5. All waste streams can be collected, monitored and managed

GAC

1,2,4,5

IX-R

1,2,3,4,5

Reverse Osmosis

1,2,5

Ozone Fracturation

3,4

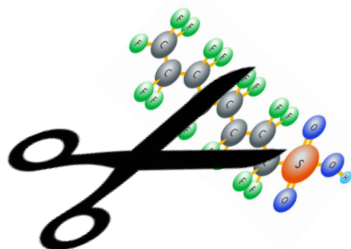
AOP

2,5

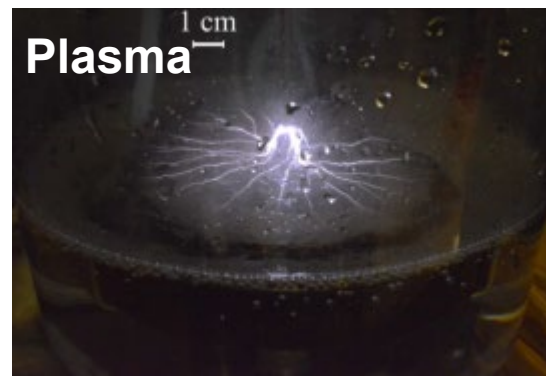
EO

1,3,4,5

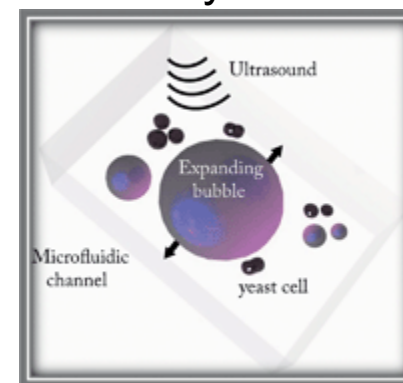
# Emerging PFAS Destruction Technologies



- Thermal technologies
- UV Photolysis
- Advanced oxidation
- Ozone Fractionation
- Electrochemical oxidation
- Sonolysis
- Plasma



Sonolysis



- PFAS destroyed on site
- Eliminate offsite incineration
- Reduce liabilities permanently

Under Development  
and Pilot

# Special Patented Electrodes

## $\text{SnO}_2$ -, $\text{RuO}_2$ - or $\text{PbO}_2$ -based hybrid electrodes

- Not effective for PFOS
- Limited life time
- Dissolution of toxic metals

## Boron Doped Diamond (BDD) electrode

- Effective for PFOA and PFOS
- Inconsistent results
- Expensive, not scalable
- Fragile on silicon base

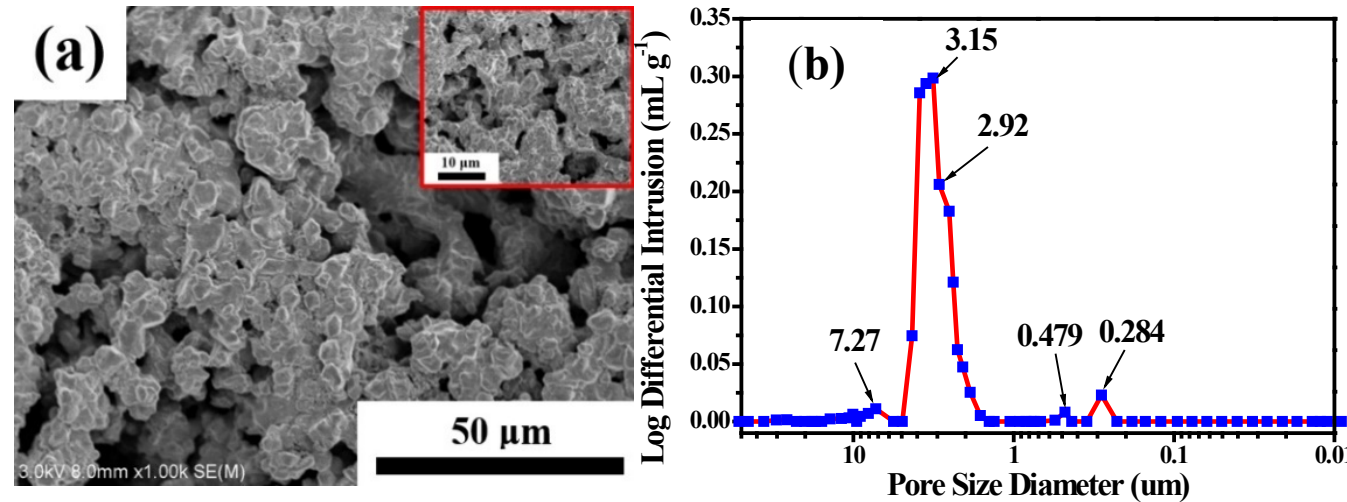
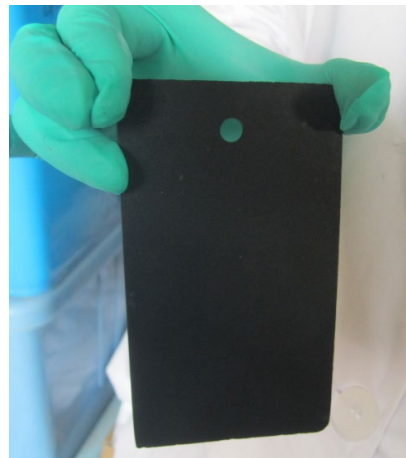
## UGA Electrode

Effective for PFOS and PFOA

- Physically and chemically stable
- Excellent electrochemical performance
- Cost-effective, scale-up applications are available

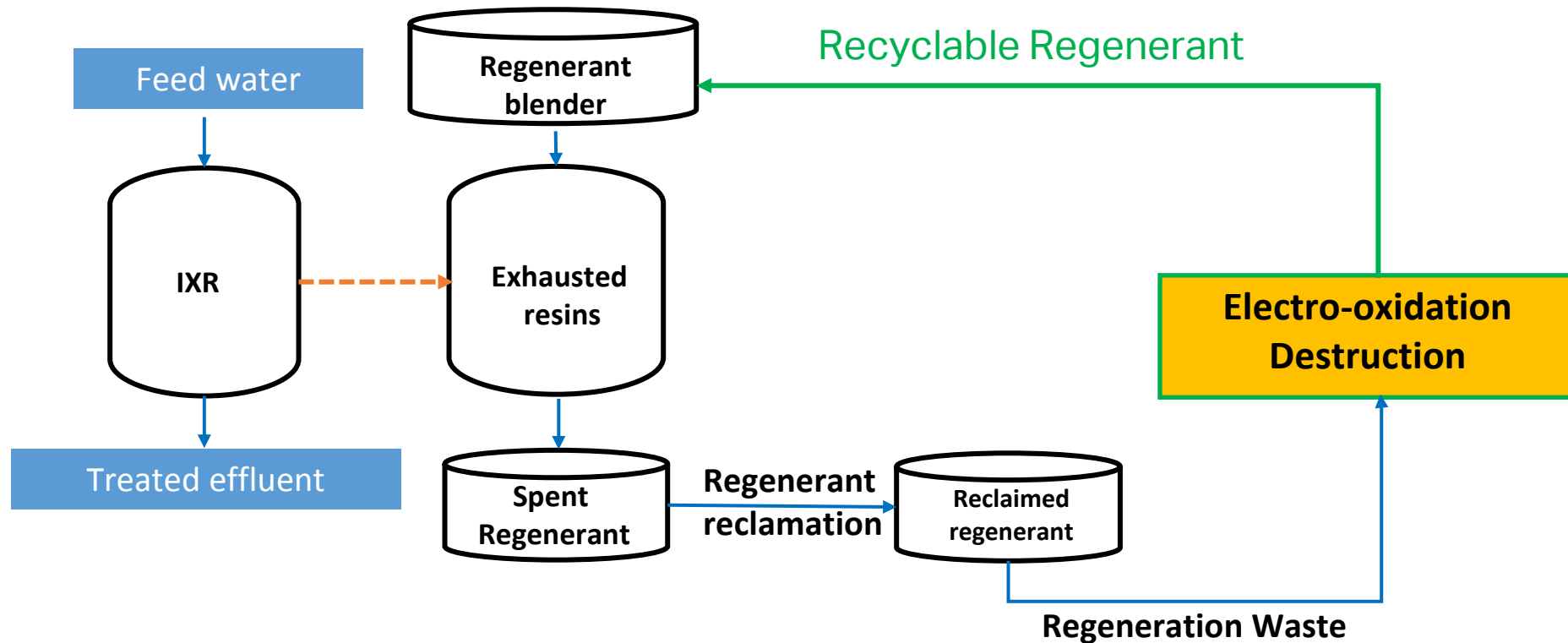


Inexpensive non-toxic oxide powder



# Coupling separation and destruction

## Coupling Ion Exchange Resin with Electrochemical Oxidation

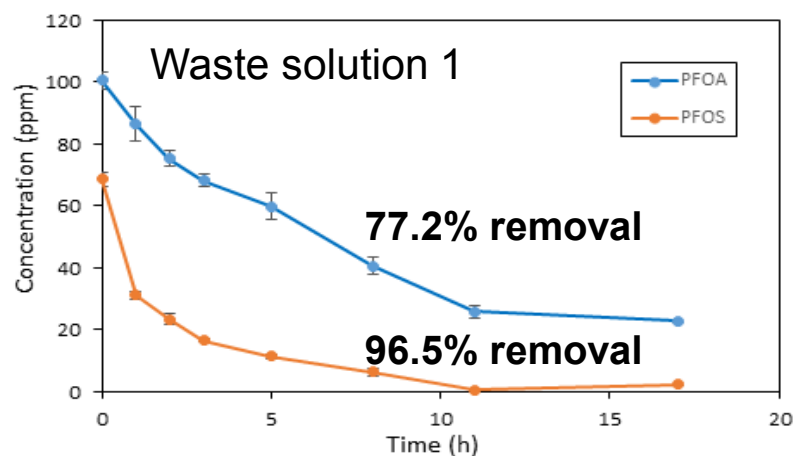


Regeneration requires solvent & 6% salt

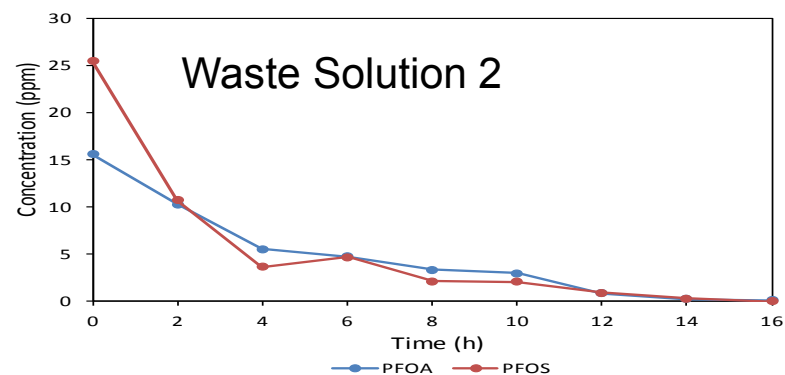
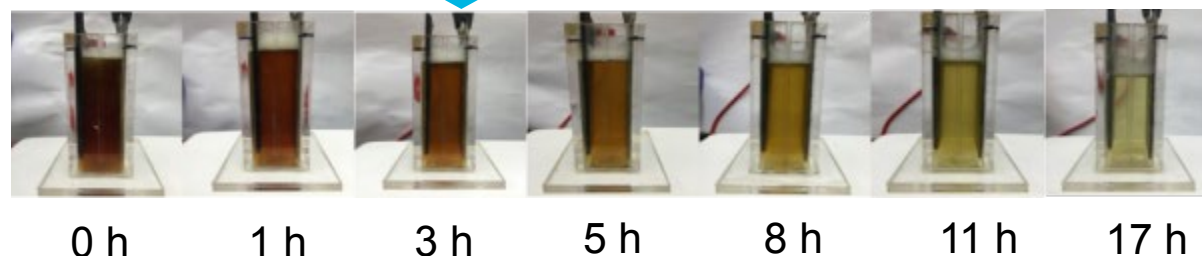


# Coupling Ion Exchange Resin and EO

TOC (ppm)	Conductivity ( $\mu\text{S}/\text{cm}$ )	PFOA (ppm)	PFOS (ppm)	PFHxS (ppm)	PFHxA (ppm)	PFHpA (ppm)	PFPeA (ppm)	PFBS (ppm)
7861	2939	100.5	68.6	55.1	18.7	10.2	5.3	1.9



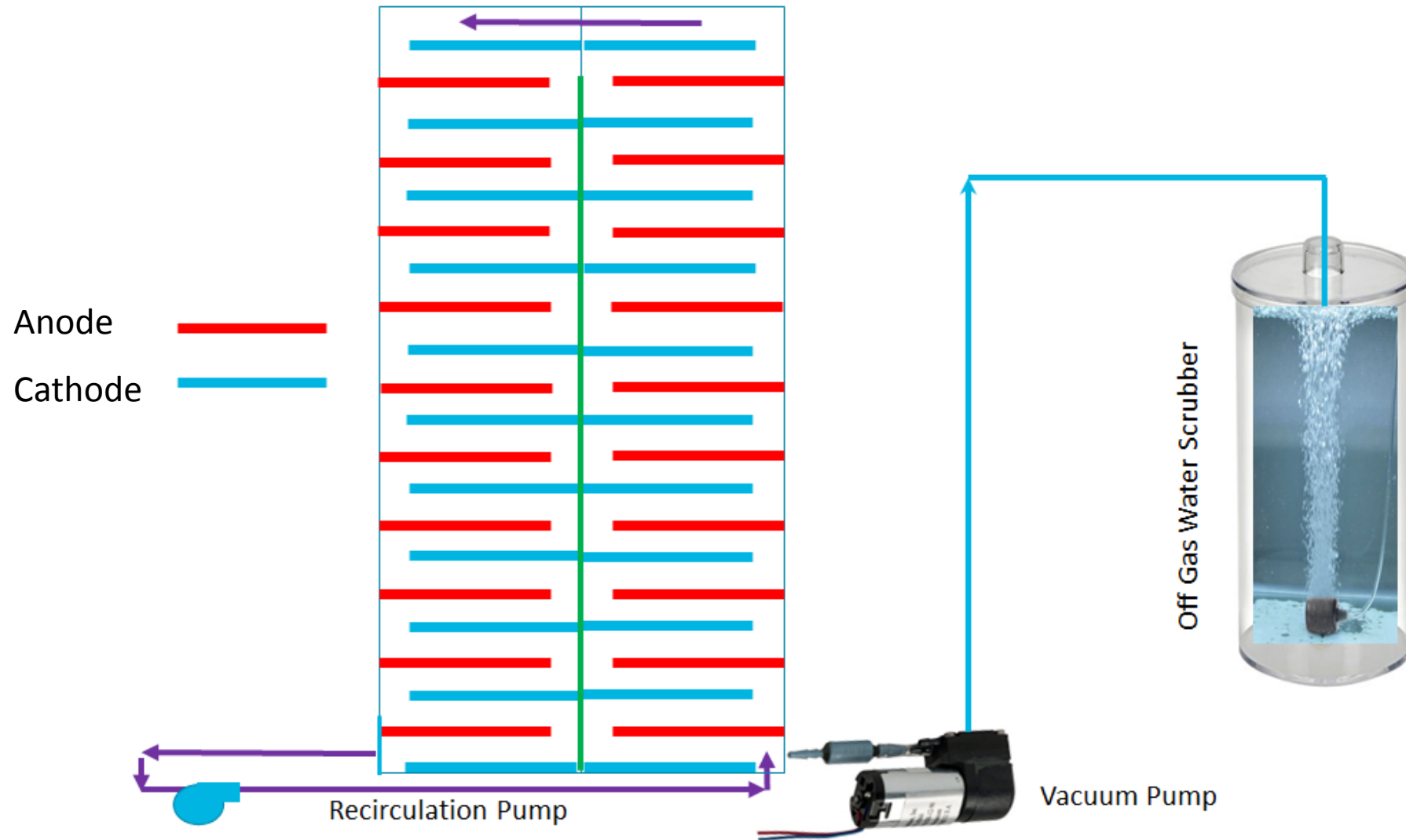
Ion exchange resin was used to treat PFOS/PFOA, regeneration process generated the regeneration waste for this study



	Fluoride (ppm)	Chloride (ppm)
T0	1	3534
17-HR sample	836	2874

Test condition  
 Current density: 10 mA/cm<sup>2</sup>  
 Cell voltage: 7.0 V  
 pH: 12.0 (initial), 9.0 (final)

# Basic Concept of EO Pilot System



# AECOM EO Pilot Unit



# Preliminary Pilot Shows Promising Results

- Spiked solution tested in March 2018
- Achieved **95%** destruction
- AECOM team is currently optimizing pilot system design to enhance performance

## Next Steps:

- Develop facility requirements and implementation plan
- Develop preliminary level capital and life cycle costs

