Per- and Polyfluoroalkyl Substances (PFASs): Chemistry, Occurrence, Regulation, Mobility and Remediation

Remediation Technologies Symposium 2016

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ch2m℠

Per- and Polyfluoroalkyl Substances Introduction

- Heat, oil, stain, and grease resistant coatings
  - Clothing
  - Furniture
  - Food packaging
  - Non-stick cooking surfaces
  - Electrical wire insulation
- Fluorosurfactants
  - **Aqueous film-forming foam (AFFF)**
    - **Electrochemical vs fluorotelomer based**
  - Chromium plating mist suppressants
  - Photolithographic chemicals
  - Many other uses

PFASs Chemistry

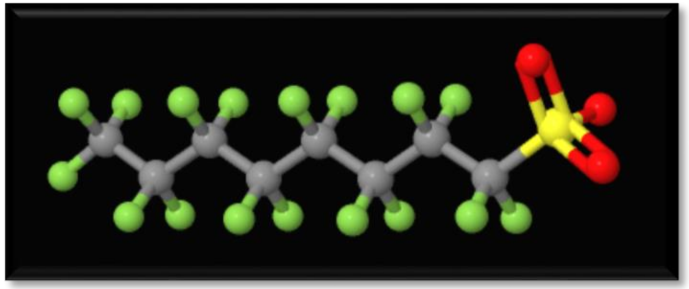
- Stable, recalcitrant, mobile
- Hydrophobic and oleophobic
- C8 Panel identified effects on human health:

Ulcerative colitis	High cholesterol	Pregnancy-induced hypertension
Thyroid disease	Testicular Cancer	Kidney cancer

- Half-life in humans 5.4 years for PFOS and 3.8 years for PFOA

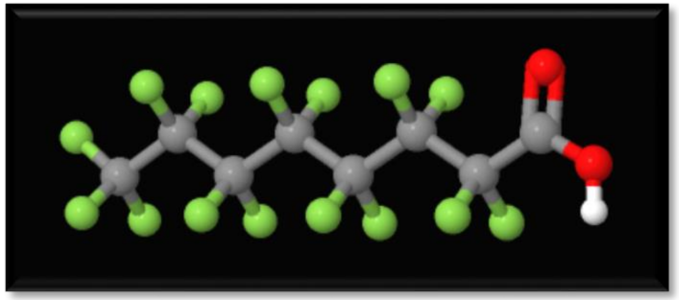
Perfluorooctane sulfonate (PFOS)

$C_8HF_{17}O_3S$



Perfluorooctanoic acid (PFOA)

$C_8HF_{15}O_2$



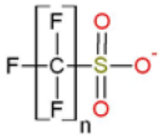
Images from Chemspider.com

PFASs Chemistry (Cont'd)

Perfluoroalkyl Carboxylates[L]

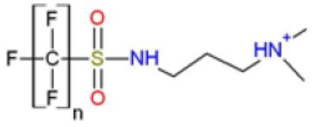
PFPrA	n = 2
PFBA	n = 3
PFPeA	n = 4
PFHxA	n = 5
PFHpA	n = 6
PFOA	n = 7
PFNA	n = 8
PFDA	n = 9
PFUdA	n = 10
PFDoA	n = 11
PFTrA	n = 12
PFTeA	n = 13

Perfluoroalkyl Sulfonates[L]



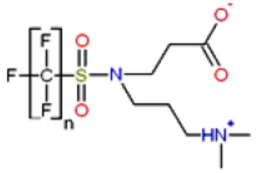
PFEtS	n = 2
PFPrS	n = 3
PFBS	n = 4
PFPeS	n = 5
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFNS	n = 9
PFDS	n = 10

Perfluoroalkyl Sulfonamido Amines[N]



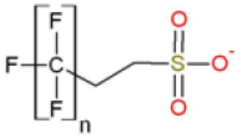
PFPrSaAm	n = 3
PFBSaAm	n = 4
PFPeSaAm	n = 5
PFHxSaAm	n = 6
PFHpSaAm	n = 7
PFOSaAm	n = 8

Perfluoroalkyl Sulfonamide Amino Carboxylates[N]



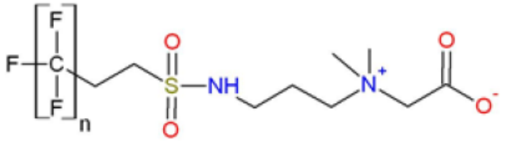
PFPrSaAmA	n = 3
PFBSaAmA	n = 4
PFPeSaAmA	n = 5
PFHxSaAmA	n = 6
PFHpSaAmA	n = 7
PFOSaAmA	n = 8

Fluorotelomer Sulfonates[L]



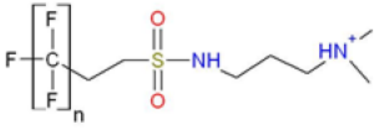
4-2 FtS	n = 4
6-2 FtS	n = 6
8-2 FtS	n = 8

Fluorotelomer Sulfonamido Betaines[N]



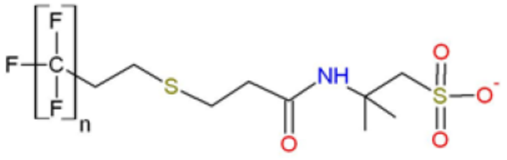
4-2 FtSaB	n = 4
6-2 FtSaB	n = 6
8-2 FtSaB	n = 8
10-2 FtSaB	n = 10
12-2 FtSaB	n = 12

Fluorotelomer Sulfonamido Amines[N]



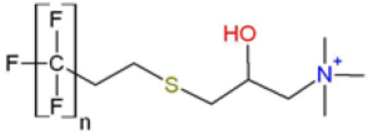
4-2 FtSaAm	n = 4
6-2 FtSaAm	n = 6
8-2 FtSaAm	n = 8
10-2 FtSaAm	n = 10

Fluorotelomer Thio Amido Sulfonates[N]



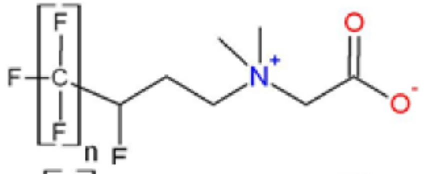
4-2 FtTAoS	n = 4
6-2 FtTAoS	n = 6
8-2 FtTAoS	n = 8
10-2 FtTAoS	n = 10
12-2 FtTAoS	n = 12
14-2 FtTAoS	n = 14

Fluorotelomer Thio Hydroxy Ammonium[N]

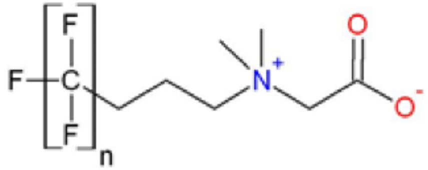


6-2 FtTHN^{+}	n = 6

Fluorotelomer Betaines[N]



5-1-2 FtB	n = 5
7-1-2 FtB	n = 7
9-1-2 FtB	n = 9



5-3 FtB	n = 5
7-3 FtB	n = 7
9-3 FtB	n = 9

After Backe, et al, 2013; Place and Field, 2012; D'Agostino and Maybury, 2014; and Barzen-Hanson and Field, 2015

PFASs Chemistry

- Quantification is by LC-MS/MS, QTOF
- BUT we only detect a subset of PFASs, the rest are precursors
- PFASs accumulate at surfaces, including glassware
- Perfluoroalkyl portions are stable, functional groups are not
- Precursors transform to PFOS and PFOA through oxidation or biologically
- No "standard" method for precursors
- Total Oxidizable Precursors (TOP) Assay
- Total organic fluorine detection
- Combustible ion chromatography

PFASs Chemistry

- ISO 25101:2009 and US EPA Method 537 (+/- mod) use LC-MS/MS
- Australian National Association of Testing Authorities (NATA) Accreditation
  - ALS, Eurofins, Envirolab
  - Some using in house modified methods
- US DOD ELAP Certified labs
  - Method 537 (DW): TestAmerica, Maxxam, SGS Accutest, Weck, ALS, Jupiter
  - Method 537 MOD (GW, soils, sediment): Vista, AXYS, Eurofins, Jupiter
- Issues with branched vs linear isomers
  - Some labs calibrated with linear only but site samples have both
  - Results could be off by 30-40%
  - US EPA Technical memorandum last month addresses this

WORLD RECOGNISED ACCREDITATION

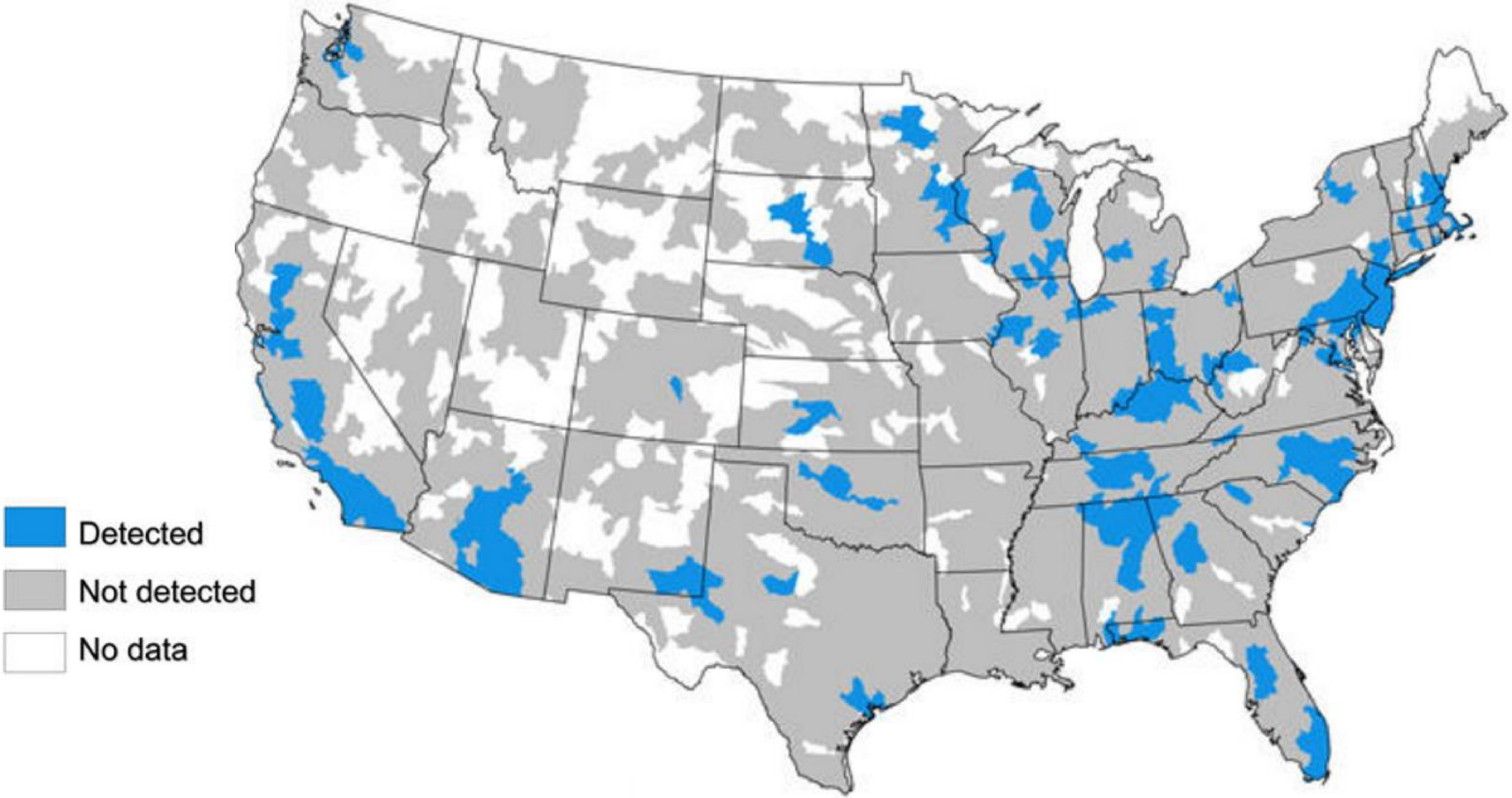
PFAS Sampling Interferences

- CH2M working with Hope College using Total Organic Fluorine test (PIGE) and OSU using LC-MS/MS analysis
- Assessment of Total Organic Fluorine performed on 169 objects, including
  - Sampling equipment, pumps, tubing
  - Paper/notebooks/note pads/paper towels
  - Permanent markers, labels
  - Duct tape, packing tape, plastic bags
  - Fast food wrappers, sunscreen, bug spray
- Results for both tests will be compared
- Publication in early 2017

OSU Oregon State UNIVERSITY

HOPE COLLEGE

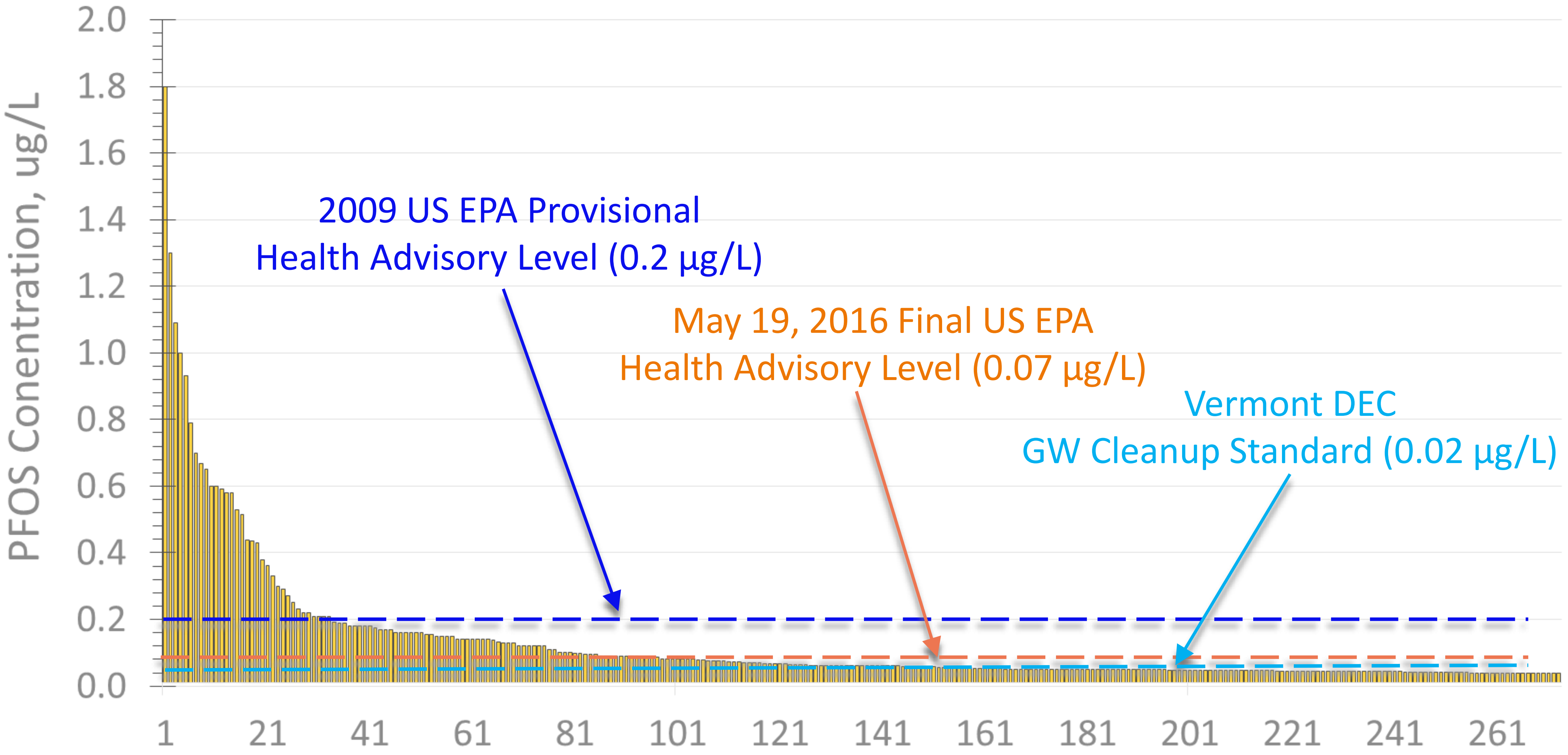
PFASs Occurrence in US Drinking Water Hydrologic Basins



(After Hu, et al, 2016)

US Drinking Water Analytical Results (January 2016)

273 Detections out of 35,060 Analyses = 0.8% Detection Rate



(USEPA, March 2016)

Canadian Standards

Drinking Water Screening Values for 9 Perfluoroalkyl Substances (PFAS) for Human Consumption (Health Canada, 2016)		
	PFAS name	DWSV (mg/L)
1	Perfluorooctanoic acid (PFOA)	0.0002
2	Perfluorooctane sulfonate (PFOS)	0.0006
3	Perfluorobutanoate (PFBA)	0.03
4	Perfluorobutane sulfonate (PFBS)	0.015
5	Perfluorohexanesulfonate (PFHxS)	0.0006
6	Perfluoropentanoate (PFPeA)	0.0002
7	Perfluorohexanoate (PFHxA)	0.0002
8	Perfluoroheptanoate (PFHpA)	0.0002
9	Perfluorononanoate (PFNA)	0.0002
Notes: DWSV - Drinking Water Screening Value, Health Canada, 2016		

Representative International Drinking Water Screening Levels

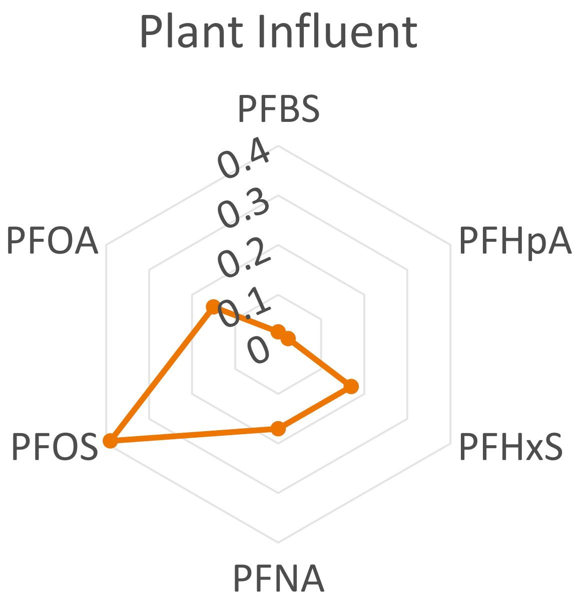
Country / Type (year) (µg/L)	PFOA	PFOS	Other PFAS
Australia / interim drinking water values (2016) Australia / recreational water quality guideline (2016)	5 50	0.5 5	PFHxS
Canada / drinking water screening value (2016)	0.2	0.6	PFBA, PFBS, PFHxS, PFPeA, PFHxA, PFHpA, PFNA
Denmark / health-based criteria (2015); if all 3 present, sum of ratios of conc: SL should be <1.	0.3	0.1	0.1 (PFOSA)
Germany / precautionary value, long-term (2006)	0.1 (PFOA + PFOS)		
Netherlands / provisional DW standard (2010)		0.53	
Sweden / maximal tolerable level (2014)	0.09 (sum of 7 PFAS)		PFHxS, PFBS, PFHpA, PFHxA, PFPeA
UK / DW quality guideline (2009)	10	0.3	

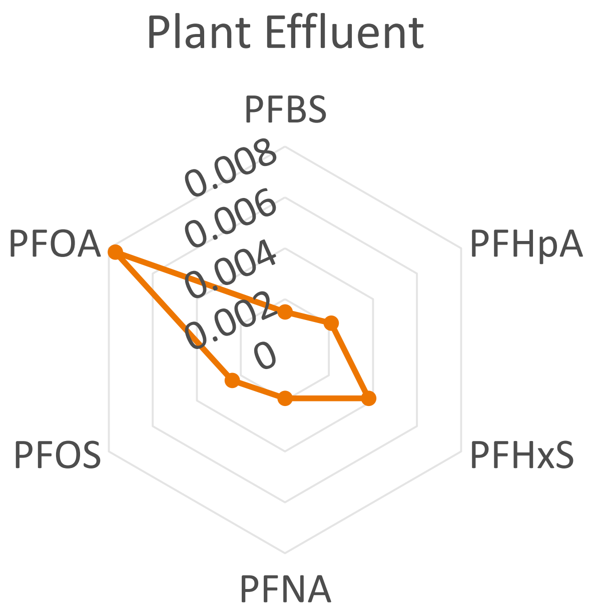
Alternative Foams to AFFF

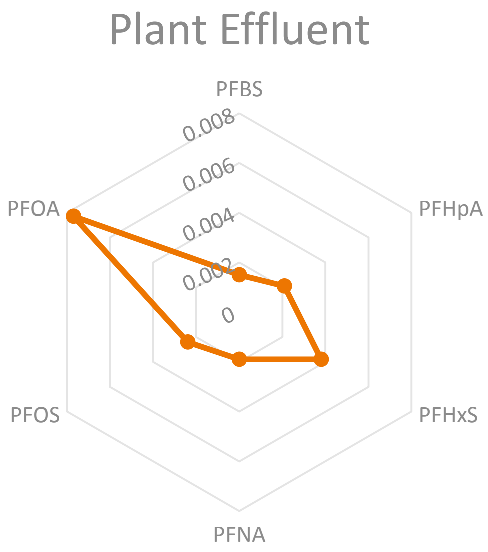
- US Refineries, tank farms, and petrochemical industry storing ~10-20 million litres of AFFF
- 6:2 Fluorotelemer-based products less toxic and less bioaccumulative; but are they safe?
- Fluorine Free Foams (F3) much less effective (4x slower, 4x more foam needed, faster burnback), and includes greater proportion of surfactants/detergents

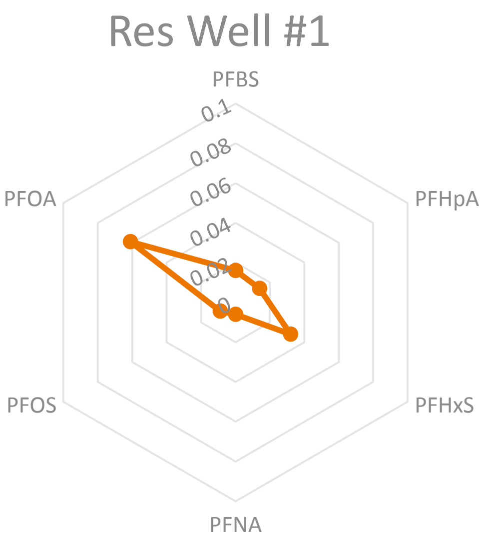
- Some regulatory guidance suggests F3 can be safely washed into streams, but huge BOD load from organics can be detrimental

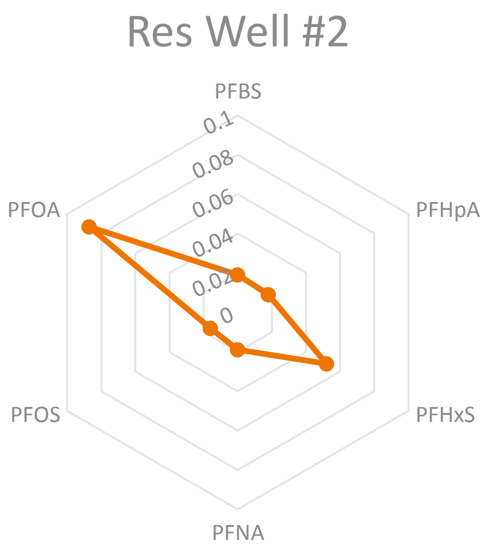
PFAS Treatment/Distribution

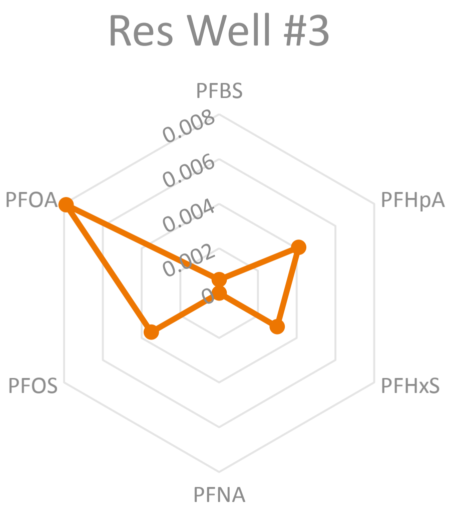


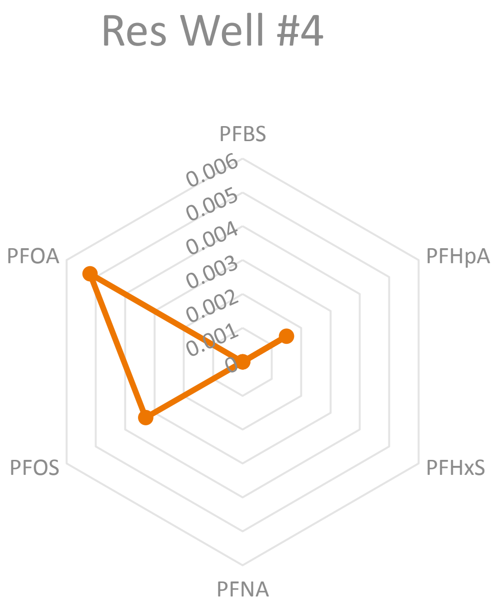


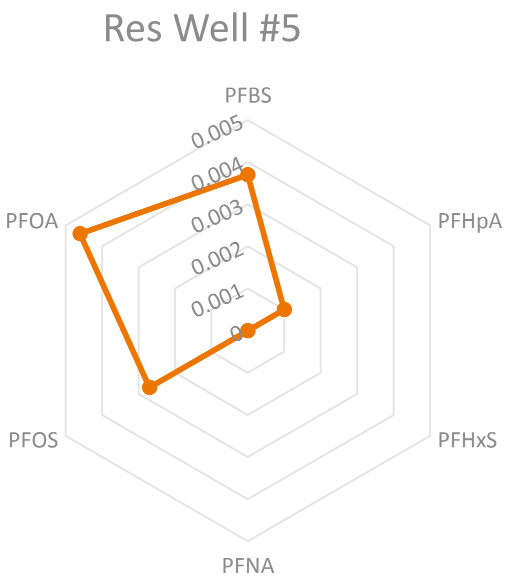

Plant Effluent
PFBS
PFHpA
PFHxS
PFNA
PFOS
PFOA
0.008
0.006
0.004
0.002
0


Res Well #1
PFBS
PFHpA
PFHxS
PFNA
PFOS
PFOA
0.1
0.08
0.06
0.04
0.02
0


Res Well #2
PFBS
PFHpA
PFHxS
PFNA
PFOS
PFOA
0.1
0.08
0.06
0.04
0.02
0


Res Well #3
PFBS
PFHpA
PFHxS
PFNA
PFOS
PFOA
0.008
0.006
0.004
0.002
0


Res Well #4
PFBS
PFHpA
PFHxS
PFNA
PFOS
PFOA
0.006
0.005
0.004
0.003
0.002
0.001
0


Res Well #5
PFBS
PFHpA
PFHxS
PFNA
PFOS
PFOA
0.005
0.004
0.003
0.002
0.001
0

PFAS Treatment Technologies

Soil Remedial Technologies

Ex situ options have been demonstrated:

- Isolation/Capping
- Excavation with offsite disposal in landfill
- Excavation with offsite incineration (>1,100° C)

In situ technologies somewhat demonstrated:

- Stabilization/sorption:
  - RemBind (Ziltek's activated carbon, activated alumina, kaolin clay)
  - Plume Stop (Regenesis' colloidal biomatrix)
  - MatCare (CRC CARE's amine-modified clay)

Soil Treatment Results

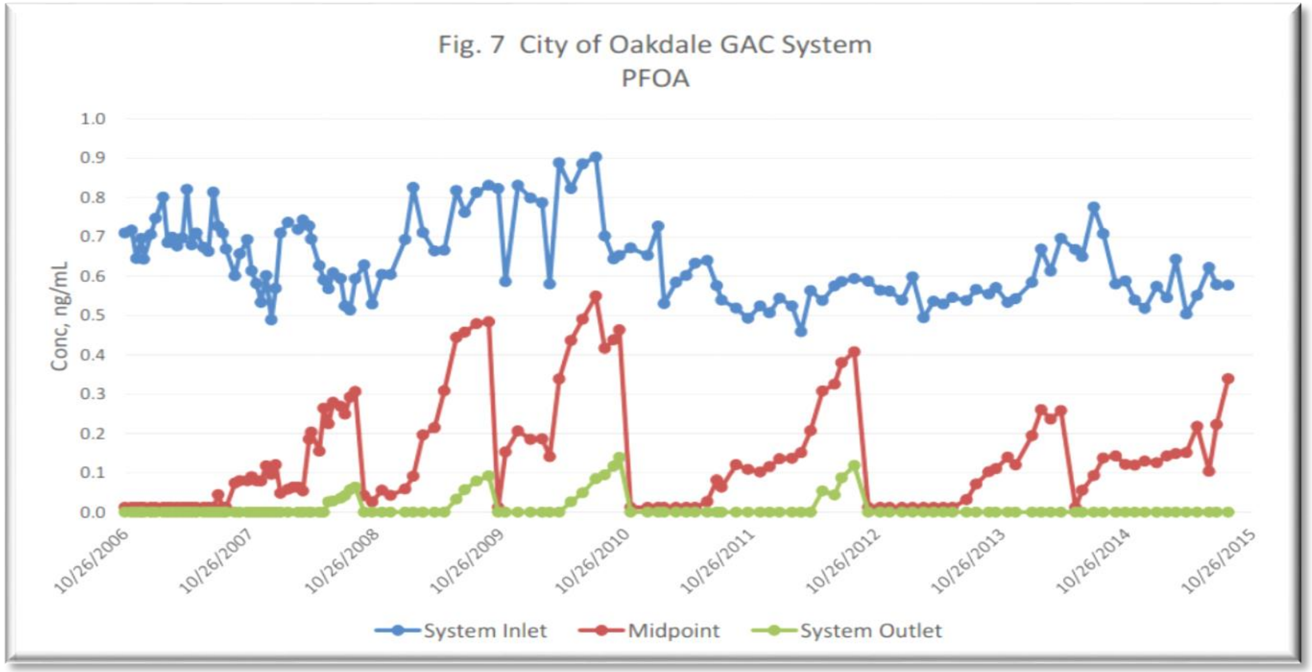
	PFOS* µg/L	PFOS % Reduction	PFOA* µg/L	PFOA % Reduction
Control	62.5	-	2.7	-
RemBind	0.39	99%	0.12	95%
RemBind Plus	<0.02	>99%	<0.02	>99%

*Australian Standard Leaching Protocol

http://www.ziltek.com.au/pdf/Z082-03_RemBind_Case_Study_PFOS_web.pdf

Water Technologies - Sorption

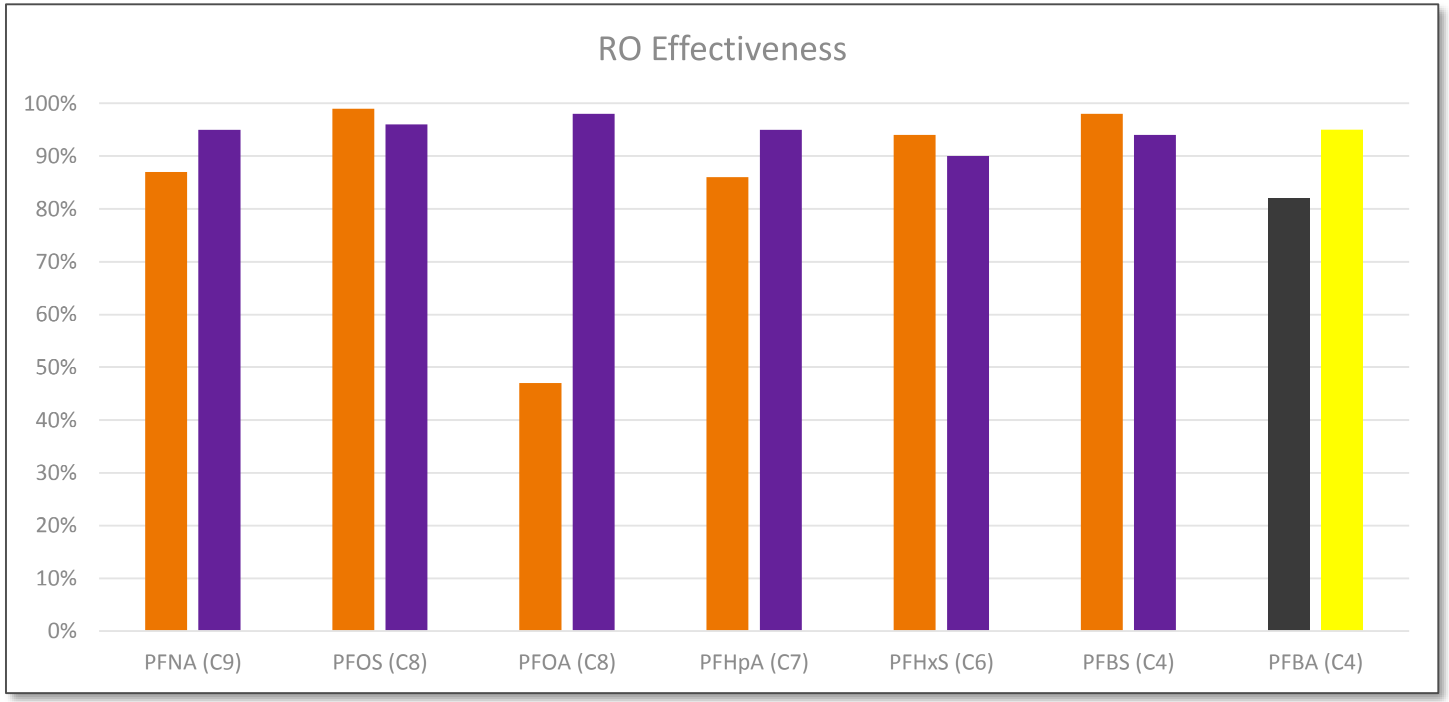
- Sorption technologies: GAC, PAC, MatCare, RemBind, PlumeStop
- Most tests validated with only PFOS/PFOA, less effective with short-chains



- ECT2 working with Dow anion exchange resins
  - Evidence of sorption of PFOS, PFOA, short-chain PFASs and precursors
  - Field pilot studies scheduled in 2016

Water Technologies - Filtration

- Reverse osmosis (RO) has been shown to be effective in several studies
- Ultrafiltration/microfiltration less effective
- Short-chain PFASs effectively filtered
- Down side is dealing with reject stream



(After Appleman, et al, 2014)

Water Technologies - Chemical Oxidation

- C-F chain resistant to oxidation, bonds are blocked by the F atoms
- Marginally effective on PFOS/PFOA
- Transforms precursors to PFOS
- Persulphate used for the Total Oxidizable Precursor Assay
- May require production of super oxides, as well as reductants

Berkeley UNIVERSITY OF CALIFORNIA

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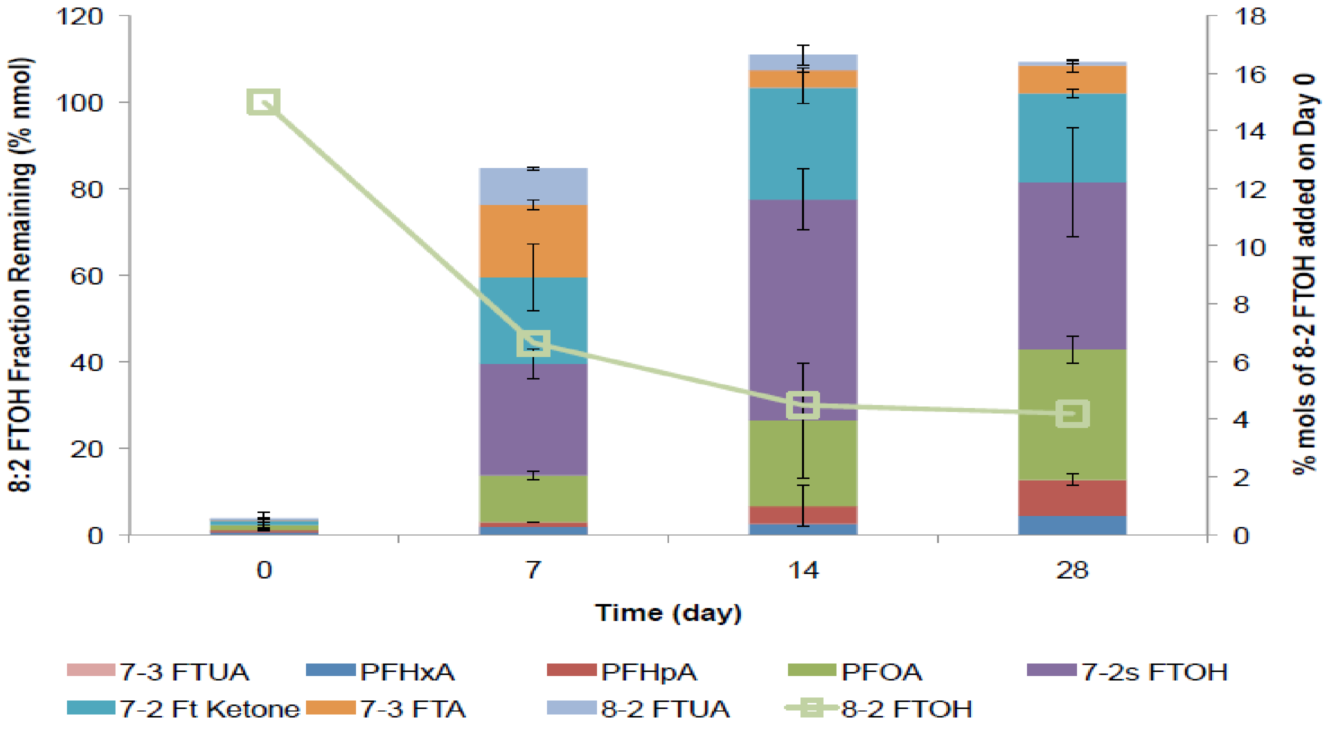
Water Technologies - Biodegradation

- Biological processes exist that are capable of degrading functional groups (e.g., transforming precursors)
- Some may also degrade C-F chains
- Catabolic or co-metabolic degradation not demonstrated



PFAS Remediation Technology Research

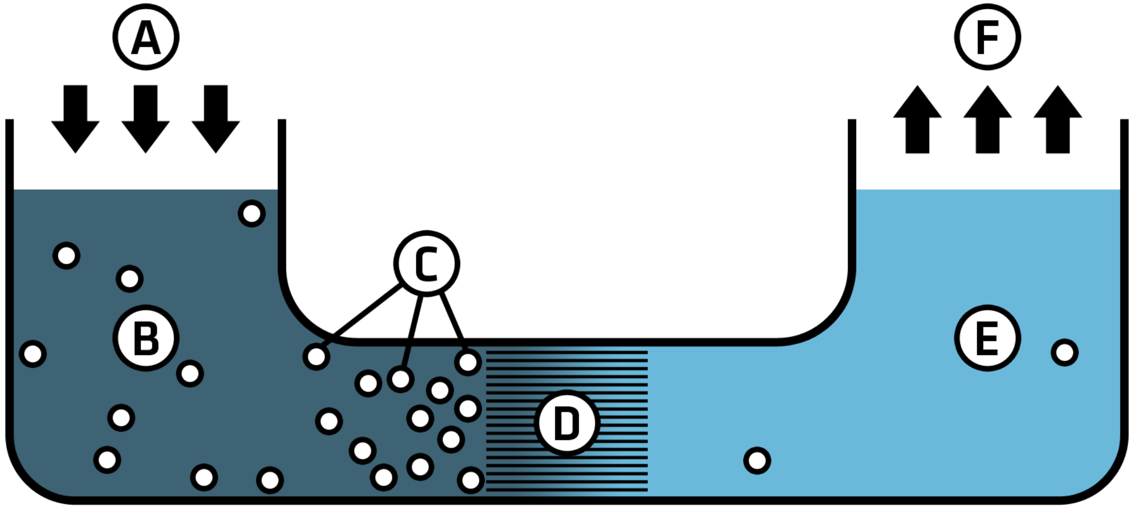
Granular Activated Carbon

- Under contract to the US Navy
- Drinking water and wastewater impacted
- Recipients presently on bottled water
- Evaluating multiple brands/types of GAC (e.g., coconut shell, coal-based, etc.) in shaker tests and residential canister units
- Column tests to define breakthrough and longevity, and determine isotherms
- Coal based activated carbon (e.g., Calgon Filtrasorb 400) performed best
- Design of drinking water and wastewater treatment systems based on findings

https://upload.wikimedia.org/wikipedia/commons/2/2d/Activated_Carbon.jpg

GAC and Reverse Osmosis

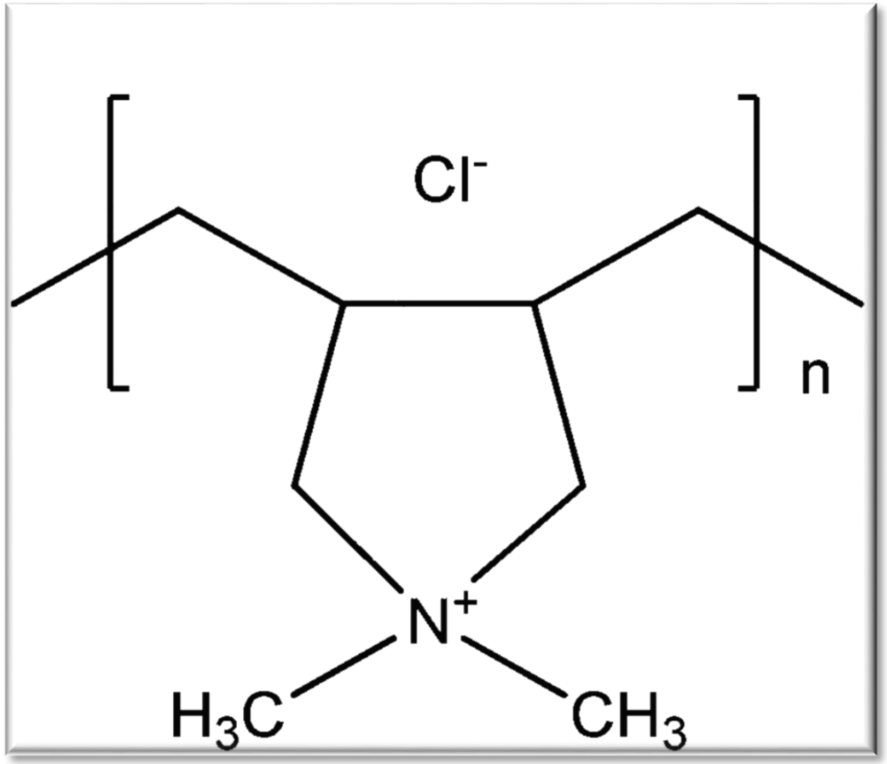
- Municipal water supply impacted from AFFF usage upgradient
- Evaluating isotherms, breakthrough and longevity of coal-based GAC
- Evaluating efficacy of Reverse Osmosis on various PFAS, beyond simply PFOS and PFOA
- Looking at existing drinking water system to assess optimal modifications (e.g., different membrane?)



https://upload.wikimedia.org/wikipedia/commons/9/99/Simple_RO_schematic.png

In Situ Sequestration

- UMN and Tufts University SERDP
- Cationic surface modification of aquifer materials may enhance sorption/sequestration
- Polydiallyldimethyl ammonium chloride (polyDADMAC) showed the best results
- Presently looking at longevity analysis to see whether sequestration is permanent
- Also looking at coagulant enhancement of GAC



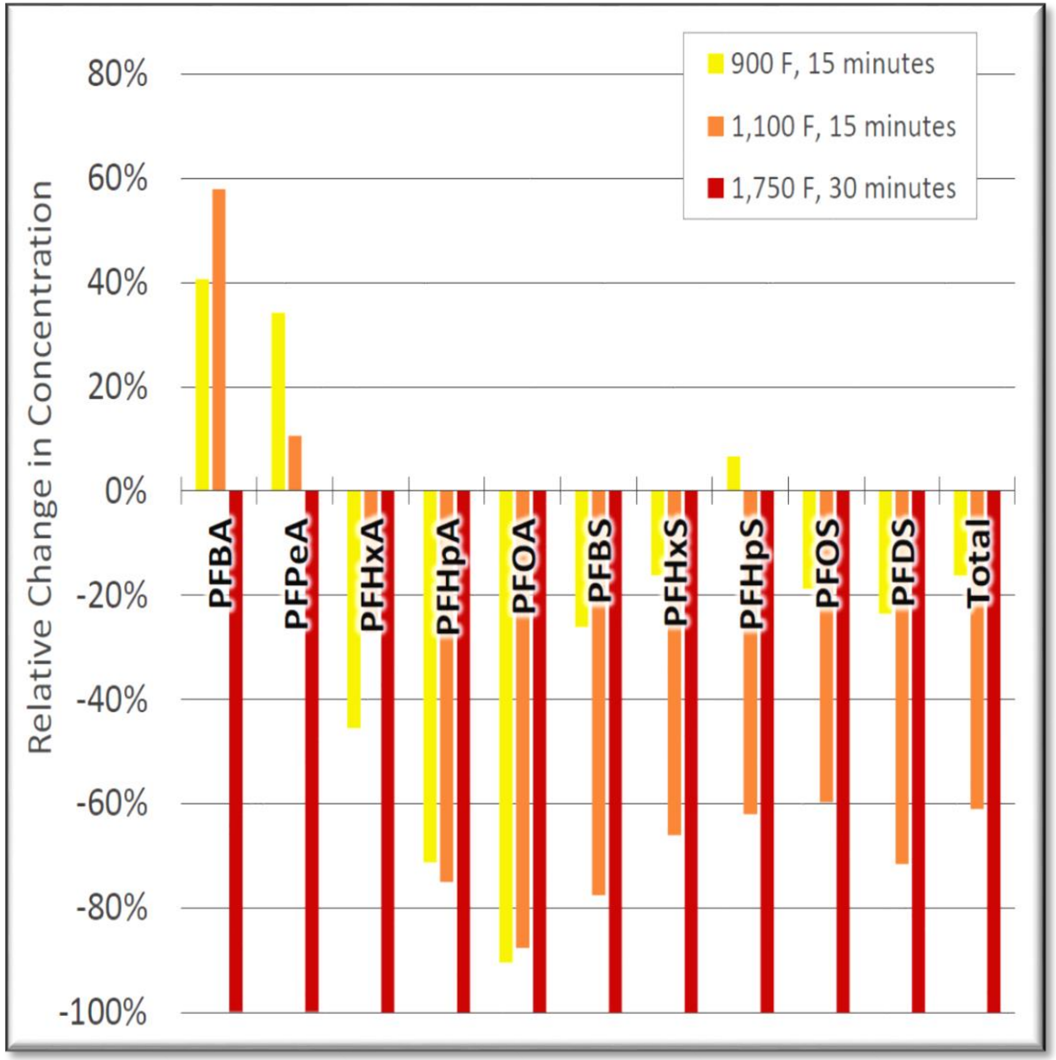
University of Minnesota
Driven to Discover℠

Tufts University

SERDP
DOD • EPA • DOE

Thermal Treatment

- Tested at "moderate" temperature (600-900°C)
- Vapors scrubbed with "acid trap" which is caustic and should capture PFCs
- Vapors then oxidized/burned at >1000°C
- Tests conducted with telomer-based AFFF
- Initial testing results showed complete removal from soil at 950°C (1750°F)
- Putting together field pilot scale follow-on project with lower temp batch process



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Endpoint.
Strategy. Science. Sustainability.

Thank you for your time

Questions?

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