

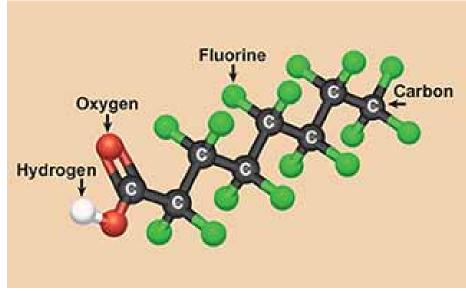
### PFAS: SCIENCE, ENGINEERING, AND PUBLIC POLICY

DRWW General Membership Meeting Feb. 16, 2023

Adrienne Nemura 734.476.0357 anemura@Geosyntec.com



History & Background
PFAS Health Effects & Criteria
Sampling & Laboratory Techniques
Treatment Challenges
Regulatory Actions



https://www.niehs.nih.gov/health/topics/agents/pfc/index.cfm

# HISTORY & BACKGROUND

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## PER- AND POLYFLUOROALKYL SUBSTANCES

#### Group of manufactured chemicals

- One of strongest bonds (carbon-fluorine) in organic chemistry
- Resistant to fire, degradation

Used in industry & consumer products since 1940s – polymers, surfactants, lubricants, etc.

#### Ambiguous and conflicting definitions

- EPA's master list has 12,000\*
- Includes other fluorinated organic compounds (pesticides, pharmaceuticals, veterinary drugs)\*\*
  - · Lipitor, Prozac, Flonase, Pavloxid



\*\* Fluorinated Compounds (mass.gov)



### PERFLUOROOCTANOIC ACID (PFOA)



Keeps coatings like Teflon from clumping

Animal and human health impacts studied since the 1960s

1998 call to corporate attorney by his grandmother's neighbor about his cattle in Parkersburg, WV\*

Required a 2000 Court Order to obtain studies

Epidemiological study of 70,000 people (exposed for decades) links to diseases

Dupont ceases production and use of PFOA in 2013

http://www.nytimes.com/2016/01/10/magazine/the-lawyer-who-became-duponts-worst-nightmare.html? r=0

<sup>\*</sup> https://www.chicagotribune.com/news/environment/ct-pfas-history-20220710-iqrm53d4qrdt3dzbxr5exvvfli-htmlstory.html

### PERFLUOROOCTANESULFONIC ACID (PFOS)

Key ingredient in Scotchguard

PFOS and PFOA used to make aqueous film forming foam (AFFF)

3M had documented adverse effects in animals in 1970s – did not pursue findings of PFAS in breast milk of animals or elevated rates of prostate cancer in factory workers

2002 - Minnesota Pollution Control Agency

- Requests MDH develop Health Based Values\* for PFOA (700 ng/L) and PFOS (100 ng/L)
- Extensive investigation at 3M Cottage Grove manufacturing facility in Twin Cities

2018 - State settles with 3M for \$850M

Chemical	Revised Minnesota HBV (ng/L)	Year
PFOA	35	2017
PFOS	15	2019
PFHxS	47	2019
PFHxA	200	2021
PFBS	100	2022
PFBA	7	2022

<sup>\*</sup> Lifetime drinking water source

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## New Hollywood film 'Dark Waters' highlights the shocking reality of PFAS pollution

February 4, 2020 By Eleanor Hawke



Dark Waters is the most important American film in a decade, although it squanders an opportunity to fully portray PFAS\* contamination as the nationwide human health epidemic it has become. The film leaves out half of the story and that involves the military's role.

SCREENPLAY BY MARIO CORREA AND MATTHEW MICHAEL CARNAHAN DIRECTED BY TODD HAYNES





















# PFAS HEALTH EFFECTS & CRITERIA

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## PFAS SCIENCE IS "FULL OF UNCERTAINTIES AND INCONSISTENT INTERPRETATIONS BY SCIENTISTS"

PFOA <u>may</u> be associated with kidney and testicular cancer

PFOS and PFOA <u>may</u> be associated with

- Increased cholesterol
- Decreased vaccine response for children
- Kidney disease

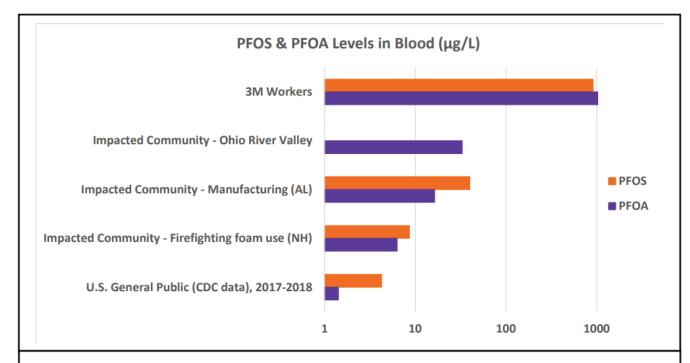
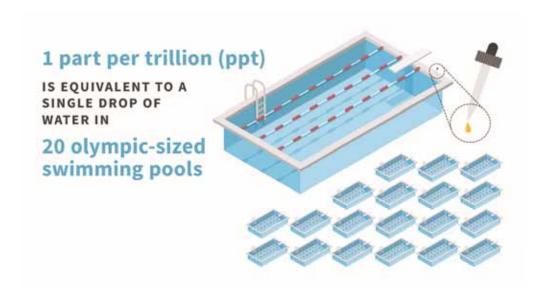
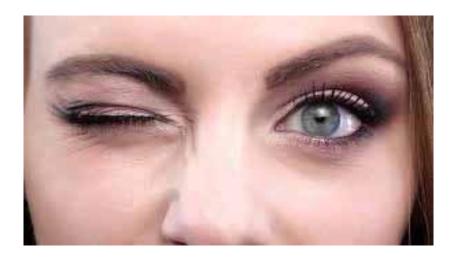


Figure 3. Comparison of exposure to PFOS and PFOA between different groups of people. Data (log scale) adapted from ATSDR (<a href="https://www.atsdr.cdc.gov/pfas/health-effects/us-population.html">https://www.atsdr.cdc.gov/pfas/health-effects/us-population.html</a>).



 $\frac{https://www.michigan.gov/-/media/Project/Websites/PFAS-Response/Images/PPT-Swimming-Pool.pdf?rev=5104c6f80cc74cf79fcb5e2add3c9088$ 



If you were 31.8 million years old, 1 part per quadrillion (ppq) or a picogram per liter is equivalent to a blink.

### **CHANGING (AND LOW) TARGETS & CRITERIA**

**USEPA HAS PFOA = 0.004 PFOS = 0.020**HFPO-DA = 10
PFBS = 2,000

Table is promulgated for drinking water

All concentrations are **ppt** (or ng/L)

	State	PFOA	PFOS	PFHxS	PFHxA	PFBS	PFBA	PFNA	PFHpA	HFPO-DA
	CA	10	40			5,000				
	MA	20	20	20				20	20	
	MI	8	16	51	400,000	420		6		370
	MN	35	15	47	200	100	7			
	NH	12	15	18				11		
	NJ	14	13					13		
	NY	10	10							
	PA	14	18							
	RI	20	20	20						
	VT	20	20	20				20	20	
	WA	10	15	65		345		9		
-Λ	NTC									40

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PFAS — Per- and Polyfluoroalkyl Substances (itrcweb.org)

THE US EPA LIFETIME DRINKING WATER HEALTH ADVISORIES FOR PFOS AND PFOA ARE OFTEN LOWER THAN THEIR RESPECTIVE LEVELS IN RAINWATER AND THE DANISH DRINKING WATER LIMIT VALUE FOR  $\Sigma 4$  PFAS IS ALSO OFTEN LOWER THAN THE LEVEL OF  $\Sigma 4$  PFAS IN **RAINWATER** 

THE EUROPEAN UNION (EU) ENVIRONMENTAL QUALITY STANDARD (EQS) FOR PFOS FOR FRESHWATERS IS OFTEN LOWER THAN LEVELS IN

**RAINWATER** 

THE CYCLING OF PFAAs IN THE WORLD'S HYDROSPHERE MEANS THAT LEVELS OF PFAAs IN RAINWATER WILL BE PRACTICALLY **IRREVERSIBLE** 



pubs.acs.org/est



Perspective

Outside the Safe Operating Space of a New Planetary Boundary for Per- and Polyfluoroalkyl Substances (PFAS)

Ian T. Cousins,\* Jana H. Johansson, Matthew E. Salter, Bo Sha, and Martin Scheringer

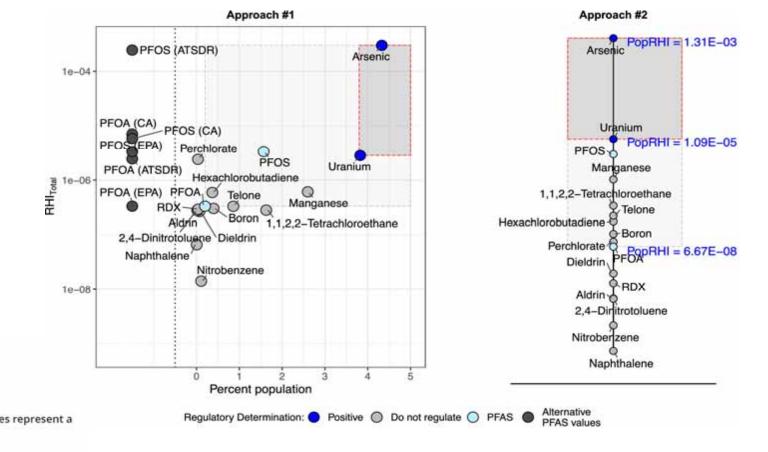




PFAS (ng/L)	USEPA HAs	Tibetan Rain	Antarctic Rain
PFOA	0.004	0.055	0.22
PFOS	0.020	0.005	0.106

Does regulating per- and polyfluoroalkyl substances represent a meaningful opportunity for health risk reduction?

If PFOA & PFOS were present in 100% of our drinking water systems, levels of 227 ng/L PFOS and 2295 ng/L PFOA would be needed to exceed the minimum threshold of percent population to justify "meaningful opportunity"





Katherine Alfredo 🙉 Chad Seidel, Amlan Ghosh

First published: 14 September 2021 | https://doi.org/10.1002/aws2.1240 | Citations: 1

Calculations with PFOA and PFOS at 70 ng/L

#### Water & Health Advisory Council

Chemical & Engineering News: Letter to the Editor of PFAS Drinking Water Advisories - Water & Health Advisory Council (wateradvisory.org)

- Debate on study EPA relied on
- Advisories' credibility is doubtful
- Misdirecting drinking-water priorities and expenditure
- Serious peer review is essential

Everyone agrees that per- and polyfluoroalkyl substances (PFAS) are environmentally and biologically persistent and should be managed. Exposures occur from many sources, including household products and fabrics, some foods, and food contact containers. Their manufacture, uses, and exposures are being reduced by company and government agreements from the early 2000s. Human blood levels of PFOA and PFOS in the US are more than 70–85% less than they were in 1999. Some drinking waters are exposure sources, usually at low parts per trillion, especially some groundwaters, where they may persist for many years.

The EPA's calculations are based partly on a study in the Faeroe Islands with an inverse relationship between child blood levels and antibody titers for diphtheria and tetanus. There is debate on the study's applicability. Even if the finding is valid, the US Centers for Disease Control and Prevention's data show no relationship with cases in the US. Cases of diphtheria are extremely low. Vaccinations are very effective, so those health advisories are protecting against a nonexisting consequence at high cost.

The advisories' credibility is doubtful, and those unmeasurable numbers raise public concern and result in major expenditures in the over 150,000 public water systems in the US. They also misdirect drinking-water priorities and expenditures that should deal with decaying water distribution systems and water-related legionellosis, a deadly waterborne disease.

The EPA must reexamine its scientific risk assessments and provide a more credible scientific basis for its health advisories. Serious peer review is essential.

### SAMPLING AND LABORATORY TECHNIQUES

#### **SAMPLING TECHNIQUES**

#### Avoid

- Clothes washed with fabric softener
- Clothes made or washed with stain resistant chemicals
- Certain insect repellents and sunscreens
- Certain personal care products
- Pre-wrapped food or snacks



Polypropylene (or HDPE)
Trizma® (pH 7)
from qualified lab
Watch carpets &
car interiors



Wash hands Powderless nitrile gloves Place bottles on PFAS-free surfaces (not the ground) Bag samples in LDPE resealable storage bags

#### Decontamination

- Alconox, Liquinox, and Citranox
- PVC brush to remove particles
- Triple rinse with PFAS-free deionized water

"even the smallest cross-contamination could contribute to a false positive sample" <a href="https://www.michigan.gov/pfasresponse/investigations/sampling-guidance">https://www.michigan.gov/pfasresponse/investigations/sampling-guidance</a>

#### **USEPA LABORATORY TECHNIQUES**

USEPA Method 537 Revision 1.1 (SPE and LC/MS/MS)

For 18 PFAS in finished drinking water samples

USEPA Method 533 (Isotope Dilution Anion Exchange SPE and LC/MS/MS)

• Isotope dilution method targeting 25 "short-chain" PFAS in finished drinking water samples

USEPA Method 8327 (External Standard Calibration and MRM LC/MS/MS)

• Direct injection method for 24 analytes in groundwater, surface water and wastewater

Draft Method 1633 (3<sup>rd</sup> draft in Dec. 2022)

- Direct injection method for 40 PFAS in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue (single lab validation)
- EPA and DoD collaborating with a multi-laboratory validation study
- EPA recommending for use in individual NPDES permits

#### **USEPA LABORATORY TECHNIQUES - TOTAL**

Method 1621 (multi-laboratory validation ongoing)

Adsorbable organofluorines in wastewater and surface waters

Total Organic Fluorine (TOF) – in development

Total PFAS presence and absence

Total Organic Precursors (TOP) – under consideration

- Identify PFAS precursors that may transform to more persistent PFAS
- TOP methods are commercially available

32 accredited labs (including American Water Central Laboratory in Belleville, IL)

# TREATMENT CHALLENGES

#### TREATMENT CHALLENGES

Relied upon technologies focus on PFAS removal, not destruction

- Granulated activated carbon (GAC)
- Ion exchange (IX)
- Reverse osmosis (RO)

Produce a concentrated residual stream that must be treated

- Hazardous waste landfill
- Incineration

No demonstrated in situ treatment technologies



"An under-sink RO filter integrates with the plumbing under your kitchen sink to provide treated drinking water for you and your family. The concentrated PFAS brine is discharged directly down the drain, so there is not waste to manage or dispose of."

# TREATMENT OPPORTUNITIES

## Next generation technologies

- Both in-situ and ex-situ approaches
- Primary focus
  - Treatment trains
  - PFAS destruction
- Significant R&D investments by the Department of Defense



2022	١
Workshop Report:	
PFAS R&D Needs	
	•

		Creation of AFFF Reference Material		Ecotoxicity of PFAS- Free AFFF		Ecotoxicity of Mixtures	
SERDP RESEARCH PROJECTS		Source Zones		Alternative Formulations for PFAS-Free AFFF		Ecotoxicity in the Marine Environment	AFFF Impacted Concrete and Asphalt
		Investigation Derived Waste		Biodegradation		Ecotoxicity & Risk in Avian Species	Stormwater Management
2011 In Situ Groundwater Remediation		In Situ & Ex Situ Groundwater Remediation	PFAS Multilab Method Validation	Passive Sampling Methodologies		PFAS-Impacted Matrices Treatment	Transformation in Soil and Groundwater
2014 In Situ Groundwater Remediation	Co-Occuring Chemicals in Groundwater	Ecorisk/Assessing Remediation Effectiveness	Ecological Risk Characterization	Analytical Methods to Assess Leaching and Mobility	Thermal Destruction Technologies for AFFF	PFAS-Free Fire Suppressant Enhancements	PFAS-Free Firefighting Agents Performance
2016 Ecotoxicity	PFAS-Free Aqueous Film Forming Foam	PFAS-Free Aqueous Film Forming Foam	Analytical and Environmental Sampling Methods	Forensic Methods for Source Tracking and Allocation	Amendments for In Situ PFAS Groundwater Remediation	Thermal Degradation of Polymeric PFAS in Munitions	PFAS-Free Firefighting Agents Testing
2011 - 2016	2017	2018	2019	2020	2021	2022	2023
2015 FAQs Regarding PFAS at DoD Sites	Thermally-Enhanced Persulfate Oxidation Followed by P&T	Ion Exchange & Low Energy Electrical Discharge Plasma Process	Mobile Lab-Based Real Time PFAS Analytical Methods	Demonstration/ Validation of AFFF Cleaning from Firefighting Systems	PFAS-Impacted Materials Treatment Demonstration/ Validation	Demonstration/ Validation of PFAS- Free AFFF	
2016 Characterization of		Life Cycle	Sub-Micron				
the Nature and Extent of PFAS at DoD Sites		Comparison of Ex Situ Treatment Technologies	Powdered Activated Carbon & Ceramic Membrane Filter System	Demonstration/ Validation of PFAS- Free AFFF	In Situ Treatment Demonstration/ Validation	In Situ Treatment Demonstration/ Validation	
		Comparison of Ex Situ Treatment	Carbon & Ceramic Membrane Filter	Validation of PFAS-	Demonstration/	Demonstration/	
of PFAS at DoD Sites	emonstration Projects	Comparison of Ex Situ Treatment	Carbon & Ceramic Membrane Filter System Source Zone Treatment	Validation of PFAS- Free AFFF PFAS Monitoring and	Demonstration/ Validation  PFAS Monitoring and	Demonstration/ Validation  PFAS-Impacted Materials Treatment Demonstration/	











## REGULATORY ACTIONS

#### NPDES PROGRAM – USEPA DEC. 5, 2022 MEMO

Quarterly monitoring for 40 PFAS

Best management practices (BMPs) - product substitution, reduction, or elimination of PFAS

BMPs to address firefighting foams for stormwater permits

Technology-based effluent limits (TBELs) based on best professional judgment

Water-quality based effluent limits (WQBELs) including numeric translation of narrative water quality standards

INDUSTRIAL DISCHARGERS (Effluent Limit Guidelines)

- OCPSF (Spr. 2024)
- Metal finishing
- Electroplating (Dec. 2024)
- Electric and electronic components
- Landfills (TBD)
- Pulp, paper, & paperboard (phasing out)
- Leather tanning & finishing
- · Plastics molding & forming
- Textile mills (lack of data)
- Paint formulating
- Airports (phasing out)

#### NPDES PROGRAM – USEPA DEC. 5, 2022 MEMO

#### For POTWs:

Effluent, influent, and biosolids monitoring

Update industrial user inventories

Use BMPs and pollution prevention

Notify potentially affected public water systems of draft permits with PFAS-monitoring, BMPs, or other conditions

#### **VARIETY OF STATE ACTIONS**

Maine – statewide ban on biosolids application

Michigan – organized MPART – statewide sampling of influent, effluent, biosolids

Led to "industrially impacted" approach

Focus on source reduction and restricting biosolids application when necessary

California – statewide sampling of targeted industries

Illinois – initiating discussion with Illinois Association of Wastewater Agencies

Consideration of drafting model NPDES permit language

Begin sampling of major municipal and industrial wastewater treatment plants

"McKinsey analysis suggests that new PFAS requirements could lead to a threefold increase in PFAS-related annual capital spending between 2021 and 2025."

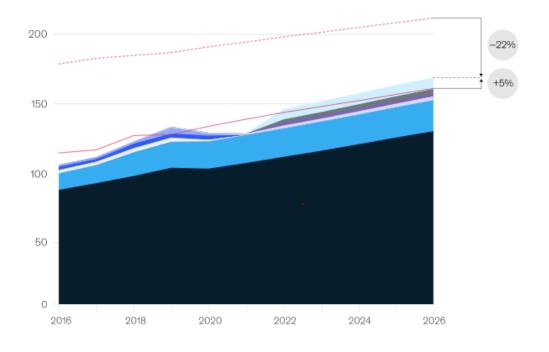
#### OTHER FUNDING NEEDS:

- Lead and copper rule
- Fixing water leaks
- Cybersecurity
- Combined sewer overflows
- Nutrients
- Climate resilience

https://www.mckinsey.com/industries/electric-power-and-natural-gas/our-insights/us-water-infrastructure-making-funding-count

A fivefold increase in federal funding would raise total funds in the industry by about 5 percent in the short term, but funding would still fall 22 percent short of the necessary capital.







THE ROANOKE TIMES Monday, September 20, 2004



STEPHANIE KLEIN-DAVIS | The Roanoke Times

Mellisa Williamson, 35, a Bullitt Avenue resident, worries about the effect on her unborn child from the sound of jackhammers.

## TRAFFIC: Official says wait for end result

**EXTRA SLIDES** 

#### **SMOLDERING**

Low-cost / energy thermal technique to treat contaminated soils and media

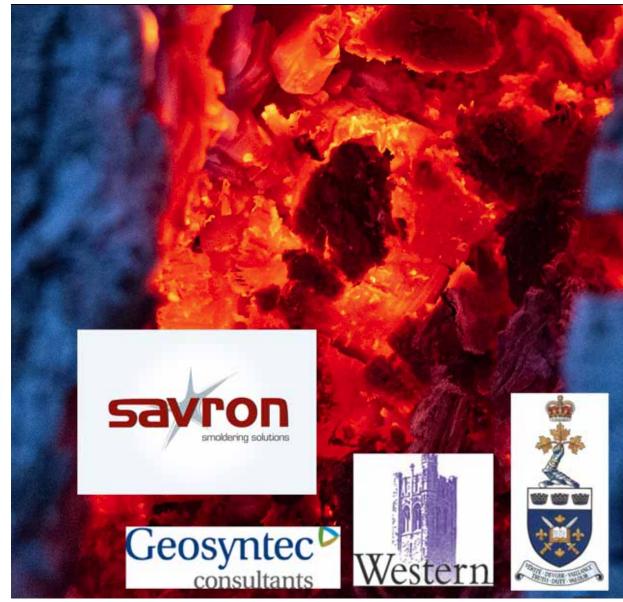
- Temperatures > 700°C
- Use GAC to support





<u>Demonstration of Smoldering Combustion Treatment of PFAS-impacted Investigation-Derived Waste (serdp-estcp.org)</u>

<u>Innovations – Savron (savronsolutions.com)</u>



## ULTRA-VIOLET ACTIVATION WITH STABLE PHOTOCATALYST

