Pace Analytical®

Per– and Polyfluoroalkyl Substances (PFAS)

Paul R. Jackson, Program Manager
Pace - Emerging Contaminants

ADEM

Safety Moment

Don’t be THAT guy.

Pace Locations

- Founded 1978
- Largest American owned environmental laboratory company
- 3 Divisions and nearly 2,600 employees nationwide

Pace Analytical®
PRIDE IN AMERICAN OWNERSHIP
SINCE 1978
CELEBRATING 40 YEARS

About Pace Analytical

- 40 laboratory locations and 50 service centers
- Provides microbiology, inorganic, organic capabilities - specializing in the analysis of trace level contaminants in air, waters, soil, biota and waste
- Specialty Analytical Services:
  - PFAS - Per- and polyfluoroalkyl substances
  - 1,4-Dioxane
  - Low-level Hexavalent Chromium & Mercury
  - Dioxins
  - Radiochemistry
  - Environmental Forensics
  - Air
  - Biota
  - Microcystins
  - Unregulated Contaminants
  - Drinking & Bottled Water

PFAS – The Environmental Wild West Show

- Lack of federal regulation
- Non-uniformity of state regulation
- Non-uniformity of test methods
- Lack of environmental test methods
- Variety of compound lists
- Thousands of PFAS compounds
- Low DLs vs contaminated matrices
- Ultra restrictive field sampling guidance
- All this conspires to lead to uncertainty & a highly consultative process

Per- and Polyfluoroalkyl Substances (PFAS)

- Sources
- PFAS Classes
- Basic Chemistry
- Naming Conventions
- Analytical Methods
- Regulatory Update

Per- and Polyfluoroalkyl Substances (PFAS)

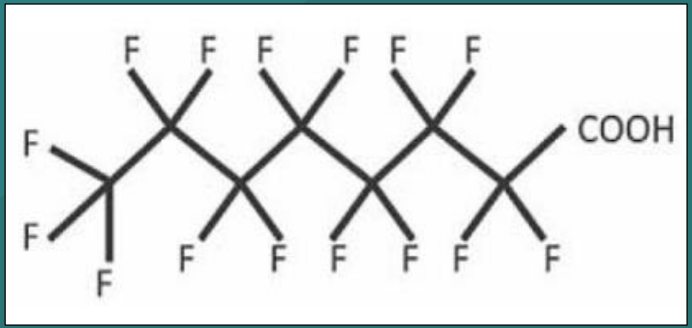
Per- and polyfluoroalkyl substances (PFAS) are a large, diverse group of manufactured compounds used in a variety of industries, such as aerospace, automotive, apparels, food packaging, fire-fighting foams, non-stick coatings/cookware, carpeting, and metal plating.

PFAS are anthropogenic chemicals and do not occur naturally in the environment.

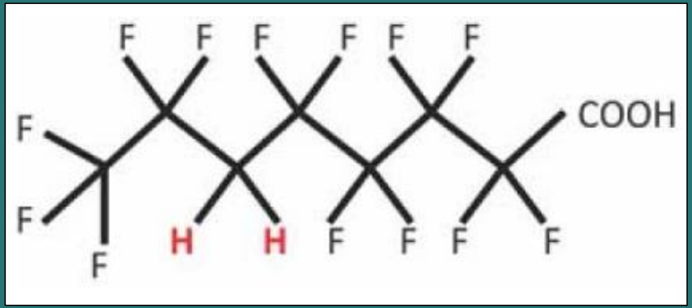
Phonetically: PFAS = PF 

P F A S

Perfluorinated substances are those in which all the hydrogens on the carbons are replaced by fluorine.

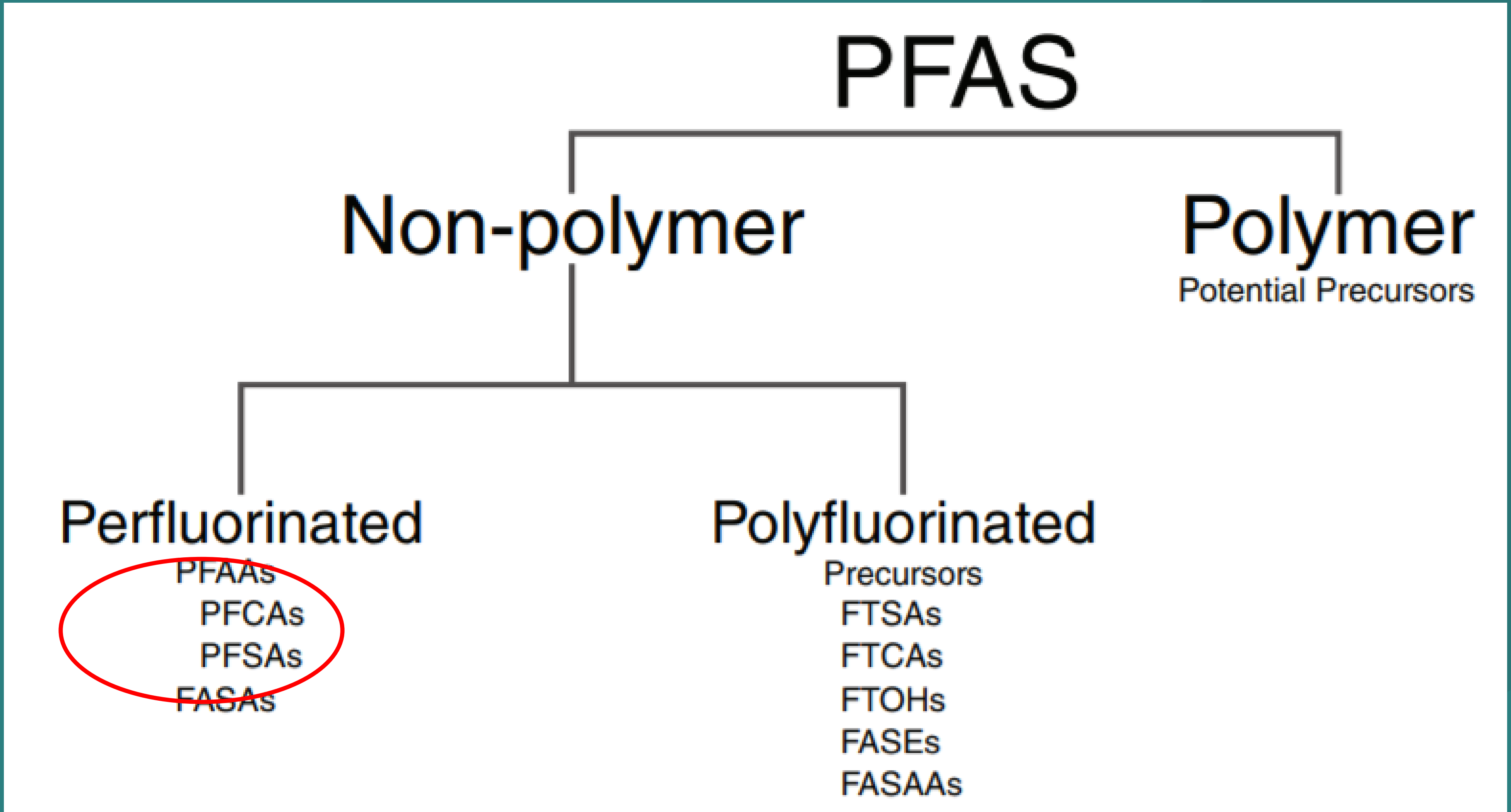


Polyfluorinated substances apply to chemicals in which not all the hydrogens on the carbons of the molecule are replaced by fluorine.

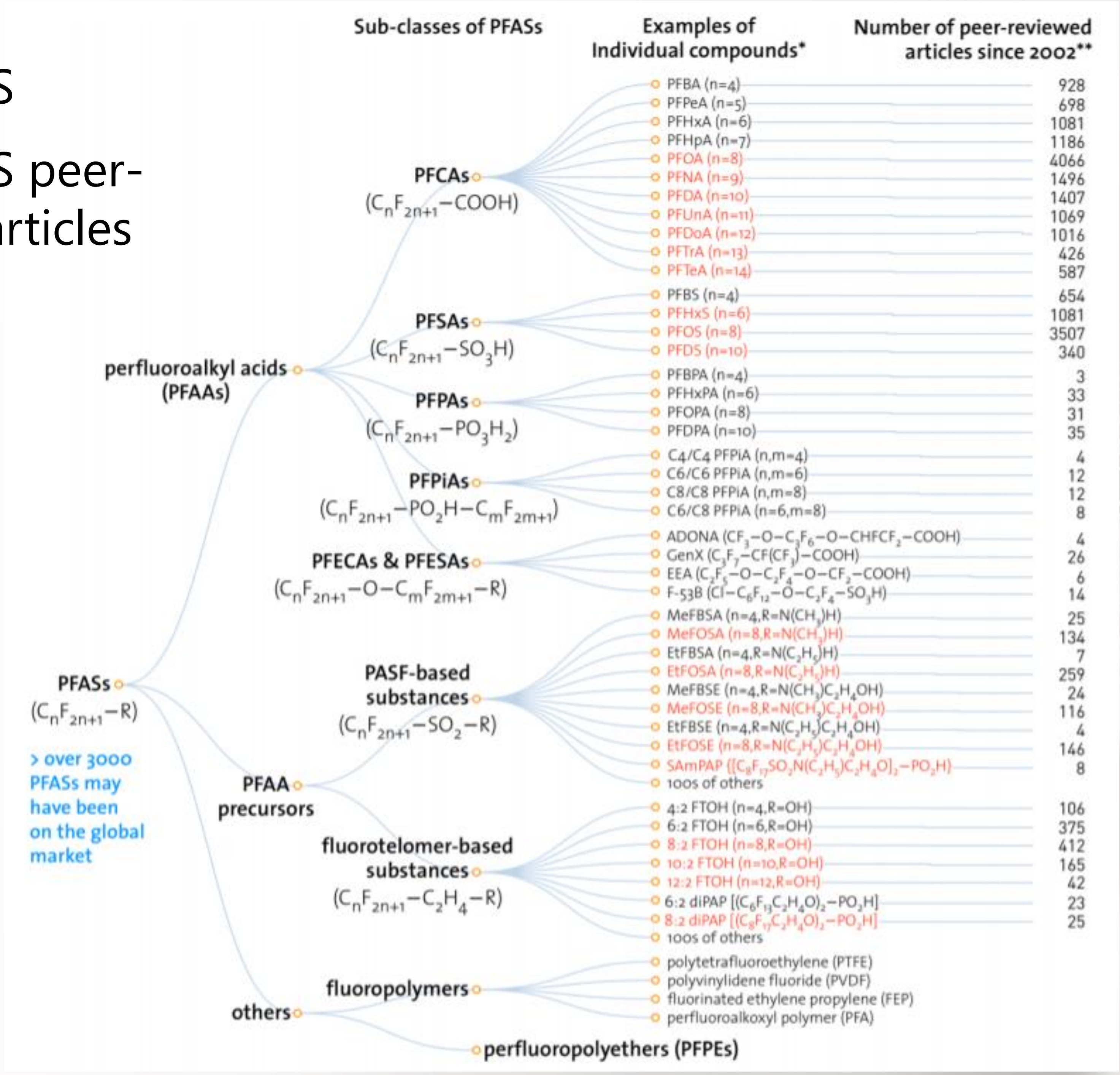


When referring to mixtures of perfluorinated and polyfluorinated substances, it is more correct to use the term per- and polyfluoroalkyl substances or **PFAS**.

PFAS CLASSES



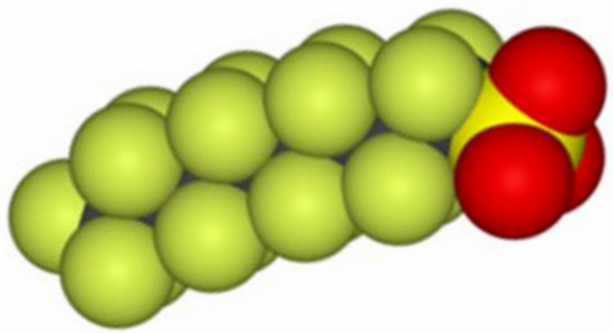
- Many PFAS
- Many PFAS peer-reviewed articles



Source: Wang, et al 2017

BASIC CHEMISTRY: **Perfluoroalkyl Acids**

- **Perfluoroalkyl Acids (PFAAs)**
  - Fully fluorinated chain (2 or more carbon "tail")
  - Functional group ("head")
    - **PFCAs**: Carboxylate group (COO^-)
    - **PFSAs**: Sulfonate group (SO_3^-)



Perfluorooctane sulfonate (PFOS)

Tail | $F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2$ — SO_3^- | Head

Perfluorooctane carboxylate (PFOA)

Tail | $F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2$ — CO_2^- | Head

BASIC CHEMISTRY: **Polyfluorinated**

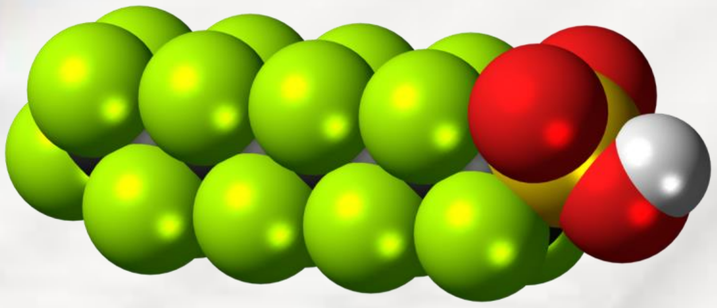
- **Partially fluorinated**
  - Non-fluorine atom (usually H or O) attached to at least one, but not all, of the carbon atoms in the "tail"
  - Creates a "weak link" susceptible to biotic or abiotic degradation
  - Often named using a "n:x" prefix
    - n = number of fully fluorinated carbons
    - x = number of non-fully fluorinated carbons

$$\overbrace{F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2}^{8}\text{-}\overbrace{CH_2CH_2}^{2}\text{-}OH$$

8:2 FTOH (8:2 fluorotelomer alcohol)

PFAS PROPERTIES

- **C – F is the shortest and strongest bond in chemistry**
  - Small, highly electronegative fluorine atoms "shield" the carbon from chemical reactions
  - No biotic or abiotic degradation of PFAA under natural conditions
  - PFAAs thermally degrade only at high temperatures (> 900°C)



- **Perfluoroalkyl acids (PFAAs) are negatively charged**
  - Interact and sorb on positively charged minerals
  - Mediated by pH, chain length, and functional group

PFAS PROPERTIES

- **PFAAs generally have low volatility**
  - Air transport may occur for PFAAs sorbed to particulates or dissolved in water droplets
  - May be formed from volatile precursors (e.g. FTOHs)

- **PFAAs may be linear or branched in linear**
  - May affect partitioning and/or bioaccumulation - not well understood yet

$F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$

Linear Perfluorooctane sulfonate (PFOS)

$$F_3C\text{-}\overset{\displaystyle CF_3}{\overset{|}{C}}F\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$$

Branched Perfluorooctane sulfonate (PFOS)

PFAS NAMING CONVENTIONS

- **PFXY**
  - **PF** = perfluoro
  - **X** = number of carbons
    - Same naming convention as hydrocarbons
  - **Y** = functional group
    - S = sulfonate
    - C = carbonxylate

- **Example**:
  - **X**: 8 carbons = “octa”
  - **Y**: S = sufonate

Perfluorooctane sulfonate (PFOS)

X	Y	Acronym	Name	Formula	CAS No.
B = buta (4 carbon)	A = Carboxylate or carboxylic acid	PFBA	Perfluorobutanoate	$C_3F_7CO_2^-$	45048-62-2
			Perfluorobutanoic acid	C_3F_7COOH	375-22-4
	S = Sulfonate or sulfonic acid	PFBS	Perfluorobutane sulfonate	$C_4F_9SO_3^-$	45187-15-3
			Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	375-73-5
Pe = penta (5 carbon)	A = Carboxylate or carboxylic acid	PFPeA	Perfluoropentanoate	$C_4F_9CO_2^-$	45167-47-3
			Perfluoropentanoic acid	C_4F_9COOH	2706-90-3
	S = Sulfonate or sulfonic acid	PFPeS	Perfluoropentane sulfonate	$C_5F_{11}SO_3^-$	NA
			Perfluoropentane sulfonic acid	$C_5F_{11}SO_3H$	2706-91-4
Hx = hexa (6 carbon)	A = Carboxylate or carboxylic acid	PFHxA	Perfluorohexanoate	$C_5F_{11}CO_2^-$	92612-52-7
			Perfluorohexanoic acid	$C_5F_{11}COOH$	307-24-4
	S = Sulfonate or sulfonic acid	PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_3^-$	108427-53-8
			Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	355-46-4
Hp = hepta (7 carbon)	A = Carboxylate or carboxylic acid	PFHpA	Perfluoroheptanoate	$C_6F_{13}CO_2^-$	120885-29-2
			Perfluoroheptanoic acid	$C_6F_{13}COOH$	375-85-9
	S = Sulfonate or sulfonic acid	PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_3^-$	NA
			Perfluoroheptane sulfonic acid	$C_7F_{15}SO_3H$	375-92-8
O = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
			Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
	S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
			Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1
N = nona (9 carbon)	A = Carboxylate or carboxylic acid	PFNA	Perfluorononanoate	$C_8F_{17}CO_2^-$	72007-68-2
			Perfluorononanoic acid	$C_8F_{17}COOH$	375-95-1
	S = Sulfonate or sulfonic acid	PFNS	Perfluorononane sulfonate	$C_9F_{19}SO_3^-$	NA
			Perfluorononane sulfonic acid	$C_9F_{19}SO_3H$	474511-07-4
D = deca (10 carbon)	A = Carboxylate or carboxylic acid	PFDA	Perfluorodecanoate	$C_9F_{19}CO_2^-$	73829-36-4
			Perfluorodecanoic acid	$C_9F_{19}COOH$	335-76-2
	S = Sulfonate or sulfonic acid	PFDS	Perfluorodecane sulfonate	$C_{10}F_{21}SO_3^-$	126105-34-8
			Perfluorodecane sulfonic acid	$C_{10}F_{2}1SO_3H$	335-77-3

Common acronyms – CAS numbers are crucial!

Source: ITRC Naming Conventions and Physical Chemical Properties factsheet

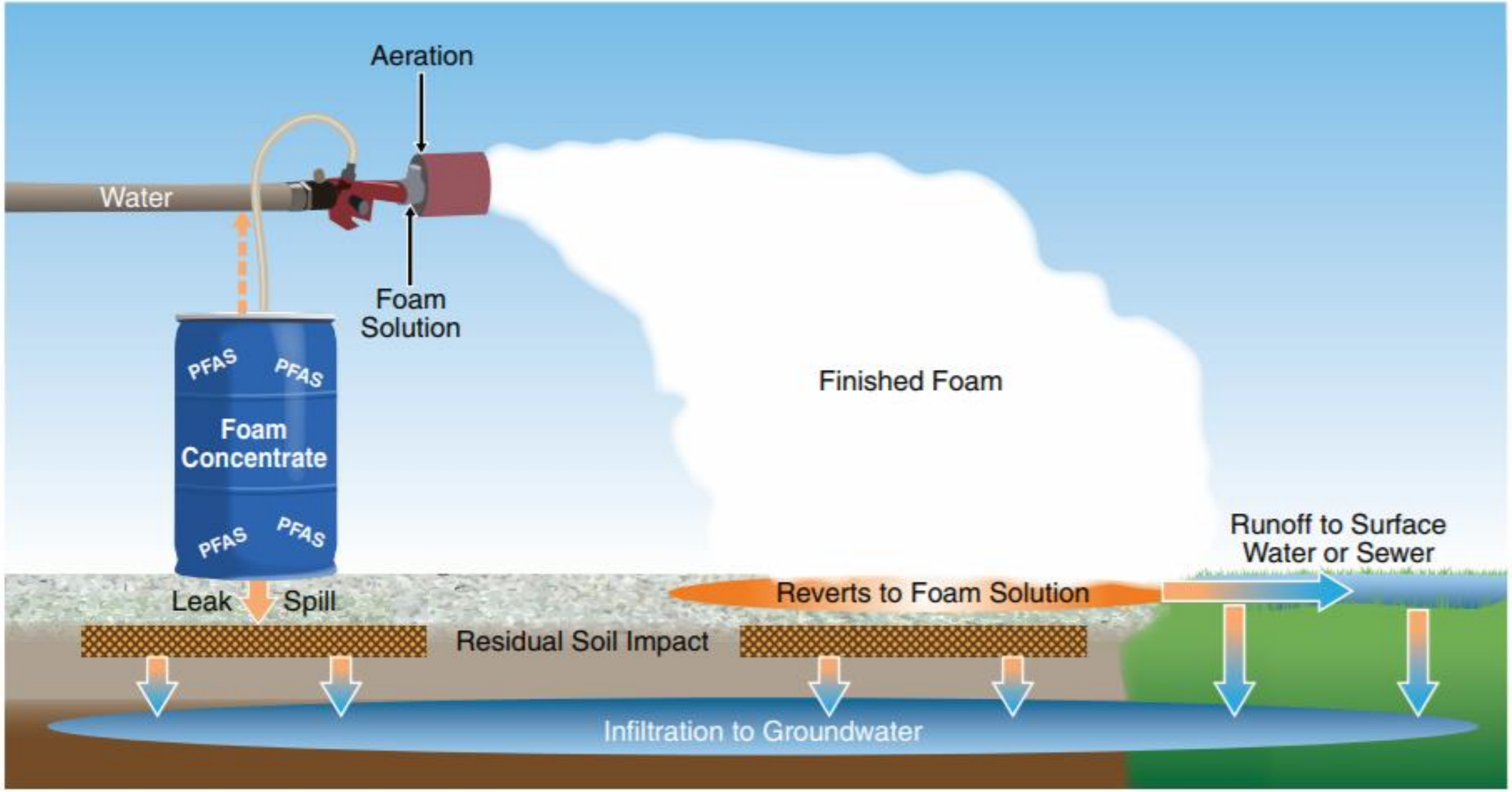
PFAS **SOURCES**

Aqueous Film Forming Foam (AFFF)

These foams have been stored and used for fire suppression, fire training, and flammable vapor suppression at hundreds of military installations and civilian airports (Hu et al. 2016), as well as at petroleum refineries and storage facilities, and chemical manufacturing plants throughout the United States.

PFAS **SOURCES**

Aqueous Film Forming Foam (AFFF)



PFAS **SOURCES**

Aqueous Film Forming Foam (AFFF)

- DoD Knowledge Based Corporate Reporting System show that 594 DoD facilities have been categorized as Fire/Crash/Training Sites
- As of August 2017, DOD has identified 401 active and BRAC installations where there are one or more areas with a known or suspected release of PFOS or PFOA to groundwater that may impact drinking water off an installation
- As of August 2017, the Military Departments have sampled over 2,600 groundwater wells for PFOS/PFOA (on 90 installations) with 1,621 sampling results exceeding the EPA LHA.

PFAS **SOURCES**

Production and Manufacturing Facilities

Due to the solubility and persistence of many PFAS, environmental release mechanisms associated with these facilities include:

- Air emission and dispersion
- Spills
- Disposal of manufacturing wastes and wastewater

Potential impacts to air, soil, surface water, stormwater, and groundwater are present not only at release areas but potentially over the surrounding area.

PFAS **SOURCES**

NORTH CAROLINA *Environmental Quality*

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Home » GenX found in rainwater samples collected near Chemours facility

GenX found in rainwater samples collected near Chemours facility

- GenX concentrations in rainwater 1-3 miles away from facility ranges from 5.2 ppt to 630 ppt.
- 25 ppt found in rainwater 70 miles away from facility.
- State health goal is 140 ppt for drinking water.

GenX found in rain

Tags: GenX

Posted February 21
Updated February 23

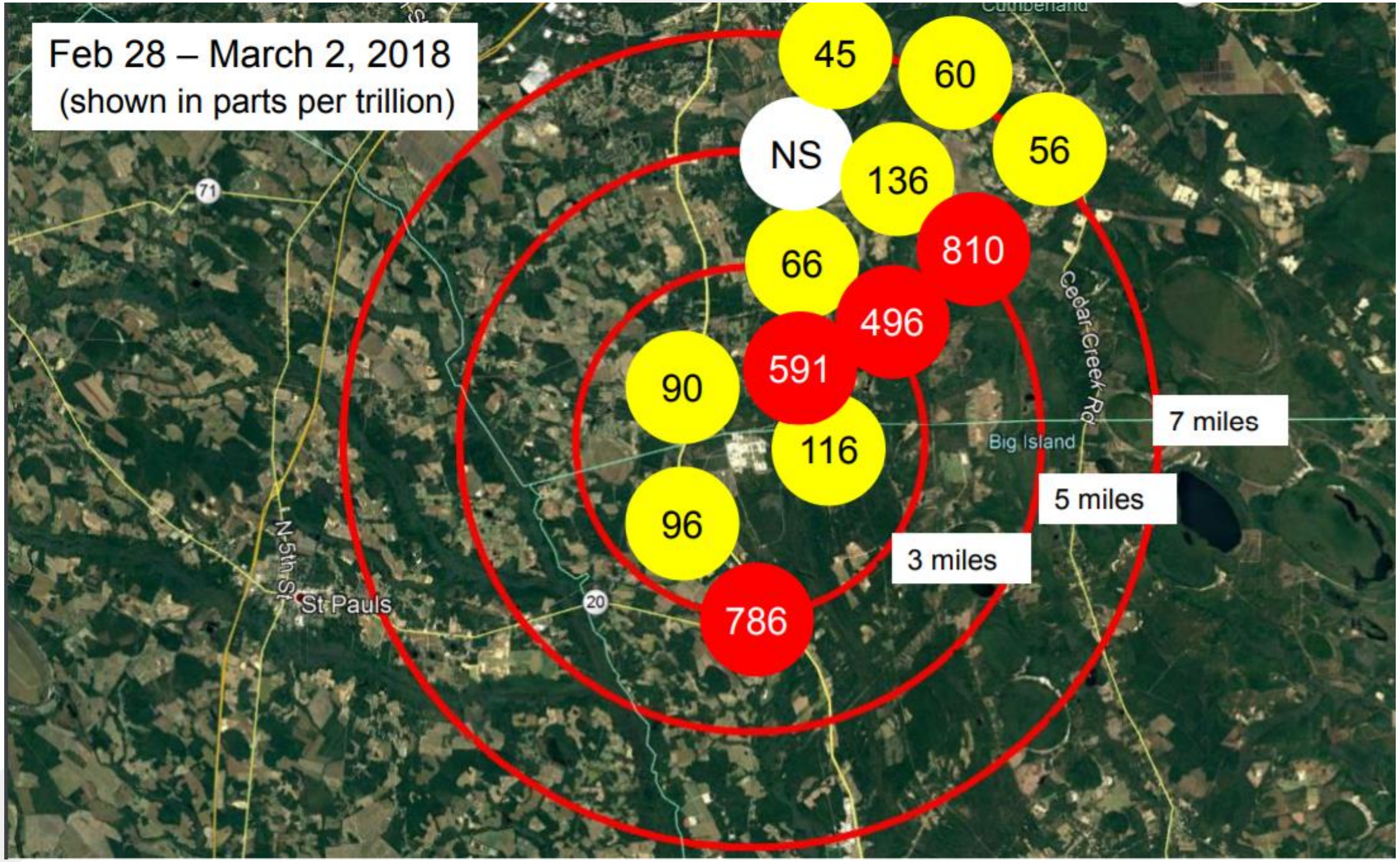
415 Share 40 Reactions

By Travis Fain, WRAL statehouse reporter

RALEIGH, N.C. — Researchers at the University of North Carolina at Wilmington found trace amounts of GenX in rainwater on campus, a university scientist told state legislators Wednesday.

PFAS **SOURCES**

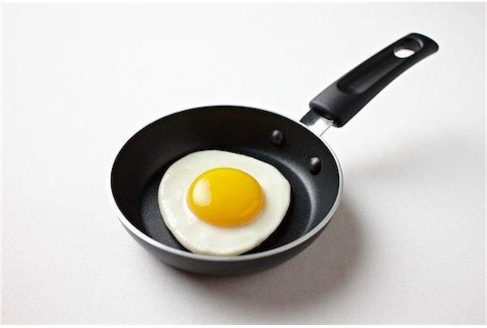
GenX Rainwater Data around Chemours facility



PFAS **SOURCES**

Production and Manufacturing Facilities

- Textiles and Leather: factory and consumer applied coating to repel water, oil, and stains
- Paper Products: surface coatings to repel grease and moisture
- Metal Plating and Etching: corrosion prevention, wear reduction, surfactant, fume suppressant
- Wire Manufacturing: coating and insulation
- Pesticides, cleaning products, polishes, photo processing


PFAS **SOURCES**

Checkout

Whole Foods Ranked Worst on Cancer-Linked Package Chemicals

By Tiffany Kary and Deena Shanker
December 11, 2018, 10:11 AM CST *Updated on December 11, 2018, 6:18 PM CST*

HEALTH

Study finds toxic substances in all 12 carpets tested

Ecology Center says carpets can be dangerous

By Hank Winchester - Reporter, Frank McGeorge - Reporter, Derick Hutchinson

Posted: 6:31 PM, December 13, 2018
Updated: 6:31 PM, December 13, 2018

Four billion pounds of carpets are dumped in landfills or burned in incinerators, releasing deadly pollutants into the air, soil and water.

PFAS **SOURCES**

Waste Disposal (Landfills)

- PFAS production facilities waste disposal
  - Secondary manufacturing sites waste disposal
  - Facilities that incorporate PFAS into the manufacturing process

- Municipal Solid Waste Facilities
  - Disposal of consumer goods coated with PFAS
  - Leachate

PFAS **SOURCES**

Wastewater Treatment

Consumer and industrial use of PFAS-containing materials, including disposal of landfill leachate and firefighting foam, results in the discharge of PFAS to waste water treatment plants (WWTPs).

WWTP Operations

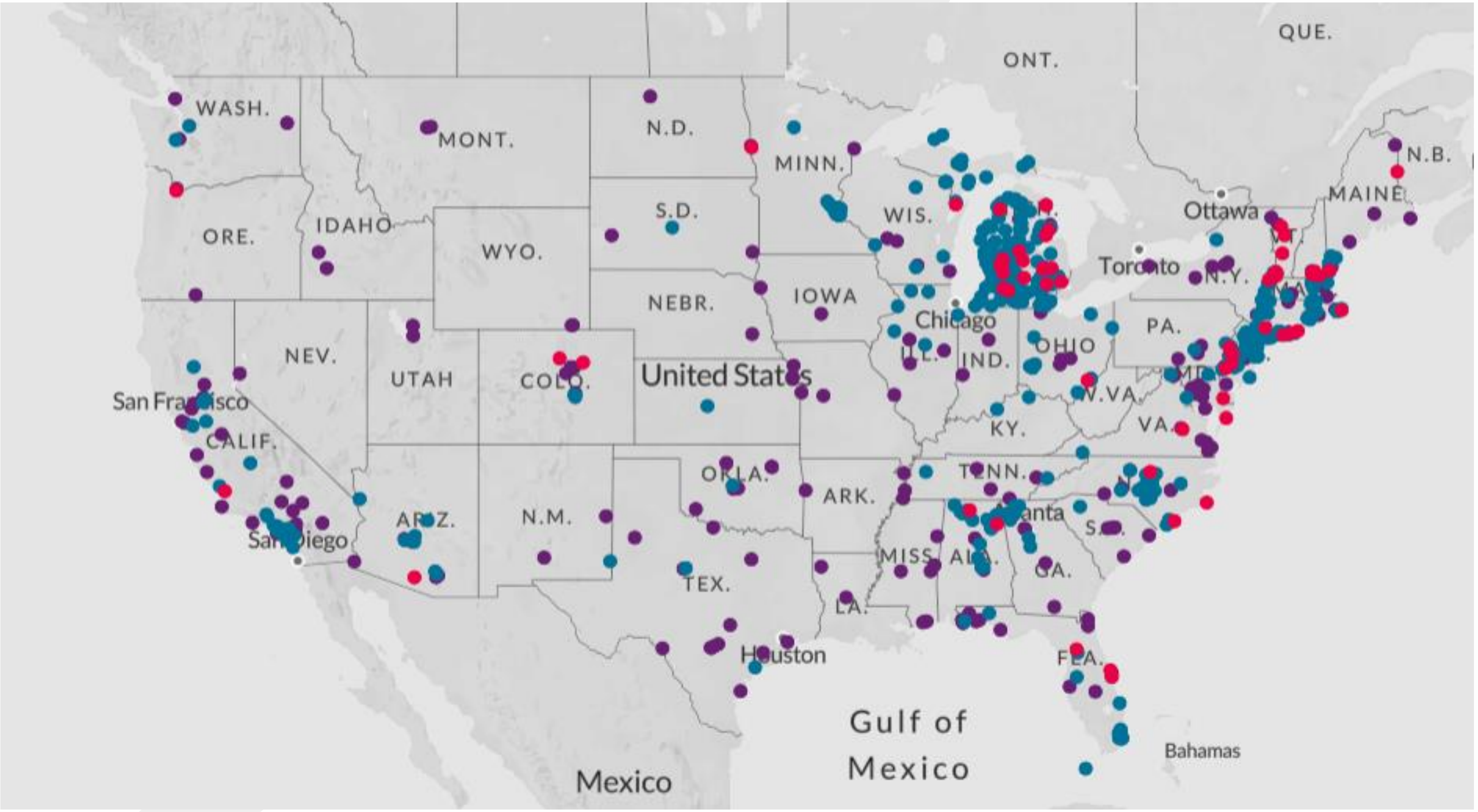
- Conventional sewage treatment methods do not efficiently remove PFAAs
- Conventional treatment processes can change PFAS concentrations
  - Increase in PFAA due to transformation of precursor PFAS

PFAS **SOURCES**

WTTP Biosolids

- PFAS have been found in domestic sewage sludge
- more than half of the sludge produced in the United States is applied to agricultural land as biosolids
- Application of biosolids as a soil amendment can result in a transfer of PFAS to soil
- PFAAs can enter the food chain through the use of biosolids-amended soil
- PFAS concentrations can be elevated in surface and groundwater in the vicinity of agricultural fields that received PFAS contaminated biosolids

PFAS **SOURCES**



https://www.ewg.org/interactive-maps/2019_pfas_contamination/map/

PFAS **METHODS**

	EPA 537 v1.1	EPA 537.1	EPA 537M	ISO 25101	ASTM D7979-16	DoD QSM 5.1	DoD QSM 5.2
Matrix	Drinking water	Drinking water	All Matrices	Drinking, ground, surface water	Water & wastewater	Matrices other than drinking water	Matrices other than drinking water
Analytes	14	18	24+	2 (PFOA, PFOS)	21	24	25
Sample size	250 mL	250 mL	250 mL	~ 500 mL	5 mL	As received	As received
Holding time	14/28	14/28	14/28	14	28	14/28	14/28
Surrogate	3	4	3	-	9	19	19
Extraction	SPE	SPE	SPE	SPE	Liquid/liquid filtration	SPE, ENVI-Carb cleanup	SPE, ENVI-Carb cleanup
RLs (ng/L)	2 -14	2-14	2 -14	2 - 10	10-300	2+	2+
Quantification	Internal Std.	Internal Std.	Internal Std.	Internal Std.	External Std.	Isotope dilution or internal std.	Isotope dilution or internal std.
Branch isomer	Yes	Yes	Yes	No	No	Yes	Yes

PFAS METHODS – **WHAT'S NEXT**

	EPA Method 8327 (Draft)	EPA Method 8328 (Draft)
Matrix	non-potable waters	non-potable waters and solids
Analytes	24	24
Extraction	Direct Injection	SPE
Quantification	Internal Standard (?)	Isotope Dilution
Notes	screening method	DoD will assist with external lab validation

- SW-846 8327 was issued for 30 days of public comment on 6/21/19.
- SW-846 8328 in the works for soil.
- UCMR 5 – EPA has proposed yet another DW method – 533.

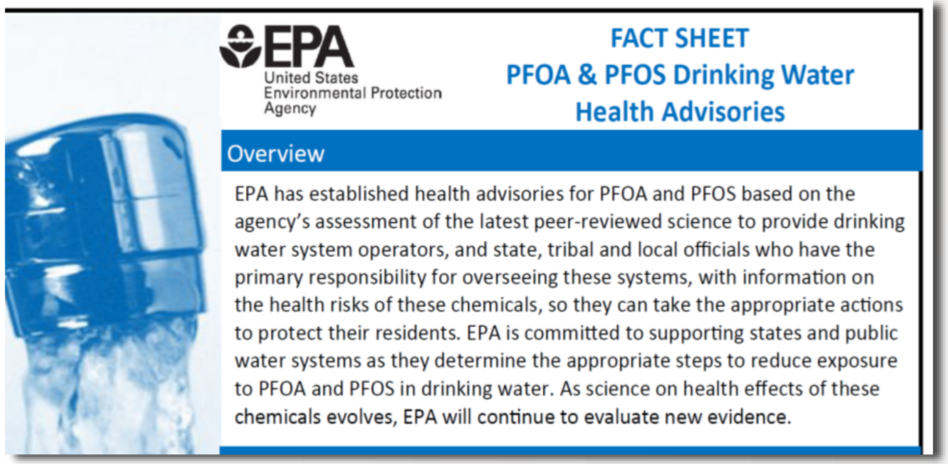
PFAS **RESOURCES**

Interstate Technology and Regulatory Council (ITRC)

1. Naming Conventions and Physical and Chemical Properties
2. Regulations, Guidance, and Advisories
3. History and Use
4. Environmental Fate and Transport
5. Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods
6. Remediation Technologies and Methods
7. Aqueous Film Forming Foam

See https://pfas-1.itrcweb.org/

PFAS **REGULATORY HISTORY**



EPA
United States Environmental Protection Agency

FACT SHEET
PFOA & PFOS Drinking Water Health Advisories

Overview

EPA has established health advisories for PFOA and PFOS based on the agency's assessment of the latest peer-reviewed science to provide drinking water system operators, and state, tribal and local officials who have the primary responsibility for overseeing these systems, with information on the health risks of these chemicals, so they can take the appropriate actions to protect their residents. EPA is committed to supporting states and public water systems as they determine the appropriate steps to reduce exposure to PFOA and PFOS in drinking water. As science on health effects of these chemicals evolves, EPA will continue to evaluate new evidence.

2013 - 2015 – PFAS included in UCMR 3, Pace analyzes over 3,000 samples. Since then Pace has analyzed over 10,000 samples.

May 2016 - EPA issues Health Advisory recommending a combined drinking water limit for PFOA and PFOS of 70 parts per trillion.

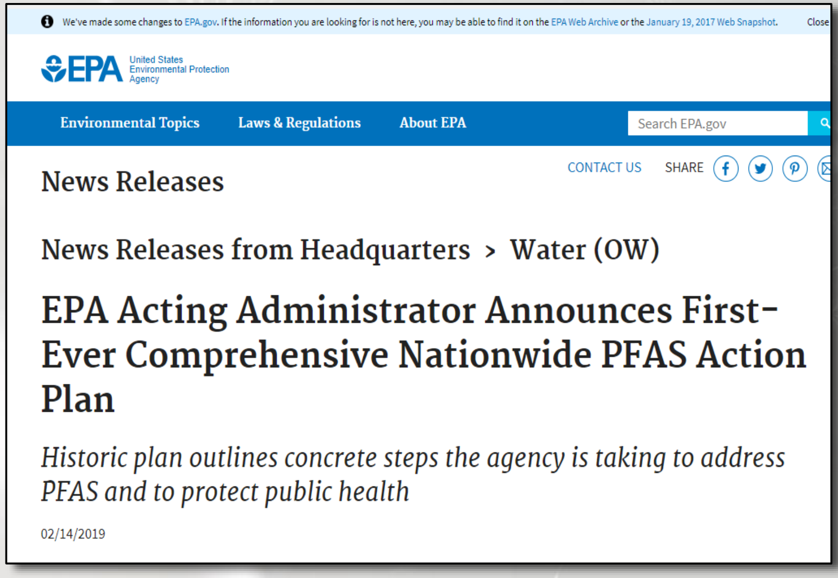
2016 to date – Numerous sites including DoD and industrial facilities are investigated and being investigated, and found to be contaminated. Many are impacting public and private water supplies.

PFAS **REGULATORY HISTORY**

Late 2018 - Bottled and package water producers association (IBWA) directed its members to test all products in 2019 for PFAS.

2/14/19 – Andrew Wheeler, EPA Administrator, announces PFAS Action Plan:

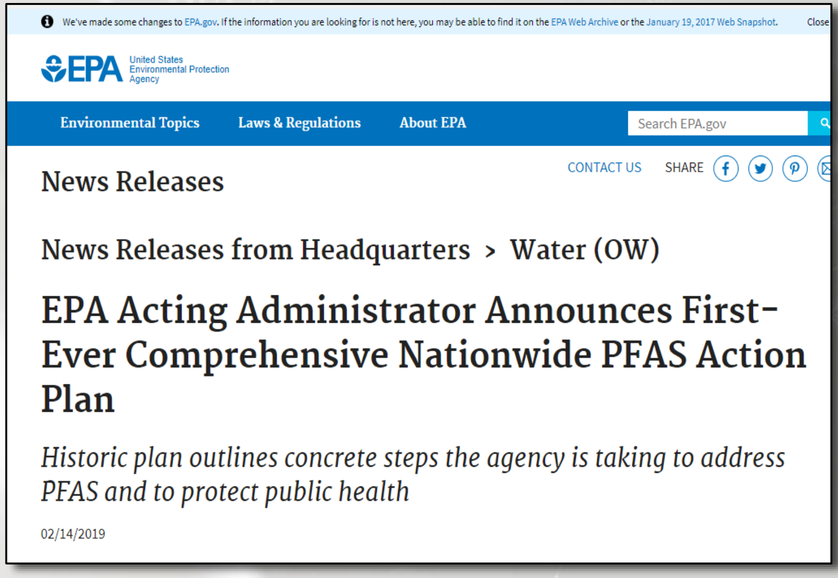
- Implement process to add PFOA & PFOS to the SDWA MCL and the Hazardous Substance list in 2019.
- Monitoring - nationwide drinking water monitoring for extended list of PFAS under the next UCMR monitoring cycle (UCMR 5) in 2023-2025.



PFAS **REGULATORY HISTORY**

2/14/19 – Andrew Wheeler, EPA Administrator, announces PFAS Action Plan:

- Clean-up - EPA continues strengthening enforcement authorities and clarifying cleanup strategies through actions such as designating PFOA and PFOS as **hazardous substances** and developing interim groundwater cleanup recommendations.
- Toxics - EPA is considering the addition of PFAS chemicals to the Toxics Release Inventory and rules to prohibit the uses of certain PFAS chemicals (TSCA).



PFAS REGULATORY HISTORY

April 25, 2019 - USEPA Draft Interim Recommendations to Address Groundwater Contaminated with PFOA and PFOS issued

- Open for comment for 45 days (June 10, 1019)
- Screening Level
  The draft interim screening level is 40 parts per trillion (ppt) for each compound individually. As stated by EPA, “screening” is “the process of identifying and defining areas, contaminants, and conditions at a particular site that may warrant further attention.” They are not technically cleanup levels, but indicate that further risk assessment activities are warranted.

PFAS **REGULATORY HISTORY**

April 25, 2019 - USEPA Draft Interim Recommendations to Address Groundwater Contaminated with PFOA and PFOS issued

- Preliminary Remediation Goals (PRGs)
  - Using the PFOA and PFOS HAs of 70 ppt as the PRG for groundwater that is a current or potential source of drinking water, where no state or tribal MCL or other applicable or relevant and appropriate requirements (ARARs) exist
  - In situations where groundwater is being used for drinking water, EPA expects that responsible parties will address levels of PFOA and/or PFOS over 70 ppt
  - Screening levels and PRGs are not drinking water standards established under the Safe Drinking Water Act

PFAS **REGULATORY HISTORY**

April 25, 2019 - USEPA Draft Interim Recommendations to Address Groundwater Contaminated with PFOA and PFOS issued

- Eliminated an entire section that would have addressed how it would respond to what it has described as "immediate threats posed by hazardous waste sites."
- Analytical Perspective
  - The draft levels the agency announced on April 25 appear to only pertain to groundwater that is or could be used as drinking water.
  - EPA only has an approved PFAS test method for drinking water; the EPA is working on two SW-846 methods for other matrices with the intent to publish later this year.

PFAS **REGULATORY HISTORY**

September 2018 – NJDEP adopted DW MCL of 13 PPT for PFNA.

March 2019 - DEP directs Solvay, DuPont, Dow DuPont, Chemours, and 3M to provide a detailed accounting of use and discharge of PFAS, and notifies each of the state's intent to hold them financially responsible. Established interim GW standards for PFOA and PFOS at 10 PPT.

PFAS REGULATORY HISTORY

April 11, 2019 - PDEP announces plan to prioritize and sample Public Water Systems (400 in Phase 1) for PFAS based on relative risk, i.e. proximity to:

- Military bases
- Fire training schools/sites
- Landfills
- HSCA sites
- Superfund sites
- Manufacturing facilities

pennsylvania
DEPARTMENT OF ENVIRONMENTAL PROTECTION

PFAS **REGULATORY HISTORY**

May 28, 2019 - ADEM announces that all Public Water Systems that did not participate in UCMR 3 will be required to sample for PFAS starting in October 2019.

- 266 Public Water Systems required to sample
- Surface Water/GWUDI systems – quarterly for 12 months at each Entry Point
- Groundwater systems – semi-annually for 12 months at each Entry Point

Alabama Department of Environmental Management

PFAS REGULATORY HISTORY

WaterWorld

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PFAS bill passes in Senate Committee

The bill directs EPA to set a drinking water standard for PFOS and PFOA, potentially other PFAS within two years.

Jun 21st, 2019

Credit — Photo by Skitterphoto from Pexels.

WASHINGTON, DC, JUNE 21, 2019 -- On Wednesday, the Senate Environment and Public Works Committee (EPW) approved a bipartisan bill to address per- and polyfluoroalkyl substances (PFAS). The bill combines a few other PFAS bills into one legislative package by amending S. 1507, the PFAS Release Disclosure Act.

June 21, 2019 - Growing pressure in Congress to speed EPA regulatory process

- Note **Senate** Environment & Public Works Committee bill approval
- Note 2 year limit to regulate
- Note "potentially other PFAS"
- Note this bill combines others into 1 package
- Note "bipartisan"
- The sponsors intend to add the bill to this week's Defense Authorization Act

PFAS REGULATORY HISTORY

July 8, 2019 – Cuomo directs NY State Department of Health to adopt PFOA/PFOS DW limits

- Department of Health to immediately begin process of implementing limits
- MCL of 10 PPT for each compound
- Applicable to all PWSs regardless of size
- Most PWSs will be required to submit first round of sampling within 3 months of rule adoption

PFAS **REGULATORY HISTORY**

July 18, 2019 – NH issues final rule establishing DW & GW limits for 4 PFAS

- PFOA 12 PPT
- PFOS 15 PPT
- PFHxS 18 PPT
- PFNA 11 ppt

PFAS **REGULATORY HISTORY**

SUSTAINABILITY VIEW MORE STORIES >

PHASING OUT PRODUCTS CONTAINING PFAS

September 17, 2019

In partnership with suppliers, The Home Depot is working diligently to offer products that are innovative and safer for the enviro
minimizing the environmental impact of the products on its store shelves and has led the industry in creating chemical standard

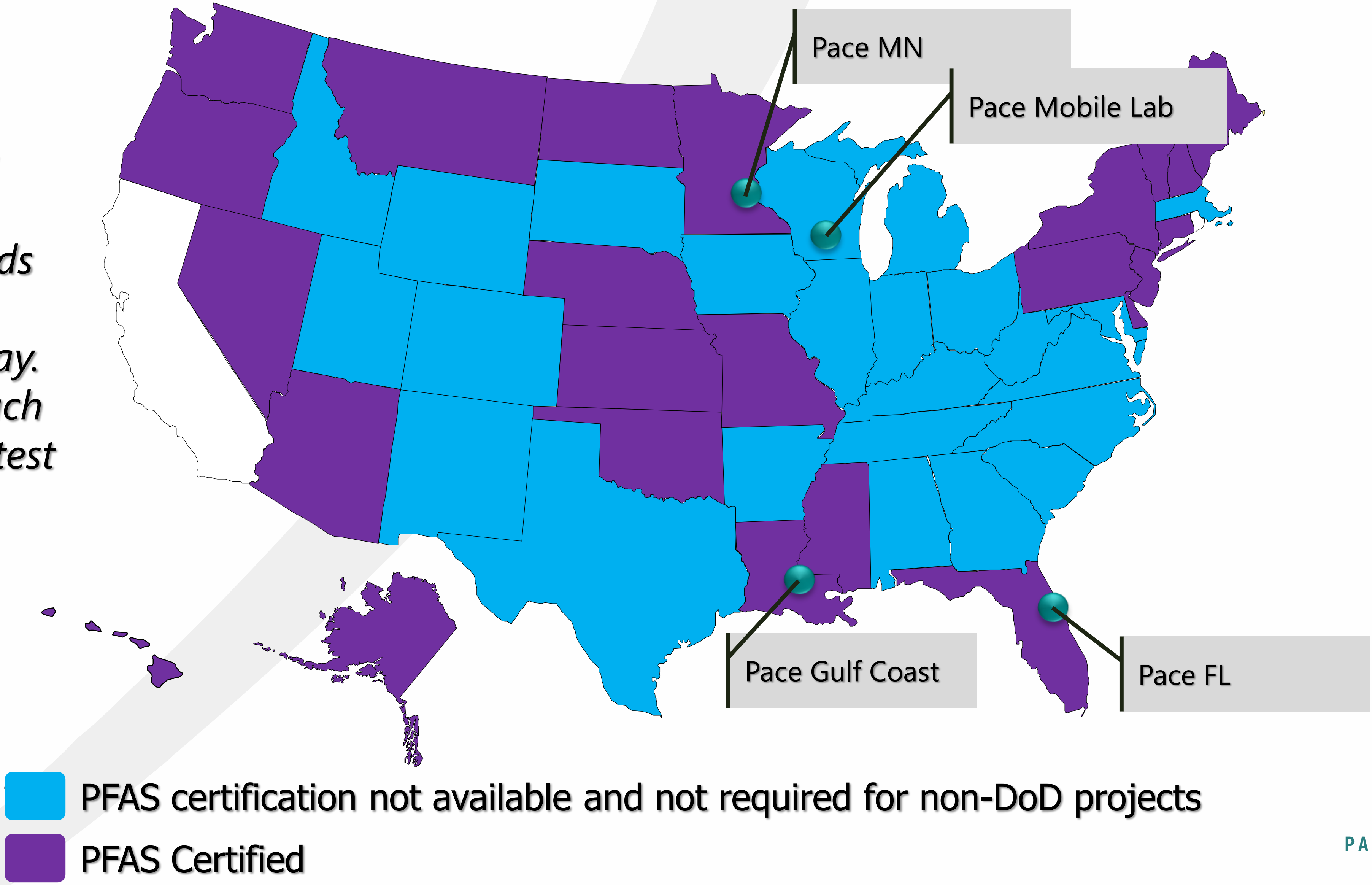
To build upon the strategy, The Home Depot will be phasing out Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) December
rugs.

PFAS **SAMPLING GUIDANCE**

- California - https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/pfos_and_pfoa/ddw_pfas_sampling_guidance_4_8_19.pdf
- ITRC - https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_site_characterization_3_15_18.pdf
- New Hampshire - https://www.des.nh.gov/organization/commissioner/documents/pfas-faq.pdf
- Michigan - https://www.michigan.gov/documents/pfasresponse/General_PFAS_Sampling_Guidance_634597_7.pdf
- ASDWA - https://www.asdwa.org/wp-content/uploads/2018/10/ASDWA-PFAS-Lab-Testing-Primer-10-10-18-Final.pdf

PFAS **AT PACE ANALYTICAL**

The market is rapidly changing and Pace with it. Certs and methods are all subject to change day by day. Contact us for each project for the latest info.



QUESTIONS

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