Per – and Polyfluoroalkyl Substances (PFAS)

Sources, Classes, Basic Chemistry, Naming Conventions, Methods, and Resources

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Per-and Polyfluoroalkyl Substances (PFAS)

- PFAS Classes
- Basic Chemistry
- Naming Conventions
- Analytical Methods

Per-and Polyfluoroalkyl Substances (PFAS)

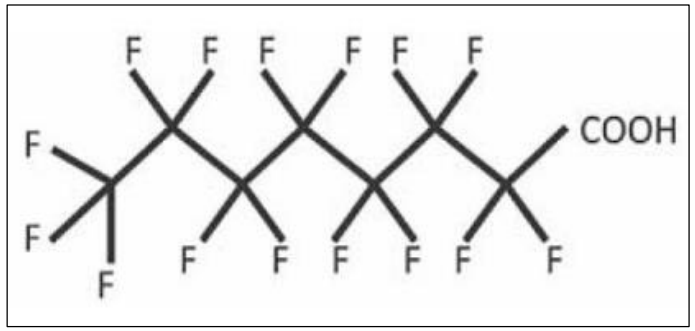
Per- and polyfluoroalkyl substances (PFAS) are a large, diverse group of manufactured compounds used in a variety of industries, such as aerospace, automotive, apparels, food packaging, fire-fighting foams, non-stick coatings/cookware, carpeting, and metal plating.

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

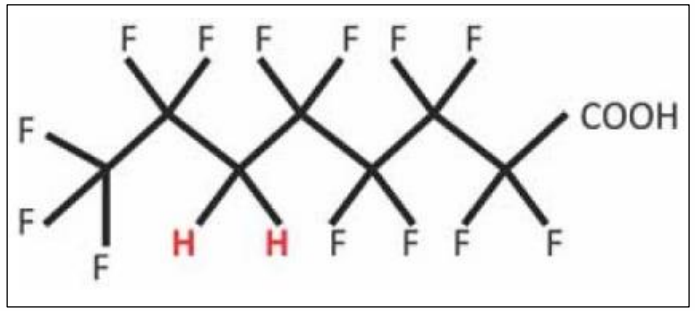
Phonetically: PFAS = PF + 

Per-and Polyfluoroalkyl Substances

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

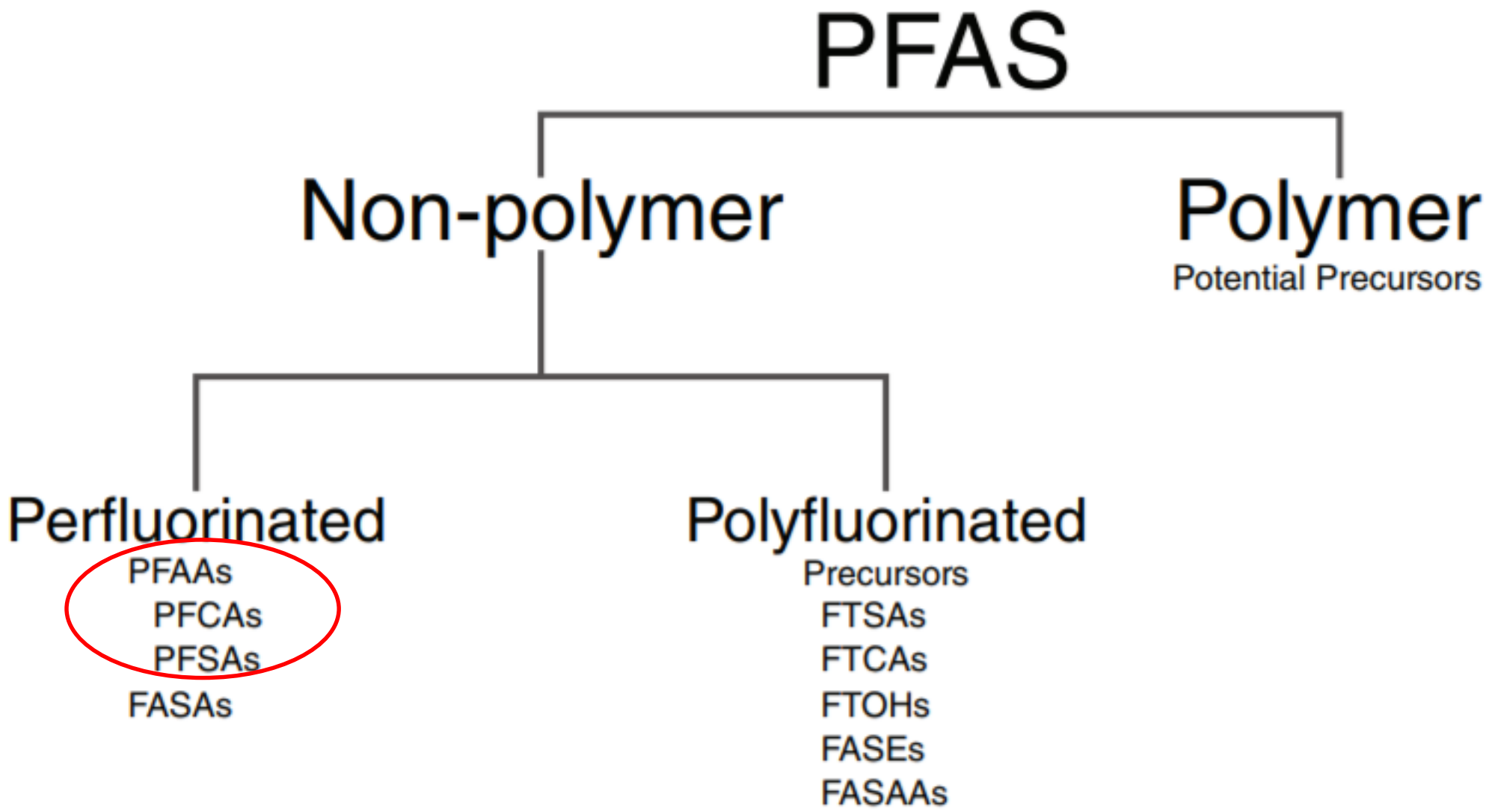


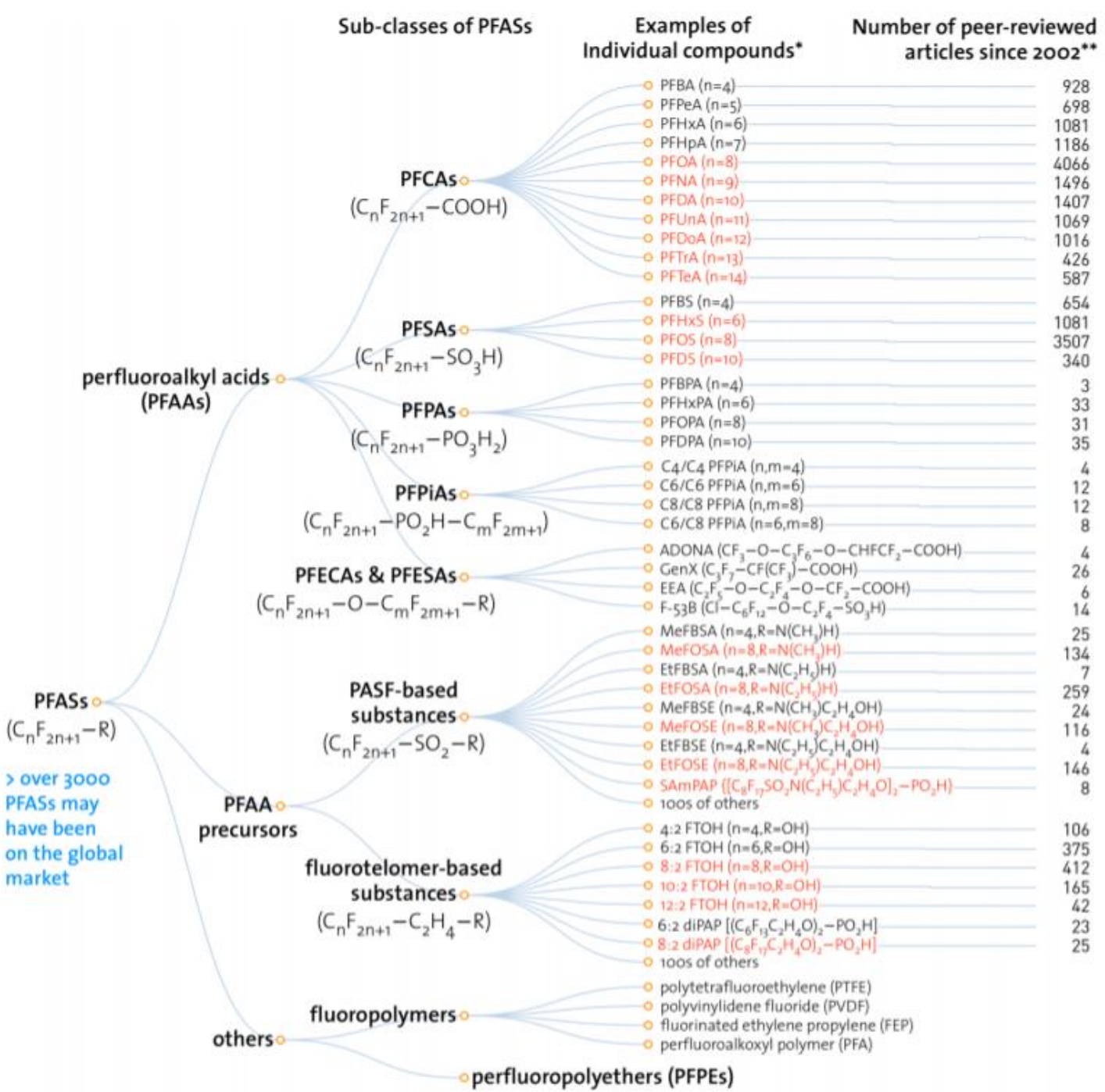
Polyfluorinated substances apply to chemicals in which <u>not all</u> the hydrogens on the carbons of the molecule are replaced by fluorine.



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

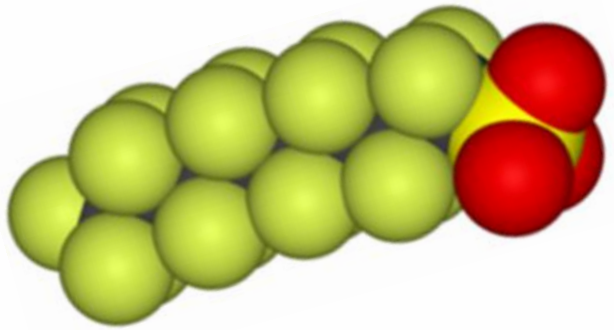




Source: Wang, et al 2017

BASIC CHEMISTRY: PFAA STRUCTURE

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

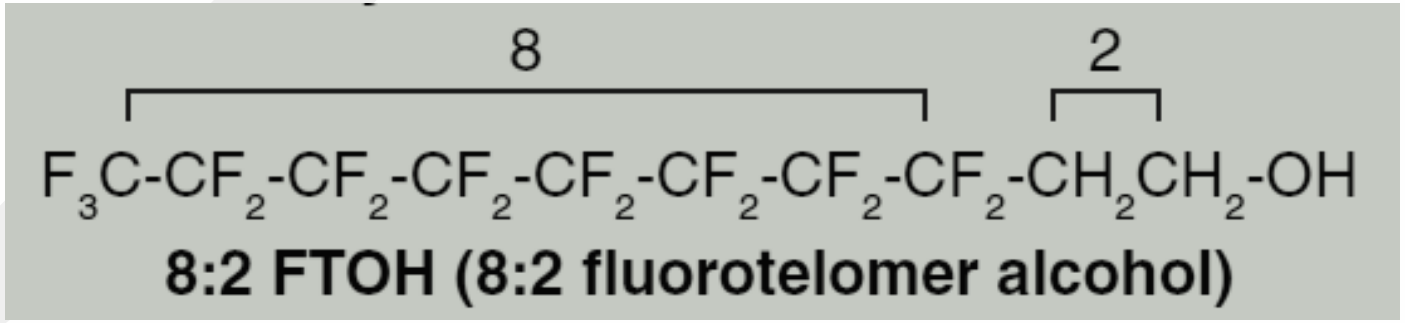


Perfluorooctane sulfonate (PFOS)

Perfluorooctane carboxylate (PFOA)

POLYFLUORINATED BASIC STRUCTURE

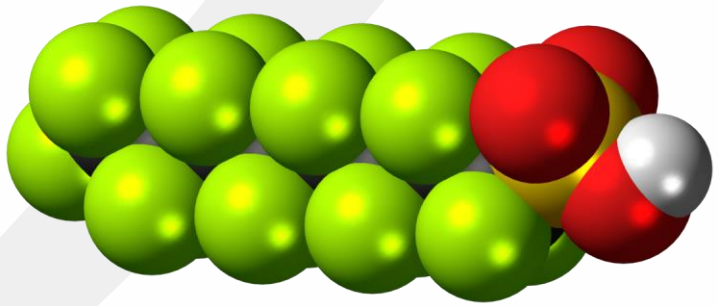
- **Partially fluorinated**
  - Non-fluorine atom (usually H or O) attached to at least one, but not all, of the carbon atoms in the “tail”
  - Creates a “weak link” susceptible to biotic or abiotic degradation
  - Often named using a “n:x” prefix
    - n = number of fully fluorinated carbons
    - x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



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^{o}C)

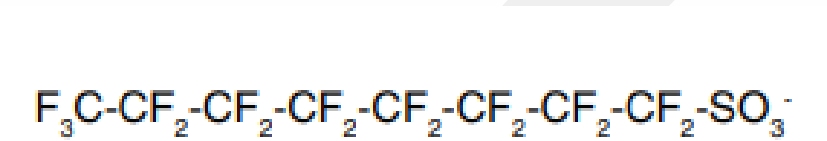


- **Perfluoroalkyl acids (PFAAs) are negatively charged**
  - Interact and sorb on positively charged minerals
  - Mediated by pH, chain length, and functional group

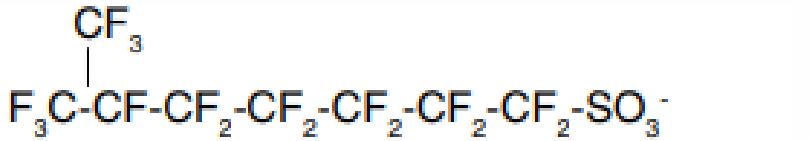
PFAS PROPERTIES

- **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

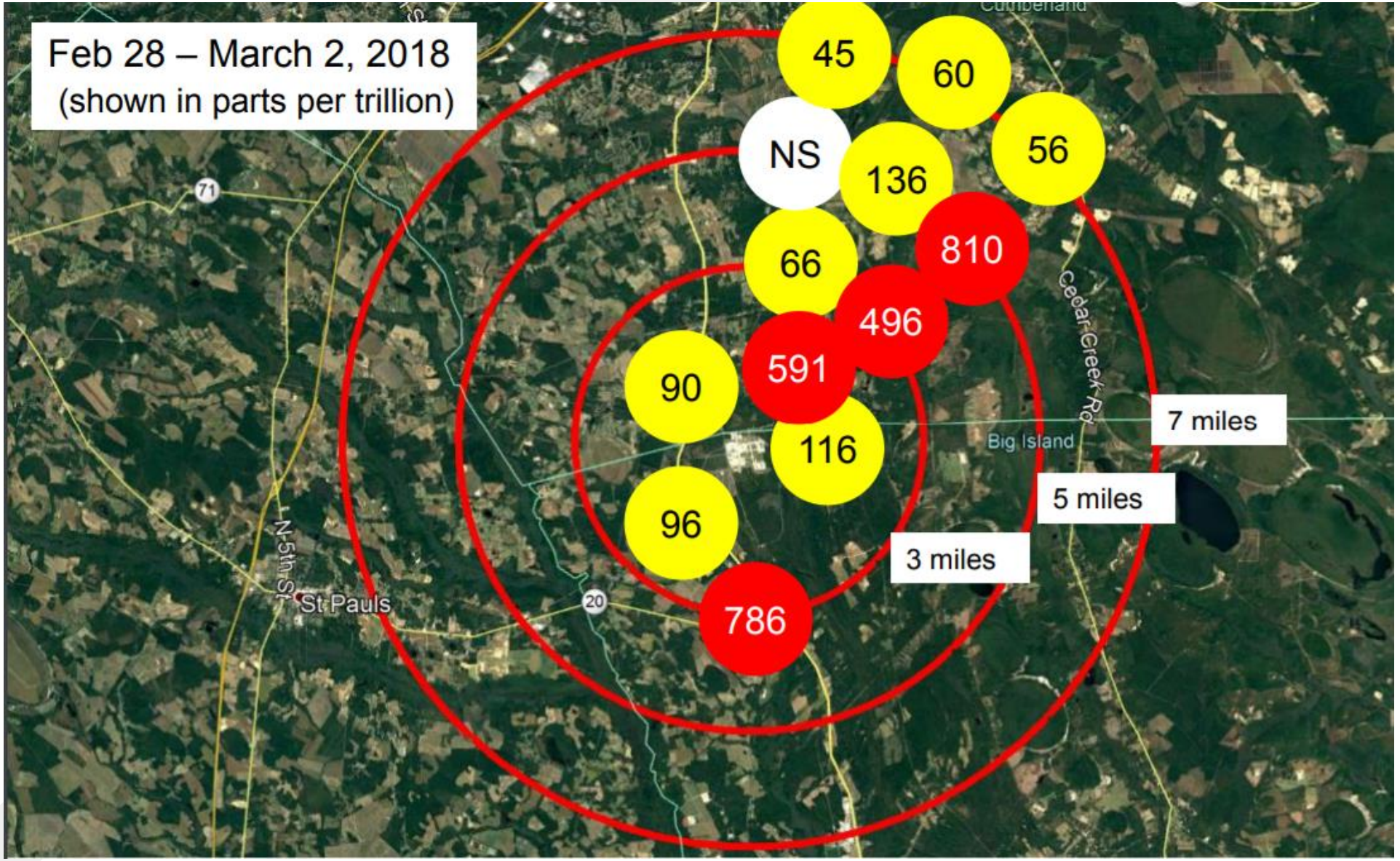


Linear Perfluorooctane sulfonate (PFOS)



Branched Perfluorooctane sulfonate (PFOS)

GenX Rainwater Data around Chemours



PFAS PROPERTIES

- PFAS typically have a carbon-fluorine “tail” and a non-fluorinated “head”
- The tail is hydrophobic (water fearing) and lipophobic (fat fearing)
- The head groups are polar and hydrophilic (water loving)
- The competing tendencies of the head and the tail can lead to a wide distribution in the environment

Perfluorooctane sulfonate (PFOS)

Perfluorooctane carboxylate (PFOA)

Source: ITRC Environmental Fate and Transport factsheet

PFAS PROPERTIES

Polar bears that hunt furthest north in the Barents Sea area – part of the Arctic Ocean – have 30-35% higher concentration of PFASs in their blood compared with coastal bears, a Norwegian-Russian study has found

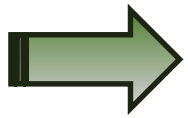
Source: ChemWatch July 2018

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	$C_{10}F_21SO_3H$	335-77-3

Source: ITRC Naming Conventions and Physical Chemical Properties factsheet

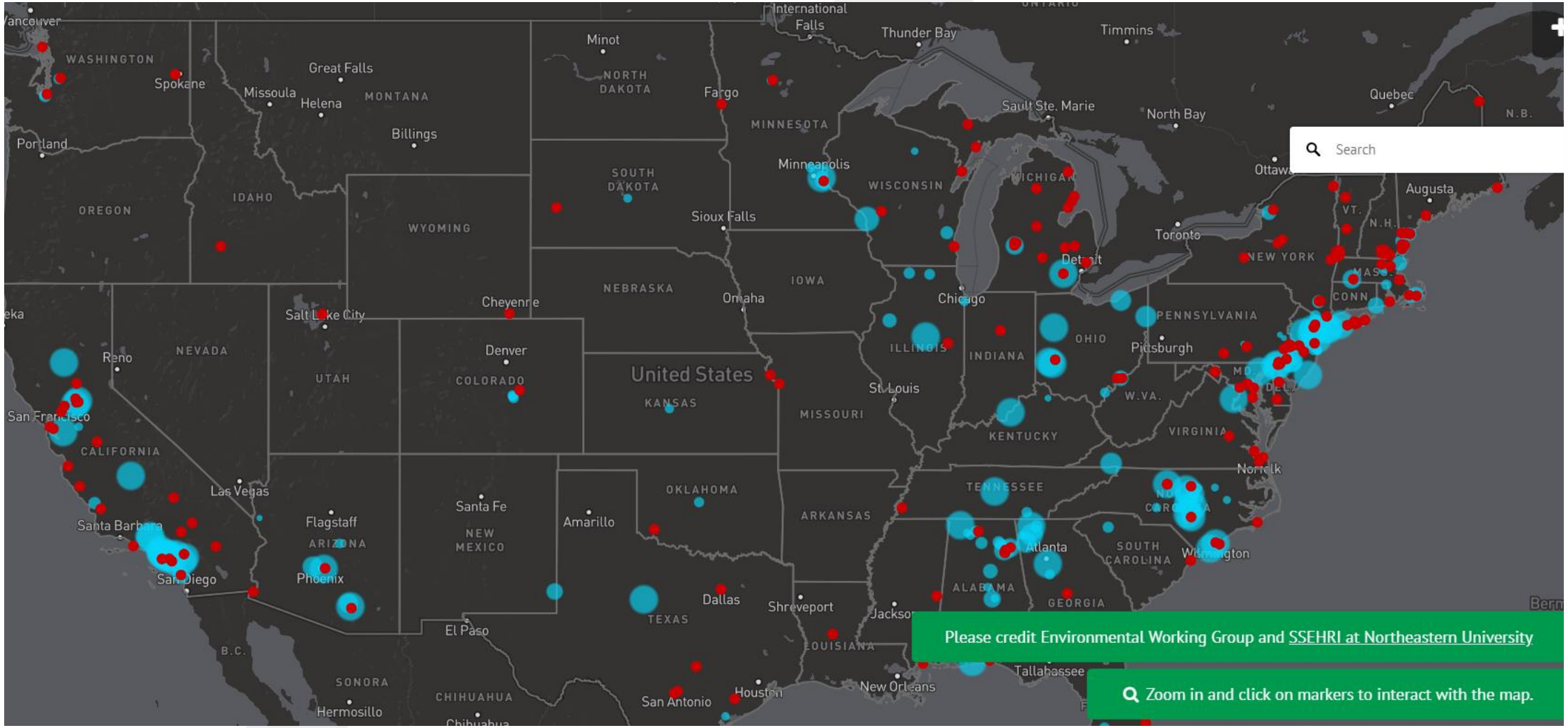
PFAS METHODS

	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)	EPA Method 8329 (Draft)
Matrix	non-potable waters	non-potable waters and wastewater	solids
Analytes	24	24	24
Extraction	Direct Injection	SPE	SPE
Quantification	Internal Standard (?)	Isotope Dilution	Isotope Dilution
Notes	screening method	DoD will assist with external lab validation	Pace in EPA lab validation program for this matrix

PFAS RESOURCES



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

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

QUESTIONS?

EPA PFAS REGULATORY UPDATE

- **May 2018**
  - Following its national PFAS leadership summit, the EPA first announced that it was developing groundwater cleanup recommendations

- **February 14, 2019**
  - EPA releases PFAS Action Plan

    - Drinking Water - EPA is moving forward with the Maximum Contaminant Level (MCL) process for PFOA and PFOS

EPA PFAS REGULATORY UPDATE

- **PFAS Action Plan (continued)**
  - 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)

  - Monitoring - EPA will propose nationwide drinking water monitoring for PFAS under the next UCMR monitoring cycle (UCMR5)

EPA PFAS REGULATORY UPDATE

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

  - Open for comment for 45 days (June 10, 1019)

  - <u>Screening Level</u>
    - 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

EPA PFAS REGULATORY UPDATE

- **USEPA Draft Interim Recommendations (continued)**
  - 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

EPA PFAS REGULATORY UPDATE

- **USEPA Draft Interim Recommendations (continued)**
  - 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 analytical method for drinking water; the EPA is working on methods for other matrices, including groundwater, but the agency has yet to publish other methods for review