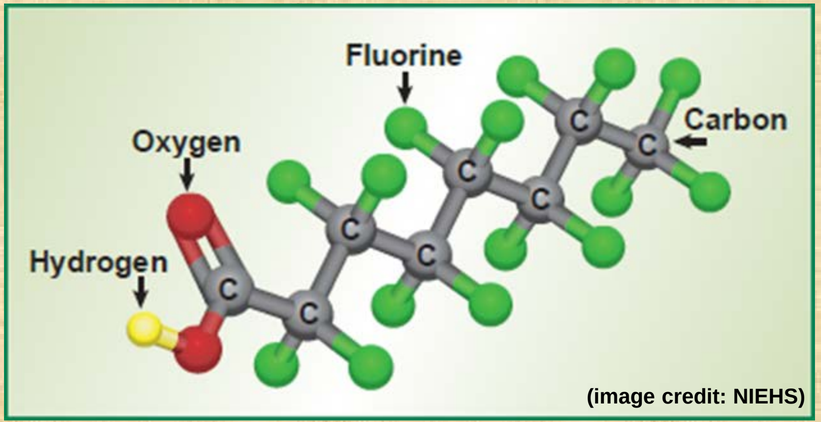
The Occurrence and Fate of Per- and Poly-fluoroalkyl substances (PFAS) in the Environment



Mark Brusseau

February 2019

Superfund Research Program
The University of Arizona

Contaminant Transport Group
University of Arizona

PFAS in the News

PBS NEWS HOUR

Menu

By Mark Scialla

0 comments

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What are PFASs, the toxic chemicals being found in drinking water?

Science Aug 12, 2016 12:15 PM EDT

SILENT-ER SPRING

The DDT of this generation is contaminating water all over the US and Australia

By Zoë Schlanger • September 7, 2018

Bloomberg

Business

3M Settles Minnesota Lawsuit for $850 Million

By Tiffany Kary

February 20, 2018, 1:53 PM MST *Updated on February 20, 2018, 5:02 PM MST*

- 2010 suit alleged cancers, colitis linked to Scotchgard toxin
- Chemicals not a health risk at current exposures, 3M said

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MMM
3M CO
208.77 USD
▲ +0.36 +0.17%

MINNESOTA POLLUTION CONTROL
Private Company

3M Co. has settled a lawsuit with Minnesota's Attorney General Lori Swanson for $850 million, putting an end to eight years of litigation over a former Scotchgard ingredient that got into the state's drinking water.

The funds will be used to finance projects that involve drinking water and water sustainability, according to statements from 3M and the state, after Minnesota alleged that chemicals known as PFCs could cause harm to citizens.

The agreement materialized just as jury selection got underway Tuesday, and after Judge Kevin S. Burke urged the parties to compromise, saying that it wasn't in the best interests of the state's citizens or 3M's shareholders for the case to drag on.

Senators Announce Funding For Research, Remediation Of PFAS Chemicals

By LUCAS WILLARD • APR 11, 2018

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0:53

New York's U.S. Senators have announced federal funding to support research and remediation efforts for communities facing contamination from the chemicals PFOA and PFOS.

Democrats Charles Schumer and Kirsten Gillibrand said the recently passed omnibus spending bill includes $63.8 million for the research and remediation of perfluoronated chemicals.

PFAS in the News

KGUN 9 ON YOUR SIDE > NEWS > LOCAL NEWS

Tucson Water shuts down contaminated wells near DM

Posted: 11:43 AM, Jun 18, 2018 **Updated:** 6:58 PM, Jun 18, 2018

By: Valerie Cavazos

TUCSON WATER

Tucson, Marana sue 3M, 4 other companies over water contaminants

By Joe Ferguson Arizona Daily Star Nov 8, 2018

Upgrade at Tucson Water treatment plant to remove more PFAS pollutants

By Tony Davis Arizona Daily Star Dec 13, 2018

Statements

The Madrid Statement:

"As scientists and other professionals from a variety of disciplines, we are concerned about the production and release into the environment of an increasing number of poly- and perfluoroalkyl substances (PFASs) for the following reasons:"

Perspectives | Brief Communication

Environmental Health Perspectives • VOLUME 123 | NUMBER 5 | May 2015

The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

http://dx.doi.org/10.1289/ehp.1509934

Outline

- What are PFAS
  - terminology
  - uses
  - sources & occurrence
  - exposure & health effects
  - regulations
- PFAS Properties
  - chemical structure
  - transport and fate in the environment
- Case Study

Terminology

- Originally referred to as PFCs --- Perfluorinated chemicals

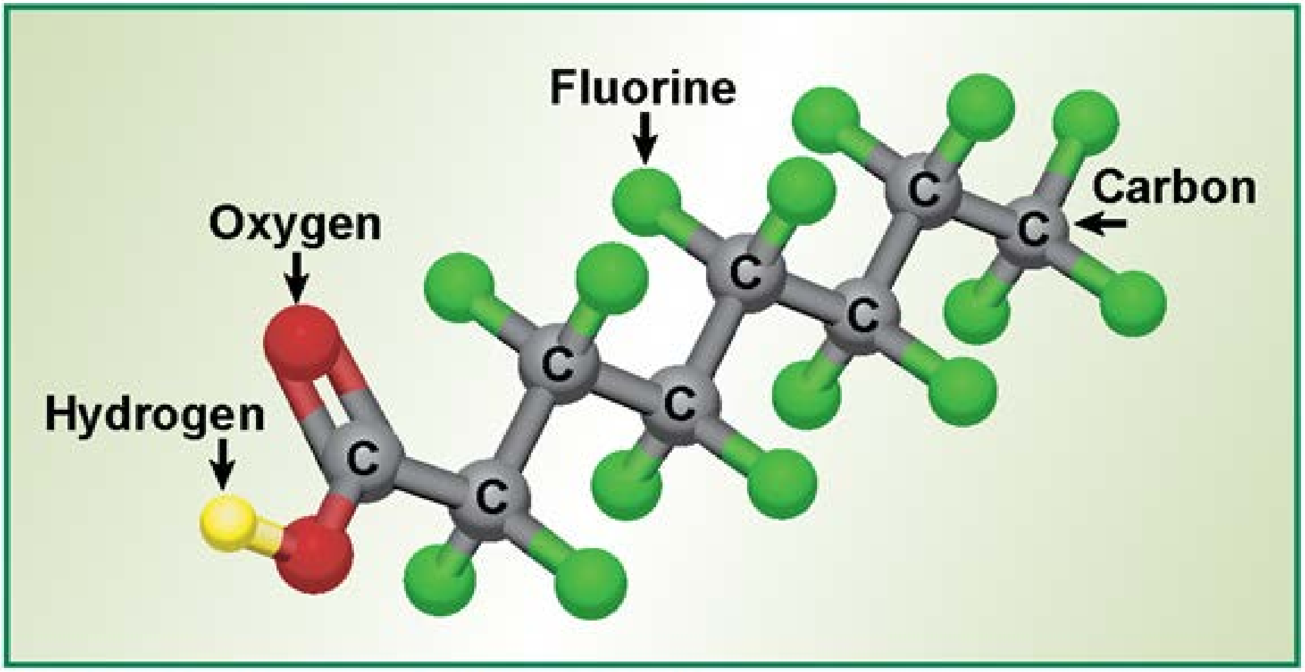
  - Confusion with perfluorocarbons (refrigerants)

- EPA standardizing terminology

  - Per- and poly-fluorinated compounds (PFAS) or (PFASs)

PFAS Compounds

PFAS Molecule (example):

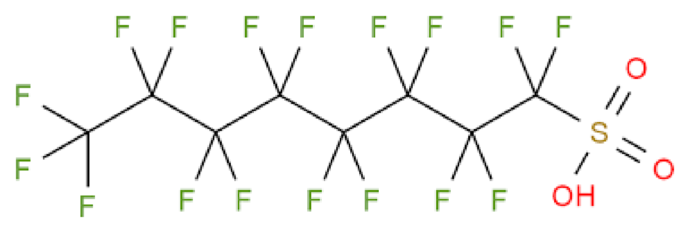


PFOA, also known as C8, has 8 carbons.

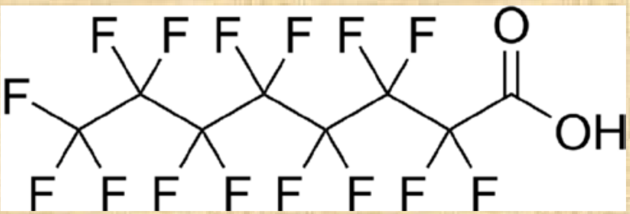
(image credit: NIEHS)

PFAS Compounds

The two most widely investigated & regulated PFAS:

PFOS: 

= perfluorooctanesulfonic acid

PFOA: 

= perfluorooctanoic acid

PFAS Compounds

PFAS comprise a large family of compounds (example):

Compound	Formula
Perfluorocarboxylic acids (PFCAs)	
PFBA (perfluorobutanoic acid)	C4 H F7 O2
PFPeA (perfluoropentanoic acid)	C5 H F9 O2
PFHxA (perfluorohexanoic acid)	C6 H F11 O2
PFHpA (perfluoroheptanoic acid)	C7 H F13 O2
PFOA (perfluorooctanoic acid)	C8 H F15 O2
PFDA (perfluorodecanoic acid)	C10 H F19 O2
PFUnA (perfluoroundecanoic acid)	C11 H F21 O2
PFDoA(perfluorododecanoic acid)	C12 H F23 O2
PFTriA (perfluorotridecanoic acid)	C13 H F25 O2
Perfluorosulfonic acids (PFSAs)	
PFBS (perfluorobutanesulfonic acid)	C4 H F9 S O3
PFHxS (perfluorohexanesulfonic acid)	C6 H F11 S O3
Fluorotelomer sulfonates (FTSs)	
4:2 FTS	C6 H5 F9 S O3
6:2 FTS	C8 H5 F13 S O3
10:2 FTS	C10 H5 F17 S O3
Polyfluoroalkyl phosphate diesters (diPAPs)	
6:2-8:2-diPAP	C18 H9 F30 O4 P
8:2-8:2-diPAP	C20 H9 F34 O4 P
Polyfluorinated ethers (PF ethers)	
C5 polyfluoro ether	C5 H F9 O5
C6 polyfluoro ether	C6 H F11 O6

PFAS Compounds

Organisation for Economic Co-operation and Development

May 2018

TOWARD A NEW COMPREHENSIVE GLOBAL DATABASE OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs):

SUMMARY REPORT ON UPDATING THE OECD 2007 LIST OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs)

"In total, 4730 PFAS-related CAS numbers have been identified and manually categorised in this study"

CAS = Chemical Abstracts Service

Uses

The FluoroCouncil is a global organization representing the world’s leading FluoroTechnology companies

https://fluorocouncil.com/

Uses

PFAS have been used for many purposes (examples):

- Consumer products
  - Nonstick materials--- Teflon
  - Stain-resistant textiles--- Scotchguard, Stainmaster
  - Water-resistant textiles--- Gore-Tex
  - Personal care products (cosmetics, shampoo)
  - Cleaning products
  - Paints
  - Food packaging (fast foods)

- Fire-fighting foams→ major issue at many military installations

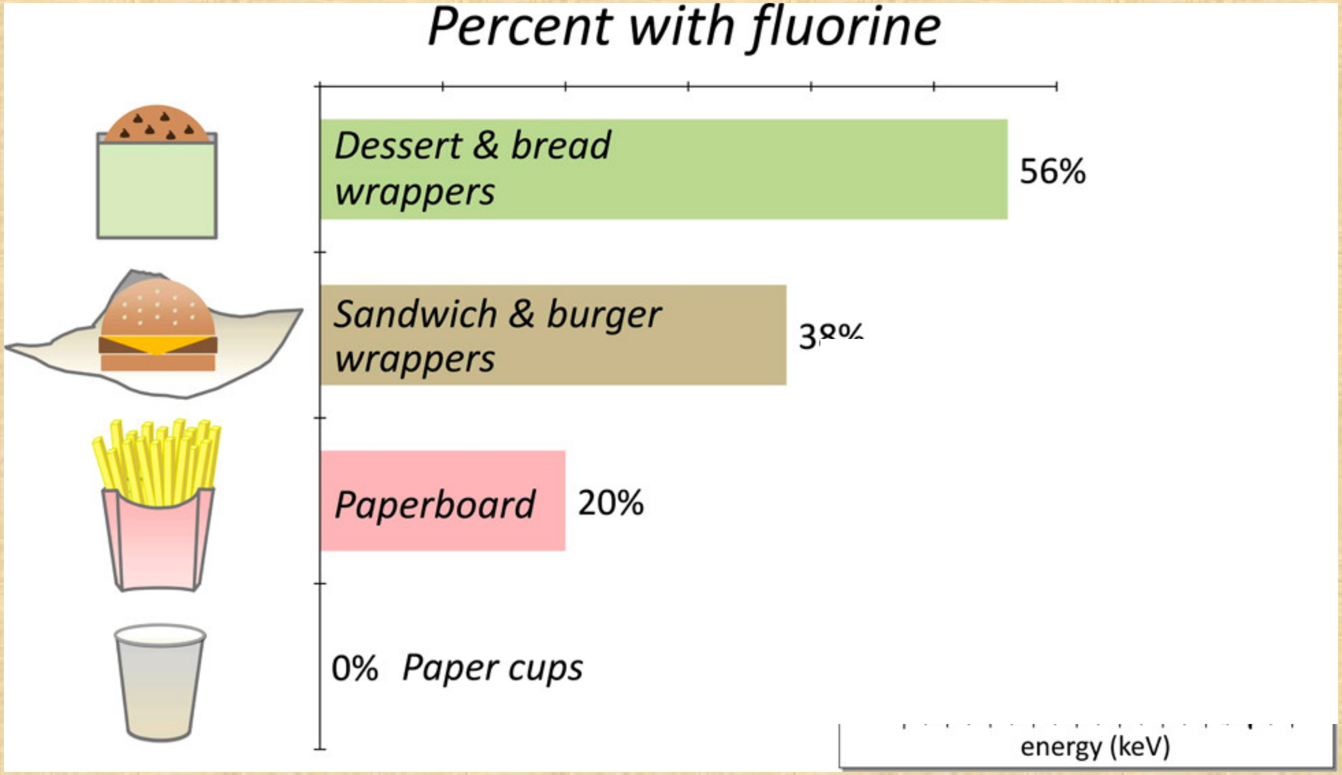
- Engineered coatings
- Plastics

Uses- Coatings & Textiles

- Non-stick and stain-, grease-, and water-resistant properties

Uses- Food Packaging

Fluorinated Compounds in U.S. Fast Food Packaging



From: Schaider et al., 2017

Uses- Fire Fighting Foam

- AFFF- aqueous film forming foam
  - for Class B: flammable liquids (hydrocarbons)

- Airports

- Military Bases

Sources to the Environment

- Manufacturing facilities

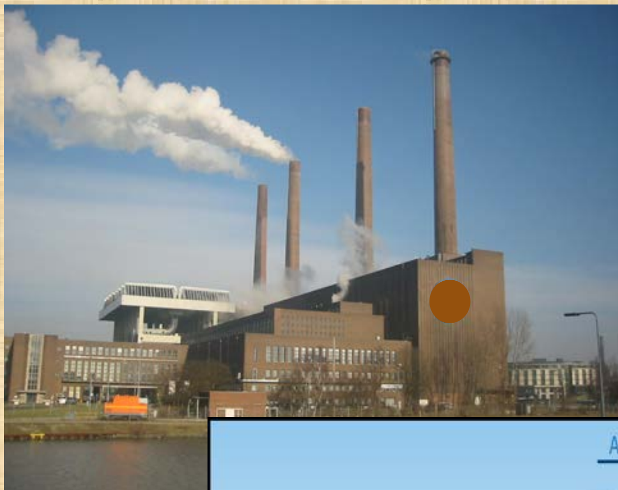
>>> Output to:

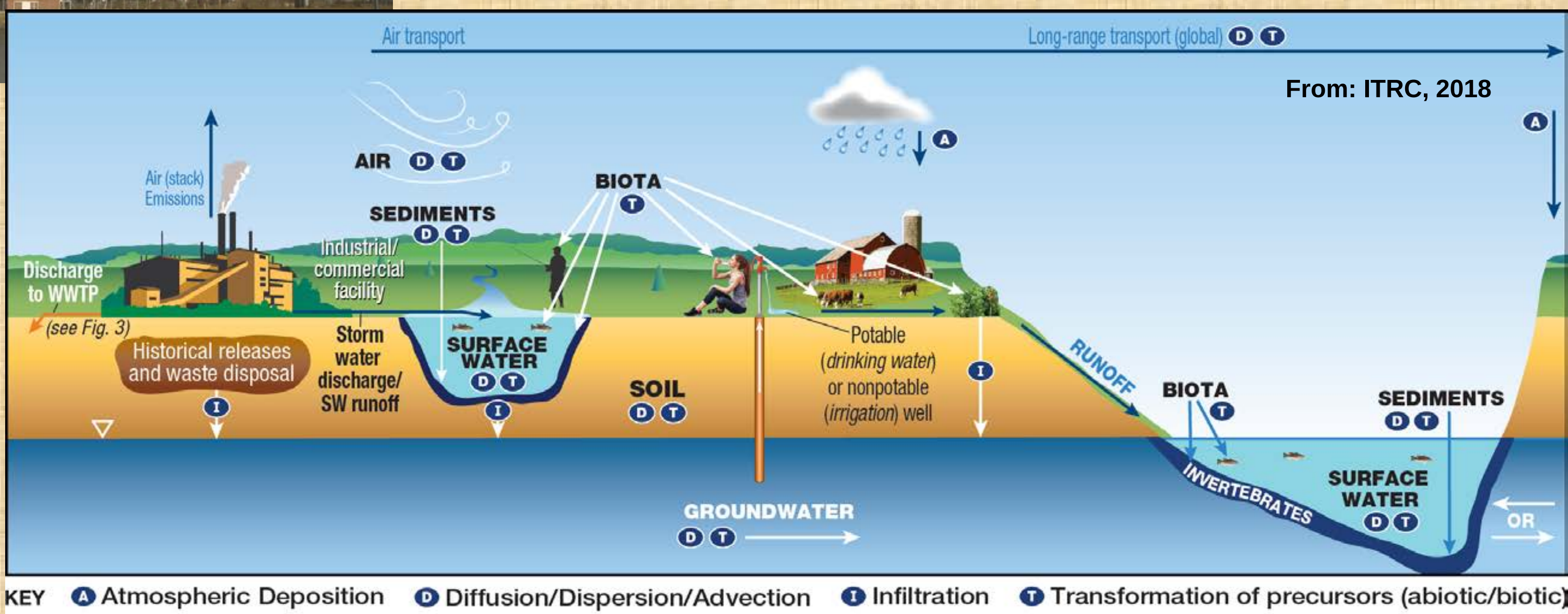
-atmosphere

-surface water

-soil

-groundwater





From: ITRC, 2018

Figure 2. Conceptual site model for industrial sites.

Sources to the Environment

- Point of use Sites
  - Fire-training facilities

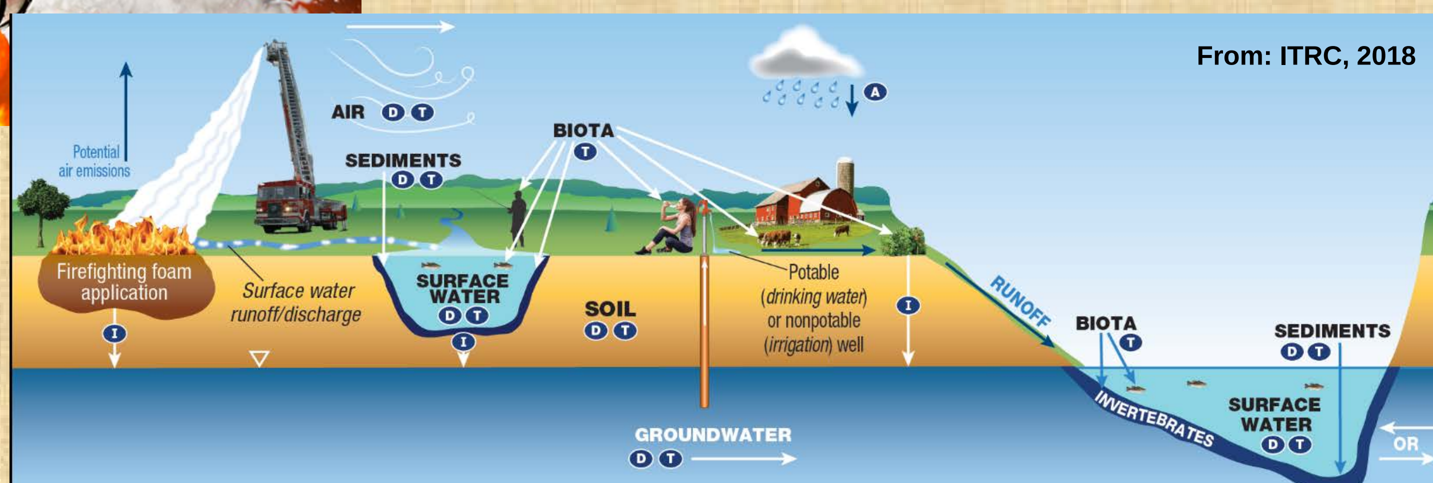
>>> Output to:

-atmosphere

-surface water

-soil

-groundwater



KEY A Atmospheric Deposition D Diffusion/Dispersion/Advection I Infiltration T Transformation of precursors (abiotic/biotic)

Figure 1. Conceptual site model for fire training areas.

Sources to the Environment

- Disposal Sites

Landfills

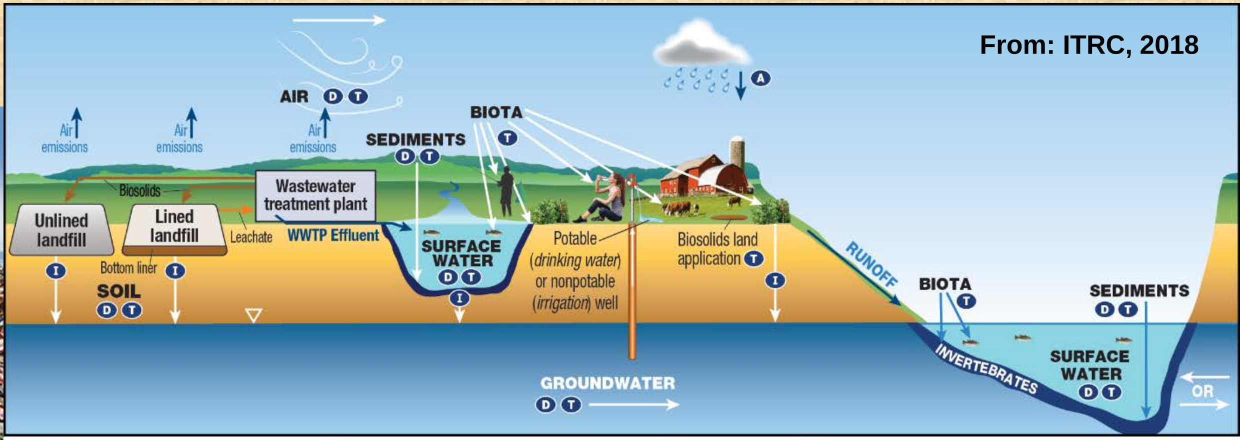


Figure 3. Conceptual site model for landfills and WWTPs.

Wastewater treatment plants

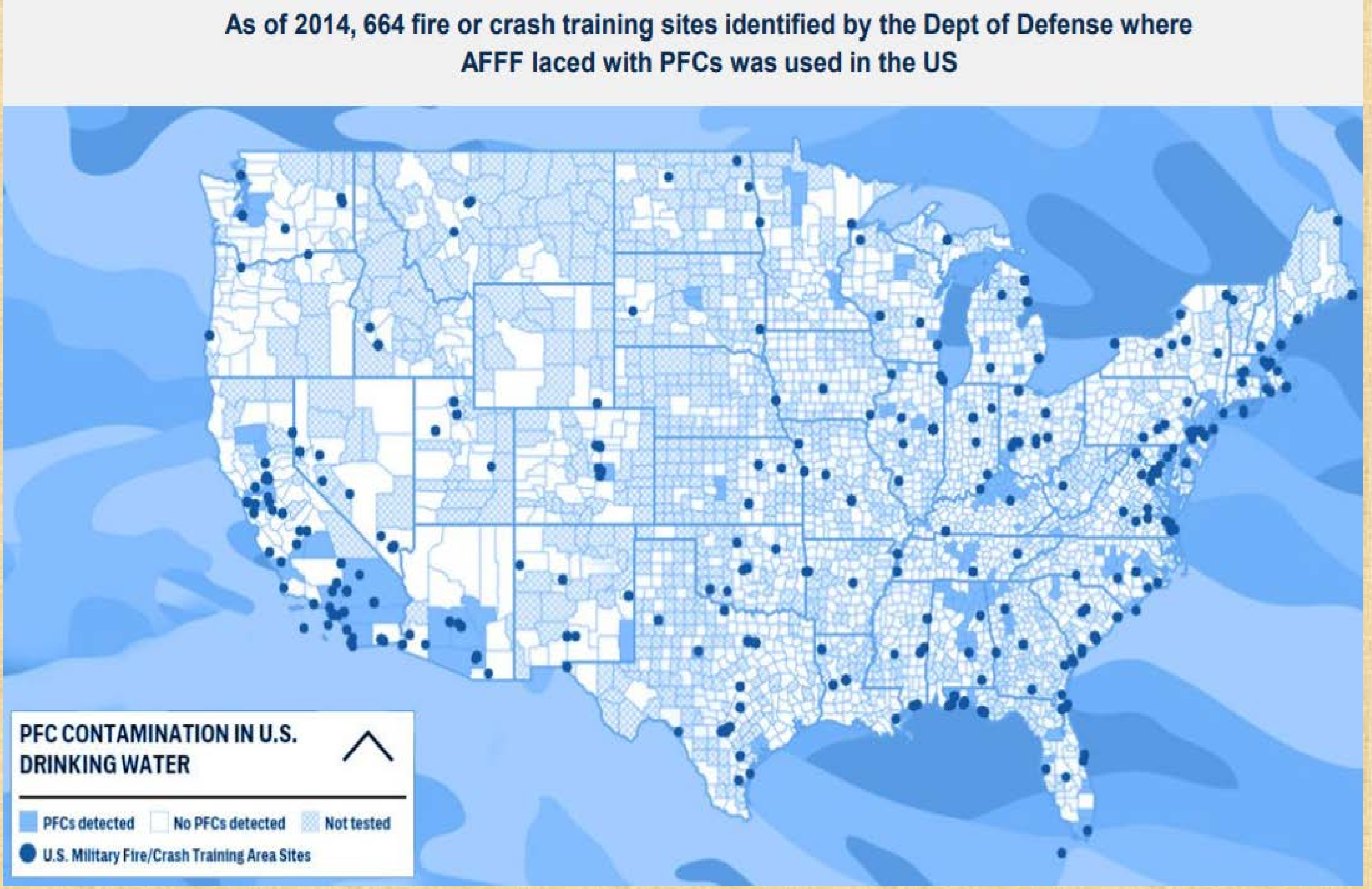
Biosolids application sites

Occurrence

- Present at many military installations
- Present at airports
- Present at manufacturing plants
- Drinking water

Occurrence – DOD Sites

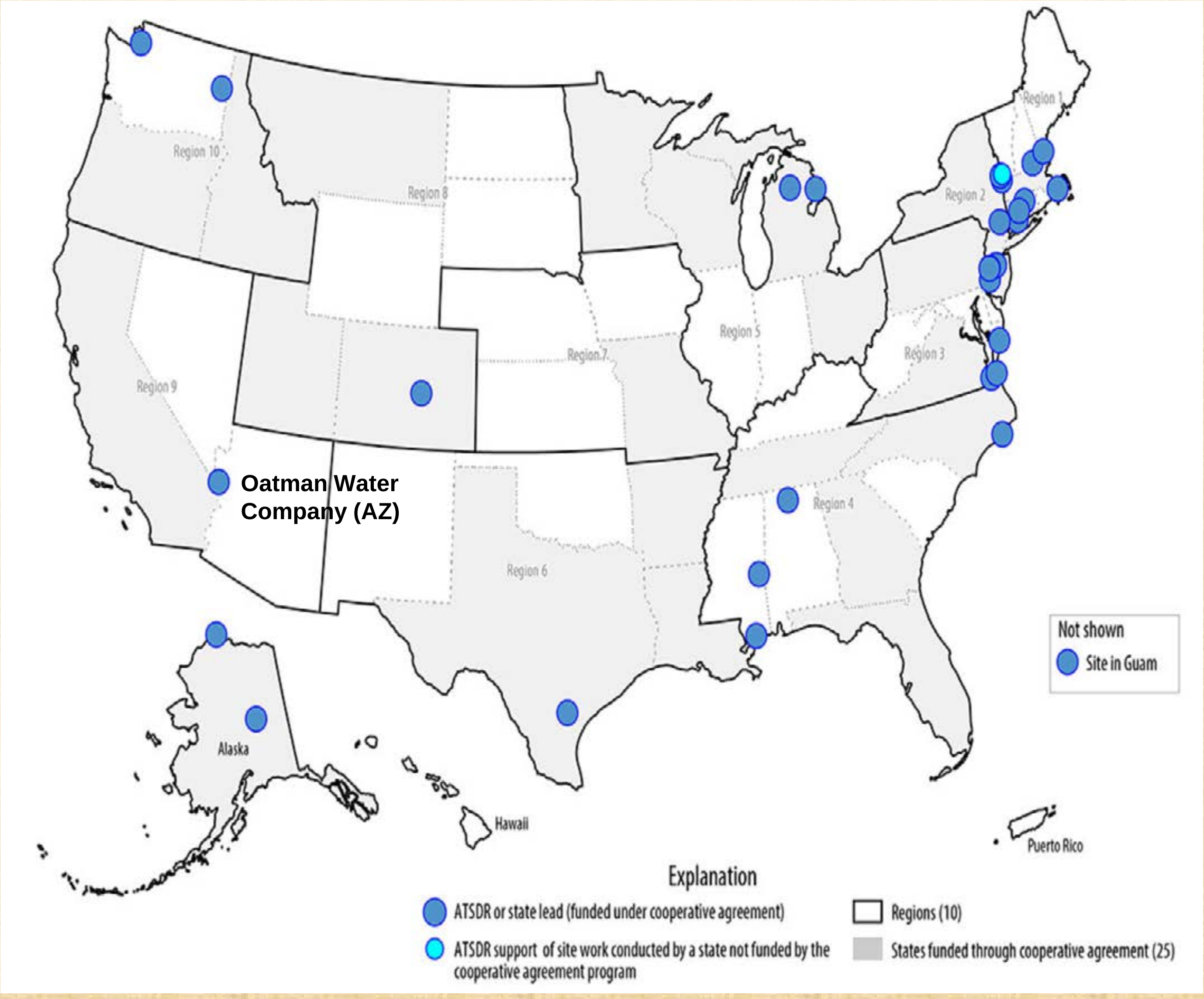
From: Testing for Pease, 2017



Occurrence – ATSDR Sites

PFAS sites with ATSDR involvement [Agency for Toxic Substances and Disease Registry]
https://www.atsdr.cdc.gov/pfc/atsdr_sites_involvement.html

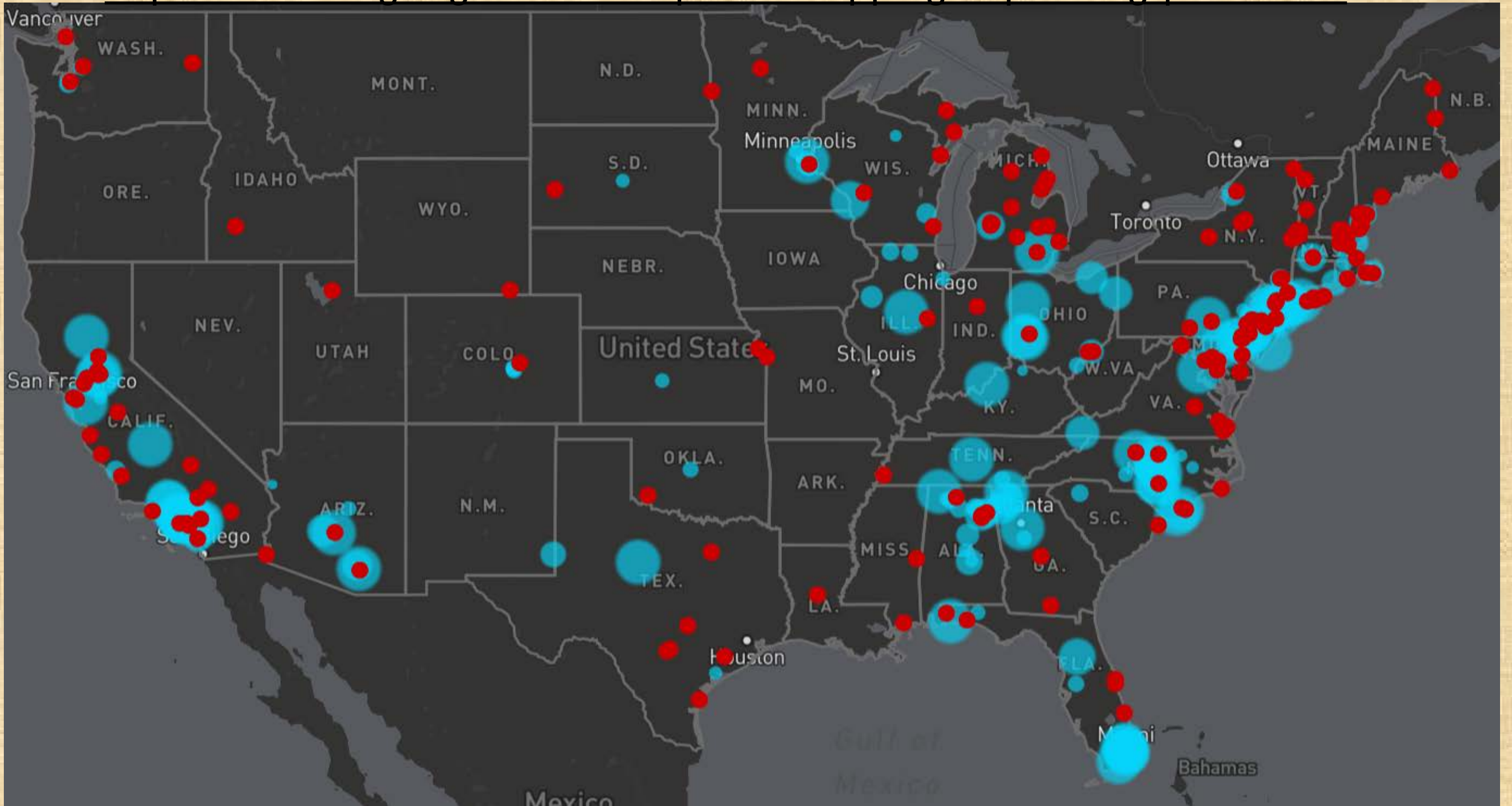
~30 Sites



EWG Study- 2018

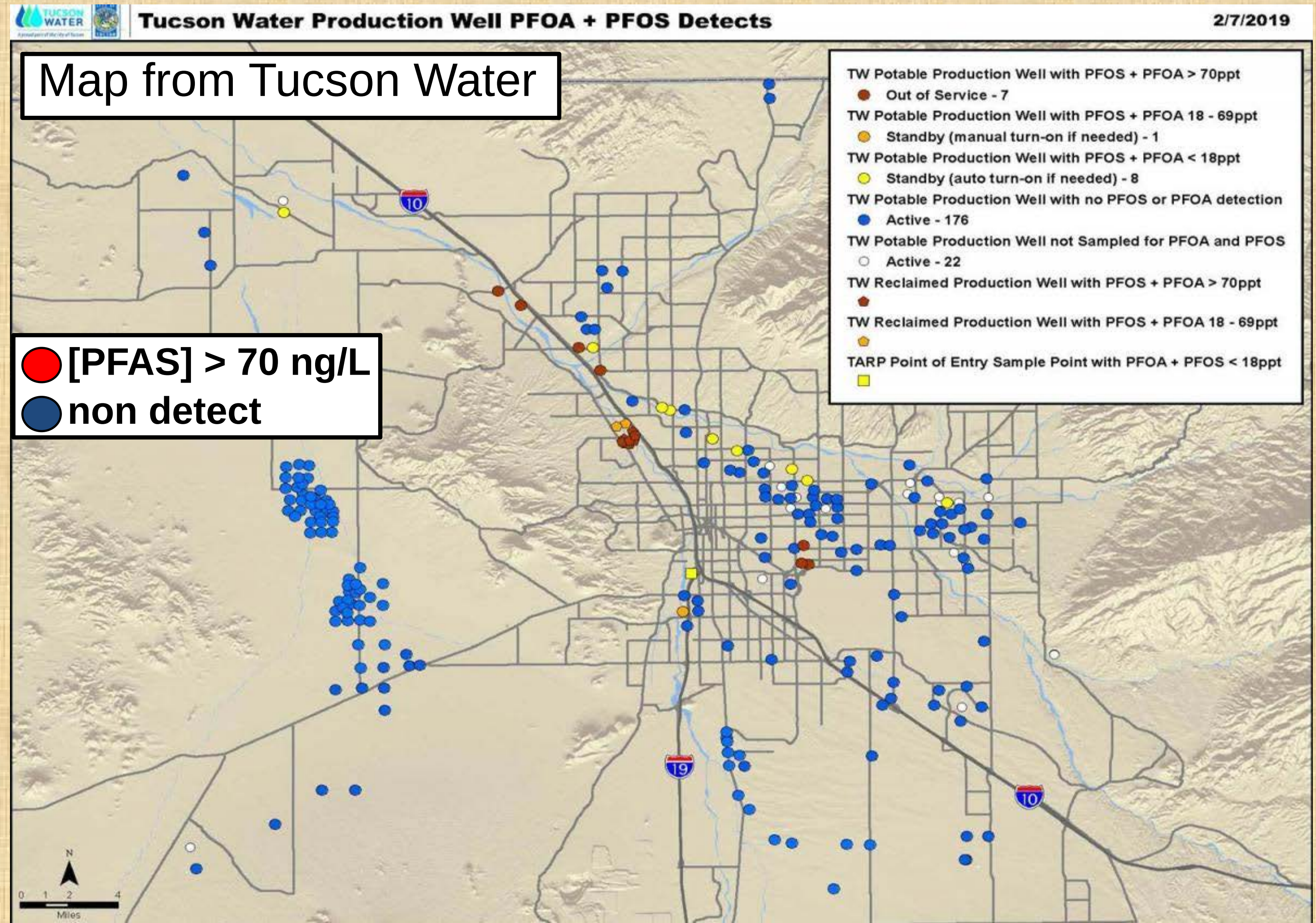
- Public water supply with PFAS detection--- 16 M people affected
- Site with identified PFAS in groundwater--- 172 sites

Source: Environmental Working Group & SSEHRI-Northeastern University
https://www.ewg.org/research/update-mapping-expanding-pfas-crisis



PFOA & PFOS in Tucson GW

https://www.tucsonaz.gov/water/pfas



PFAS in US Drinking Water

Recent survey was conducted to determine the occurrence of select PFAS in drinking water for all 4064 public water supplies that serve >10,000 individuals in the US.

Drinking water supplies for 6 million U.S. residents exceed US EPA's lifetime health advisory for PFOS/PFOA

From: Hu et al., 2016.

*Used EPA data

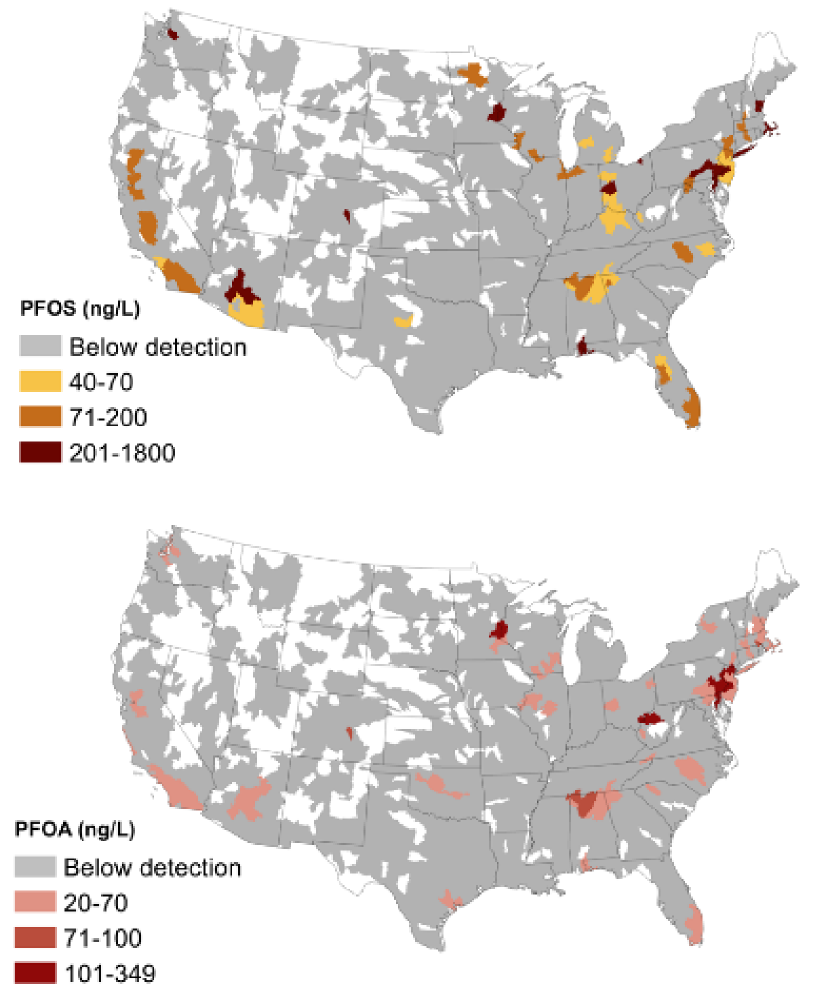
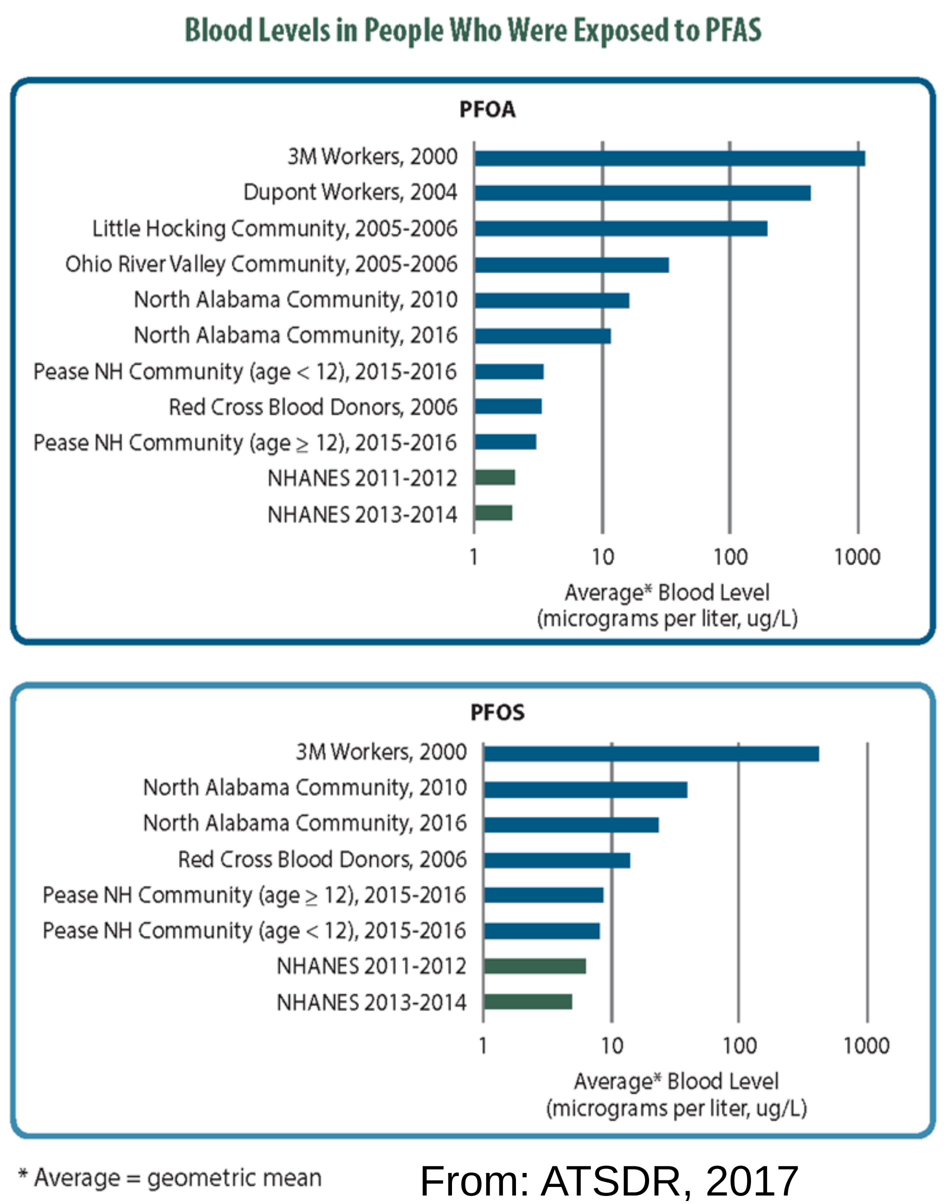


Figure 1. Hydrologic unit codes (eight-digit HUCs) used as a proxy for watersheds with detectable PFOA and PFOS in drinking water measured in the US EPA's UCMR3 program (2013−2015). Blank areas represent regions where no data are available.

Human Exposure

- CDC National Health and Nutrition Examination Survey
  - PFAS detection in blood of humans
  - Most people (97%) in the US have one or more PFAS in their blood

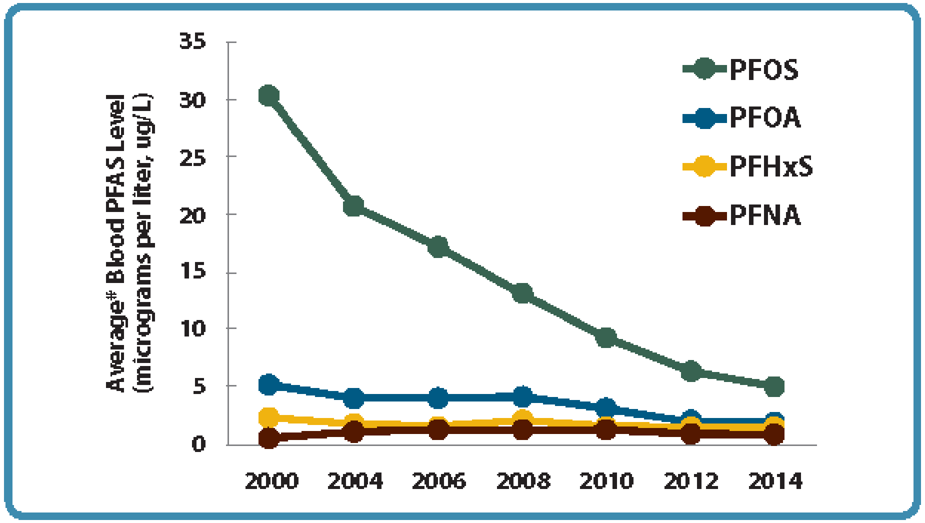


From: ATSDR, 2017

Human Exposure

- CDC National Health and Nutrition Examination Survey
  - from 2000 to 2014, PFOS & PFOA blood levels have declined

Blood Levels of the Most Common PFAS in People in the United States from 2000-2014



* Average = geometric mean

Data Source: Centers for Disease Control and Prevention. Fourth Report on Human Exposure to Environmental Chemicals, Updated Tables, (January 2017). Atlanta, GA: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention.

From: ATSDR, 2017

Health Effects

- **From ATSDR website**:

Some, but not all studies in humans have shown that certain PFAS may:

- affect growth, learning, and behavior of infants and children
- lower a woman's chance of getting pregnant
- interfere with the body's natural hormones
- increase cholesterol levels
- affect the immune system
- increase the risk of cancer

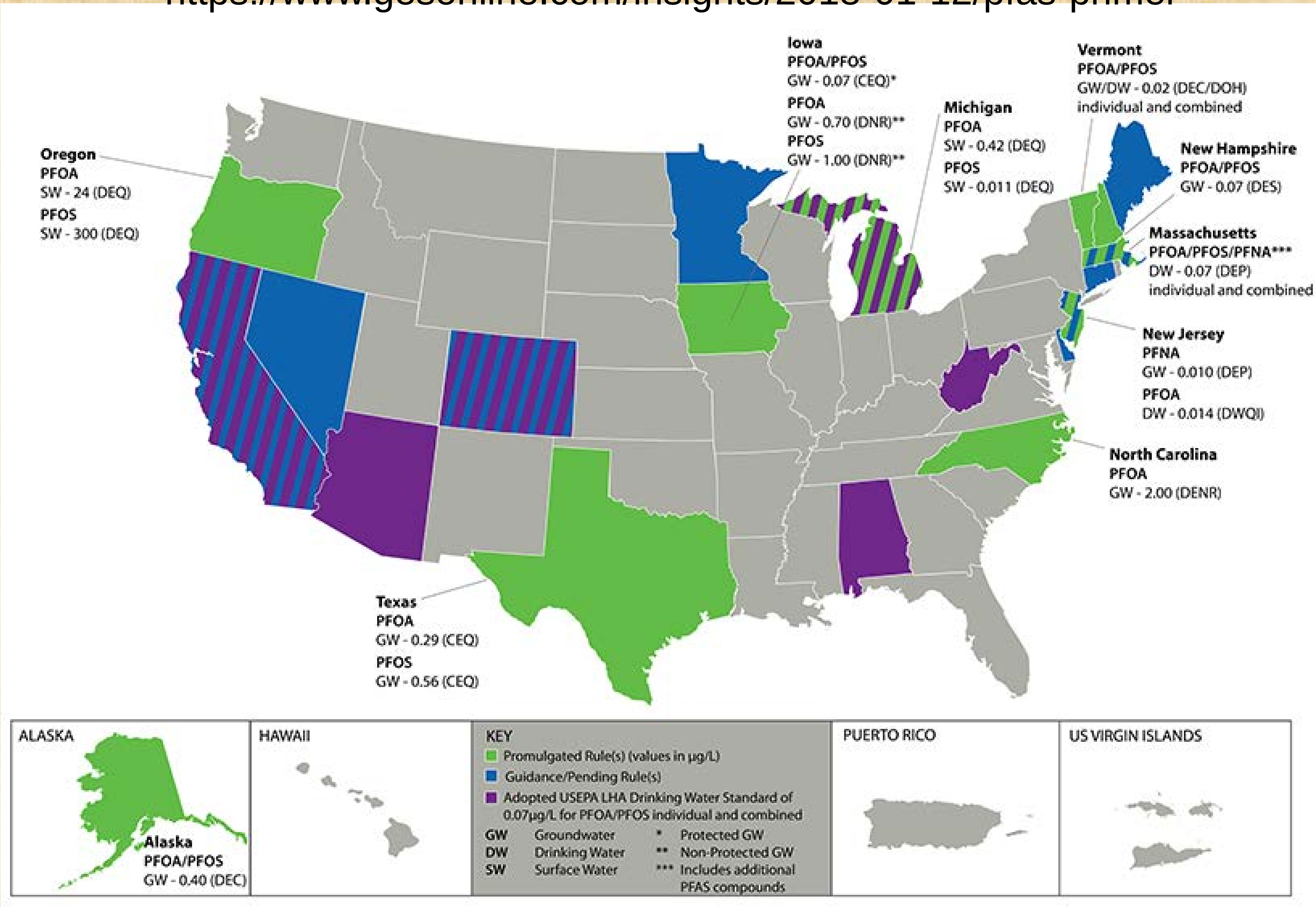
- EPA– ongoing toxicological research

Regulations

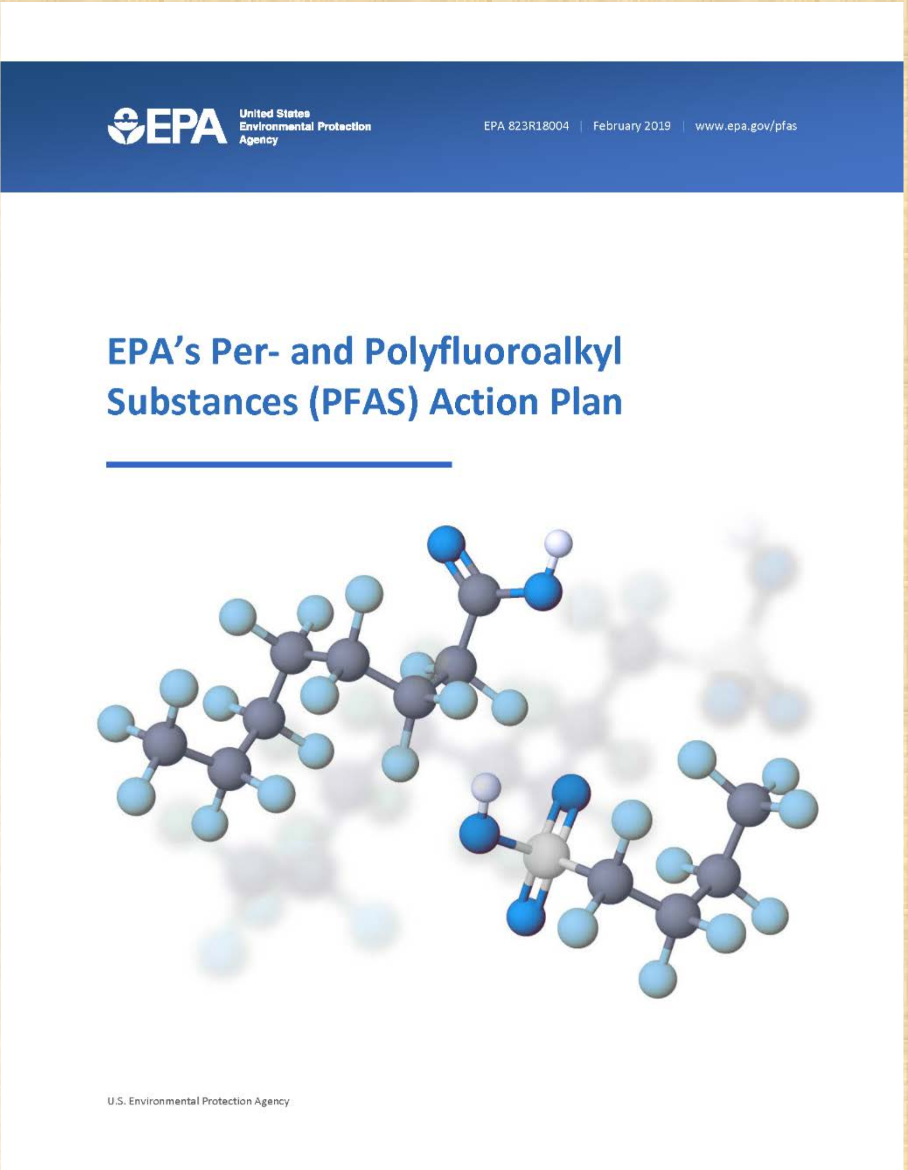
- PFAS <u>not</u> regulated under the Safe Drinking Water Act
  - No national primary drinking water regulations (MCLs)
- PFOS & PFOA listed in the EPA **Contaminant Candidate List 3** - 2009
- EPA issued lifetime health advisories (LHAs) for long-term exposures to PFOA and PFOS through drinking water (2016)
  - **70 ng/L (combined)→ parts per trillion**

State-level Regulatory Activity

From: GES – Groundwater & Environmental Services, Inc
https://www.gesonline.com/insights/2018-01-12/pfas-primer



Regulations



Plan Includes:

- Evaluate the need for a maximum contaminant level (MCL) for PFOA and PFOS

- Beginning the necessary steps to propose designating PFOA and PFOS as "hazardous substances"

- Developing groundwater cleanup recommendations for PFOA and PFOS at contaminated sites

https://www.epa.gov/pfas/epas-pfas-action-plan

Regulations

- May 2000: Following negotiations between EPA and 3M, the company announced that it would voluntarily phase out PFOS

- 2006: EPA established a voluntary stewardship program with 8 chemical manufacturers to phase out production of PFOA by 2015

- Toxic Substances Control Act (TSCA): EPA issues Significant New Use Rules (SNURs) for chemical manufacturing

  - Since 2002, issued a series of SNURs affecting dozens of PFAS chemicals

- Stockholm Convention--- **Persistent Organic Pollutants (POPs)**
  - PFOS is listed
  - PFOA under consideration

Phase-out & Replacement

- Initial PFAS used in products are starting to be phased out and replaced

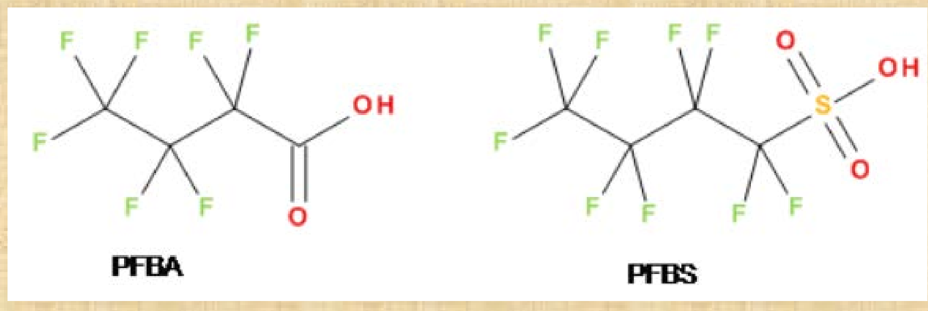
DOD Denix- 2011:
PFOS use in AFFF phased out after 2000

Gorefabrics.com- Jan 2014:
GORE completes elimination of PFOA from raw material of its functional fabrics

CNBC- Dec 2018:
Whole Foods removes packaging with a cancer-linked chemical from its stores

Short-Chain PFAS Alternatives

- Less potential for bioaccumulation
- Higher mobility
- Less research available about the environmental and human health impacts



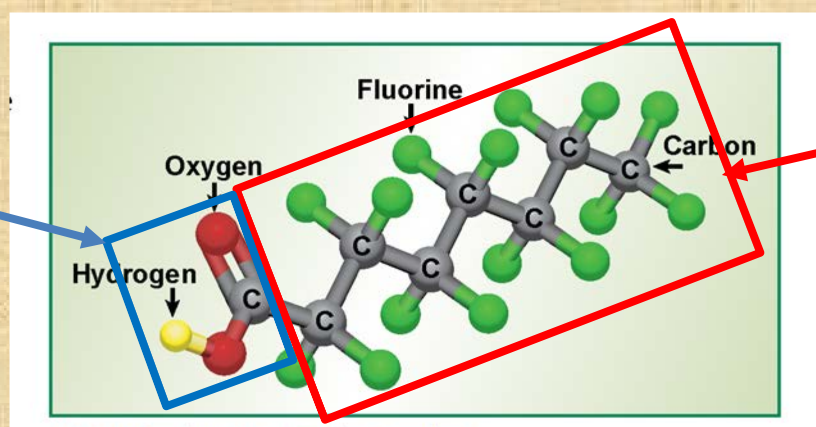
Perfluorobutanoic acid   Perfluorobutane sulfonic acid

Physicochemical Properties

PFAS have a unique set of properties:

- Many PFAS are **<u>surfactants</u>**

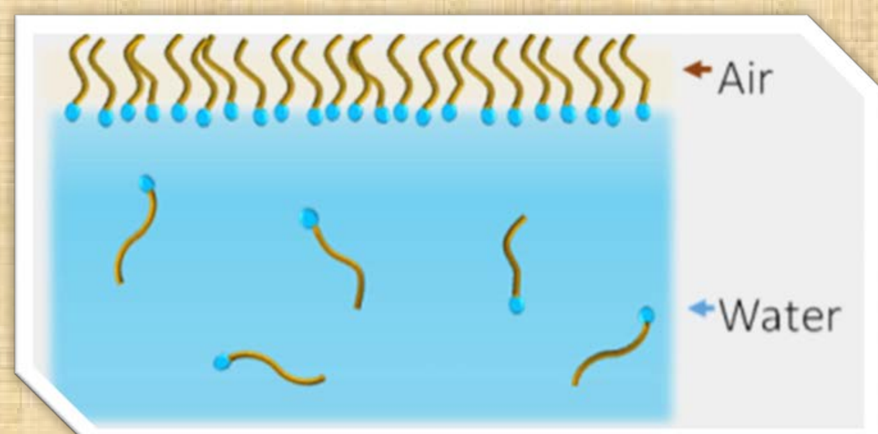
Hydrophilic Headgroup



PFOA, also known as C8, has 8 carbons.

Hydrophobic & Oleophobic Tail

*Provides water <u>and</u> oil repellency

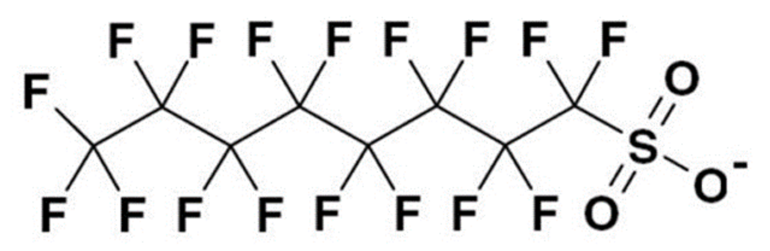


Physicochemical Properties

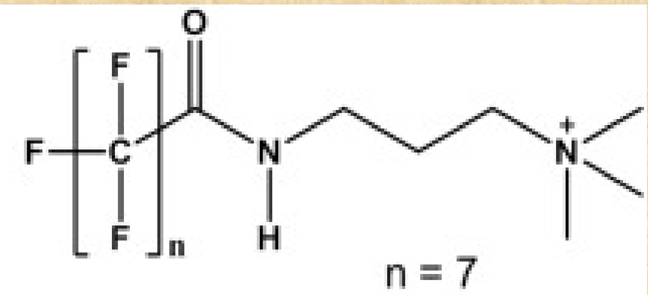
PFAS have a unique set of properties:

- Several different classes of compounds--- different surfactant headgroups

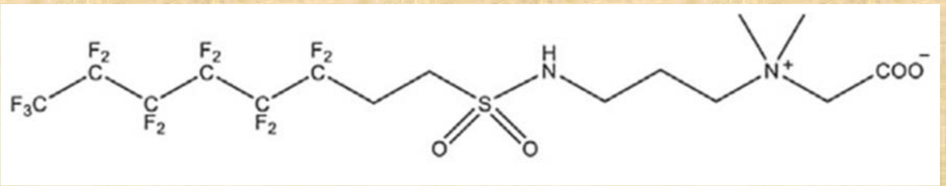
Anionic



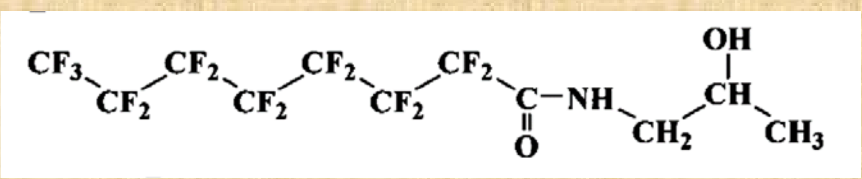
Cationic



Zwitterionic



Nonionic

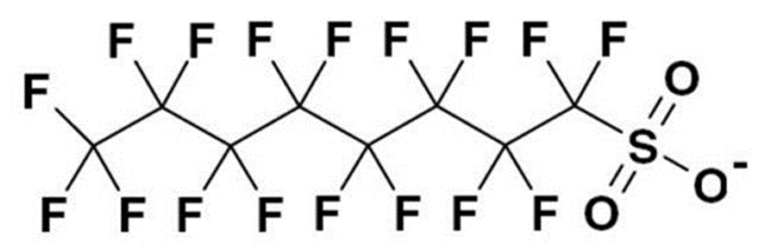


Physicochemical Properties

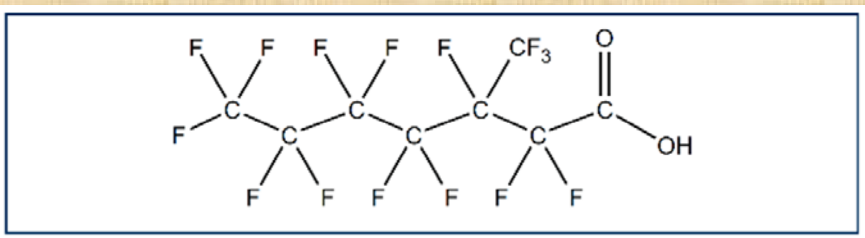
PFAS have a unique set of properties:

- Several different structures

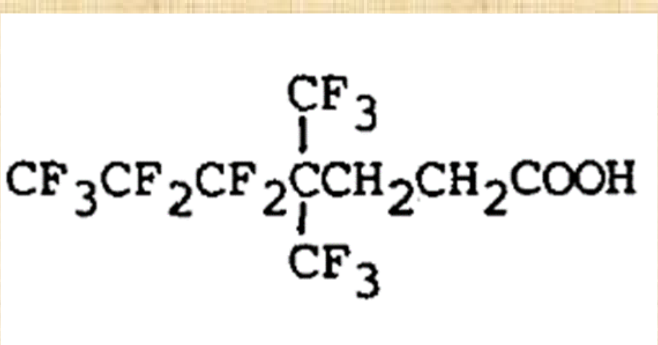
Straight-chained perfluoroalkyls

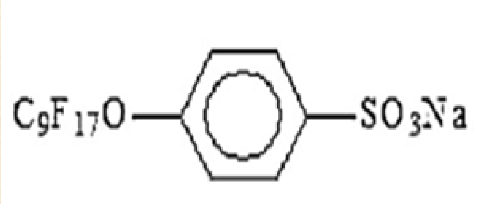


Branched perfluoroalkyls



Polyfluoroalkyls



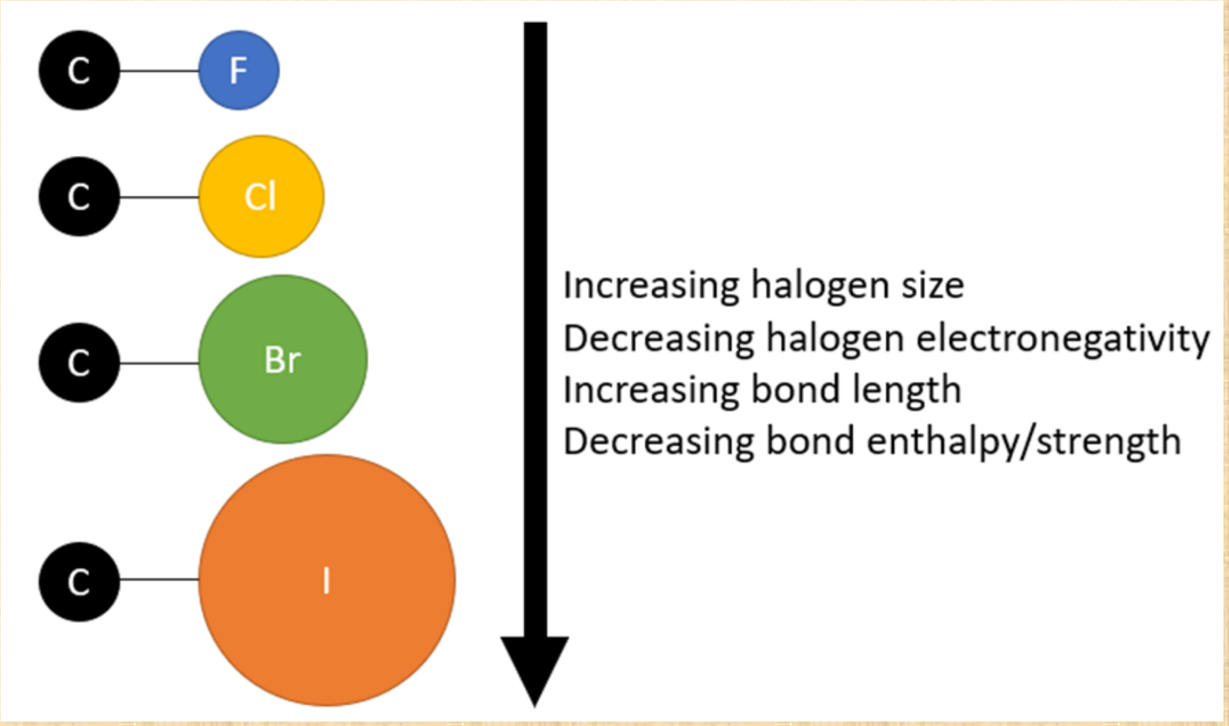


$CF_3CF_2CF_2$-O-CF(CF_3)CF_2-O-CF(CF_3)COONa

Physicochemical Properties

PFAS have a unique set of properties:

- Possess extremely strong carbon-fluorine bonds
  - very resistant to transformation reactions→ **persistent**



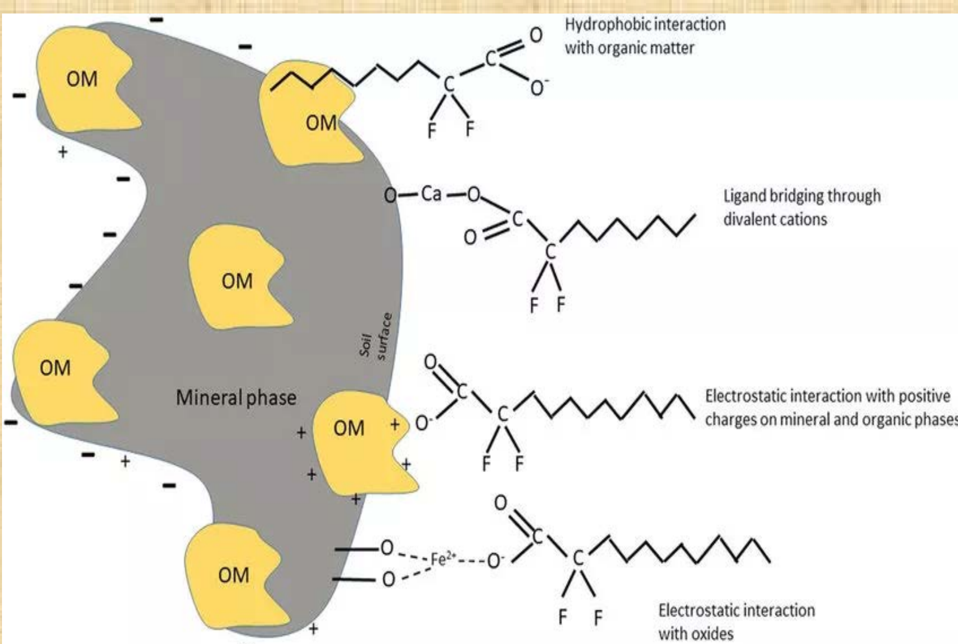
Prepared by S. Van Glubt

Transport & Fate

- Transport and fate behavior is a function of molecular structure
- General behavior
  - Low volatilities
  - Relatively high aqueous solubilities
  - Low transformation potential (except for “precursors”)
  - Often present as mixtures
  - Retention processes
    - Sorption by solid phases (soil, sediment, aquifer material) has been a major focus of study for past decade

Transport & Fate

- Sorption of PFAS by soil, sediment, and aquifer material (geomedia) is complex
- Function of PFAS molecular structure and the geochemical properties of the geomedia



From: Li et al., 2018

Geomedia are heterogeneous

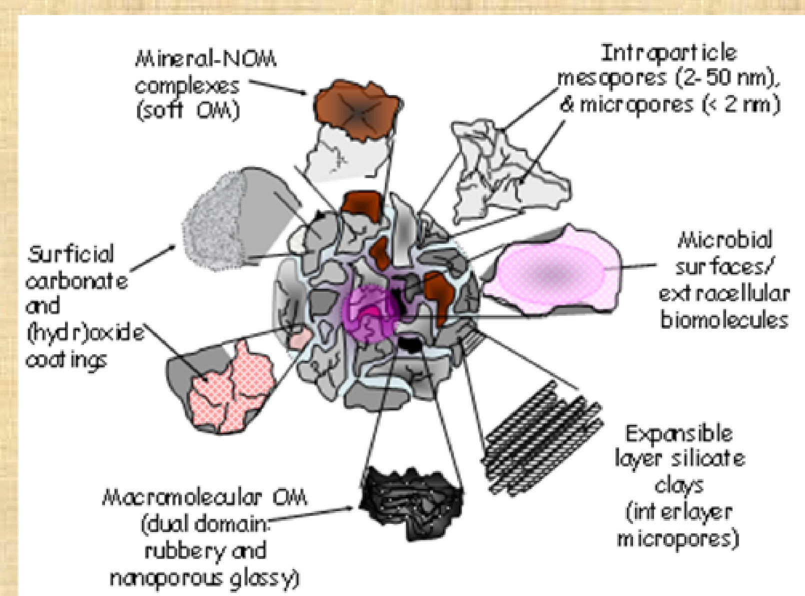
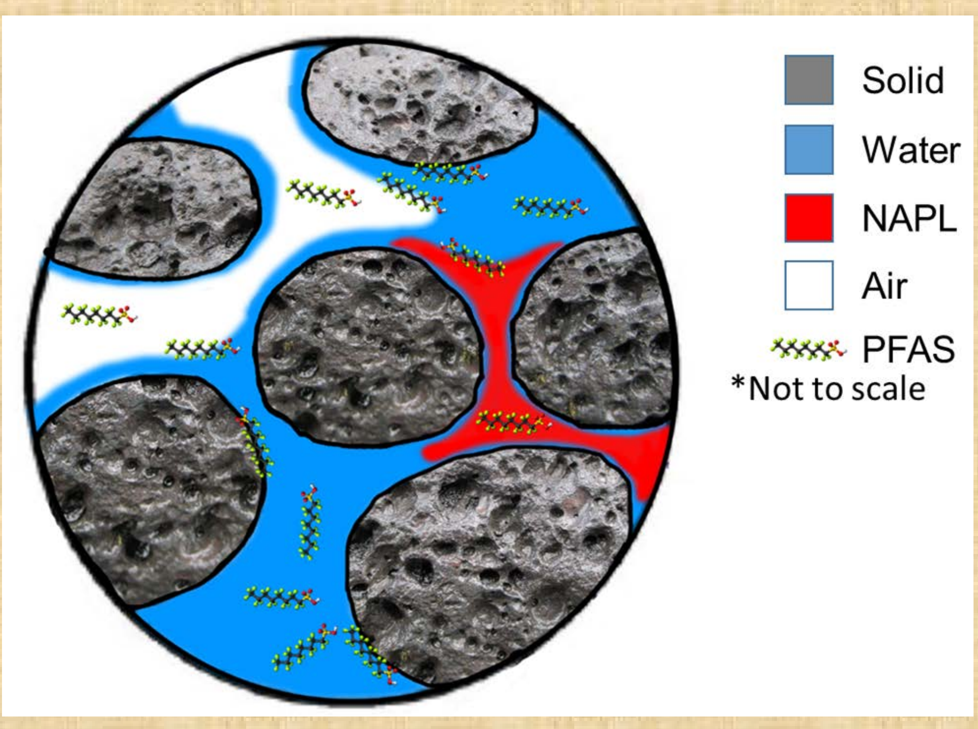


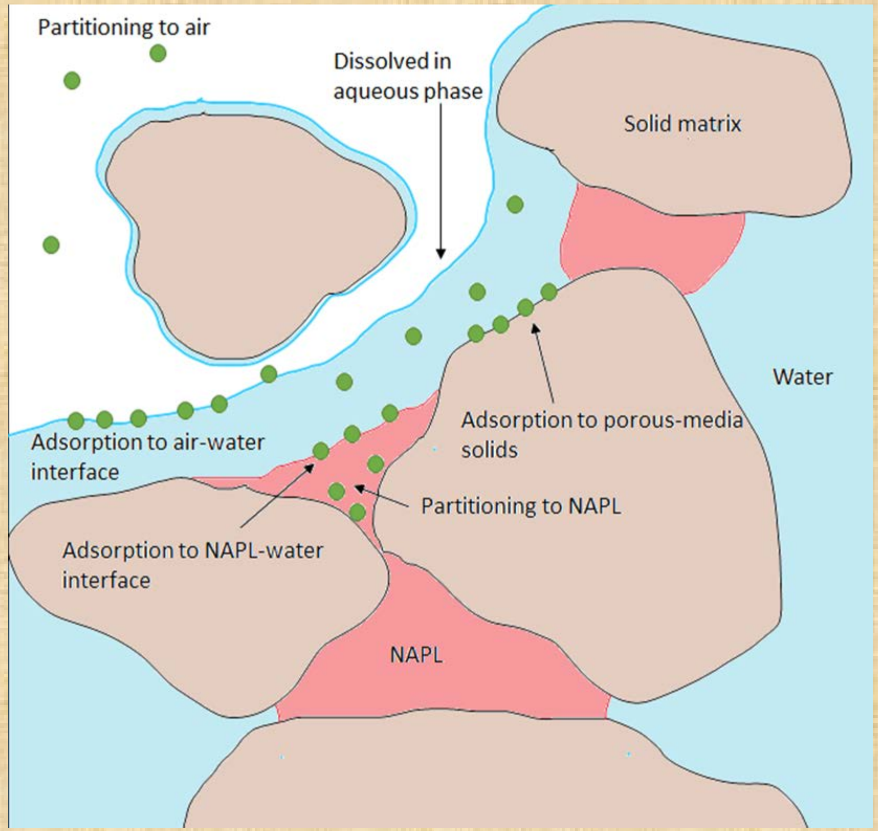
Figure A. Biogeochemically-reactive solid-water interfaces present in natural and waste-impacted geomedia (from Chorover and Brusseau, 2008)

Transport & Fate

- Transport and fate of PFAS in source zones even more complex: Additional retention processes:



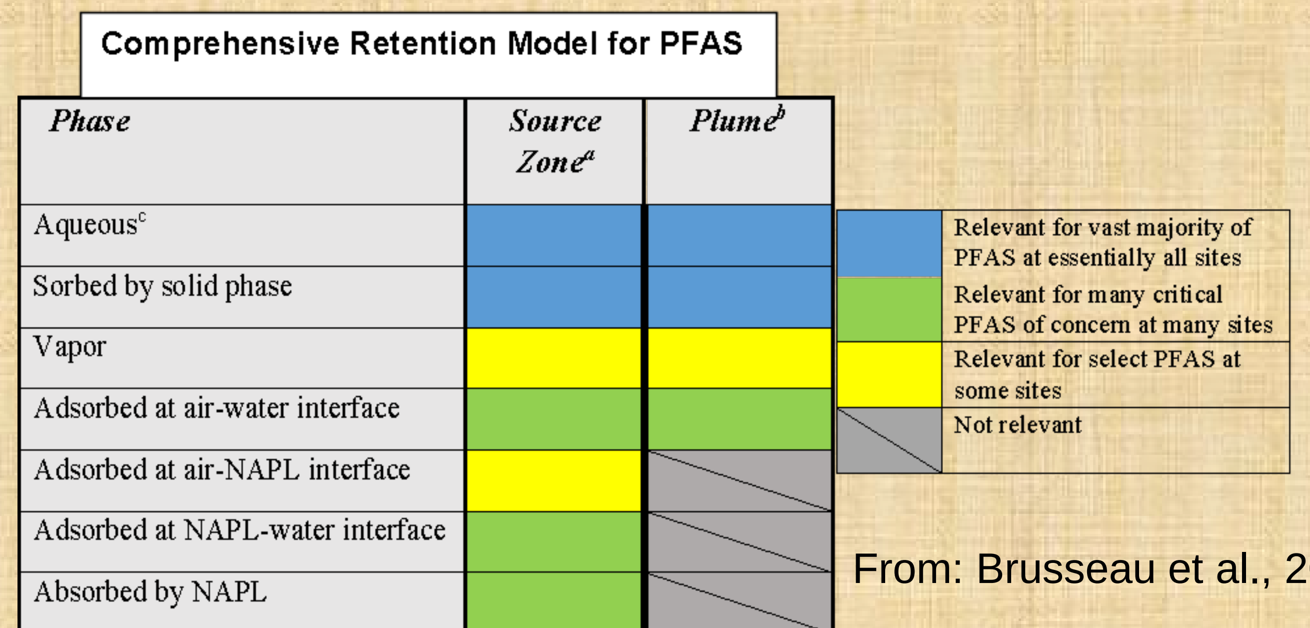
From: Brusseau, 2018



Prepared by S. Van Glubt

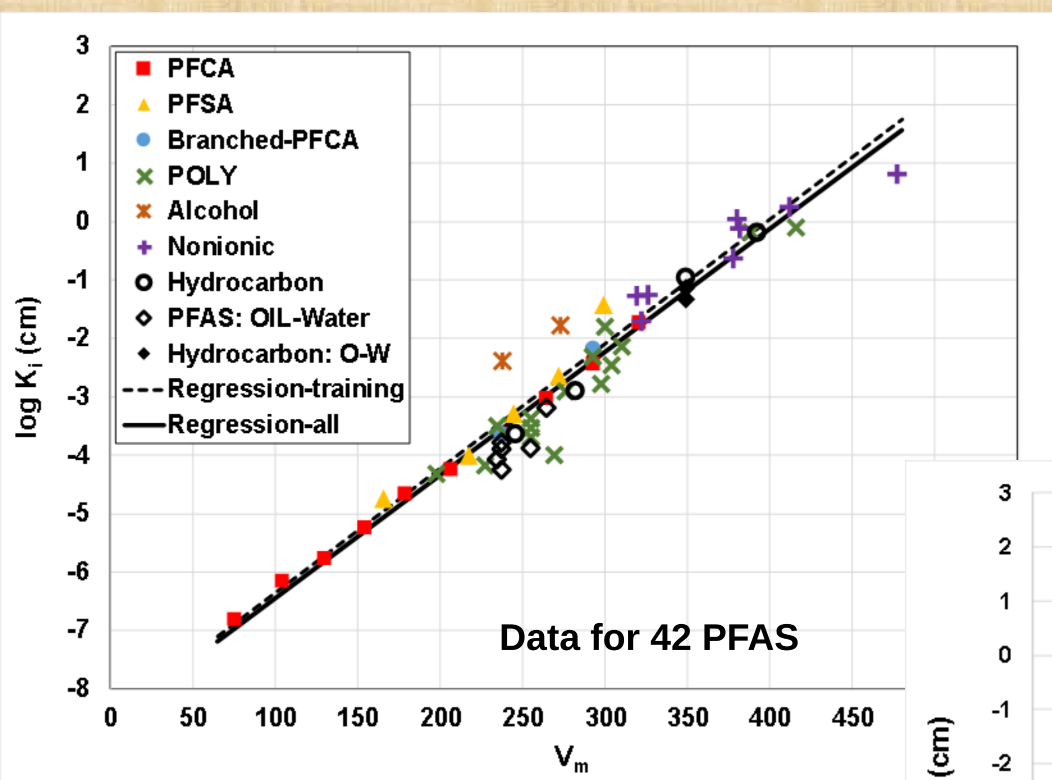
Transport & Fate

- Transport and fate of PFAS in source zones even more complex: Additional retention processes:
  - Adsorption at the air-water interface in vadose zone
  - Adsorption at the NAPL-water interface in NAPL source zones
    - NAPL = nonaqueous-phase liquid → chlorinated solvents, fuels

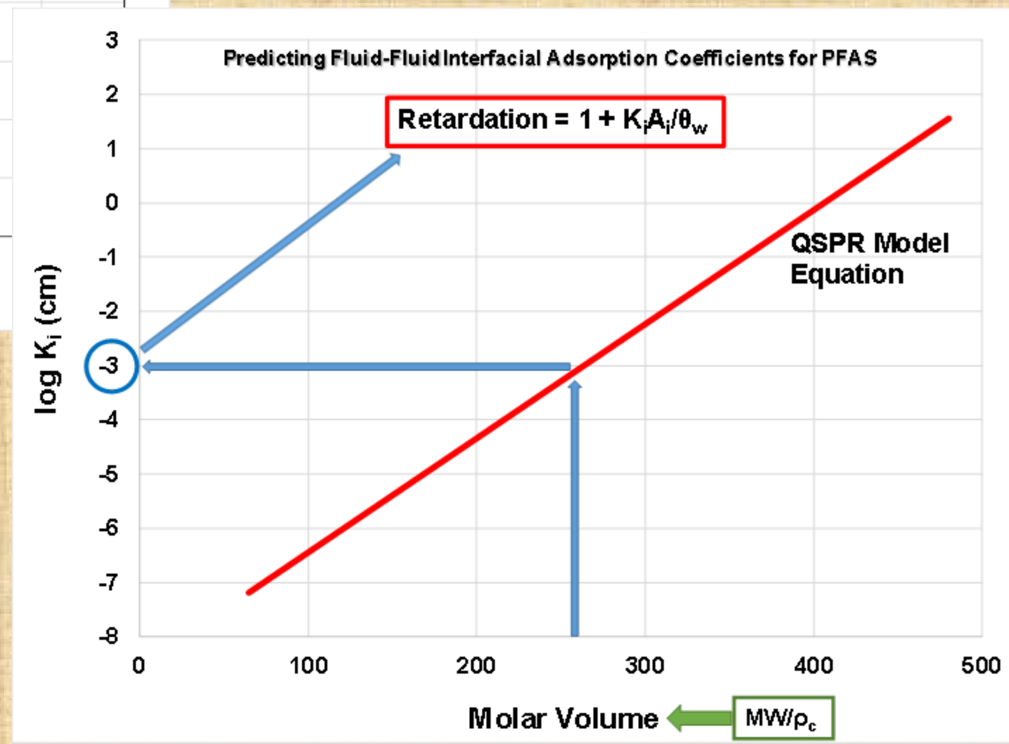


From: Brusseau et al., 2019

Transport & Fate



From: Brusseau, 2019



Case Study

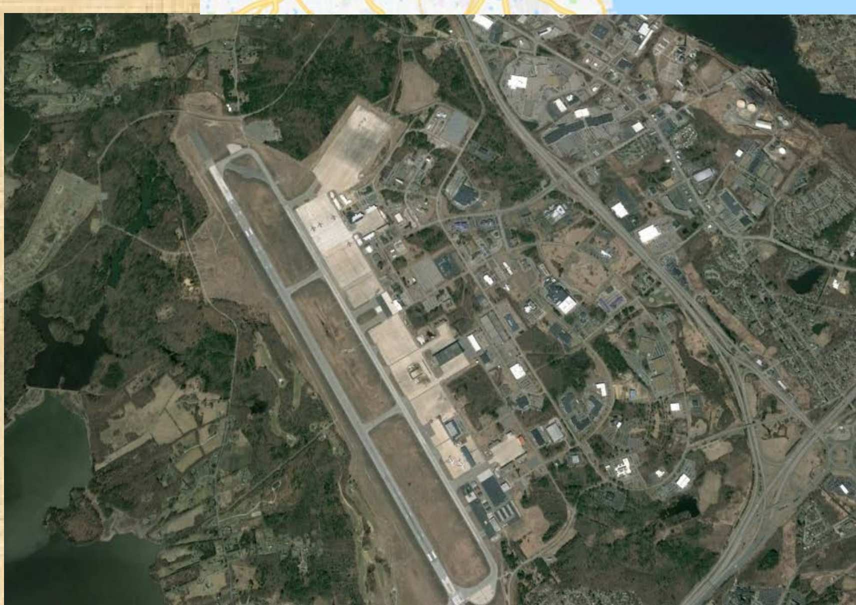
Redevelopment of Pease AFB, NH

- 1989- Closure decision finalized
  - officially closed in 1991

- Listed on the NPL in 1990
  - 41 hazardous waste sites (chlorinated solvents)
  - 63 petroleum release sites
  - Multiple remedial actions implemented

- The original remediation effort did not include PFAS

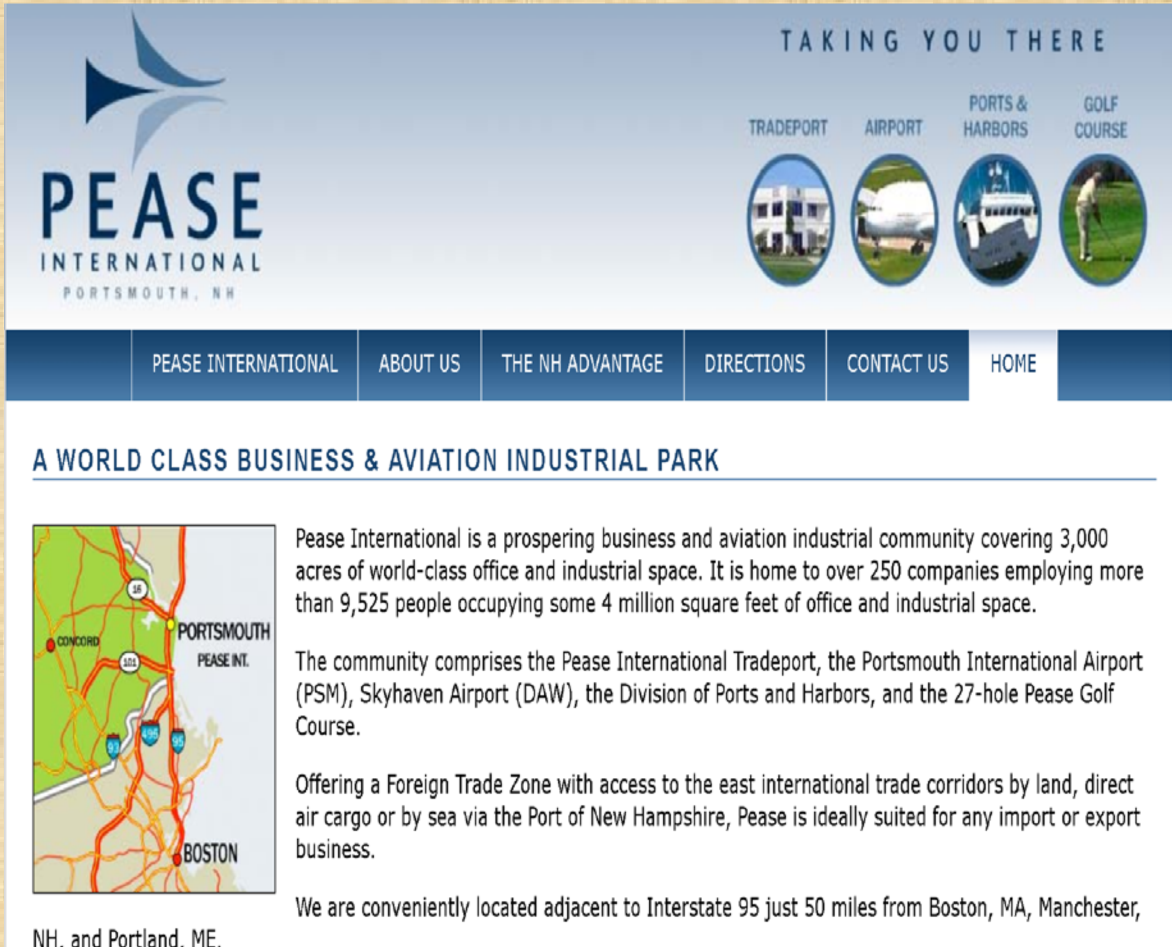
>>>PFAS-based foam used at fire-training areas on base



Case Study

<u>Redevelopment of Pease AFB, NH</u>

- Early 1990's- AFB redeveloped into a tradeport
  - 250+ businesses
  - 2 daycare facilities
  - Hotels, restaurants
  - Healthcare facilities
  - ~8000 workers



Case Study

Redevelopment of Pease AFB, NH

- Three wells on the former AFB used to supply potable water to the Tradeport facility

- 2013- sampling of site groundwater revealed presence of PFAS
  - 2014 sampling of water supply wells
  - 2015 EPA issues Admin Order to Air Force to investigate & remediate
  - Air Force has spent ~$55M to date (http://nhpr.org/post/air-force-give-update-cleanup-efforts-pease)

- Concern over long-term exposure of workers, children, and prior AFB personnel

Case Study

Redevelopment of Pease AFB, NH

- 2014 groundwater data

From: City of Portsmouth, 2014

Sample Location	Collection Date	Perfluorobutane sulfonate	Perfluorodecanoic acid	Perfluorododecanoic acid	Perfluoroheptanoic acid	Perfluorohexane sulfonate	Perfluorohexanoic acid	Perfluorononanoic acid	Perfluorooctane sulfonate (PFOS)	Perfluorooctanoic acid (PFOA)	Perfluoropentanoic acid	Perfluoroundecanoic acid
PHA (µg/L)		--	--	--	--	--	--	--	0.2	0.4	--	--
HAVEN	16-Apr-14	0.051	0.0049 J	ND	0.12	0.83	0.33	0.017	**2.5**	0.35	0.27	ND
HAVEN	14-May-14	0.051	0.0043 J	ND	0.12	0.96	0.35	0.017	**2.4**	0.32	0.26	ND
HARRISON	16-Apr-14	0.002 J	ND	ND	0.0046 J	0.036	0.0087	ND	0.048	0.009	0.0079	ND
HARRISON	14-May-14	0.0019 J	ND	ND	0.0042 J	0.032	0.01	ND	0.041	0.0086	0.0084	ND
SMITH	16-Apr-14	0.00094 J	0.0044 J	0.012	0.0025 J	0.013	0.0039 J	ND	0.018	0.0035 J	0.0035 J	0.017
SMITH	14-May-14	0.00087 J	ND	ND	0.002 J	0.013	0.004 J	ND	0.015	0.0036 J	0.0034 J	ND

Notes:

Grey text indicates the parameter was not detected.

[pink box] indicates concenetration above PHA

J - estimated value

all results in µg/L

ND - non detect

PHA - Provisional Health Advisory

-- indicates no established PHA

Final LHA = 0.07 ug/L

Summary

- PFAS have many uses and sources
- Widespread in the environment
- Significant analytical constraints
- Persistent in the environment
- Complex transport behavior
- Difficult to treat

Difficult & costly to assess and mitigate risk

Resources

Rapidly Evolving Field

Resources:

- EPA: https://www.epa.gov/pfas
- ITRC: https://www.itrcweb.org/Team/Public?teamID=78
- ATSDR: https://www.atsdr.cdc.gov/pfas/
- NIEHS: https://www.niehs.nih.gov/health/topics/agents/pfc/index.cfm
- NGWA: https://www.ngwa.org/what-is-groundwater/groundwater-issues/Groundwater-and-PFAS
- Enviro Wiki: https://www.enviro.wiki/index.php?title=Perfluoroalkyl_and_Polyfluoroalkyl_Substances_(PFASs)

Thank You

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Citations

- ATSDR. 2017. Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in the U.S. Population. https://www.atsdr.cdc.gov/pfc/docs/PFAS_in_People.pdf

- Brusseau, M.L. 2018. Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface. Science Total Environ., 613-614, 176-185.

- Brusseau, M.L. 2019. The influence of molecular structure on the adsorption of PFAS to fluid-fluid interfaces: Using QSPR to predict interfacial adsorption coefficients. Water Research, 152, 148-158.

- Brusseau, M.L., N. Yan, S. Van Glubt, Y. Wang, W. Chen, Y. Lyu, B. Dungan, K.C. Carroll, F.O. Holguin. 2019. Comprehensive retention model for PFAS transport in subsurface systems. Water Research, 148, 41-50.

- City of Portsmouth. 2014. April and May 2014 PFC Analytical Results. https://www.cityofportsmouth.com/publicworks/water/pease-tradeport-water-system.

- Chorover, J. and Brusseau, M.L. Kinetics of Sorption-Desorption. Chapter 4 in: Kinetics of Water-Rock Interaction, Brantley, S. L., Kubicki, J.D., and White, A.F., eds. Springer, NY, NY, 2008.

- Hu, X.C., Andrews, D.Q., Lindstrom, A.B., Bruton, T.A., Schaider, L.A., Grandjean, P., Lohmann, R., Carignan, C.C., Blum, A., Balan, S.A., Higgins, C.P., Sunderland, E.M. 2016. Detection of poly- and perfluoroalkyl substances (PFAS) in U.S. drinking water linked to industrial sites, military fire training areas and wastewater treatment plants. Environ. Sci. Technol. Lett. 3, 344–350.

- ITRC. 2018. Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances. https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_fate_and_transport__3_16_18.pdf

- Li, Y., D.P. Oliver, and R.S. Kookana. 2018. A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). Science Total Environ., 628-629, 110-120.

- OECD. 2018. Toward a New Comprehensive Global Database of Per-and Polyfluoroalkyl Substances (PFASs). http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV-JM- MONO(2018)7&doclanguage=en

- Schaider, L.A., S.A. Balan, A. Blum, D.Q. Andrews, M.J. Strynar, M.E. Dickinson, D.M. Lunderberg, J.R. Lang, and G.F. Peaslee. 2017. Fluorinated Compounds in U.S. Fast Food Packaging. *Environ. Sci. Technol. Lett.*, 2017, 4, pp 105–111.

- Testing for Pease. 2017. The PFAS Contamination at Pease:A Community Perspective. Presented by A. Amico, A. Davis, and M. Dalton at the Highly Fluorinated Compounds –Social and Scientific Discovery conference, held at Northeastern University, June 14, 2017. https://pfasproject.com/wp-content/uploads/2017/06/community-organizing-military-amico.pdf.