United States Environmental Protection Agency

EPA Tools and Resources Webinar

Investigating PFAS Occurrence in the Environment: *EPA ORD Collaborative Projects with States and Tribes*

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August 18, 2021

EPA United States Environmental Protection Agency

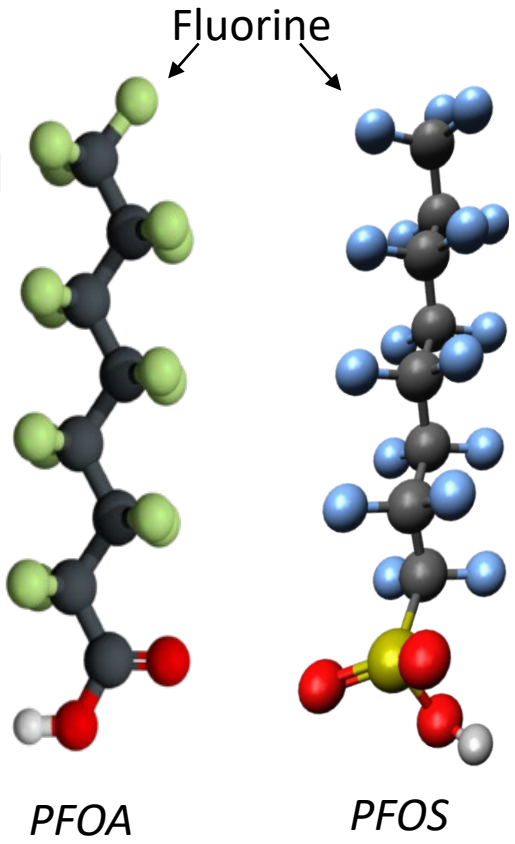
Presentation Outline

- PFAS background and problem statement
- ORD innovative techniques for identifying PFAS
- Examples of collaborative projects investigating PFAS occurrence in the environment conducted by states and tribes with ORD assistance
- Shared value from these projects
- How to engage with ORD in initiating a project

What are PFAS (perfluoroalkyl substances)?

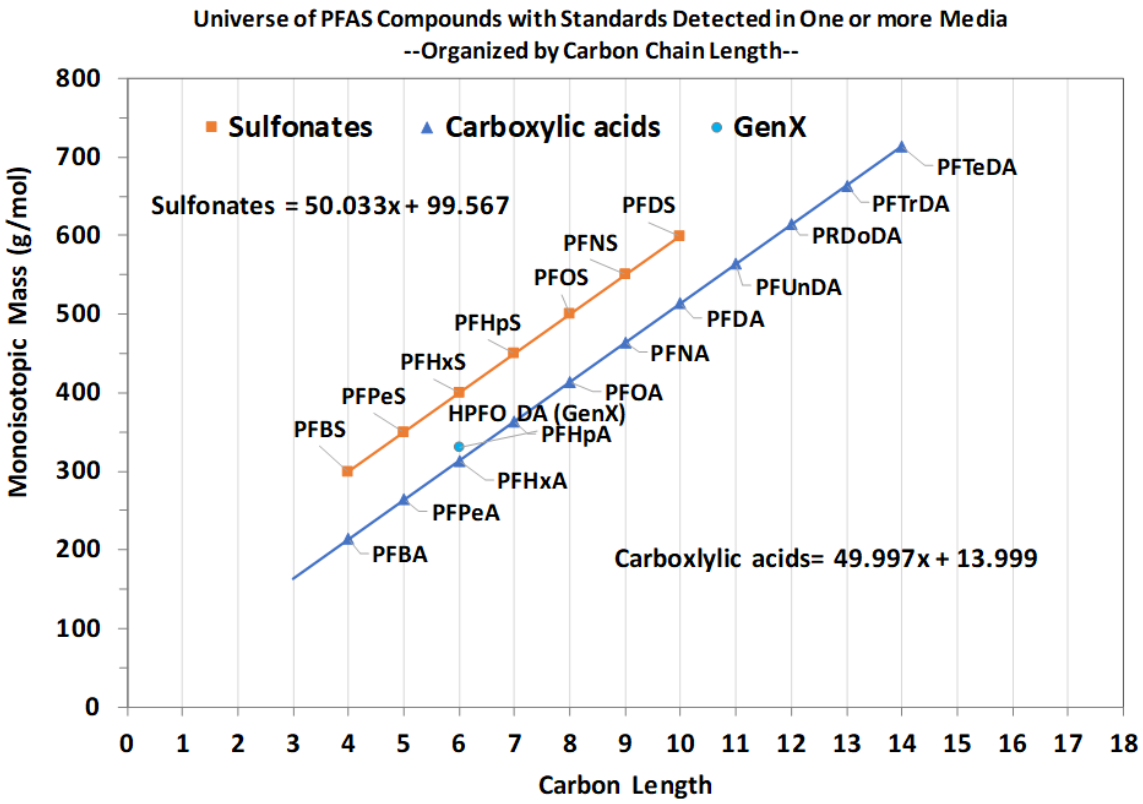
A class of man-made chemicals

- **Chains** of carbon (C) atoms surrounded by fluorine (F) atoms, with different terminal ends
- **Complicated chemistry** – thousands of different variations exist in commerce
- Desirable properties for many industrial and commercial applications
  e.g., resistant to degradation



PFOA *PFOS*

Families of PFAS compounds



Problem: Why the Concern with PFAS?

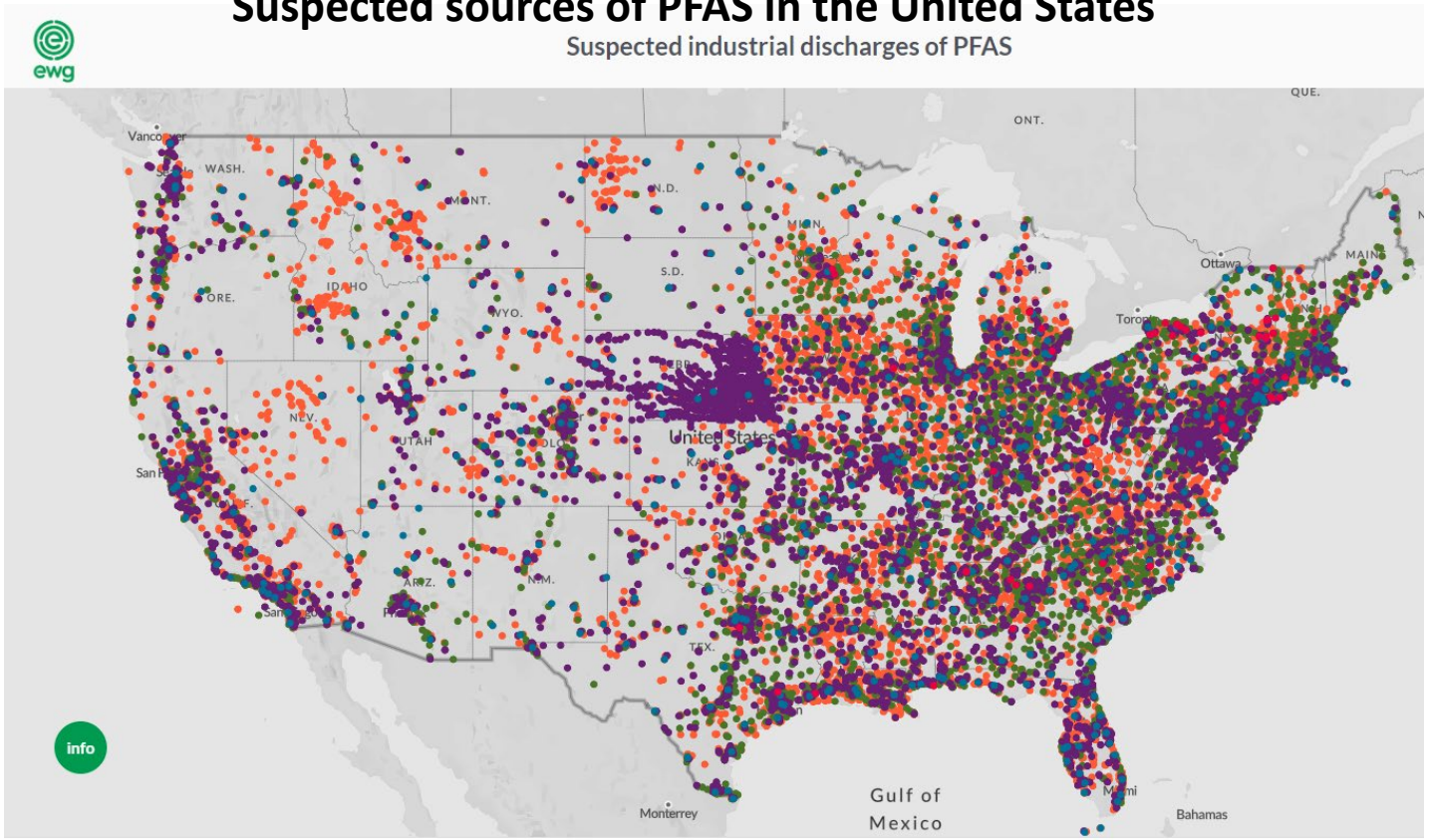
Widespread unregulated use in multiple consumer products and manufacturing processes since the 1950's

- Industrial Uses
  - Electroplating
  - Metal finishing
  - Vapor/mist suppression
  - Electronics production
  - Metal coatings
  - Production of plastics and rubber

- Aqueous film-forming foams (AFFFs) for firefighting

- Commercial Products
  - Stain repellants (e.g. Scotch guard)
  - Paper and textile coatings
  - Non-stick cookware
  - General household maintenance products
  - Toothpaste, shampoo, cosmetics, dental floss
  - Waterproof fabrics
  - Prescription and nonprescription drugs
  - Lubricants and greases

Suspected sources of PFAS in the United States

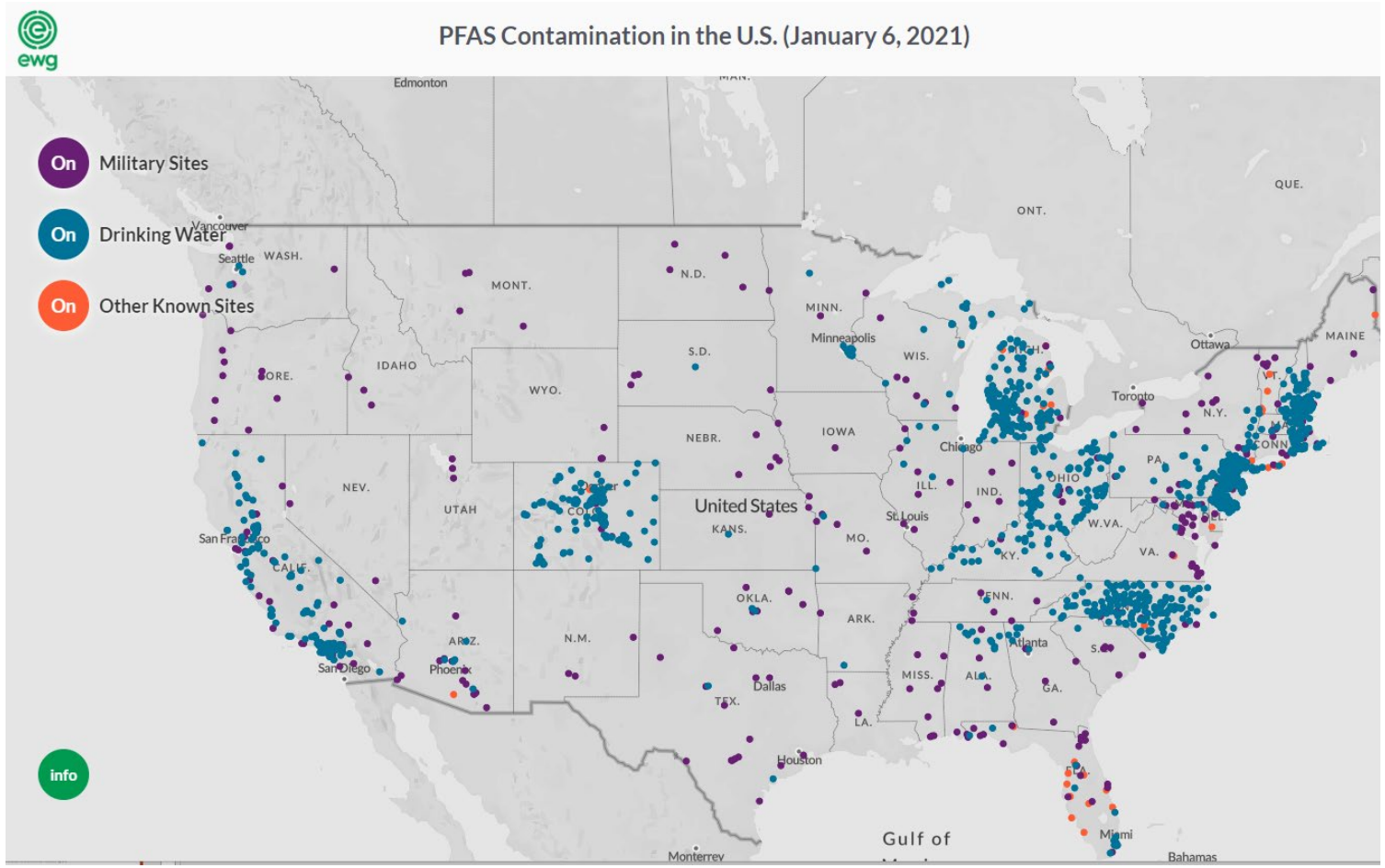


Map by EWG.ORG https://www.ewg.org/interactive-maps/2021

Map includes industrial dischargers, landfills and waste disposal sites, sewage treatment facilities, airports and military bases

Documentation of PFAS Contamination is Growing

- Classified as “Contaminants of Emerging Concern”
- Pervasive, persistent, and bioaccumulative in the environment
- It is estimated that >98% of people in the U.S. have measurable amounts of PFAS in their bodies—main routes of exposure:
  - Drinking contaminated water
  - Eating food that was packaged in material that contains PFAS
- Can result in a variety of health effects, including cancer
- Scarcity of information in the scientific literature



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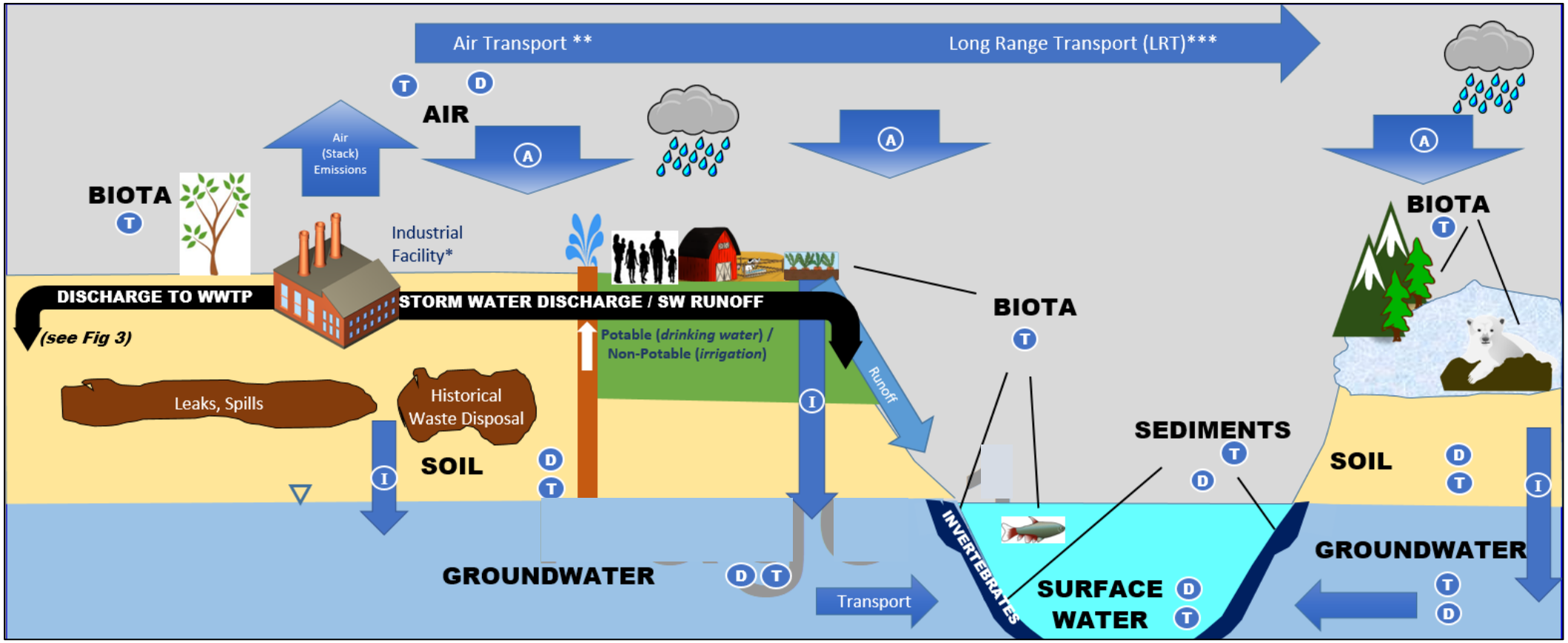
PFAS Have Been Found in Many Media with Many Pathways for Delivery



- PFAS do not break down in the environment and have been discovered at concentrations of concern in groundwater, surface water and drinking water.
- They are also known to bioaccumulate in fish and wildlife tissues and accumulate in the human body.

EPA and States Have Recognized the Need for Better Understanding of PFAS through Research

- Determine how different PFAS compounds migrate within and between environmental media such as air, surface water, sediment, wastewater, stormwater, groundwater, soil, etc.
- Fingerprinting techniques to associate specific manufacturing processes or sites to specific suites of PFAS compounds
- Effective techniques for management and remediation of PFAS
- Expand site investigations for PFAS sources and contamination
- Timely collection of environmental PFAS data

EPA
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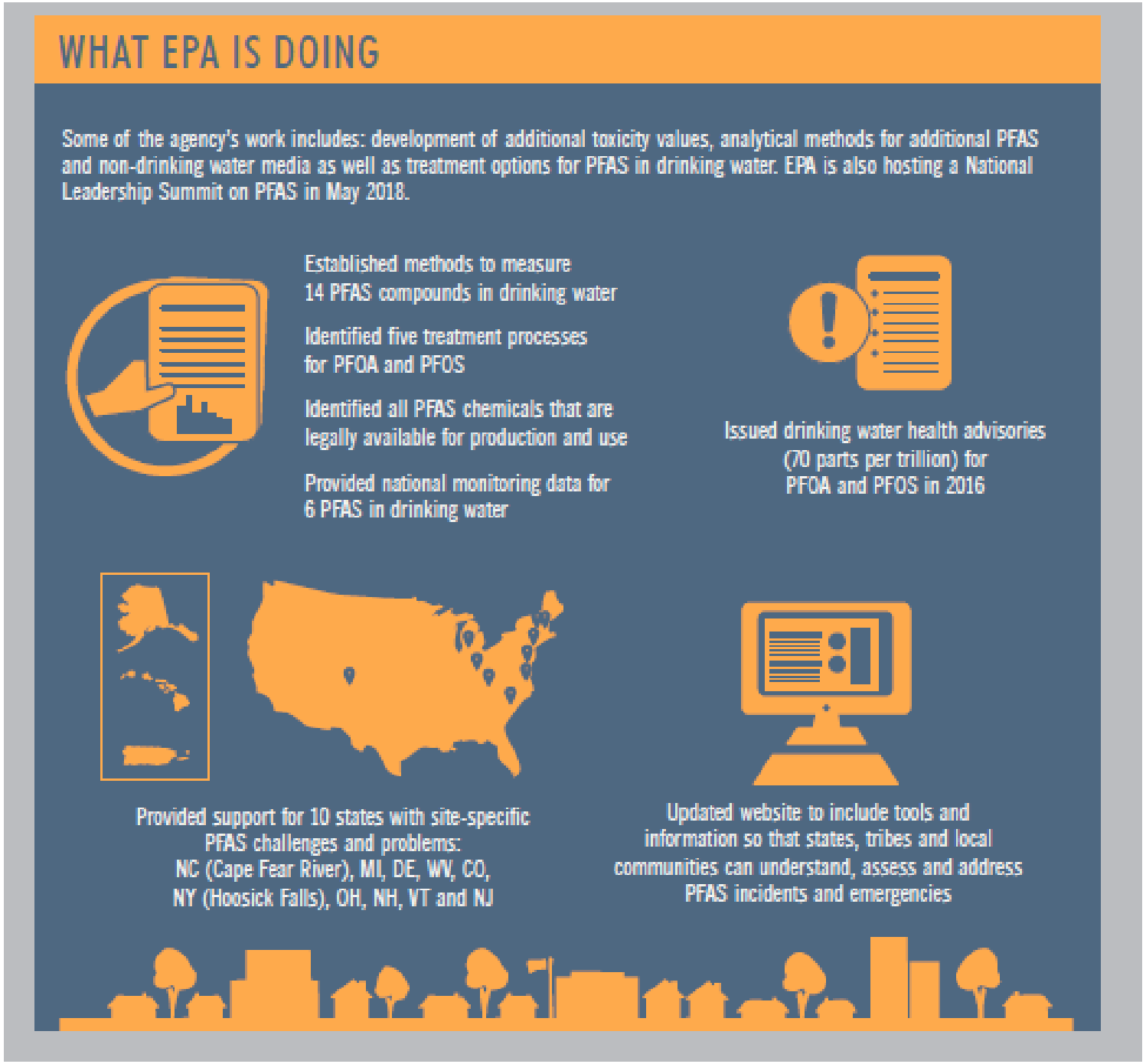
EPA has launched a major initiative to understand and manage human and environmental risk from exposure to PFAS

Considerable focus on drinking water exposures

EPA's Office of Research and Development (ORD) has launched numerous research efforts investigating PFAS chemicals



Problem:

Measurement of PFAS is a significant barrier to evaluating the presence and abundance of the wide array and constantly evolving family of compounds

- With over 5,000 known PFAS compounds, it is not currently possible to include every single PFAS compound on the standard analyte list
- Only 36 PFAS compounds can be quantitated by certified laboratories at this time (and not all laboratories can do all)
- PFAS sampling is complex
  - The presence of these compounds in many everyday consumer products requires protocols and care in avoiding contamination during sampling
  - New methods are needed for comprehensive measurement of PFAS in air an important route for introducing chemicals into the environment

Analytical Barriers to Understanding PFAS

1) Lack of certified standards and approved methods for many PFAS compounds
2) It is difficult and expensive to test for an analyte in the parts per trillion range where effects levels appear to be
3) Commercial laboratory analytical limitations for handling more complex sample matrices
4) Unknown nature of the compounds because they are proprietary, manufacturing byproducts or degradation compounds contained in raw materials
5) Constantly evolving products in use and substitution of similar compounds
6) Lack of expertise and experience associated with advanced fluorochemistry and fate and transport properties

PFAS Technical Support Program

- ORD's Center for Environmental Measurement and Modeling (CEMM) has chemistry experts who have researched methods to identify and quantify the family of PFAS compounds in a variety of media
- ORD is making those experts available to assist states/tribes in conducting studies that enable them to take action before the full complement of research addressing these compounds is available
- ORD also views these projects as an opportunity to learn from real-world situations for feedback into our other PFAS research programs

PFAS Technical Service Capabilities

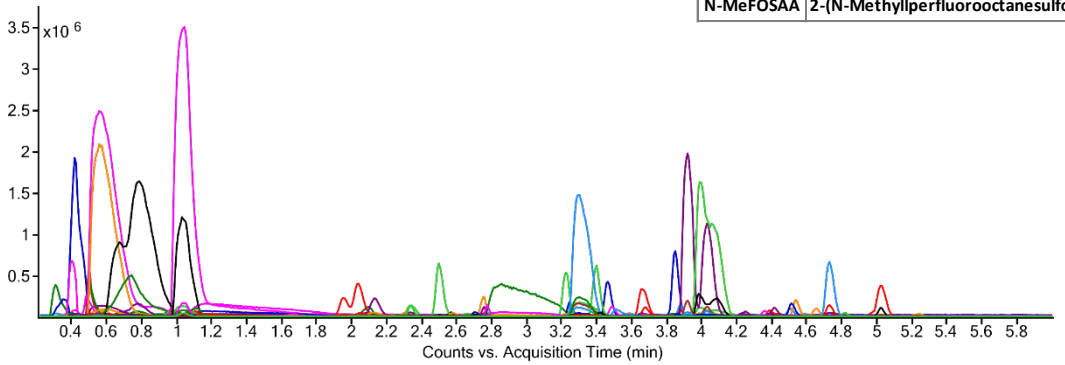
Standard Quantitation (Targeted Analysis)
Based on LC/MS technology

- We know exactly what we're looking for using standard laboratory analytical techniques and authentic chemical standards (like a commercial lab)
- ORD can determine concentrations of 10s to 100s of PFAS chemicals, a somewhat broader set of compounds than presently available in many commercial laboratories
- ORD can quantify concentrations within complex mixtures

Product:
Concentrations of PFAS analytes

ORD's targeted analyte list has grown with experience

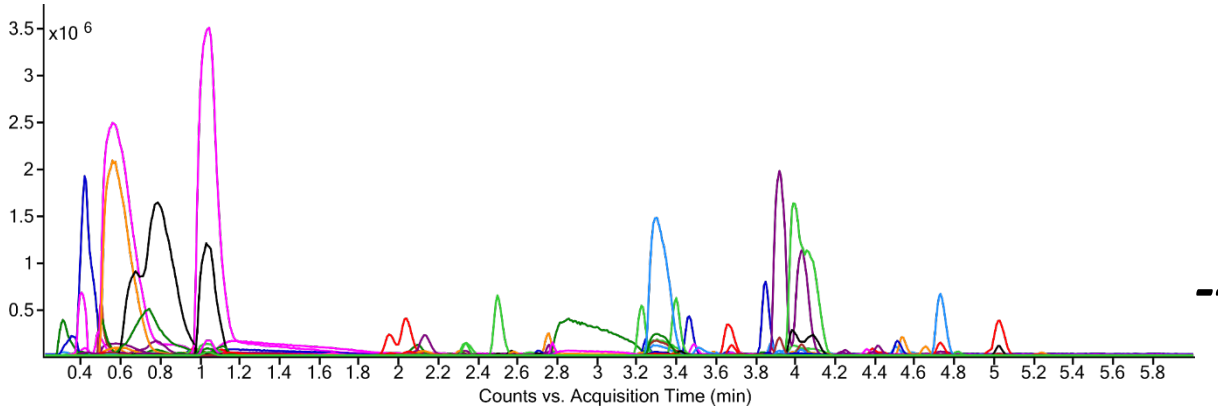
Short Name	Chemical Name
PFBA	Perfluorobutanoic Acid
PFPeA	Perfluoropentanoic Acid
PFHxA	Perfluorohexanoic Acid
PFHpA	Perfluoroheptanoic Acid
PFOA	Perfluorooctanoic Acid
PFNA	Perfluorononanoic Acid
PFDA	Perfluorodecanoic Acid
PFUnDA	Perfluoroundecanoic acid
PFDoDA	Perfluorododecanoic
PFTrDA	Perfluorotridecanoic acid
PFTeDA	Perfluorotetradecanoic acid
PFBS	Perfluorobutane Sulfonate
PFPeS	Perfluoropentanesulfonic acid
PFHxS	Perfluorohexane Sulfonate
PFHpS	Perfluoroheptanesulfonic acid
PFOS	Perfluorooctane Sulfonate
PFNS	Perfluorononanesulfonic acid
PFDS	Perfluorodecanesulfonic acid
PFOSA	Perfluorooctanesulfonamide
4:2 FTS	Fluorotelomer sulphonic acid 4:2
6:2 FTS	Fluorotelomer sulphonic acid 6:2
8:2 FTS	Fluorotelomer sulphonic acid 8:2
HFPO-DA	Perfluoro(2-methyl-3-oxahexanoic) acid
N-EtFOSAA	2-(N-Ethylperfluorooctanesulfonamido) acetic acid
N-MeFOSAA	2-(N-Methyllperfluorooctanesulfonamido) acetic acid



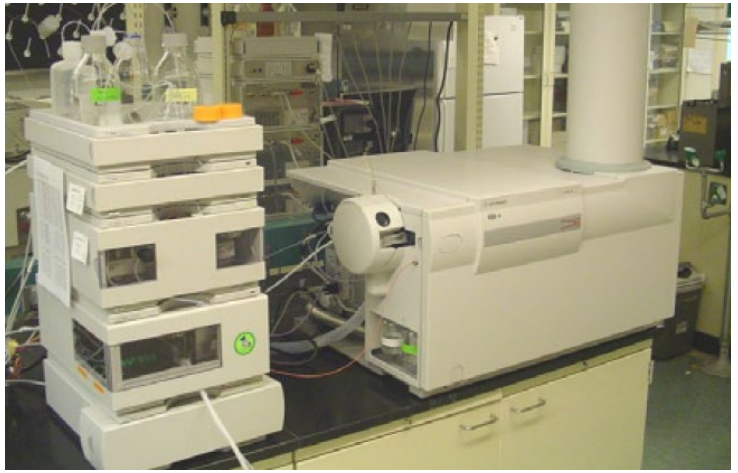
PFAS Technical Service Capabilities

Search for Novel Chemicals with Non-Targeted Analysis (NTA)

- Approach: We have no pre-conceived notions or lists
- Experts interpret LC/MS analytical results to identify a broader array of PFAS
- Dust, soil, food, air, water, products, plants, animal tissue, etc.



--Analyze with LC/MS Analytical Instruments



--Match with Chemical Databases

EPA United States Environmental Protection Agency | Home
Chemistry Dashboard

PubChem

--Researchers' Expertise and Experience

EPA United States Environmental Protection Agency

PFAS Technical Service Capabilities

Non-Targeted Analysis (NTA) Products

NTA results are inherently more uncertain

Compound Identification	• **Name and formula** • **Formula only** • **Mass only**
Compound Abundance	• Results reported in Peak Area • Semi-quantitative abundance can be used for comparisons with care

Approach: Use ORD capabilities to assist with field studies

- Conduct collaborative projects with states and tribes
  - Problem statement defined by State or Tribe
  - Sampling plan designed by State or Tribe
  - Samples are collected through State or Tribal actions
  - ORD provides laboratory analysis of samples

Due to lower certainty with NTA, projects should be considered exploratory in nature

These ORD Technical Service Projects **do not** conduct risk assessments or interpret risk of sampling results

PFAS Technical Service Projects: Project Collaborator Roles

State or Tribe	EPA ORD	EPA Region
• Formulate problem statement and project goals • Sampling design • Conduct Sampling	• Perform analysis of samples • Consult on sample design/chemistry	• Facilitate and coordinate communications

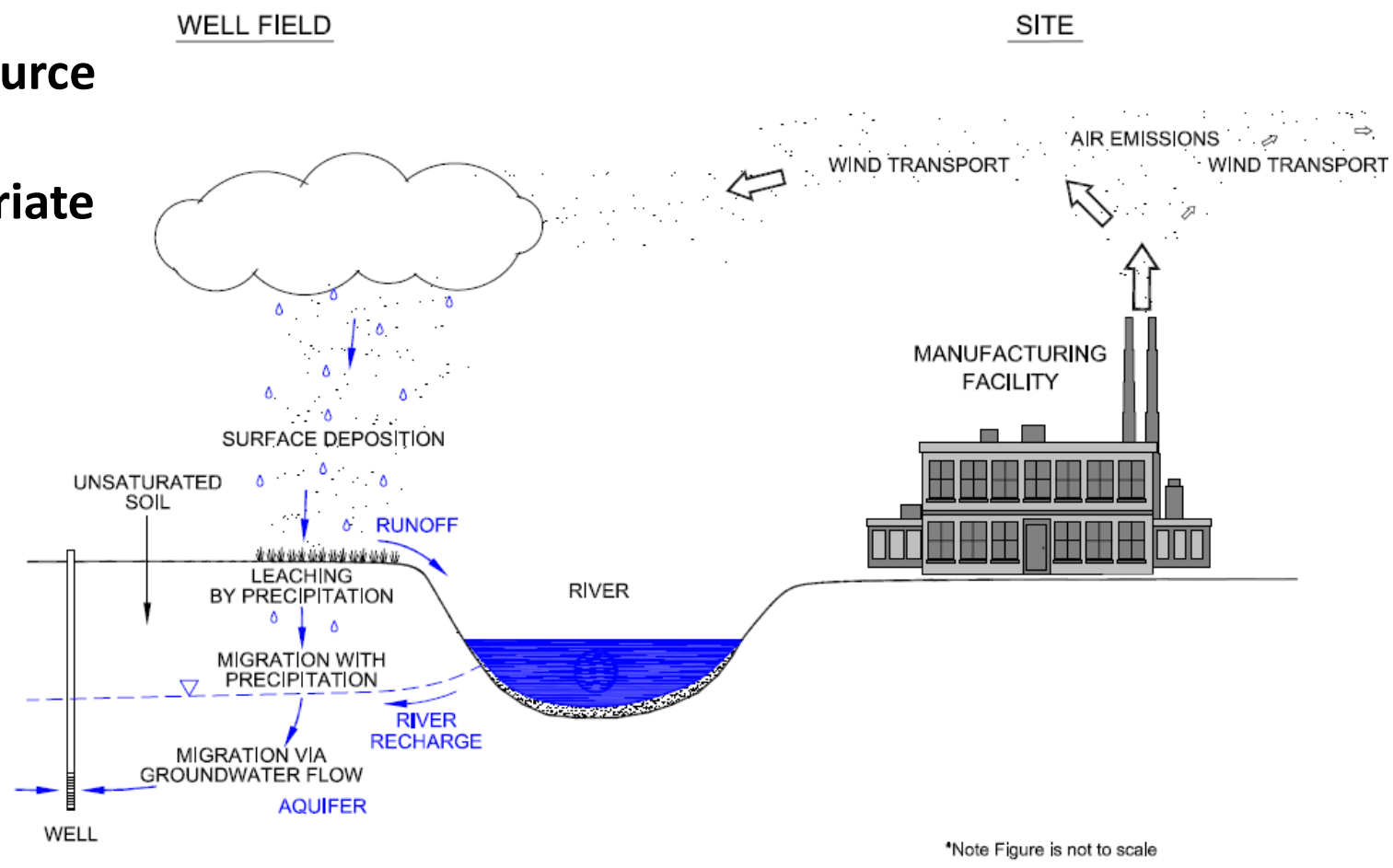
We encourage NGOs who have an interest in sampling PFAS to enlist your state environmental agency to support and implement the project

Example Projects

A number of our technical service projects have been near a known source of PFAS (e.g. manufacturing facility, airport), but any situation is appropriate

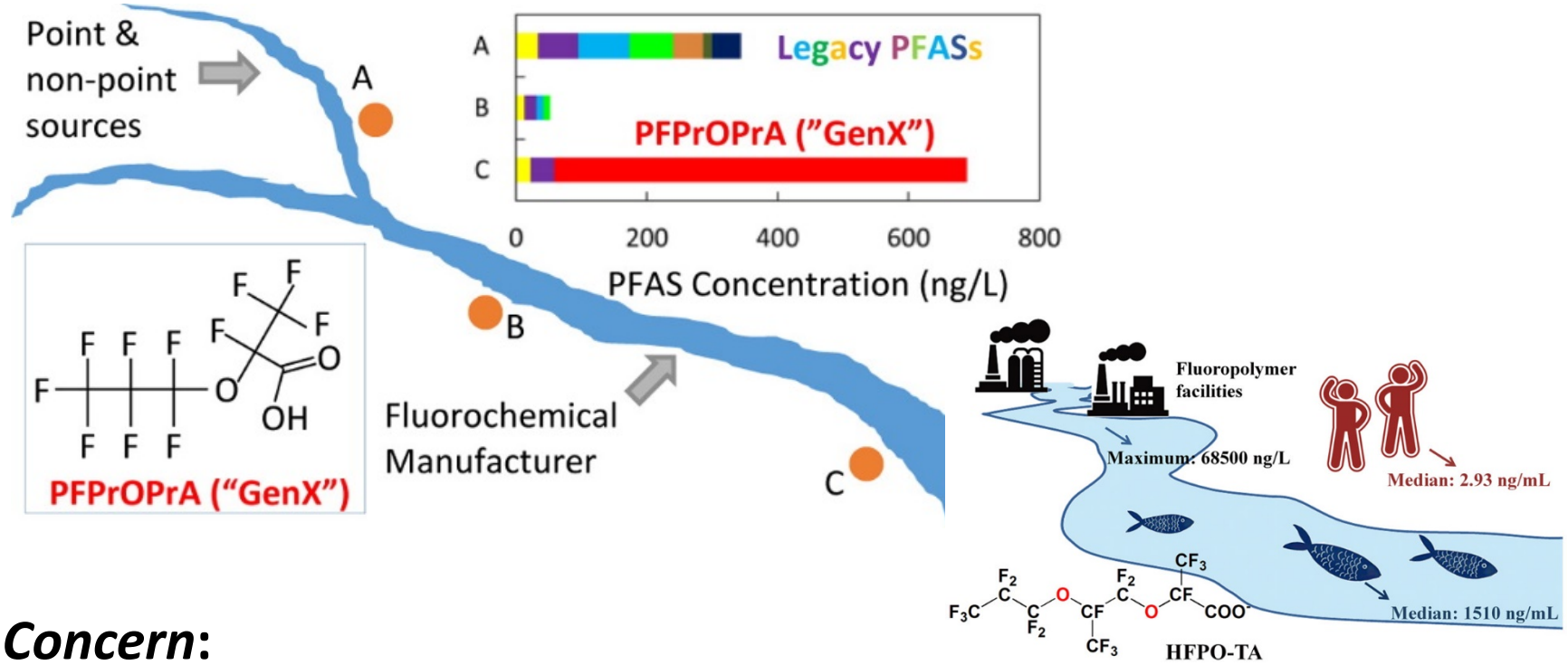
General shared objectives :

- Identify novel PFAS
- Identify any compounds unique to a facility that could be used as a signature
- Check if novel compounds are found in multiple media, especially groundwater
- Role of air emissions in larger scale contamination
- Assess whether control measures appear to be successful



PFAS contamination of the Cape Fear River and local drinking water supplies

- ***Collaborator***:
  North Carolina Department of Environmental Quality (NCDEQ) and EPA Region 4
- ***Where:***
  Cape Fear River in eastern NC
- ***Project:***
  Use NTA to identify PFAS in surface water, wastewater, groundwater, sediments, fish, human blood and sera



Concern:

Contamination of the Cape Fear River and drinking water resulting from discharges of PFAS in water and air from the Chemours chemical manufacturing facility

What PFAS are present in addition to PFOS and PFOA?

Novel PFAS in air and wastewater from a plastics manufacturing facility in New Hampshire

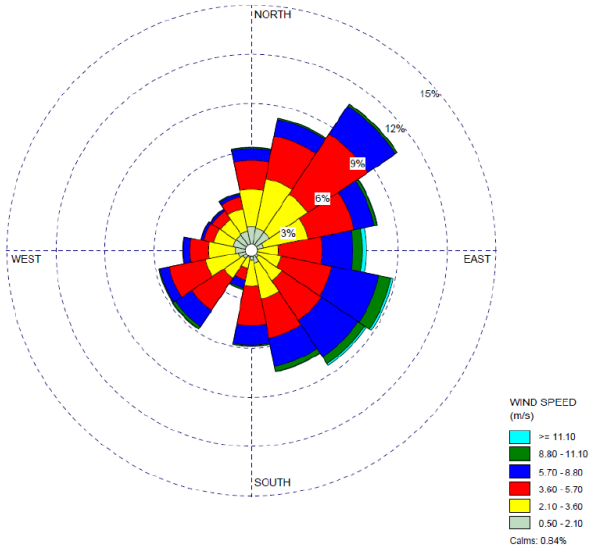
- ***Collaborator*:**
  New Hampshire Department of Environmental Services (NHDES) and EPA Region 1
- ***Where:***
  Within and surrounding the Saint-Gobain Performance Plastics manufacturing site in Merrimack, NH
- ***Project:***
  Use NTA to identify novel PFAS that may be in wastewater and air emissions from a manufacturing facility and their presence in soil and water in the surrounding vicinity

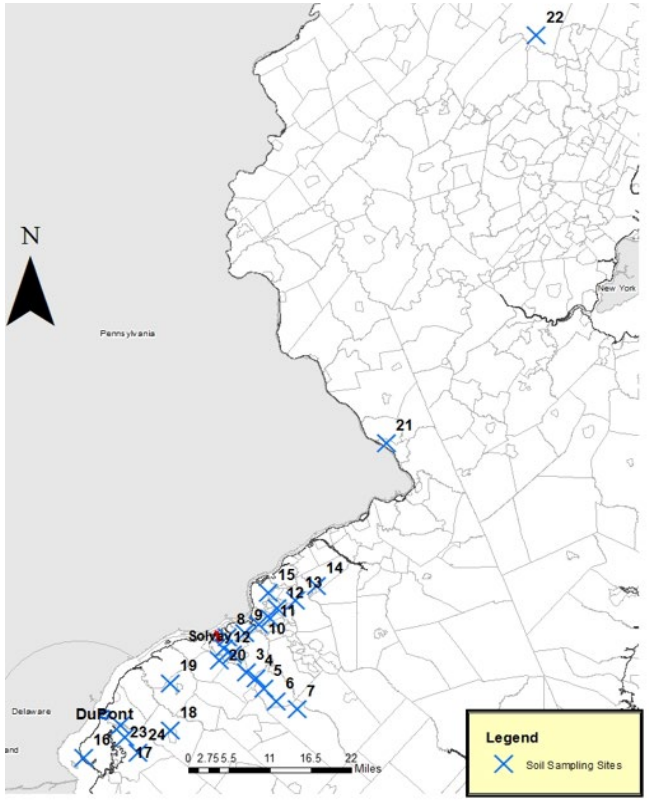
Concerns:

- Need to understand the multimedia environmental distribution of a known source of fluorinated compounds generated in the wastewater and air emissions from the Saint-Gobain plasticizing facility, including the Merrimack River
- Ensure air emission systems designed to remove PFOA and PFOS are also able to remove other PFAS compounds and associated degradates

Novel PFAS in air and wastewater from chemical manufacturing facilities in New Jersey

- ***Collaborator*:**
  New Jersey Department of Environmental Protection (NJDEP) and EPA Region 2
- ***Where:***
  Within and surrounding the Chemours and Solvay manufacturing facilities in SW NJ
- ***Project:***
  Use NTA to identify novel PFAS that may be in emissions from a manufacturing facility and their presence in soil and water in the surrounding vicinity





Concerns:

- Sampling of public supply wells and domestic wells in the vicinity of two chemical manufacturing facilities had found high levels of PFNA, presence of other PFAS not certain
- Ensure drinking water treatment systems and remediation systems designed to remove PFOA and PFOS are also able to remove other PFAS compounds and associated degradates

Example Result of NTA Analysis of POET[1] Treated Wells (GAC[2])

Multiple PFAS present in groundwater influent—most reduced or removed after GAC treatment

PEAK AREA -- Not Equivalent to Concentration

Compound	Well 1		Well 2		Well 3		Well 4		Well 5		Well 6	
	Influent	After treatment	Influent	After treatment	Influent	After treatment	Influent	After treatment	Influent	After treatment	Influent	After treatment
PFPeA	155,000	<RL	171,000	<RL	<RL	<RL	90,200	<RL	78,100	<RL	171,000	<RL
PFHxA	293,000	<RL	351,000	<RL	41,800	<RL	55,100	<RL	130,000	<RL	242,000	<RL
PFHxA	<RL	<RL	2,230	<RL	1,610	<RL	1,670	<RL	<RL	<RL	182,000	<RL
PFHpA	266,000	<RL	233,000	<RL	227,000	<RL	140,000	<RL	102,000	<RL	304,000	<RL
PFHpA	3,370	<RL	9,650	<RL	14,800	<RL	7,290	<RL	3,710	1,150	225,000	<RL
PFOA	1,153,000	<RL	1,077,000	<RL	283,900	<RL	836,000	<RL	427,200	<RL	2,315,000	<RL
PFNA	265,640	<RL	1,664,700	<RL	931,000	<RL	3,285,900	<RL	227,480	82,230	7,537,000	<RL
PFDA	<RL	<RL	<RL	<RL	<RL	166,000	<RL	<RL	50,100	<RL	60,000	<RL
PFUDA	<RL	<RL	9,070	<RL	<RL	<RL	<RL	<RL	<RL	<RL	86,100	<RL
PFBS	51,700	<RL	134,000	<RL	10,900	<RL	28,400	<RL	17,200	<RL	144,000	13,000
PFPeS	<RL	12,300	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	138,000	<RL
PFHxS	69,700	<RL	222,000	<RL	61,800	269,000	318,000	<RL	90,700	<RL	1,020,000	<RL
PFHpS	53,600	<RL	11,000	<RL	2,390	772	13,600	<RL	5,160	<RL	119,000	<RL
PFOS	540,800	<RL	342,300	<RL	<RL	480,000	411,880	<RL	324,520	<RL	4,178,000	<RL
Chloro-perfluoro-polyether-carboxylate congeners (ClPFPECA)(0,	3,290	<RL	65,900	<RL	<RL	<RL	<RL	<RL	2,250	<RL	1,270,000	593
Perfluoro-4-(perfluoroethyl)cyclohexylsulfonic acid	6,900	<RL	17,900	<RL	18,600	<RL	36,500	2,790	2,200	816	234,000	<RL
Perfluoro-4-(perfluoroethyl)cyclohexylsulfonic acid	<RL	<RL	5,780	<RL	6,620	<RL	11,600	<RL	<RL	<RL	55,500	<RL
2,2,3,3-Tetrafluoro-3-{[1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl]oxy}propanoic acid	7,160	<RL	224,000	529	<RL	<RL	1,020	<RL	8,980	<RL	2,090,000	2,400

[1] POET – Point-of-Entry Treatment

[2] GAC – Granular Activated Carbon

Fume suppressants used at chromium electroplating facilities as a source of PFAS in wastewater

- ***Collaborator*:**
  Michigan Department of Environment, Great Lakes, and Energy (EGLE) and EPA Region 5
- ***Where:***
  11 chrome etching facilities operating in MI agreed to participate in the project
- ***Project:***
  Use NTA to identify PFAS in fume suppressant products used at facilities and in discharged wastewater

According to Michigan EGLE **more than 1.5 million residents have been drinking water** contaminated with PFAS, and there could be as many as 11,300 potential sites where PFAS may have been used.

Concern:

PFOS contamination discovered in rivers and the Great Lakes was traced to chrome plating facilities, among other sources

- Are new fume suppressants used at the facilities PFAS-free?
- What other PFAS are in the wastewater?

PFAS in Air Stack Emissions from a Chemours Plant

- ***Collaborator***:
  West Virginia Department of Air Quality (WVDAQ) and EPA Region 3
- ***Where:***
  Chemours Washington Works facility in Parkersburg, WV
- ***Project:***
  Perform targeted and non-targeted analysis on air stack testing samples collected with MM-0010 methods to determine concentrations of HFPO-DA[1] and identify other PFAS present

Concern:

Chemours was required to test air emissions for PFOA and a "novel" PFAS (GenX). WVDEP's Division of Air Quality was not confident in the results provided by a commercial laboratory at the time.

- Does ORD agree with TestAmerica sample quantitation?
- What other PFAS are in the emissions?
- Are emissions controlled?

[1]HFPO-DA – hexafluoropropylene oxide-dimer acid

Example Result of NTA Analysis of Air Emission Samples

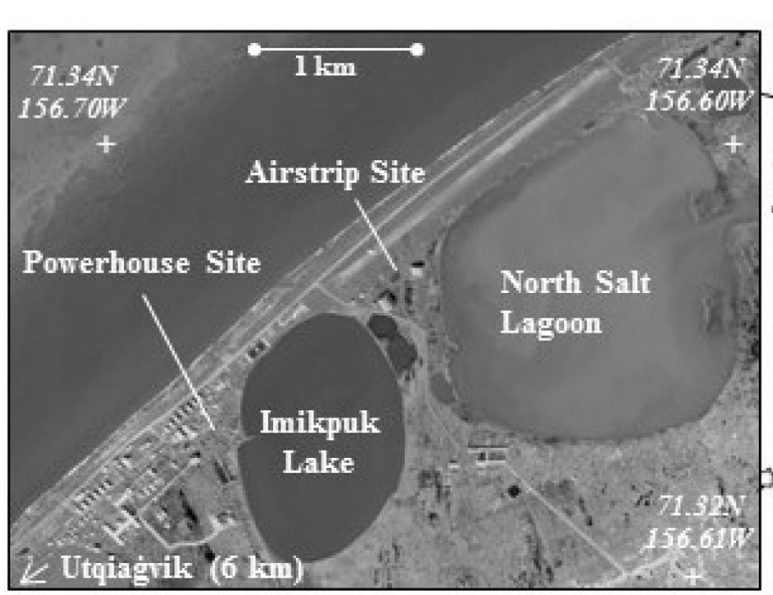
- PFOA present in only small amounts
- GenX present in air emission stack inlets in high amounts
- A number of other PFAS were also present, some in high amounts
- Scrubber controls were effective at removing all from final emissions

		Perfluorooctanoic acid (PFOA)	Perfluoro-2-methyl-3-oxahexanoic acid (HFPO-DA)	Perfluorohexanoic acid (PFHxA)	Perfluoroheptanoic acid (PFHpA)	Perfluorononanoic acid (PFNA)	Perfluorodecanoic acid (PFDA)	Perfluoroundecanoic acid (PFUnDA)	Perfluorododecanoic acid (PFDoDA)	Perfluorotridecanoic acid (PFTrDA)	Perfluorotetradecanoic acid (PFTeDA)	Perfluoro-1,10-decanedicarboxylic acid	Hexacosafluoro-13-(trifluoromethyl)myristic acid	Fluoro(heptafluoropropoxy)acetic acid	CAS 919005-26-8	C3F6O Polymer (n=5)	C3F6O Polymer (n=6)	C3F6O Polymer (n=7)	C3F6O Polymer (n=8)	C3F6O Polymer (n=9)	9-H-Perfluorononanoic acid	7-H-Perfluoroheptanoic acid	11-H-Perfluoroundecanoic acid	2,3,3,3-Tetrafluoro-2-(pentafluoroethoxy) propanoic acid	1,1,2,2-Tetrahydroperfluorotetradecyl acrylate
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Inlet Line	FH filter fraction composite	<RL	12,856,667	29,785	12,655	<RL	376,333	<RL	695,333	<RL	1,851,333	5,515,333	235,667	<RL	641	34,333,333	168,888,888	152,184,888	184,333,333	78,666,667	522,888	11,838,888	3,856,667	241	463,667
	BH filter fraction composite	275,888	18,733,333	35,233	47,567	751,888	525,888	<RL	28,758	<RL	<RL	237,667	<RL	<RL	<RL	7,815,333	34,333,333	41,488,888	15,888,888	1,456,667	272,667	218,888	1,682,888	1,783	1,558,667
	Impinger condensate	2,845,333	285,333,333	22,288	265,667	5,316,667	3,476,667	577,588	578,333	<RL	<RL	2,288,888	<RL	<RL	548	4,188,333	18,348,888	28,476,667	15,736,667	5,388,888	4,545,333	2,376,667	25,788,888	2,888	2,658,888
	XAD-2 Resin Tube	<RL	521,333	333	<RL	<RL	28,488	<RL	<RL	<RL	<RL	4,657	<RL	<RL	<RL	15,567	151,888	258,888	181,888	<RL	5,858	7,333	77,588	<RL	28,233
Inlet Line	FH filter fraction composite	<RL	27,258,888	28,727	<RL	<RL	278,833	536,888	757,888	<RL	1,577,667	5,418,188	277,888	<RL	<RL	15,836,667	75,266,667	117,466,667	33,188,888	34,633,333	684,888	12,536,667	1,784,888	463	<RL
	BH filter fraction composite	381,888	28,866,667	185,667	35,258	<RL	376,667	<RL	161,367	<RL	142,367	347	<RL	<RL	1,585	8,345,667	36,233,333	33,866,667	17,456,667	<RL	186,367	224,888	1,123,333	2,344	<RL
	Impinger condensate	778,667	142,366,667	11,473	165,667	763,667	447,633	<RL	<RL	<RL	38,567	275,388	<RL	<RL	257	1,258,333	7,638,888	12,553,333	7,456,667	1,344,333	1,645,667	242,333	4,446,667	1,525	17,433
	XAD-2 Resin Tube	<RL	264,888	638	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	3,758	<RL	<RL	<RL	<RL
Scrubber Outlet	FH filter fraction composite	<RL	<RL	<RL	<RL	<RL	81,888	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	15,123	35,888	21,858	<RL	<RL
	BH filter fraction composite	<RL	544,888	35,688	35,788	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	5,528	<RL	<RL	<RL
	Impinger condensate	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
	XAD-2 Resin Tube	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL

Analysis of MM5 Train Sample Fractions

Imikpuk Lake, North Slope Alaska

- ***Collaborator***:
  Iñupiat Community of the Arctic Slope (ICAS) and EPA Region 10
- ***Where:***
  north of the village of Utqiaġvik (formerly Barrow, AK)
- ***Concern***:
  - Long history of petroleum spills and AFFF fire-fighting foam from former naval air base
  - Contamination of community drinking water supply and food resources
  - Effect on Bowhead whale health
- ***Project:***
  NTA analysis of water, sediment and fish tissue collected from Imikpuk Lake and other impacted locations



US Navy has instituted clean-up measures for a variety of organic compounds after the base closed, and has identified the presence of PFOS and PFOA in recent years

What other PFAS are there?

PFAS in Precipitation in Wisconsin

- ***Collaborator***:
  Wisconsin Department of Natural Resources and EPA Region 5
- ***Where:***
  8 precipitation stations in the National Atmospheric Deposition Program network distributed throughout WI
- ***Project:***
  Analyze precipitation samples collected through the summer of 2020 for legacy PFAS (WSLH[1]), and novel PFAS (ORD)

As part of a nationwide effort, Wisconsin is evaluating rainwater for 36 legacy PFAS

Are novel PFAS also present?

[1]WSLH – Wisconsin State Laboratory of Hygiene

EPA United States Environmental Protection Agency

Impact of ORD's PFAS Technical Service Projects

- Have shed light on the scope of contamination in the environment surrounding manufacturing facilities
- Allowed states to independently assess information provided by manufacturing facilities
- Allowed states to pursue control activities on manufacturing facilities
- Provided states additional insight into the potential exposures beyond the known universe of PFAS compounds
- Provided an indication of the effectiveness of control technologies such as GAC on the novel compounds
- Increased understanding of product substitutions and ramifications

Contact

For more information about ORD/CEMM's PFAS State and Tribal Technical Service Projects and help with how to get started:

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