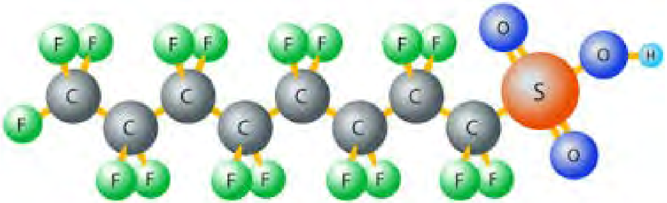
Get to Know Emerging Drinking Water Contaminants: Per- and Polyfluoroalkyl Substances (PFAS)



Syracuse University – Environmental Finance Center

Smart Management for Small Water Systems

August 6, 2019

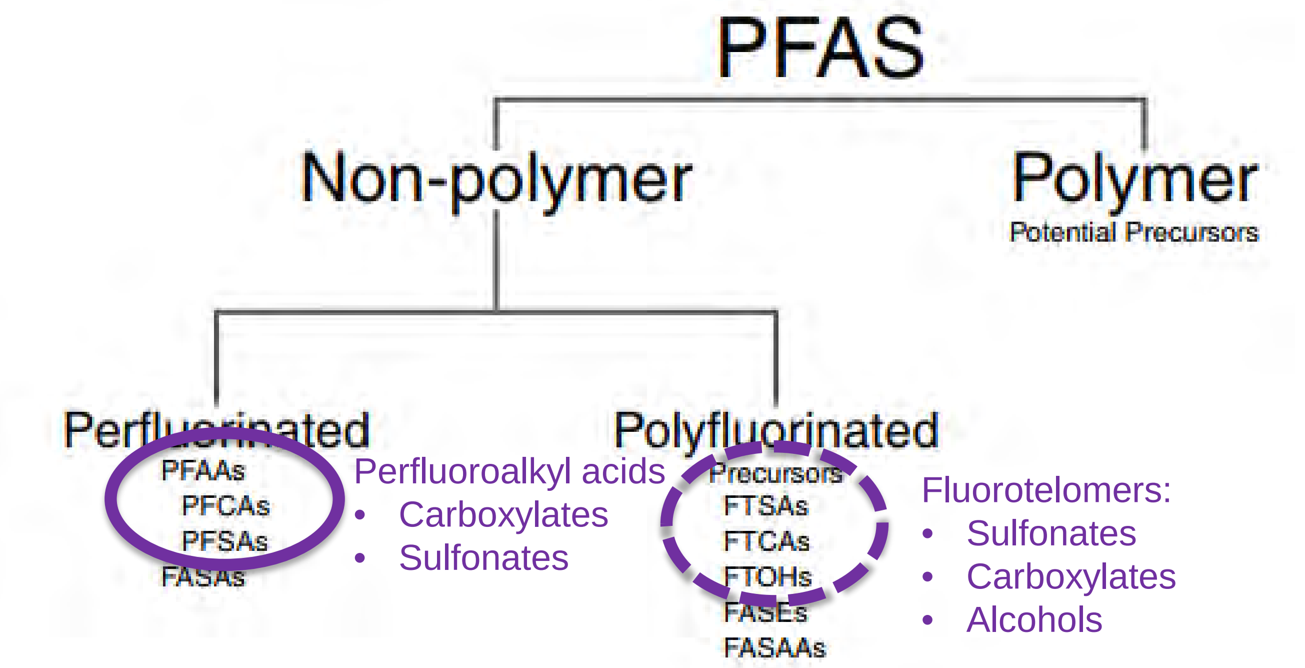
PFAS Emerging Contaminants
Presentation Overview

- **PFAS Background**
- **Toxicology and Regulatory Status**
- **Sampling, Fate & Transport**
- **Case Study: Bennington, VT**
- **Case Study: Portsmouth, NH**
- **Case Study: Burrillville, RI**
- **Questions**

What are PFAS?

- PFAS are a diverse group of manmade compounds resistant to heat, water, and oil. For decades, they have been used in hundreds of industrial applications and consumer products.
- Stable chemicals that include long carbon chains
- The most commonly observed are PFOA and PFOS. PFOS and PFOA are fully fluorinated, organic compounds and have been produced in the largest amounts within the United States. Voluntary phase out of manufacture and use in 2002.
- Shorter chain PFAS and more complex PFAS chemistries (GenX) have been used as “replacement” compounds.
- Have unique lipid- and water-repellent characteristics, used as surface-active agents in various high-temperature applications and as a coating on surfaces that contact with strong acids or bases and for Aqueous Fire Fighting Foams (AFFF)

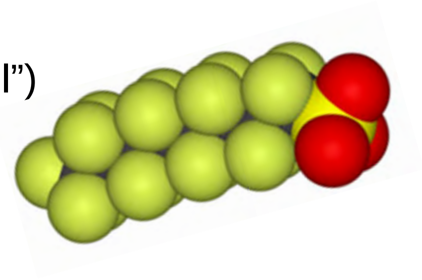
The General Classes of Per- and Polyfluoroalkyl Substances (PFAS)

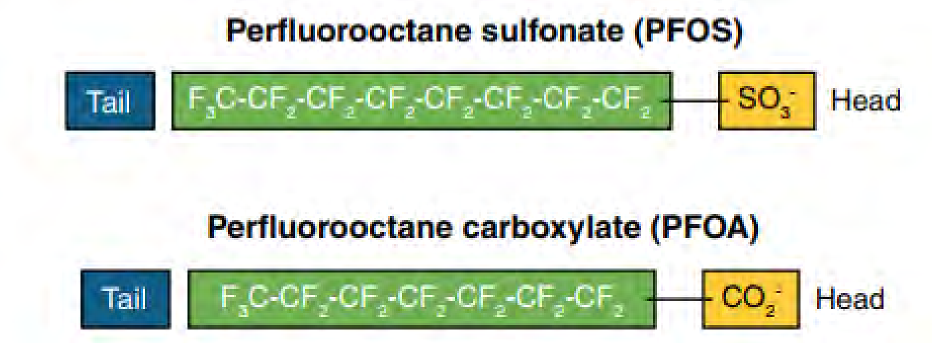


Source: ITRC Naming Conventions and Physical Chemical Properties factsheet

Basic 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^-)





Source: ITRC Naming Conventions and Physical Chemical Properties factsheet

PFAA Naming System

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

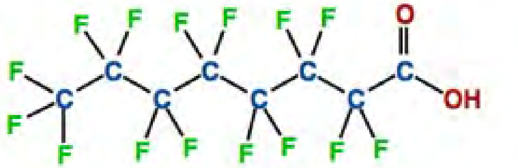
Source: ITRC Naming Conventions and Physical Chemical Properties factsheet

Structural Makeup

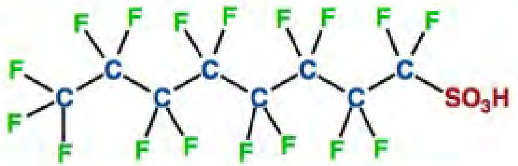
- Anionic <u>Per</u>fluorinated Alkyl Acids (Terminal, NO BREAKDOWN)
  - Negatively charged
  - Low vapor pressure
  - Water soluble

PFAAs generally act as surfactants with tail in the air and head in water

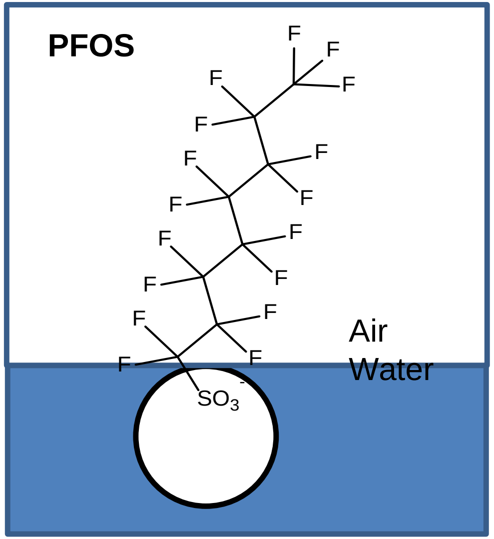
Perfluorinated TAIL   Anionic HEAD



PFOA - perfluorooctanoic acid

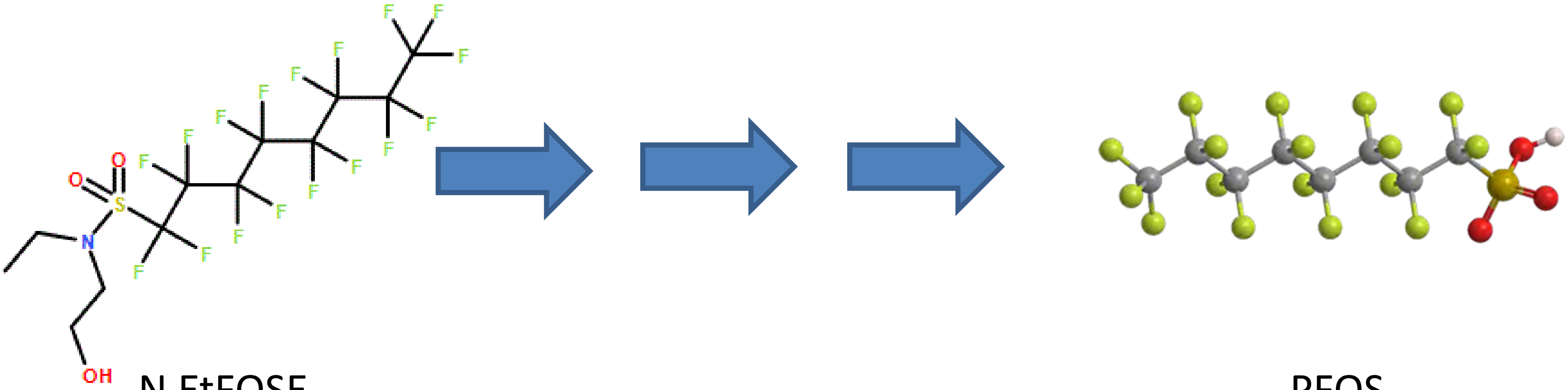


PFOS - perfluorooctanesulfonic acid



Precursors

- Polyfluorinated Substance (Abiotic and Biotic Breakdown Possible)
  - State of charge may dominate retardation
    - Anions > Cations > Zwitterions
  - Short Chains generally migrate faster
  - Cation exchange onto soils may be significant….on par with organic carbon
  - **Transformation into Perfluorinated end products may occur with distance from source and/or oxidization.**

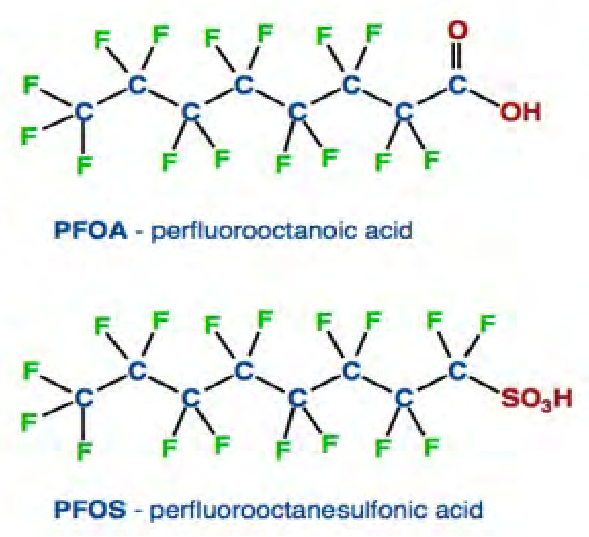


N EtFOSE

PFOS

Primary Uses of PFAS

- Used in fire fighting foams, Aqueous Film-Forming Foam (AFFF)
- Also used in industrial and commercial products including:
    - ➢ Textiles and leather products (Gore-Tex, Polartec)
    - ➢ Metal plating
    - ➢ Stain-resistant carpet
    - ➢ Photographic industry and photolithography
    - ➢ Semi-conductors
    - ➢ Paper and packaging (fast food wrappers)
    - ➢ Coating additives (Teflon)
    - ➢ Cleaning products
    - ➢ Pesticides
- PFOA and PFOS voluntarily phased out in US



PFAS Uses

Where is it?

- Airports
- Air Force Bases
- Naval Facilities
- Fire Fighting Academies
- Manufacturing Facilities
- Wastewater Treatment Facilities
- Landfill Leachate

Source Type

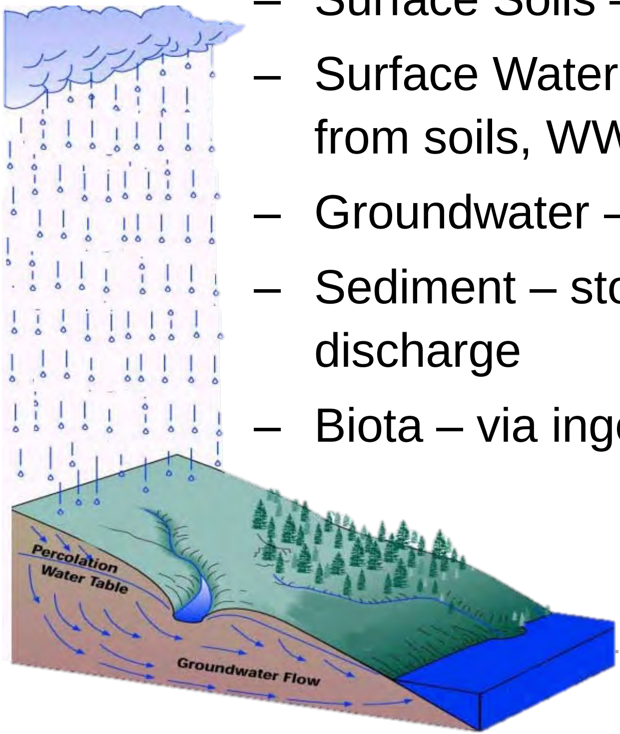
- AFFF Sources
  - AFFF is a mixture of compounds - <5% PFAS
  - There can be many PFAS (short and long) and precursors
  - Hydrocarbons from fire source
  - "Complex Mixture" in source area may effect advection, adsorption, precursor breakdown
- Manufacturing Sources
  - Can have single PFAS source or complex PFAS mixture
  - Additional compounds may be present
- Landfill Leachate
  - "Complex Mixture" in source area may effect advection, adsorption, precursor breakdown
- Wastewater Treatment Facilities
  - Multiple inputs may be present (industries, humans, surface water)
  - Treatment may cause oxidation of precursors
  - Concentration of PFAS in biosolids due to high TOC
  - Biosolids drying, composting, spreading

Release Sources

- "Traditional" Release Methods
  - Airborne Emissions from Manufacturing Facilities
  - Fire Training Facilities
  - Fire Responses
  - Spills
  - Landfill Disposal
  - WWTF Discharge
- "Non-Traditional" Releases/Redistribution Methods
  - Land Application of WWTF Sludge
  - On-Site Septic Disposal Fields
  - Irrigation

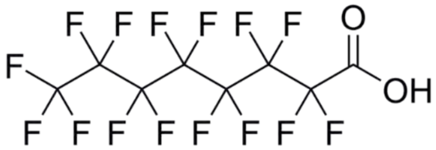
Release Mechanisms

- Use/Release of PFAS can result in impacts to:
  - Air– atmospheric transport can result in large impacted areas,
  - Surface Soils – air deposition, AFFF use, infiltration of runoff water
  - Surface Water – via direct discharge, infiltration from soils, runoff from soils, WWTF discharges
  - Groundwater – via infiltration, wastewater disposal and soil
  - Sediment – storm water infiltration, runoff of soils, groundwater discharge
  - Biota – via ingestion of impacted water, plants?, other biota



Toxicology and Regulatory Status

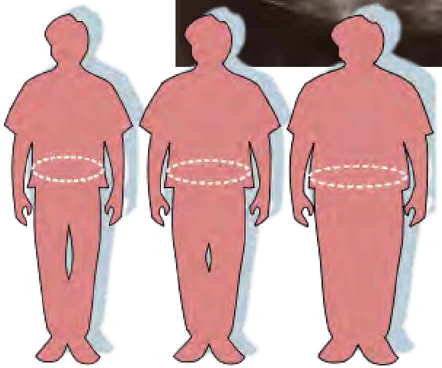
PFAS Toxicology



- Toxicology poorly known
- Possible link to diabetes, weight gain
- In 2006, the EPA Science Advisory Board suggested that PFOA are “likely to be carcinogenic to humans” (pancreatic, liver and kidney cancers)
- PFOS exposure also associated with cancers
- Potential developmental, reproductive and other systemic effects
- Bioaccumulation at different rates per species

Health Effects in Humans

- Fetal growth
- Child/adult adiposity
- Breastfeeding
- Potential Carcinogens
- Others



Other Health Effects

Wide Range of Other Health Effects from PFAS observe in animal and/or human studies:

- Skeletal variation – reduced bone growth
- Testicular and kidney caner
- Persistent liver effects – tissue damage
- Immune effects (e.g., antibody production and immunit
- Thyroid effects
- Accelerated puberty (observed in animal studies)

USEPA's Lifetime Health Advisory

- 70 ng/L based on developmental study in mice
  - Lowest effects level of 1 mg/kg-d decreased ossification and hastened male puberty
  - Adjusted to 0.0053 mg/kg-d to account for much longer half-life in humans
  - Applied safety factors total 300: 10 (sensitive individuals), 3 (inter-species) and 10 (LOAEL to NOAEL) to get reference dose of 0.00002 mg/kg-d (0.02ng/kg-d)
  - Assumed 20% of exposure from drinking water

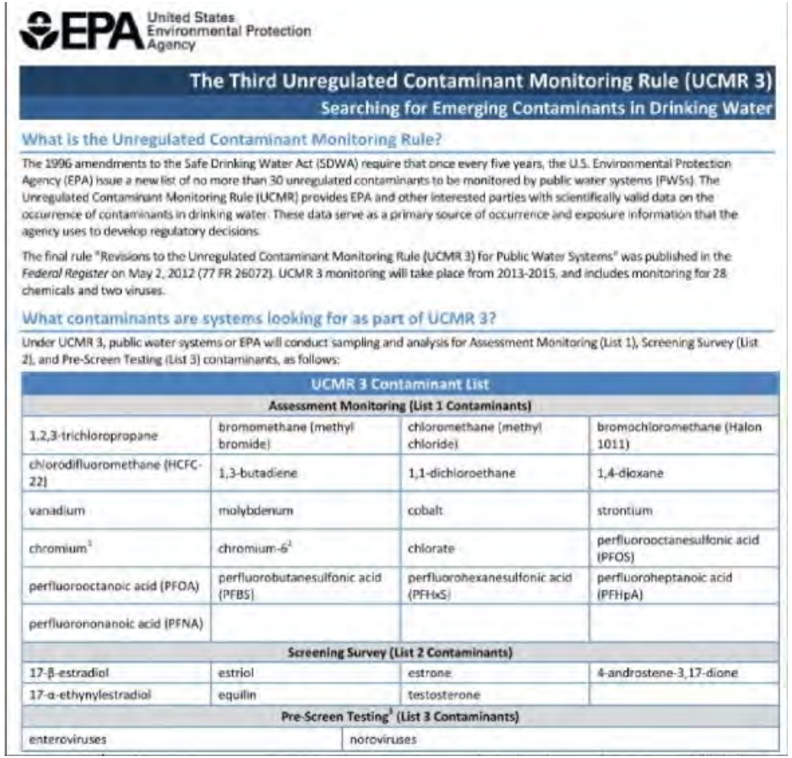
Exposure Should Be Decreasing

- Manufacturers in US phased out PFOA/PFOS production and PFOA/PFOS usage in 2002.

- Stockpiles of AFFF are slowly decreasing

- PFOA/PFOS concentrations in blood serum decrease once exposure stopped

Unregulated Contaminant Monitoring Rule



United States Environmental Protection Agency

The Third Unregulated Contaminant Monitoring Rule (UCMR 3)

Searching for Emerging Contaminants in Drinking Water

What is the Unregulated Contaminant Monitoring Rule?

The 1996 amendments to the Safe Drinking Water Act (SDWA) require that once every five years, the U.S. Environmental Protection Agency (EPA) issue a new list of no more than 30 unregulated contaminants to be monitored by public water systems (PWSs). The Unregulated Contaminant Monitoring Rule (UCMR) provides EPA and other interested parties with scientifically valid data on the occurrence of contaminants in drinking water. These data serve as a primary source of occurrence and exposure information that the agency uses to develop regulatory decisions.

The final rule "Revisions to the Unregulated Contaminant Monitoring Rule (UCMR 3) for Public Water Systems" was published in the *Federal Register* on May 2, 2012 (77 FR 26072). UCMR 3 monitoring will take place from 2013-2015, and includes monitoring for 28 chemicals and two viruses.

What contaminants are systems looking for as part of UCMR 3?

Under UCMR 3, public water systems or EPA will conduct sampling and analysis for Assessment Monitoring (List 1), Screening Survey (List 2), and Pre-Screen Testing (List 3) contaminants, as follows:

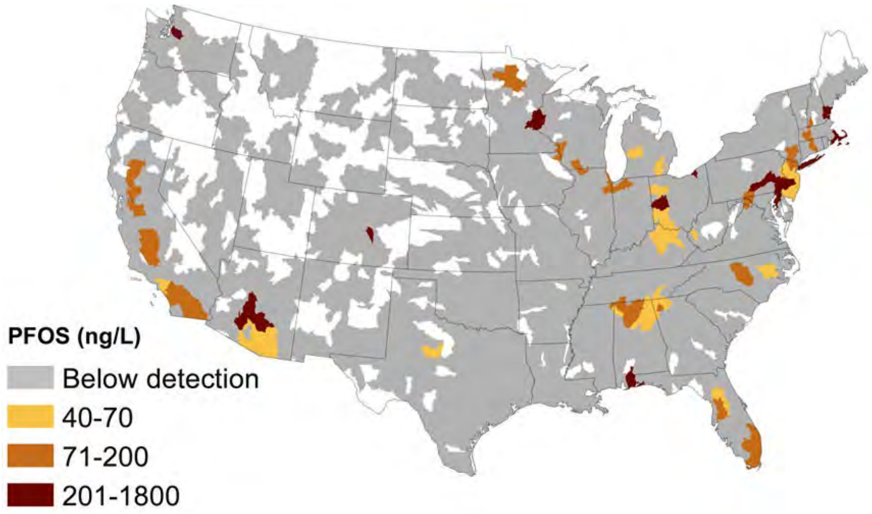
UCMR 3 Contaminant List			
Assessment Monitoring (List 1 Contaminants)			
1,2,3-trichloropropane	bromomethane (methyl bromide)	chloromethane (methyl chloride)	bromochloromethane (Halon 1011)
chlorodifluoromethane (HCFC-22)	1,3-butadiene	1,1-dichloroethane	1,4-dioxane
vanadium	molybdenum	cobalt	strontium
chromium[1]	chromium-6[2]	chlorate	perfluorooctanesulfonic acid (PFOS)
perfluorooctanoic acid (PFOA)	perfluorobutanesulfonic acid (PFBS)	perfluorohexanesulfonic acid (PFHxS)	perfluoroheptanoic acid (PFHpA)
perfluorononanoic acid (PFNA)			
Screening Survey (List 2 Contaminants)			
17-β-estradiol	estriol	estrone	4-androstene-3,17-dione
17-α-ethynylestradiol	equilin	testosterone	
Pre-Screen Testing[3] (List 3 Contaminants)			
enteroviruses	noroviruses		

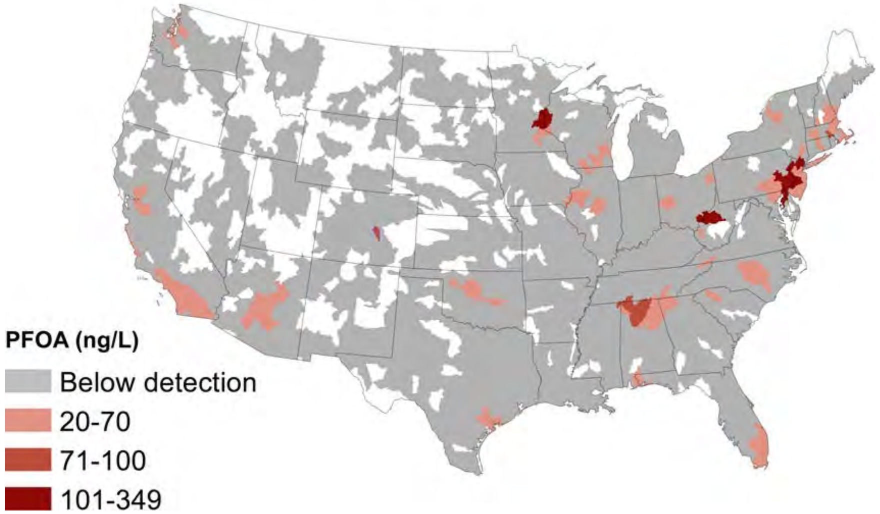
List included (MRL/% >MRL):

- PFOS (0.04 µg/L, 1.9%)
- PFOA (0.02 µg/L, 2.4%)
- PFBS (0.09 µg/L, 0.2%)
- PFHxS (0.03 µg/L, 1.1%)
- PFHpA (0.01 µg/L, 1.7%)
- PFNA (0.02 µg/L, 0.3%)

PFOS & PFOA in Public Drinking Water

Xindi C. Hu et al. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environmental Science & Technology Letters* **2016** *3* (10), 344-350. DOI: 10.1021/acs.estlett.6b00260





State Standards and Guidelines

Drinking Water	PFAS Listed	Concentrration
• EPA Guideline	PFOS & PFOA	70 ng/L (ppt)
• ~~New Hampshire Standard~~	~~PFOS & PFOA~~	~~70 ng/L~~
• Rhode Island Standard	PFOS & PFOA	70 ng/L
• Connecticut Action Level	Sum of 5	70 ng/L
• Vermont Standard	Sum of 5	20 ng/L
• Massachusetts Guideline	Sum of 6	20 ng/L
• New Hampshire Standard	PFOA, PFOS, PFHxS, PFNA	12, 15, 18, 11 ng/L
• New York Recommended Standard	PFOA & PFOS	10 ng/L

Clean Water Infrastructure Act 2017 - $2 Billion for Water and Wastewater Upgrades

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Per- and Polyfluoroalkyl Substances (PFAS)

Per- and Polyfluoroalkyl Substances (PFAS)

Per- and Polyfluoroalkyl Substances (PFAS) are a group of chemicals used to make fluoropolymer coatings and products that resist heat, oil, such as water-repellent clothing, furniture, adhesives, paint and varnish, food packaging, heat-resistant non-stick cooking surfaces and insula

Chemicals in this group include perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS)

PFOA/PFOS Facility Identification Survey

If a respondent indicated that the facility used/stored/disposed PFOA/PFOS substances, it does not necessarily mean that there is an environmental/public health concern associated with the facility. DEC is in the process of reviewing/evaluating the returned surveys to determine if additional follow-up or study is needed

Return rate: *164 surveys were sent to facilities; 152 were returned completed as of June 20, 2017.*

Questions 1 & 2 relate to name and address; questions 3-5 relate to facility ownership.

Q. 6: Is PFOA/PFOS or a PFOA- or PFOS-containing material currently used at the facility?
Q. 7: Was PFOA/PFOS or a PFOA- or PFOS-containing material formerly used at the facility?
Q. 8: Is PFOA/PFOS or a PFOA- or PFOS-containing material currently stored at the facility?
Q. 9: Was PFOA/PFOS or a PFOA- or PFOS-containing material formerly stored at the facility?
Q. 10: Is PFOA/PFOS or a PFOA- or PFOS-containing material currently manufactured at the facility?
Q. 11: Was PFOA/PFOS or a PFOA- or PFOS-containing material formerly manufactured at the facility?
Q. 12: Is PFOA/PFOS or a PFOA- or PFOS-containing material currently being disposed of or released at the facility?
Q. 13: Was PFOA/PFOS or a PFOA- or PFOS-containing material formerly disposed of at the facility?

Facility ID	facility name	facility address	county	Survey complete?	Q. 6	Q. 7	Q. 8	Q. 9	Q. 10	Q. 11	Q. 12	Q. 13
MFG0014	3M - Honeoye	127 East Lake Rd Honeoye, NY	Ontario	YES	NO	NO	NO	NO	NO	NO	NO	NO
MFG0015	3M - Rochester	1999 Mt Read Blvd Rochester, NY	Monroe	YES	NO	NO	NO	NO	NO	NO	NO	NO
MFG0016	3M - Tonawanda	305 Sawyer Ave Tonawanda, NY	Erie	YES	NO	NO	NO	NO	NO	NO	NO	NO
MFG0017	3M/Dynacolor - Brockport	180 State St Brockport, NY	Monroe	YES	NO	NO	NO	NO	NO	NO	NO	NO
MFG0019	Aalborg Instruments & Controls, Inc	20 Corporate Dr Orangeburg, NY	Rockland	YES	NO	NO	NO	NO	NO	NO	NO	NO
MFG0020	Acme Plastics, Inc	570 Union Ave Westbury, NY	Nassau	YES	NO	NO	NO	NO	NO	NO	NO	NO
MFG0021	Acrilex, Inc	188A Miller Pl Hicksville, NY	Nassau	YES	NO	NO	NO	NO	NO	NO	NO	NO
MFG0010	Albany Valve & Fitting Co dba Swagelok Westchester	8 Sprout Creek Ct Ste 3 Wappingers Falls, NY	Dutchess	YES	NO	NO	NO	unknown	NO	unknown	NO	unknown
MFG0022	Aljo-GEFA Precision Manufacturing	205 Bethpage Sweet Hollow Rd Old Bethpage, NY	Nassau	YES	NO	unknown	NO	unknown	NO	unknown	NO	unknown
MFG0023	AlliedSignal Fluogas Division	20 Peabody St Buffalo, NY	Erie	YES	NO	YES	YES	YES	NO	NO	NO	YES
MFG0024	ALLMETAL Screw Products Corp	31 Prospect Pl Deer Park, NY	Suffolk	YES	NO	NO	NO	NO	NO	NO	NO	NO
MFG0025	Allstate Gasket & Packing, Inc	31 Prospect Pl Deer Park, NY	Suffolk	YES	NO	NO	NO	NO	NO	NO	NO	NO
MFG0026	American Combining Corp	Arverne, NY	Queens	NO								

Department of Health Individuals/Families Providers/Professionals Health Facilities Search

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New York State's Water Quality Rapid Response Team Announces New Actions to Address Water Contamination In Washington County

Water Quality Rapid Response TeamFinds PFOA and PFOS Contamination at Paper CompostingFacility

DEC Directs Facility to Cease Distribution of Finished Compost Until Investigation is Complete

Initial Investigation Reveals No Impact to Public Water Systems and Private Wells Tested Below Health Advisory Level

DEC and DOH Launch Statewide Investigation of Recycled Paper Mill Sludge and Processing Facilities

ALBANY, N.Y. (March 13, 2017 - New York State's Water Quality Rapid Response Team today announced new actions to address water contamination in Washington Countyafter releasing the preliminary results of an investigation at the CTI Agri-Cycle compost facility in Cambridge, NY. The in DOH) with support from the Department of Agriculture and Markets, revealed the presence of six perfluorinated compounds (PFCs), including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), in papermill sludge, finished compost material, and water flowing from the cor collection pond.

The Team has been sampling private wells in Cambridge since May, and launched an initial investigation into the CTI Agri-Cycle facility in January after receiving a tip from a private well owner in December. To date, no public water systems have been impacted and nine private wells in the imm he U.S. Environmental Protection Agency (EPA) lifetime health advisory level of 70 parts per trillion (ppt) for PFOA and PFOS combined.To date, four residents have requested and received point of entry treatment (POET)systems. DOH has made initial attempts to reach an additional 10 home residents will continue.

"New York State is committed to ensuring every community has access to clean drinking water. DEC will continue to investigate threats to water contamination in any community while holding polluters accountable," **said DEC Commissioner Basil Seggos.**"Our job is not done until we have ide environment."

"The Water Quality Rapid Response Team continues to work proactively to investigate potential sources of contamination and ensure they are not impacting drinking water supplies," **said DOH Commissioner Dr. Howard Zucker.**"We are taking an aggressive approach throughout the state to

The CTI Agri-Cycle compost facility processes yard waste such as leaves and grass clippings, along with paper mill sludge, which is a byproduct of paper manufacturing used to create compost material that is applied to farm fields near the facility as a soil amendment toincrease organic matter sludges meet current regulatory requirements, but currently does not include testing for the emerging contaminants PFOA and PFOS. The Team will conduct further investigations to determine the source(s) of the PFC contamination at the facility, and may require additional actions by CTI Agri-C

The Team's continued investigation of CTI Agri-Cycle will include thesamplingof farm fields, pond water, and monitoring wellsto evaluate the extent of the PFC contamination.Additionally, DEC will evaluate CTIAgri-Cycle's water management operations and revisit the facility's current State Pollu for facility operations.Concurrently, DOH will continue to sample private wells in the vicinity of the facility to identify whether these wells are impacted by PFCs and whether actions are necessary to reduce exposure.The Team will continue toshare the results of the ongoing investigation with resi

DEC has directed the company to immediately cease any transportation of compostfrom the facility.The Team has launched an expanded investigation of other paper mill sludge-generating andprocessing facilities statewide to track down anyother potential cases of PFCs in paper sludge, thus f sludge as well assix facilities, in addition to Agri-Cycle,that use recycled papersludge in their manufacturing processes.Additionally, the Team has commenced an investigation and immediate mapping of each facility to determine proximity to public and private water supplies along with extensive

As part of the Executive Budget, Governor Cuomo is proposing legislation to mandate the testing of regulated drinking water systems for unregulated contaminants, including PFOA and PFOS. Under the EPA Unregulated Contaminant Monitoring Rule, public water supplies that serve less than Yorkers on untested systems. Through the Governor's proposal, water systems would begin testing for PFOA and PFOS this year, and small community water supplies will be eligible to receive financial hardship funding.

In January, Governor Cuomo also announced the Clean Water Infrastructure Act of 2017 to invest a record $2 billion in critical water infrastructure across New York State. The $2 billion Clean Water Infrastructure Act will provide the capital dollars needed to upgrade municipal drinking water sys additional support for the state Superfund program.

This historic investment in drinking water and wastewater infrastructure, and in addition to source water protection actions will enhance community health and wellness, safeguard our most important water resources, and create jobs. Funding for projects will prioritize regional and watershed leve

CAPE FEAR PUBLIC UTILITY AUTHORITY, NC

PFAS compounds have consistently been detected in raw water from the Cape Fear, even after state regulators suspended Chemours' privilege to discharge its wastewater in November 2017. Since then PFAS levels have fluctuated, spiking to 297 ppt in September 2018. The overall trend of raw water concentrations since permitted discharges ceased appears to be about 100 ppt, according to the authority.

Officials said the variability of PFAS concentrations in river water could be tied to river flow and other factors. Lower river flows appear to result in higher total PFAS concentrations.

"Stopping Chemours' permitted discharges have helped reduce PFAS in the Cape Fear River," said CFPUA Executive Director Jim Flechtner. "But what we've seen in our monitoring indicates that we can expect to see PFAS in our raw water at varying concentrations for many years to come."

The authority plans to begin construction in November of eight deep-bed granular activated carbon filters at the Sweeney plant. The $46 million project is to be operational by early 2022 and is expected to reduce PFAS levels by an average of 90%.

Gov. Roy Cooper asked for $6 million for new equipment and 37 positions to handle the additional workload generated by PFAS oversight and regulation. DEQ recently mandated testing for PFAS and other compounds for 25 public water systems in the Cape Fear River basin.

From Coastal Review 6/21/19

Evolving Landscape

- New and changing toxicological data
- Improved analytical testing has allowed for detection limits in single part per trillion range

- Increased detections
- CONFUSION ABOUNDS

Sampling, Fate and Transport

PFAS Sampling Methods

EPA Method 537.1 is the ONLY certified drinking water method

- 250 mL, HDPE bottles, Trizma preservative, NO Teflon lined caps
  - 2 bottles per sample location
  - Field Blank collected at EVERY location - Pour PFAS free water from provided bottle into preserved bottle
- Ship on Ice
- Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)
- Fortified with Surrogates
- Solid Phase Extraction/Filtration
- Detection Limits in the 1 – 5 ng/L

No EPA certified method for any other media….yet

- DoD QSM 5.1 – Soil, Sludge, Groundwater, Leachate
- ASTM Methods – High Detection Limits, QA/QC issues

PFAS Sampling Concerns

Real or Just Potential

Material of Concern	Potential Alternative
PPE	
Coated Tyvek	Untreated Tyvek
Treated Clothing (waterproof, stain resistant, water resistant)	Synthetic or natural fiber clothing
New Clothing	Well washed clothing
Clothing with Fabric Softener	Do not use fabric softeners
Treated Boots (waterproof, stain resistant, water resistant)	PVC boots
Deodorant	Do not use
Cosmetics, Lotions, Sunscreen, Insect Repellant	Do not wear, all natural ingredients, DEET
Food Containers/Wrappers	Do not have in sampling area
Sampling Equipment	
PTFE, FEP, ETFE, LDPE (anything with "fluoro" in the name)	Do not use
Rite in the Rain Notebooks	loose leaf paper
Post Its	Do not use
Decon 90	Alconox
Glass containers	Polypropylene or HDPE
Teflon lined lids	Unlined lids
Chemical Ice	Ice (double bag to keep melt away from samples)
Aluminum foil	HPDE Sheeting
Sharpies	Ball point pen

PFAS Sampling Concerns

ARE THE NUMBERS "REAL"?

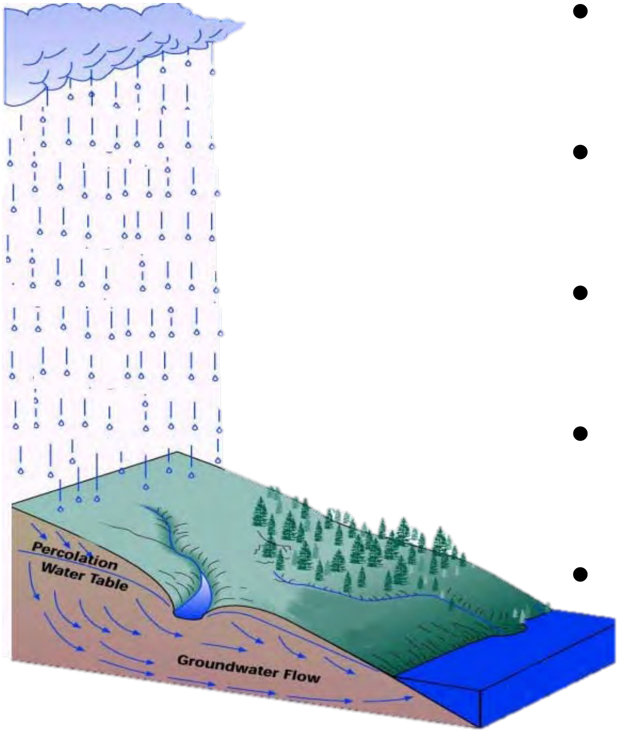
- **The potential for false positive results is accentuated by the very low detection limits.**
  - **Detection limits of 2-5 ng/L (parts per trillion).**
  - **1 person in 2 world populations = 70ppt**

- **"Background" concentrations of PFAS are present everywhere.**
  - **PFAS found in blood serum of polar bears, Pacific Ocean waters**
  - **Wastewater, carpet dust, clothes, sampling materials**

- **Quality Assurance and Quality Control are more important than ever**
  - **Frequent Duplicates**
  - **Frequent Equipment Blanks**
  - **Frequent Rinsate Blanks**
  - **Frequent Field Blanks (bottle to bottle) (EPA Method says EVERY SAMPLE)**

- **Use a well proven lab and get to know how to read their QA/QC**
  - **EPA 537.1 is for Drinking Water ONLY**
  - **Qualifiers?**
  - **Isotope Dilution?**
  - **SPME "clean up"?**

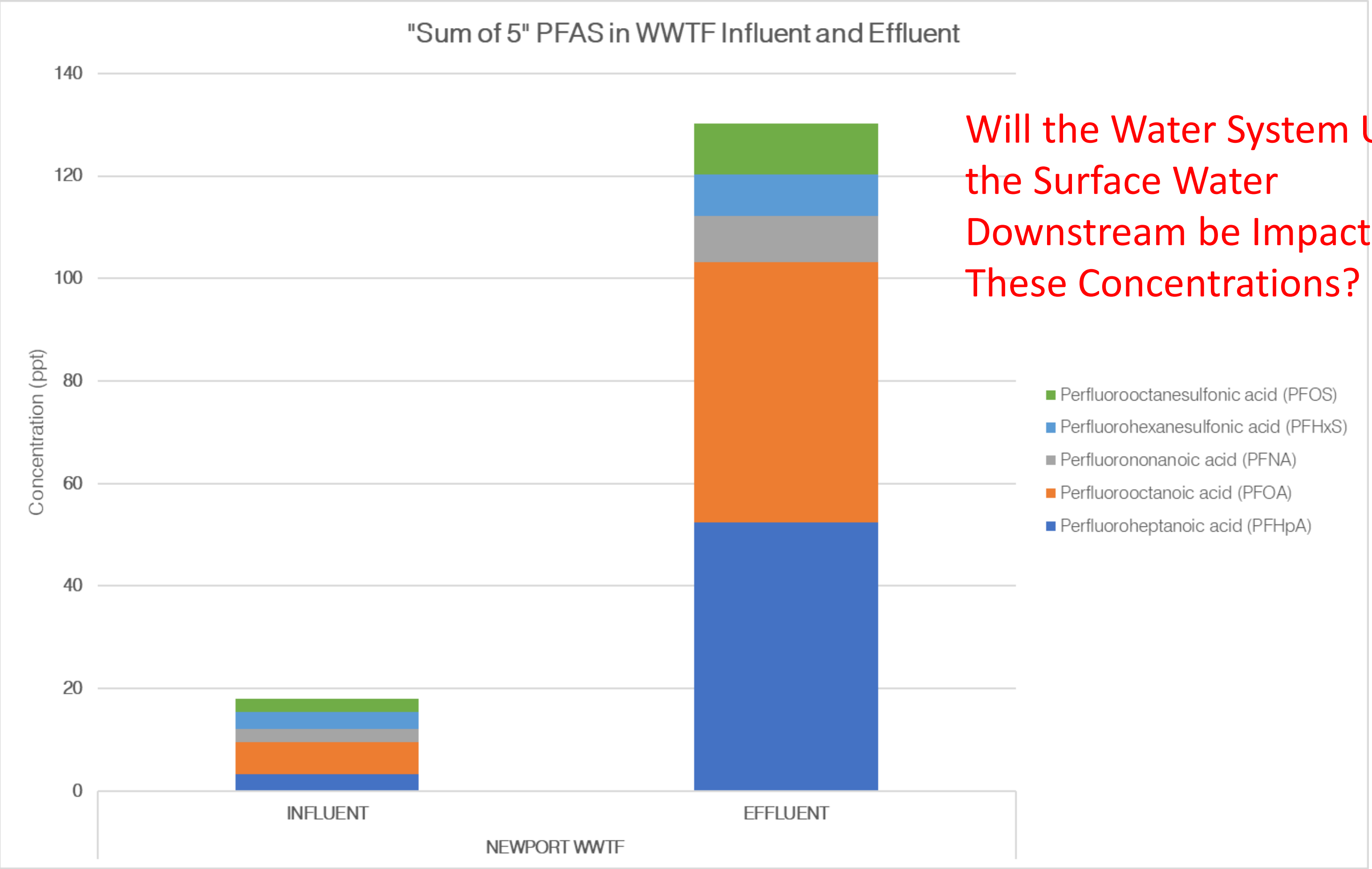
Fate & Transport



- Use of PFAS in manufacturing can result in releases to air, water, and soil
- PFAS released to air is readily adsorbed to particles and settles to the ground
- PFAS deposited into/onto soil can be transported to and contaminate groundwater and surface water
- Very resistant to biodegradation and therefore very persistent
- FOREVER CHEMICALS

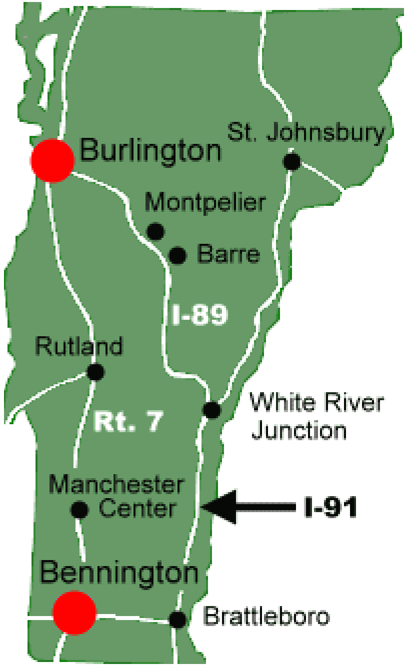
WWTF Related Potential Issues

Analyte	Units	RANDOLPH WWTF SBR		BARRE WWTF ACTIVATED SLUDGE		NEWPORT WWTF		MONTPELIER WWTF ACTIVATED SLUDGE	
		INFLUENT	EFFLUENT	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT
Perfluorobutanoic acid (PFBA)	ng/l	ND/< 13.7	**15.8**	ND/< 13.7	**11.5**	**43.3**	**77.7**	**126.0**	**51.5**
Perfluoropentanoic acid (PFPeA)	ng/l	ND/< 6.83	**7.03**	ND/< 6.83	**13.3**	ND/< 6.81	**57.7**	**66.8**	**28.9**
Perfluorohexanoic acid (PFHxA)	ng/l	**4.10**	**20.9**	ND/< 3.33	**19.3**	**7.39**	**87.4**	**117.0**	**62.2**
Perfluoroheptanoic acid (PFHpA)	ng/l	ND/< 1.50	**4.94**	ND/< 3.33	**3.52**	ND/< 3.32	**52.5**	**33.8**	**16.0**
Perfluorooctanoic acid (PFOA)	ng/l	ND/< 1.50	**20.2**	ND/< 3.33	**8.78**	**6.27**	**50.6**	**93.9**	**44.1**
Perfluorononanoic acid (PFNA)	ng/l	**1.12**	**1.86**	ND/< 0.666	**0.357**	**2.45**	**9.07**	**5.91**	**3.50**
Perfluorodecanoic acid (PFDA)	ng/l	**0.96**	**0.70**	ND/< 0.666	**0.162**	**1.21**	**30.8**	**5.17**	**5.14**
Perfluoroundecanoic acid (PFUnA)	ng/l	ND/< 0.500	**0.08**	ND/< 0.500	ND/< 0.0598	ND/< 0.498	**1.47**	**0.61**	**0.0810**
Perfluorododecanoic acid (PFDoA)	ng/l	ND/< 0.700	ND/< 0.084	ND/< 0.700	ND/< 0.0837	ND/< 0.698	**1.17**	ND/< 0.706	ND/< 0.0841
Perfluorotridecanoic acid (PFTrDA)	ng/l	ND/< 0.500	ND/< 0.060	ND/< 0.500	ND/< 0.0598	ND/< 0.498	**0.17**	ND/< 0.504	ND/< 0.0601
Perfluorotetradecanoic acid (FTeDA)	ng/l	ND/< 0.667	ND/< 0.080	ND/< 0.666	ND/< 0.0797	ND/< 0.665	ND/< 0.0798	ND/< 0.672	ND/< 0.0801
Perfluorobutanesulfonic acid (PFBS)	ng/l	*ND/< 1.25*	**1.25**	ND/< 3.33	**4.73**	ND/< 3.32	**67.6**	**101**	**41.2**
Perfluoropentanesulfonic acid (PFPeS)	ng/l	ND/< 3.17	ND/< 0.379	ND/< 3.16	ND/< 0.379	ND/< 3.16	ND/< 0.477	**3.26 J**	ND/< 0.470
Perfluorohexanesulfonic acid (PFHxS)	ng/l	*ND/< 1.25*	**2.06**	ND/< 3.33	**1.74**	ND/< 3.32	**8.20**	**11.7**	**7.55**
Perfluoroheptanesulfonic acid (PFHpS)	ng/l	ND/< 3.17	ND/< 0.379	ND/< 3.16	ND/< 0.379	ND/< 3.16	ND/< 0.379	ND/< 3.19	ND/< 0.380
Perfluorooctanesulfonic acid (PFOS)	ng/l	**9.29**	**1.18 J**	ND/< 2.66	**1.17 J**	ND/< 2.66	**9.83**	**16.0 J**	**4.92**
Perfluorononanesulfonic acid (PFNS)	ng/l	ND/< 3.17	ND/< 0.379	ND/< 3.16	ND/< 0.379	ND/< 3.16	ND/< 0.379	ND/< 3.19	ND/< 0.380
Perfluorodecanesulfonic acid (PFDS)	ng/l	ND/< 3.33	ND/< 0.399	ND/< 3.33	ND/< 0.399	ND/< 3.32	ND/< 0.399	ND/< 3.36	ND/< 0.400
Perfluorododecanesulfonic acid (PFDoS)	ng/l	ND/< 3.17	ND/< 0.379	ND/< 3.16	ND/< 0.379	ND/< 3.16	ND/< 0.379	ND/< 3.19	ND/< 0.380
Perfluorooctanesulfonamide (PFOSA)	ng/l	ND/< 3.33	**0.690**	ND/< 3.33	**0.857**	ND/< 3.32	**3.64**	**3.94**	**0.455**
N-Methylperfluorooctanesulfonamidoacetic acid (N-MeFOSAA)	ng/l	ND/< 3.33	**0.693**	ND/< 3.33	ND/< 0.399	ND/< 3.32	**10.5**	**4.74**	**1.16**
N-Ethylperfluorooctanesulfonamidoacetic acid (N-EtFOSAA)	ng/l	ND/< 3.33	**0.426**	ND/< 3.33	ND/< 0.399	ND/< 3.32	**4.96**	**7.79**	**0.596**
4:2 Fluorotelomer sulfonate (4:2 FTS)	ng/l	ND/< 0.500	ND/< 0.060	ND/< 0.500	ND/< 0.0598	ND/< 0.50	**0.715**	ND/< 0.504	**0.252**
6:2 Fluorotelomer sulfonate (6:2 FTS)	ng/l	**3.01**	**5.73**	**2.66**	**1.07**	**20.4**	**11.2**	**58.2**	**24.6**
8:2 Fluorotelomer sulfonate (8:2 FTS)	ng/l	ND/< 2.67	**0.458**	ND/< 2.66	ND/< 0.319	ND/< 2.66	ND/< 0.319	**2.9**	**0.592**



Will the Water System Using the Surface Water Downstream be Impacted by These Concentrations?

Case Study: Bennington



Case Study: Bennington

- After learning the source of Hoosick Falls, NY PFOA contamination originated from a ChemFab plant, local legislators request Vermont Department of Environmental Conservation sample several private and public water supply wells surrounding the former ChemFab plant in North Bennington.
- ChemFab processed high tech fabrics using PFOA and Teflon in North Bennington from the 1960s to 2012.
- Weston & Sampson developed a sampling plan and collected samples from 4 residences close to the former plant and 2 public water supplies.
- All 4 residences reported PFOA ranging from **41 to 2,330 ppt**.

Case Study: Bennington

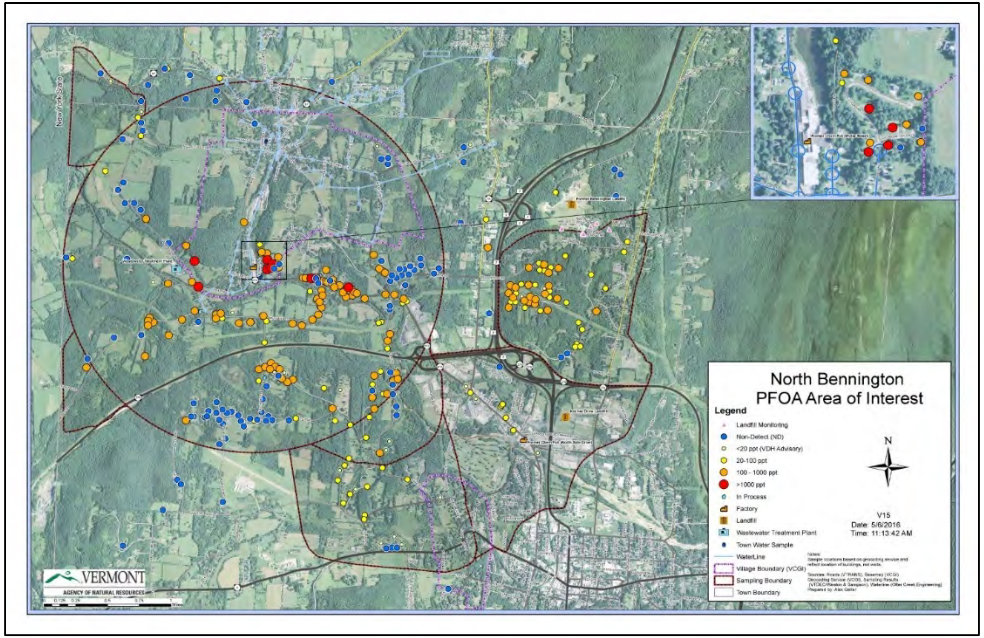
- A local response center: Collect contact information, water supply information, water quality samples and answer questions from all residents.

Case Study: Bennington

- Three AOCs were developed: around ChemFab plant, around a second (smaller) ChemFab plant, and around a closed landfill.

- All 3 AOCs merged into 1 comprehensive AOC.

- “Dog Ears” added to the AOC as data indicates “ND line” not achieved.



Case Study: Bennington

- Impractical to report large amounts of data by hand.

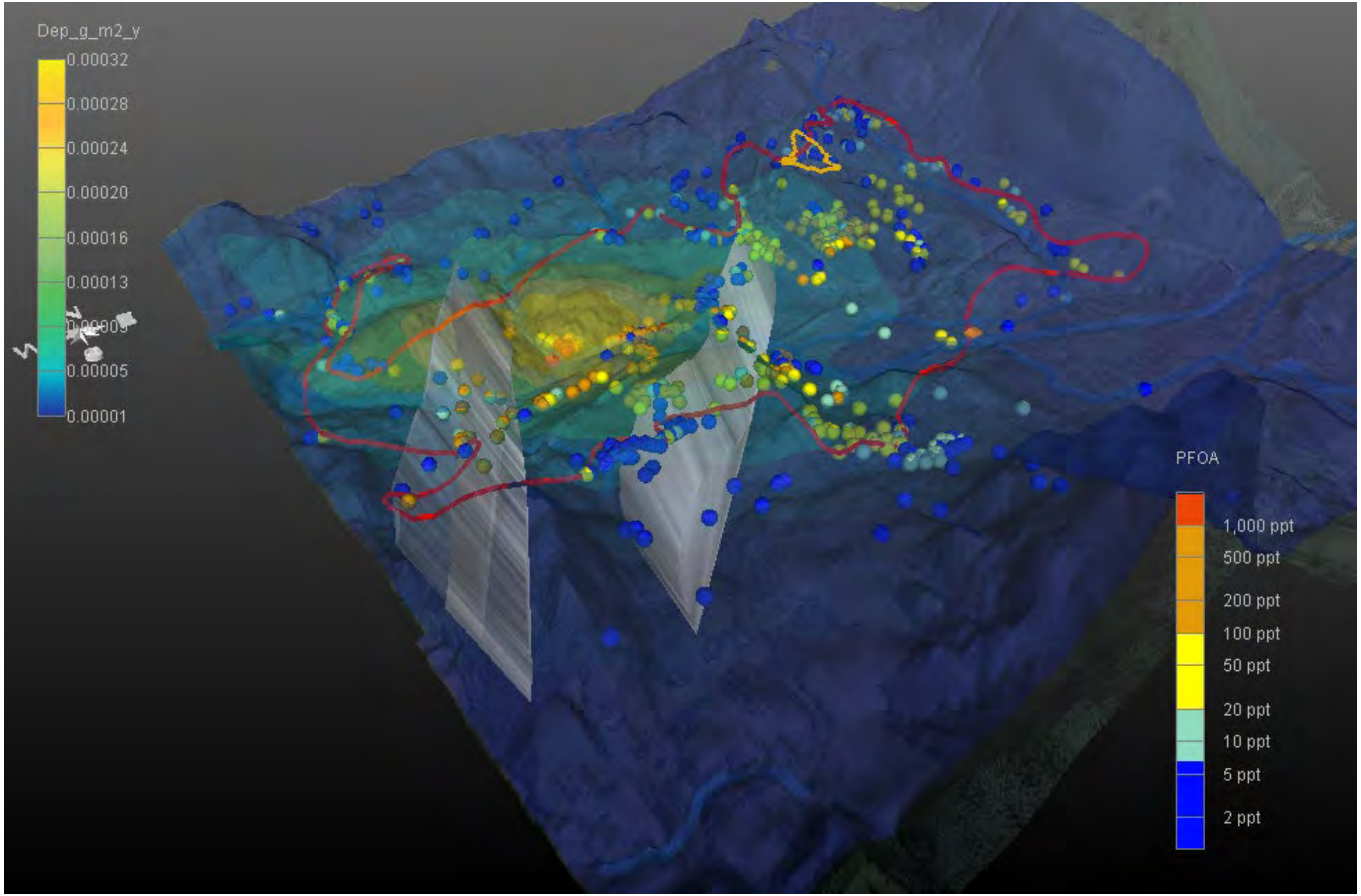
- A web based form was provided to ease the process of collecting resident requests for sampling.

Case Study: Bennington

WATER SUPPLY IMPACTS

- 553 Wells Sampled associated with all 3 AOCs
  - 270 Wells > 20ppt.
  - 80 Wells < 20ppt.
  - 203 Wells ND.
- Resampling of initially <20 ppt water supplies performed.
- <u>Approx. 10% reported as >20 ppt during EVERY resampling.</u>

amec foster wheeler



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Case Study: Bennington

- Multiple Sources of PFOA.
- The ChemFab process produced highly contaminated exhaust output likely resulting in airborne transport and deposition.
- Transport mechanisms are extremely complicated
  - Airborne
  - Groundwater (shallow and bedrock)
  - Soil Erosion/Sedimentation
  - Surface Water
  - WWTF, manure spreading, “re-circulation” via on-site septic
- Therefore, distribution of the contaminants is widespread and unpredictable.
- THE LAST USE OF PFOA WAS 14 YEARS AGO.

Case Study: Burrillville

Case Study: Burrillville

Groundwater Quality Standard

PFOA & PFOS = 70ng/L (ppt)

- http://www.dem.ri.gov/programs/benviron/water/quality/pdf/pfoa.pdf

RIDPH and Brown sampled 38 small public water systems

– Several between ND and 70 ppt
– Oakland Association public well impacted at >100 ppt

Immediate RIDEM Response

– All Oakland Association users given spring water deliveries
– All private water supply wells in a ¼ mile radius of Oakland Association Well
– Public meeting to inform impacted customers and nearby private well users
– Feasibility for extension of neighboring public water system to affected residences evaluated

Case Study: Burrillville

Potential PFAS Source Identification

- Similar to Phase I Environmental Site Assessment Research
- Multiple Potential Sources Identified

Initial Private Drinking Water Well Data Plotted via GIS

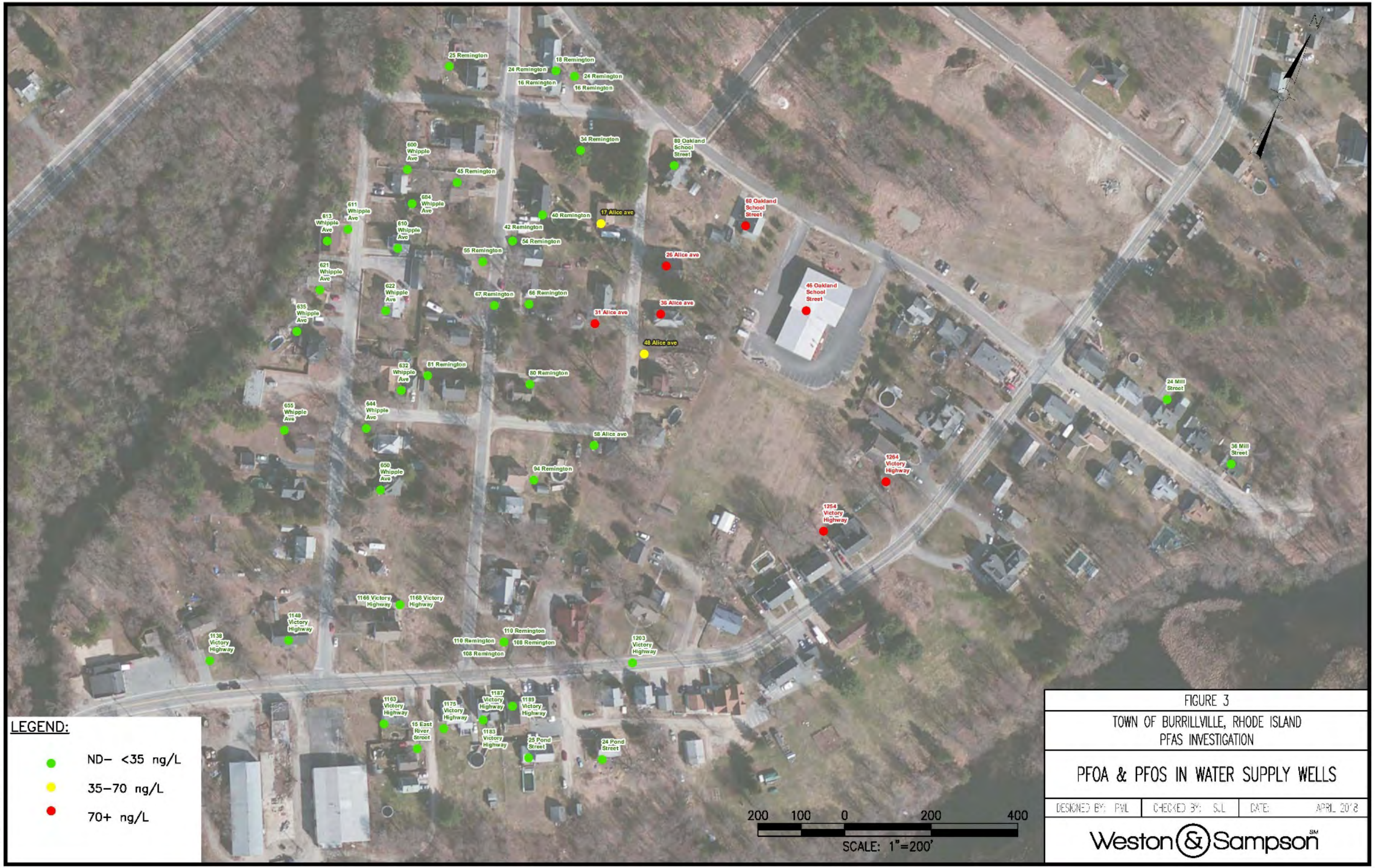
- Developed a Conceptual Site Model for PFAS makeup and distribution.
- Identified area for field data collection based on CSM to isolate source(s).

Targeted Site Investigation

- Single Mobilization
- Collection of discrete interval soil and groundwater samples
  - (shallow, intermediate, atop bedrock)
- Installed permanent monitoring wells
- Data evaluation and reporting

Weston & Sampson

Weston & Sampson



LEGEND:

- ND– <35 ng/L
- 35–70 ng/L
- 70+ ng/L

FIGURE 3

TOWN OF BURRILLVILLE, RHODE ISLAND
PFAS INVESTIGATION

PFOA & PFOS IN WATER SUPPLY WELLS

DESIGNED BY: PWL	CHECKED BY: SJL	DATE: APRIL 2018

Weston & Sampson

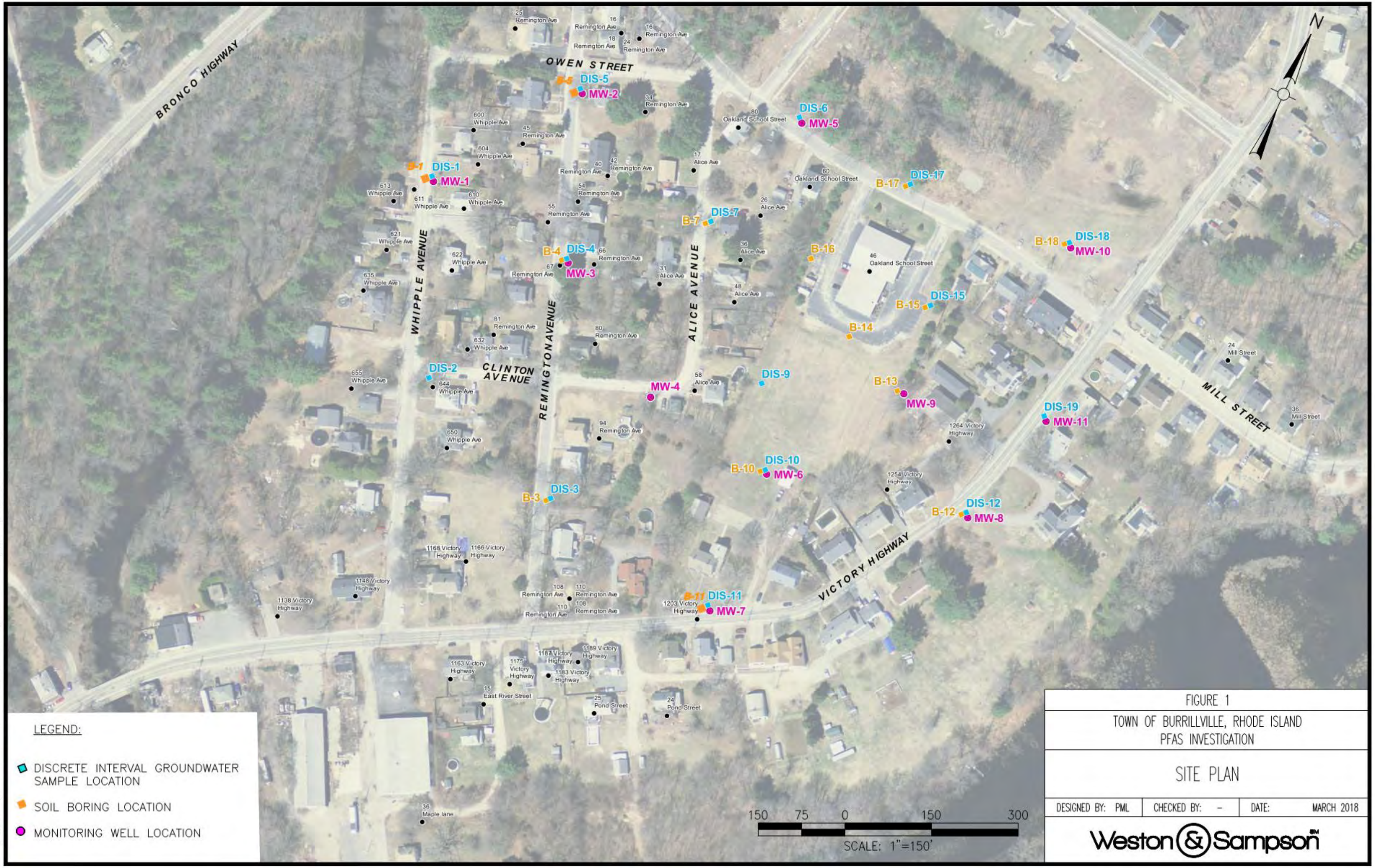


FIGURE 1

TOWN OF BURRILLVILLE, RHODE ISLAND
PFAS INVESTIGATION

SITE PLAN

DESIGNED BY: PML	CHECKED BY: –	DATE: MARCH 2018

Weston & Sampson

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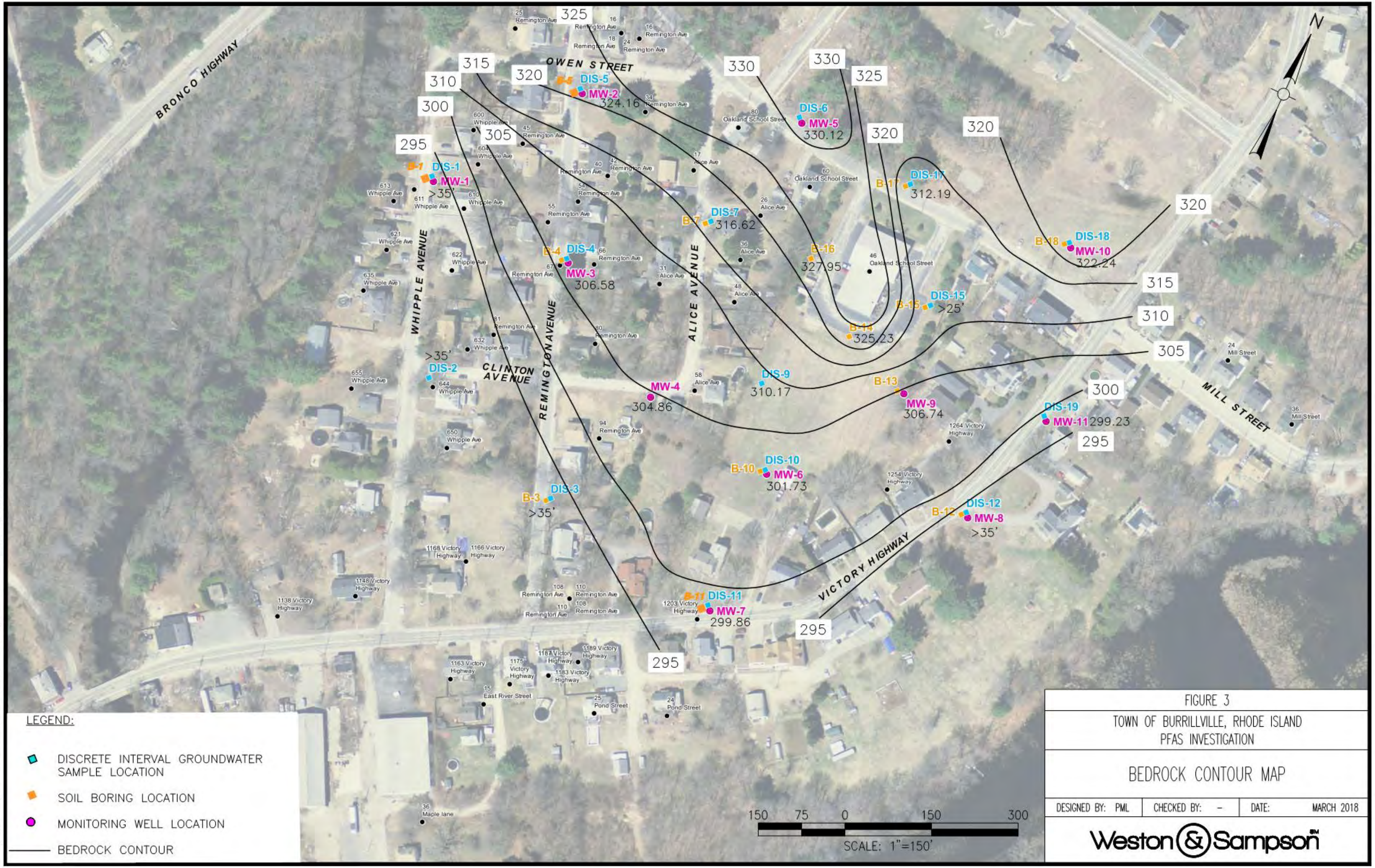

LEGEND:

- DISCRETE INTERVAL GROUNDWATER SAMPLE LOCATION
- SOIL BORING LOCATION
- MONITORING WELL LOCATION
- BEDROCK CONTOUR

FIGURE 3

TOWN OF BURRILLVILLE, RHODE ISLAND
PFAS INVESTIGATION

BEDROCK CONTOUR MAP

DESIGNED BY: PML	CHECKED BY: –	DATE: MARCH 2018

Weston & Sampson

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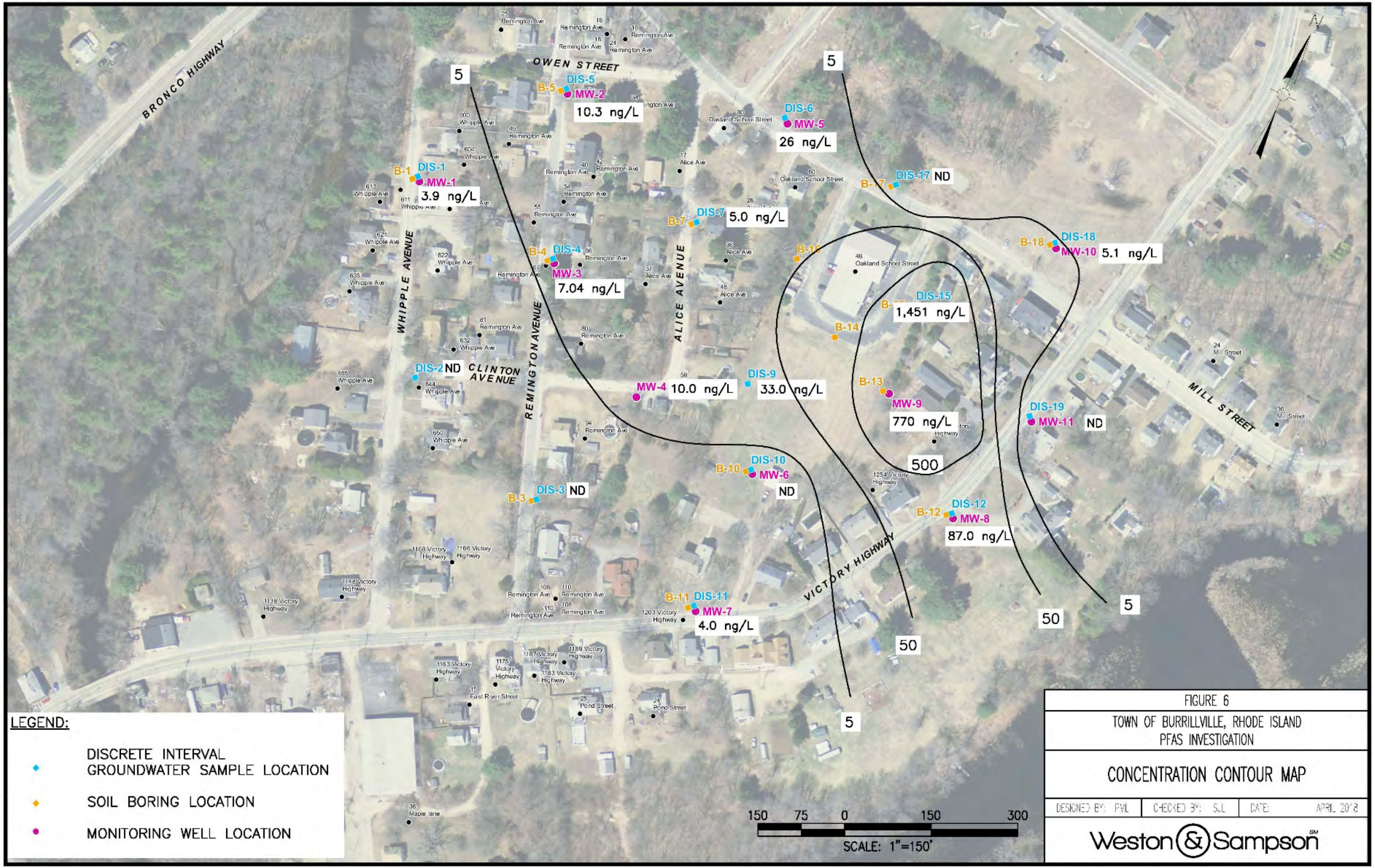


FIGURE 6

TOWN OF BURRILLVILLE, RHODE ISLAND
PFAS INVESTIGATION

CONCENTRATION CONTOUR MAP

DESIGNED BY: PWL | CHECKED BY: SJL | DATE: APRIL 2018

Weston & Sampson

Case Study: Burrillville

- PFAS identified characteristic of AFFF
- Multiple PFAS quantified on soils at very low concentrations
- Shallow and Bedrock aquifer plumes are centered around Fire Department Building
  - AFFF stored on site
  - Fire Department officials report no AFFF training on site
- Review of Fire Department construction plans indicate storm water infiltration gallery collects floor drains and parking lot waters
  - Contaminated equipment washdown water and inadvertent spills enter the infiltration gallery
  - The stormwater infiltration gallery has intermittent shallow groundwater table beneath it. Infiltration waters directly enter bedrock when shallow groundwater is not present.
- More site characterization is needed to fully delineate impacts and determine remediation actions.

IMPORTANT WEBSITES

ITRC FACT SHEETS
https://pfas-1.itrcweb.org/fact-sheets/

EPA PFAS Webpage
https://www.epa.gov/pfas

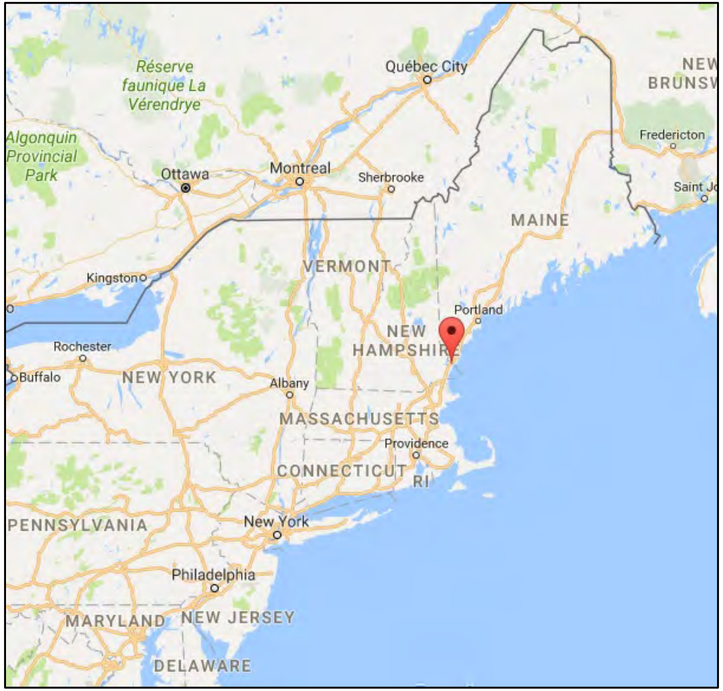
Northeastern University PFAS Project
https://pfasproject.com/

Questions?

Weston & Sampson

transform your environment

Case Study: Former Pease Air Force Base



- Portsmouth, NH
- Shut down in 1991
- Airport with split use between commercial flights and Air National Guard
- Expanding office space with some light industrial, college buildings, golf course, restaurants, day care centers

Pease Well Is Shut Down After Unregulated Contaminant Discovered

By SAM EVANS-BROWN • MAY 22, 2014

May 2014

Tweet Share Google+ Email

Article published May 22, 2014

Contaminated well shut down at Pease Tradeport

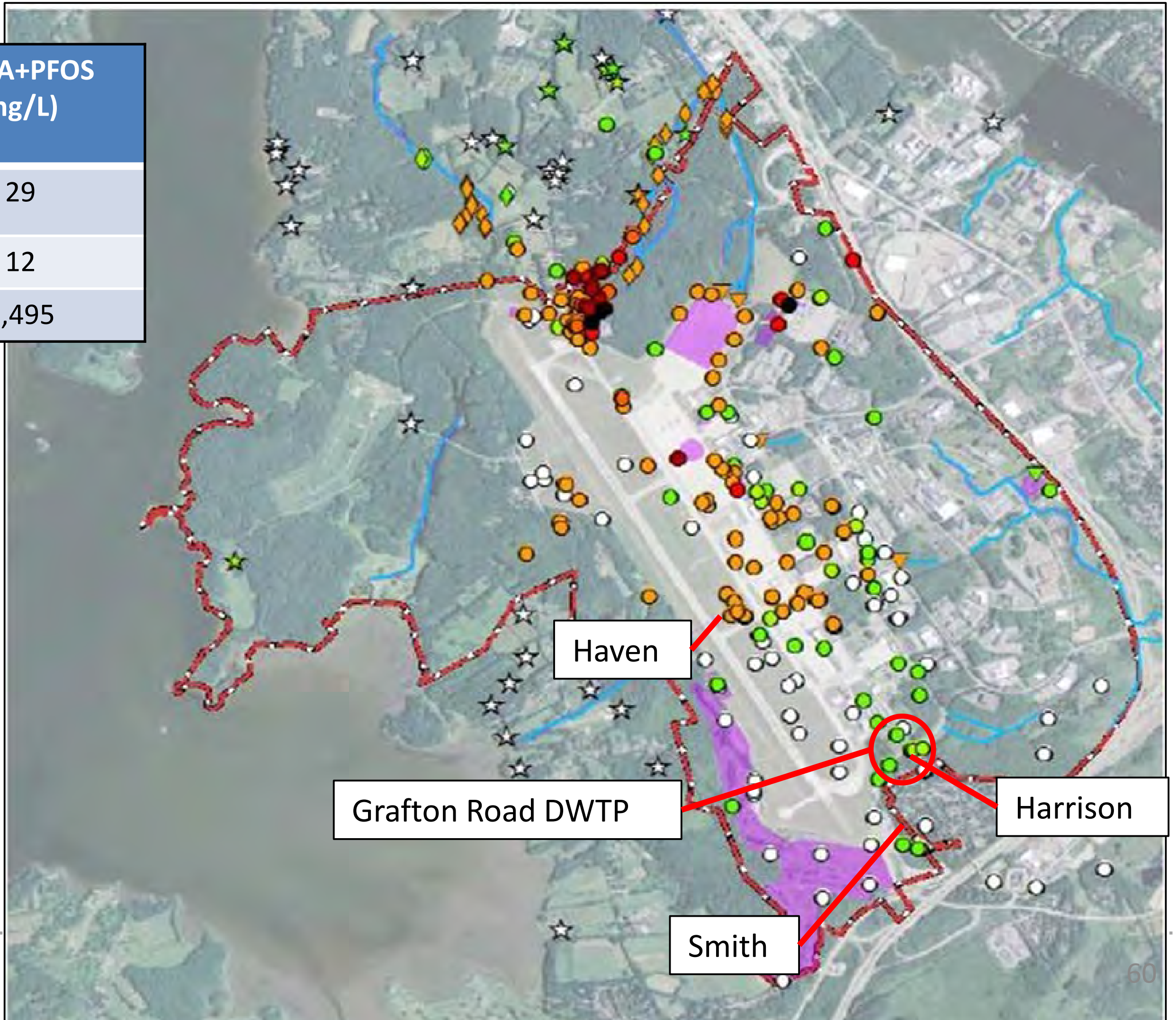
PORTSMOUTH — A well that serves the Pease International Tradeport has been shut down after testing positive for a chemical contaminant, according to the state Department of Environmental Services.

Local and Federal Legislative Delegation

March 18, 2015 - Senator Shaheen addresses Pease PFC contamination to U.S. Air Force

2016 – Governor (now Senator) Hassan meets with Testing for Pease representatives

Well	Flow Rate (gpm)	PFOA+PFOS (ng/L)
Harrison	286	29
Smith	343	12
Haven	534	1,495

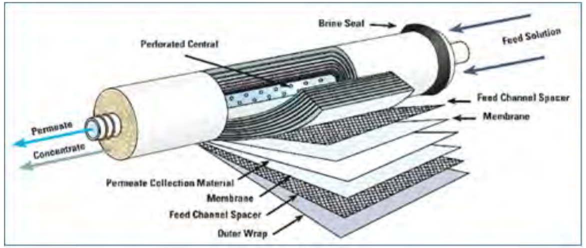


Drinking Water Treatment Technologies

- ## Granular Activated Carbon
  - Advantages – cost effective, several systems in use, PFAS can be transported offsite for destruction
  - Disadvantages – may be costly to changeout for short chain breakthrough

- ## Ion Exchange Resins
  - Advantages – custom designed treatment, long service life, smaller vessels required
  - Disadvantages – expensive if single useta

- ## Membranes
  - Advantages – near 100% removals
  - Disadvantages – waste stream, high capital and O&M costs, expertise required to operate system



GAC Piloting – Harrison and Smith

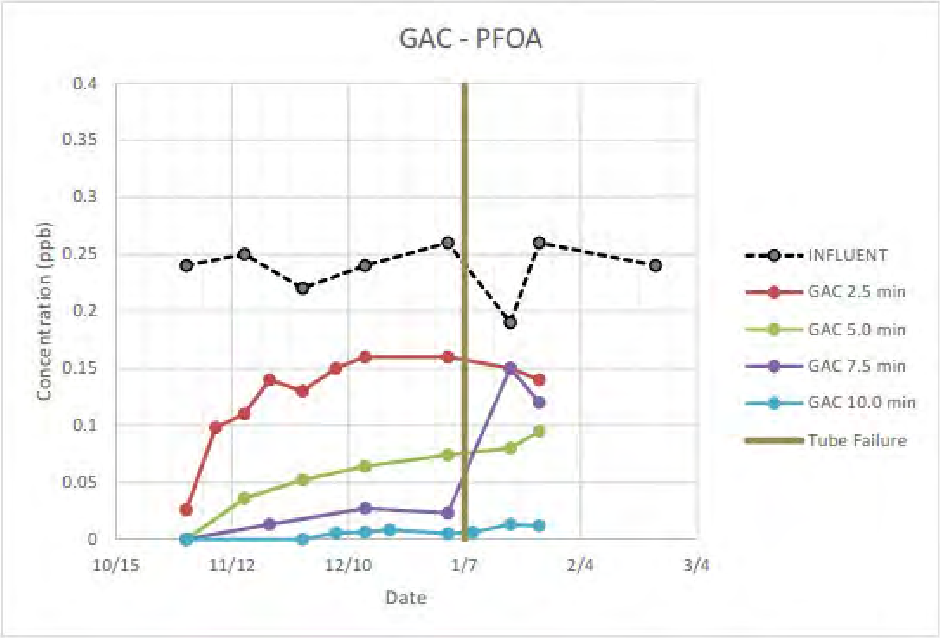
Purpose – monitor GAC effects on pH

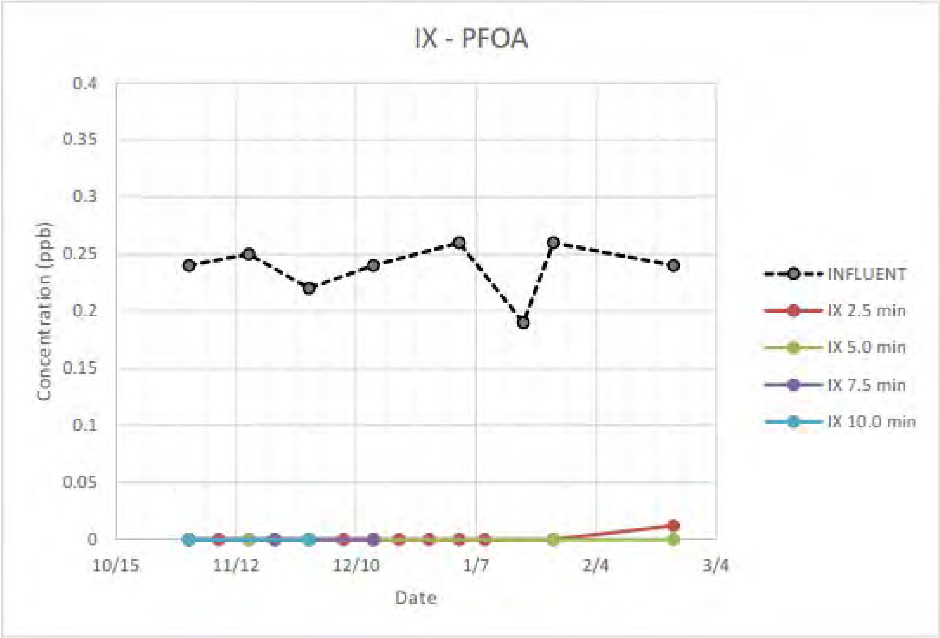
- Potential issues with orthophosphate effectiveness

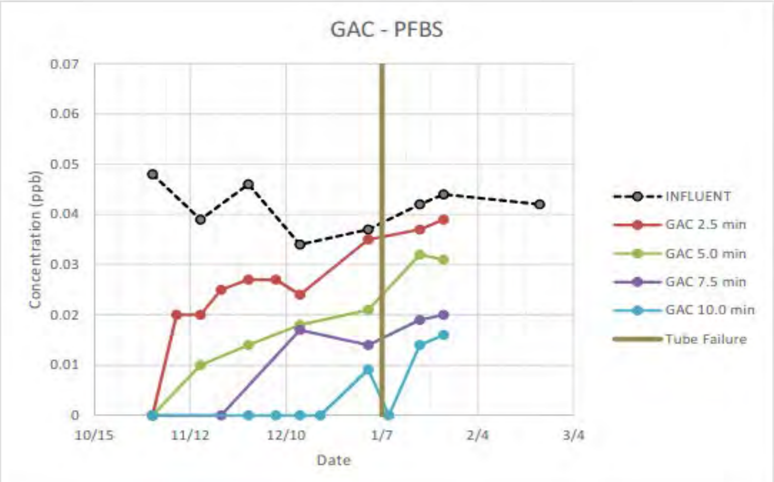
Haven Pilot Setup

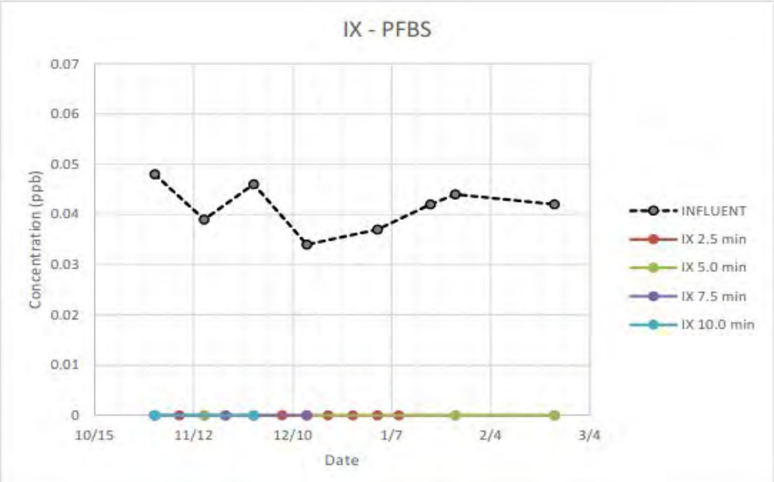
- Fabricated dual sided pilot skid for side-by-side testing: IX Resin vs. GAC
  - Each side:
    - Design flowrate of 112 gpd
    - 4 columns in series, 2.5-min EBCT each
    - 1.25-inch column diameter
    - 30-inch media bed height
- Sampled & analyzed for 23 PFAS compounds out of each column

Treatment Methods

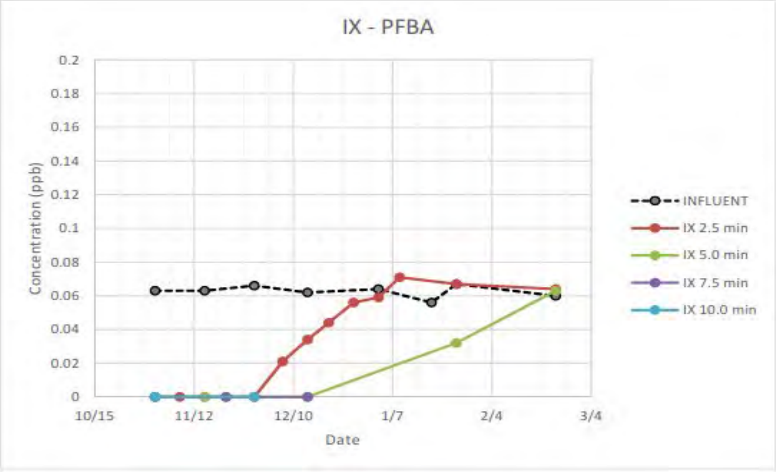




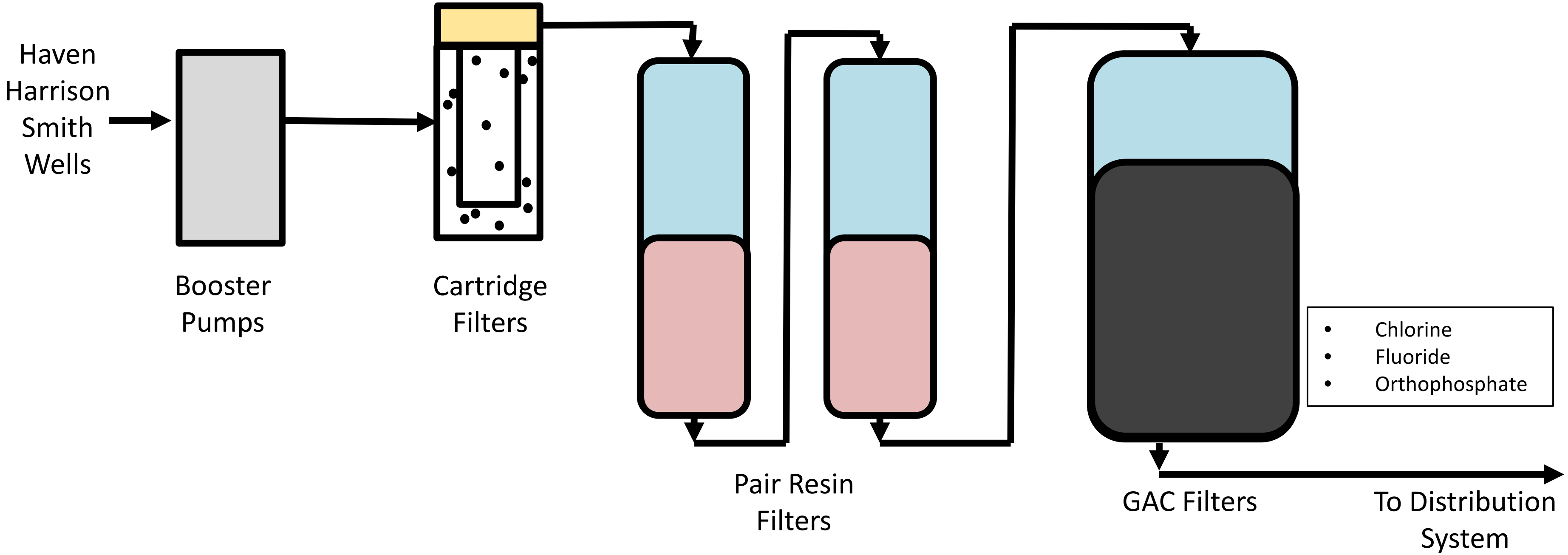

GAC - PFBS
Concentration (ppb)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
10/15
11/12
12/10
1/7
2/4
3/4
Date
INFLUENT
GAC 2.5 min
GAC 5.0 min
GAC 7.5 min
GAC 10.0 min
Tube Failure


IX - PFBS
Concentration (ppb)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
10/15
11/12
12/10
1/7
2/4
3/4
Date
INFLUENT
IX 2.5 min
IX 5.0 min
IX 7.5 min
IX 10.0 min

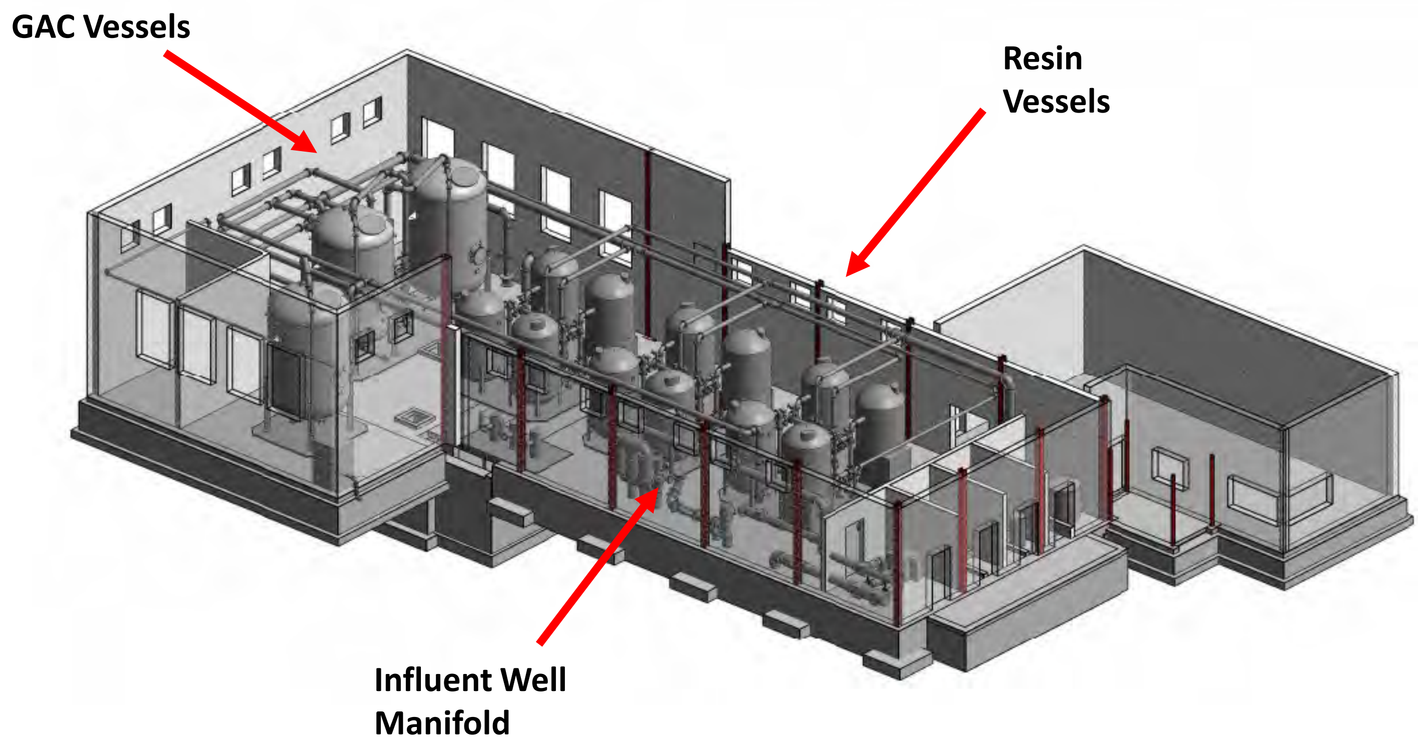

GAC - PFBA
Concentration (ppb)
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
10/15
11/12
12/10
1/7
2/4
3/4
Date
INFLUENT
GAC 2.5 min
GAC 5.0 min
GAC 7.5 min
GAC 10.0 min
Tube Failure


IX - PFBA
Concentration (ppb)
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
10/15
11/12
12/10
1/7
2/4
3/4
Date
INFLUENT
IX 2.5 min
IX 5.0 min
IX 7.5 min
IX 10.0 min

Grafton Road Water Facility Process Schematic
New Treatment System



Proposed Final Layout



National Assessment of Municipal Treatment

GAC Filtration

- Ann Arbor, MI
- Aqua America, PA
- Barnstable, MA
- Hoosick Falls, NY
- Issaquah, WA
- Little Hocking, OH
- Merrimack Village District, NH
- New Castle, DE
- Newburgh, NY
- Oakdale, MN
- Portsmouth, NH (temporary filters)
- Suffolk County Water Authority, NY
- Westfield, MA

Resin Filtration

- Horsham, PA (with carbon)
- Portsmouth, NH (with carbon)
- Widefield WSD, CO (resin only)

Membrane Filtration

- West Morgan – East Lawrence, AL (expressed interest)