

### Per- and Polyfluoroalkyl Substances (PFAS) in Groundwater

Presented by Brandon Kernen, Manager of Hydrology and Conservation Drinking Water and Groundwater Bureau

> Connecticut Private Well Conference April 11, 2018



# NH PFAS Investigation <u>https://www4.des.state.nh.us/nh-pfas-investigation/</u>



#### Welcome

Posted on September 1, 2017 by Jana Ford

Welcome. This website will be used to update interested parties on NHDES' current investigation into the presence of Per- and Polyfluoroalkyl Substances (PFASs) in New Hampshire. You can access our previous webpage for archived information: https://www.des.nh.gov/organization/commissioner/pfoa.htm .

#### Posted in Uncategorized

#### NHDES Extends Bottled Water Delivery Area

Posted on September 13, 2017 by Jim Martin

NHDES has extended bottled water delivery area to additional properties in Merrimack and Litchfield. The complete list of eligible properties can be found on the Bottled Water Delivery Area page.

https://www4.des.state.ph-us/ph-pfas-investigation/uchfield, Merrimack, St. Gobain

#### ADDITIONAL RESOURCES

Water Line Extension Projects Investigation Documents Be Well Informed Guide Pease Tradeport Investigation Archive

#### EMAIL ALERTS

CONTACT INFORMATION

#### **Jim Martin**

(603) 271-3710 NHDES Public Information Officer

RECENT POSTS

NHDES Extends Bottled Water



## **PFAS Challenges**

- Unique chemical properties
  - Expansive uses
  - Mobile and persistent
  - Challenging to remediate
- Health impacts
  - Bioaccumulative
  - Known or suspected toxicity at very low concentrations
  - Sensitive receptor endpoint
- Emerging understanding
  - Heightened public awareness
  - Stakeholder knowledge evolving
  - Analytical capabilities evolving



Check each box where the answer to any of the following questions is YES

#### Sampling Results

During the most recent monitoring event, were any <u>new</u> compounds detected at any sampling point?

Well/Compound:

Are there any detections of contamination in drinking water that is untreated prior to use?

Well/Compound:SW103/PFOAs SW112S/PFOAs SW104D/PFOAs SW112D/PFOAs

Do compounds detected exceed AGQS? At this time there is no AGQS for

PFOAs only an EPA health advisory limit

Was free product detected for the <u>first time</u> in any monitoring point? Surface Water (*visible sheen*) Groundwater (1/8" or greater thickness)



### PFAS

### Just Not Another New Contaminant

- Two sites in NH Contaminated by Air Emissions
  - Undermines traditional waste site investigation/source water protection
  - Has caused contamination over standard over 30-40 sq. miles
- Its presence in drinking water is measurable in our residents' blood – health implication is not known
- Currently have standards for two out of thousands PFAS
- Short-term exposure is considered a health risk
- Public in NH is demanding "0". Other states contemplating standards 3-5 times lower than EPA's recommended concentration

## Magnitude of the Issue

- Over 40 million dollars has been allocated for addressing PFAS at a couple of sites in NH. A full state-wide assessment is just beginning......
- In the southern region of NH, groundwater/drinking water has been contaminated over a 30-40 square mile area
- Three significant water supply sources in NH contaminated over health standards
- Since March 2016 NH has sampled over 3,000 sources of drinking water for PFAS
  - 600+ homes on private wells are being provided bottled water
  - Public water systems are being extended to these homes (20+ miles of pipe)

### Concept of Regulating a Contaminant to "0"

- No state drinking water standard is set at 0 or non-detect.
- Detection limits keep getting lower. At some level there is no such thing as non-detect.
- Standards need necessary justification
  - Public health improvement
  - Consistent with public health protection approach for other contaminants
- NH provides information on how homeowners can treat to non-detect for \$200-\$3000.
- Standards must be based on real-world limitations
  - Treatment technologies/Analytical limitations
  - Simultaneous compliance with other drinking water regulations



## **General PFAS Timeline**

1930s and 1940s	1950s and 1960s	1970s
<ul> <li>PFAS research</li> <li>PTFE (Teflon®) patented by DuPont; production begins</li> </ul>	<ul> <li>Consumer products (e.g., Scotchguard, Zonyl)</li> <li>PFOS-based AFFF developed</li> </ul>	<ul> <li>Company worker exposure studies</li> <li>AFFF expands beyond military activities</li> </ul>
1980s and 1990s	2000s	2010s
<ul> <li>Detection in global environment</li> <li>Analytical capabilities</li> <li>Toxicological studies published</li> <li>PFOA found in drinking water in WV and OH</li> </ul>	<ul> <li>PFOA Stewardship Program begins - C8 phase-out</li> <li>PFOS production phase- out in U.S.</li> <li>Replacement chemistries (shorter chain)</li> <li>Large scale PFAS production begins in China</li> <li>AFFF formulations modified</li> <li>EPA studies &amp; Provisional Health Advisories</li> <li>Water system testing begins</li> </ul>	<ul> <li>PFOS included as POP on Stockholm Convention</li> <li>C8 phase-out by 2015 (PFOA stewardship program)</li> </ul>



## New Hampshire Timeline



- Haven Well 2,500 ng/L PFOS
- Class B Use at Pease Tradeport
- Private wells up to 1,600 ng/L PFOA
- Public wells up to 140 ng/L PFOA
- Industrial Air Emissions in Southern NH

Statewide assessments

PFAS are used in a wide variety of industries and commercial products for their valuable properties, including fire resistance, dust suppression, and oil, stain, grease, and water repellence. (Some examples of uses are on the following slides)

Fire fighting foams (AFFF) used in military and civilian airports as well as some other industrial facilities.



From: Hillary Thornton, USEPA Region 4

- Polishes, waxes, paints
- Stain repellants (carpets, clothing and upholstered furniture)
- Cleaning products





From: Hillary Thornton, USEPA Region 4

 Food surfaces (Teflon<sup>1</sup> pans, pizza boxes, popcorn bags, food wrappers)



<sup>1</sup> <u>https://en.wikipedia.org/wiki/Polytetrafluoroethylene</u> PFOA, which used to be a key ingredient in making Teflon, has been phased out, however there is little evidence that the chemicals that have replaced PFOA are much safer.

<sup>2</sup> Shaider, *Environ. Sci. Technol. Lett.*, Publication Date (Web): February 1, 2017 http://pubs.acs.org/doi/ipdf/10.1021/acs.estlett.6b00435

From: Hillary Thornton, USEPA Region 4





- Dust suppression for chrome plating
- Electronics manufacturing
- Oil and mining for enhanced recovery
- Performance chemicals (hydraulic fluid, fuel)





Landfills

- Land where biosolids from wastewater treatment plants treating PFAS-containing wastewater was applied
- Direct release of PFAS products into the environment – such as use of AFFF in training and at crash sites

From: Hillary Thornton, USEPA Region 4



## **Expansive Use of PFAS**

C	ommercial Products	Industrial Uses				
•	Nonstick Cookware	•	Photo Imaging			
•	Fast Food Containers	•	Metal Plating			
•	Candy Wrappers	•	Semiconductor Coatings			
•	Microwave Popcorn Bags	•	Aviation Hydraulic Fluids			
•	Personal Care Products (Shampoo, Dental	•	Medical Devices			
	Floss)	•	Class B Firefighting Foam (e.g., Aqueous			
•	Cosmetics (Nail Polish, Eye Makeup)		Film Forming Foam)			
•	Paints and Varnishes	•	Insect Baits			
•	Stain Resistant Carpet	•	Printer and Copy Machine Parts			
•	Stain Resistant Chemicals	•	Chemically Driven Oil Production			
•	Water Resistant Apparel	•	Textiles, Upholstery, Apparel and Carpets			
•	Cleaning Products	•	Paper and Packaging			
•	Electronics	•	Rubber and Plastics			
•	Ski Wax	•	Pesticides			
•	Soil amendments					
•	Pesticides					
•	Potting soils					



EPA/600/R-09/033 March 2009

#### Perfluorocarboxylic Acid Content in 116 Articles of Commerce

Zhishi Guo, Xiaoyu Liu, and Kenneth A. Krebs U.S. Environmental Protection Agency, Office of Research and Development National Risk Management Research Laboratory, Research Triangle Park, NC 27711

and

Nancy F. Roache

ARCADIS, 4915 Prospectus Dr., Suite F, Durham, NC 27713

## Solar Panels??

- Teflon/PTFE are included in some solar panels
- Solar panels are often located near drinking water sources
- New Hampshire has not observed PFAS contamination near solar panels(3 known sites)
  - Have not specifically studied run-off near solar panel installations
  - Have not reviewed solar panel designs to date in NH to identify if PFAS was used





#### Environmental Services Human Exposure Pathway

- Major<sup>1,2</sup>
  - Diet (bioaccumulation)
    - Fish and seafood
    - Produce
  - Drinking water
  - Incidental soil/dust ingestion
- Usually insignificant or minor
  - Dermal absorption
  - Inhalation

1 Oliaei et al., 2013. Environ. Sci. Pollut. Res. Manag. 20:1977-1992 2 Domingo, 2012. Environment International 40:187-195





From: Hillary Thornton, USEPA Region 4



## **PFOA/PFOS Exposure Decreasing**

- Most people have been exposed to PFOA/PFOS through everyday commercial products
- In 2006, PFOA/PFOS manufacturers joined an EPA global stewardship program:
  - Phased out by the end of 2015
- Materials imported not really addressed
- PFAS chemistry is complex and PFOA and PFOS still show up in processes using other types of PFAS
- PFOA and PFOS being replaced by other PFAS with no health information



Surface Water Sampling

Wastewater/ Biosolids Assessment

> Groundwater Discharge Permits 100+ sites

Identify Potential Sources +Targeted Well Sampling

> Voluntary Public Water Supply Sampling– 400+sources

Class B Foam Outreach – Letters & online forms

Waste Sites Sampling 400+ sites ~2,900 water samples ~2,300 sample locations ~2,000 samples collected by NHDES (as of March 14, 2018)



\_eyenu

PFASResults\_GroundWater



### **Detection Frequency**



- Compounds detected in one or more samples (as of October 2017)
- Results biased by targeted sampling near southern NH fabric coating sources





## Water Supply Testing

- Public Water Supplies
  - UCMR 3
  - Voluntary sampling request (>4,000 sources)
  - ~500 samples from ~400 sources
- Targeted private supply well sampling around potential sources





### Surface Water

Site	PFOA (ng/L)	PFOS (ng/L)
Pond Near Landfill #1	10	<4
Stream Near Landfill #2	850	400
Pond at Fire Training Area	270	3,000
Me, MI, MN Standards	50 - 12,000	6 - 12

#### No NH Surface Water Standard

- Site-specific screening level for Coakley Landfill
  - 760 ng/L PFOA
  - 760 ng/L PFOS







#### Investigation Around Saint-Gobain Performance Plastics







Davis et al., 2007, Chemoshpere



### Landfills

PFOA + PFOS up to ~3,700 ng/L

- Exceedances at ~60% of unlined
- Exceedances at ~40% of lined
- Total PFAS up to ~6,600 ng/L
   (9 compounds)
- Groundwater impacts fairly localized
- No typical "fingerprint"





### **Chrome Plating**



PFOA: 1,070 PFOS: 90 *Total PFAS (12): 3,461* 

PFOA: 44 PFOS: 3,130 *Total PFAS (12): 3,437* 

Results in ng/L (ppt)

Adapted from Ransom, August 2017 and Sanborn Head, October 2017





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#### **KEY MANUFACTURERS**



#### Simoniz Shield Special Teflon Formulation Lemon

Product ID: ASCWS-T37760

Choose One:	~
Quantity:	

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A clear coat sealer containing Teflon" that will provide gloss and protection. It should be followed by a final rinse.

This product is listed in these Categories...

📢 Polishes & Sealants

previous | next >

Client:	New Hampshire Department of Environmental Services	Service Request: K1610470
Project:	Regulated Car Wash	Date Collected: 09/01/16 11:40
Sample Matrix:	Water	Date Received: 09/07/16 09:30
Sample Name:		Units: ng/L
Lab Code:	K1610470-002	Basis: NA

#### Perfluorinated Sulfonic Acids and Perfluorinated Carboxylic Acids by HPLC/MS

Analysis Method:	PFC/537M
Prep Method:	EPA 3535A

## +9000 PPT PFAS in groundwater at a

La	waji					
Analyte Name	Result	MRL	Dil.	Date Analyzed	Date Extracted	Q
HFPO-DA	ND U	4.6	1	09/28/16 03:35	9/26/16	*
Perfluorobutanoic Acid	640	93	10	09/30/16 04:30	9/26/16	*
Perfluoropentanoic Acid	3400	46	10	09/30/16 04:30	9/26/16	*
Perfluorobutane Sulfonate	5.3	4.6	1	09/28/16 03:35	9/26/16	340
Perfluorohexanoic Acid	3500	46	10	09/30/16 04:30	9/26/16	340
Perfluoroheptanoic Acid	1200	46	10	09/30/16 04:30	9/26/16	340
Perfluorohexane Sulfonate	4.9	4.6	1	09/28/16 03:35	9/26/16	*
Perfluorooctanoic Acid	33	1.9	1	09/28/16 03:35	9/26/16	340
Perfluorononanoic Acid	ND U	4.6	1	09/28/16 03:35	9/26/16	*
Perfluorooctane Sulfonate	19	4.6	1	09/28/16 03:35	9/26/16	*
Perfluorodecanoic Acid	350	4.6	1	09/28/16 03:35	9/26/16	*
Perfluoroundecanoic Acid	ND U	4.6	1	09/28/16 03:35	9/26/16	*
Perfluorodecane Sulfonate	ND U	4.6	1	09/28/16 03:35	9/26/16	*
Perfluorododecanoic Acid	ND U	4.6	1	09/28/16 03:35	9/26/16	*
Perfluorooctylsulfonamide	ND U	4.6	1	09/28/16 03:35	9/26/16	**
Perfluoro-n-tridecanoic acid	ND U	4.6	1	09/28/16 03:35	9/26/16	*
Perfluoro-n-tetradecanoic acid	ND U	4.6	1	09/28/16 03:35	9/26/16	*
Perfluoroheptane sulfonate	ND U	4.6	1	09/28/16 03:35	9/26/16	*
N-ethylperfluoro-1-octanesulfonamide	ND U	4.6	1	09/28/16 03:35	9/26/16	*
N-methylperfluoro-1-octanesulfonamide	ND U	4.6	1	09/28/16 03:35	9/26/16	*
2-(N-ethylperfluoro-1-octanesulfonamido)-	ND U	4.6	1	09/28/16 03:35	9/26/16	*
ethanol						
2-(N-methylperfluoro-1-octanesulfonamido)	ND U	4.6	1	09/28/16 03:35	9/26/16	*



# WWTF Effluent Sampling in NH (ppt)

WWTF	PFBS	PFBA	PFHPA	PFHXS	PFHXA	PFOA	PFOS	PFPEA	Total PFAS
А	C4-S	C4	C7	C6-S	C6	C8	C8	C5	
В	<4	7	<4	<4	46	6	7	21	86
С	<4	<4	<4	<4	17	8	<4	16	41
D	<5	12	<5	<5	47	15	9	9	92
E	<4	<4	<4	6	11	11	10	16	53
F	4	<4	<4	<4	18	4	4	5	35
G	<4	<4	<4	<4	6	11	<4	16	33
Н	<4	12	<4	<4	52	7	<4	73	144
I	<4.8	<9.6	5	8	20	15	14	9	71
J	<4	73	19	<4	195	49	<4	101	437
К	<4	<4	<4	<4	10	10	14	7	40
L	5	12	14	6	65	54	14	57	227
М	5	<4	<4	<4	26	7	<4	10	<b>47</b> <sup>37</sup>



### Wastewater Sludge/Biosolids

		Α	В	С	D	E	F	G	н
		Sludge	Sludge	Sludge	Sludge	Compost	Sludge	Sludge	Ash
PFBS	C4-S	<1.1	<0.81	0.54	<8.8	5.20	Not Detected	<9.8	<0.98
PFBA	C4	Not	Not	Not	<u>~8 8</u>	12.00	1 20	< <u>0</u> 8	<0 98
		Tested	Tested	Tested	\0.0	12.00	1.20	<b>\</b> J.0	NO. 30
PFDS	C10	Not	Not	Not	6 70	Not	Not	Not	<0.08
		Tested	Tested	Tested	0.70	Tested	Tested	Tested	NU.90
PFDA	C10	Not	Not	Not	2.60	Not	Not	Not	<0.08
		Tested	Tested	Tested	2.00	Tested	Tested	Tested	<0.98
PFDOA	C12	Not	Not	Not	F 60	Not	Not	Not	<0.08
		Tested	Tested	Tested	5.00	Tested	Tested	Tested	<0.90
PFHPA	C7	<1.1	1.00	<1	<8.8	2.80	0.52	4.60	<0.98
PFHXS	C6-S	3.20	73.00	2.30	<8.8	0.48	3.50	<9.8	<0.98
PFHXA	<b>C</b> 6	Not	Not	2 20	4 00	72.00	10.00	1 20	<u> </u>
		Tested	Tested	5.50	4.90	75.00	10.00	1.50	<0.98
PFNA	С9	1.90	3.60	<1	<8.8	3.40	1.50	<9.8	<0.98
PFOA	C8	4.40	6.50	1.10	<8.8	13.00	3.40	<9.8	<0.98
PFOS	C8	46.00	390.00	7.20	17.00	8.70	15.00	17.00	<0.98
PFPEA	C5	Not	Not	~1.0	<u>~0 0</u>	27.00	1 70	2 90	<u> </u>
		Tested	Tested	<1.0	<0.0	27.00	1.70	5.00	<0.98
Total PFAS		56	474	14	37	146	37	27	0

Units in parts-per-billion



## Human Blood Testing in NH

95<sup>th</sup> Percentile PFC Levels by Community (As of 7/31/17)



## **Residential Scale Water Treatment**

- NHDES developed a PFAS Treatment Factsheet
- Need to pay attention to "traditional contaminants"
- Point of Entry (whole house) Treatment Options
  - Granular activated carbon

- Engineered resins may be an option in the future
- Point of Use (treatment for a single fixture) Treatment Options
  - Granular activated carbon (only addresses PFAS and a few other contaminants)
  - Reverse osmosis (addresses PFAS and most other contaminants)

#### Typical Design of a Point of Entry Carbon Treatment for a Home



Available information suggests treatment systems with two (2 cubic foot) granular activated carbon vessels may be adequate.

## **Point of Use Carbon Treatment**



FROM POINT OF USE (POU) TREATMENT SYSTEMS WORK PLAN – 11/30/16 (NHDES SITE # 1997 12005)

### **Point of Use Reverse Osmosis**



http://waterquality.cce.cornell.edu/publications/CCEWQ-04-ReverseOsmosisWtrTrt.pdf



### **Analytical Guidance**

<u>http://des.nh.gov/organization/commissioner/documents/</u> <u>pfoa-testing-labs.pdf</u>

- Lab capabilities growing
- Only standard method is for drinking water labs develop own methods
  - EPA 537 Rev 1.1 (6 to 14 compounds)
  - New EPA methods... soon?
  - Recommend Modified 537 with isotope dilution



- Accuracy of +/- 50% is considered acceptable
  - NHDES QA/QC testing shows +/-25% accuracy is typical but that results for PFOA/PFOS/PFHxS are typically underreported
- Analytical process evolving
  - One lab study identified 20 to 30% variability between certified standards

### **Discrepancies and Inconsistencies with Lab Reports**

- Lab reports and electronic data deliverables are problematic
  - Different labs are reporting different forms of PFAS compounds
    - same acronym but different properties
  - Form of compound can affect the concentration reported
  - Lab reports/electronic data deliverables contain mismatching CAS #s and chemical names/forms
  - EPA's health advisory & NHDES standards reference the acid form

X	Y	Acronym	Name	Formula	CAS No.
O = octa (8 carbon)	A = Carboxylate or	DEOA	Perfluorooctanoate	C <sub>7</sub> F <sub>15</sub> CO <sub>2</sub> <sup>-</sup>	45285-51-6
	carboxylic acid	PFUA	Perfluorooctanoic acid	C <sub>7</sub> F <sub>15</sub> COOH	335-67-1
	S = Sulfonate or	PFOS	Perfluorooctane sulfonate	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> <sup>-</sup>	45298-90-6
	sulfonic acid		Perfluorooctane sulfonic acid	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> H	1763-23-1

#### Table 3-1. Basic naming structure and shorthand for perfluoroalkyl acids (PFAAs)



## Current PFAS/PFAS Related Compounds in Use

- GenX is receiving a lot of national attention as a replacement to PFOA
  - Not a chemical it is a process using two chemicals to make fluoropolymers without PFOA
  - Chemicals associated with GenX not detected in hundreds of samples collected in NH
  - Unlikely to be detected unless sampling near facilities producing PFAS chemicals
- PFHxA is detected frequently and is a replacement for PFOA
- EPA Office of Research and Development is assisting with identifying highly fluorinated compounds currently in use.



What's next?

- Legislative activity in NH
- More information needed:
  - Drinking, ground, and surface water quality guidance for other PFAS
  - Soil leaching guidance
  - Air emission information

- Additional toxicological studies
- Standardized analytical methods
- Reporting use of PFAS (TRI, SDS)?

USEPA's PFAS National Leadership Summit will be in Washington, D.C. on May 22–23, 2018.



Questions??

- Media coverage on PFAS see PFASproject.com
- Technical resources of PFAS see <u>https://pfas-</u> <u>1.itrcweb.org/</u>
- NHDES's website des.nh.gov