Assessment and Regulation of Per- and Polyfluoroalkyl Substances in New Hampshire's Drinking Water

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Rep to ACWI from the Association of State Drinking Water Administrators

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March 28, 2017

Acknowledgements

Substantial expertise and assistance has been provided by USEPA Headquarters and Regional Offices

- Superfund
- Drinking Water
- Pre-remedial
- Laboratories
- Health and Ecological

Objectives of the Presentation

1. Provide an overview of Per- and Polyfluoroalkyl Substances (PFAS)
   a) Sources
   b) Occurrence in the environment
   c) Public health concerns

2. New Hampshire's Experience with PFAS

3. Identify areas where more information and assistance are needed to address PFAS (ten specific recommendations)

Magnitude of the Issue

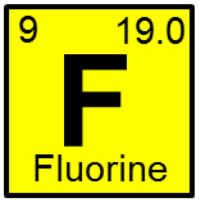
- Over 30 million dollars has been allocated for addressing PFAS at a couple of sites in NH. A full state-wide assessment is just beginning……
- In the southern region of NH, groundwater/drinking water has been contaminated over a 30-40 square mile area
- Three significant water supply sources in NH contaminated over health standards
- Since March 2016 – NH has sampled over 2,000 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)

PFAS
Just Not Another New Contaminant

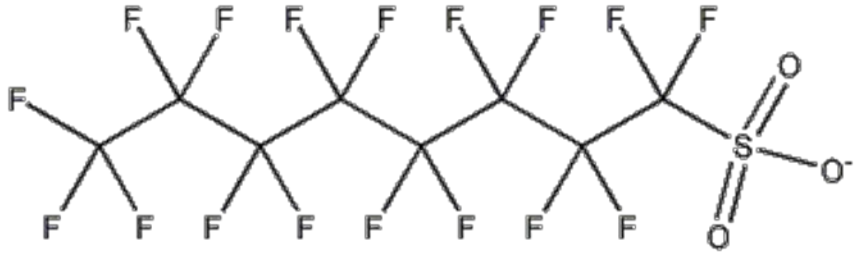
- Two sites in NH Contaminated by Air Emissions
  - Undermines traditional waste site investigation/source water protection
  - Has caused contamination over standard over 30-40 sq. miles
- Its presence in drinking water is measurable in our residents' blood – health implication is not known
- Currently 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

Introduction to PFAS

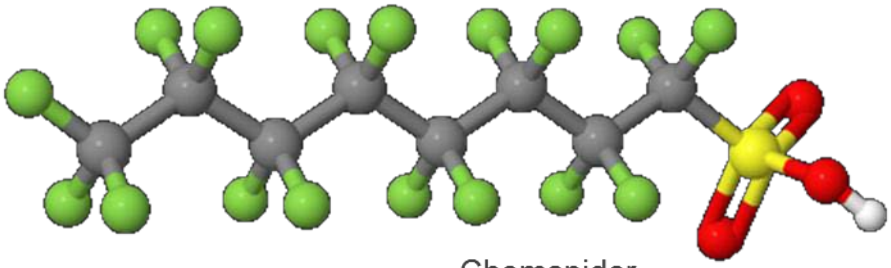
- A large family of synthetic organic compounds that contain multiple Fluorine (F) atoms.



- The 2 most studied PFAS are
  - Perfluorooctanoic Acid (PFOA)
  - Perfluorooctane Sulfonate (PFOS)
- PFAS family = thousands of diverse compounds



Conder et al. (2008)



Chemspider

Example molecular structures for perfluorooctane sulfonate (PFOS)

From: Hillary Thornton, USEPA Region 4

Introduction to PFAS

- A class of chemicals that are ubiquitous due to
  - Wide variety of uses
  - Persistence
  - High Mobility
- They are a concern due to:
  - Known or suspected toxicity, especially for PFOS and PFOA
  - Bioaccumulation
  - Some have very long half lives (several years), especially in humans
- Information on PFAS is rapidly evolving

From: Hillary Thornton, USEPA Region 4

Uses & Sources of PFAS

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.

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Uses & Sources of PFAS

- Food surfaces (Teflon[1] pans, pizza boxes, popcorn bags, food wrappers)

[1] https://en.wikipedia.org/wiki/Polytetrafluoroethylene 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.

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

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Uses & Sources of PFAS

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

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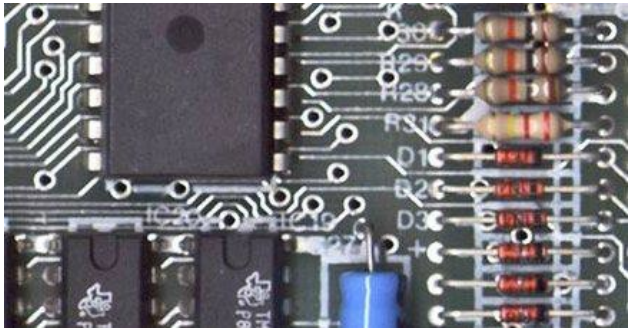
Uses & Sources of PFAS



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

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Uses & Sources of PFAS

- 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

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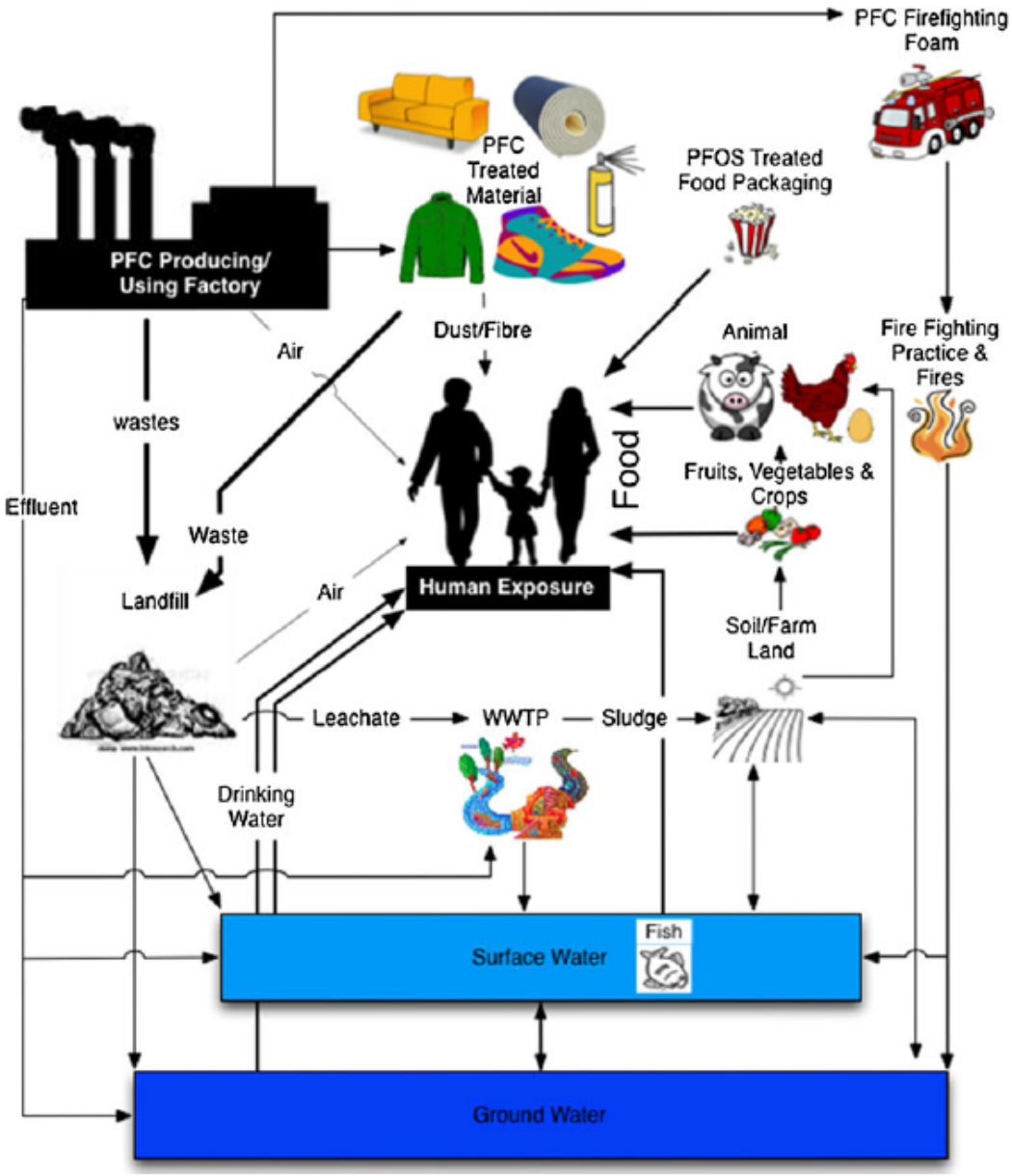
Possible Sources of PFAS Releases



Used for decades to make products that resist heat, oils, grease, stains and water

- Textiles, Upholstery, Apparel and Carpets
- Paper, Packaging, Non Woven Fibers
- Metal Plating (mist suppressant)
- Semiconductor
- Wire Coating
- Firefighting Aqueous Film-Forming Foam

From Oliaei 2013, Environmental Science Pollution Research

Human Exposure Pathway

- Major[1,2]
  - Diet (bioaccumulation)
    - Fish and seafood
    - Homegrown 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

Toxicology

- Non-cancer effects[1,2]
  - USEPA reference doses (RfD for PFOA and PFOS (non-cancer hazard only)
    - PFOS: 0.00002 mg/kg*day (reduced birth weight)
    - PFOA: 0.00002 mg/kg*day (developmental effects in bones, accelerated puberty)
- Immunotoxicity potential[3,4]
- Potential carcinogenic/mutagenic properties[5]
  - "Cancer Slope Factor (CSF) for PFOA: 0.07 (mg/kg*day)
    - Risk-based drinking water threshold for cancer endpoint higher (less conservative) than non-cancer endpoint

[1]Lau, 2012. Clinical and Environmental Toxicology, Experientia Supplementum 101; [2]ATSDR, 2015. Draft Toxicological Profile for Perfluoroalkyls; [3]Grandjean et al., 2012. JAMA; [4]Granum et al., 2013. J Immunotox.; [5]USEPA, 2016. Drinking Water Health Advisories for PFOA and PFOS

From: Hillary Thornton, USEPA Region 4

Toxicology

- Many epidemiology studies (used qualitatively in support of RfDs and CSF)[1,2]

- PFAS other than PFOA and PFOS
  - Very limited information available in peer-reviewed literature and chemical registration information (REACH dossiers, TSCA submittals)
  - NH is frequently detecting: Perfluorobutanoic acid (PFBA)
    Perfluoropentanoic acid (PFPeA)
    Perfluorohexanoic acid (PFHxA)
    Perfluoroheptanoic acid (PFHpA)
    Perfluorononanoic acid (PFNA)
    Perfluorobutanesulfonic acid (PFBS)
    Perfluorohexanesulfonic acid (PFHxS)

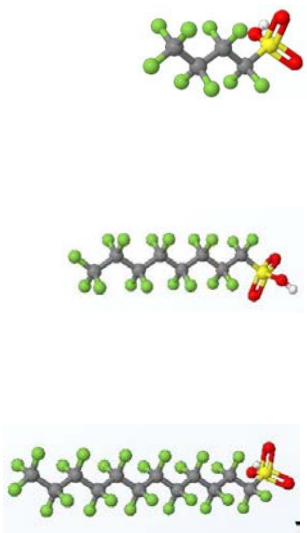
[1] C8 Science Panel (http://www.c8sciencepanel.org);
[2] Olsen et al., 2009. Reproductive Toxicology 27:212-230

From: Hillary Thornton, USEPA Region 4

Bioaccumulation of PFOA/PFOS

- PFASs are detectable in nearly any biological tissue
- Many PFASs bioaccumulate, especially longer PFASs and sulfonated PFASs (e.g., PFOS)
- Partition to protein, not fat
  - Blood, liver, kidney, muscle are primary repositories
- Not metabolized, or metabolized to persistent PFASs

Less Bioaccumulative



More Bioaccumulative

Conder et al., 2008. Environ Sci Technol . 42:995-1003

From: Hillary Thornton, USEPA Region 4

Lifetime Health Advisory (HA) replaces Provisional Health Advisory (PHA)

- New Lifetime Drinking Water HA[1,2] was released May 2016 by USEPA and replaces the 2009 PHA
  - Much lower value of 0.07 ug/L (70 ppt) for PFOA and PFOS combined
  - Provides peer reviewed reference dose and cancer slope factor
  - NH reviewed the HA and adopted 70 ppt as an enforceable drinking water and clean-up standard under an emergency rule
    - Vermont has adopted a standard of 20 ppt for PFOA+PFOS
    - New Jersey is considering a standard of 14 ppt for PFOA
- Until May 2016, EPA's Office of Water's 2009 provisional health advisory (PHA) levels were in effect with much higher values:
  - PFOA 0.4 ug/L (400 ppt)
  - PFOS 0.2 ug/L (200 ppt)

From: Hillary Thornton, USEPA Region 4

NH Regulatory Standards

- AAL – Ambient Air Limits (Env-A 1400)
  - Ammonium perfluorooctanoate (APFO)
  - 0.050 µg/m^3 (24-hr)
  - 0.024 µg/m^3 (annual)

- Soil guidance – direct contact
  - PFOA – 0.5 mg/kg (500 ppb)
  - PFOS – 0.5 mg/kg (500 ppb)
  - No leaching based standard

- No surface water standard

NEW HAMPSHIRE DEPARTMENT OF Environmental Services

NEW HAMPSHIRE DEPARTMENT OF Environmental Services

Status of NH PFAS Investigation

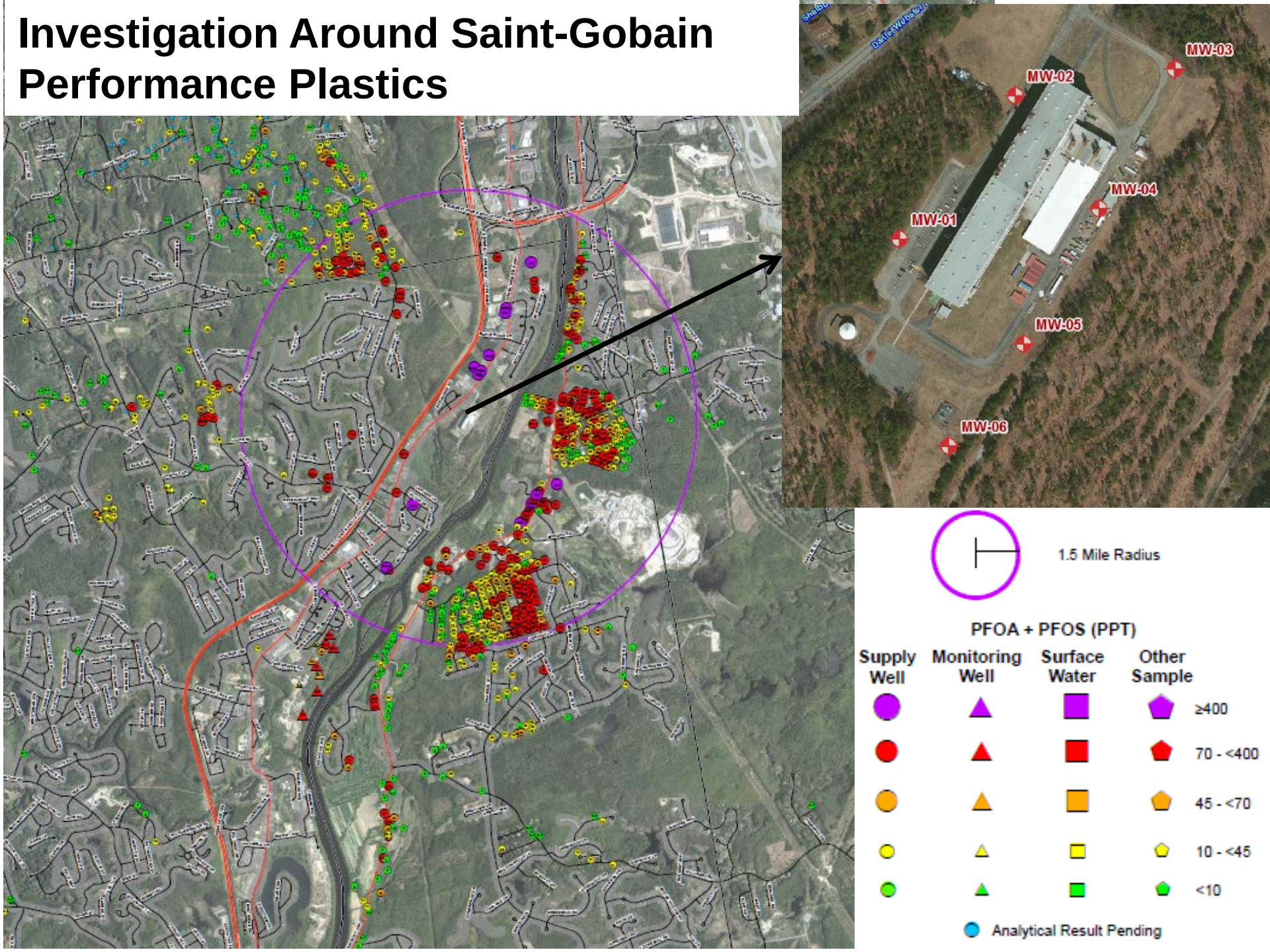
PFAS INVESTIGATION
SAMPLING SUMMARY - MOST RECENT RESULT FROM ALL DISCRETE SAMPLING LOCATIONS
(GROUNDWATER / DRINKING WATER / SURFACE WATER / WASTEWATER)
FEBRUARY 21, 2017

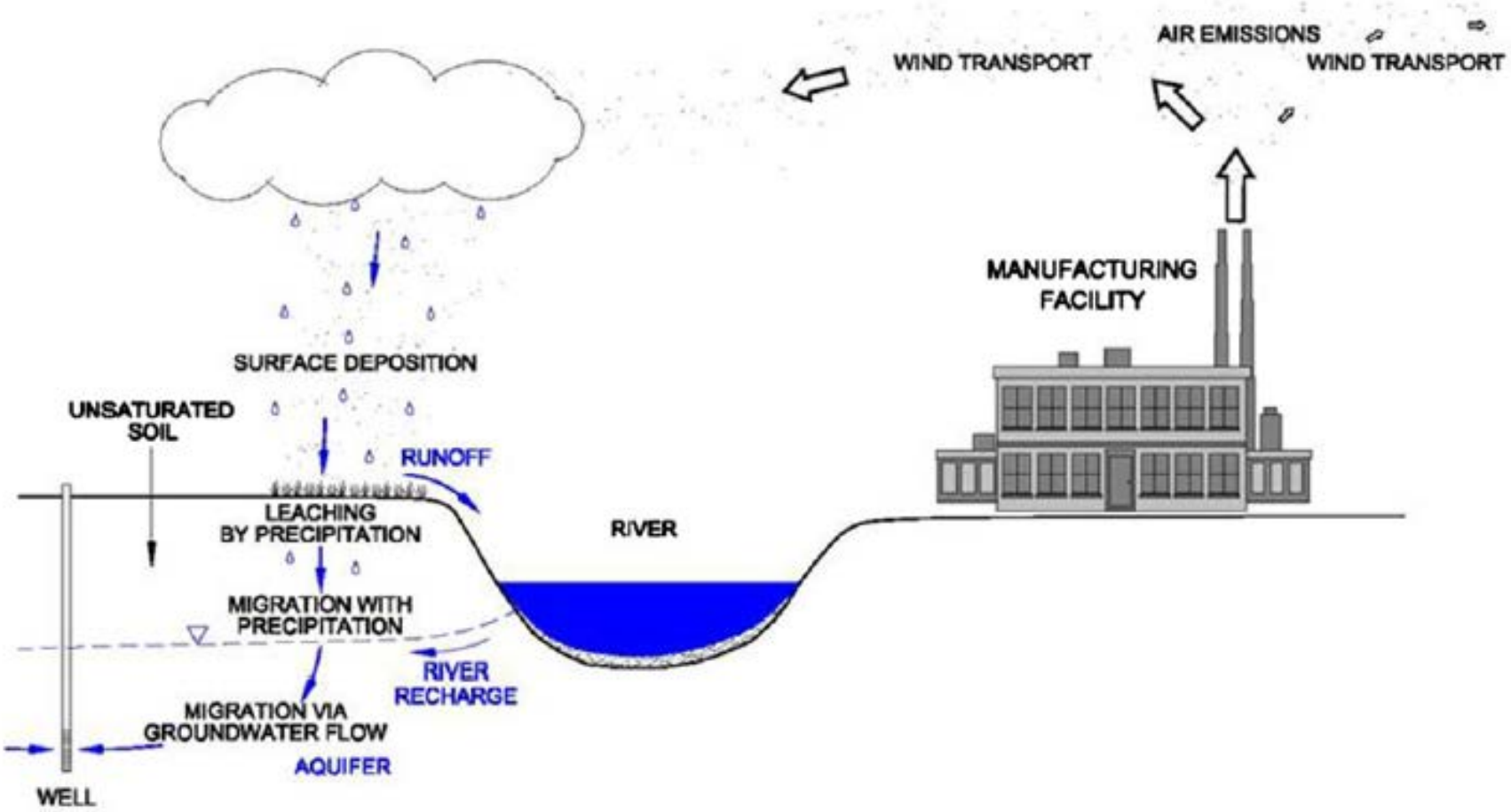
SITE	SAMPLES	APPOINT-MENTS SCHEDULED	RESULTS RECEIVED	PFOA & PFOS <10	PFOA & PFOS 10 - <45	PFOA & PFOS 45 - <70	PFOA & PFOS ≥70
SGPP	903	13	880	271	333	87	189
TCI AMHERST	246		245	129	78	15	23
MERRIMACK LF	116		116	75	38	1	2
LYDALL	16		16	7	4		5
LLS LF	44		44	41	3		
SOUHEGAN LF	30		30	30			
COAKLEY LF	83	1	82	68	9		5
BEDFORD LF	28		28	18	8	2	
MEADOWOOD	8		6	5	1		
ROCKINGHAM COUNTY COMPLEX	21		21	17	1		3
KINGSTON FD	46		46	23	18	1	4
NEW BOSTON FD	17		17	13	3	1	
TROWBRIDGE DR	15		15	3	10		2
MAMMOTH RD	30	1	28	19	7		2
AMHERST RD	9		9	6	2	1	
HAMPSTEAD MS	16		16	9	3	4	
MARLOW ELEMENTARY	4		4	3			1
GILFORD MUNICIPAL	5		5	4		1	
MADBURY METALS	4		2	1	1		
FORMER PEASE AIR FORCE BASE	37		37	28	5	1	3
GENERAL INVESTIGATION	75		75	68	6	1	
TOTAL	1753	15	1722	838	530	115	239

NHDES Sampling – Wells

Site	Locations Sampled	Results Received	PFOA + PFOS (ppt)			
			<10	10 - <45	45 - <70	≥70
Total	1,674	1,591	751	496	113	231
Saint-Gobain, Merrimack	876	835	246	318	85	186
Former TCI, Amherst	243	236	124	75	15	22
Lydall, Rochester	16	10	4	2		4
Landfills (5)	299	290	223	56	4	7
Fire Training Areas / Fire Departments (7)	100	87	55	22	3	7
General Investigation	88	85	72	7	5	1
Self-Reported Homeowner Results (3 areas)	52	48	27	16	1	4

Investigation Around Saint-Gobain Performance Plastics

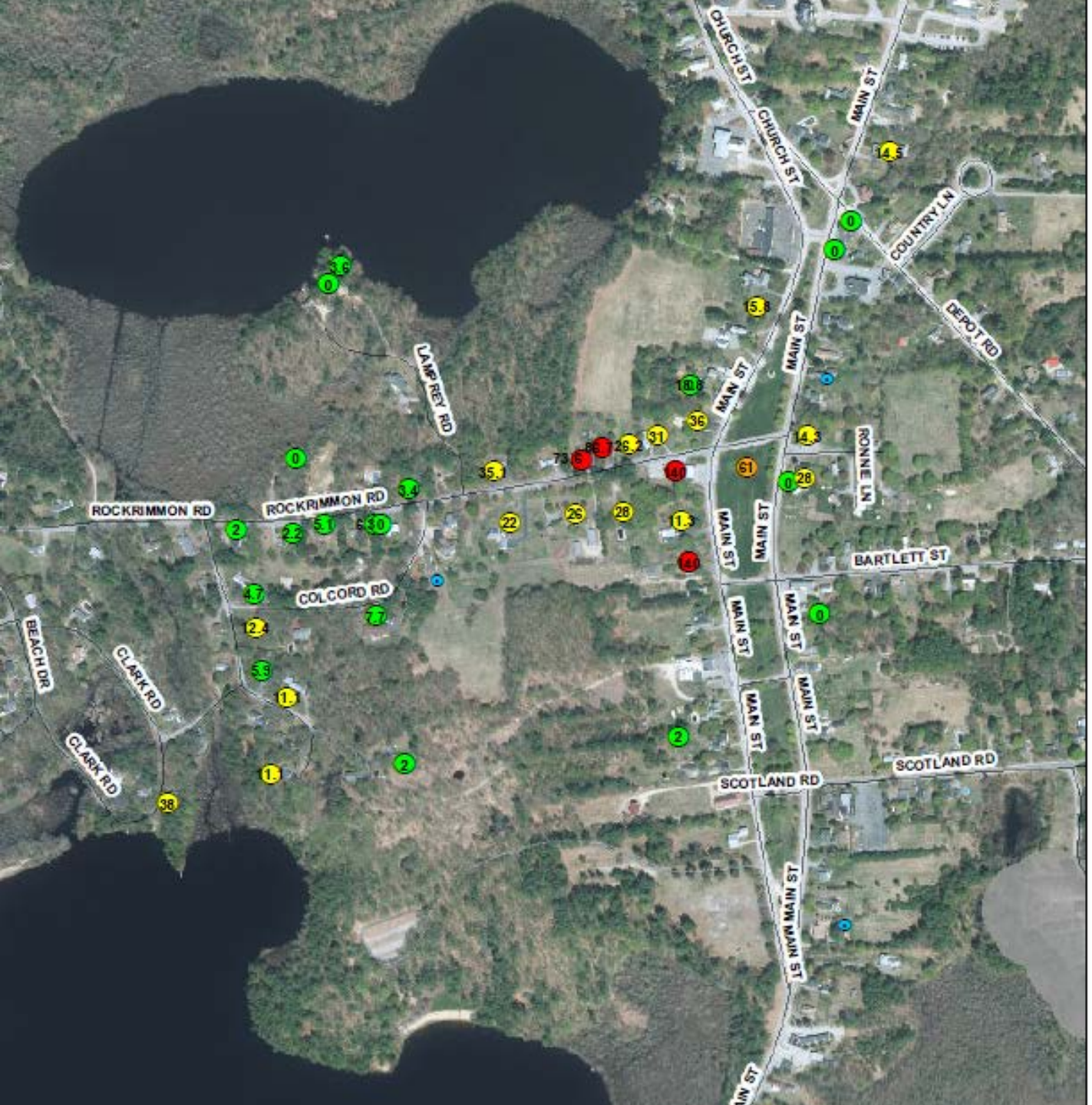




Davis et al., 2007, *Chemoshpere*

Kingston Fire Department

KINGSTON FD
PFC INVESTIGATION
FEBRUARY 8, 2017



PFOA + PFOS (PPT)

Supply Well	Monitoring Well	Surface Water	Other Sample	
●	▲	■	⬟	≥400
●	▲	■	⬟	70 - <400
●	▲	■	⬟	45 - <70
●	▲	■	⬟	10 - <45
●	▲	■	⬟	< 10
●				Analytical ResultPending

Public Water Supplies

Water Distribution

Political Boundary

1 inch equals 600 feet

NEW HAMPSHIRE DEPARTMENT OF Environmental Services

Summary of PFOA / PFOS Data Public Water System Voluntary Sampling

(partial data – does not include sources near known waste sites)

- Approximately 400 water sources have been sampled
  - 62% Not Detected (reporting limits ranged from (0.7- 40 ppt)
  - 26% <= 10 parts-per-trillion
  - 6% 10-20 parts-per-trillion
  - 6% >= 20 parts-per-trillion
- Frequency of detection increases if non-regulated PFAS are included
- Frequency of detection increases if only data with very low reporting limits are shown
- Schools/health care facilities on their own well/septic have relatively higher levels of PFAS – floor cleaning?? http://www.oecd.org/env/48125746.pdf

AUTO SHINE CAR WASH SYSTEMS OF NEW ENGLAND

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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 car wash

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	*
Perfluorohexanoic Acid	**3500**	46	10	09/30/16 04:30	9/26/16	*
Perfluoroheptanoic Acid	**1200**	46	10	09/30/16 04:30	9/26/16	*
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	*
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)-ethanol	ND U	4.6	1	09/28/16 03:35	9/26/16	*
2-(N-methylperfluoro-1-octanesulfonamido)	ND U	4.6	1	09/28/16 03:35	9/26/16	*

Occurrence Information In New Hampshire

Municipal Wastewater Discharge (no known PFAS industry)

	Perfluoro-pentanoic acid	Perfluoro-hexanoic acid	Perfluoro-hexane sulfonate	Perfluoro-octanoic acid	Perfluoro-octane Sulfonate
Influent	120	8.5	6.7	9.3	9.1
Effluent	12	8.7	47	15	9.4
Outfall	13	9.4	53	16	16

- Possible implications
  - Groundwater discharges
  - Treated wastewater aquifer recharge
  - Wastewater reuse

Current and Future Considerations

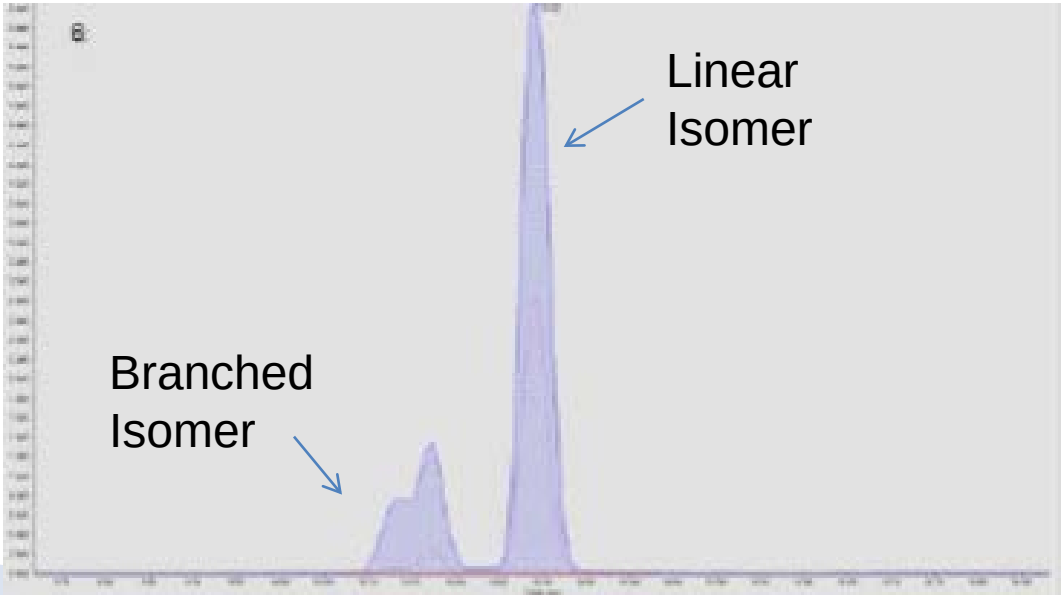
- Reviewing other potential source facilities
  - Information requests/inspections/sampling
  - Reviewing internal files/GIS
- Targeted public water supply sampling near high-risk activities
- Biosolids - Assess groundwater near land application sites
- 800 waste sites in NH will be sampling for PFAS - http://www.des.nh.gov/organization/divisions/waste/hwrb/documents/pfc-stakeholder-notification-20161122.pdf
- Voluntary Public Water System Sampling Request
- Letter to fire departments, health officers and town administrators about Class B Firefighting Foam/AFFF to be issued soon

What Level is "Non Detect"? What compounds to look for? What analytical method? What to do with results for compounds with no health guidance values?

- EPA 537 Method covers 14 compounds – most labs report 6 of these
- More modern analytical method (isotope dilution) include 20+ compounds and have lower reporting limits.
  - "In-house" lab methods
  - Should accreditation be required?
  - Do data from lab to lab compare well? – Not always
    - Need to make sure labs are reporting BOTH linear and branched isomers of PFOA
- NHDES requires/recommends lower reporting limits

Lab Discrepancies – PFOA Isomers

- Labs performing PFAS testing interpret Method 537 differently
  - Some labs only report linear isomers of PFOA only
  - Some lab report both branched and linear isomers
  - Different Types of PFOA
    - 3M PFOA (30% branched isomer / 70% linear isomer)
    - Dupont (linear isomer only)
    - NHDES split samples have varied by 20%-40% between labs when branched isomers are not accounted for
  - NHDES/EPA Region 1 staff documented this issue
    -PE sampling
    -Split sampling
  - EPA HQ recently provided guidance

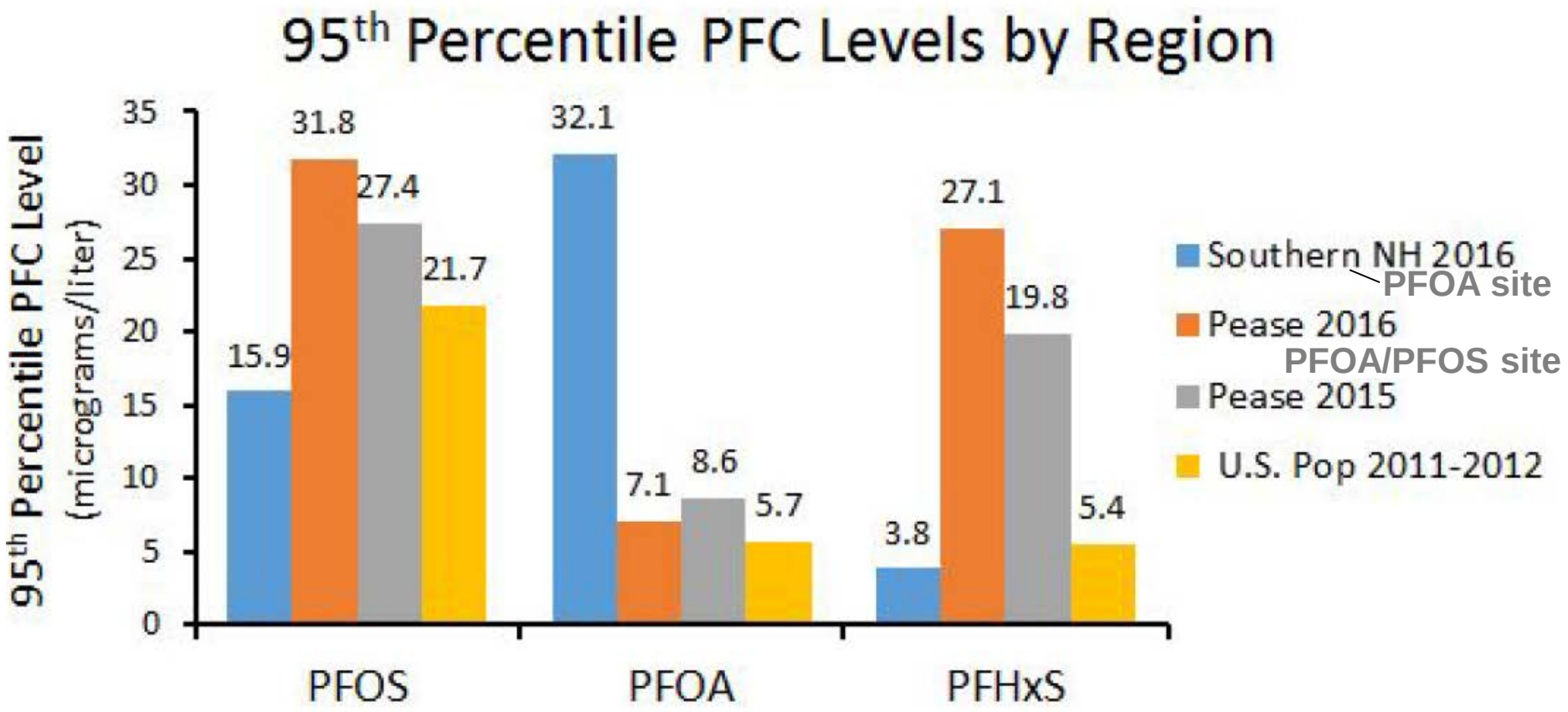


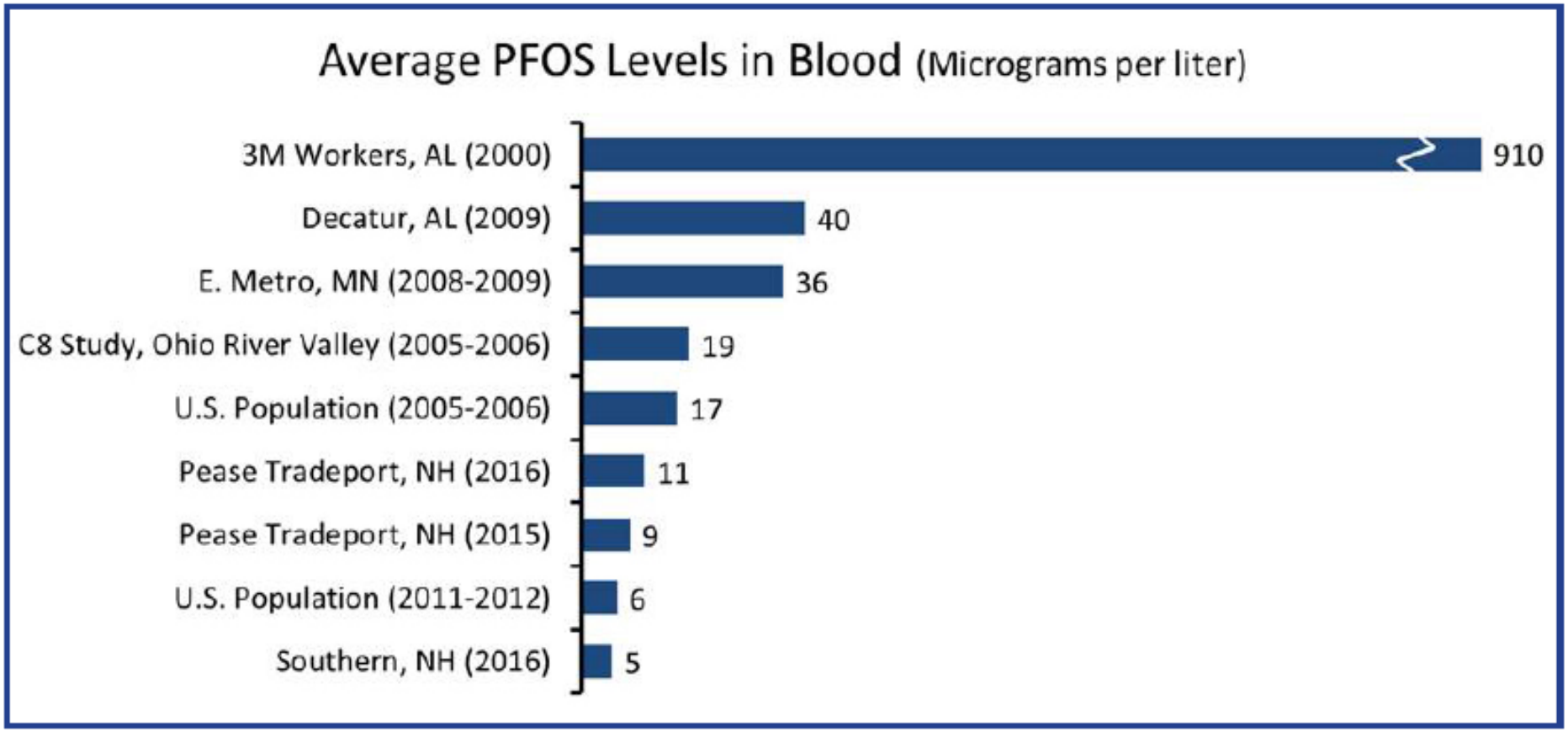
Lab Discrepancies – Certified Standard Do Not Match

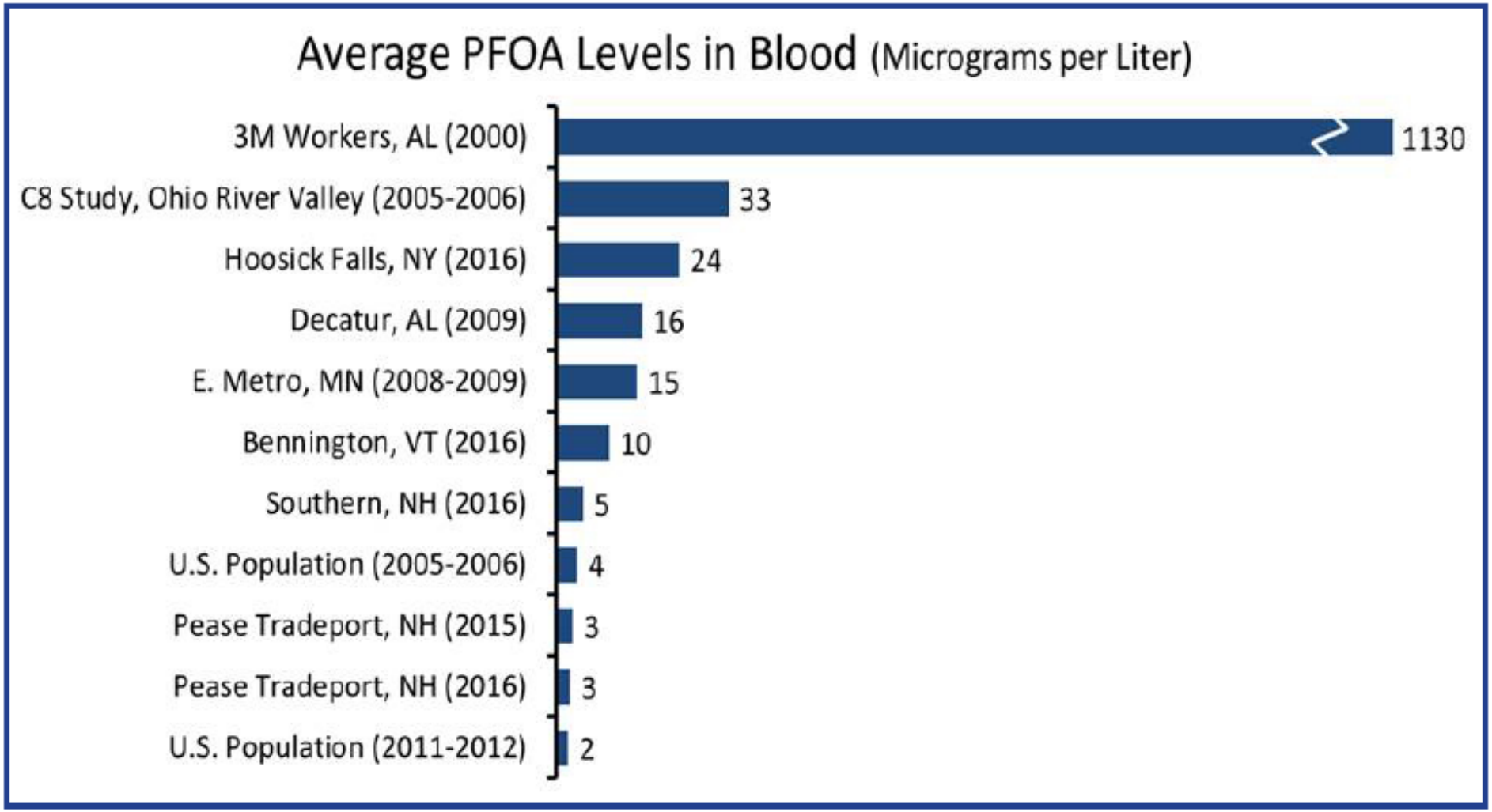
- Certified standards from two different companies cause sample results to vary by 20%-30%

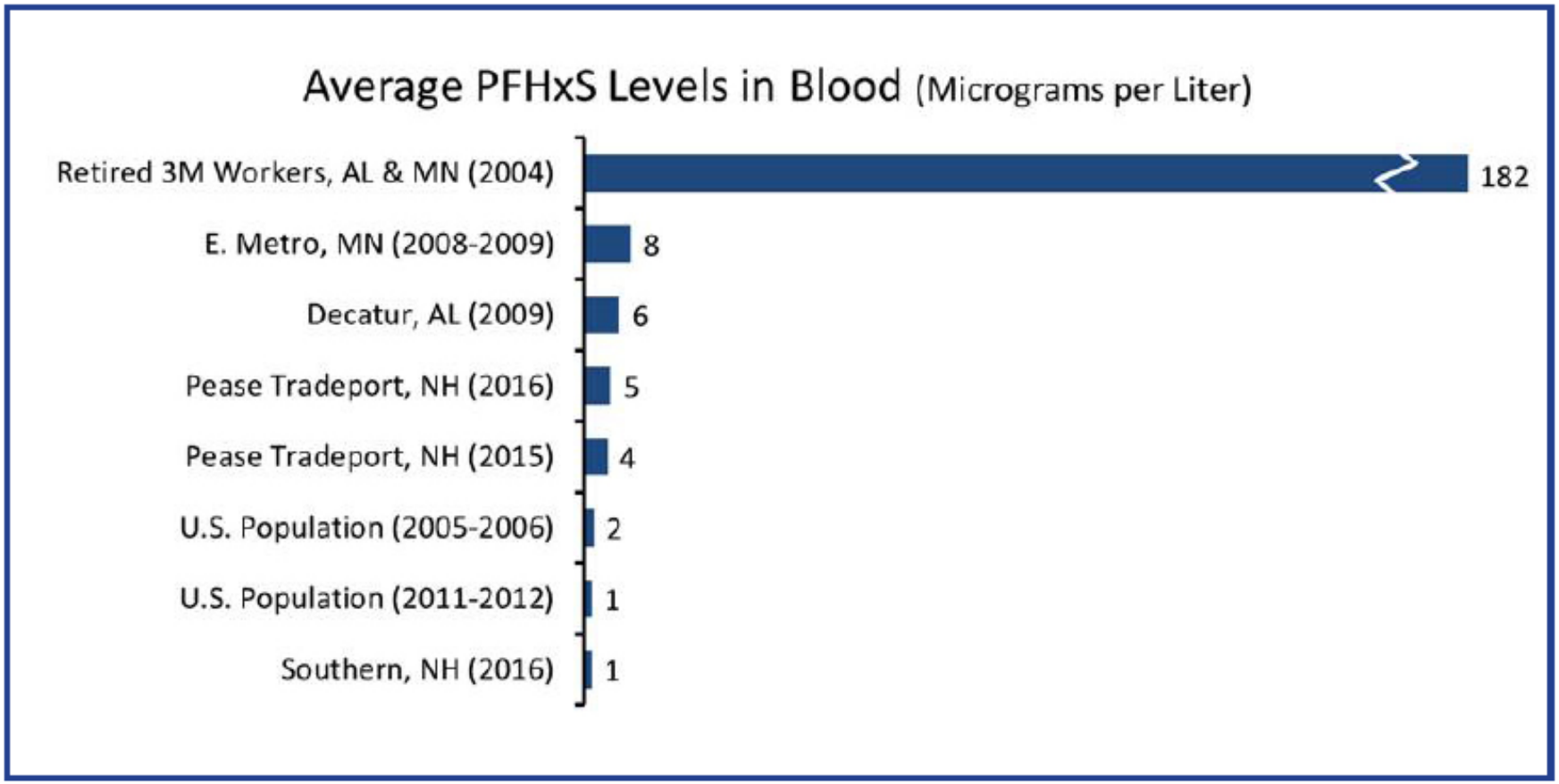
ID	Analyte	Results Using Standard "A" Calibration Curve ppb	Results Using Standard "B" Calibration Curve ppb
1	PFOA	0.059	0.079
2	PFOA	0.104	0.132
3	PFOA	0.050	0.070
4	PFOA	0.049	0.063
5	PFOA	0.061	0.076
6	PFOA	0.054	0.073
7	PFOA	0.086	0.136

PFAS – Human Blood Sampling Results in NH




Average PFOS Levels in Blood (Micrograms per liter)
3M Workers, AL (2000)
910
Decatur, AL (2009)
40
E. Metro, MN (2008-2009)
36
C8 Study, Ohio River Valley (2005-2006)
19
U.S. Population (2005-2006)
17
Pease Tradeport, NH (2016)
11
Pease Tradeport, NH (2015)
9
U.S. Population (2011-2012)
6
Southern, NH (2016)
5


Average PFOA Levels in Blood (Micrograms per Liter)
3M Workers, AL (2000)
1130
C8 Study, Ohio River Valley (2005-2006)
33
Hoosick Falls, NY (2016)
24
Decatur, AL (2009)
16
E. Metro, MN (2008-2009)
15
Bennington, VT (2016)
10
Southern, NH (2016)
5
U.S. Population (2005-2006)
4
Pease Tradeport, NH (2015)
3
Pease Tradeport, NH (2016)
3
U.S. Population (2011-2012)
2


Average PFHxS Levels in Blood (Micrograms per Liter)
Retired 3M Workers, AL & MN (2004)
182
E. Metro, MN (2008-2009)
8
Decatur, AL (2009)
6
Pease Tradeport, NH (2016)
5
Pease Tradeport, NH (2015)
4
U.S. Population (2005-2006)
2
U.S. Population (2011-2012)
1
Southern, NH (2016)
1

PFAS INFORMATION NEEDS

1) Drinking water quality guidance for PFAS
   a) Guidance for PFAS other than PFOA/PFOS

Compound Name	CAS #
Perfluorobutanoic acid (PFBA)	375-22-4
Perfluoropentanoic acid (PFPeA)	2706-90-3
Perfluorohexanoic acid (PFHxA)	307-24-4
Perfluoroheptanoic acid (PFHpA)	375-85-9
Perfluorononanoic acid (PFNA)	375-95-1
Perfluorobutanesulfonic acid (PFBS)	375-73-5
Perfluorohexanesulfonic acid (PFHxS)	355-46-4

   b) Routine re-evaluation of health guidance to assess the latest literature

PFAS INFORMATION NEEDS

Slide 2 of 5

2) Update Clean Air Act to address air emissions that may contaminate drinking water
   - Are there compounds other than PFAS that should be addressed?
   - Are emissions of PFAS with no health data appropriate?
   - What levels of PFAS (especially PFOA) emitted in air will not result in additional drinking water impacts (surface and groundwater)

PFAS INFORMATION NEEDS

Slide 3 of 5

3) Standardized analytical techniques for PFAS to reflect current technology
   - Extended list of PFAS
   - Isotope dilution
   - Standardize methods for solids, drinking water & monitoring wells
   - Additional analytical tools such as the total oxidized precursor for PFAS
4) PFAS reporting (Toxic Release Inventory, MSDS sheets) so that entities know where these compounds are being stored and used
5) Clean Water Act – Surface water quality standards (fish consumption, dermal exposure)

PFAS INFORMATION NEEDS

Slide 4 of 5

6) Soil/biosolids standards to protect water quality & food safety
   - Could impact wastewater plant/industrial pretreatment requirements
   - Could limit the type of wastes that wastewater treatment plants accept – landfill leachate??
7) FDA market basket studies to assess levels in food/Sources of PFAS in food
8) PFOA and PFOS in imported products – not addressed by the EPA C8 phase out agreement

PFAS INFORMATION NEEDS

Slide 5 of 5

9) Exposure pathways to PFAS other than drinking water and recommended mitigation measures

10) Financial assistance to sample PFAS in small community water systems and private wells.

Questions and Answers