PFAS Analytical Methods – New Hampshire's Experience

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PFAS Analytical Methods Application, Comparison, and Lab Accreditation

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NHDES

Presentation Overview

1) PFAS Sampling In New Hampshire
   - Public water systems
   - Other sites and media
2) ASDWA's Primer on Sampling for PFAS in Public Water Systems

- Analytical options
- Target analytes
- Reporting limits
- Identifying a qualified laboratory
- Causes for variability in results
- Interpreting data
- Sample collection procedures
- Development of new analytical methods

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PFAS Regulation in NH

- Ambient Groundwater Quality Standard (clean-up and enforceable drinking water standard of 70 ppt for PFOA/PFOS combined (based on health criteria only)
- Per state law, must initiate rulemaking for MCLs by 1/1/19 for PFOA, PFOS, PFNA and PFHxS (considers health benefits, costs and technical feasibility)
- Per state law, must develop a plan and budget for developing surface water quality standards by 1/1/20
- Per state law, has clear authority to regulate air emissions to protect water quality

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PFAS Sampling Timeline in NH

2013-2015 UCMR 3

(21 water systems / 80 sources)

2014 – DoD / Superfund Sampling

(3 major water supply wells)

2016 – Sampling of wells around two air emissions sites

(1000+ wells)

Present – Statewide sampling (3000+ multi-media samples)

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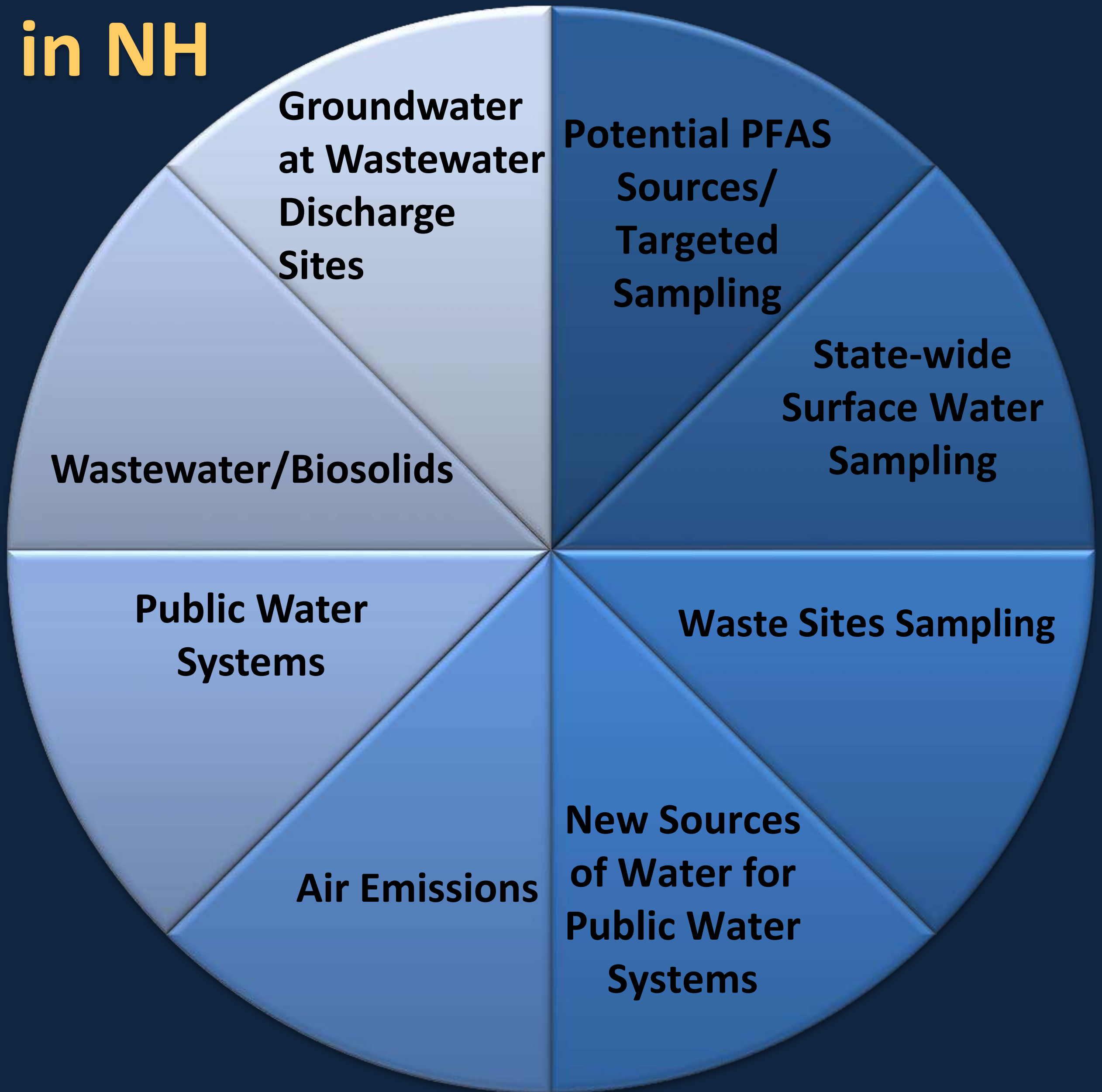
Sampling for PFAS in NH



PFAS INVESTIGATION
Updated: September 24, 2018

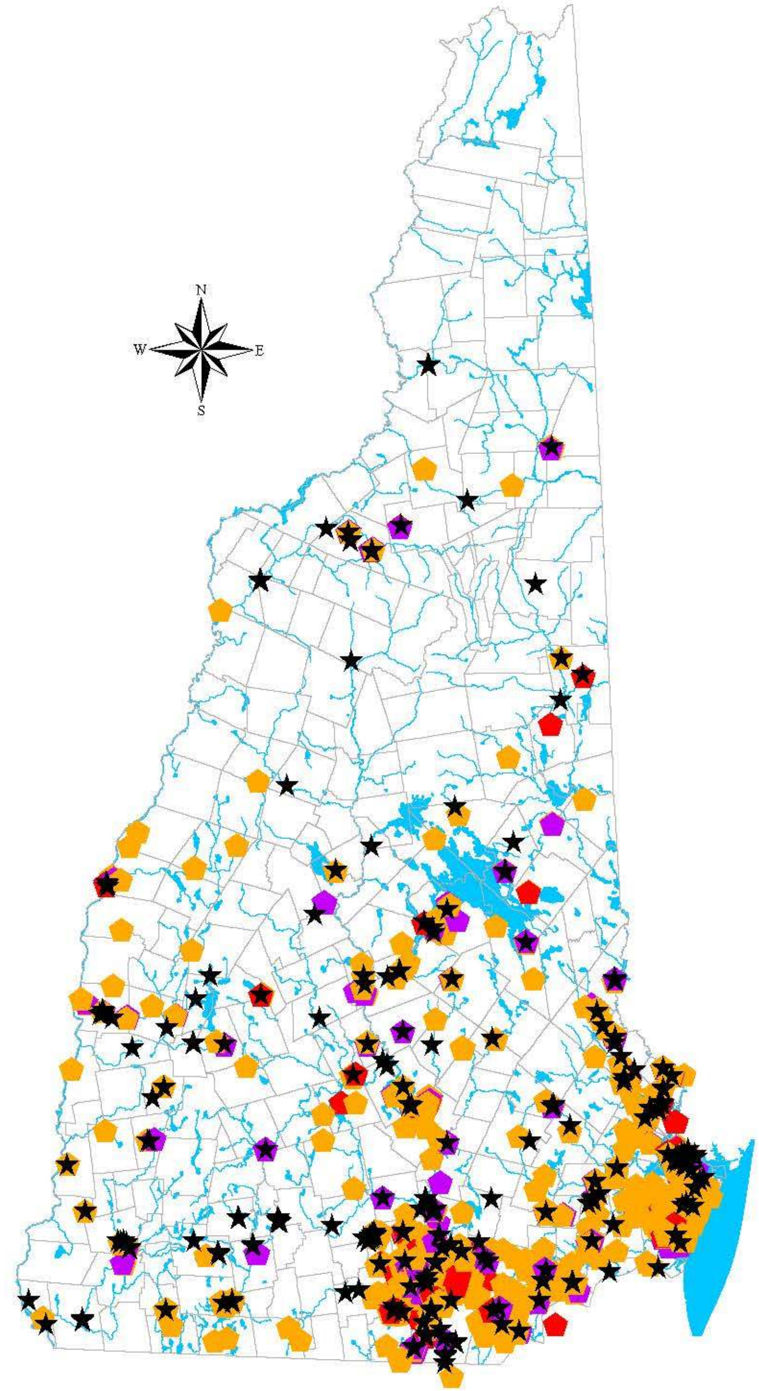
SAMPLES WITH PFAS DETECTS
TOTAL PFAS (ppt)

- 70+
- 45 - <70
- Detect - <45

- Existing Remedial Site with PFAS Detections

- Political Boundary
- Major Waterbody

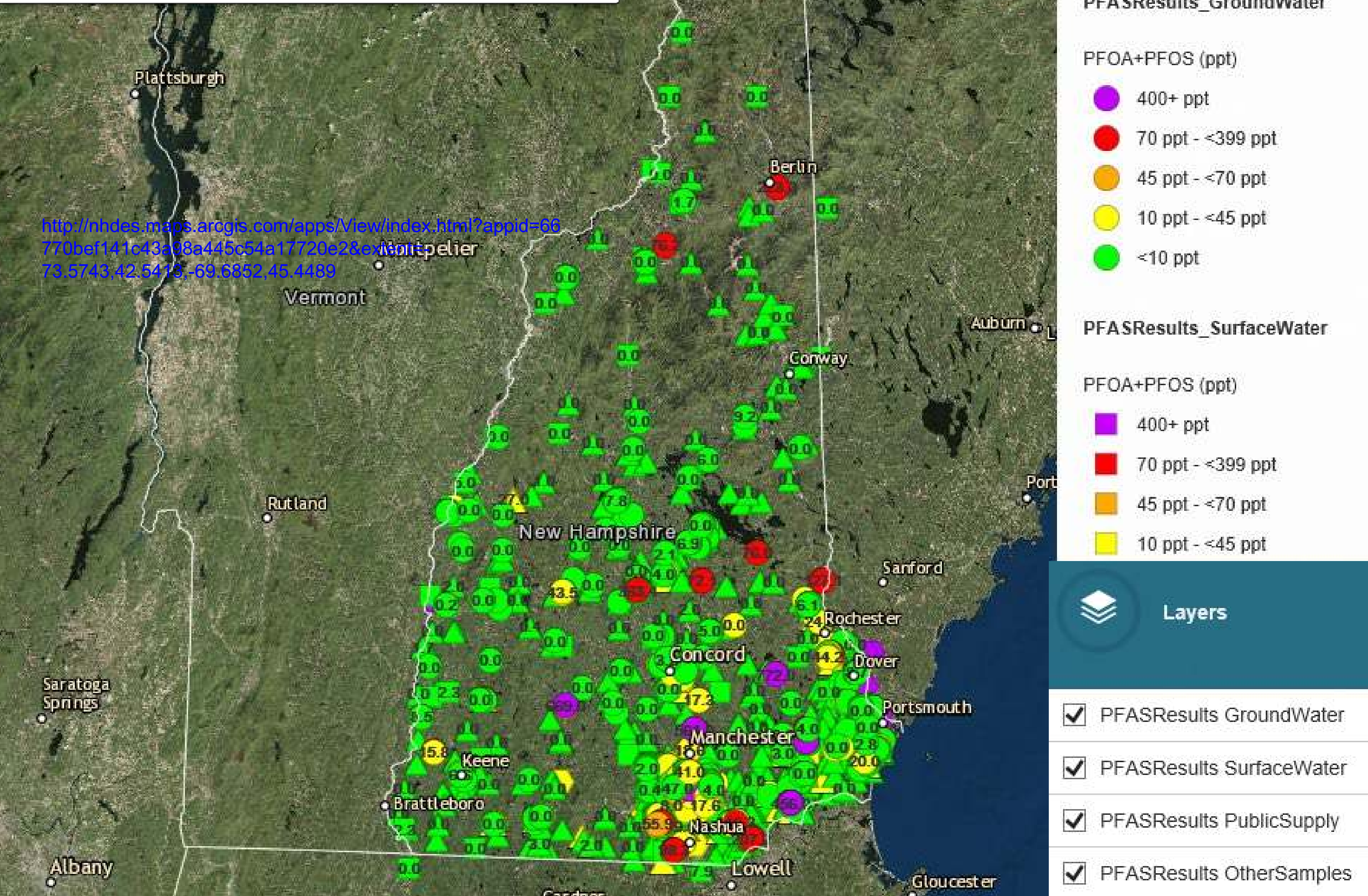
Miles
0 12.5 25 50



NEW HAMPSHIRE DEPARTMENT OF Environmental Services

~2,900 water samples
~2,300 sample locations

http://nhdes.maps.arcgis.com/apps/View/index.html?appid=66770bef141c43a98a445c54a17720e2&extent=-73.5743,42.5413,-69.6852,45.4489



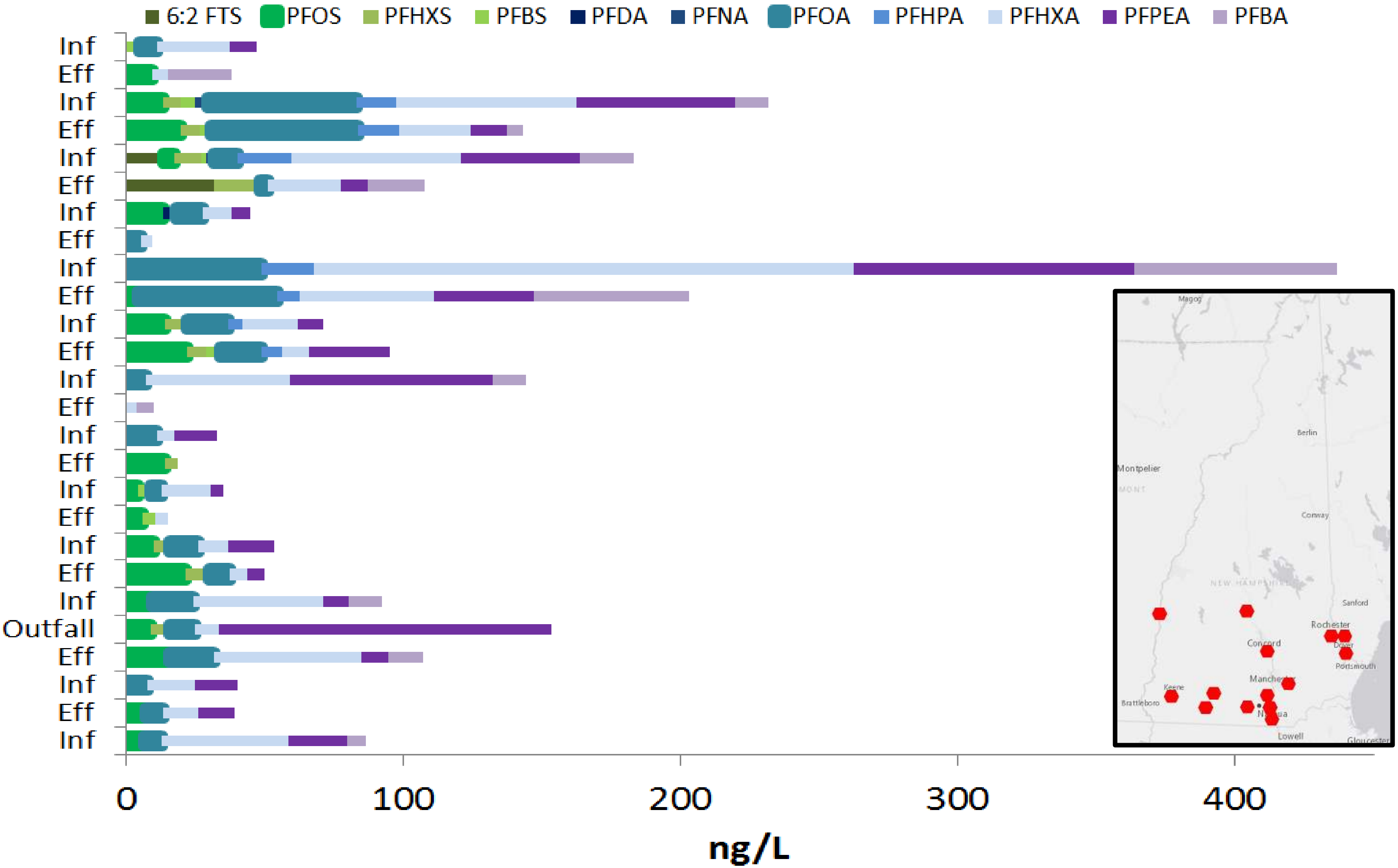
Public Water System Sampling in New Hampshire

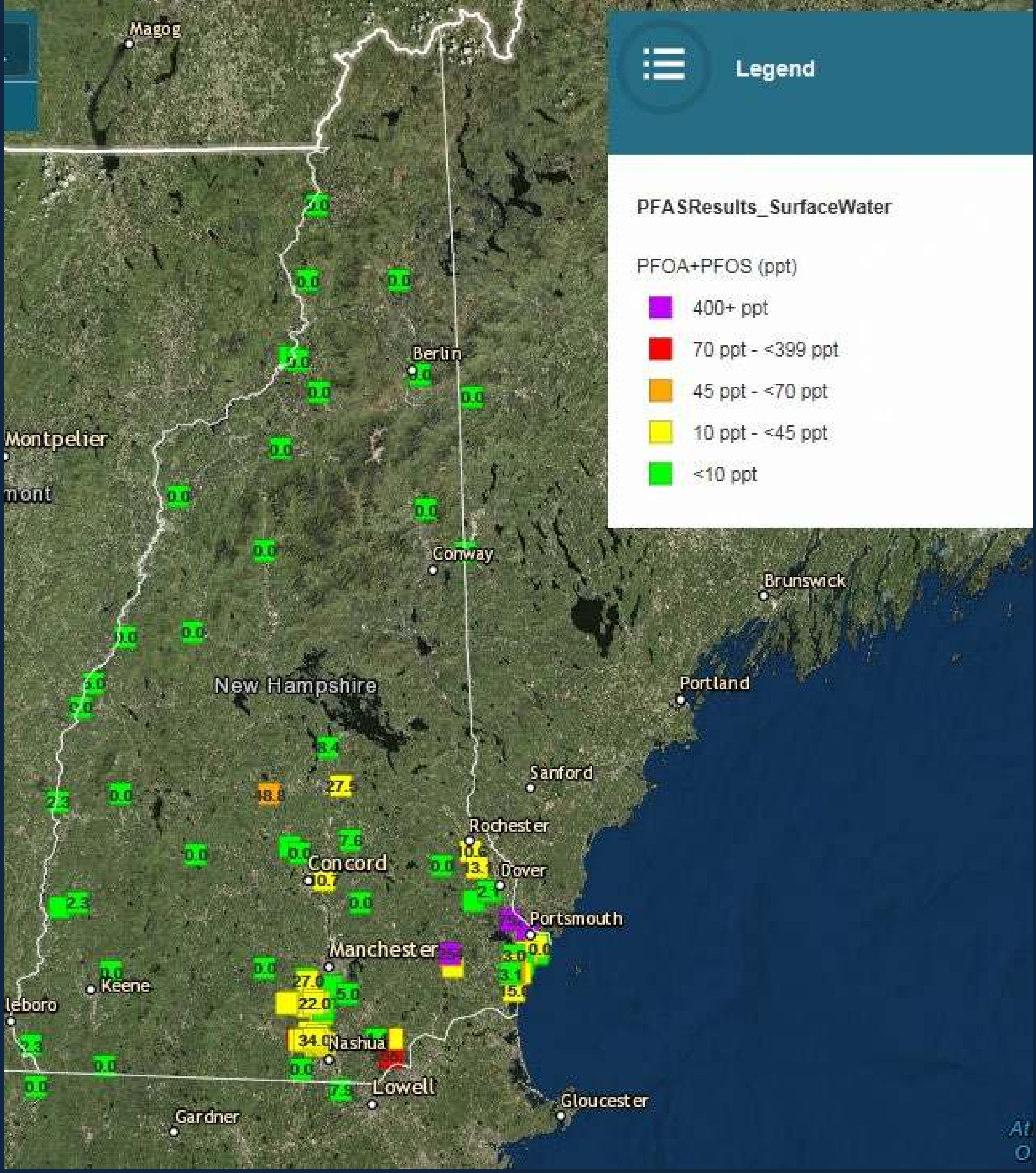
Combined PFOA & PFOS Result	Number of Public Water System Sources	Percentage
Greater than 70 ppt	7	1.6%
Greater than 60 ppt	9	2.1%
Greater than 50 ppt	9	2.1%
Greater than 40 ppt	10	2.3%
Greater than 30 ppt	17	4.0%
Greater than 20 ppt	32	7.5%
Greater than 10 ppt	57	13.3%
Greater than 5 ppt	73	17.0%
Number of Sources Tested = 429		

Non Public Water System Samples

Site Type	# Sampled	Number of Detects	Combined PFOA & PFOS > 70 ppt	Percentage Exceeding 70 ppt
Existing Waste Sites (non-petroleum)	92	79	51	54%
Existing Petroleum Sites				
Auto Salvage Yards	4	4	3	75%
Fuel Oil Bulk Storage	1	1	1	100%
Used Motor Oil Sites	1	1	1	100%
Residential Home Heating Oil Spills	2		0	0%
Gas Stations	2	2	0	0%
Landfills				
Unlined	87	83	40	46%
Lined	10	9	2	17%
Wastewater Discharge to Groundwater Sites	47	39	8	17%
Fire Departments	17	12	7	41%

Wastewater Assessments




Legend
PFASResults_SurfaceWater
PFOA+PFOS (ppt)
400+ ppt
70 ppt - <399 ppt
45 ppt - <70 ppt
10 ppt - <45 ppt
<10 ppt
Magog
Berlin
Montpelier
Conway
Brunswick
New Hampshire
Portland
Sanford
Rochester
Concord
Dover
Portsmouth
Manchester
Keene
Nashua
Lowell
Gardner
Gloucester

Topic 1: Selecting an Analytical Method

1) EPA Method 537 Rev 1.1

Pros

- Only standard method used by commercial labs
- Method developed by USEPA
- Cost less than other methods

Cons

- Includes only 14 analytes
- Not intended for non-drinking water samples
- Corrections are not made to account for matrix interference

2) Isotope Dilution

Pros

- Considered the best method by many chemists
- Can be used for non-drinking water samples
- Can include more analytes than Method 537
- Makes corrections for matrix interference

Cons

- Cost more than Method 537
- Labs use their own proprietary method/method different from lab to lab

Topic 2: Finding a Qualified Laboratory

Laboratory Accreditation Programs

- National Environmental Laboratory Accreditation Program http://lams.nelac-institute.org/Search) by selecting a common PFAS chemical such as perfluorooctanoic acid (PFOA) under the "Analyte" pulldown tool; and

- The Department of Defense https://www.denix.osd.mil/edqw/accreditation/accreditedlabs/ by selecting EPA 537 or "EPA 537 Mod" under the "Method" pull down tool.

- Some states may have their own accreditation or certification programs

Note: Isotope dilution is sometimes called "Method 537 Modified" even though it is completely different than Method 537

Other approaches to verify laboratory performance

- Periodically split samples and send to multiple laboratories
- Conduct double blind proficiency testing studies with labs you work with
- Request that the lab provides the results of historical proficiency testing

Topic 3: Which PFAS Chemicals Should Be Analyzed?

- Methods 537 includes up to 14 PFAS analytes (labs performing Method 537 do not always include all 14 compounds however)

- Isotope dilution includes up to 30 compounds
  - Many labs offer more than one testing packages
  - Options vary from lab to lab

- Six PFAS (PFOS, PFOA, PFNA, PFHxS, PFHpA and PFBS) were included in USEPA's UCMR3

- Three additional PFAS compounds are frequently detected (PFBA, PFPeA and PFHxA)

Topic 3: Which PFAS Chemicals Should Be Analyzed? (continued)

Benefits of using methods with an extended list of analytes

- Collect as much information as possible when sampling
- Assist with fingerprinting/segregating potential sources of contamination
- Future health studies may be completed and guidelines issued for additional PFAS compounds
- Some states are developing health guidelines using an additive approach/summing up the concentration of up to five PFAS compounds.

Challenges of using methods with an extended list of analytes

- The may be no health guidelines for some of the detected PFAS
- Cost per analysis may be higher
- More data processing and reporting

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 (do not assume they are the same)
- Form of compound can affect the concentration reported
- Lab reports/electronic data deliverables contain mismatching CAS #s and chemical names/forms
- Creates havoc in data management and maintaining database integrity

EPA's health advisory & NHDES standards reference the acid form

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

X	Y	Acronym	Name	Formula	CAS No.
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

http://pfas-1.itrcweb.org/wp-content/uploads/2017/10/pfas_fact_sheet_naming_conventions_11_13_17.pdf

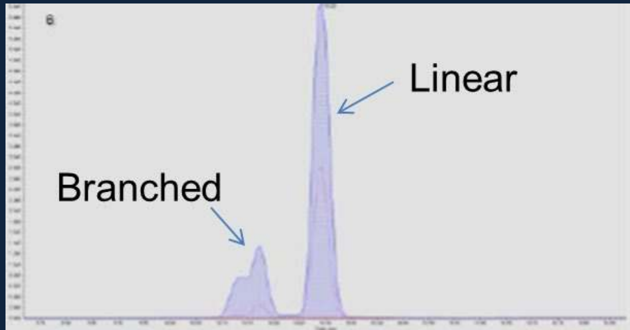
Topic 4: What Reporting Limit Should Be Used?

- Reporting limits of at least 2-4 ng/L should be utilized
- Many labs performing isotope dilution achieve limits below 1 ng/L
- Method 537 has reporting limits ranging from 2.9-14 ng/L
- Benefits of low reporting limits
  - Improve utility of the data in the event health advisories are lowered and use an additive approach
  - Track concentration trends
  - Fingerprint source of contamination

Topic 5: Topic 5: Technical Issues that Cause Variability in Testing Results

Linear and Branched Isomers

- Prior to September 2016, Method 537 did not specify if branched isomers of PFOA should be measured and reported (some labs included it & others did not)
- PFOA was produced by Dupont & 3M
  - PFOA from Dupont contained only linear isomers of PFOA
  - PFOA from 3M contained 70% linear & 30% branched isomers
- Results from some samples analyzed prior to September 2016 may be underreported by 30% if contaminated with PFOA that was manufactured by 3M



Topic 5: Topic 5: Technical Issues that Cause Variability in Testing Results (continued)

Expected Accuracy of Testing Results and Common Biases Based on NHDES' Experience

- Expected accuracy of analytical testing is +/-50% (higher than data from UCMR3 because high reporting limits were used)
- NHDES typically observed an accuracy of approximately -20% (biased low)
- NHDES split sample studies generally showed
  - Different labs reported similar results
  - Method 537 & isotope dilution reported similar results
- Occasional significant over reporting or under reporting occurred

Topic 5: Topic 5: Technical Issues that Cause Variability in Testing Results (continued)

- Standards do not exist for many PFAS with branched isomers – labs estimate concentration using linear isomers
- Labs interpret branched isomers differently because the peaks on the chromatograph are less pronounced
- Certified standard from different vendors can cause results to vary by as much as 20%

ID	Analyte	Results Using Standard "A" Calibration Curve ppt	Results Using Standard "B" Calibration Curve ppt
1	PFOA	59	79
2	PFOA	104	132
3	PFOA	50	70
4	PFOA	49	63
5	PFOA	61	76
6	PFOA	54	73
7	PFOA	86	136

Topic 6: Sample Collection Procedures

- Low detection limits combined with the widespread use of items with PFAS increases the potential for sampling errors
- However, drinking water sampling agents and operators are qualified to complete the sampling
- Sampling taps and plumbing should be free of materials containing Teflon
- Samplers should wear well laundered cotton clothing without the use of softeners
- Samplers should not wear cosmetics, moisturizers, hand cream and related products
- Avoid the use of traditional weatherproof field books/paper
- Samplers should wash hands and wear nitrile gloves
- Field blanks and trip blanks should be periodically used – With each batch of samples or some other predetermined frequency

Topic 7: Interpretation of Results

- Compare results against USEPA's health advisory or state guidance – ITRC maintains a table of standards and guidance values for other states and countries.
- The detection of low levels of PFAS do not mean there is a major source of PFAS Contamination at low levels could be associated with:
  - Teflon in components of the plumbing system??
  - Chemical feed tanks/tubing??
  - Regional septic systems or other numerous and dispersed uses and releases of PFAS.
- Lab blanks, trip blank, field blanks and duplicates are especially important when assessing low-level detections