Drivers of PFC Analytical Requirements

Are we there yet?

12 April 2016

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Welcome and introductions

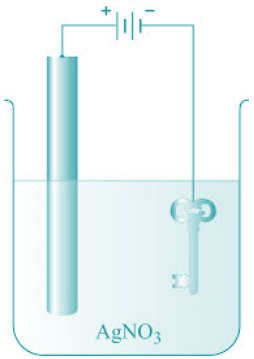
Agenda

What is driving the analytical requirements for PFCs?

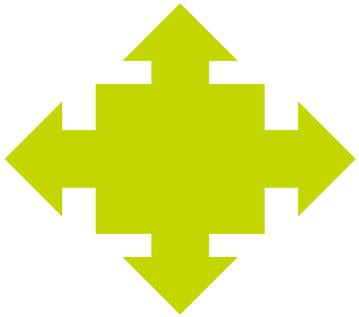
1. **Regulatory Drivers**
2. **Technical Drivers**
3. **Screening Levels**
4. **Are we there yet? Can we consistently and reliably meet these expectations?**
5. **What gaps remain?**

PFCs- Uses/sources

Oil and gas extraction

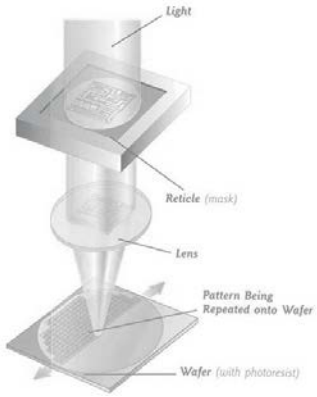


Electroplating
(mist suppressants)



Manufacturing processes/
intermediates/ by-products

Consumer products



Semiconductor
industry

Aqueous film forming
foams

Fate and transport

Low volatility and high solubility in water

Thermally, chemically, and biologically stable

Highly mobile in soil and leach to groundwater

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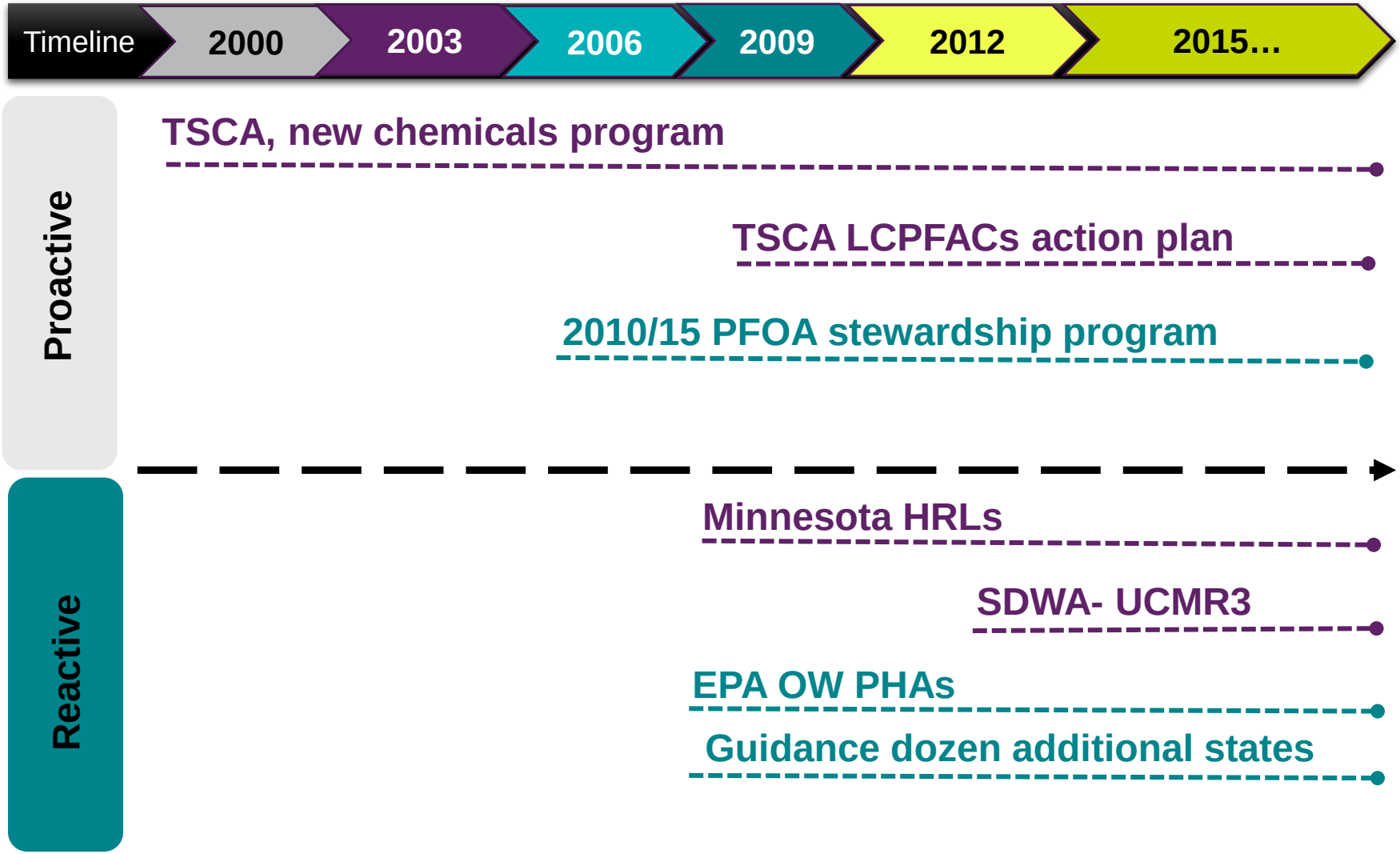
Regulatory drivers



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Regulatory drivers by state

- EPA established Provisional Health Advisory limits (water):
  - 0.2 ppb for PFOS
  - 0.4 ppb for PFOA
- EPA PHA criteria anticipated to drop by 10x

Year	U.S. EPA	PFOS	PFOA
2009	Office of Water	0.2	0.4
2016	EPA Region 2	NA	0.1
Year	**States**	**PFOS**	**PFOA**
2016	Alaska	0.6	0.4
2010	California	0.2	0.4
2015	Delaware	0.2	0.4
2013	Illinois	0.2	0.4
2016	Maine	0.56	0.13
2014/2011	Michigan	0.011	0.42
2009	Minnesota	0.3	0.3
2015	Nevada	NA	NA
2015	New Hampshire	0.2	0.4
2007/2015	New Jersey	NA	0.04
2010	North Carolina	NA	1
2009	Ohio/WV	NA	0.4
2009	Oregon	300	24
2016	Texas	0.56	0.29
2016	Vermont	NA	0.02

NOTES:
- AK, MN and TX have promulgated formal values for drinking water or groundwater cleanup
- MN, NV, NJ, OR, and TX have criteria developed for other perfluoroalkyl acids
- EPA Region 2 PFOA Criteria is site-specific response to Hoosick Falls, NY site

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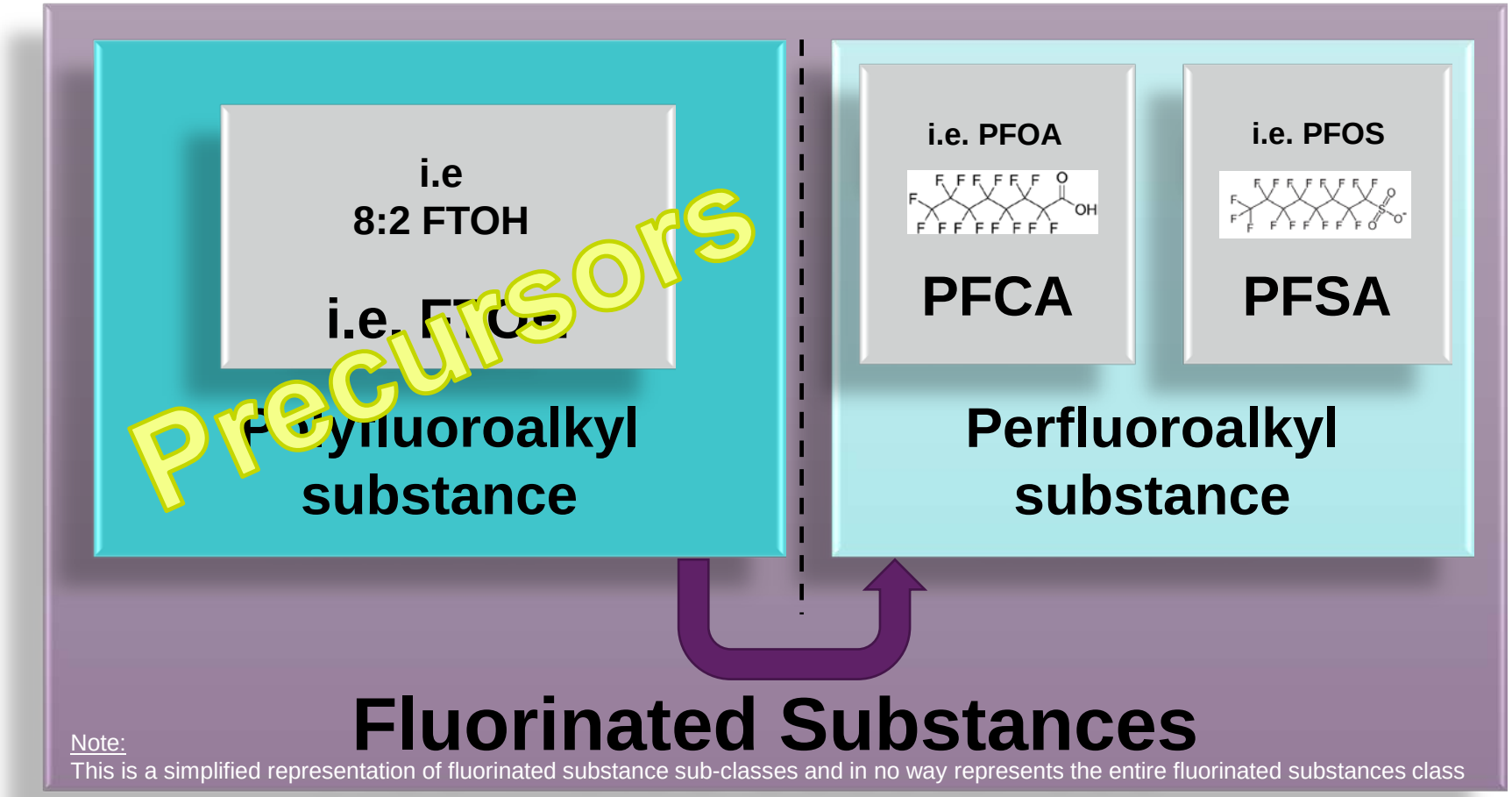
Technical drivers for analytical requirements



Note:
This is a simplified representation of fluorinated substance sub-classes and in no way represents the entire fluorinated substances class

[3] RC Buck et al. Guide to PFASs in the Environment- Integr Environ Assess Manag 7, 2011

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PFC potential compound list, screening levels

Analyte	EPA PHA (µg/L)	UCMR3	537.1	States (concentrations in µg/L)								Project-Specific		Lowest Screening Value (µg/L)	Targeted LOQ (µg/L)
				ME	MI	MN	NJ	NV	OR	TX	VT	ME	NH		
Perfluoroalkylcarboxylic Acids															
PFBA						7				71		x	x	7	0.7
PFPeA										0.093		x	x	0.093	0.0093
PFHxA			x							0.093		x	x	0.093	0.0093
PFHpA		x	x						300	0.56		x	x	0.56	0.056
PFOA	0.4	x	x	0.13	0.42	0.3	0.04		24	0.29	0.02	x	x	0.02	0.002
PFNA		x	x				0.01		1	0.29		x	x	0.01	0.001
PFDA			x							0.37		x	x	0.37	0.037
PFUnA			x							0.29		x	x	0.29	0.029
PFDoA			x							0.29		x	x	0.29	0.029
PFTrDA			x							0.29		x	x	0.29	0.029
PFTeDA			x							0.29		x	x	0.29	0.029
Perfluoroalkylsulfonates															
PFBS		x	x			7		667		34		x	x	7	0.7
PFHxS		x	x							0.093		x	x	0.093	0.0093
PFHpS													x		0.008
PFOS	0.2	x	x	0.56	0.011	0.3			300	0.56		x	x	0.011	0.0011
PFDS										0.29			x	0.29	0.029
Perfluoroalkylsulfonamides															
PFOSA													x		0.008
MeFOSA													x		0.02
EtFOSA													x		0.02
Perfluoroalkylsulfonamidoacetic acids															
MeFOSAA			x									x			0.01
EtFOSAA			x									x			0.01
Perfluoroalkylsulfonamidoethanols															
MeFOSE													x		0.02
EtFOSE													x		0.02
Fluorotelomer Sulfonates															
6:2 FTS												x	x		0.008
8:2 FTS												x	x		0.008

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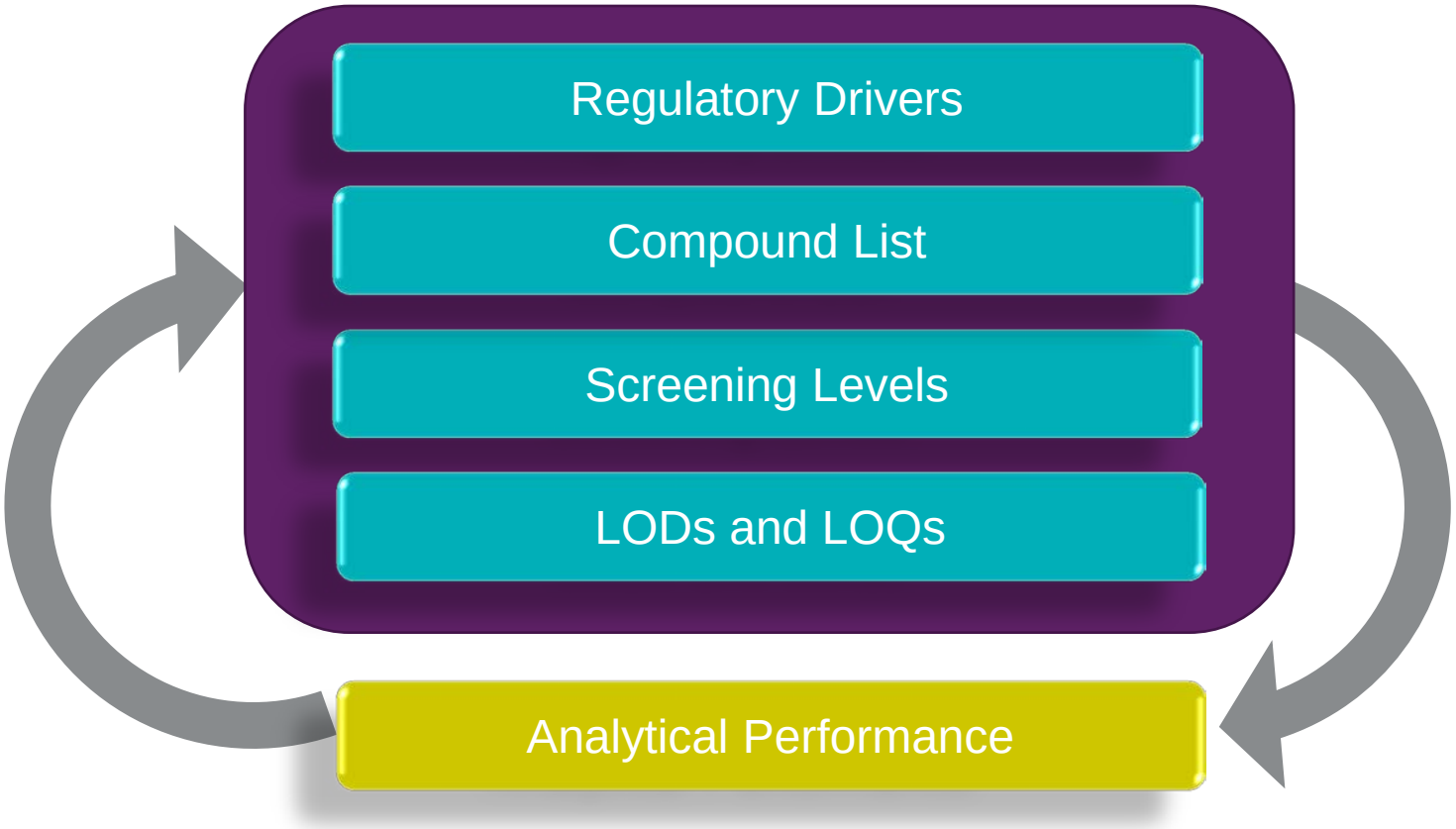
Can we consistently meet analytical requirements?



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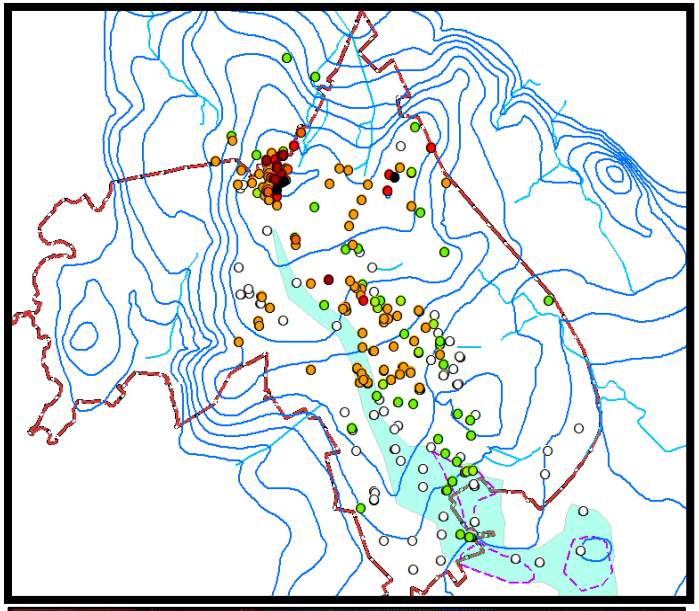
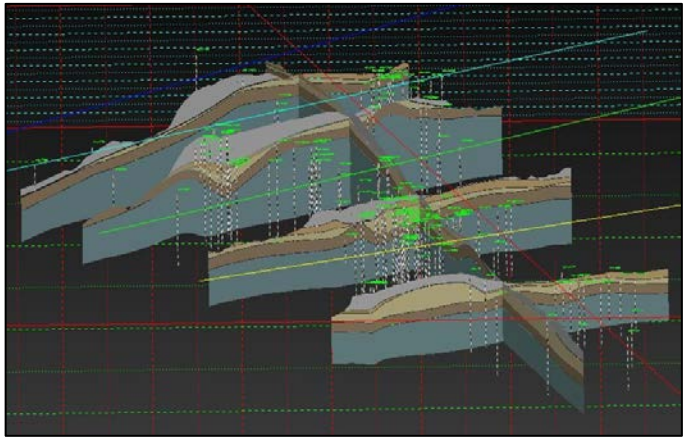
Third party controls are lacking

Measures of control for laboratory performance are limited

- Certification/accreditation programs lag behind regulatory requirements
- Method modifications vary by lab
- Performance testing is insufficient





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Certification/ Accreditation Programs

Limited options of laboratories that comply with:

- DOD ELAP, state or program certification requirements
- Covering project analyte list
- At the required screening levels to meet DQOs

Laboratory Accreditation

Verify lab meets DQOs

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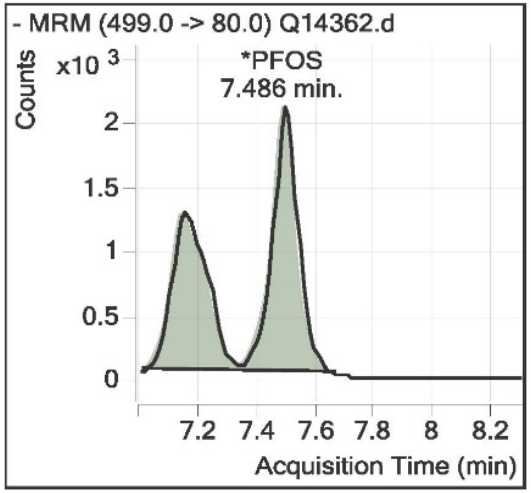
Method modifications

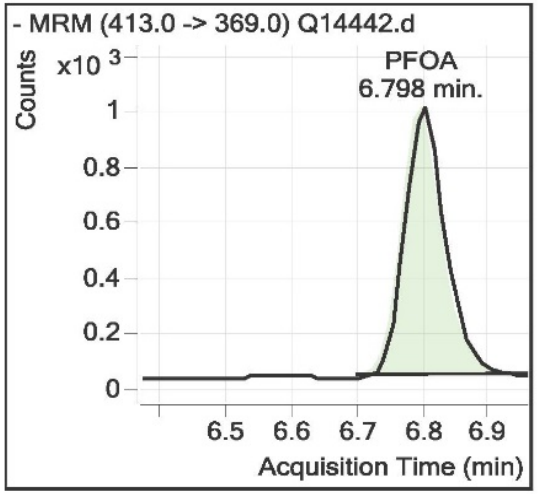
Laboratories modify basic EPA Method 537 in different ways

- Liquid chromatography tandem mass spectroscopy (LC/MS/MS)
- High resolution mass spectroscopy (HRMS)
- Chromatography resolution with branched and linear isomers
- Isotope dilution
- Analyte list
- Potential mass quantification differences

PFOS-Note peaks for branched/linear isomers



PFOA - Note single peak from linear isomer



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Performance Testing (PT)

Four laboratories evaluated single blind PT

- Analyzed 25 analytes/extended list
- Concentration ranged from 0.13 to 0.29 ug/L and
- Findings: primary 6 compounds are consistent across laboratories
- Extended lists shows method/lab limitations
- PT procured and sponsored by Air Force because not readily/commercially available for project needs

Integrate performance testing

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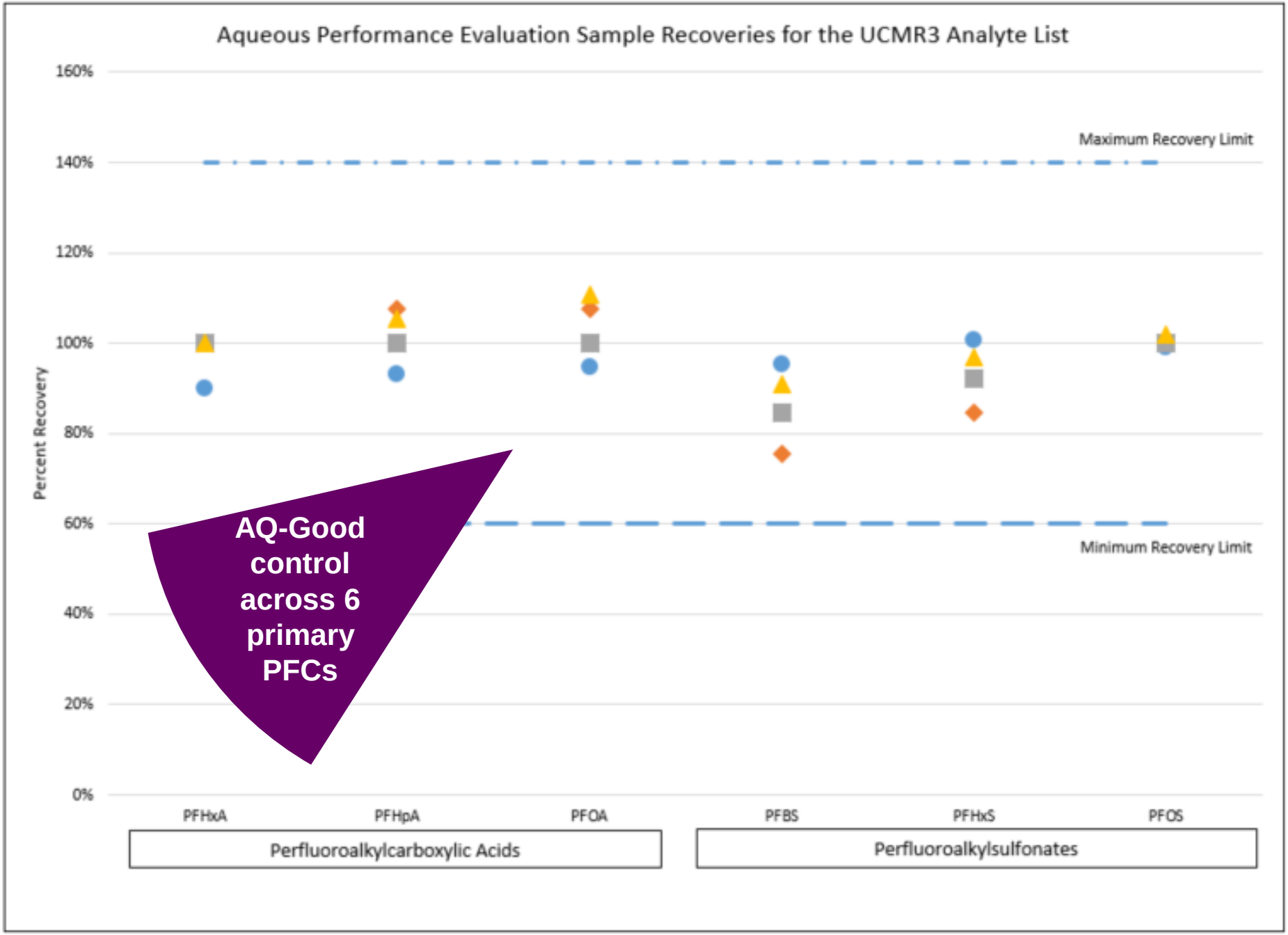
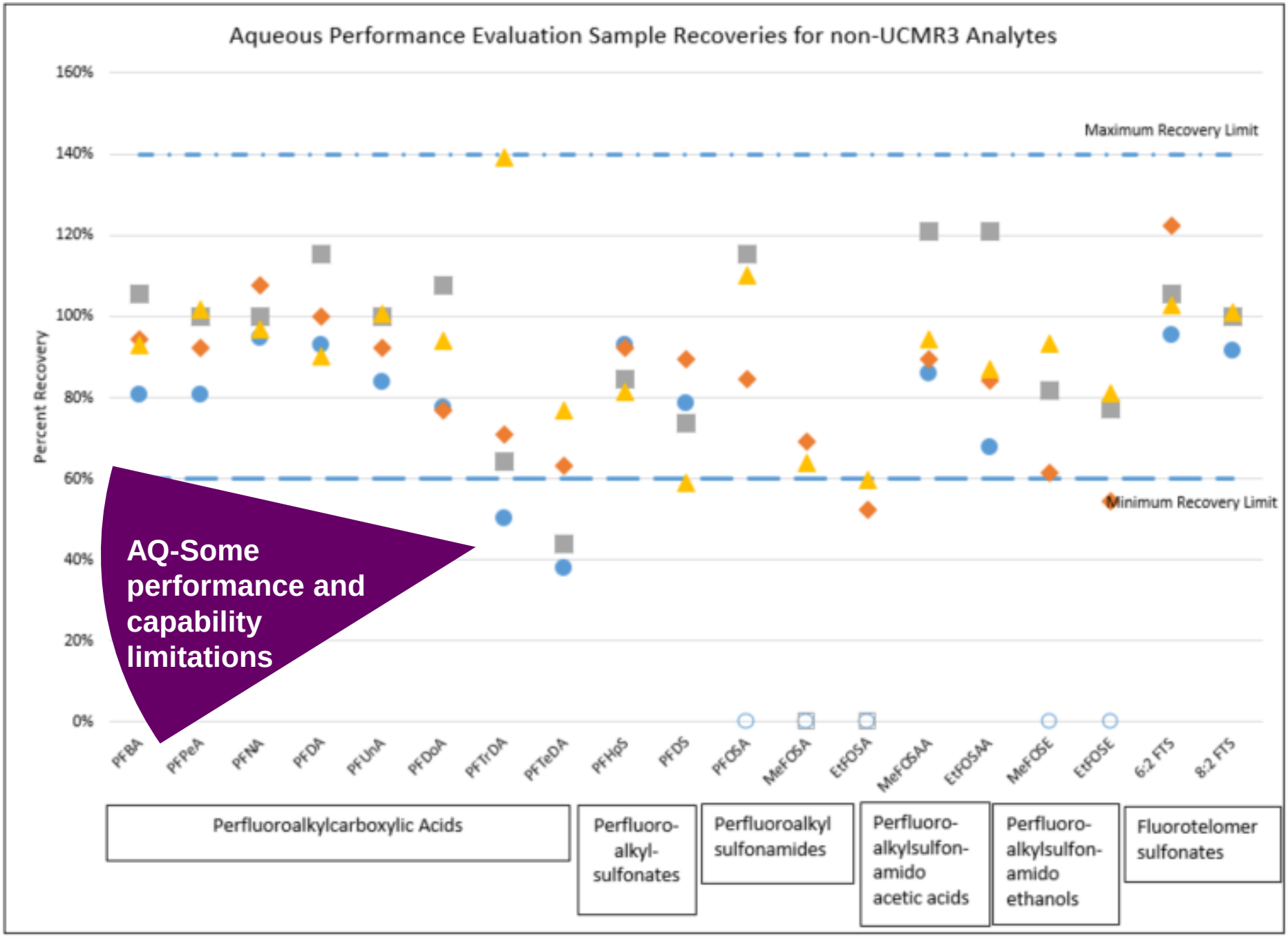
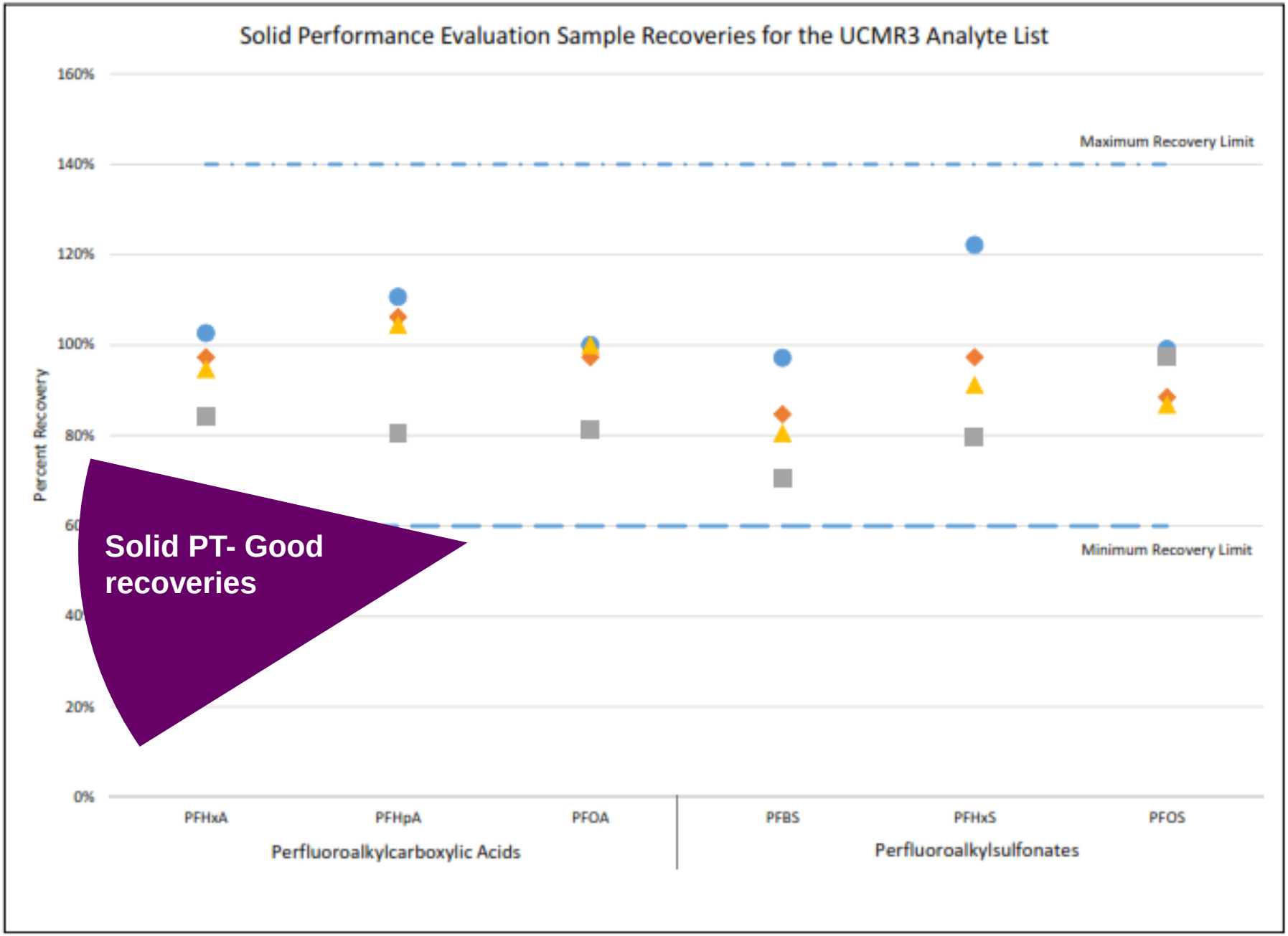
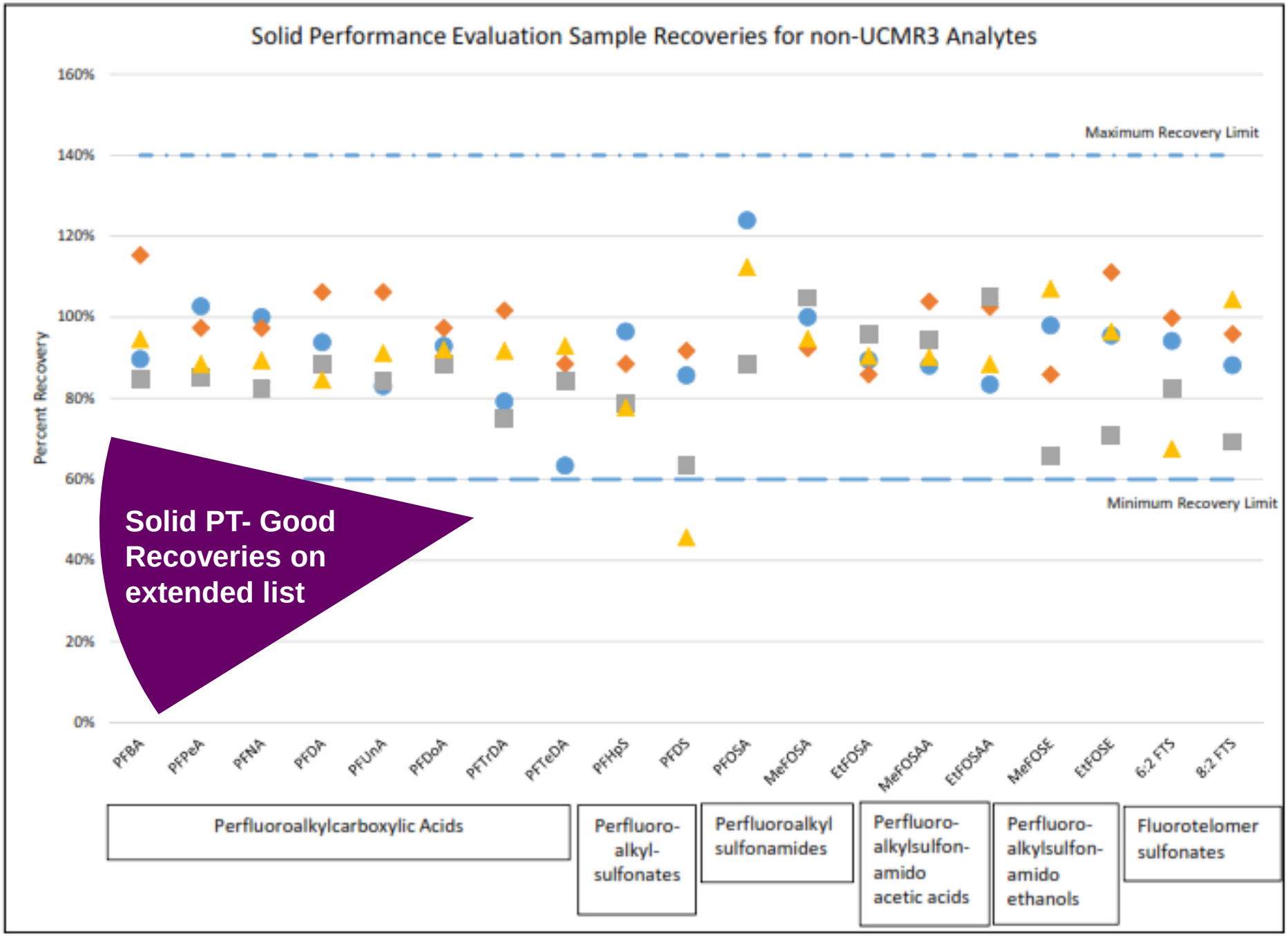

Aqueous Performance Evaluation Sample Recoveries for the UCMR3 Analyte List
160%
140%
120%
100%
80%
60%
40%
20%
0%
Percent Recovery
Maximum Recovery Limit
Minimum Recovery Limit
AQ-Good control across 6 primary PFCs
PFHxA
PFHpA
PFOA
PFBS
PFHxS
PFOS
Perfluoroalkylcarboxylic Acids
Perfluoroalkylsulfonates


Aqueous Performance Evaluation Sample Recoveries for non-UCMR3 Analytes
160%
140%
120%
100%
80%
60%
40%
20%
0%
Percent Recovery
Maximum Recovery Limit
Minimum Recovery Limit
AQ-Some performance and capability limitations
PFBA
PFPeA
PFHxA
PFDA
PFUnA
PFDoA
PFTrDA
PFTeDA
PFHpS
PFDS
PFOSA
MeFOSA
EtFOSA
MeFOSAA
EtFOSAA
MeFOSE
EtFOSE
6:2 FTS
8:2 FTS
Perfluoroalkylcarboxylic Acids
Perfluoro-alkyl-sulfonates
Perfluoroalkyl sulfonamides
Perfluoro-alkylsulfon-amido acetic acids
Perfluoro-alkylsulfon-amido ethanols
Fluorotelomer sulfonates


Solid Performance Evaluation Sample Recoveries for the UCMR3 Analyte List
160%
140%
120%
100%
80%
60
40
20%
0%
Percent Recovery
Maximum Recovery Limit
Minimum Recovery Limit
PFHxA
PFHpA
PFOA
PFBS
PFHxS
PFOS
Perfluoroalkylcarboxylic Acids
Perfluoroalkylsulfonates
Solid PT- Good recoveries


Solid Performance Evaluation Sample Recoveries for non-UCMR3 Analytes
160%
140%
120%
100%
80%
60%
40%
20%
0%
Percent Recovery
Maximum Recovery Limit
Minimum Recovery Limit
PFBA
PFPeA
PFHxA
PFDA
PFUnA
PFDoA
PFTrDA
PFTeDA
PFHpS
PFDS
PFOSA
MeFOSA
EtFOSA
MeFOSAA
EtFOSAA
MeFOSE
EtFOSE
6:2 FTS
8:2 FTS
Perfluoroalkylcarboxylic Acids
Perfluoro-alkyl-sulfonates
Perfluoroalkyl sulfonamides
Perfluoro-alkylsulfon-amido acetic acids
Perfluoro-alkylsulfon-amido ethanols
Fluorotelomer sulfonates
Solid PT- Good Recoveries on extended list

Are we there yet?

What gaps remain?

- Reliable 3rd party performance testing
- Improved performance for extended analyte list
- Recognize that screening levels may be changing as understanding of exposure risk improves
- Understand which analytical techniques may be best suited for your project DQOs

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Acknowledgement of Contributors
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Thank you

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