Evaluating Perfluorinated Compounds – A Test of Quality Systems

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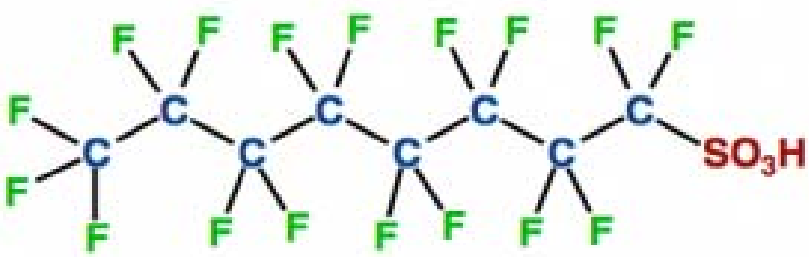
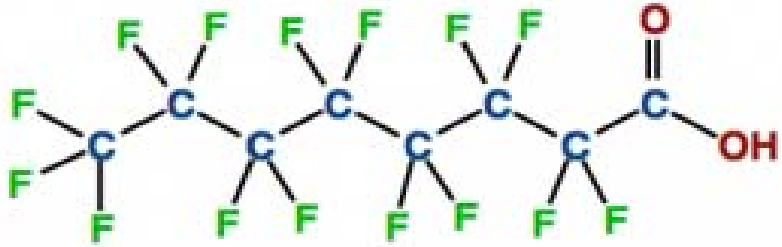
April 28, 2015

Overview

1. Perfluorinated Compounds- emerging contaminant
2. Unique challenges for quality assurance
3. Verifying method control
4. Analytical considerations
5. Next steps



PFOS - perfluorooctanesulfonic acid



PFOA - perfluorooctanoic acid

What are PFCs?

Perfluorinated compounds (PFCs)

- Human-made compounds
- Persistent, bioaccumulative
- C-F bond- shortest and strongest
- Stable in acids, bases, oxidants, heat
- Lipid and water repellent
- Used in many products

Widespread use of PFCs in products

Aqueous Film Forming Foam (AFFF)

AFFF Use- 1970 - present

- Effective for fuel-based fires
- Emergency responses (crashes, fires)
- Fire training activities
- Fire suppression systems
- Fuel storage
- AFFF still in inventory to be used as needed

Impacts of AFFF- regular use and uncontrolled releases

Toxicity Effects- PFCs

- Primary exposure routes: **inhalation and ingestion**
- **4-year half life** in humans
- Suspected **carcinogen**: Bladder, liver, and other cancers
- Detected in public **landfill leachate, WWTP effluent**
- PFCs monitored under Safe **Drinking Water** Act Unregulated Contaminant Rule for water supplies serving over 10,000- **no significant impact**
- **98% of human blood** includes trace levels of PFOS and PFOA

PFCs are persistent, bioaccumulative, and ubiquitous

Criteria in Water by State

Year	State	PFOS (ug/L)	PFOA (ug/L)
2009	**EPA PHA**	0.2	0.4
2009	Alabama	0.2	0.4
2009	Georgia	0.2	0.4
2009	Minnesota	0.3	0.3
2009	North Carolina	--	2
2009	Ohio	0.2	0.4
2009	West Virginia	0.2	0.4
2010	California	0.2	0.4
2011	Oregon	300	24
2013	Alaska	1.3	3.1
2014	Maine	--	0.1
2014	Michigan	0.011	0.42
2014	New Jersey	--	0.04
2014	Texas	0.56	0.29

EPA Provisional Health Advisory- Not regulated

- PFOS, PFOA primary PFCs
- NJ, TX, MN, OR have guidelines for additional PFCs
- MN only state with promulgated criteria
- Over 90 species of PFCs

Regulatory changes for PFCs are happening quickly

PFCs- A Test of Quality Systems

- Program sample quantities may require redundancy in labs
- EPA 537 Drinking water method (LC/MS/MS) – **modifications required**
  - Inter-laboratory difference potential
  - Labs have limited experience running PFCs
  - Conducted audits and SOP reviews
- **Standard analytical controls lacking**
  - Vendors lack standards for PFCs
  - PE sample options are very limited
  - Limited certification programs

Typical method controls are limited for PFCs

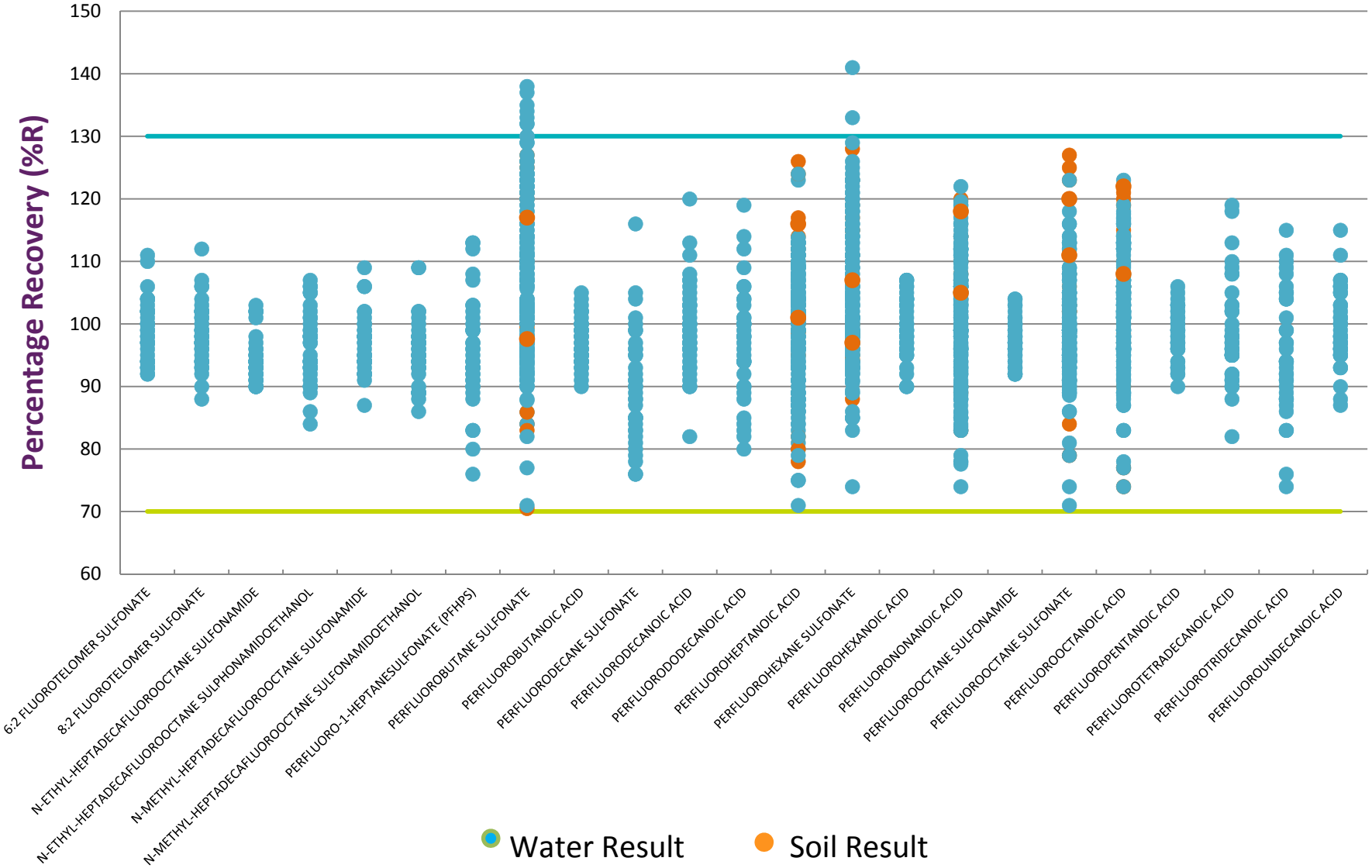
PFCs- A Test of Quality Systems

PFC Field sampling SOP designed to minimize false positive results:

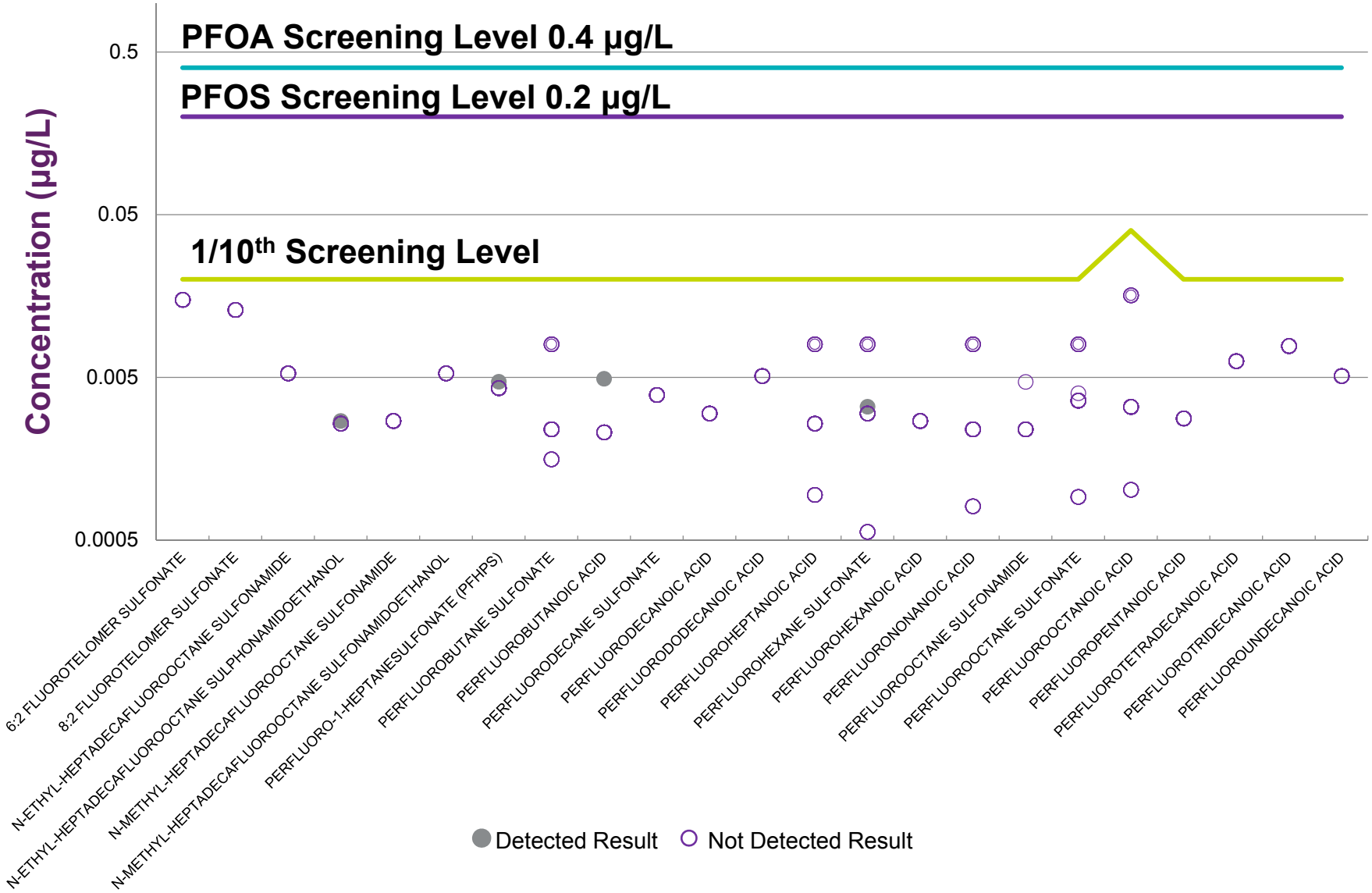
- **No Teflon** in sampling pumps, equipment, or sample containers
- **No Gore-Tex, Tyvek**, waterproof clothing
- **Natural-based products** for sunscreens, bug spray, personal care products
- **Use of vegetable oil** instead of standard drilling equipment grease

Differentiate cross-contamination from site conditions

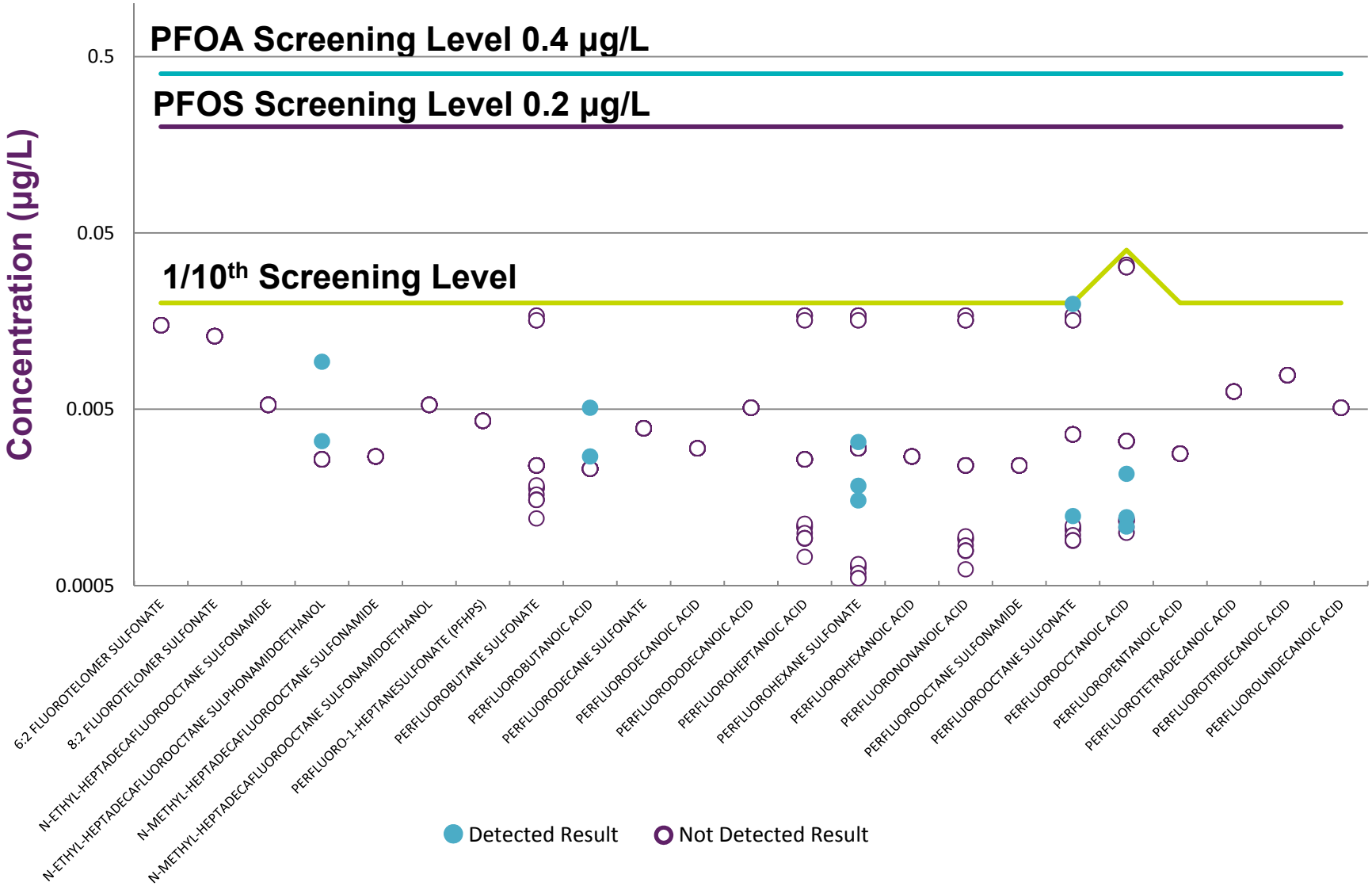
Demonstrating Method Performance
Laboratory Control Sample Recoveries



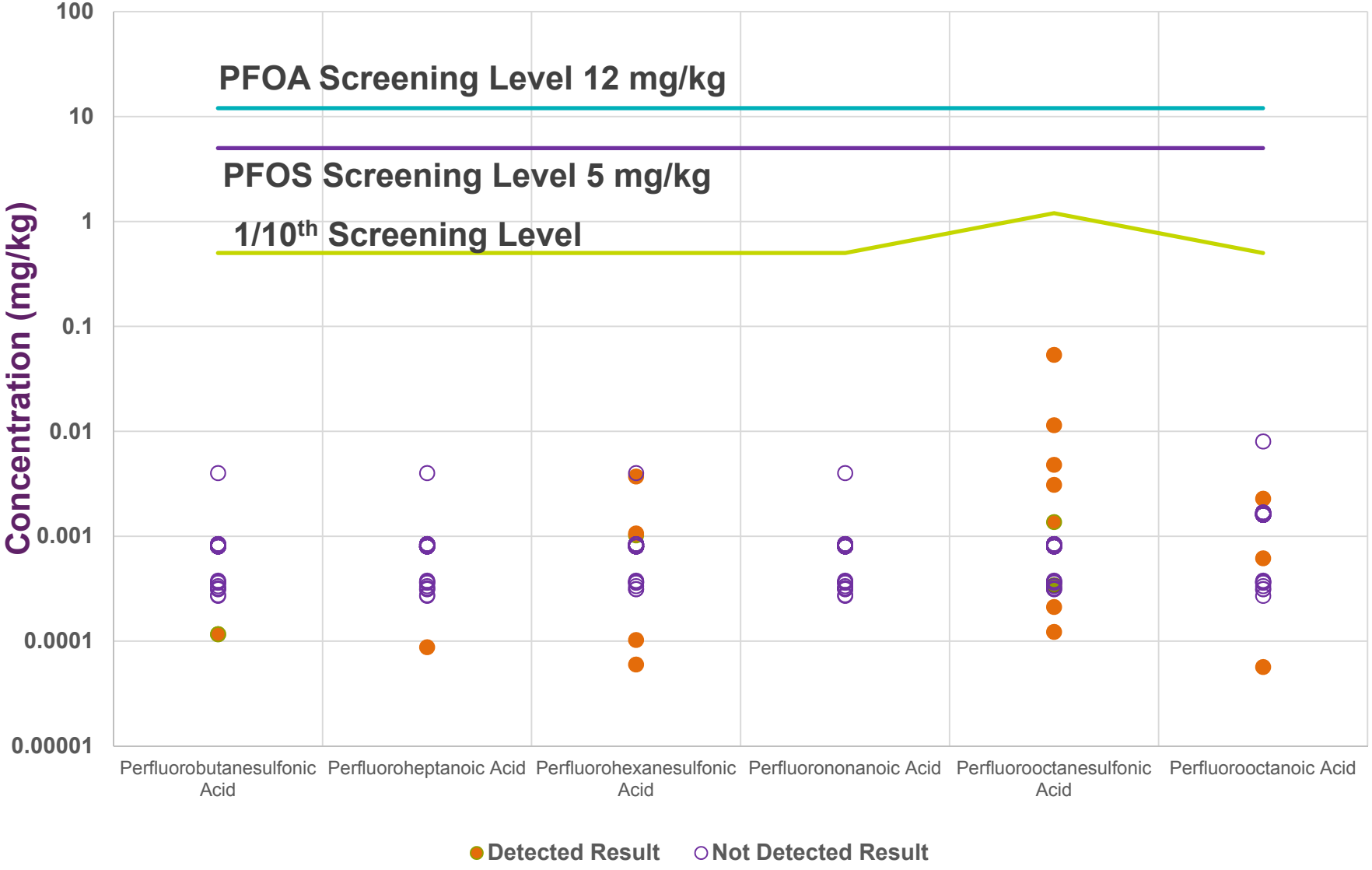
Managing Ambient Contamination
Laboratory Blanks



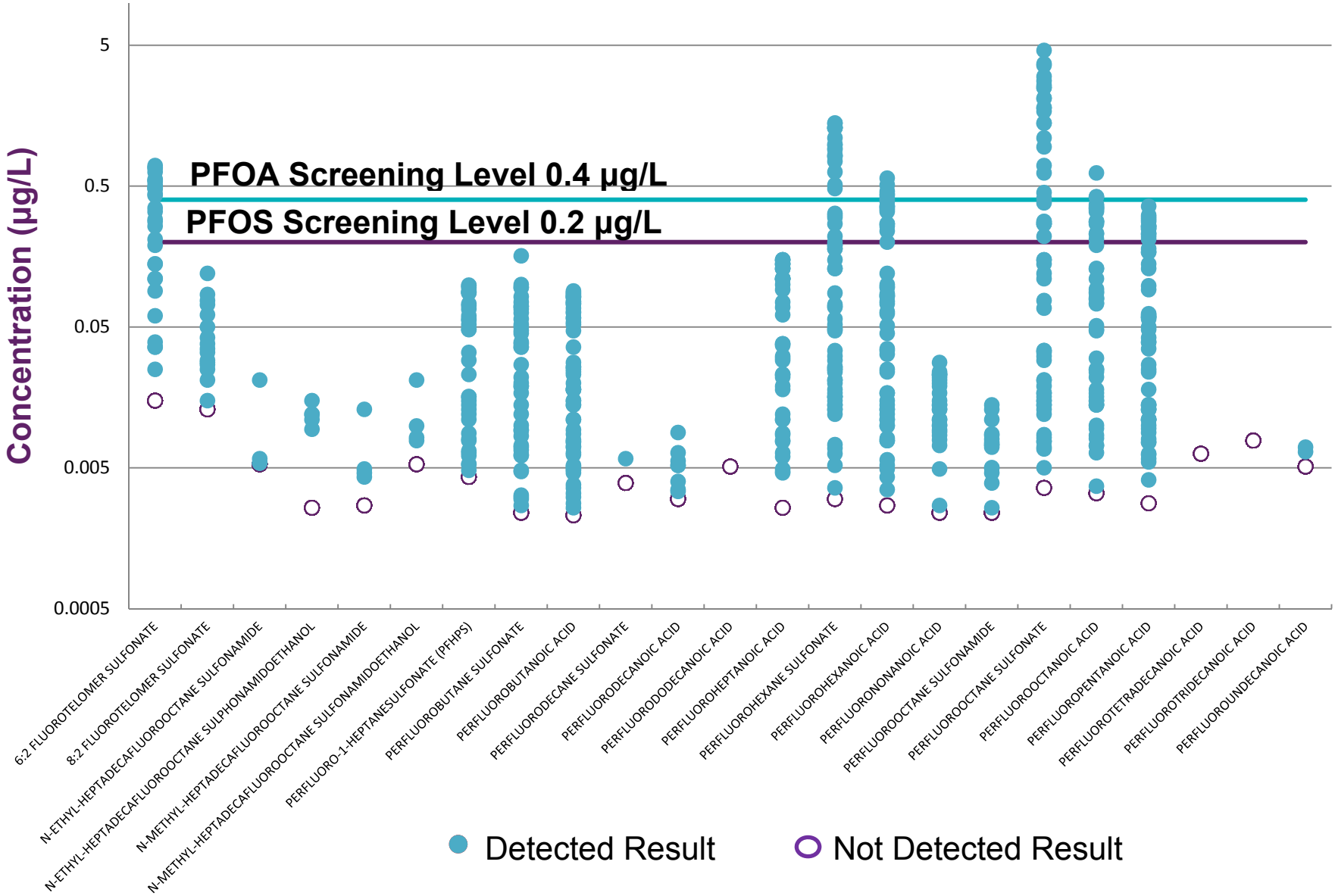
Managing Ambient Contamination
Field/Equipment Blanks- Water Samples



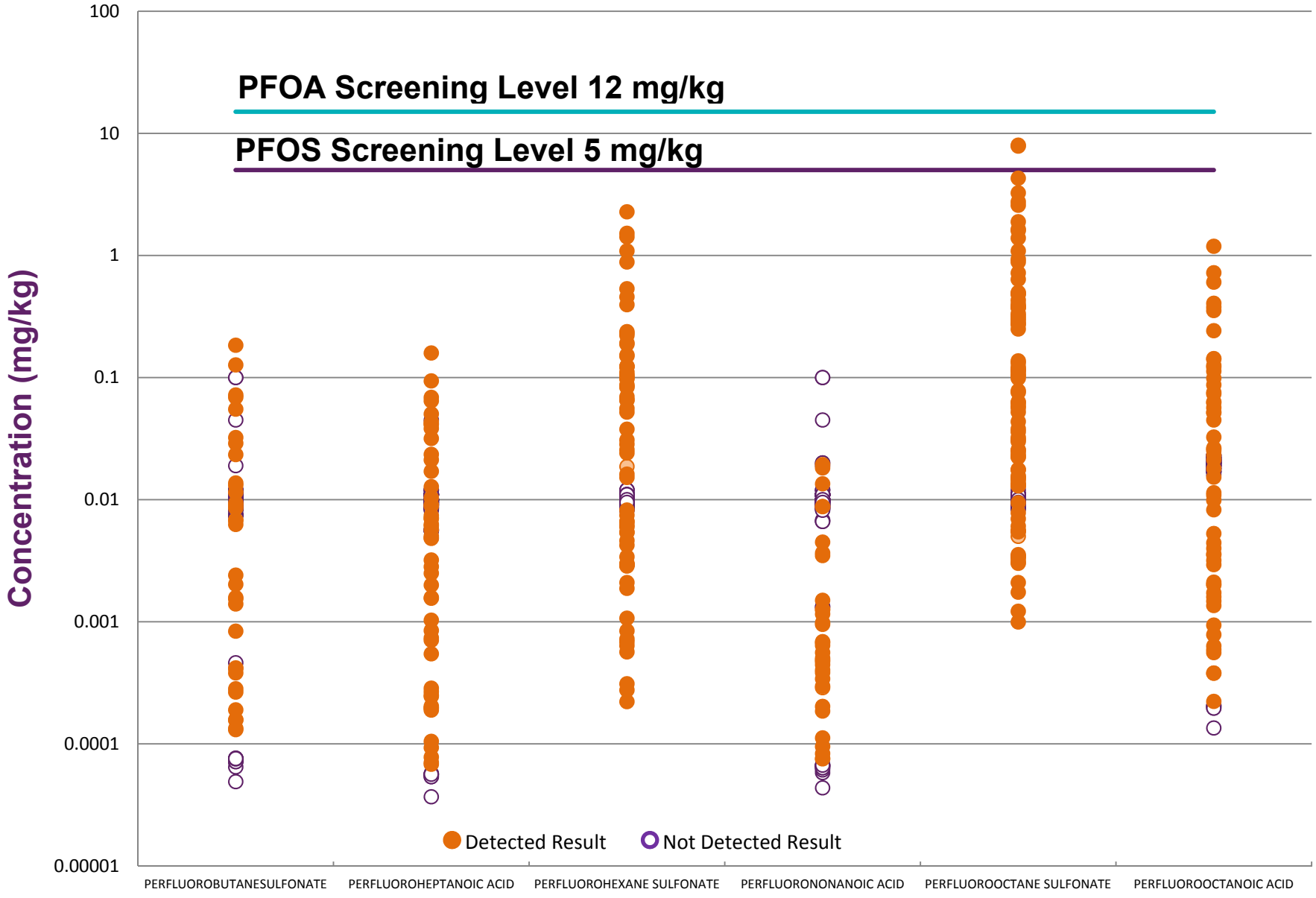
Managing Ambient Contamination
Field/Equipment Blanks- Solid Samples



Aqueous Sample Results



Solid Sample Results



Analytical Considerations

Sources of Uncertainty in PFC Monitoring

The Good News:

- Performance Evaluation samples within acceptance ranges
- LCS data across methods typically within 70-130%
- Blanks have been mostly ND or trace levels
- Inter-laboratory split samples are generally comparable (typically <40%)

Dataset control is mostly within acceptance limits

Sources of Uncertainty in PFC Monitoring

The challenges –

- **Relatively new method** for most commercial labs
- **Differences in procedures** between labs (performance-based methods) and lack of Round Robin PE programs
- **Lack of multi-laboratory validation studies**
- Container recommendations may not be correct
- **Growing target compound list** with limited standards
- The "full" 20+ target compound list covers a wide range of physicochemical properties – in a single extraction/analysis

Further study needed for improved PFC analysis

Sample Container Recommendations

Reference methods differ *slightly:*

- **EPA Method 537** – *"Due to potential adsorption of analytes onto glass,* ***polypropylene containers*** *were used for all standard, sample and extraction preparations."*
- **ASTM D7979-15** – *"Grab samples are collected in* ***polypropylene*** *containers"*
- **ASTM 7878-14** – Soil, not water method, but: *"Grab samples are collected in* ***glass or polypropylene containers****."*

Is polyethylene OK or not, and similarly for glass?

Are polypropylene containers really best?

Further modifications to recommendations are likely

Representative Samples

Sample **stratification/ sediment** issues

- How to subsample?
- Decant?
- Whole volume analysis?
- Screening levels are in **ppm for soils ppb for water**

Photo courtesy of
Axys Analytical Services, Ltd.

Project decision: decant and analyze water for **groundwater** investigations (separate soil sampling, different screening levels, limited issue). Approach will differ for other sample types and DQOs.

Consider DQOs and data needed for project decisions

Solid Matrix Extraction Procedures

There are **3 different solvent systems** used by labs**:**

- **Extraction with methanol only** (no reference method)
- **Extraction with alkaline methanol** (ASTM Method D7968 – 14)
- **Pretreatment with caustic followed by extraction with a 50:50 acetonitrile/methanol mixture** (EPA Draft Procedure for Analysis of Perfluorinated Carboxylic Acids and Sulfonic Acids in Sewage Sludge and Biosolids by HPLC/MS/MS, December 2011).

Initial performance data from all labs was acceptable

Limited data available to assess method differences

Solid Matrix Extraction Procedures

- EPA Region expressed concern over possible inter-lab differences and **potential low biases** related to the different procedures
- **Vista Labs** performing a limited study **comparing soil extraction procedures** for 23 PFCs
- Findings will be presented at Fluoros Conference July 2015

Project decision –require ASTM or EPA extraction procedure and not allow MeOH only extraction

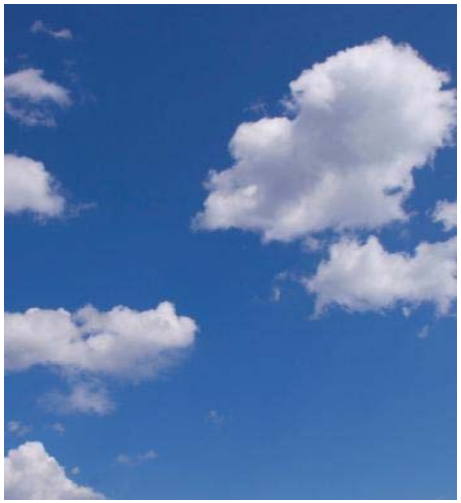
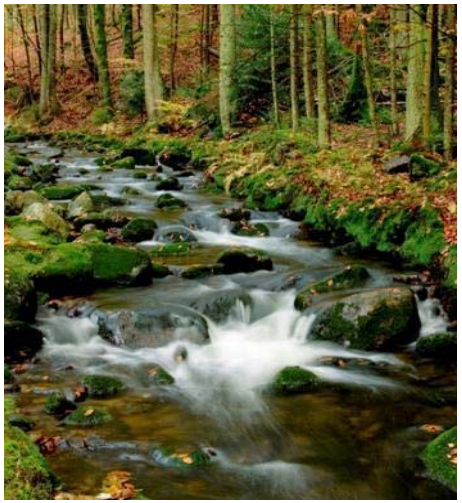
Analytical (Determinative Method) Uncertainty

- Composition and purity of standards
- Calibration Methods
- Use of internal standards
- Growing target compound list
- Performance-based method

Specific analytical techniques may be preferred for challenging matrices or lower detection limits

Next Steps for PFCs

- Public awareness is growing and regulatory action is increasing
- Confirmed use of AFFF shows high likelihood of PFC presence
- Analytical programs need further refining for data comparability
- Need better vendor support of standards and expanded compound lists
- Need to expand laboratory capability and capacity

Questions?

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