PFAS are Everywhere and Now We Have a Validated Multi-matrix Method 1633 to Find Them

Overview of the Multi-Laboratory Validation of Method 1633

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Disclaimer

The views expressed in this presentation are mine and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

PFAS Method 1633 Background

- Partnership with Department of Defense's (DoD) Strategic Environmental Research and Development Program
  - DoD funded and managed both single and multi-laboratory validation studies of the method, EPA OW and OLEM provided review
- The goal was to provide EPA OW with the documentation needed to consider publication of this method as a CWA method
  - OLEM plans to leverage the validation data to support an SW-846 method
- Based on an SOP originally developed by SGS AXYS
  - Single-laboratory validated in 2021 by SGS AXYS with DoD and EPA

Massive Undertaking

- 10 Participant Laboratories
- 3 Data Validation Companies
- 3rd party sample preparation, spiking, and shipping
- Multiple contractors for data management, lab management, data validation management, statistical analysis, report writing, etcetera
- Thank you to all who participated!
  - This effort would not have been successful without the contributions of hundreds of people who participated from the laboratories, government contractors, and government employees.

Waters Selection and Acquisition

- 7 Wastewaters Collected
  - Hospital, POTW Influent, bus washing station, chemical plant effluent, paper and pulp mixed effluent, POTW effluent, and ASTM synthetic WW*
- 3 Surface Waters
  - Ohio lake water, Washington river water, and Washington seawater
- 3 Groundwaters
  - Midwest, southwest, and Colorado sources
- These waters were tested for PFAS and water quality parameters
  - Very diverse mixture of waters tested in the study

Solids Selection and Acquisition

- 3 Soils
  - From Montana, New Mexico, and Tennessee
  - Diversity of organic content
- 3 Sediments
  - Freshwater silty-sand, sandy, and marine silty-sand

- Soil and sediments tested for PFAS and percent sand/silt/clay fractions, grain size, pH, and total organic carbon (TOC)
- 3 Biosolids
  - 2 mid-atlantic (1 dry and 1 wet), 1 west coast
  - Tested for pH

Leachate and Tissue Selection and Acquisition

- 3 Landfill Leachates
  - 3 landfills: municipal, military, primarily ash
  - Tested for water quality parameters
- 3 Aquatic Tissues
  - Freshwater low-lipid fish – walleye
  - Marine high-lipid fish - king salmon
  - Shellfish - butter clams

Matrix characterization and spiking

- DoD hired Waters ERA™ to homogenize, characterize, and spike the samples
  - Third-party sample spiking is not a requirement for CWA method validation, but it reduces the potential for variability between laboratories
- Each matrix was analyzed by SGS AXYS to determine how much PFAS was already in each sample matrix
  - Each sample was assigned a ‘high’ and ‘low’ spike for aqueous, landfill leachate, solids, biosolids, and aquatic tissue
  - The low spike was ignored from some analytes in some samples because that PFAS analyte was already present at comparable levels

Laboratory Analysis!

Special thank you to the participant laboratories!

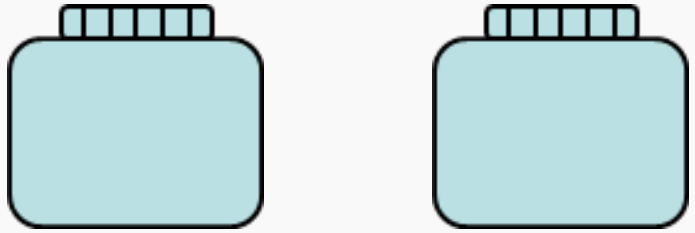
- Alpha Analytical, Mansfield, MA
- Battelle Memorial Institute, Norwell, MA
- California EPA, Pasadena, CA
- Eurofins Lancaster, Lancaster, PA
- Eurofins-Test America (ETA) West Sacramento, West Sacramento, CA
- GEL Laboratories, Charleston, SC
- Pace Analytical, Baton Rouge, LA
- Maryland Department of Health, Baltimore, MD
- SGS North America Orlando, FL
- Vista Analytical Laboratory, El Dorado Hills, CA

Aqueous Extraction/Preparation

- Sample size
  - 500 mL water
  - 100 mL leachate
- Holding Time
  - 28 days @ 0-6˚ C
  - 90 days @ ≤ -20˚ C
- Measure TSS
- Invert sample to homogenize
- Sample volume determined by weight
- Spike with EIS
- Check pH
- Ready for SPE
- Carbon cleanup
- Spike with NIS
- ~1 mL of extract for analysis

Solids Extraction/Preparation

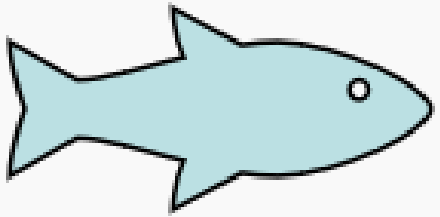
- Sample size
  - 5 g dry weight (soil and sediment)
  - 0.5 g dry weight (biosolids)
- 90 days @ 0-6˚ C or ≤ -20˚ C
- Measure % solids
- Mix with stainless steel spoon
- Remove rocks, invertebrates, foreign objects
- Transfer to centrifuge tube
- Spike with EIS
- Solvent extraction and first carbon cleanup
- Evaporation and reconstitution
- Ready for SPE and cleanup
- Spike with NIS
- ~1 mL of extract for analysis

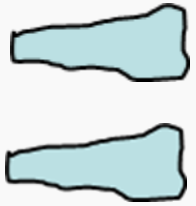


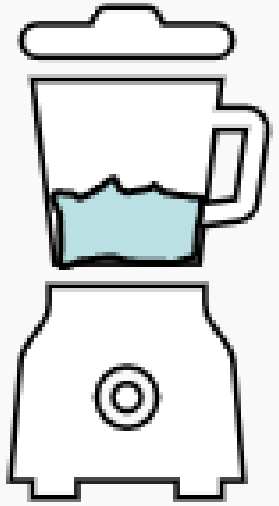
Tissue Extraction/Preparation

- 2 g homogenized tissue
- 90 days @ ≤ -20° C
- Transfer to centrifuge tube
- Spike with EIS
- Solvent extraction
- Carbon cleanup
- Evaporation and reconstitution

- Ready for SPE and second carbon cleanup
- Spike with NIS
- ~1 mL of extract for analysis







LC/MS/MS Analysis

- Individual PFAS analytes are identified through peak analysis of the quantification and confirmation ions, where applicable
- Quantitative determination of target analyte concentrations is made with respect to an isotopically labeled PFAS standard
- 40 analytes
- 24 extracted internal standards
- 7 non-extracted internal standards
  - Only determine EIS recovery, no effect on analyte quantification

Multi-Lab Analysis

- 9-point initial calibration
  - Each laboratory performed 3 initial calibrations
  - All labs achieved 20% RSE
  - Some had to eliminate a high or low calibration point for a specific analyte
- Initial Demonstration of Capability (IDOC)
  - Initial precision and recovery study (4 mid-point blank spikes)
  - MDL study
  - Different IDOC for aqueous, solids, and tissues

Multi-Lab Analysis (Cont.)

- Each laboratory analyzed 7 samples for each matrix received
  - 1 unspiked, 3 low spikes, and 3 high spikes
  - If a lab ran all the wastewater (6), surface water (3), and groundwater (3) matrices; then the laboratory would have run (6+3+3)X7 = 84 samples
  - The laboratories that ran all 8 matrix types ran 189 samples
    - Wastewater (6), surface water (3), groundwater (3). landfill leachate (3), soil (3), sediment (3), biosolids (3), and aquatic tissue (3) matrices
    - (6+3+3+3+3+3+3+3)X7 = 189

Data Review

- DoD employed three data validation companies review every laboratory data package received
  - Approximately 200,000 pages of data packages, an 80-foot stack of paper
  - Each sample has 40 analytes, 24 EIS results, 7 NIS results
  - 200,727 results were submitted by the laboratories
    - Aqueous samples: 88,372
    - Soil and sediment: 56,339
    - Landfill leachate: 13,205
    - Biosolids: 13,996
    - Aquatic tissue: 28,815
  - The data validation effort took over a year to complete
  - EPA reviewed all the data review reports and spot-checked data packages

Data Management and Statistical Analysis

- Exa Data and Mapping Services, Inc. was hired to compile all of the data into a functional database
- Institute for Defense Analyses and DoD performed statistical analysis of the data
- EPA and GDIT performed a parallel statistical analysis to determine QC criteria

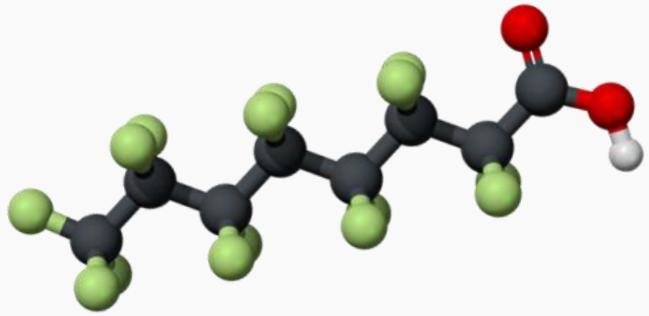
Report Writing

- DoD and EPA initiated the single-laboratory validation efforts in 2019
- Final Method 1633 and the Multi-Laboratory Validation Study Report posted on January 31, 2024

  https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

  – The Multi-Laboratory Validation Report is available in 4 volumes, by matrix

  – 667 Pages total



Method 1633 MDL Values

- Method Detection Limit – Blank Calculation (MDL_b)
  - MDL_b values rarely impacted the MDL for any laboratory
  - The pooled MDL values were almost entirely calculated from the MDL_s values
- Pooled Method Detection Limit (MDL)
  - Most aqueous values were below 1 ng/L
  - The highest: NMeFOSE - 3.8, NEtFOSE - 4.8, 7:3FTCA - 8.7, and 5:3 FTCA - 9.6 ng/L
  - Leachate MDLs are assumed to be about 10 times higher
  - Most of the solid MDLs were below 0.2 ng/g
  - The highest: 5:3 FTCA – 0.86 ng/g, and 7:3 FTCA – 0.87 ng/g
  - Biosolid MDLs are assumed to be about 5 times higher
  - Most of the tissue MDLs were below 0.4 ng/g
  - The highest: NEtFOSE – 1.77, 7:3FTCA – 2.38, and 5:3 FTCA – 2.02 ng/g

Method 1633 MLV (cont.)

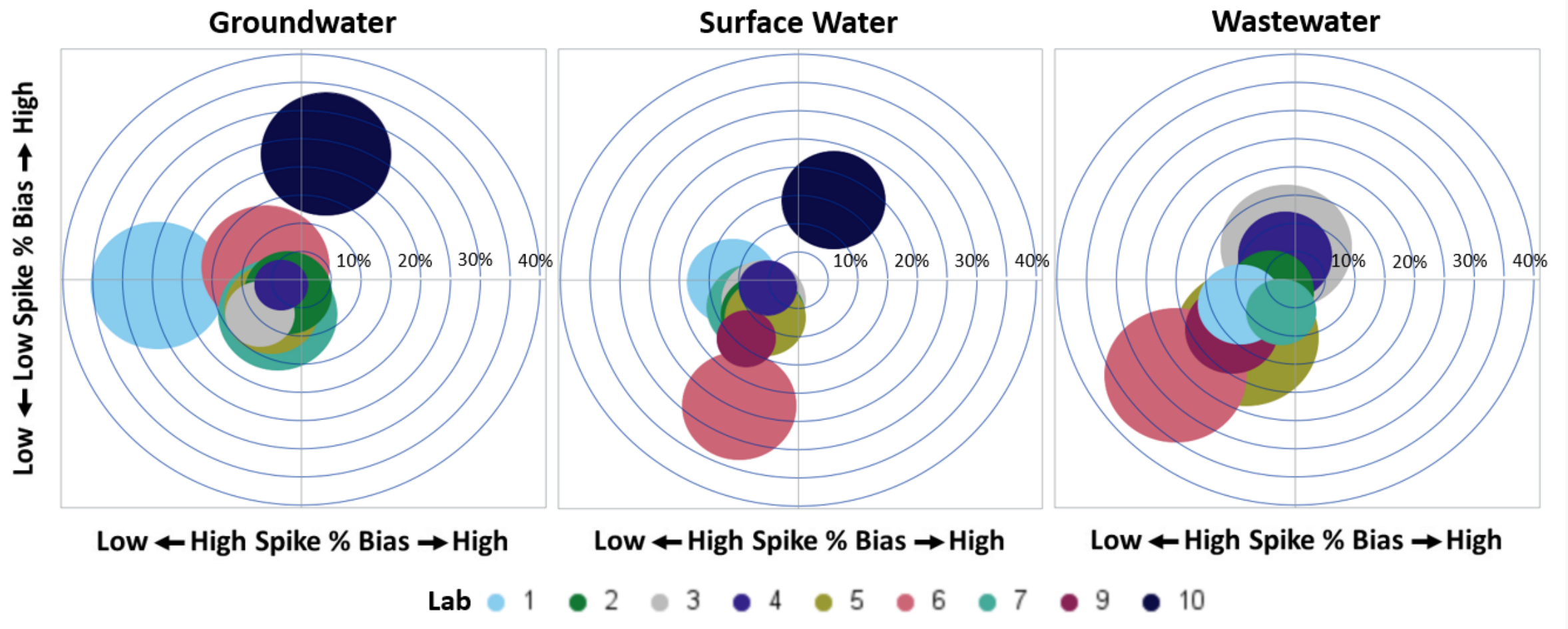
- Ongoing Precision and Recovery (OPR) Low-Level OPR (LLOPR)
  - The performance was about the same for the OPR and LLOPR, so the data were combined and used to develop a single set of criteria
  - Most criteria are inclusive of the highest and lowest observed data point from all 10 laboratories
  - No criteria are more stringent than 70-130%
  - The vast majority of the analytes were able to meet a 50-150% criteria for OPR and LLOPR analysis

Method 1633 MLV (cont.)

- 24 Extracted Internal Standards (EIS)
  - Single set of EIS criteria made from only matrix samples (no blank spikes)
  - Used a non-parametric approach (p1 and p99) and professional judgement (e.g., eliminate the EIS compound recoveries from 1 to 2 laboratories for a specific parameter)
  - No criteria are more stringent than 40-130%
  - Lower aqueous limits: 15 at 40%, 1 at 30% ($^{13}C_7$-PFUnA), 1 at 25% (D_5-NEtFOSAA), 6 at 10% ($^{13}C_2$-PFDoA, $^{13}C_2$-PFTeDA, D_3-NMeFOSA, D_5-NEtFOSA, D_7-NMeFOSE, and D_9-NEtFOSE), and 1 at 5% ($^{13}C_4$-PFBA)
  - Upper aqueous Limits: 17 at 130%, 3 at 135%, 1 at 170% (D_3-NMeFOSAA), 2 at 200% ($^{13}C_2$-4:2FTS and $^{13}C_2$-6:2FTS), and 1 at 300% ($^{13}C_2$-8:2FTS)
  - The trends were similar for the other matrices. Fish tissue was the most challenging matrix.

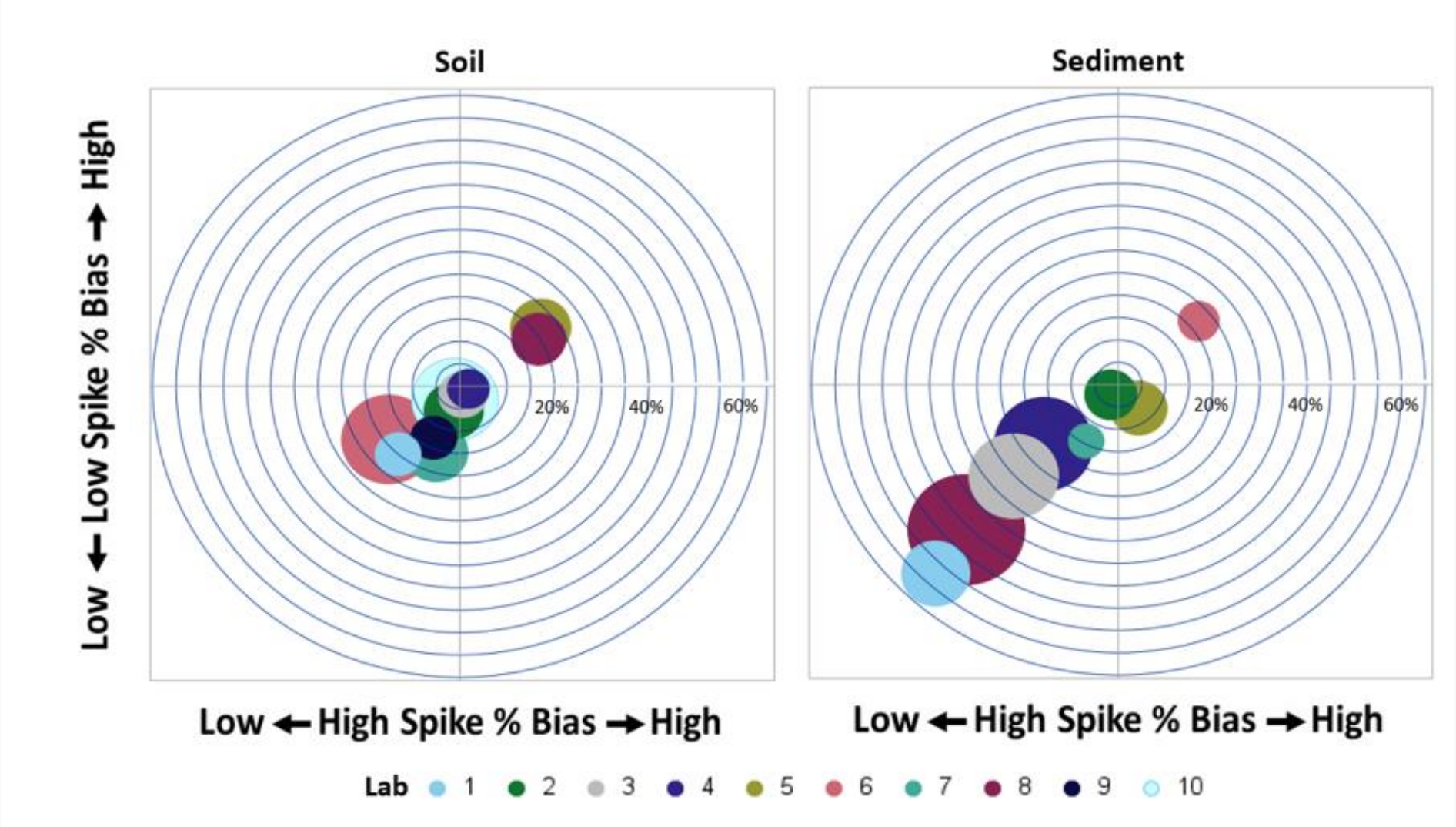
Method 1633 MLV (cont.)

- Aqueous Matrix Spike Results



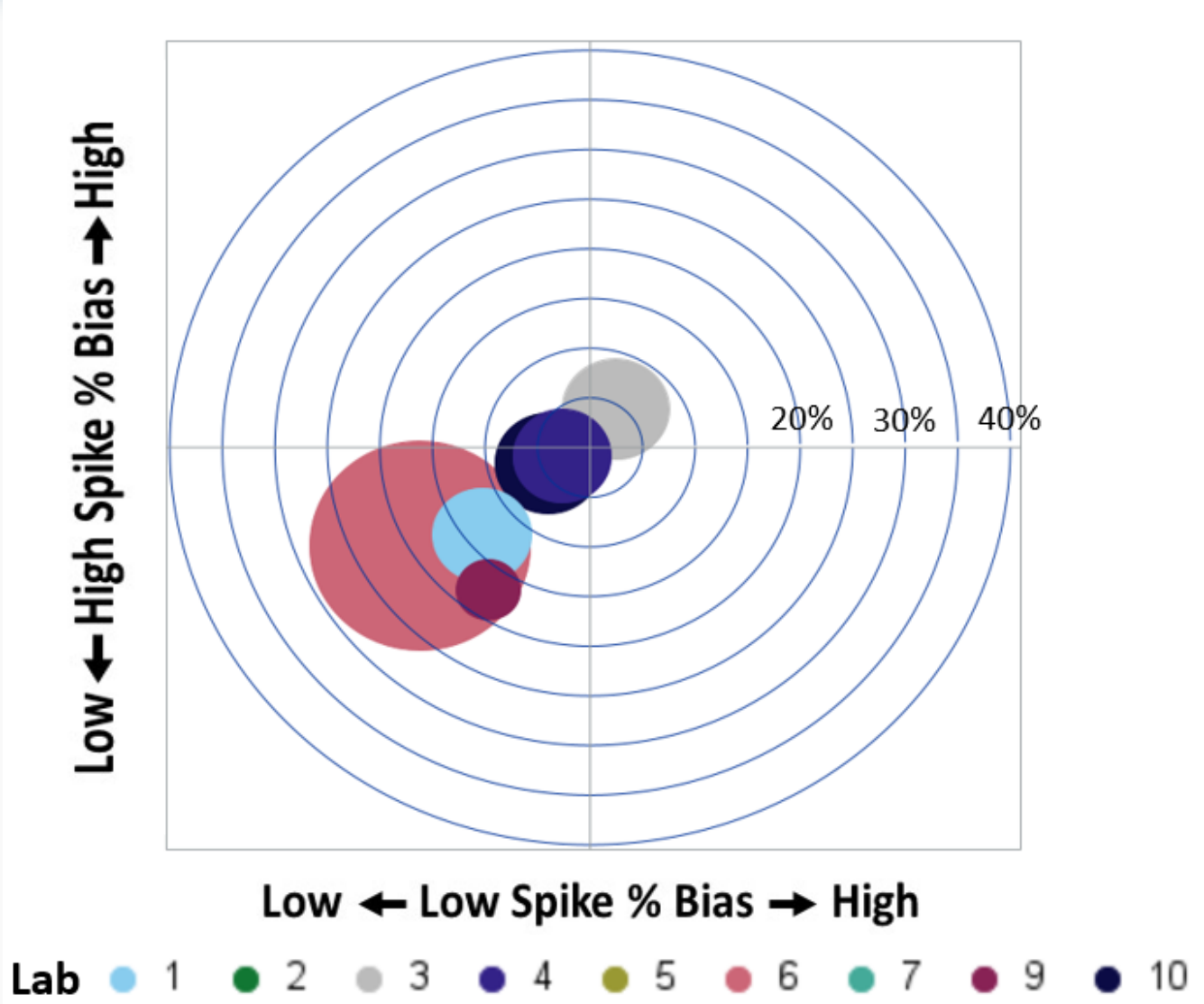
Method 1633 MLV (cont.)

Solid Matrix Spike Results



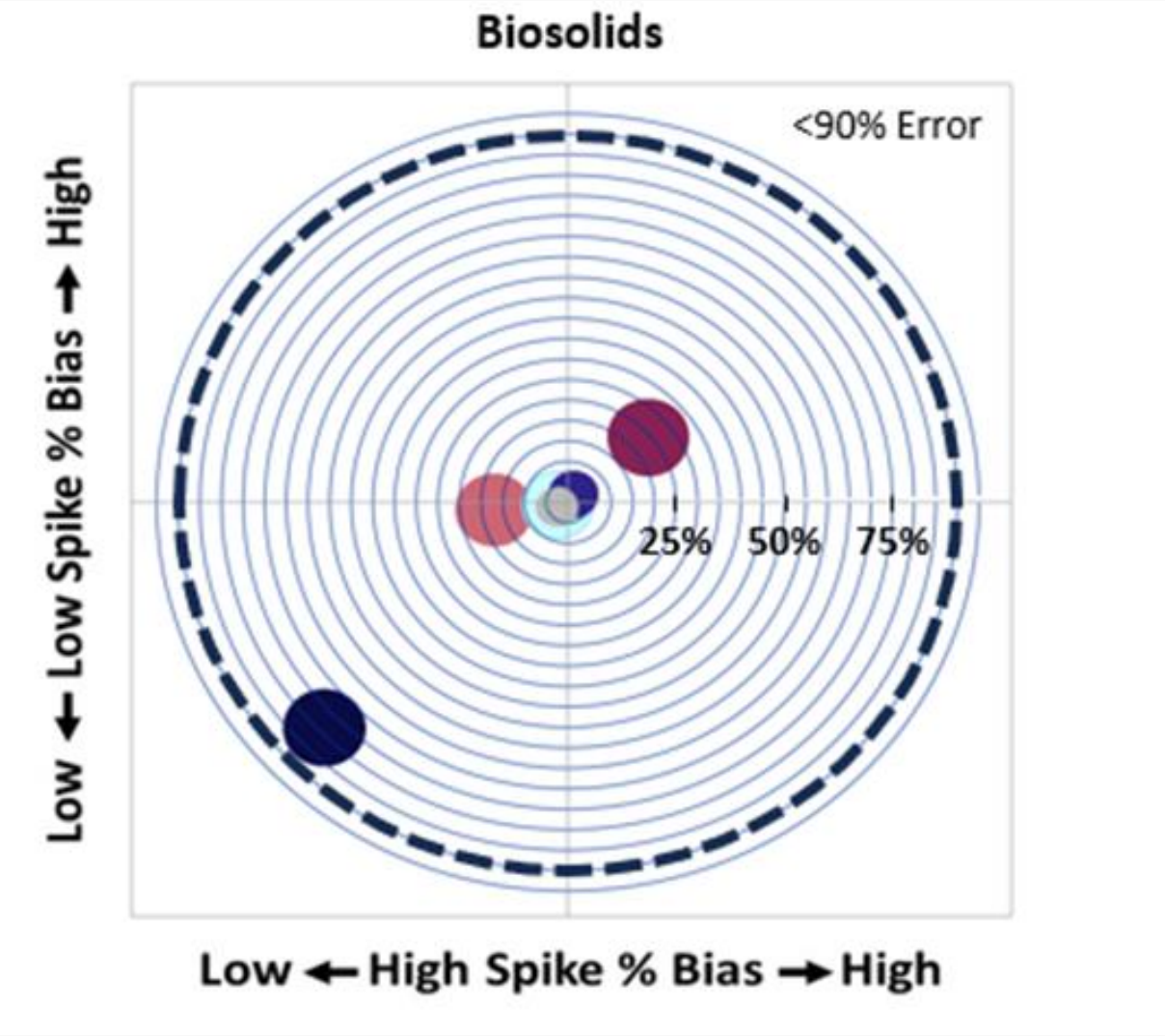
Method 1633 MLV (cont.)

Landfill Leachate Matrix Spike Results



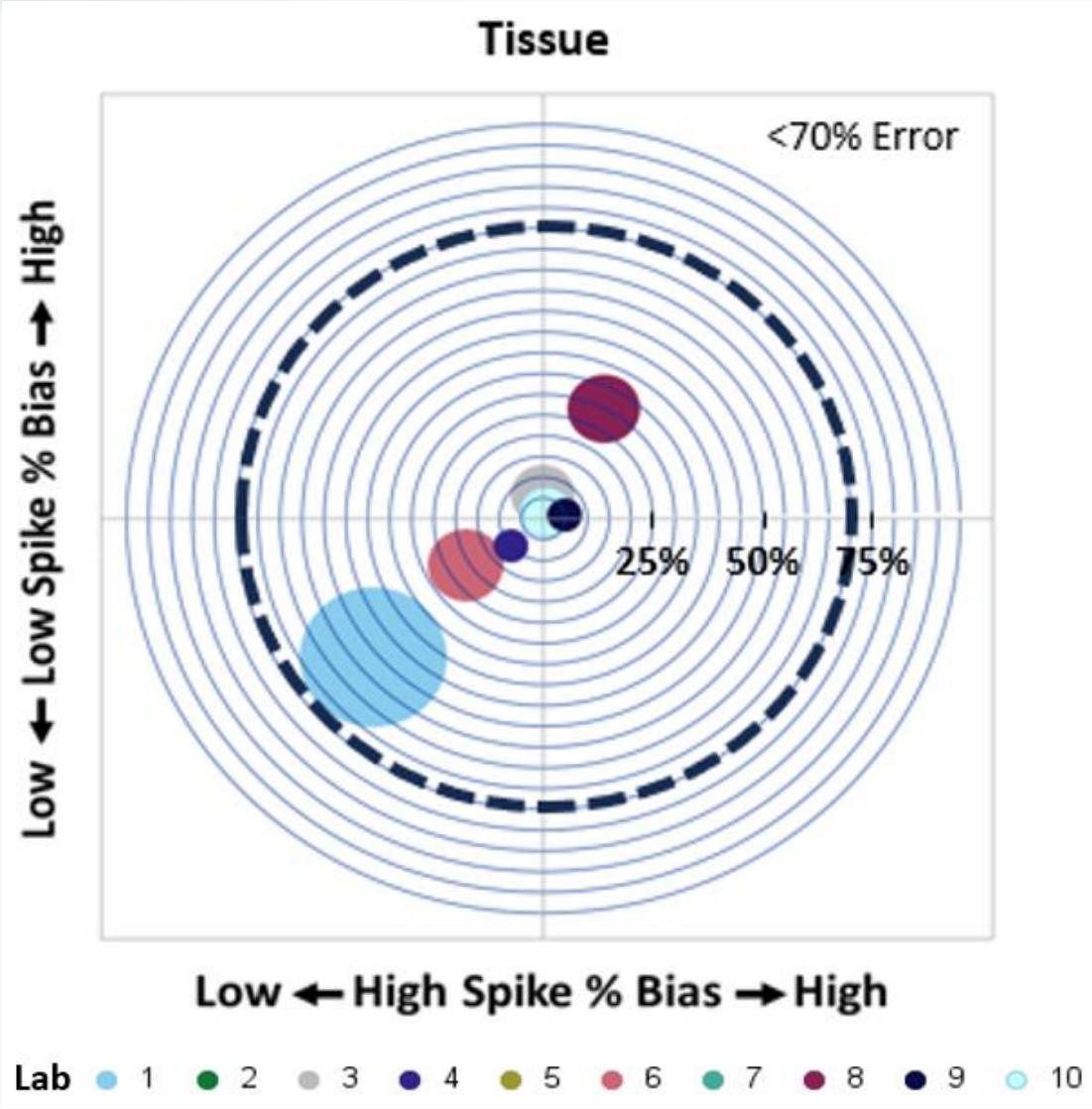
Method 1633 MLV (cont.)

Biosolid Matrix Spike Results



Method 1633 MLV (cont.)

- Tissue Matrix Spike Results



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