Public and Private Environmental Laboratory Collaboration for Oil and Gas Regulatory and Industry Dissolved Gas Methodology Study – Part 1

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Work sponsored by The Marcellus Shale Coalition (MSC)

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The Problem

- Public concern
- Data variability observed by MSC members
- Several published procedures for dissolved light gases
- No US EPA-published method
- Lack of standardization

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Milestones and Goals

- Verify (2015) high variability and uncertainty – then minimize – for the analysis of methane and other dissolved light gases.

- Refine/develop a light gas method that reduces uncertainty and capability of generating data of known quality for decision making.
  - Insert sufficient technical detail into the multi-laboratory validated method so that the published method can be employed across community.

- Provide information and validation study results to US EPA for the adoption of the light gas method.

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P1-P5 Study Sponsors, Executor, and Participants

- Select Members of the MSC Dissolved Methane Method Work Group
- Environmental Standards, Inc.
- Environmental Services Laboratories (ESL), Indiana, PA
- LGC Standards (LGC), Manchester, NH, ISO-accredited performance test (PT) provider for certified reference materials (CRMs)
- 23 Participating Laboratories total across all phases

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Private Partnership

- All laboratory results were kept anonymous.
- All laboratories performed the analyses and reported data *pro bono.*
- P1 answered 109 questions.
- P1 – P3, shared their SOPs, and provided details on instrumentation, calibration, steps they had learned to improve the precision, and the accuracy of the method with the CRM.

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Early Laboratory Testing Phases

P1 (early 2015)

Two groundwater samples across 15 laboratories including one government laboratory.

P2 (October 2016)

Four blind reference standards across 15 laboratories including one government laboratory.

P3 (January 2018)

Announced reference standard across eight non-reference (previously low) laboratories and three reference laboratories.

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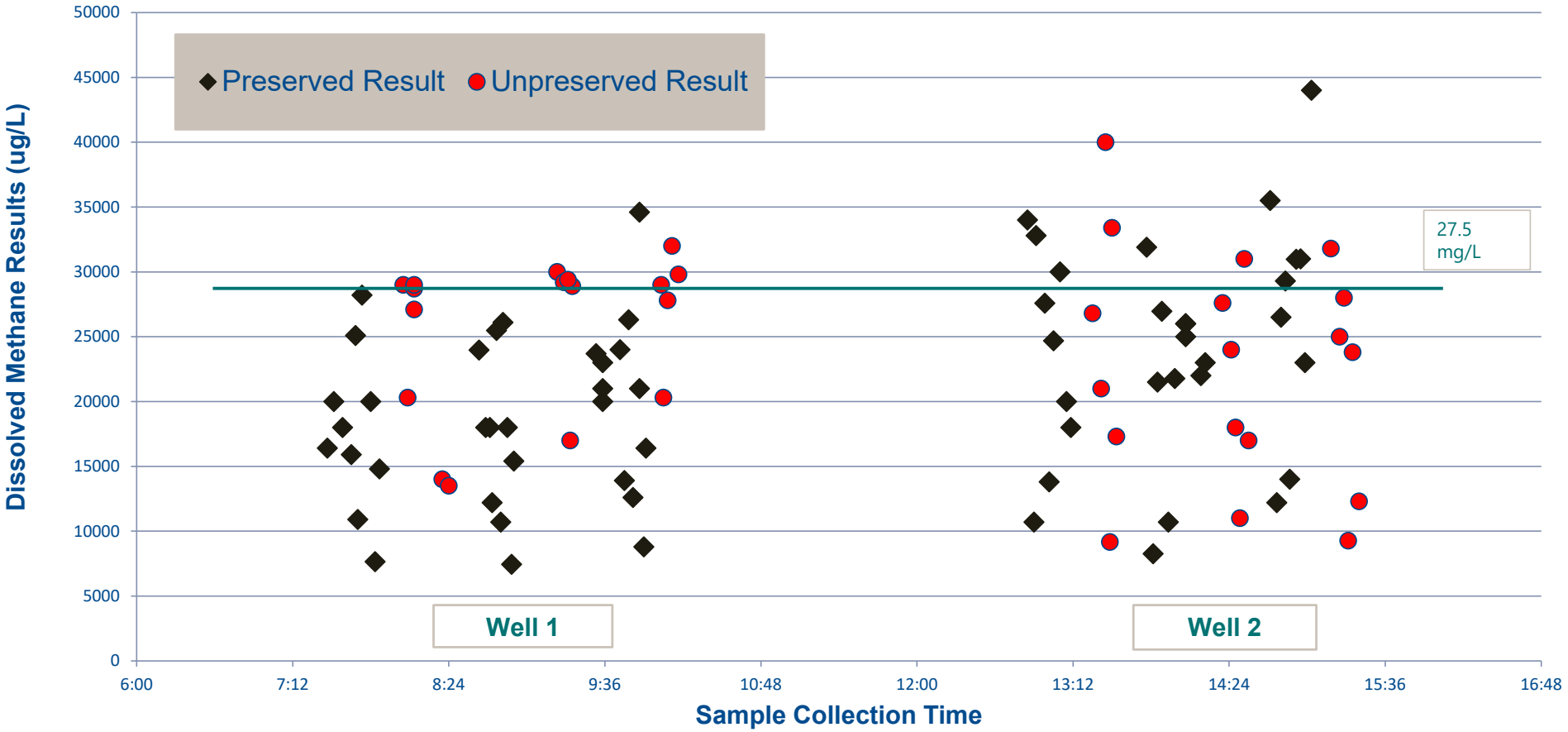
P1 (Groundwater)



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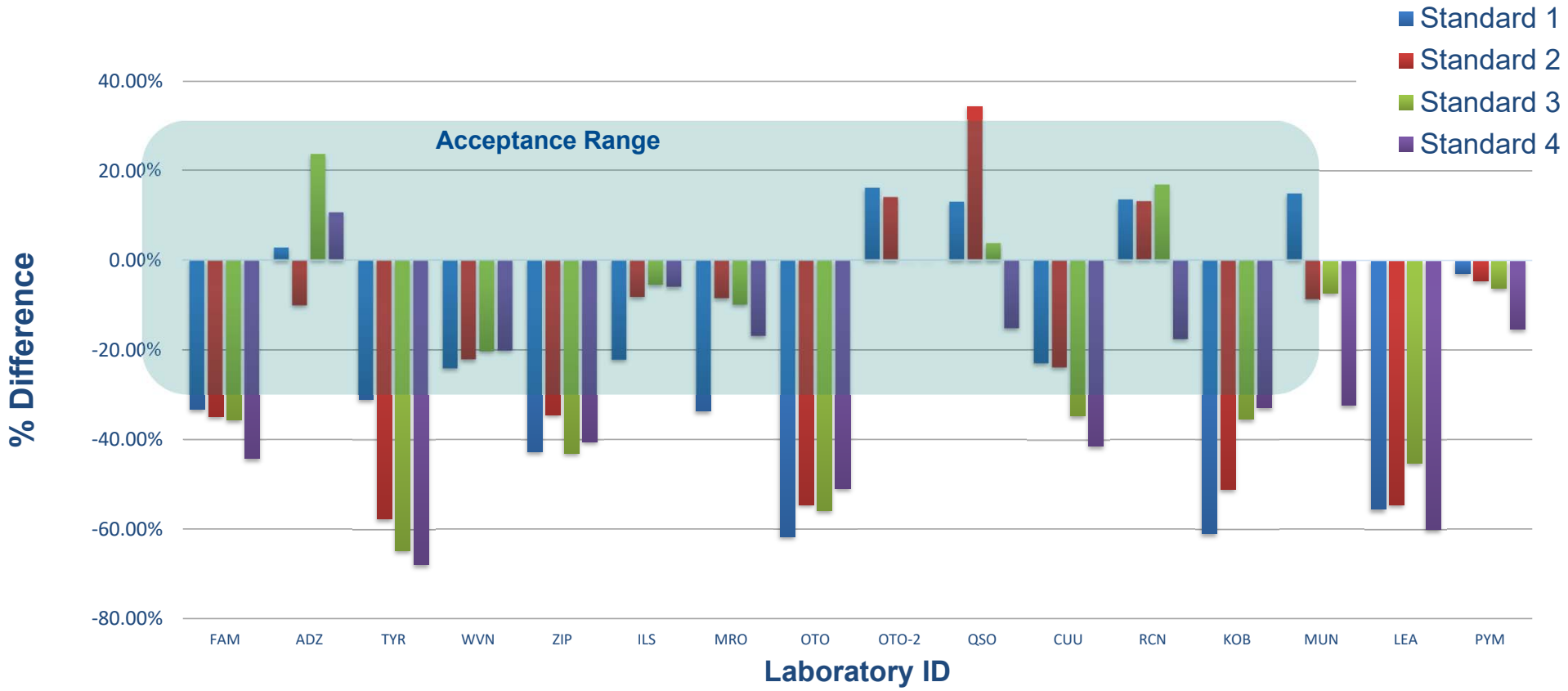
P2 - Results



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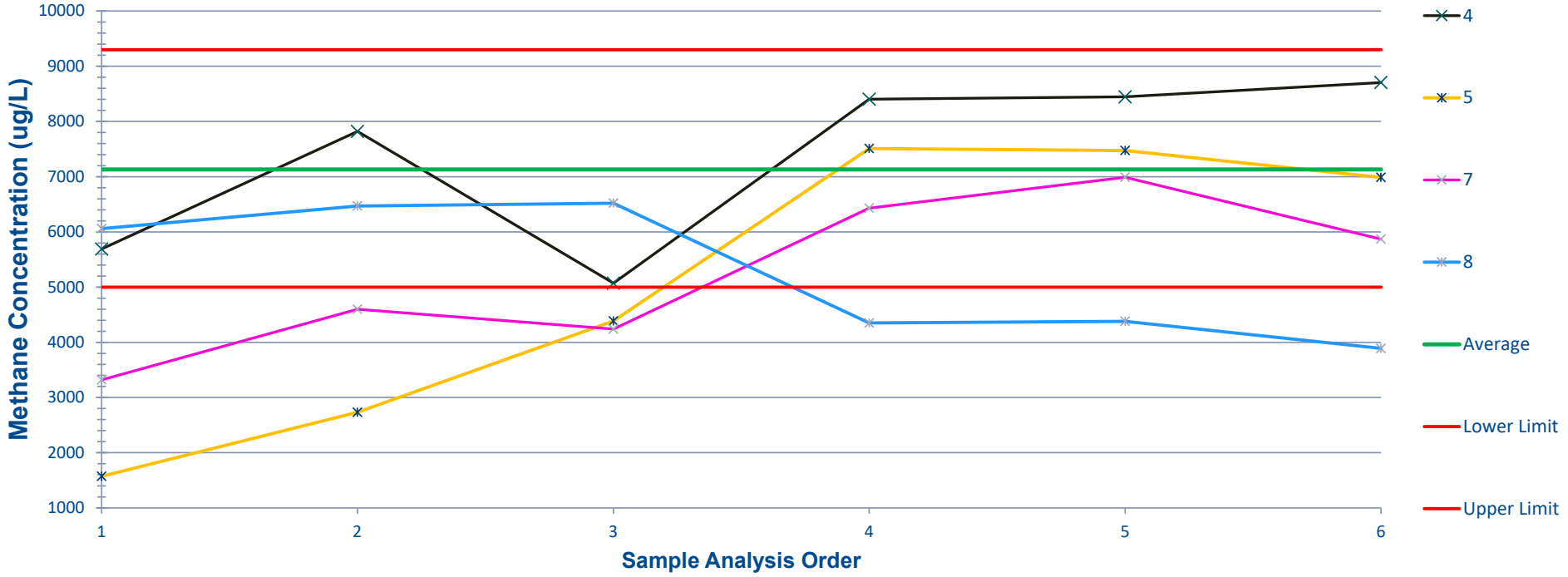
P3 Non-reference Laboratories Self Diagnosed, Some Dramatic Improvements



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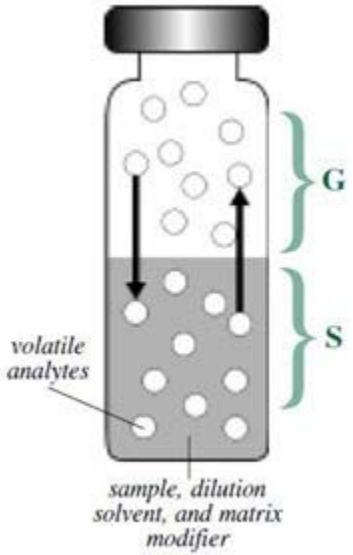
Self Diagnosis Modifications (P3) that Improved Recovery

- Handling calibration standards and samples the same.
- Performing dilutions at refrigerator temperature.
- Increasing sample warmup plus extending vortex or shaking times to ensure equilibrium.
- Sample transfer – eliminating the bubbles!
- Keeping sample pressure consistent.
- Minimizing septa piercing as much as possible.
- These details were critical to optimize the P4 procedures.



Method Validation Phases

P4 (Spring 2019)

Draft new procedure for ultimate published method.

P5 (Fall 2019)

Inter-laboratory (11) validation of method - included CRMs.

Phase 4 Procedure/Method

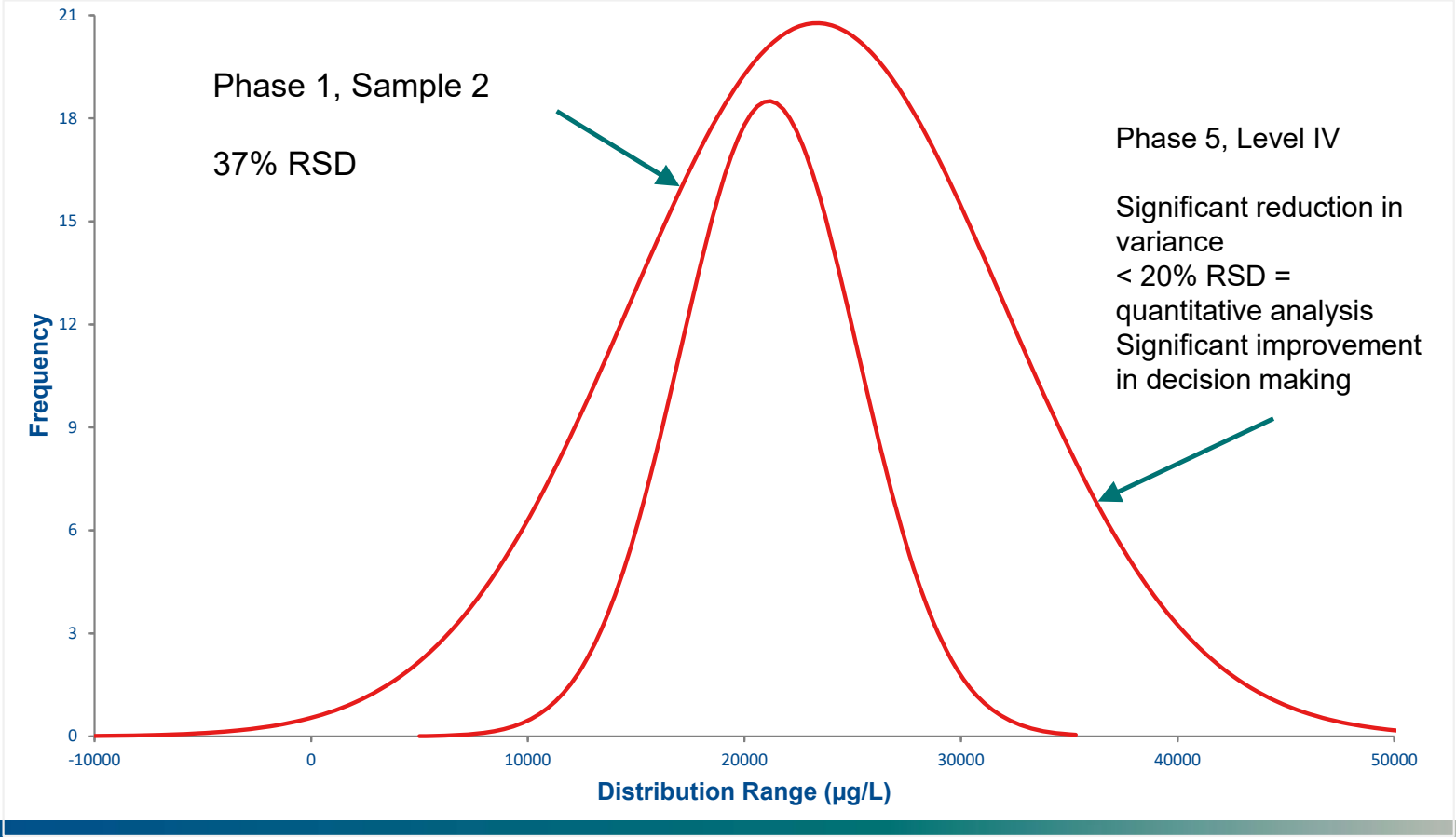
- Static Headspace
- Three calibration options using gas chromatograph (GC) and flame ionization detector (FID), thermal conductivity detector (TCD), or mass spectrometer (MS)
  - Direct gas injection (RSK-175 approach)
  - Saturated aqueous standards (most closely matrix match)
  - Prepare in vial with headspace (predominant)
- Equilibration time and steps prescriptive
- QC
  - Optional internal standard (IS), initial calibration (ICAL) using average response factor (RF) or relative error/relative standard error (RE/RSE) for linear/quadratic, continuing calibration verification (CCV) every 10 samples, retention time (RT) criteria
- CRM incorporated as accuracy assessment

P5 – Validation Study Design

- Reference Standards (methane only)
  - L01: Sample at Level 1: < 500 µg/L, (triplicates).
  - L02: Sample at Level 2: 3,000 – 8,000 µg/L, (triplicates).
  - L03: Sample at Level 3: 8,000 – 15, 000 µg/L, (triplicates).
  - L04: Sample at Level 4: >15,000 µg/L, (triplicates).

- LGC CRMs (four analytes: methane, ethane, ethene, propane [MEEP]):
  - C01: 4,000 – 8,000 µg/L, report a single analysis.
  - C02: 4,000 – 8,000 µg/L, report a single analysis.
  - C01 ≠ C02 (Youden Pairs)

Improvement !!!



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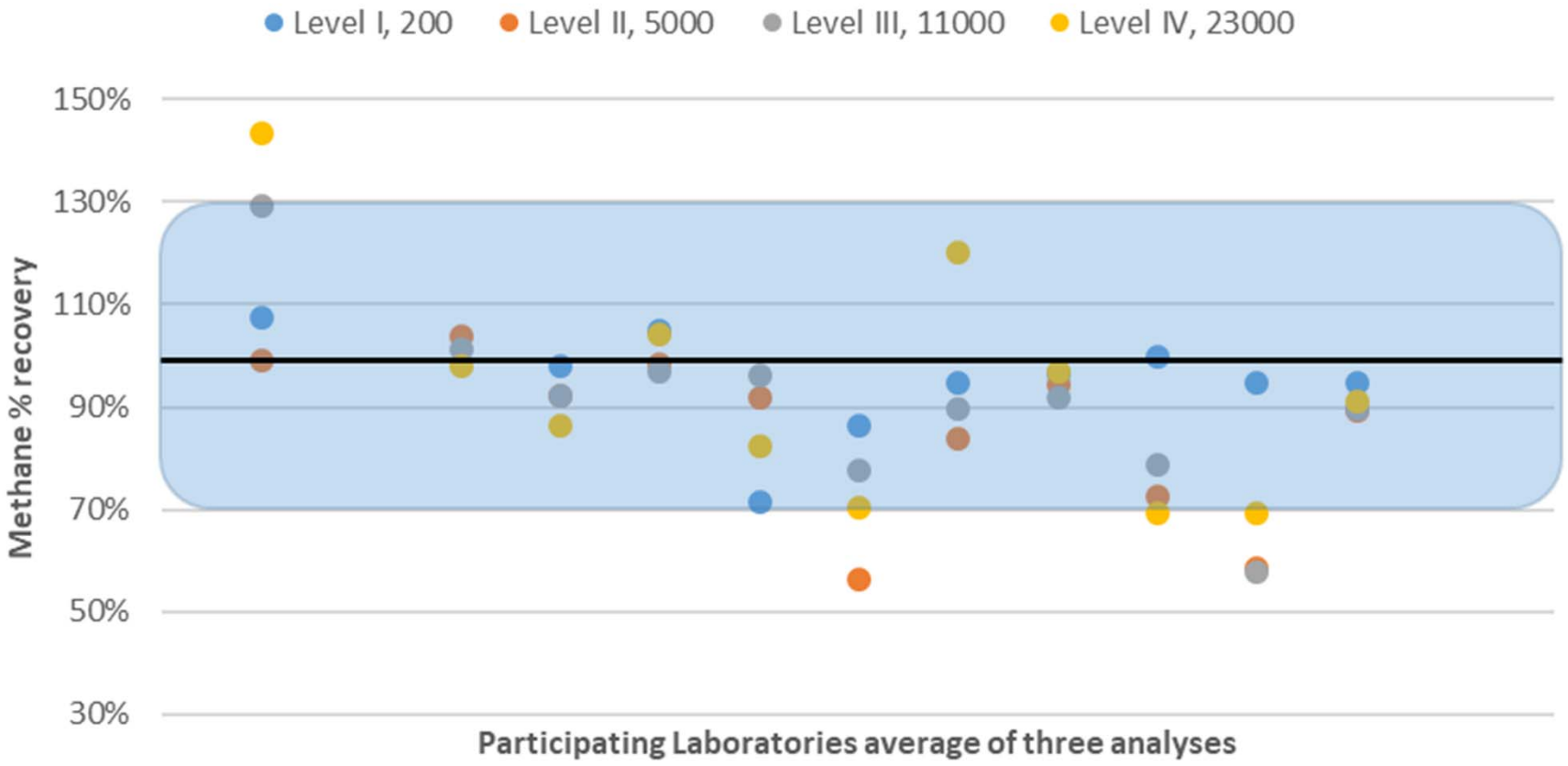
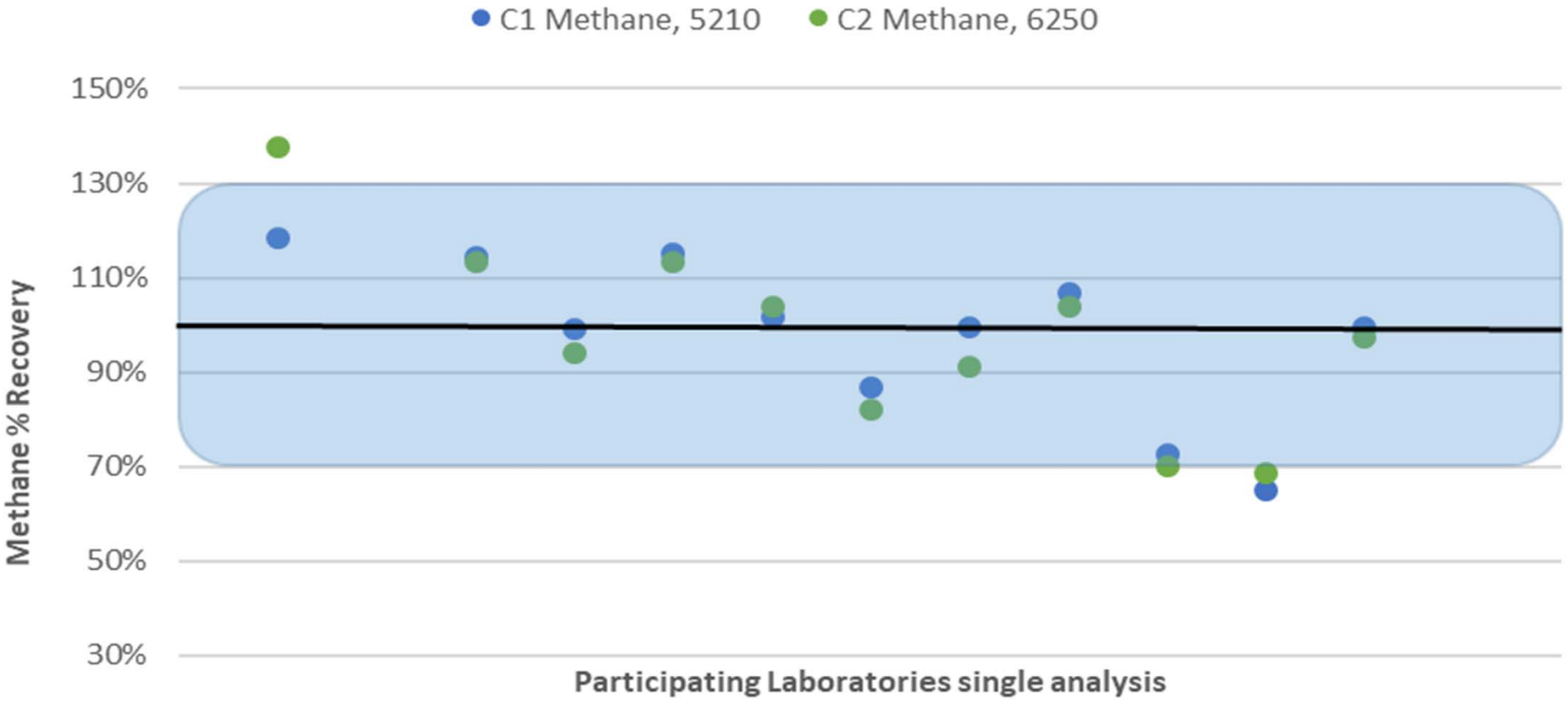
Reference Standard Performance



Certified Reference Material Performance



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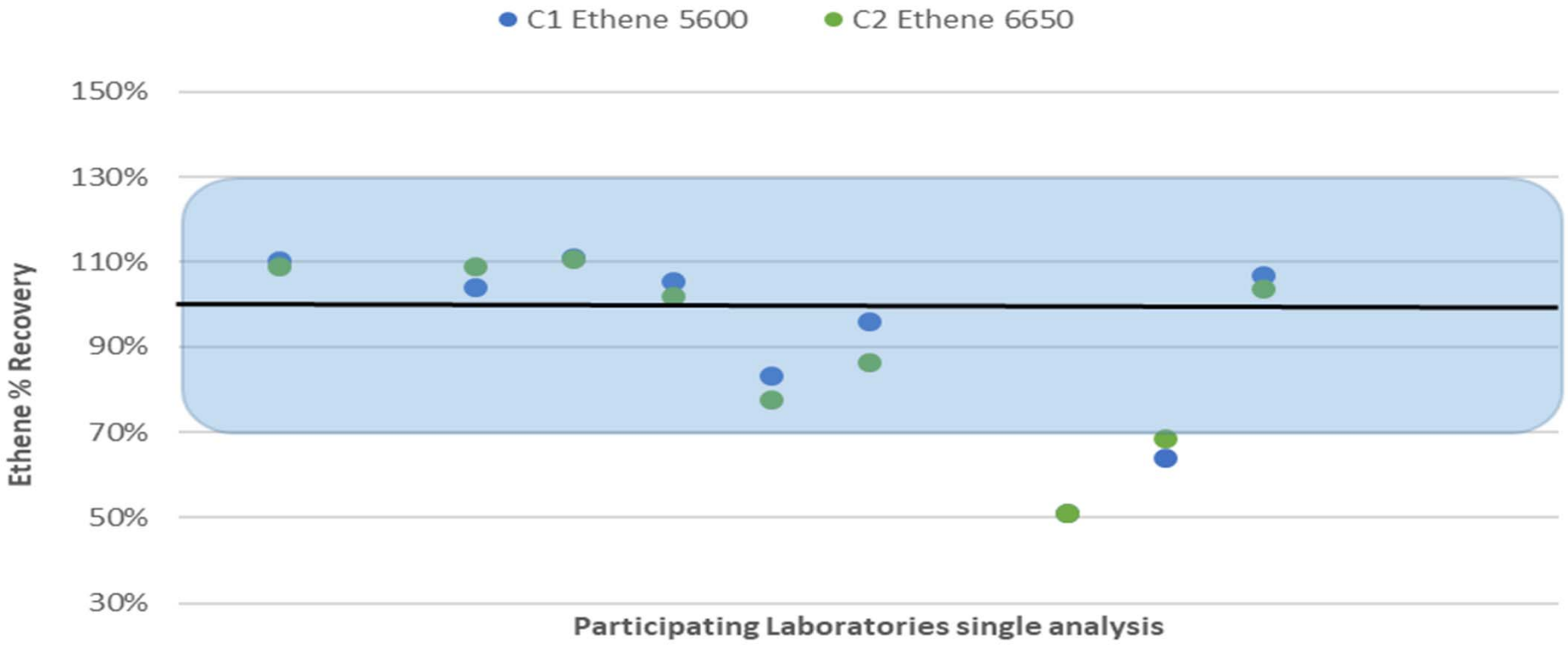

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Laboratory Name and Location	Number of Participating Phases
Air Water & Soil Laboratories, Richmond, VA	2
ALS Environmental, Middletown, PA	4
ALS Global, Rochester, NY	3
Benchmark Analytics, Inc., Center Valley, PA	1
Dolan Integration Group, Westminster, CO	3
Energy Laboratories, Billings, MT	1
Environmental Service Laboratories, Indiana, PA	4
Eurofins Lancaster Laboratories Environmental, LLC, Lancaster, PA	4
Eurofins TestAmerica, Nashville, TN	3
Eurofins TestAmerica, Pittsburgh, PA	1
Eurofins TestAmerica, Buffalo, NY	3
Eurofins TestAmerica, Canton, OH	3

Laboratory Name and Location	Number of Participating Phases
Eurofins TestAmerica, Irvine, CA	1
Eurofins TestAmerica, Savannah, GA	3
EurofinsTestAmerica, Pensacola, FL	1
Fairway Laboratories, Altoona, PA	1
Microbac Marietta, OH (merged with Benchmark)	2
PA DEP Bureau of Laboratories, Harrisburg, PA	4
Pace National (formerly ESC Laboratories), Mount Juliet, TN	4
Pace Laboratories (Microseeps), Pittsburgh, PA	1
Pace Laboratories, Long Island, Melville, NY	1
SGS (formerly Accutest Laboratories), Houston, TX	3
Shealy Laboratories, West Columbia, SC	3

Thank You
Questions?

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