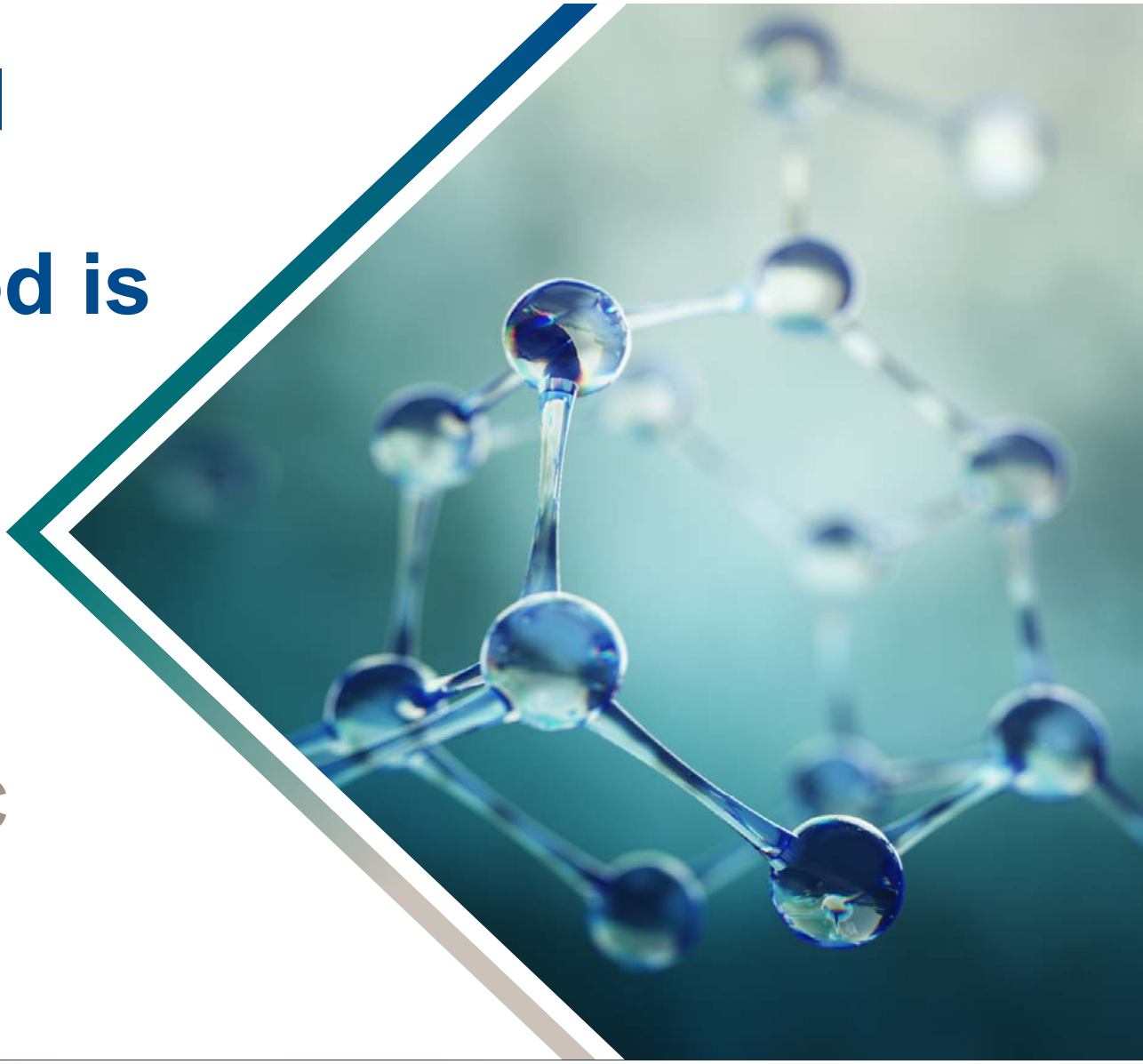
A Fix Was Found and a New Published Method is Emerging

August 10, 2020



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The Problem

- Public concern of residential well contamination
- Accreditation being issued without:
  - A US EPA (or consensus) method for dissolved light gases
  - A PT/CRM to ground laboratories to a true value
- Significant data variability observed by MSC members across samples and accredited commercial laboratories
- A total lack of standardization

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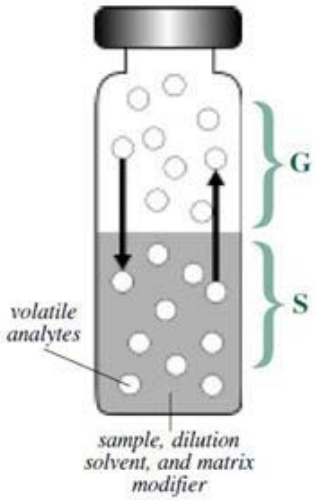
MSC Dissolved Methane Method Workgroup

- Formed to study this issue in early 2013.
- Phase 1 – Study Completed early 2015.
  - Two groundwater samples across 15 laboratories including one government laboratory.
- Phase 2 – Study Completed October 2016.
  - Four blind reference standards across 15 laboratories including one government laboratory.
- Phase 3 – Study Completed January 2018.
  - Announced reference standard across eight non-reference (previously low) laboratories and three reference laboratories
- Phases 4 and 5 – Study Initiated 2019.
  - Draft new method for Publish – US EPA and/or ASTM.
  - Inter-laboratory validation of the new written 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 Standards)
- 23 Participating Laboratories across all phases
- Environmental Services Laboratories (ESL), Indiana, Pennsylvania
- LGC Standards, Manchester, New Hampshire

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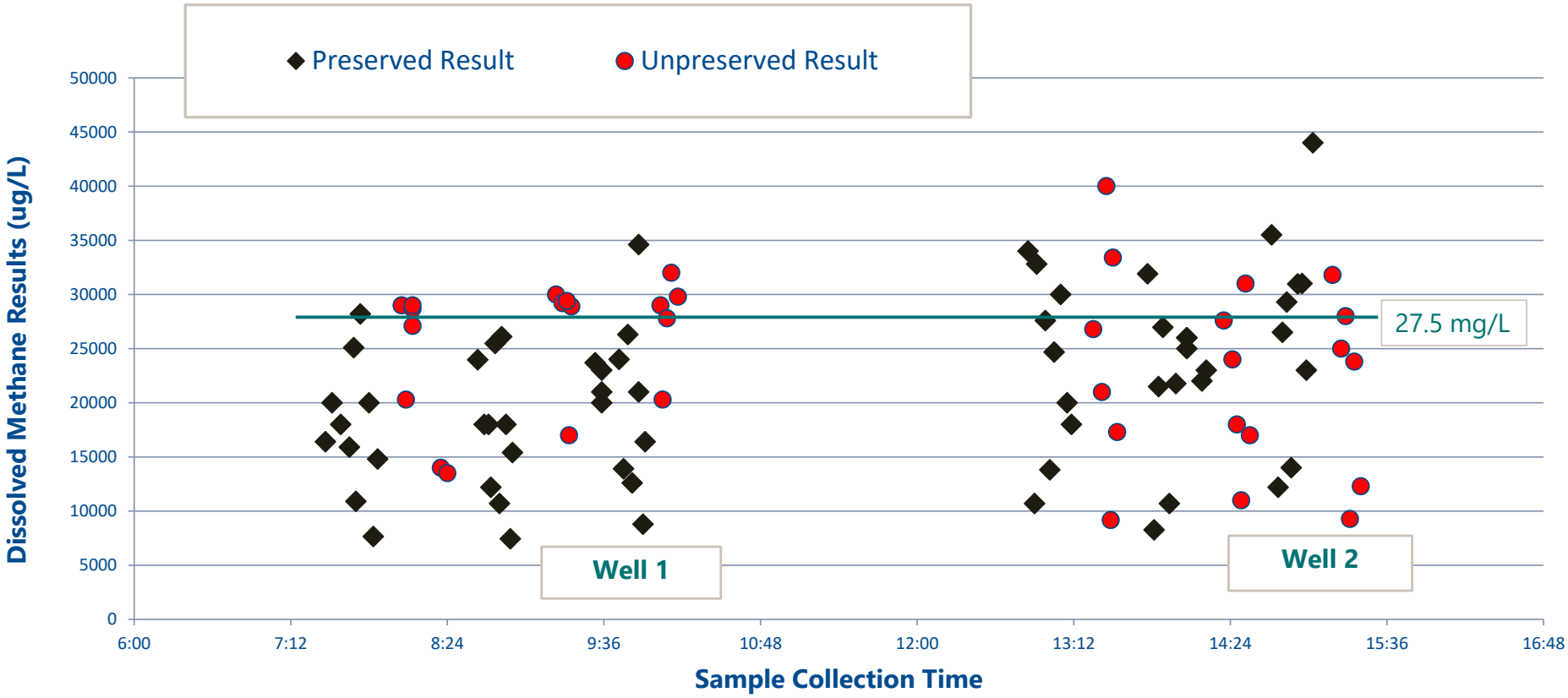
Phase 1 (P1) Design

- Infer issues that impact precision and bias.
  - Detailed questionnaires and review of laboratory SOPs.
- Inter-laboratory study of two monitoring wells.
  - Groundwater wells known to be impacted with dissolved methane.
    - In fact, both groundwater samples were saturated.
- Evaluate sampling and analytical precision and bias.
  - Three samples per well, three vials per sample, analyzed within 48 hours.
  - Vials were numbered and split across sampling so that each laboratory received vials across the multi-hour sampling period.
- Evaluate impact of preservation.
  - Both acid-preserved and unpreserved vials were submitted based on laboratory SOP (10 preserved, 5 unpreserved).

P1 – Results


Preserved Result
Unpreserved Result
Dissolved Methane Results (ug/L)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
6:00
7:12
8:24
9:36
10:48
12:00
13:12
14:24
15:36
16:48
Sample Collection Time
27.5 mg/L
Well 1
Well 2

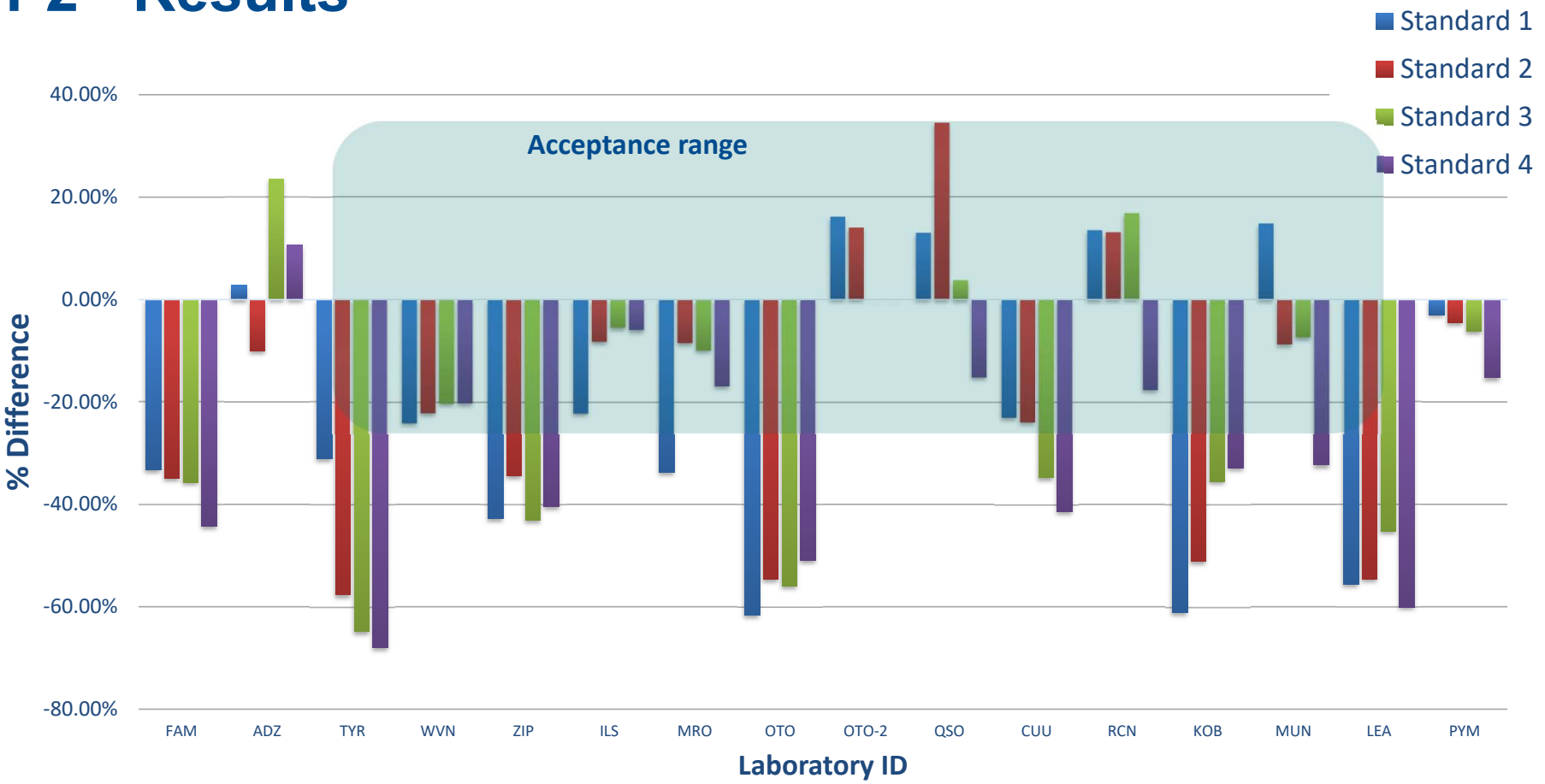
P1 - Conclusions

- Significant data variability across laboratories.
- No singular issue identified to explain spread and bias.
- Calibration varied, three general approaches.
  - Direct gas injection, Henry's Law (RSK-175)
  - Saturated aqueous solution (PA DEP 3685 and ASTM WK43267)
  - Inject gas standard into headspace above aqueous phase, establish equilibrium, then direct-inject gas phase.
- Propensity for dilution, especially at high concentrations.
- Sample preservation not an apparent factor.
- Additional testing at lower range of concentrations needed.

P2 - Design

- Provide blind reference standards (unpreserved) across concentration range and numbered each vial in order.
  - 270 µg/L; 1,080 µg/L; 2,700 µg/L; 7,015 µg/L
- Evaluate 4 different concentrations to allow for individual recovery and response model evaluation.
- Each laboratory received three vials at each of the four concentrations. Directed to report triplicate at each level.
- Controlled dilution effect by including at least one standard below calibration upper limit, to be analyzed undiluted.

P2 - Results



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P2 - Conclusions & Recommendations

- Laboratory variability continues showing a predominantly low bias.
- ***Standards vs. sample handling identified as the primary factor affecting bias.***
  - The individual steps in the sample/standard preparation processes results in the bias.
    - Sample and standard preparation differs.
    - Equilibrium must be reached.
    - Temperature control is critical.
- Recommended Phase 3 – allowing for self diagnosis for the low-recovery laboratories.

P3 - Study Participants

- Select members of the MSC Dissolved Methane Method Work Group.
- Environmental Standards, Valley Forge, PA.
- ESL, Indiana, PA. Reference standard provider.
- 8 Non-Reference Commercial Laboratories
    - Selected from those that failed Phase 1 or 2, more than a 30% difference (*e.g.*, < 70% recovery).
- 3 Reference Laboratories.

P3 – Design

- Send Laboratories a known concentration reference standard.
  - Prepare approximately 70 vials, all at a single final concentration *circa* 7,000 µg/L.
  - Request laboratories analyze vials sequentially and review against known concentration.
  - Self-diagnose after each analysis, revise preparation, handling, calibration, and analysis techniques, as needed.
  - Use what is learned to optimize a procedure/method.

P3 Reference Standard
As-Made Concentration

	Reference Laboratory 1 (µg/L)	Reference Laboratory 2 (µg/L)	Reference Laboratory 3 (µg/L)
	6600	7560	7880
	7000	7190	**7440**
	6500	**6490**	**7490**
	7100	**7465**	6820
Average	**6800**	**7176**	**7408**
%RSD	**4.3%**	**6.7%**	**5.9%**
Duplicate Analysis RPD	**8.8%**	**14%**	**0.7%**

Average of Reference Laboratories	**7130**
%RSD of Reference Laboratories	**6.4%**

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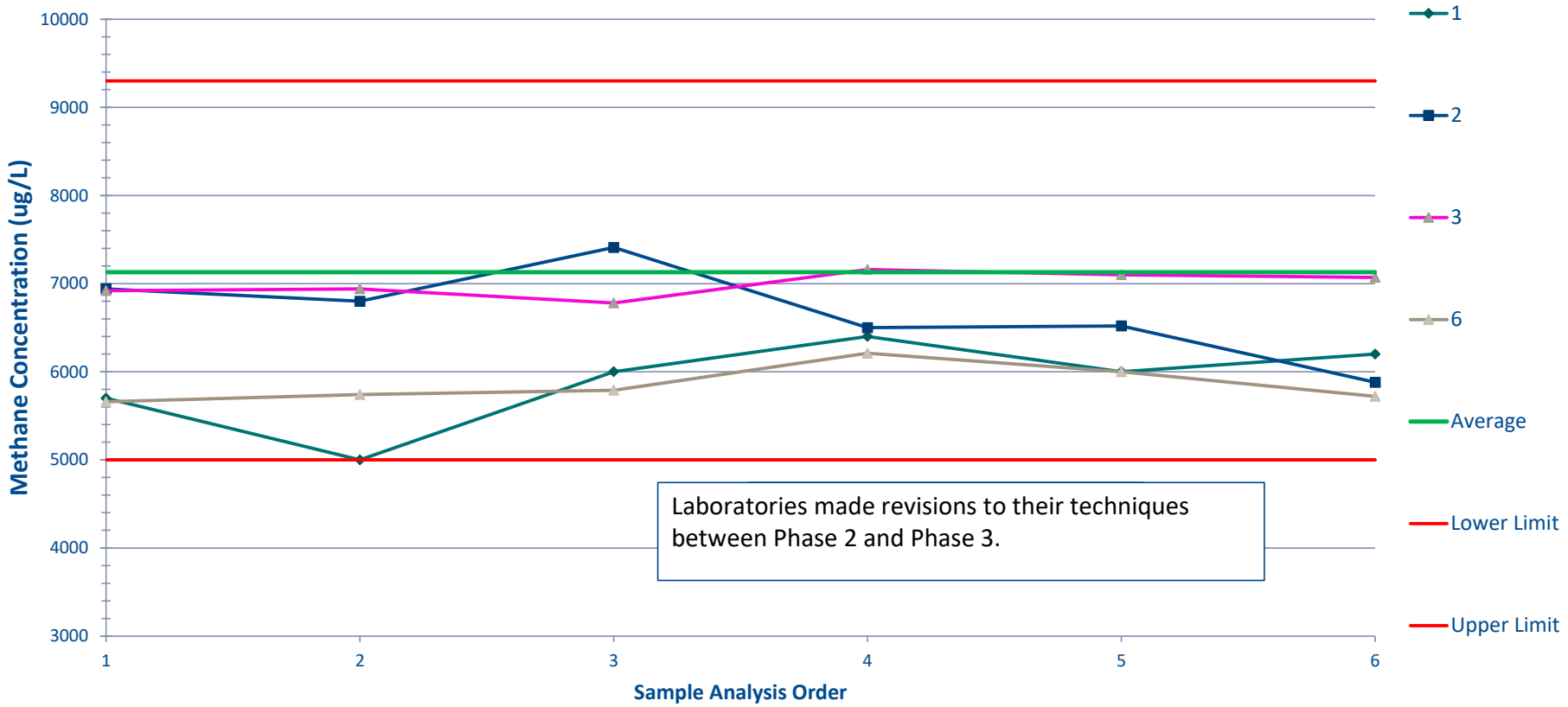
P3 Non-Reference Laboratories – Within Criteria



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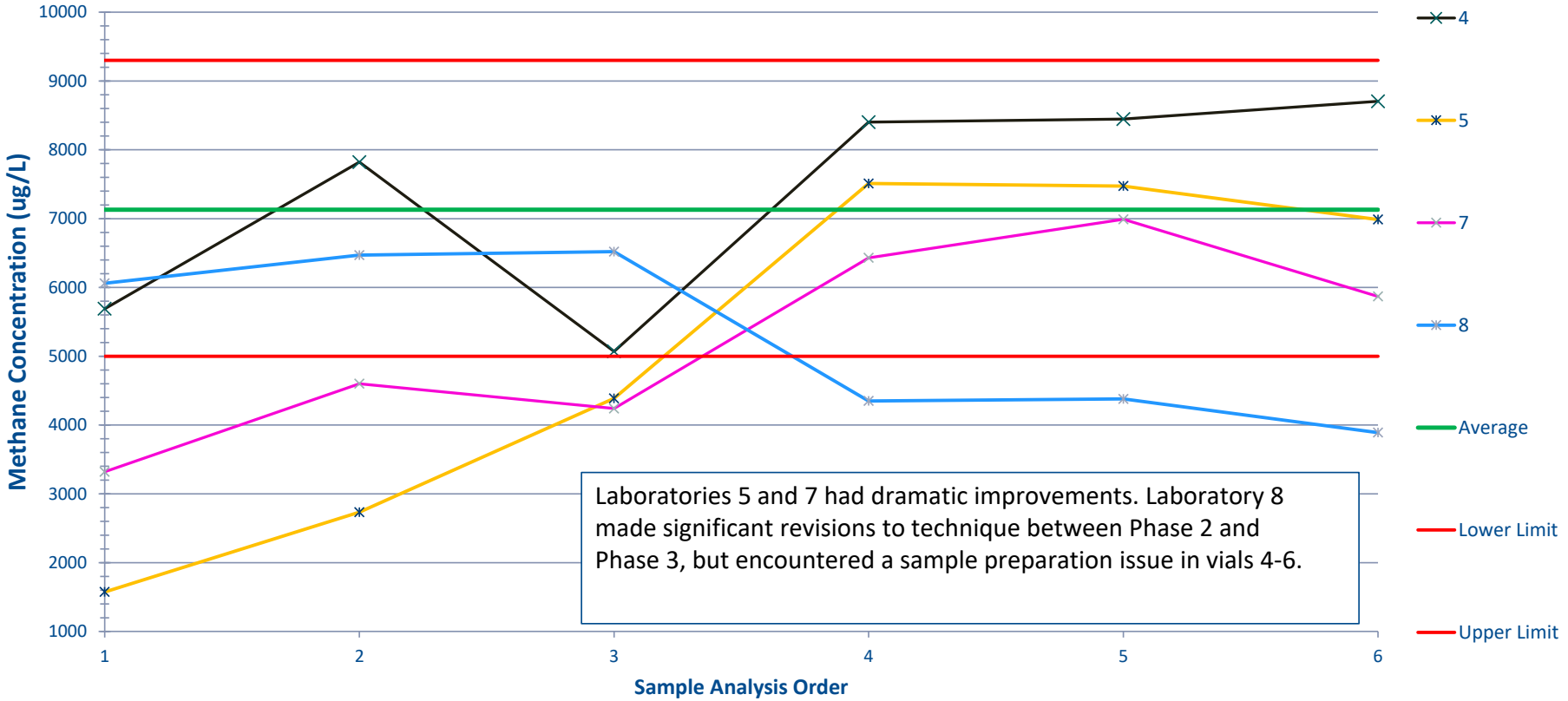
P3 Non-Reference Laboratories – Self Diagnosed, Some Dramatic Improvements



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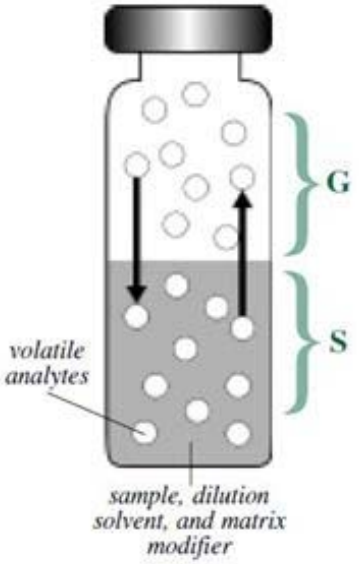
The Self Diagnosis Modifications – Success!

- Critical techniques were identified that caused the bias.
  - 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.
- Participating laboratories achieved recoveries with 70-130% of reference laboratories' average value.
  - Of equal importance, was the significant reduction in variability.



P4 and P5 - Design

- Peer review new written procedure based on P1-P3 findings
  - Written by Environmental Standards, includes three calibration approaches, but controls sample and standard handling to minimize the potential for variability and bias.
  - Reviewed by participating laboratories, regulatory agencies, and MSC Dissolved Methane Group.
  - Final draft procedure for P5 study in ASTM/US EPA method format.
- Submit dissolved methane standards to participating laboratories.
  - Mimic a large range of groundwater concentrations.
  - Laboratories analyze dissolved methane according to P4 procedure.

P4 – A Written Method From All the Lessons Learned

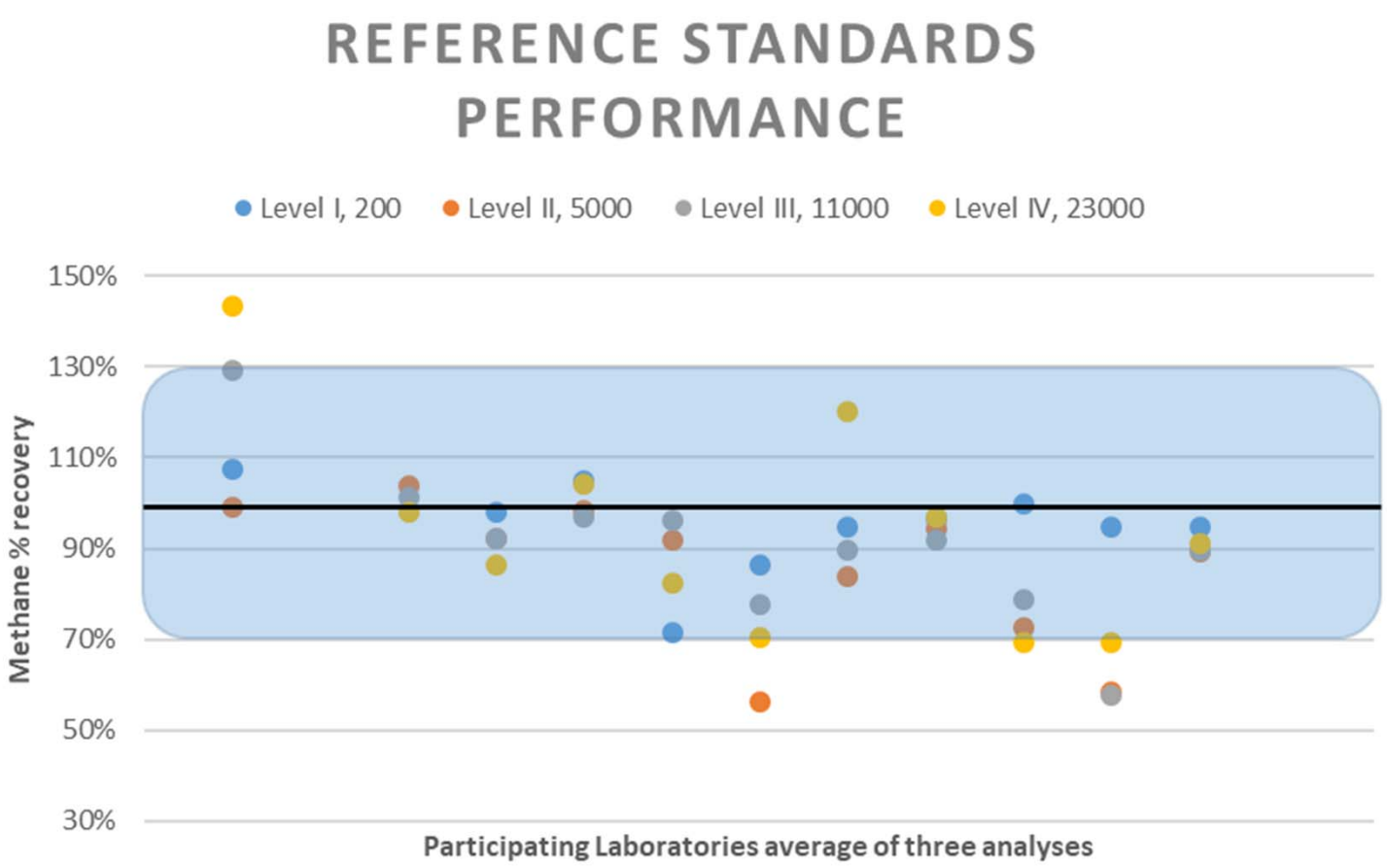
- Static headspace
- Three calibration options using GC and FID, TCD, or MS detector
  - Direct-gas injection
  - Saturated aqueous standards
  - Prepare in vial with headspace (predominant)
- Equilibration time and steps prescriptive
- QC
  - Optional IS, ICAL using Ave. RF or RE/RSE for linear/quadratic, CCV every 10 samples, RT criteria
- CRM incorporated as accuracy assessment

P5 – Study Participants

- Select members of the MSC Dissolved Methane Method Work Group.
- Environmental Standards, Valley Forge, PA.
- ESL, Indiana, PA. Reference standard provider.
- LGC Standards, Manchester, NH. Certified reference material (CRM) provider.
- 11 Commercial Laboratories.
- 1 State Agency Laboratory.

P5 – Results

- Range of concentrations: 200-23000 µg/L dissolved methane.
- Three laboratories were outliers.
- Dramatic improvement.



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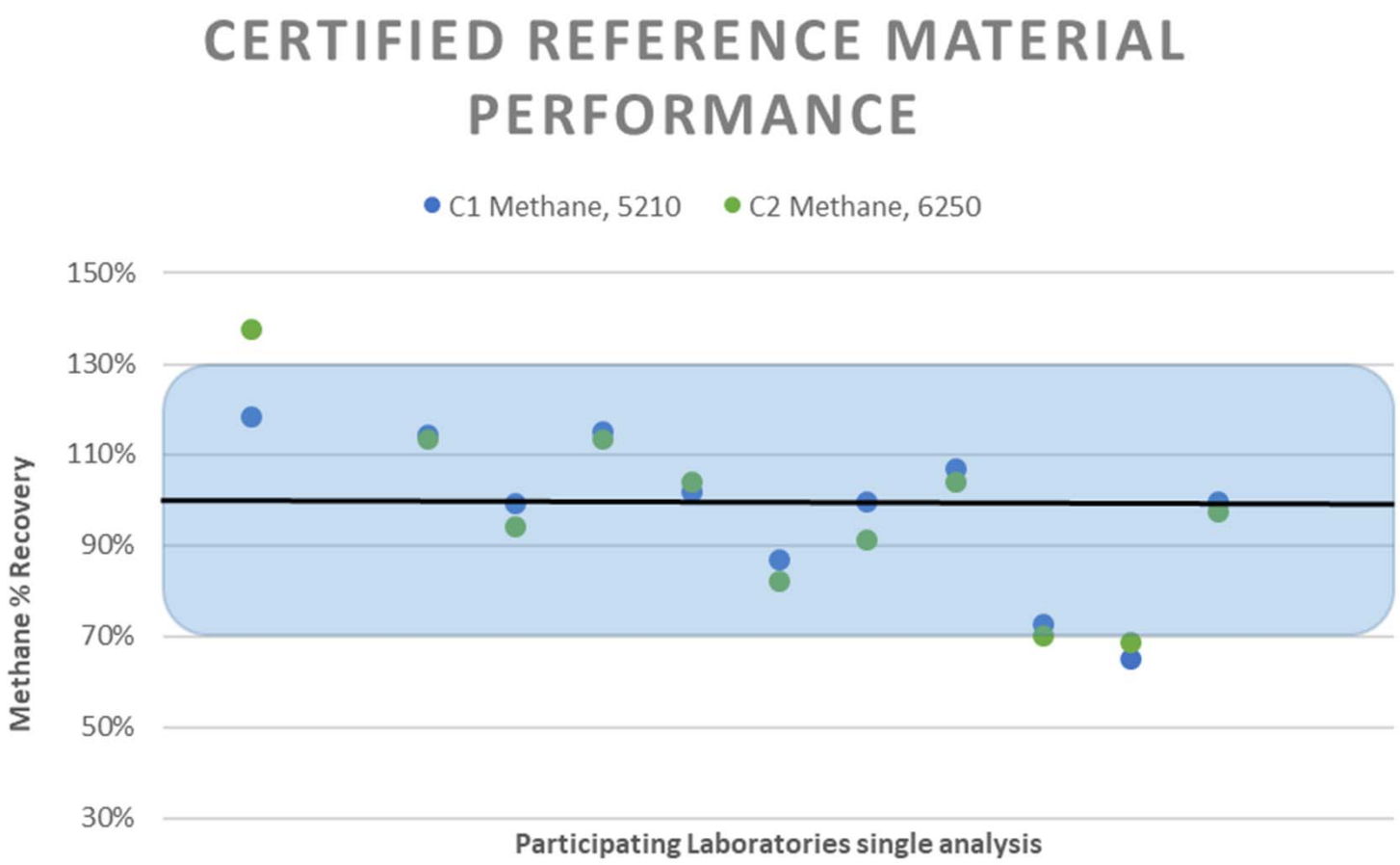
P5 – Results

- CRM mid-range concentrations.
- Two laboratories were outliers. Same outliers as Reference Standards.



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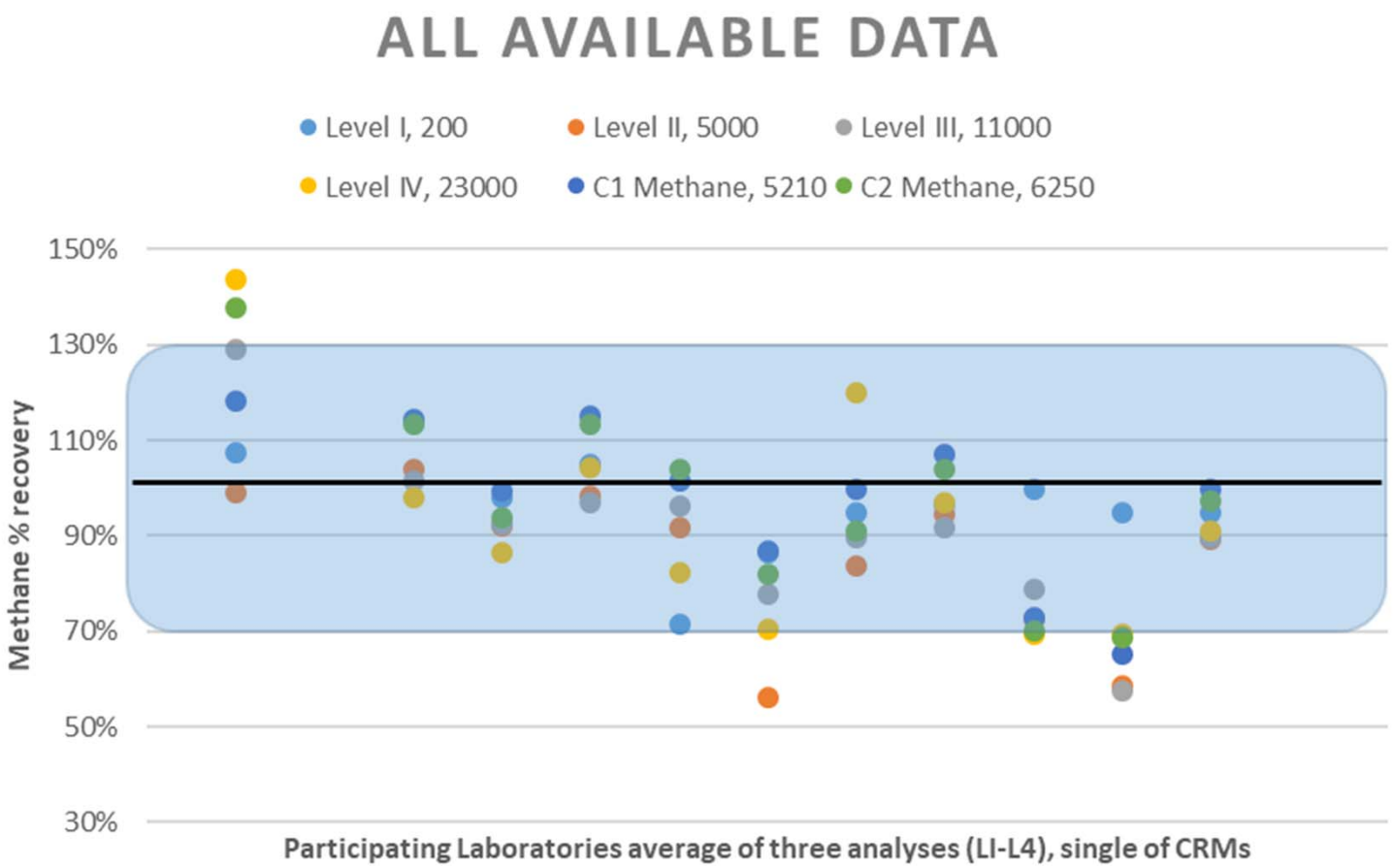
P5 – Results

- Total of 167 data points.
- One laboratory high bias.
- Two laboratories low bias.
- Perform deep dive of outliers.



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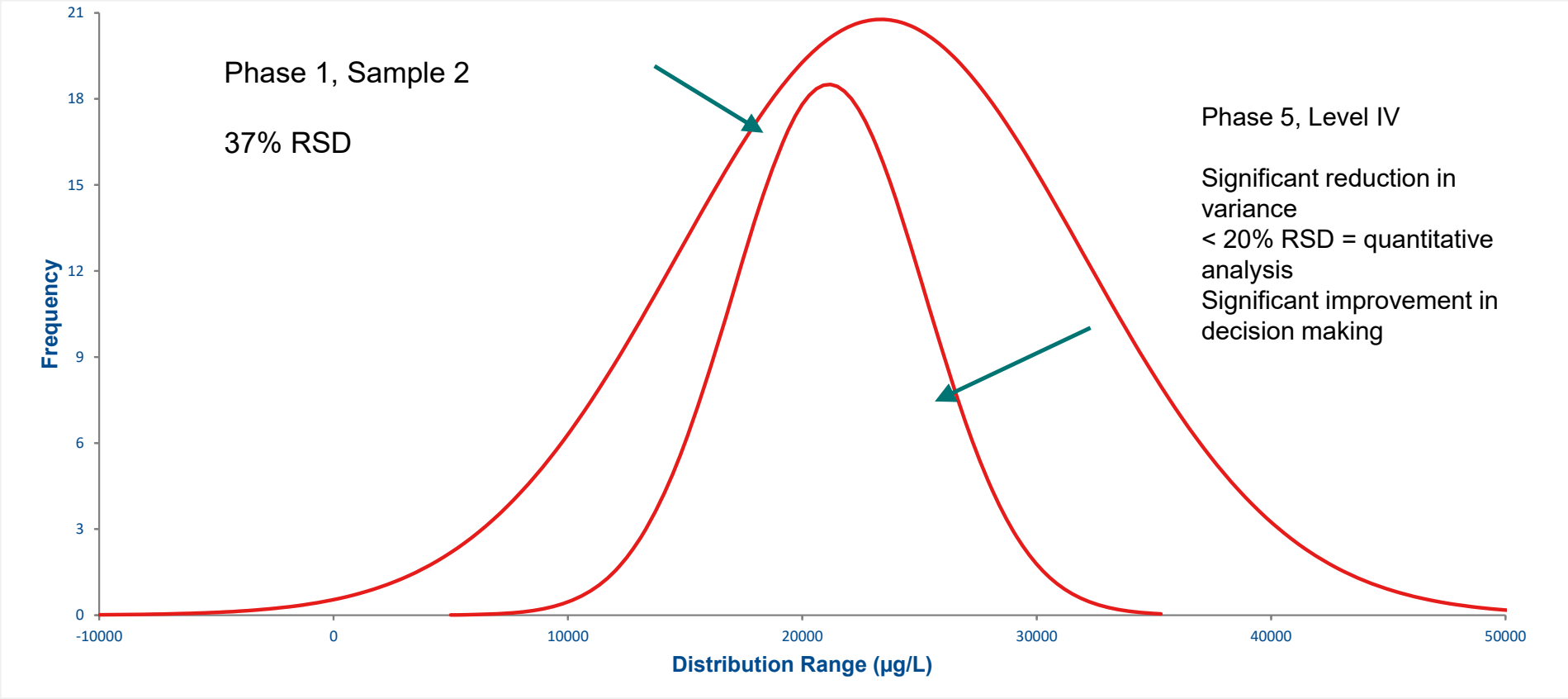
P1 to P5 - Summary

- Early phases confirmed significant bias across laboratory community.
- P3 provided self-diagnosis, captured techniques for P4 procedure used in P5 validation.
- P4 procedure also includes three options for calibration, this captures techniques across the laboratory community.
- CRM and reference standard results validate the P4 procedures used to formally write the method used in P5.
- The written method executed by the participating P5 laboratories successfully generated data of known P&A quality.

Improvement in Accuracy !!!

- Accuracy is assessed via comparison to a reference or consensus value.
  - No true references were available prior to CRM from LGC Standards.
  - Phases 1-3 prepared standard and, by default, defined this as consensus standard, but not rigorously determined (*e.g.,* ILS for consensus).
  - Phase 5 – LGC CRM.
  - With the addition of the CRM, we now have a consensus standard to assess accuracy.

Improvement in Precision



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What's Happening Now?

The Team is currently pursuing both the US EPA and ASTM to publish the new Light Gas Method.

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Questions?

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