Light Gas Analysis – from Concerns to Solutions

Presented by:
David Gratson, CEAC
Senior Technical Chemist
Prepared by Rock Vitale, David Gratson, Stephen Brower, Lydia Work

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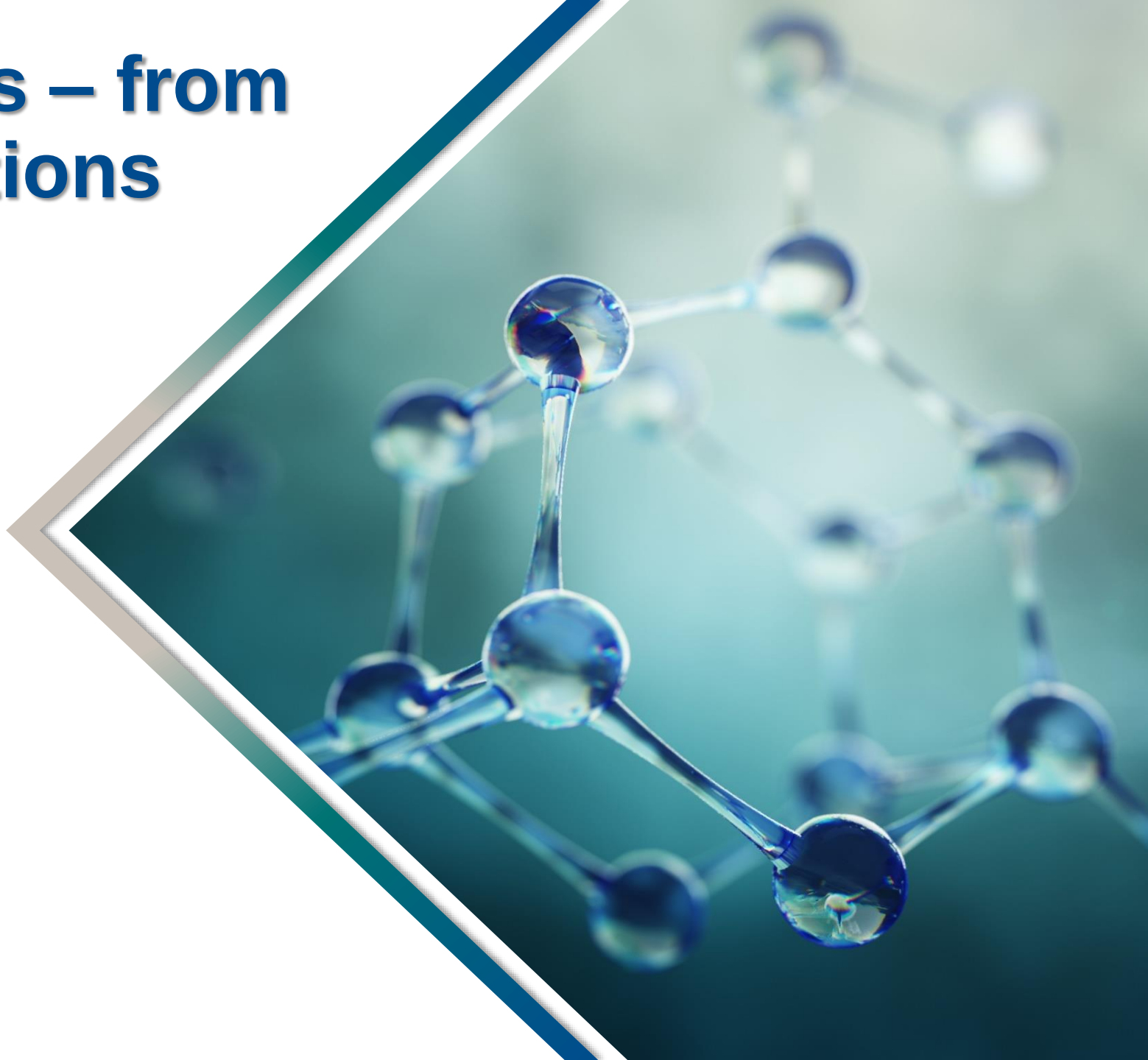

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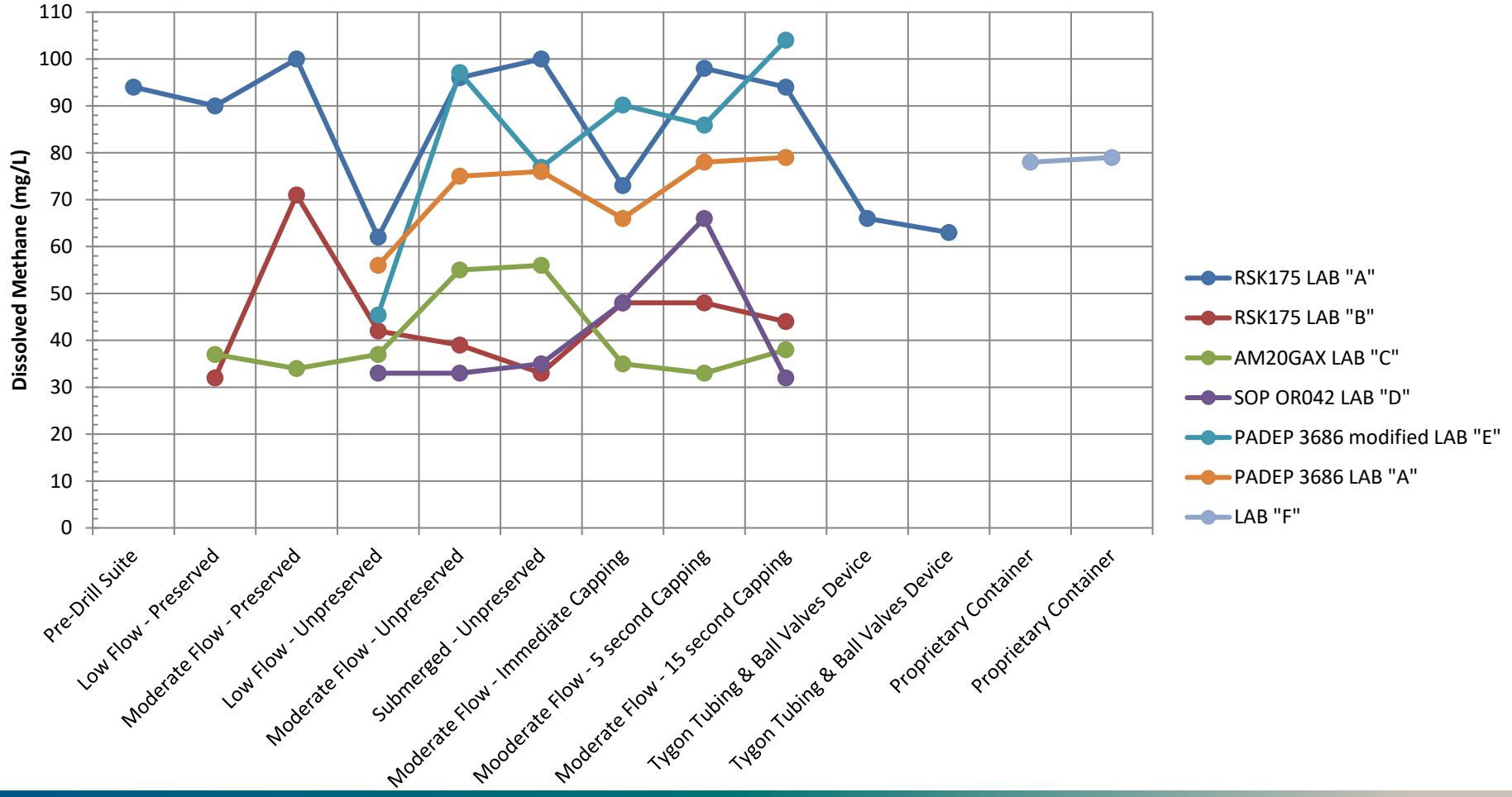
The Problems

- Public concern
- Highly variable laboratory light gas data observed by MSC members
- Lack of Standardization
  - No US EPA-published method
  - Variable laboratory procedures utilized for dissolved light gases
  - No certified reference materials (CRMs) /performance testing samples for light gases

How this all started …

Inter-Laboratory Evaluation In-House Study
Dissolved Methane and Sampling Technique Comparison
Dissolved Methane *vs.* Sampling Method



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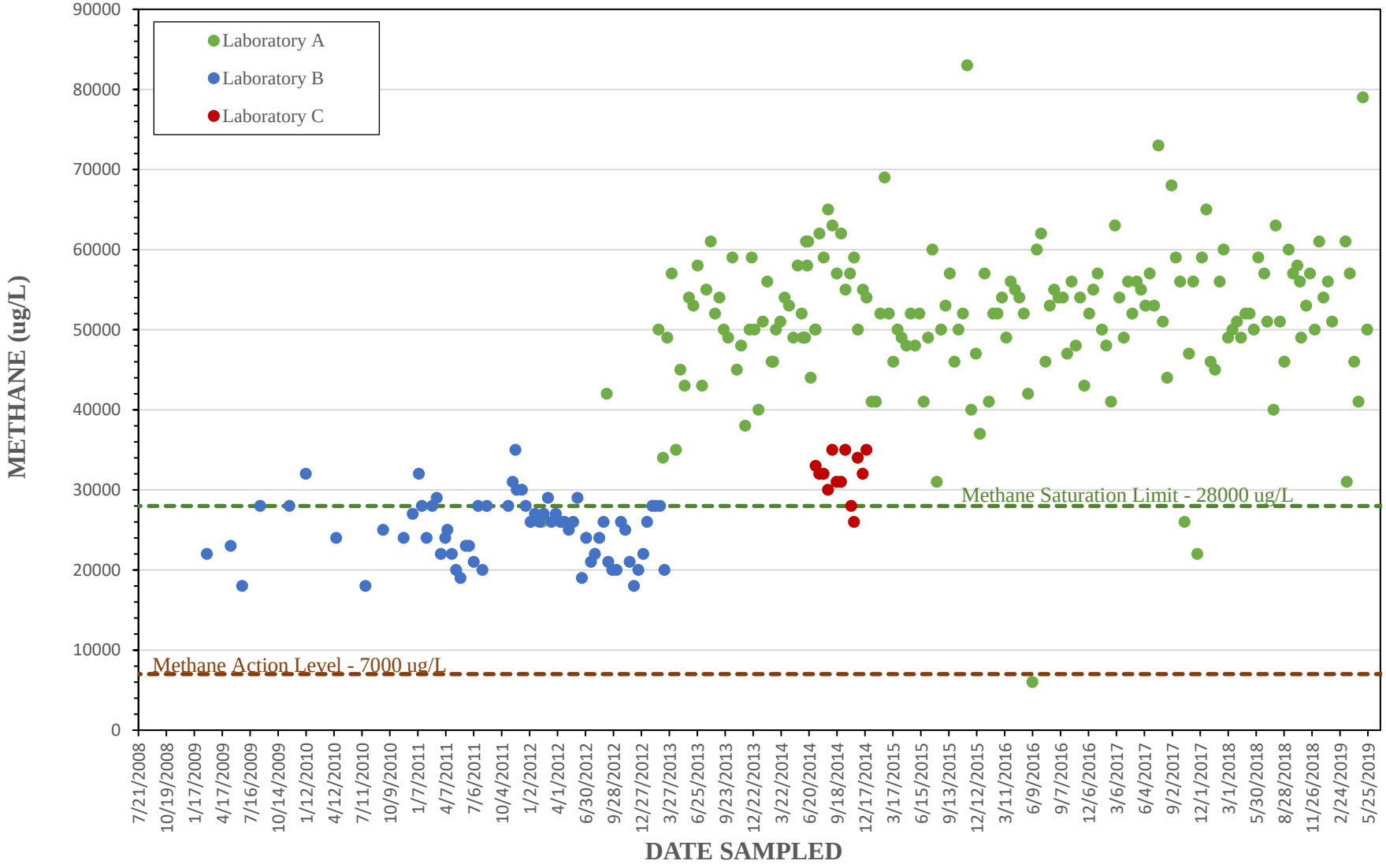
Inter-Laboratory Dissolved Methane Comparison
Environmental Groundwater Sample Results – As-Reported Results



Note: Laboratories B and C are the same laboratory.

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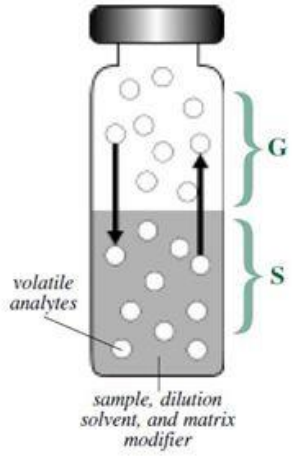
Need for Something Better

- Demonstrate method to measure light gases at concentrations of concern.
- At the time, approximately 35 commercial analytical laboratories in the U.S. providing measurement for dissolved light gases. Most reference SOP RSK-175, or PA DEP 3686.
- Citing SOP RSK-175 has proven to be unreliable – a lot of specific details on preparation and analysis were lacking.

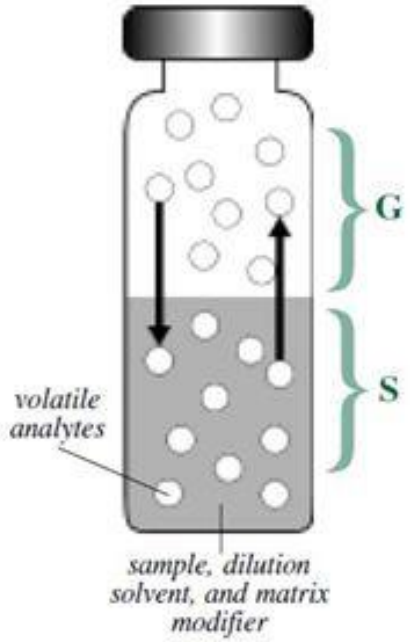


MSC Dissolved Methane Method Work Group

- Phase 1 (P1; early 2015)
  - Two groundwater samples across 15 laboratories including one government laboratory.
- Phase 2 (P2; October 2016)
  - Four blind reference standards across 15 laboratories including one government laboratory.
- Phase 3 (P3; January 2018)
  - Announced reference standards across eight non-reference (previously P2 low) laboratories and three P2 reference laboratories.

MSC Dissolved Methane Method Work Group

- Phase 4 (P4; Spring 2019)
  - Draft new procedure for the ultimately published proposed method.
- Phase 5 (P5; Fall 2019)
  - Inter-laboratory (11) validation of method – included (newly commercially available) CRMs.
- Phase 6 (P6; 2020 - 2021)
  - Discuss study results (P1 – P5) with US EPA SW-846 Methods Committee. Develop inter-laboratory study (ILS) Work Plan, with slight revisions to P4 procedure.
- Phase 7 (P7; Summer 2021)
  - Eight-laboratory with two different groundwaters spiked with methane, ethane, ethene, propane and the commercial CRM.
  - US EPA Region 9 and PA DEP laboratories participating among the eight laboratories.



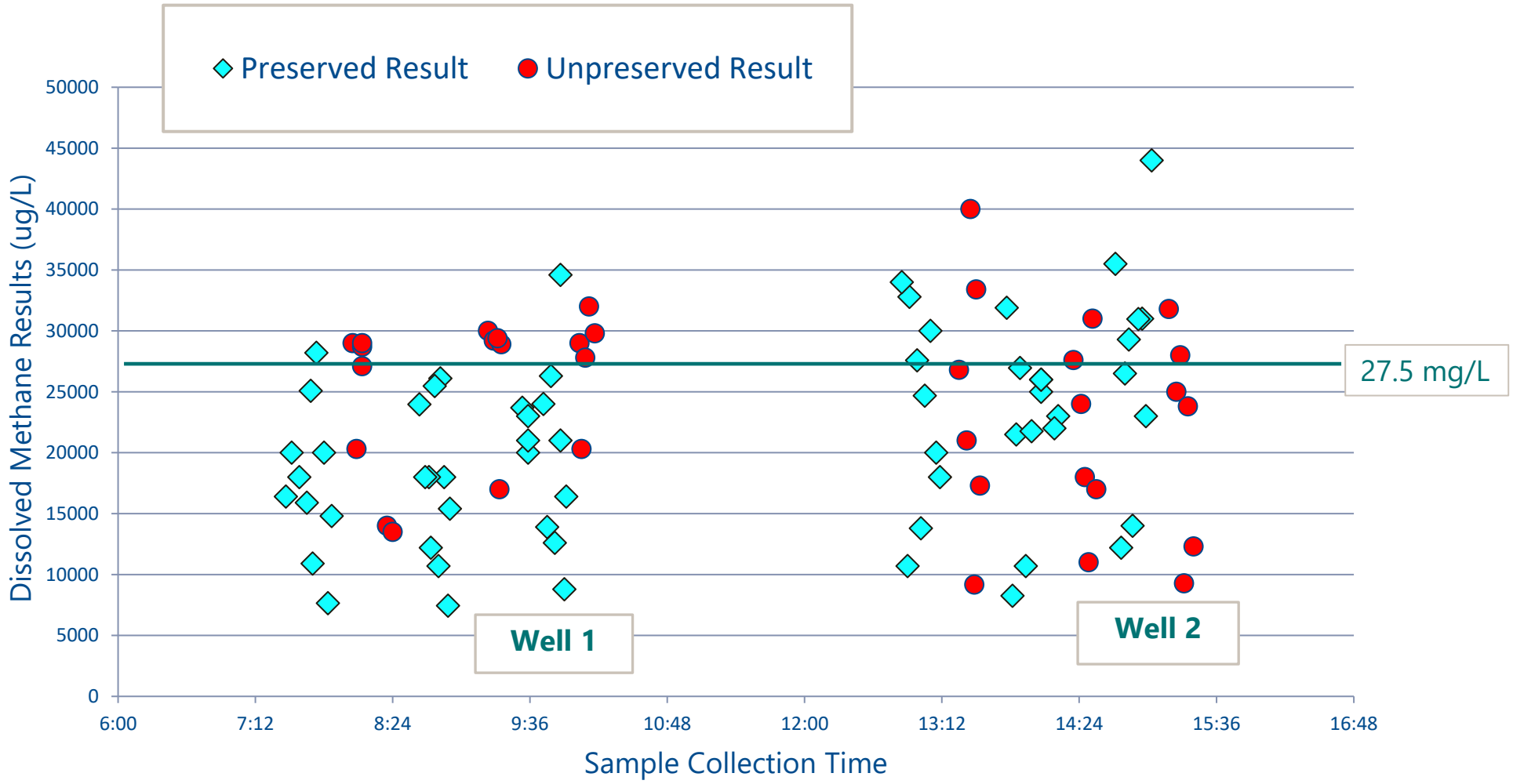
P1-P7 Study Sponsors, Executor, and Participants

- Select Members of the MSC Dissolved Methane Method Work Group
- Environmental Standards, Inc.
- Environmental Services Laboratories (ESL), Indiana, Pennsylvania
- Eurofins TestAmerica, Canton, Ohio
- LGC Standards, Manchester, New Hampshire (commercial manufacturer)
- 24 Participating Laboratories

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 and holding time
  - Both acid-preserved and unpreserved vials were submitted based on laboratory SOP (10 preserved, 5 unpreserved).
  - 17-day holding time, no statistical difference preserved *vs.* unpreserved. 7-day kept as guide for unpreserved.

P1 – Native Groundwater Methane Recovery Results



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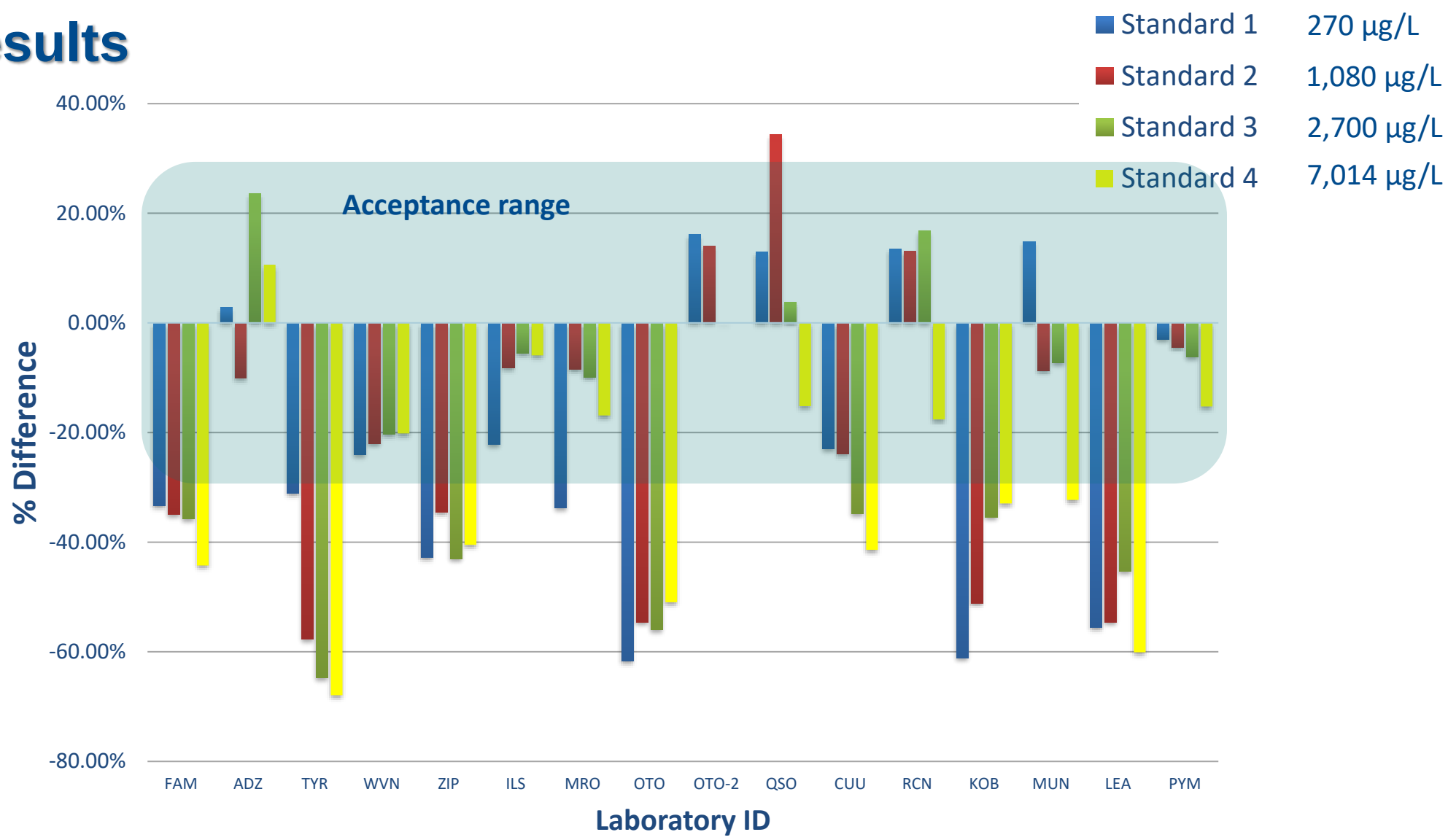
P1 - Conclusions

- 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 3686)
  - Inject gas standard into headspace above aqueous phase, establish equilibrium, then direct inject gas phase.
- Necessity for significant and variable dilutions.
- Sample preservation not an apparent factor.
- Additional testing at lower concentration ranges.

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 affect by including at least one standard below calibration upper limit, to be analyzed undiluted.

P2 - Results



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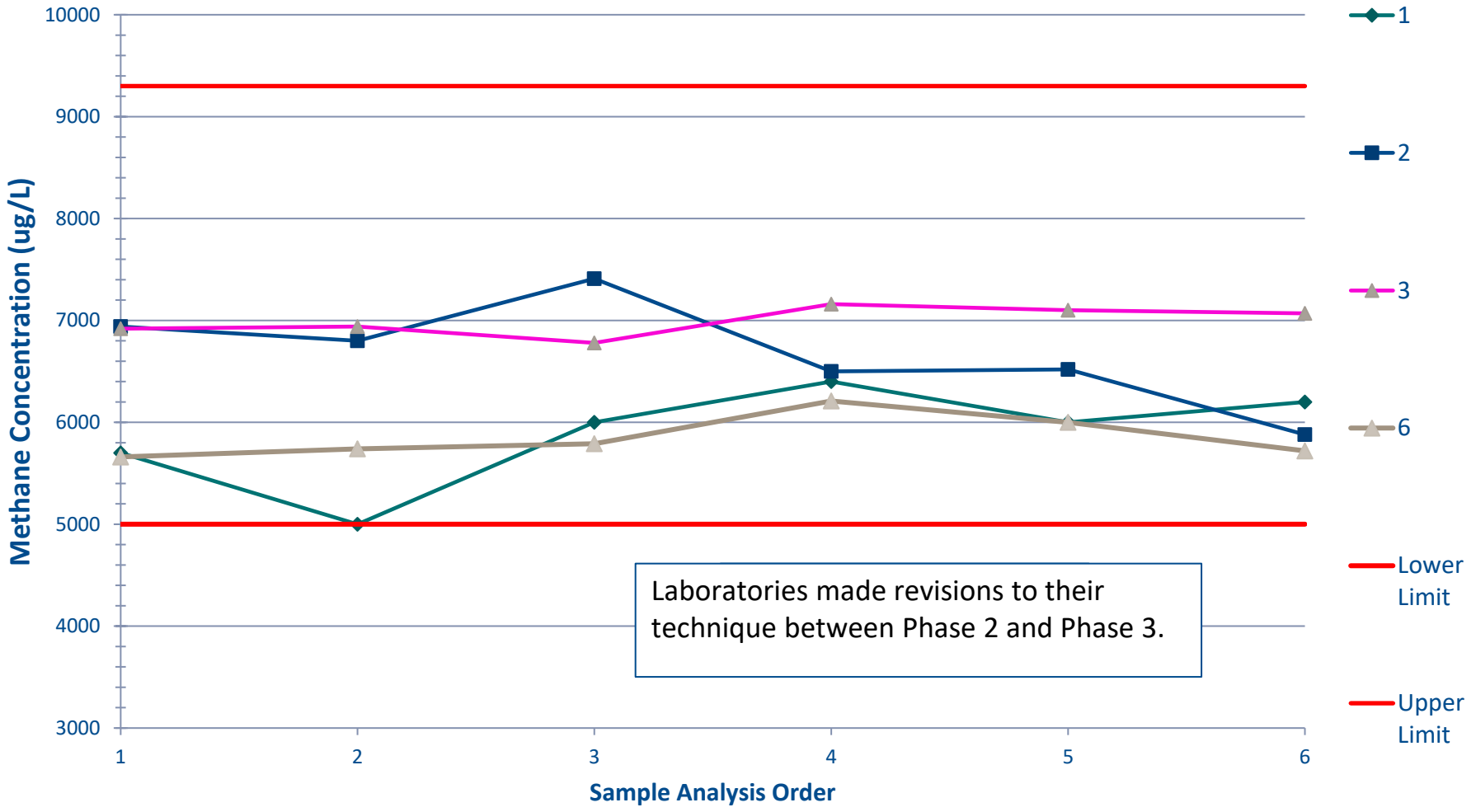
P2 - Conclusions & Recommendations

- Laboratory variability continues and shows a predominantly low bias.
- ***Standards vs. sample handling identified as the primary factor creating low 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 (non-reference) laboratories.

P3 - Design

- Send non-reference Laboratories (selected from those that failed Phase 1 or 2, more than a 30% difference of the known concentration). Send reference laboratories same vials to confirm acceptable performance.
  - Approximately 70 vials were prepared, all at a single final concentration @ ~7,000 ppb.
  - Request laboratories analyze vials sequentially and review against announced concentration.
  - If outside 30% acceptance criterion, self-diagnosis, make revisions to preparation, handling, calibration, and analysis as needed.
  - Tell us what you learned.

P3 Reference Laboratories – Within Criteria



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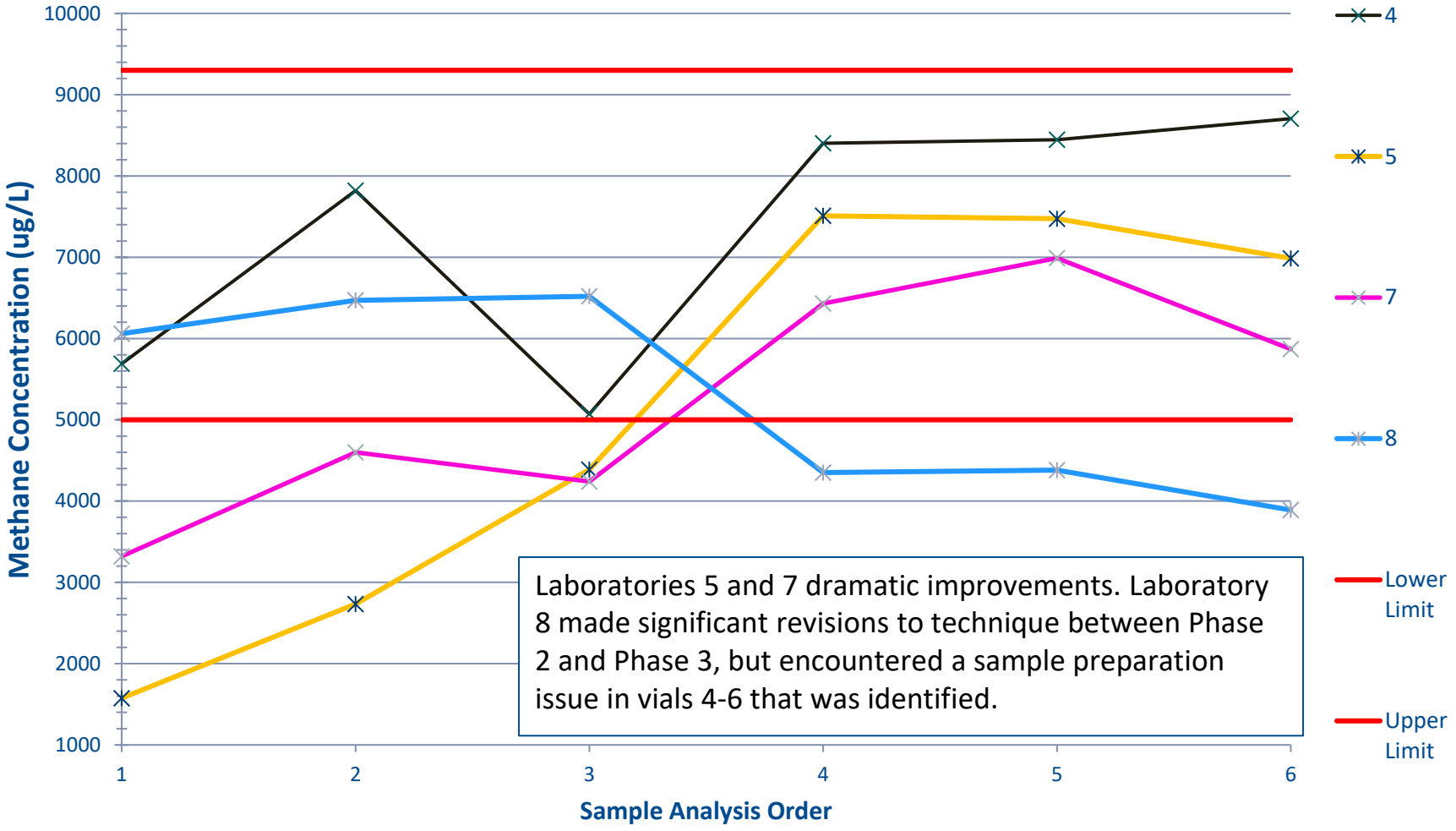
P3 Non-Reference Laboratories – Self Diagnosed, Some Dramatic Improvements



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Self Diagnosis Modifications that Improved Recovery

- Handle calibration standards and samples the same.
- Extended sample warm up times.
- Cooling prior to sample dilutions.
- Increased vortex or shaking times.
- Sample transfer – eliminate the bubbles!
- Minimize septa piercing as much as possible.
- Sample pressure increases via additional helium volume.

Phase 3 - Results

- Success!
- All participating laboratories achieved recoveries with 70-130% of prepared value.
- Significantly reduced variability.
- Critical flawed techniques were identified that caused the bias.

Statistical Summary: P1 through P3

Results by Phase	N	Mean (µg/L)	SD (µg/L)	% RSD
Phase 1, Well 1	53	21070	7052	33%
Phase 1, Well 2	50	23565	8533	36%
Phase 2, Standard 1 (lowest concentration)	45	212	70.7	33%
Phase 2, Standard 2	43	861	278	32%
Phase 2, Standard 3	40	2121	677	32%
Phase 2, Standard 4 (highest concentration)	35	4900	1450	30%
Phase 3 Accepted Values	**39**	**6590**	**870**	**13%**

SD = standard deviation, N = number of samples

P4 - Method Development

- Based on the finding of P1 – P3, a new laboratory procedure was drafted by Environmental Standards
  - Includes three calibration approaches
  - Controls sample and standard handling thereby variability and low bias.
  - Reviewed by participating laboratories, regulatory agencies, and MSC Dissolved Methane Group.
  - Final draft procedure for P5 study drafted in US EPA method format.

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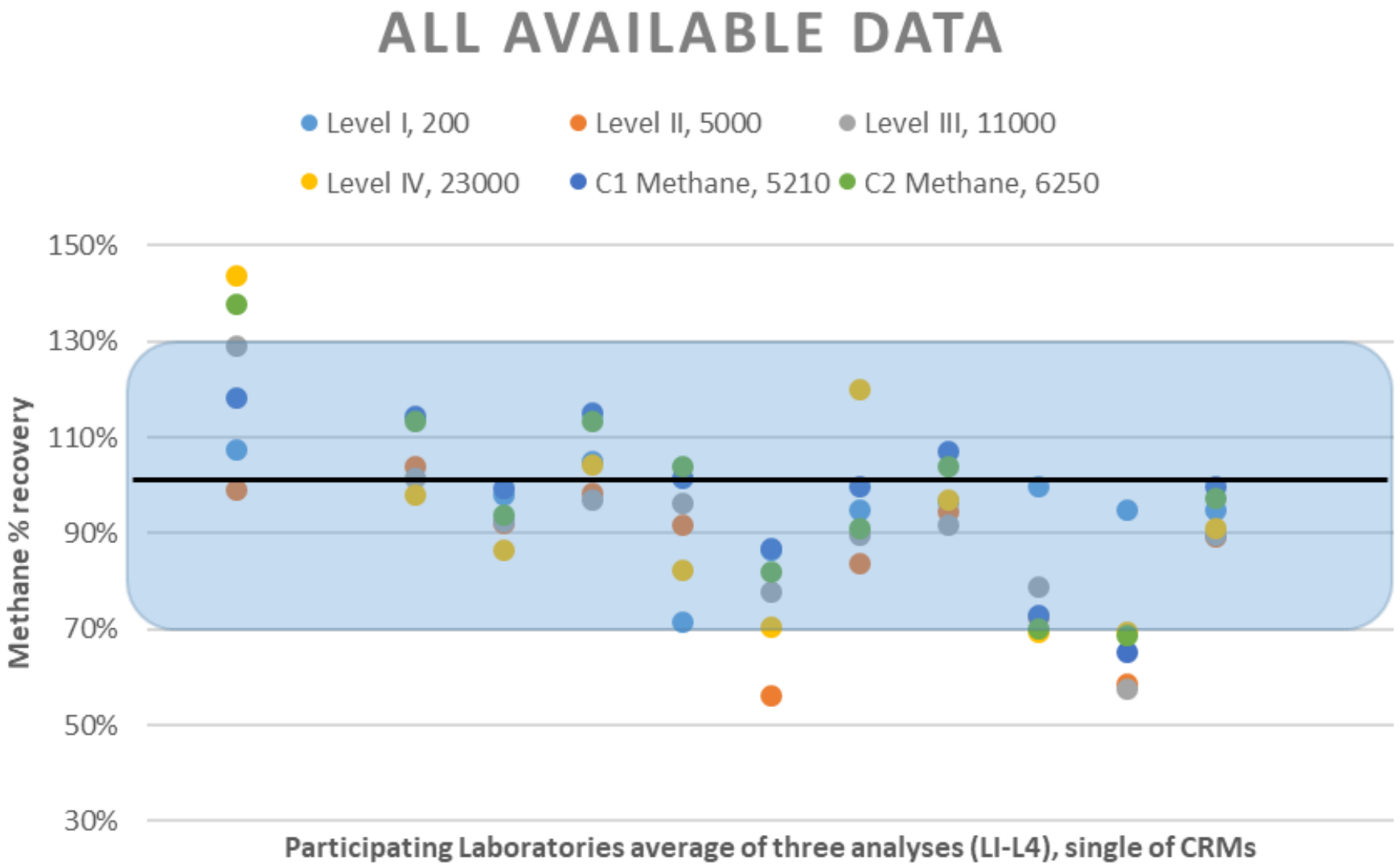
P5 – Design

- Manufacture dissolved methane standards.
  - Mimic a large range of groundwater concentrations.
  - Laboratories instructed to analyze according to P4 draft procedure.

- Summary of reference standards used in P5 study:
  - L01: Sample at Level 1: 200 µg/L, report three analyses (triplicate).
  - L02: Sample at Level 2: 5,000 µg/L, report three analyses (triplicate).
  - L03: Sample at Level 3: 11,000 µg/L, report three analyses (triplicate).
  - L04: Sample at Level 4: 23,000 µg/L, report three analyses (triplicate).
  - C01: CRM #1: 5,210 µg/L, report a single analysis.
  - C02: CRM #2: 6,250 µg/L, report a single analysis.

P5 – Results

- Total of 167 data points.
- One laboratory high bias.
- Two laboratories low bias.
- The two laboratories (9 and 10) biased low had not participated in previous rounds.



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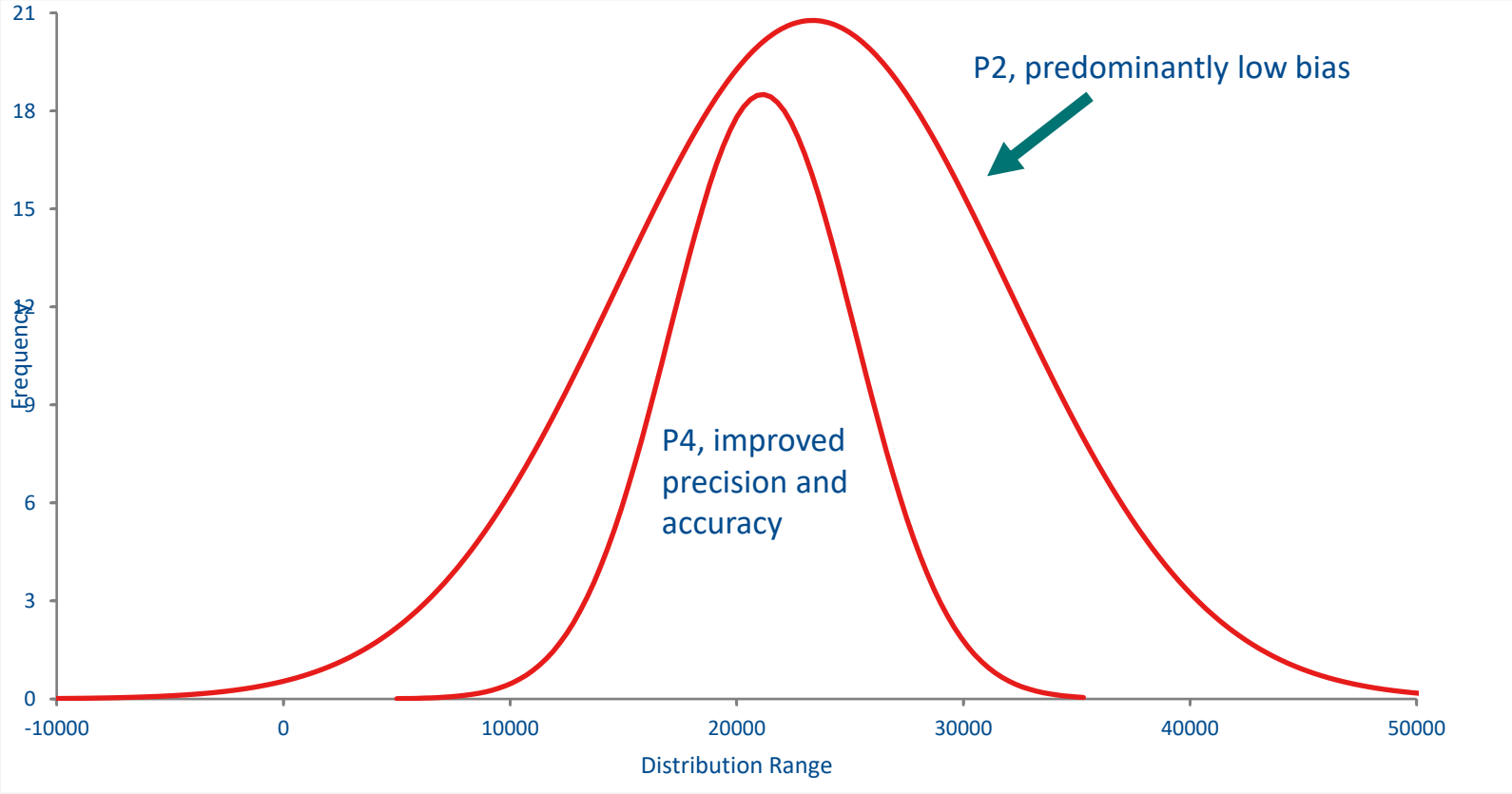
Solution– How Our Multi-laboratory Study Improved Method Precision & Accuracy



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P6- Initiate Discussions with US EPA

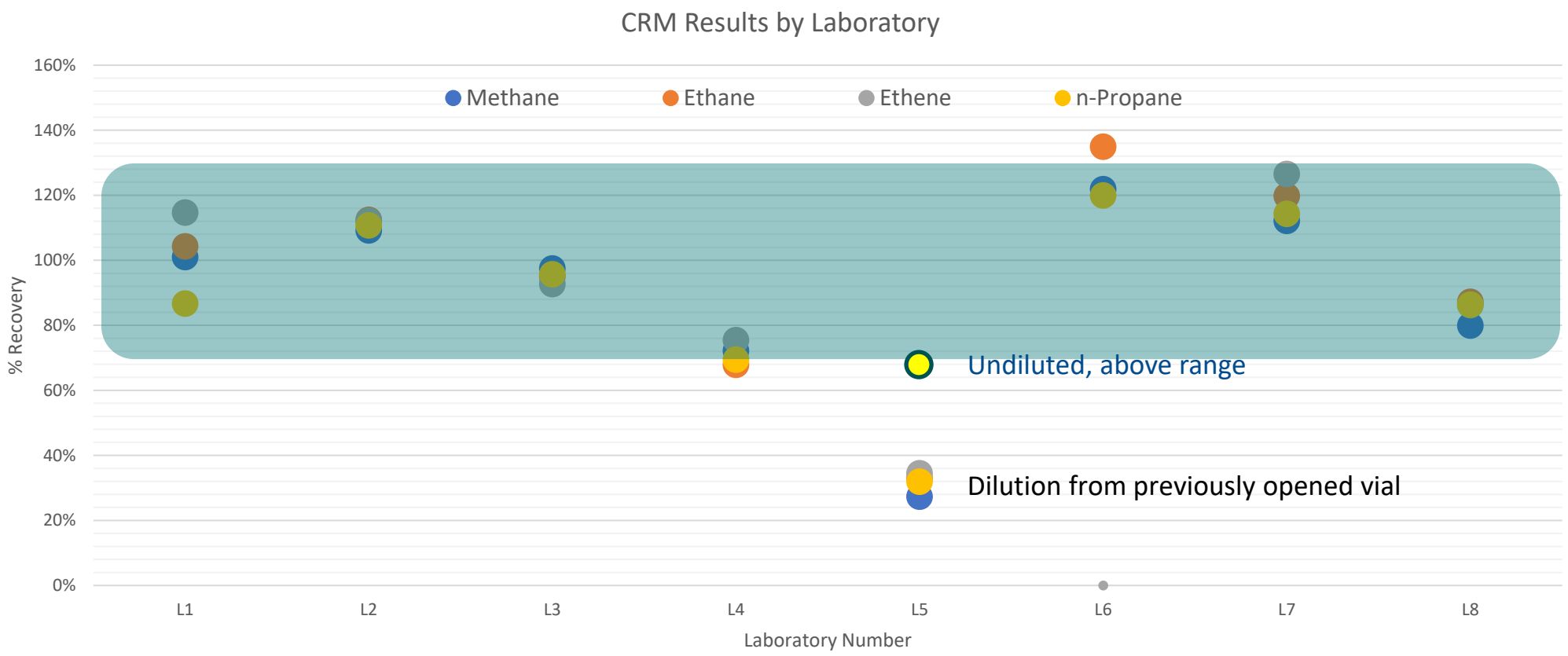
- US EPA SW-846 Methods Committee
  - Provided slide presentation P1 – P5.
  - Provided reports from prior studies.
  - US EPA requested adding ILS with groundwater due to importance to RCRA and CERCLA programs.
  - US EPA requested adding ethane and ethene analytes due to importance with monitored natural attenuation (MNA) studies.

- Slight Revisions to Procedure
  - Removed direct gas injection calibration due to minimum number of laboratories using that calibration technique.
  - Limit analytes to those validated – methane, ethane, ethene, propane (MEEP), with options for validating other gas analytes (*e.g.,* hydrogen, argon, CO, CO_2, …).
  - Several rounds of technical edits and clarifications.

P7- Design

- Submit dissolved MEEP standards prepared in two geochemically different groundwaters at two different concentrations (80 µg/L and 800 µg/L) each to participating laboratory.
  - Laboratories directed to analyze dissolved gases according to US EPA-reviewed drafted procedure.
  - Triplicate analysis at each concentration for each unpreserved groundwater prepared standard (four sample types in triplicate).
  - Laboratories directed to perform matrix spikes at lower concentrations.
  - Single-blind CRM included with the groundwater prepared standards.
  - Analyze groundwater standards and CRM within 72-hours of receipt.

P7- CRM Results



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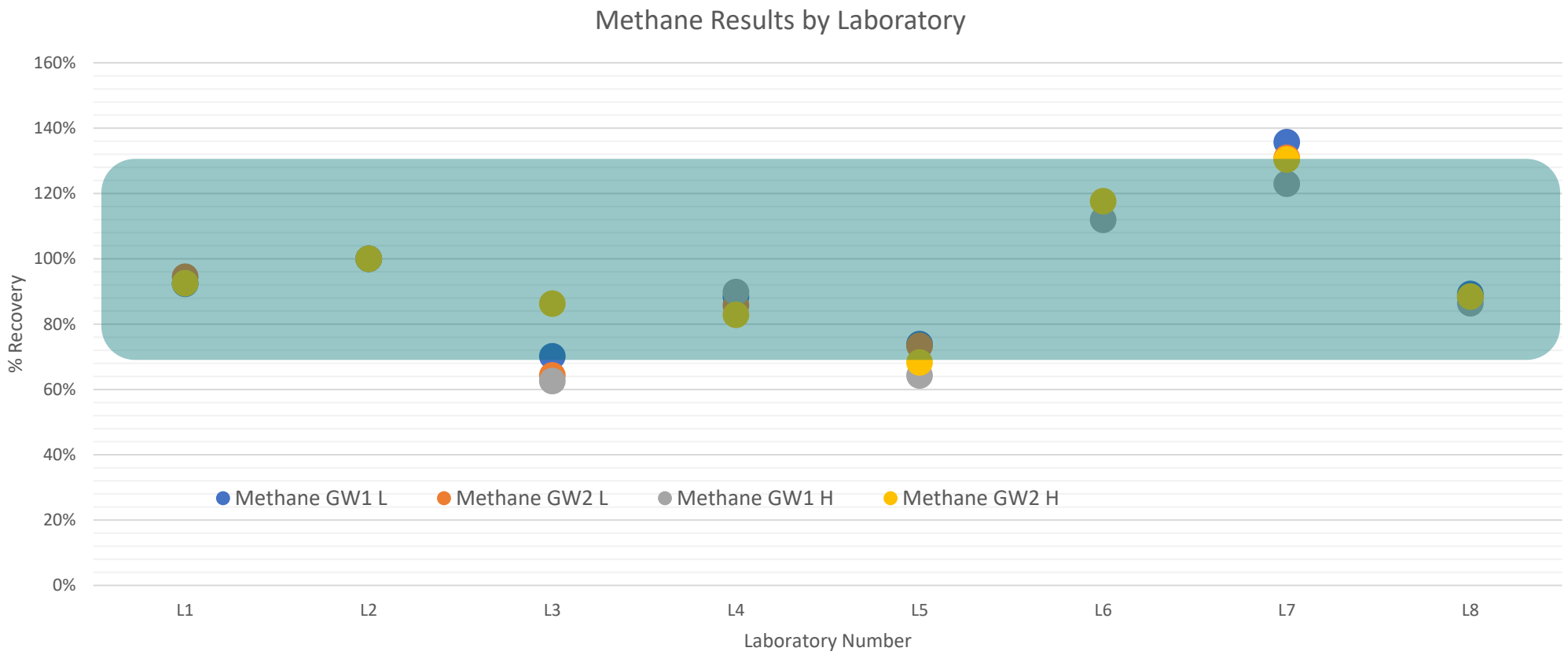
P7- GW Results - Methane



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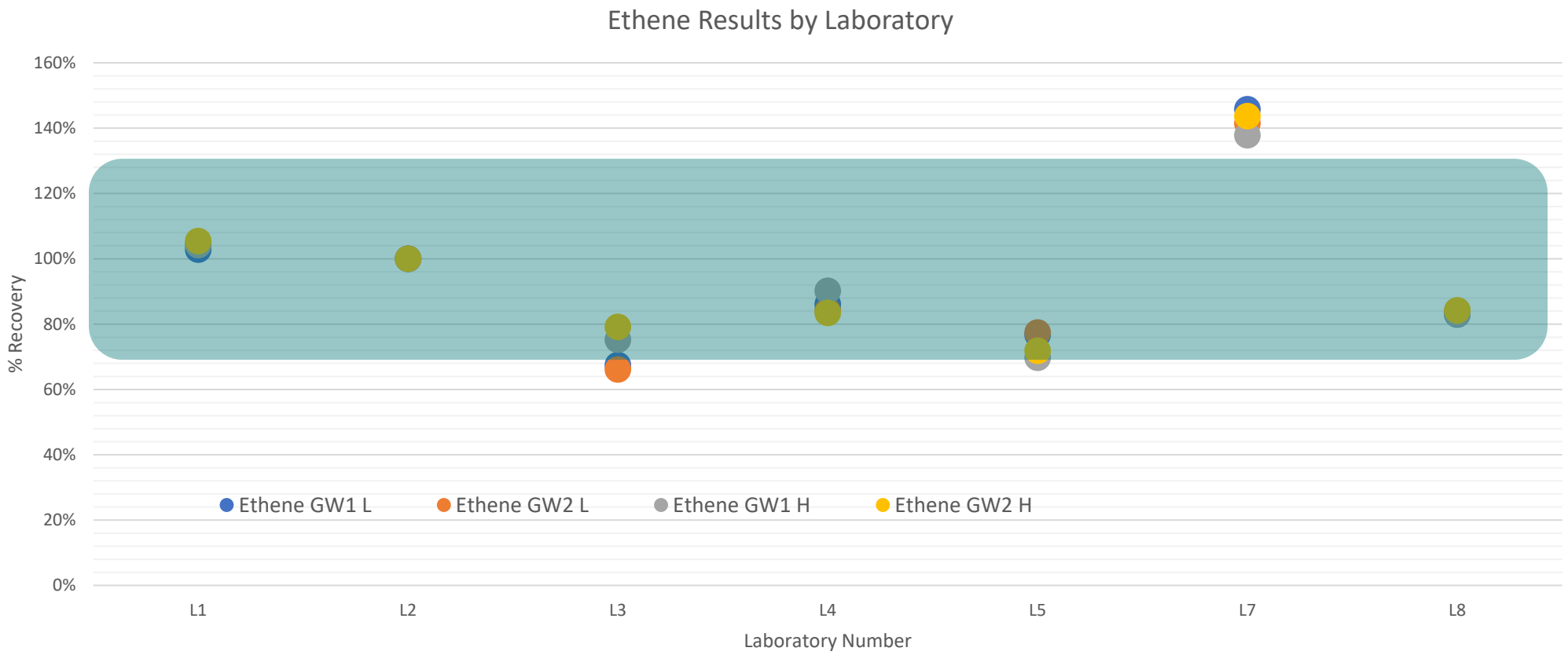
P7- GW Results - Ethene



P7 - Observations

- Laboratory 7 had a high bias in groundwater standards and CRMs, ~20+% above accepted values. Not statistically considered an outlier and would have been acted on.
- Laboratory 4 noted that it lost the spike in one of two paired matrix spike sets. The laboratory neglected to replace cap during spiking, which resulted in an incomplete seal.
- Laboratory 6 reporting limits were above the prepared concentrations, except for methane in the two high concentrations (GW1-H/GW2 – H) and the CRM.
  - Provided replicate matrix spikes with good precision and acceptable recovery for all four groundwater standards.

P7 – Observations (Cont.)

- Laboratory 5 acknowledged very low CRM recoveries and losses of spike in one MS/MSD pair due to inappropriately reusing opened vial at room temperature while preparing a matrix spike.
  - Generally accepted laboratory practice – do not reuse a pre-opened vial!
  - Method requirement to perform sample handling at refrigeration temperatures included in the procedure.
  - Laboratory 5 did not follow these prescriptive steps.

P7 – Matrix Spike Recoveries

	Pooled Average Recovery			
	GW1 -L	GW2 - L	GW1-H	GW2-H
Methane MS	108%	117%	77%	64%
Methane MSD	104%	117%	90%	18%
Ethane MS	103%	104%	95%	88%
Ethane MSD	100%	104%	92%	58%
Ethene MS	110%	116%	77%	66%
Ethene MSD	107%	118%	83%	-11%
n-Propane MS	101%	108%	92%	94%
n-Propane MSD	102%	108%	101%	77%

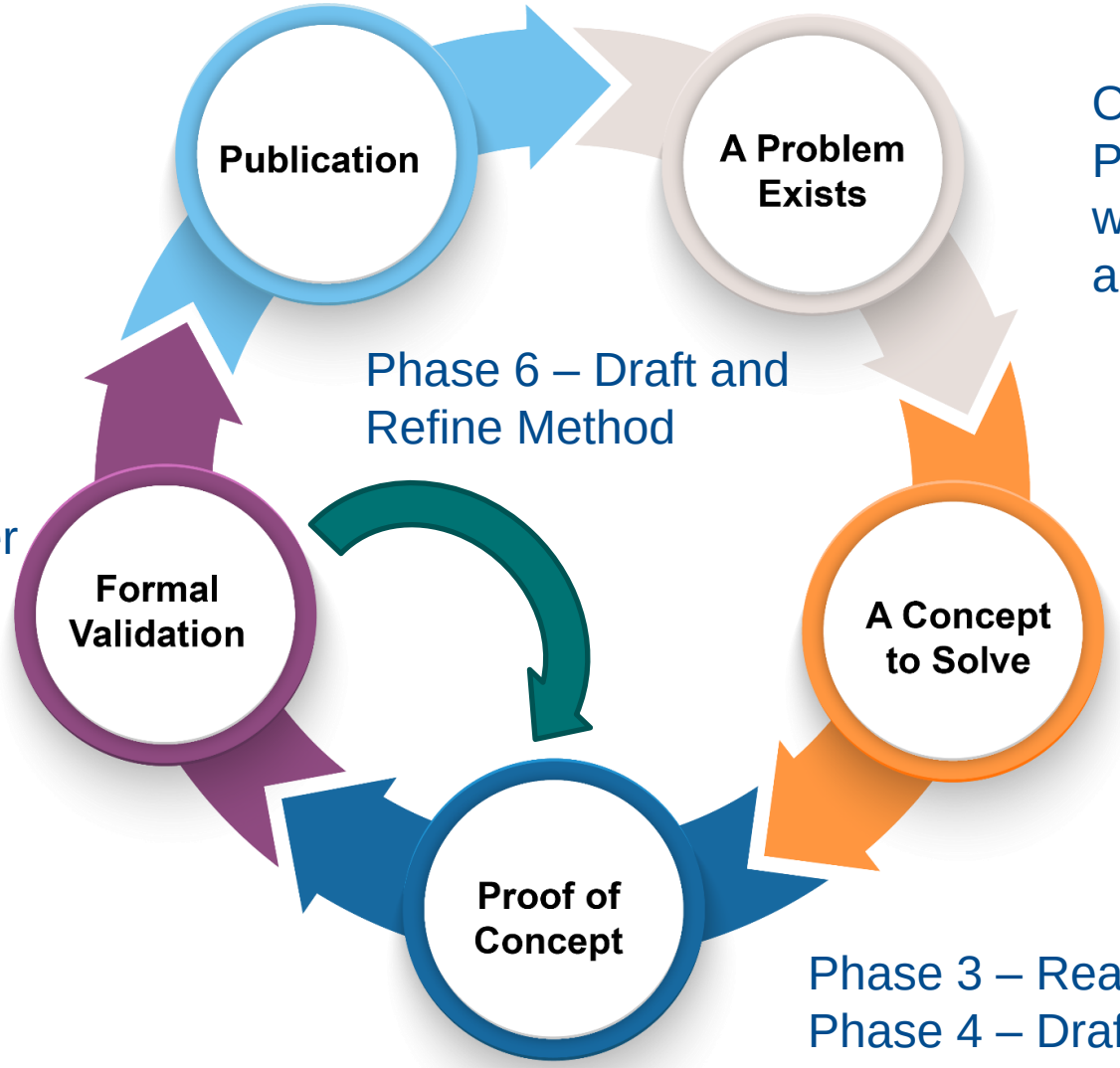
P7 – Pooled Results: Overall Excellent Recovery and Reasonable Inter- and Intra-Laboratory Precision

80 µg/L Nominal Concentration							
	GW1 - L				GW2 - L		
Target Analyte	Pooled % Recovery	Within Laboratory Relative Precision	Between Laboratory Relative Precision		Pooled % Recovery	Within Laboratory Relative Precision	Between Laboratory Relative Precision
Methane	93%	4.0%	22%		91%	3.5%	21%
Ethane	89%	3.9%	22%		89%	4.1%	23%
Ethene	96%	2.9%	29%		94%	3.5%	25%
***n*-Propane**	84%	4.4%	26%		83%	4.0%	22%

P7 – Pooled Results: Overall Excellent Recovery and Reasonable Inter- and Intra-Laboratory Precision (Cont.)

800 µg/L Nominal Concentration							
	GW1 - H				GW2 -H		
Target Analyte	Pooled % Recovery	Within Laboratory Relative Precision	Between Laboratory Relative Precision		Pooled % Recovery	Within Laboratory Relative Precision	Between Lab Relative Precision
Methane	91%	2.1%	20%		96%	3.5%	18%
Ethane	91%	3.2%	21%		90%	4.6%	23%
Ethene	94%	2.9%	23%		95%	2.7%	24%
n-Propane	85%	2.7%	23%		85%	4.2%	24%

Concern to Solution



Oil & Gas & NMA Projects
Phase 1 & 2 (native saturated wells) – confirmed inaccurate and poor precision.

Phase 6 – Draft and Refine Method

Build on RSK-175 and PA DEP3686 procedures considering laboratory community capabilities.

Phase 5 – Reagent Water

Phase 7 - Groundwater

Phase 3 – Reagent Water and Self Diagnosis
Phase 4 – Draft Procedure

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What's next …

- Continue Discussions to Finalize new SW-846 Light Gas Method (fingers crossed).

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Thank You
QUESTIONS?

David Gratson, CEAC
Senior Technical Chemist
dgratson@envstd.com

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