

Alarming Differences in Dissolved Methane across Commercial Laboratories – Finding a Fix

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The Problem

- Public concern of light gases
- Data variability
- Several published procedures, but no US EPA-published method



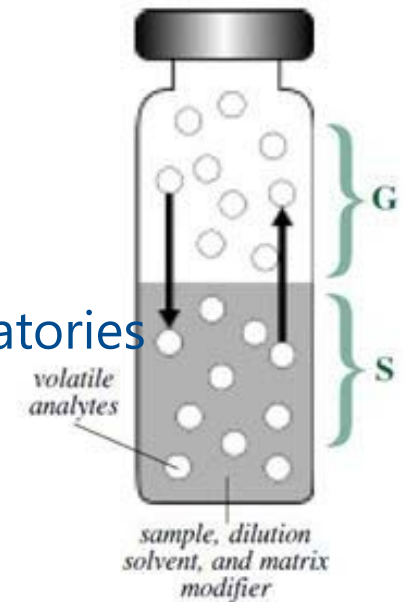
Study Sponsors, Executor, and Participants

- Members of the MSC Dissolved Methane Work Group Formed in early 2013
- Environmental Standards, Inc.
- 19 Participating Laboratories



MSC Dissolved Methane Method Workgroup

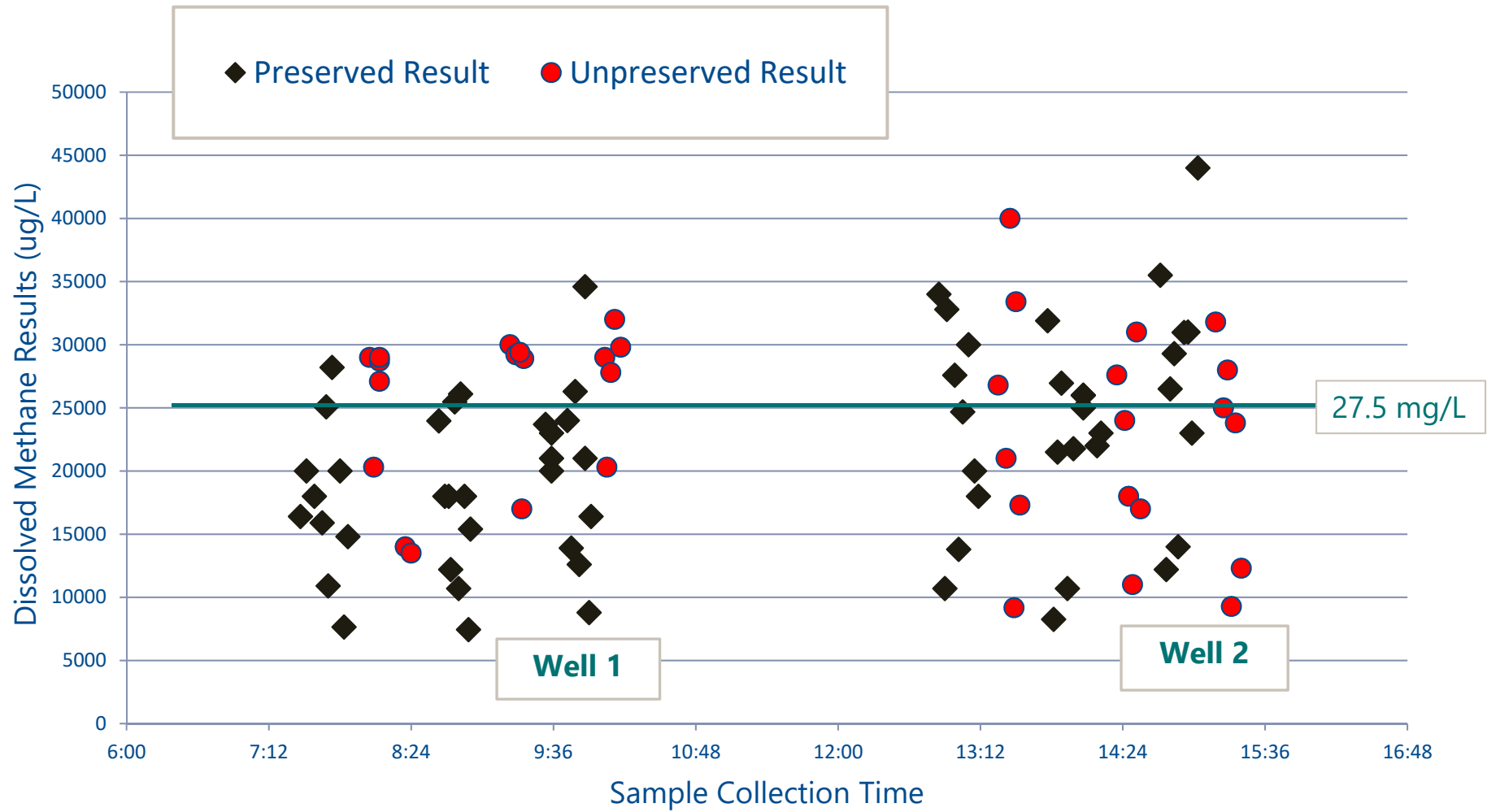
- Compared notes and reviewed information:
 - Split samples showed highly variable methane.
 - Each laboratory's protocols were equally variable.
- Phase 1 Study Completed Early 2015.
 - Two groundwater samples were submitted to 15 laboratories including one government laboratory.
- Phase 2 – Study Completed October, 2016.
 - Four blind reference standards were submitted to 15 laboratories including one government laboratory.
- Phase 3- Study Completed June, 2018.
 - Announced reference standards were submitted to 8 non-reference (previously low) laboratories and 3 reference laboratories.



Phase 1 (P1) Design

- Inter-laboratory study of two groundwater wells.
 - Groundwater wells were known to be impacted with dissolved methane.
- Infer issues that impact precision and bias.
 - Detailed questionnaire and review of laboratory SOPs.
- Evaluate sampling and analytical precision and bias.
 - 15 laboratories, 3 samples per well, 3 vials per sample.
 - Sampled vials number 1 through ~90 for each well.
 - Triplicate vials from each well analyzed within 48 hours.
 - Vials split across sampling so that each laboratory received vial across sampling period.
 - Evaluate impacts of preservation – both preserved and unpreserved, submitted based on laboratory SOP (10 preserved, 5 unpreserved).

P1 – Results



P1 - Conclusions

- Confirmed that there is significant data variability across laboratories.
- No singular issue was 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.
- Additional testing at lower range of concentrations is needed.

Phase 2 (P2) Study Participants

- MSC Dissolved Methane Method Work Group
- Environmental Standards, Inc., Valley Forge, Pennsylvania
- Environmental Services Laboratory, Indiana, Pennsylvania -Reference Standard provider
- 15 Participating Laboratories (14 commercial, 1 government)
 - One commercial laboratory reported two sets of data, using two different techniques.

P2 - Design

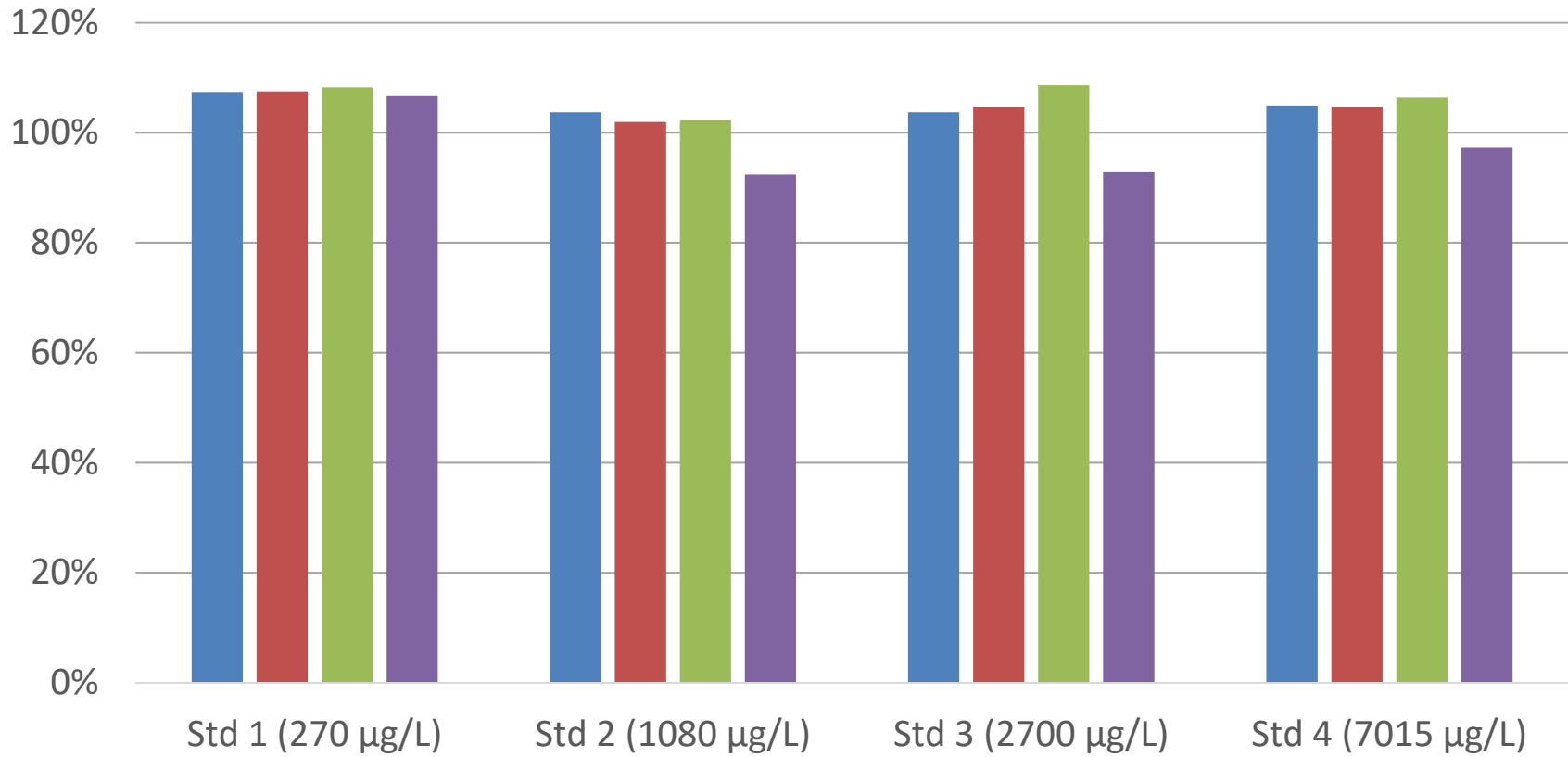
- Provide blind reference standards (unpreserved) across concentration range and number each vial in order.
- Evaluate four different concentrations to allow for individual recovery and response model evaluation.
- Control dilution effect by including at least one standard below calibration upper limit.

P2 - Design

- Provide Blind Reference Standards (unpreserved) across four concentration ranges.
 - 0.27 mg/L, 1.08 mg/L, 2.70 mg/L, 7.01 mg/L
- Each laboratory received 3 vials at each of the four concentrations. Report one at each level undiluted, duplicate analysis of remaining two vials.
- Control dilution effect by including at least one standard below calibration upper limit.
 - Laboratories instructed to only perform dilutions if required.

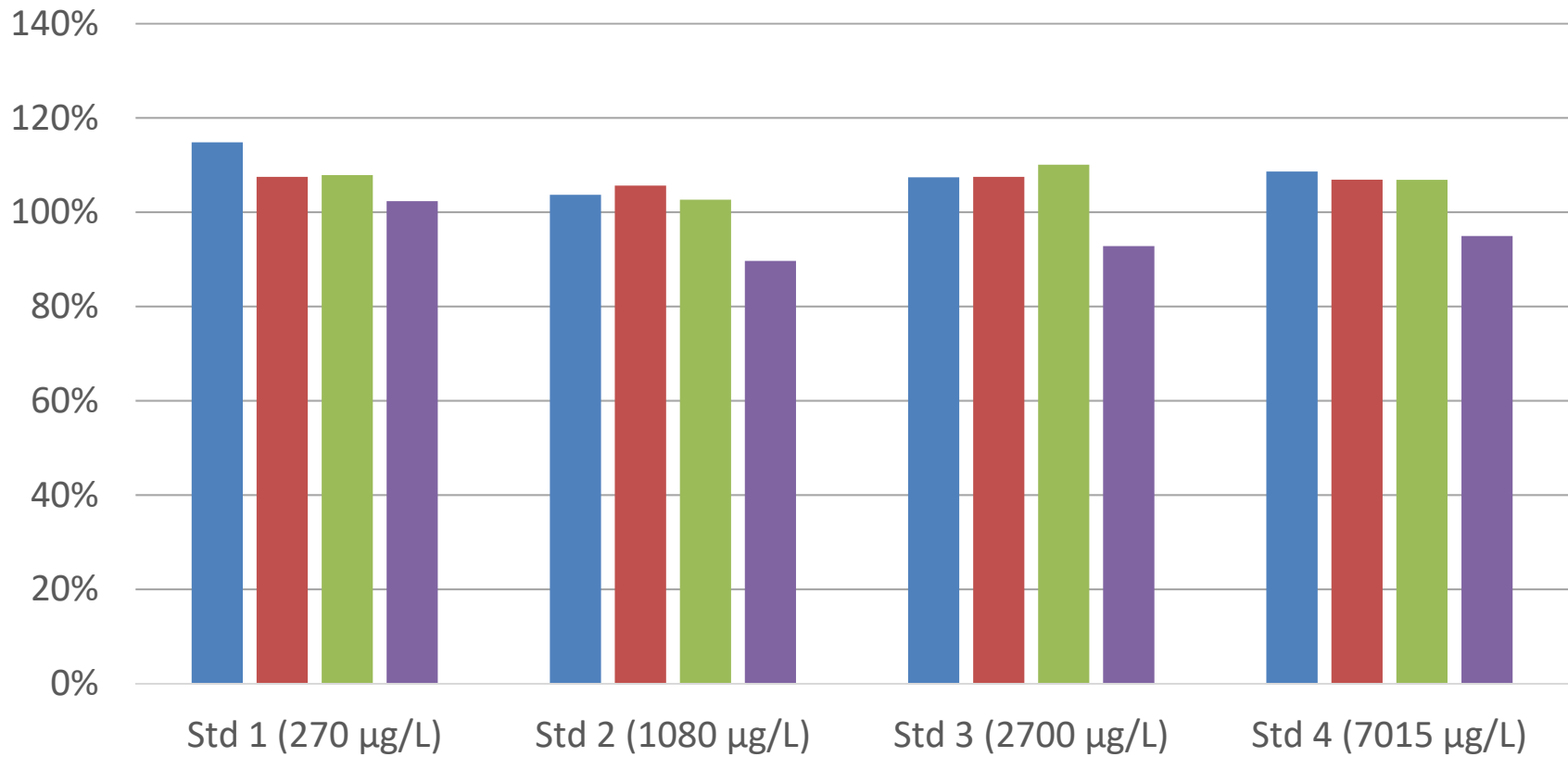
P2 - Reference Standard Provider Results

48-Hour Results

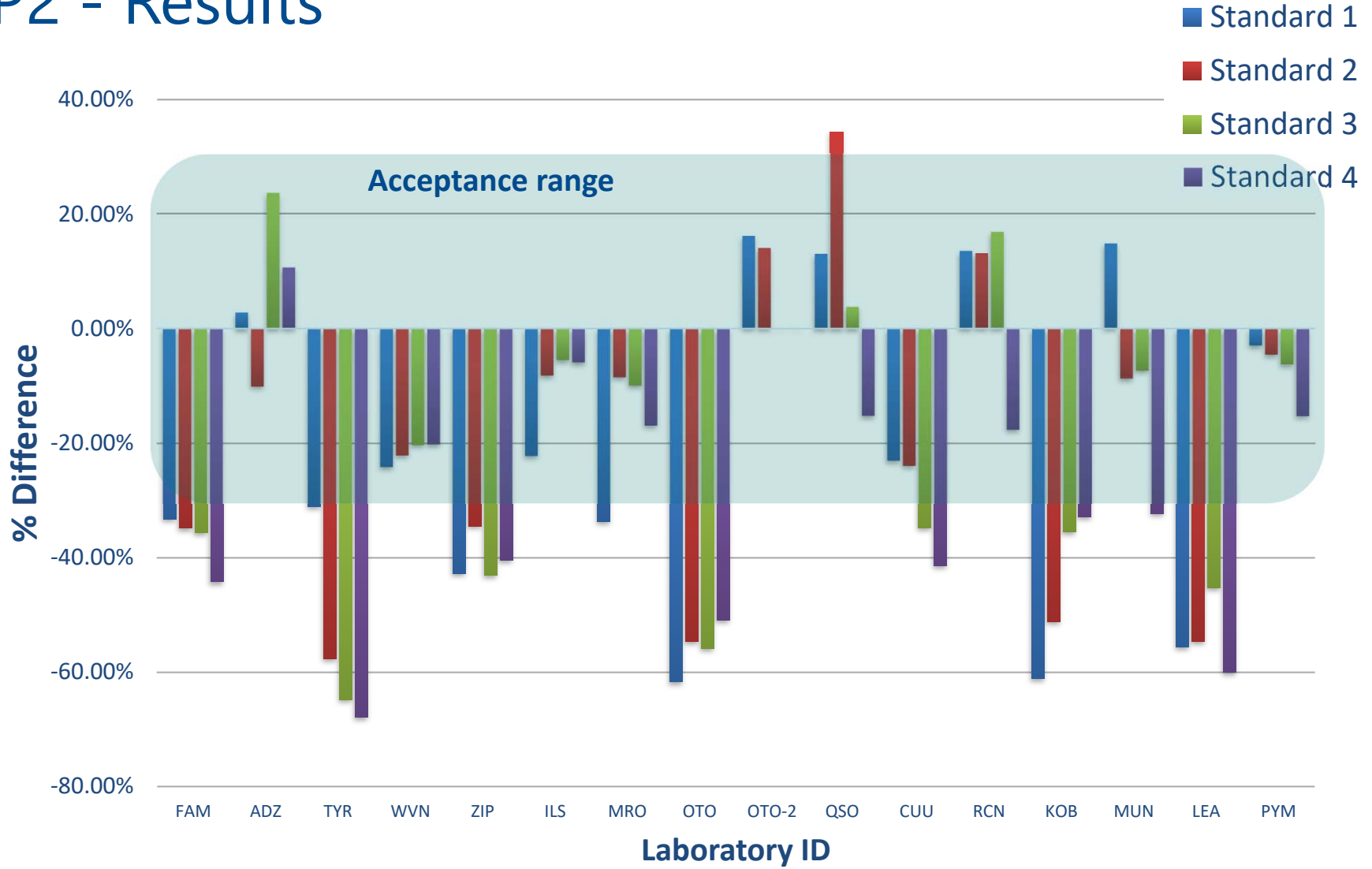


P2 - Reference Standard Provider Results

7-day Results

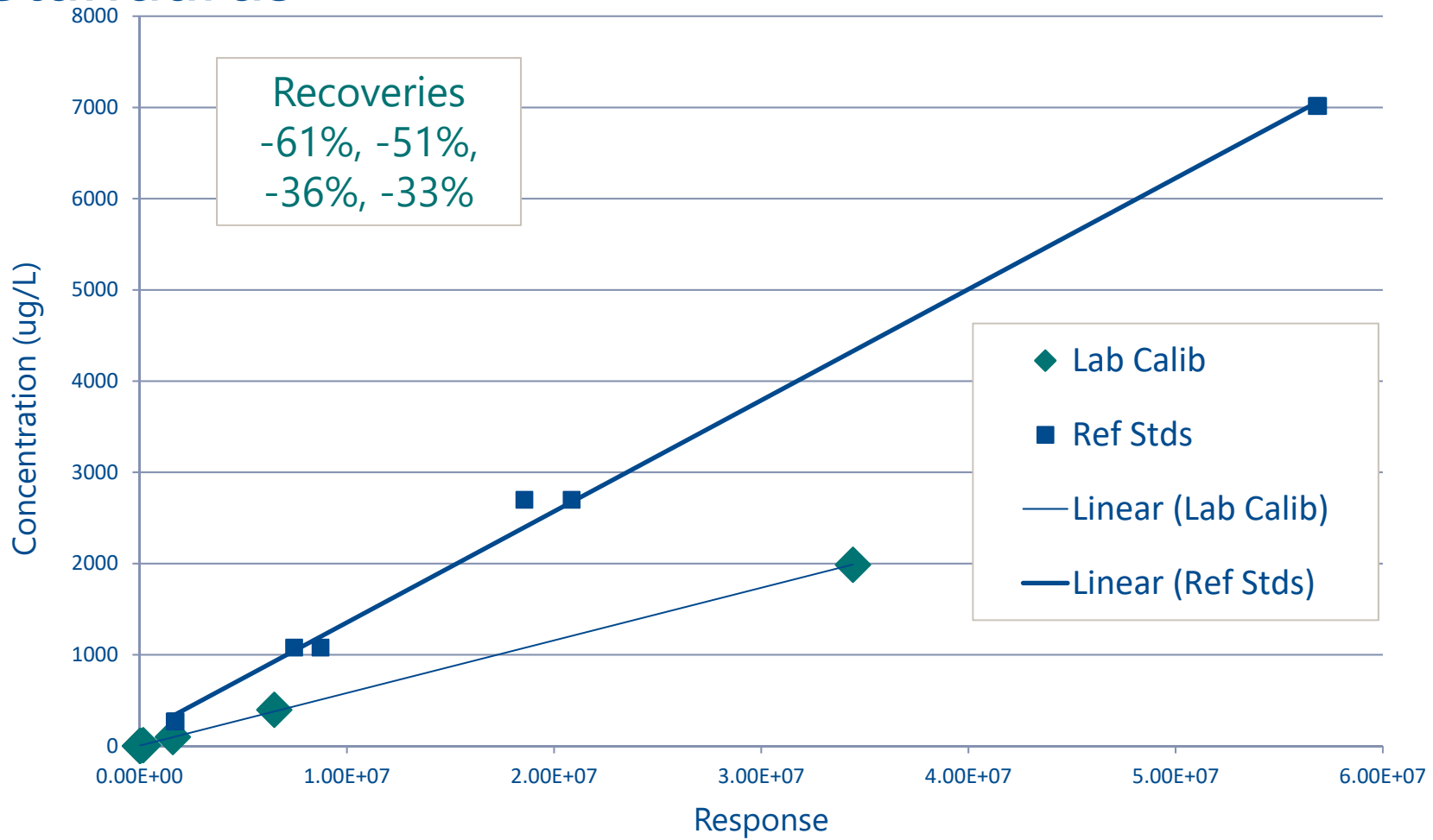


P2 - Results



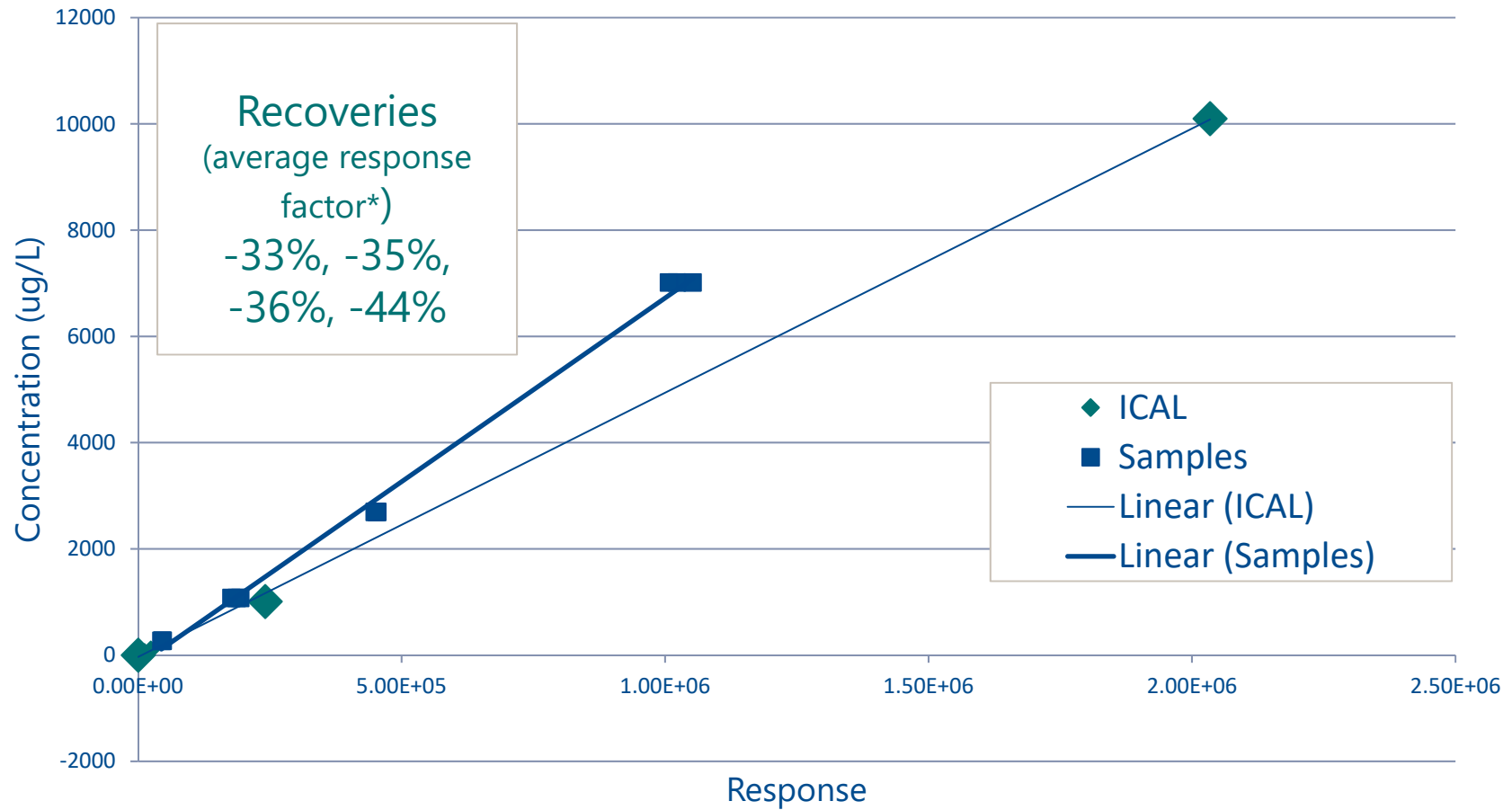
P2 - Calibration vs. Four Unknown Standards

Laboratory 13



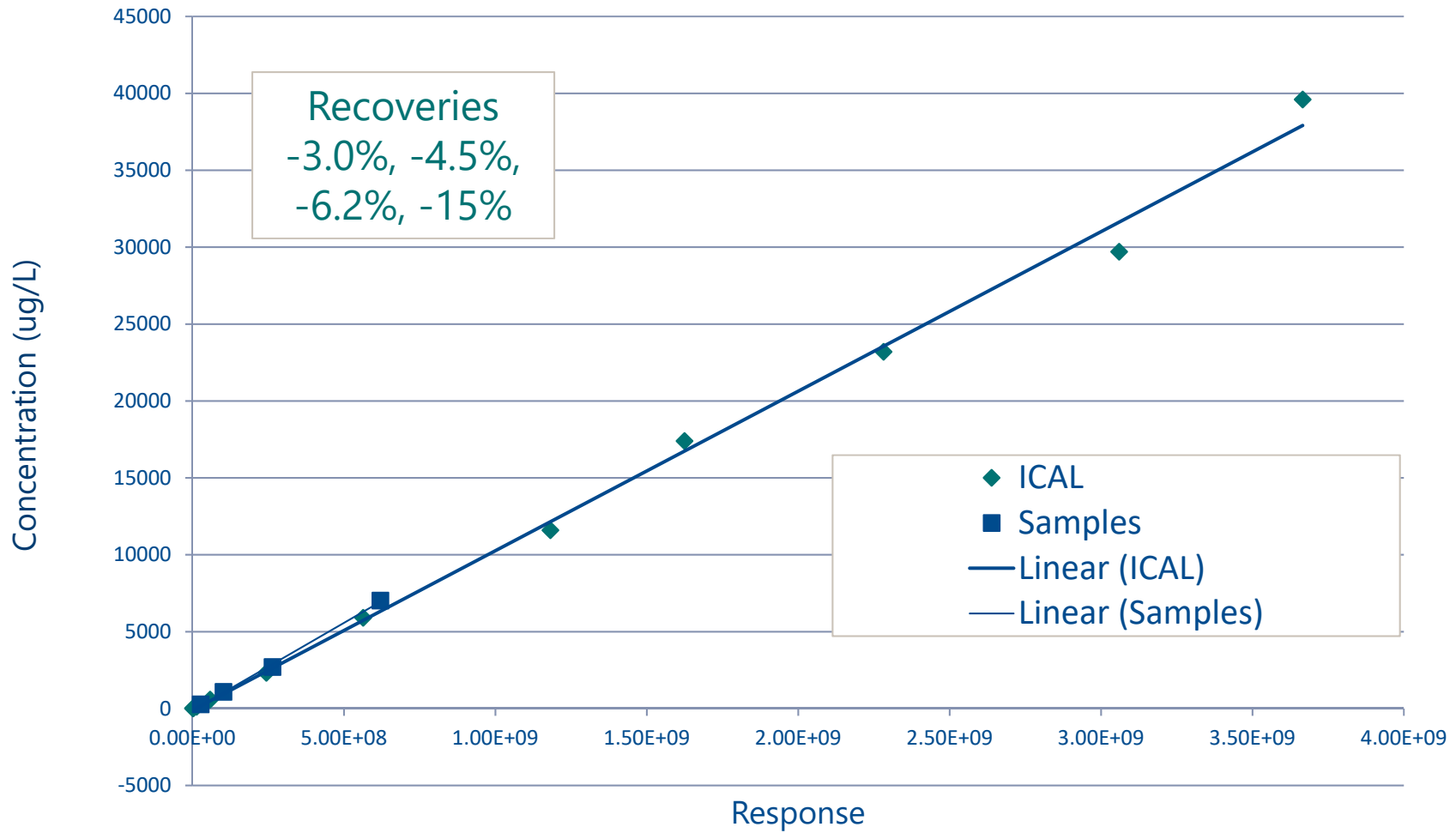
P2 - Calibration vs. Four Unknown Standards

Laboratory 1



P2 - Calibration

Laboratory 16



P2 - Conclusions & Recommendations

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

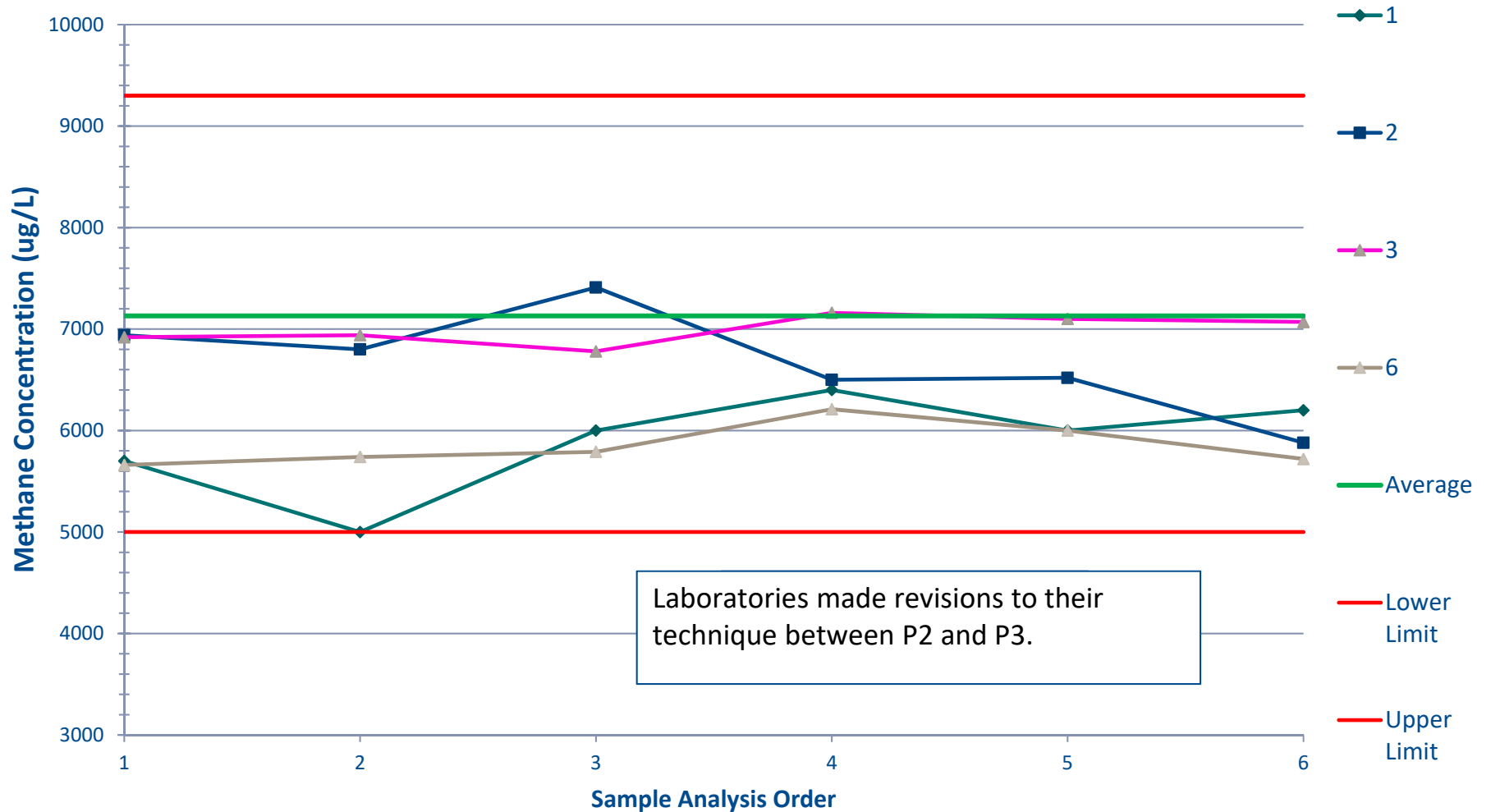
Phase 3 (P3) Study Participants

- MSC Dissolved Methane Method Work Group
- Environmental Standards, Inc., Valley Forge, Pennsylvania
- Environmental Services Laboratory, Indiana, Pennsylvania -Reference Standard provider
- 8 Non-Reference Commercial Laboratories
 - Selected from those that failed P1 or P2 at 30% difference mark.
- 3 Reference Laboratories (2 commercial and 1 government)

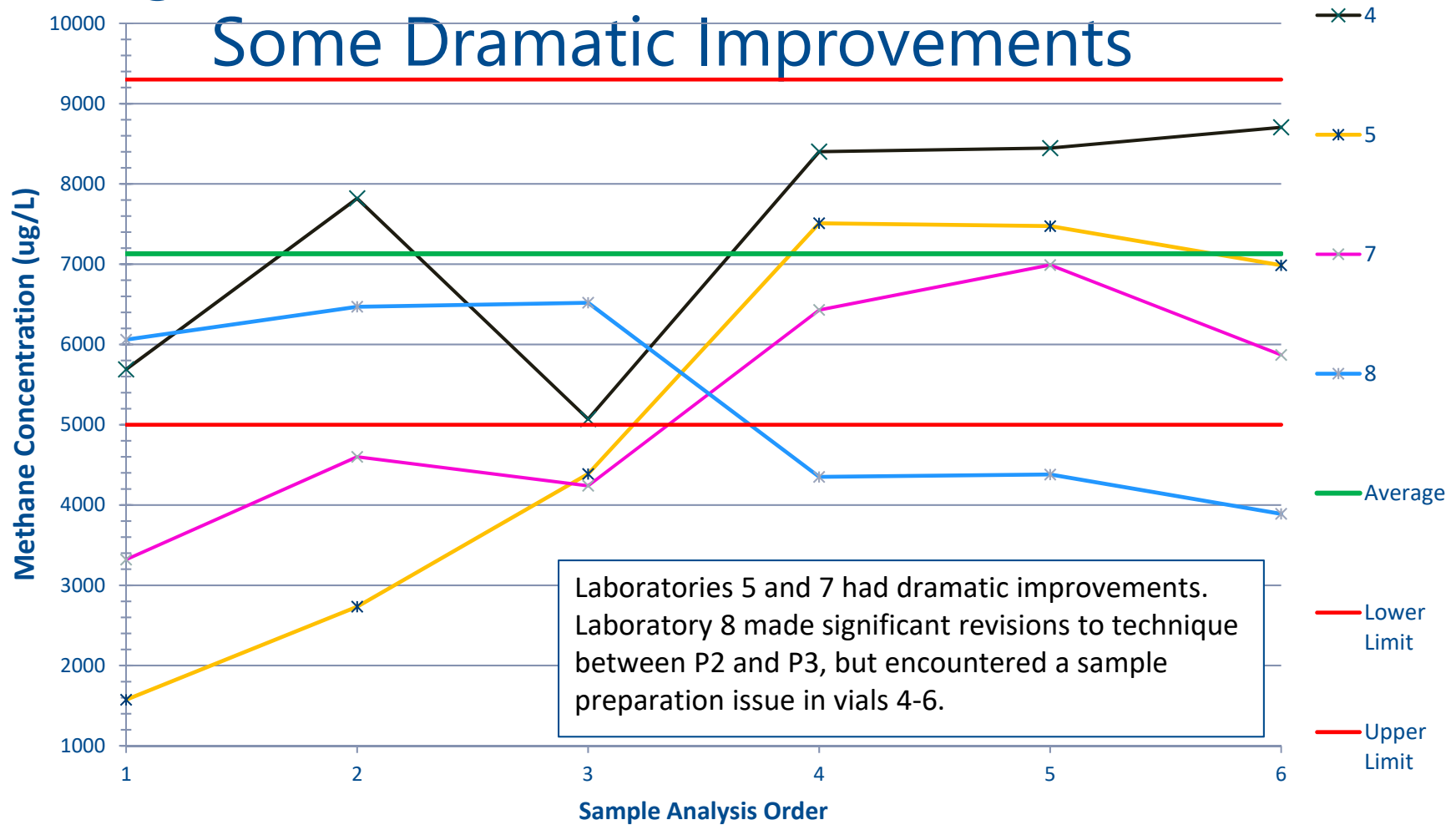
P3 - Design

- Send Laboratories multiple vials of a known and labeled concentration standard.
 - Approximately 70 vials were prepared, all at a single final concentration @ ~7,000 ppb.
 - Laboratories were requested analyze vials sequentially and review their results against the known 7,000-ppb concentration.
 - If outside 30% acceptance criterion, **self-diagnose**, make revisions to preparation, handling calibration, analysis and technique as needed.

P3 - Non-Reference Laboratories – Within Criteria



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



Statistical Summary: All Phases

Results by Phase	N	Mean (µg/L)	SD (µg/L)	% RSD
P1, Well 1	53	21070	7052	33%
P1, Well 2	50	23565	8533	36%
P2, Standard 1 (lowest concentration)	45	212	70.7	33%
P2, Standard 2	43	861	278	32%
P2, Standard 3	40	2121	677	32%
P2, Standard 4 (highest concentration)	35	4900	1450	30%
P3 Accepted Values	39	6590	870	13%

SD = standard deviation, N = number of samples RSD = relative standard deviation

Next Steps

Phase 4 – Draft the Laboratory Method

- Document the proven laboratory method.
- Submit the laboratory method to laboratories and select state agencies for review.
- Update final draft laboratory method based on **P3**.
- Engage US EPA Office of Water, and select state agencies to lay the groundwork for regulatory approval.

Next Steps

Phase 5 – Laboratory Round-Robin Study using Final Draft Method

- Invite 22 laboratories to participate.
- Create four standards (concentrations) to distribute to the participating laboratories.
- Include a certified dissolved-gas standard, which was recently made available.
- Request that laboratories strictly follow the final draft method and provide data and feedback.

Next Steps

Phase 6 – Method Preparation and Submission

- Submit detailed summary report from Phase 5.
- Prepare a final dissolved light gases method for submission to US EPA Office of Water.
- Option to also submit to select state agencies.

Thank You

QUESTIONS?



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