Multi-Laboratory Study of ICP-MS for Analysis of Selenium and Arsenic in FGD Wastewater

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Presentation Overview

- Project Background & Approach
- FGD Wastewater Sample Characterization Study
- Multi-laboratory Study
- Method Variability Evaluation
- Conclusions & Recommendations
- Acknowledgements

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Project Background

- Effluent Limitations Guidelines (ELG) for U.S. coal-fired power plants set stringent limits for flue gas desulfurization (FGD) wastewaters

- Arsenic (As) and selenium (Se) quantification in FGD wastewater below the ELG limits will be highly challenging
  - Interferences from dissolved salts
  - Instrument limits on total suspended solids
  - Potential interferences from rare earth elements (REE)

Parameter	Long-term Average	Maximum Daily Limit	Monthly Average Limit
Total arsenic, µg/L	5.98	11	8
Total selenium, µg/L	7.5	23	12

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Characteristics of Typical FGD Wastewaters

- FGD wastewaters contain high concentrations of sodium, magnesium, calcium, strontium, silicon, boron, chloride and sulfate at parts-per-million to percent levels

Parameter	Low (mg/L)	High (mg/L)
Calcium	680	5,700
Chloride	1,100	23,000
Magnesium	210	5,800
Sodium	50	1,900
Sulfate	1,200	13,000
Total Dissolved Solids (TDS)	3,000	42,000
Total Suspended Solids (TSS)	6.0	65

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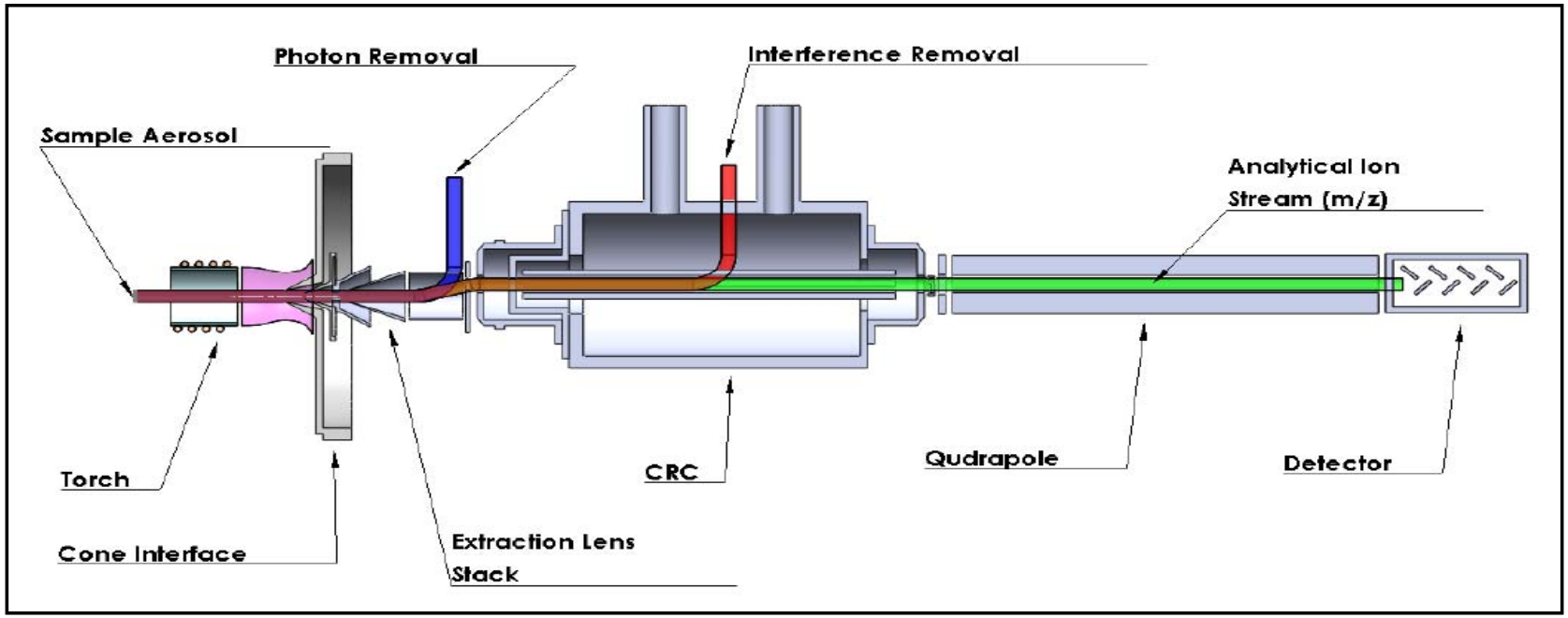
ICP-MS with Interference Reduction Technology

- Inductively Coupled Plasma Mass Spectrometry (ICP-MS) – EPA Methods 200.8/1638
  - Collision reaction cell (CRC)
  - Dynamic reaction cell (DRC)
  - Triple quadrupole (QQQ)



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Examples of Interferences for Arsenic and Selenium

- Biases due to:
  - Spectral interferences
  - Physical interferences
  - Ionization enhancement
  - Memory effects
  - High total dissolved solids
  - Other chemical additives
    - Bromine used in mercury control
    - Reduced sulfur additives

Element	Mass	Interferences
As	75	$^{59}Co^{16}O^{+}$, $^{36}Ar^{38}Ar^{1}H^{+}$, $^{36}Ar^{39}K^{+}$, $^{40}Ar^{35}Cl^{+}$, $^{38}Ar^{37}Cl^{+}$ $^{43}Ca^{16}O_2^{+}$, $^{23}Na^{12}C^{40}Ar^{+}$, $^{12}C^{31}P^{16}O_2^{+}$, $^{40}Ca^{37}Cl^{+}$, $^{150}Nd^{++}$, $^{150}Sm^{++}$
Se	78	$^{40}Ar^{38}Ar^{+}$, $^{38}Ar^{40}Ca^{+}$, $^{41}K^{37}Cl^{+}$, $^{156}Gd^{++}$, $^{156}Dy^{++}$

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Project Objectives

- Help laboratories improve ICP-MS techniques
  - Use appropriate sample preservation
  - Achieve the necessary sensitivity
  - Overcome analytical interferences
  - Develop good quality control procedures
- Expand the pool of qualified laboratories
  - Communicate best practices
  - Provide samples for self-evaluation
- Educate power plant environmental staff
  - Selecting a commercial laboratory
  - Evaluating ICP-MS data

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Project Approach

- Prescreen candidate biologically treated FGD wastewaters (Se, As < ELG limits)
- Select 4 wastewaters for multi-lab study
  - Obtain bulk samples
  - Prepare and distribute homogenized samples to participating laboratories
  - Prepare and distribute one synthetic FGD wastewater
- Collect, review and summarize laboratory data, recommend enhanced techniques

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FGD Wastewater
Sample Characterization Study

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Sample Characterization Study

- Objective: Identify appropriate samples for study
  - Study effects of container type, preservative, and digestion method
  - Measure total recoverable Se, As, sample stability over 1 month
  - Measure rare earth element (REE) interferences
    - Neodymium, samarium interference on As
  - Verify stability of Se, As for one month from collection

REE: Neodymium

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Study Variables

- Sample bottles
  - HDPE bottles
  - Glass bottles
- Sample preservation
  - Unpreserved
  - 1% nitric
  - 1% nitric, 1% hydrogen peroxide
- Sample digestion
  - EPA 200.8 hot block digestion
  - EPA 200.8 modified with closed-vessel, oven bomb digestion
- Analytical instrument
  - ICP-QQQ-MS
  - ICP-CRC-MS (subset of samples)

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Closed Vessel Digestion

- A sample aliquot was placed into a PFA closed-vessel oven bomb
- Samples preserved to a final 2% (v/v) nitric acid and 1% (v/v) hydrogen peroxide concentration
- Heated to a minimum of 85°C for at least 4 hours to ensure complete metal dissolution

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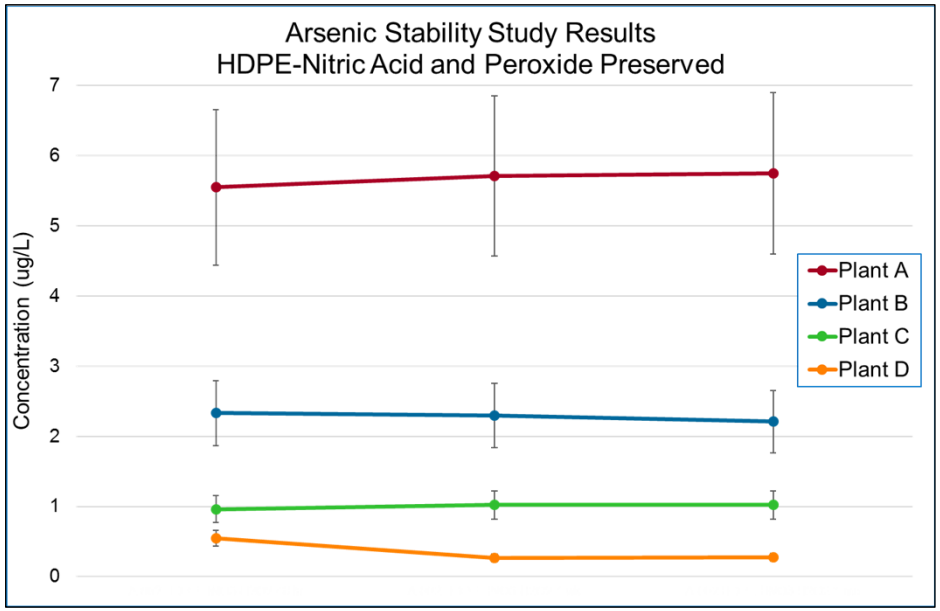
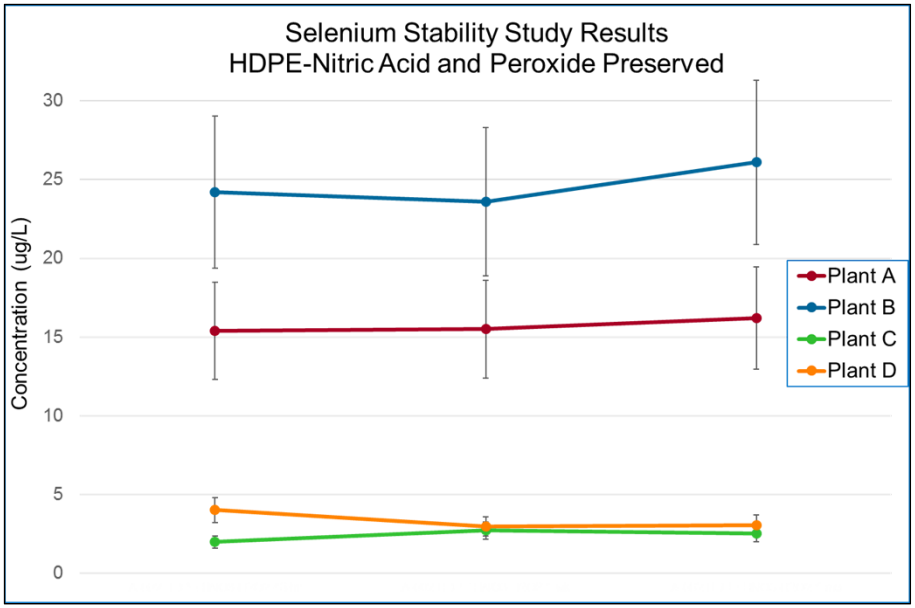
Sample Stability Study

- Samples were stable over 1 month
  - When stored in HDPE or borosilicate glass
  - When preserved with
    - 1% nitric
    - 1% nitric : 1% peroxide
    - Unpreserved





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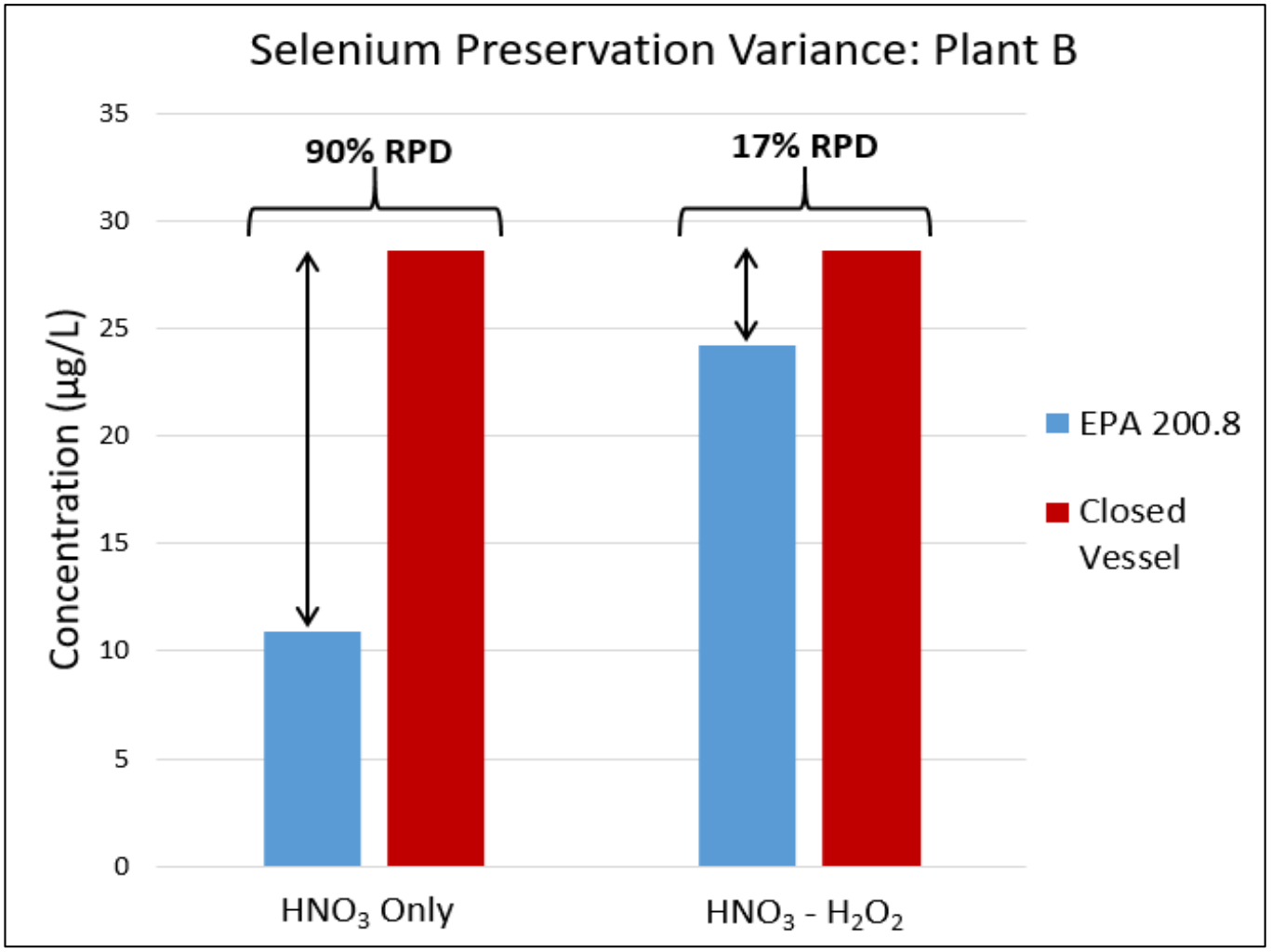
Selenium Digestion and Preservative Effect

- Low bias seen with open digestion, but effect not seen when samples were preserved with 1% nitric : 1% peroxide.



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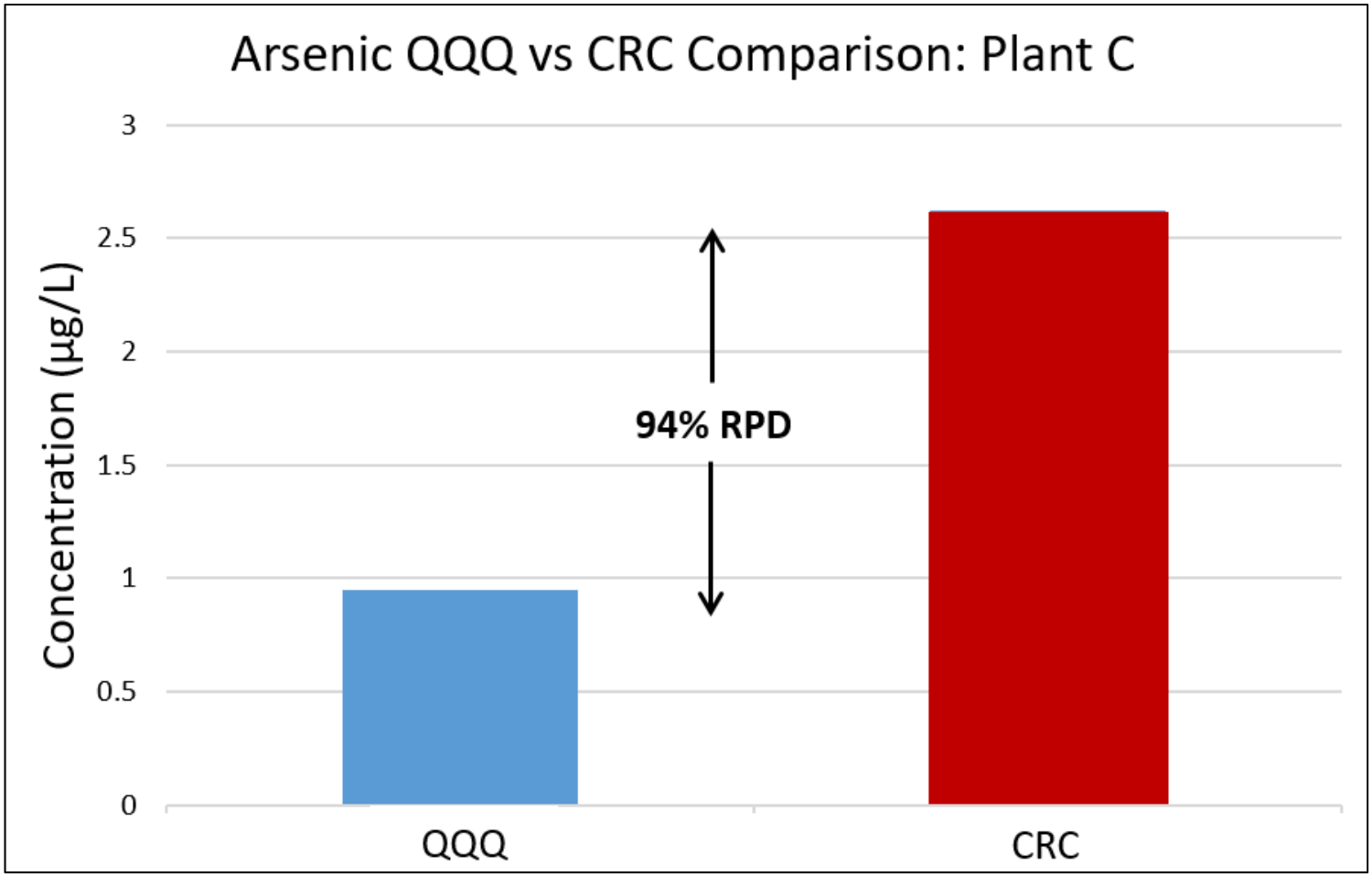
Arsenic Instrumentation Effect

- Potential high bias for *some waters* when analyzed by ICP-CRC-MS vs. ICP-QQQ-MS.



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Multi-laboratory Study

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Multi-Lab Study Scope

- 16 participating laboratories
  - 10 utility labs
  - 6 commercial labs
- 4 biologically treated FGD wastewaters (3 blinded replicates)
  - Only one site from the prescreening study was available for use in the multi-lab study
  - Fortified with selenium and arsenic to ~ 8 ppb (target)
  - Preserved with 1% nitric, 1% hydrogen peroxide
- 1 synthetic FGD samples (3 blinded replicates)
- Short-term stability study
  - Analysis by within 48 hours of receipt, at 1 week from receipt, and again at 1 month from receipt

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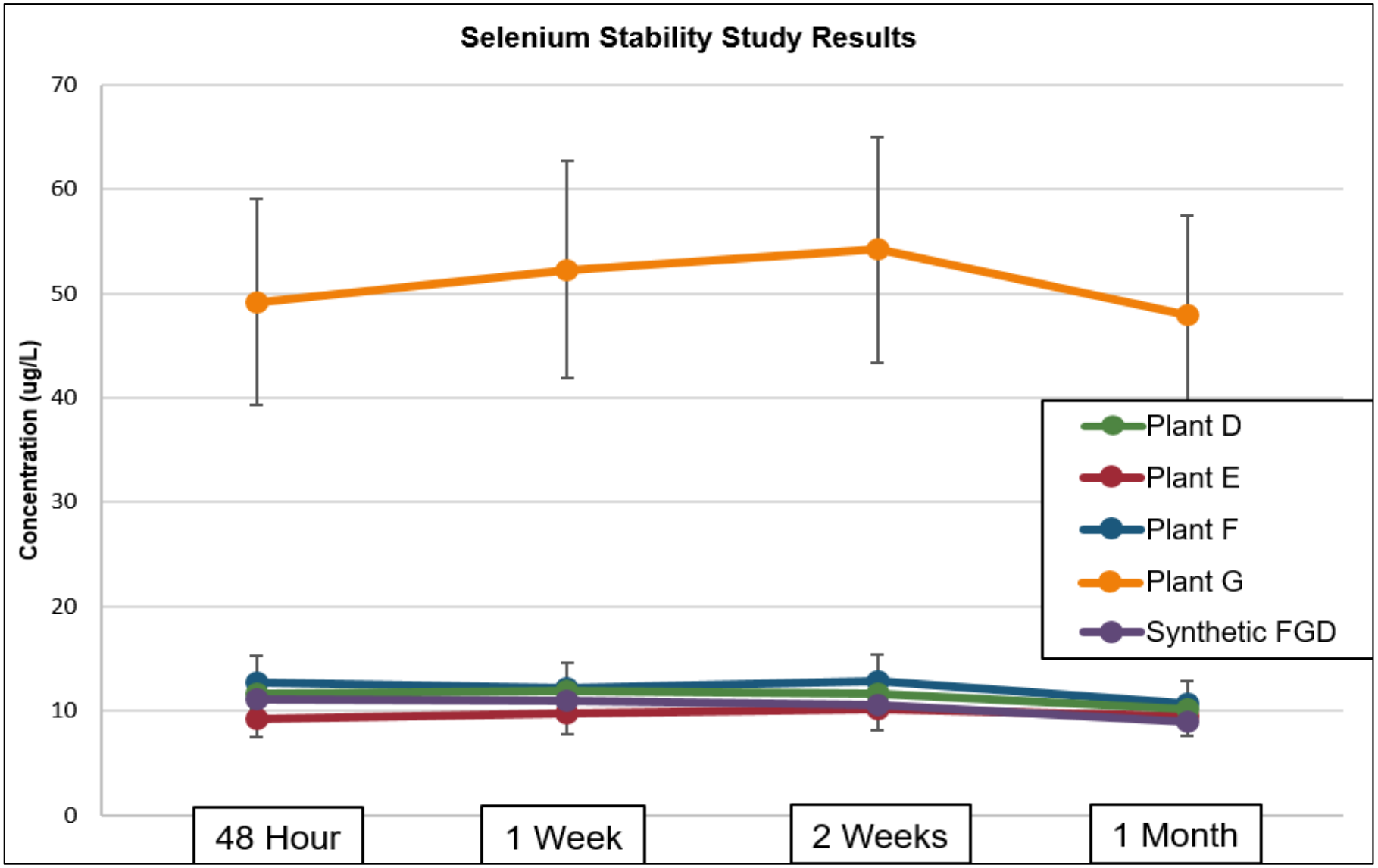
Selenium Stability Study



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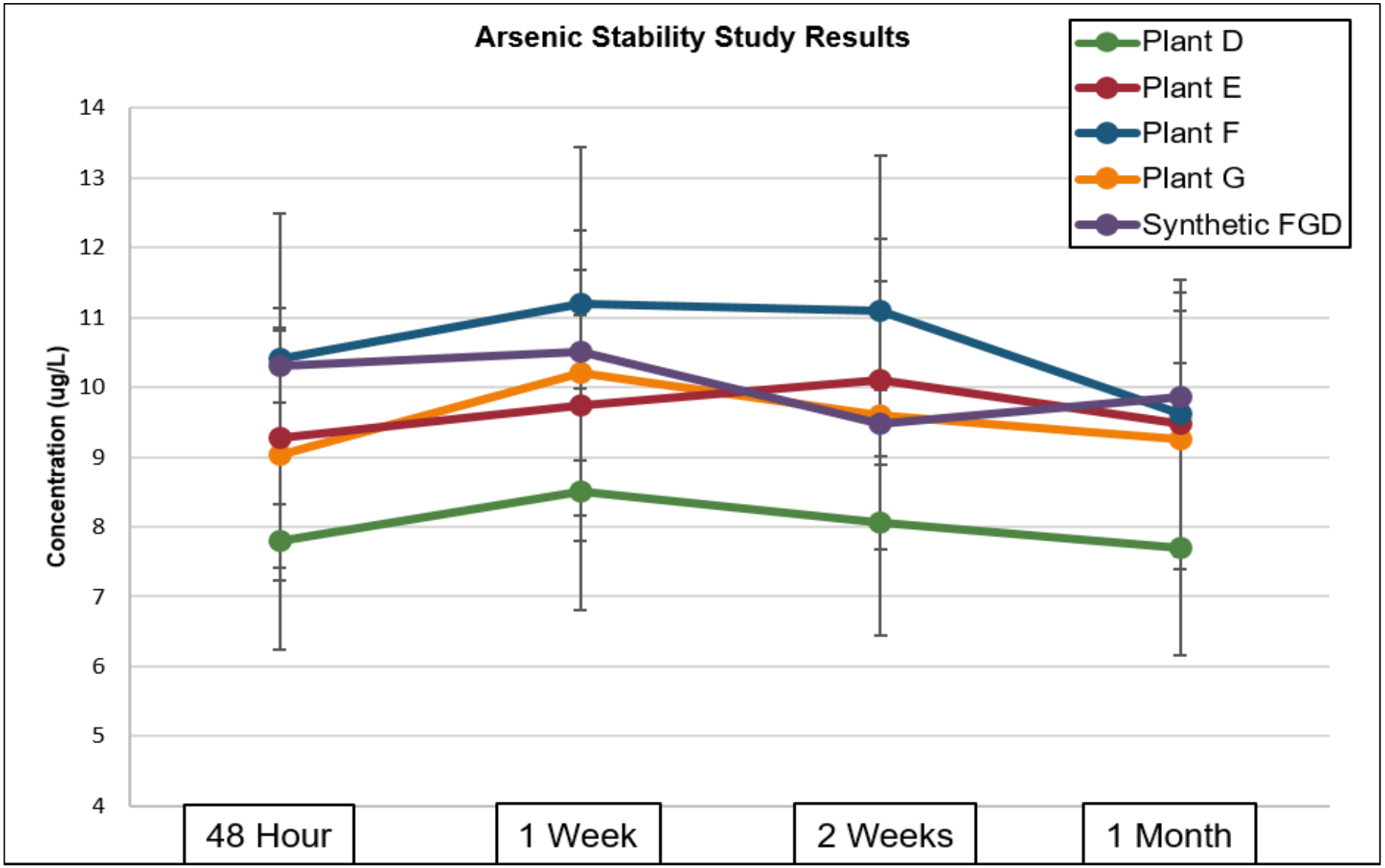
Arsenic Stability Study



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Multi-Laboratory Study Evaluation

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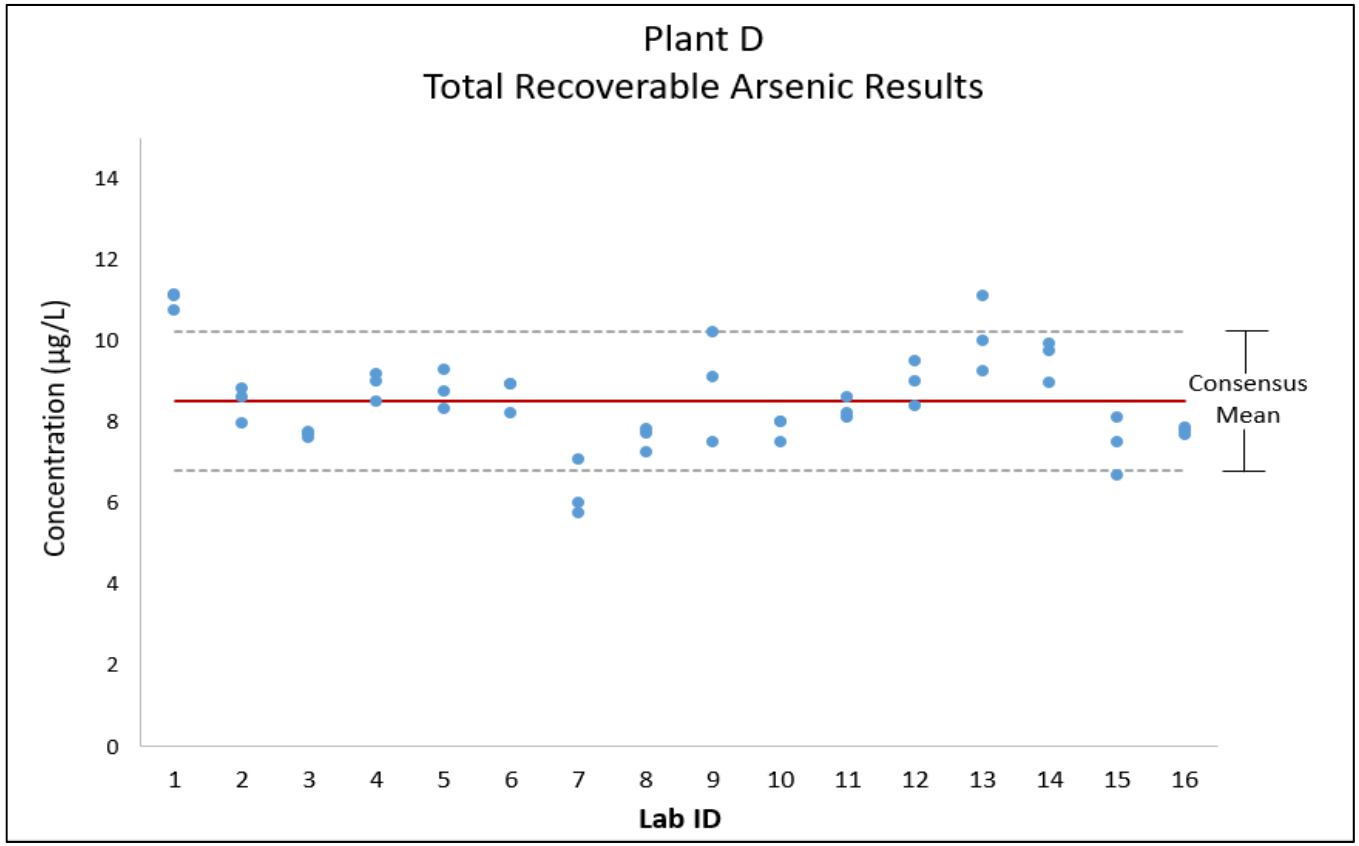
Multi-Laboratory Study Evaluation

- Most laboratory results were within +/- 20% Difference of the consensus mean value.
  - Potential laboratory bias was estimated if results fell outside this window.



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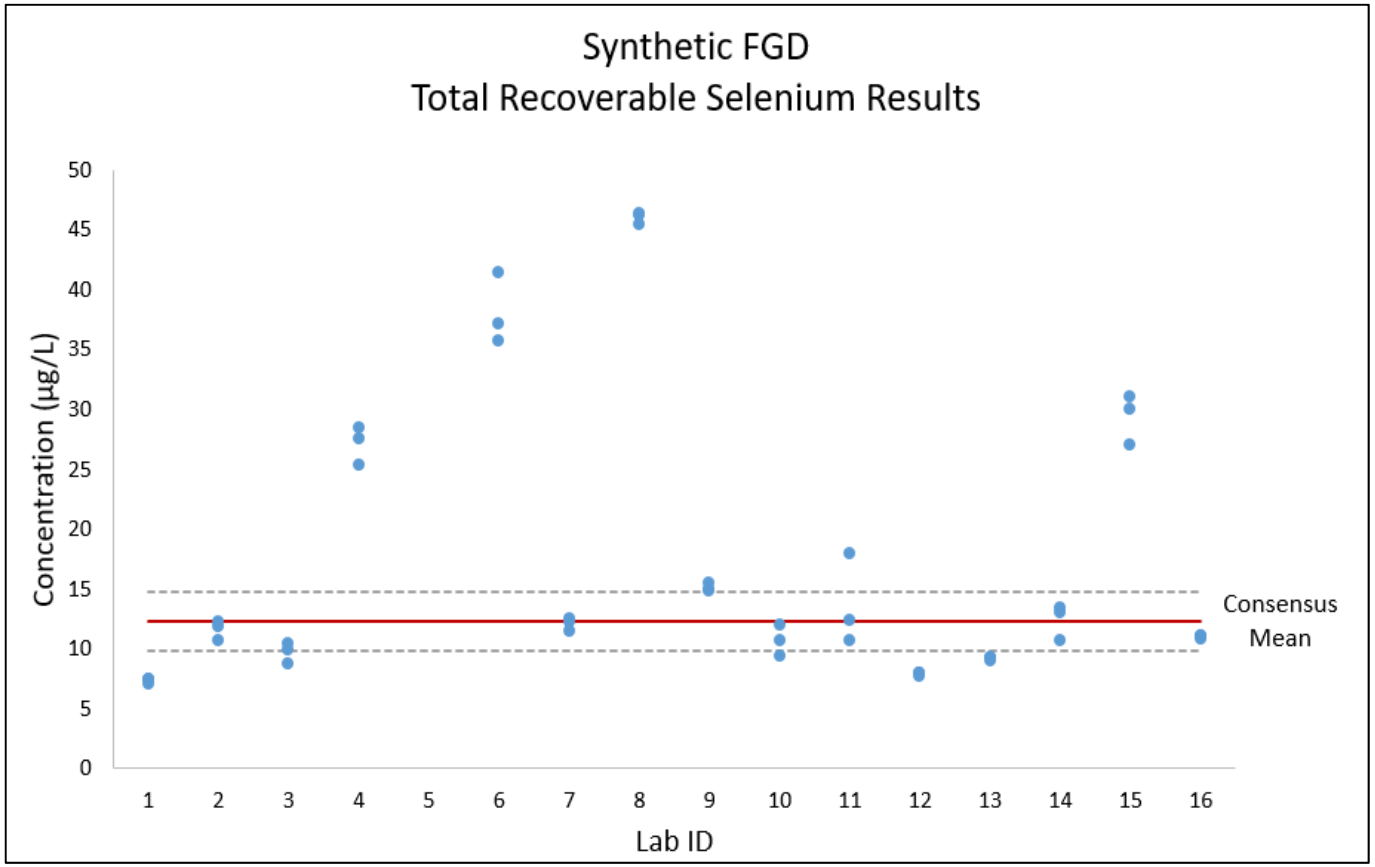
Multi-Laboratory Study Evaluation

- The Synthetic FGD results were highly variable.
  - Arsenic (8.2 µg/L to 310 µg/L)
  - Selenium (7.1 µg/L to 210 µg/L)



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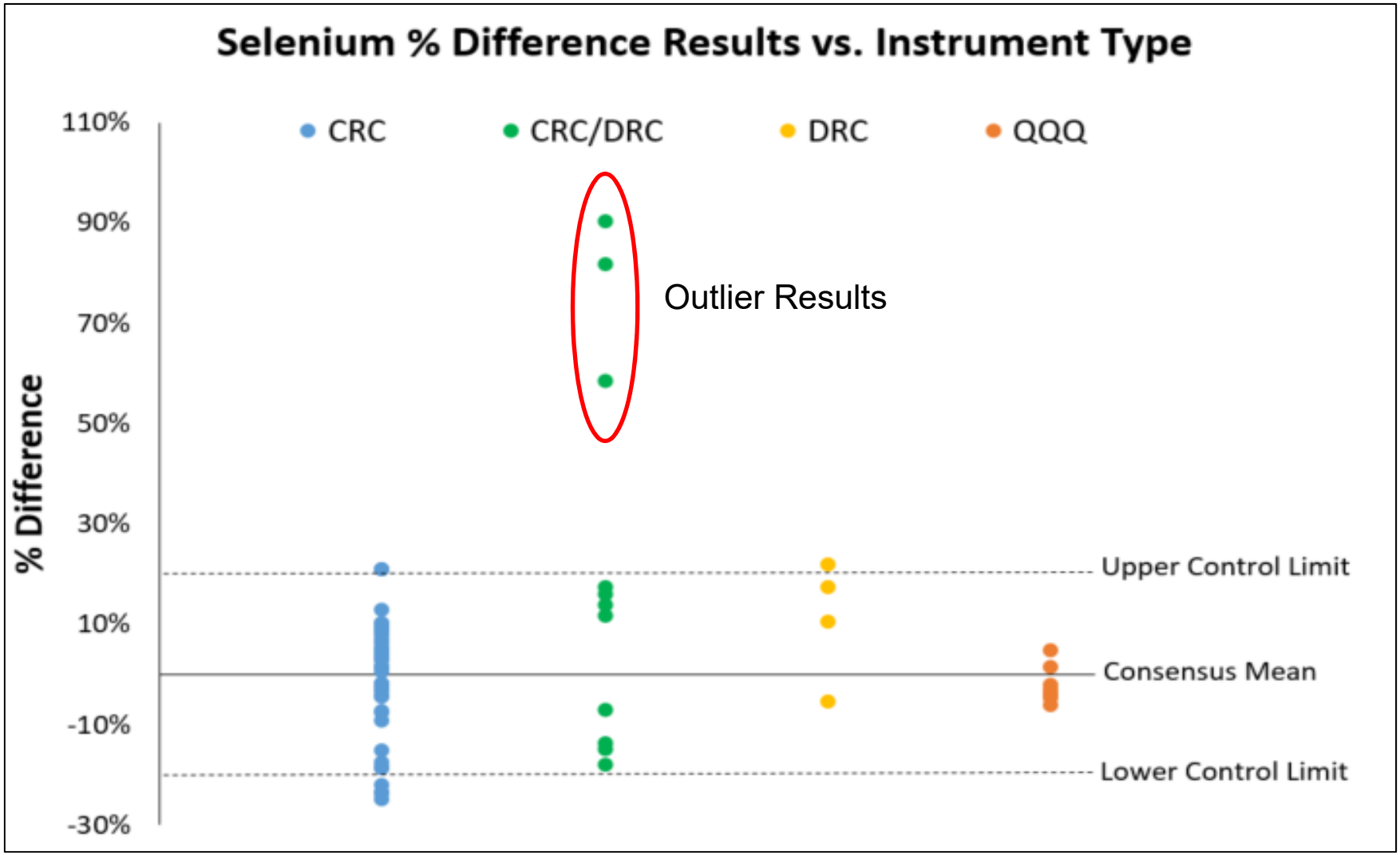
Interference Reduction Type Variability - Selenium



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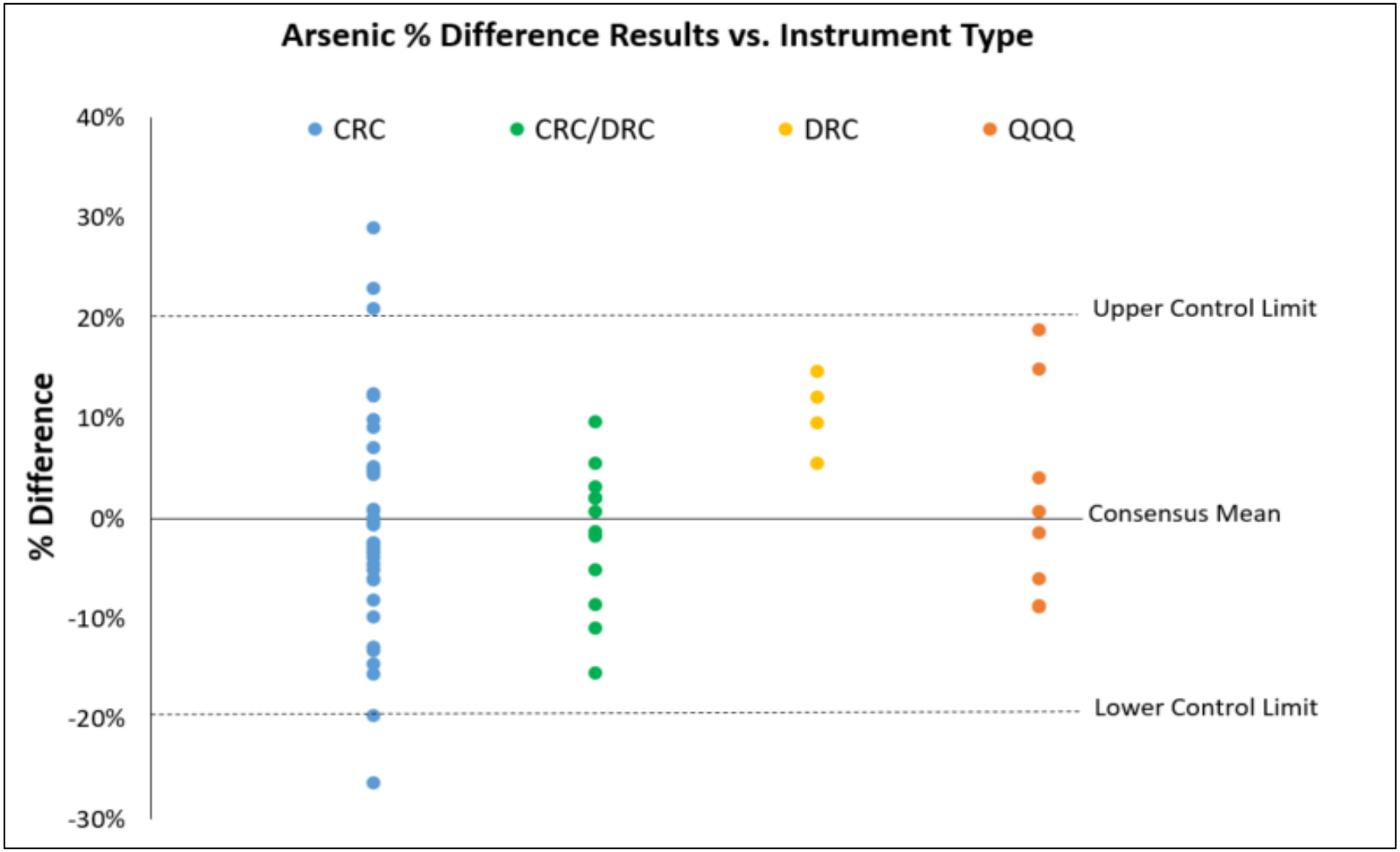
Interference Reduction Type Variability - Arsenic



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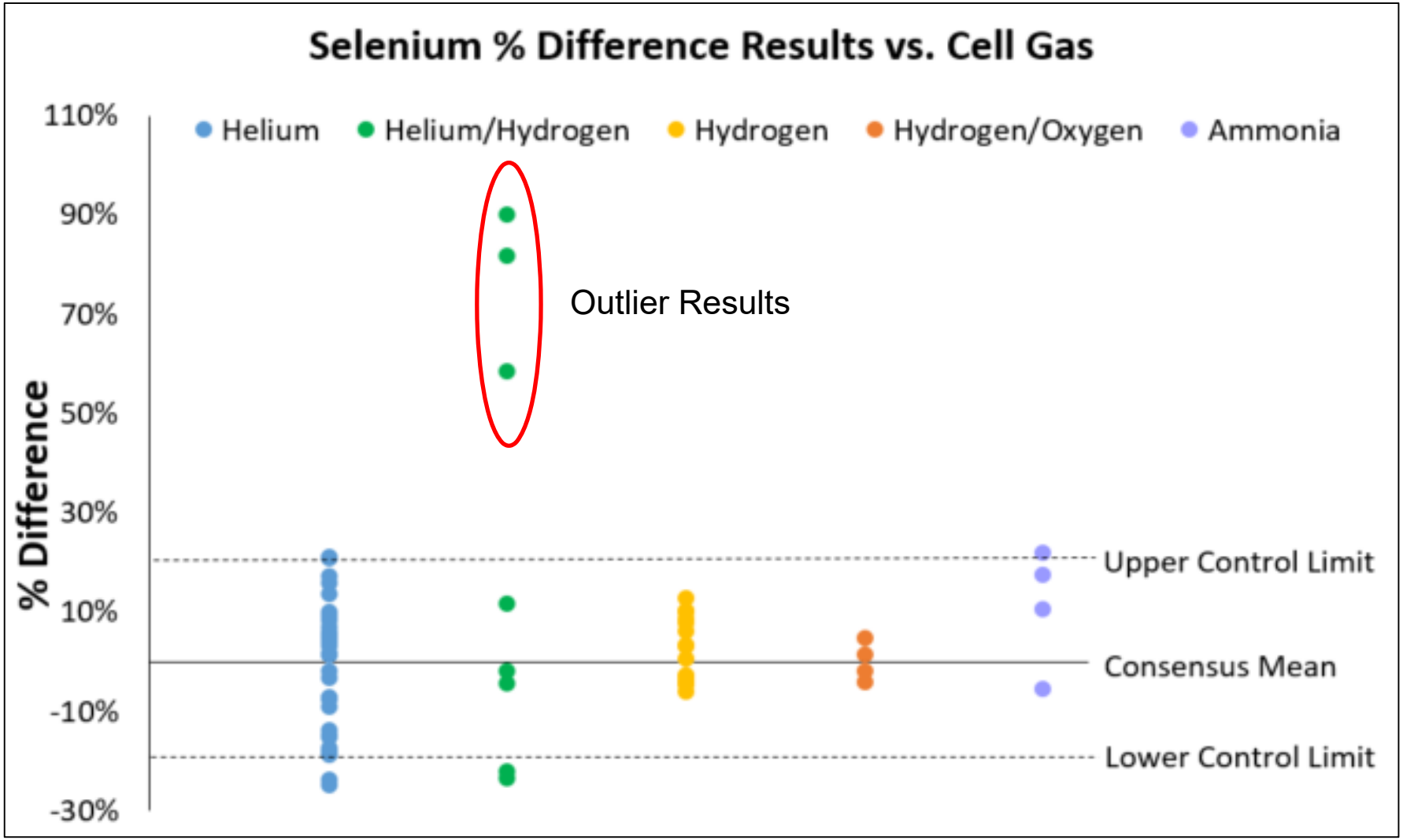
Cell Gas Type Variability - Selenium



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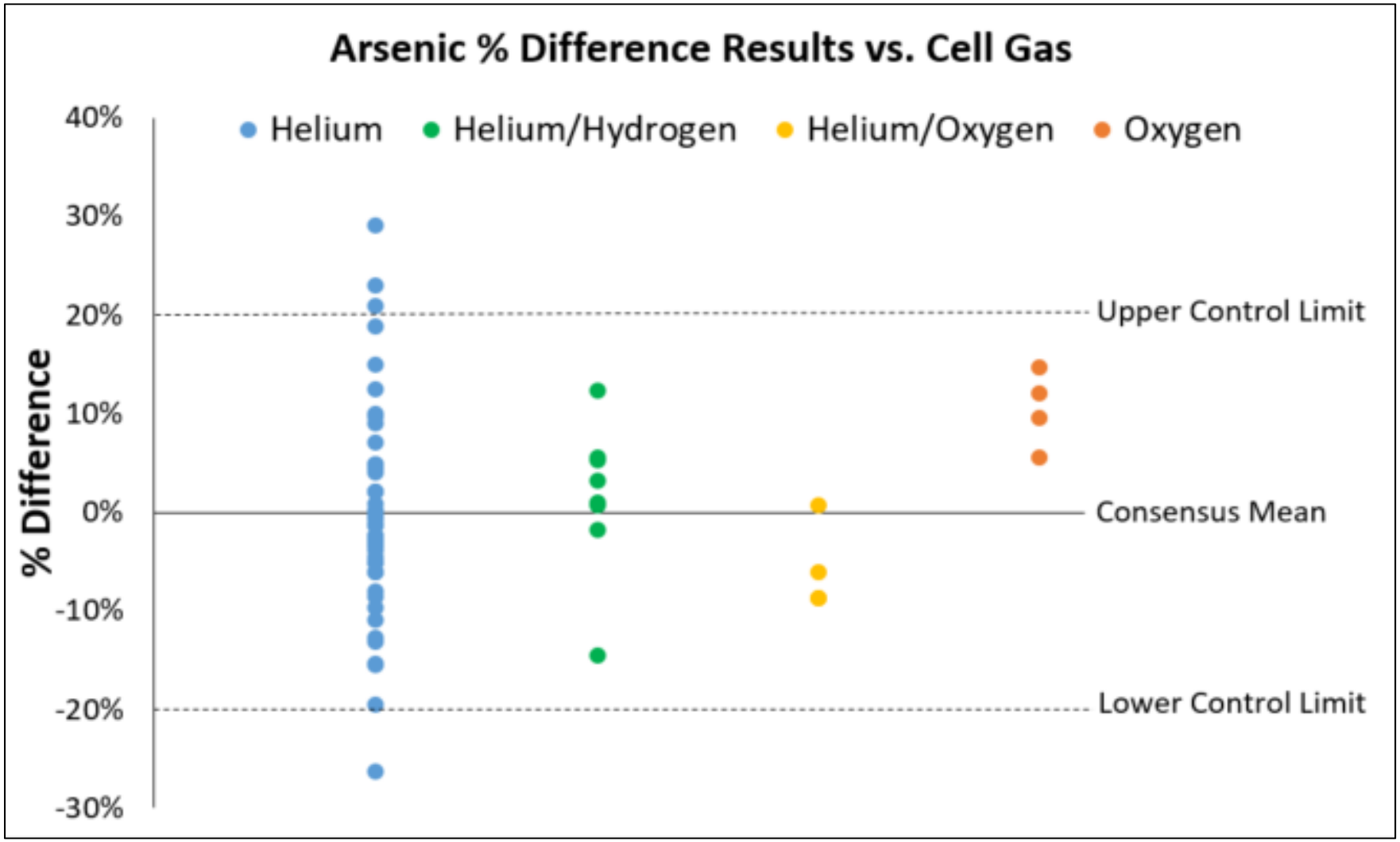
Cell Gas Type Variability - Arsenic



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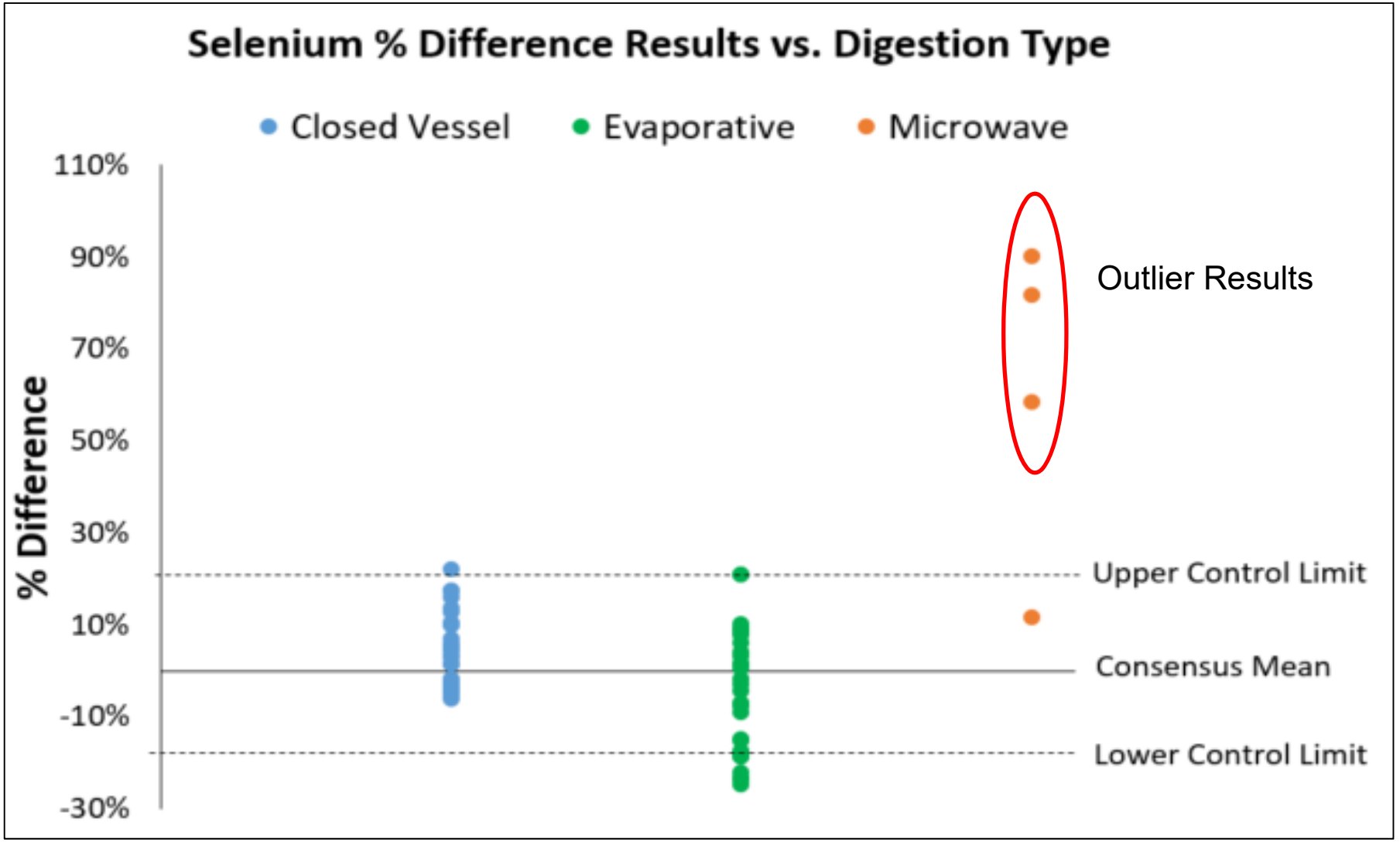
Digestion Type Variability - Selenium



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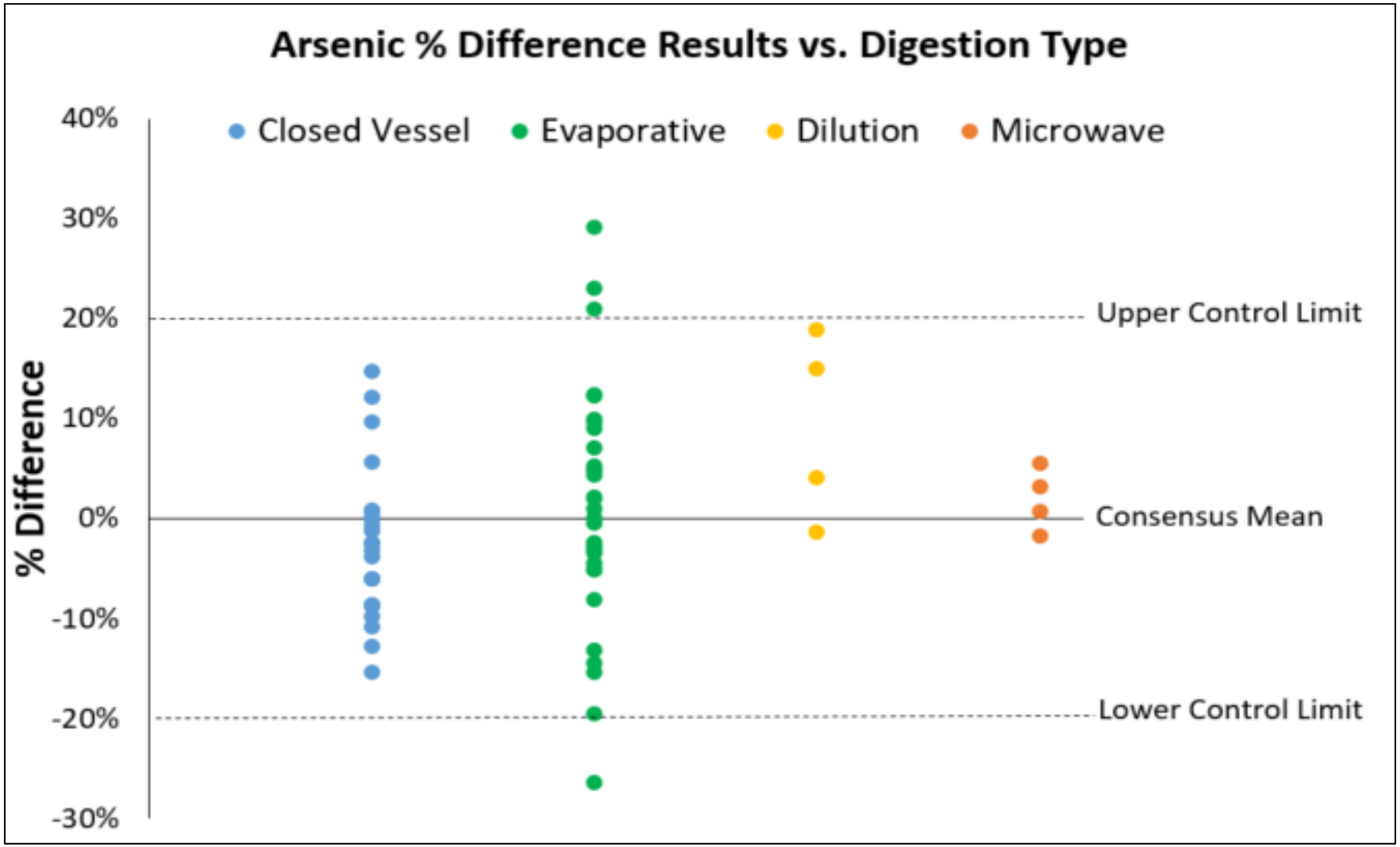
Digestion Type Variability - Arsenic



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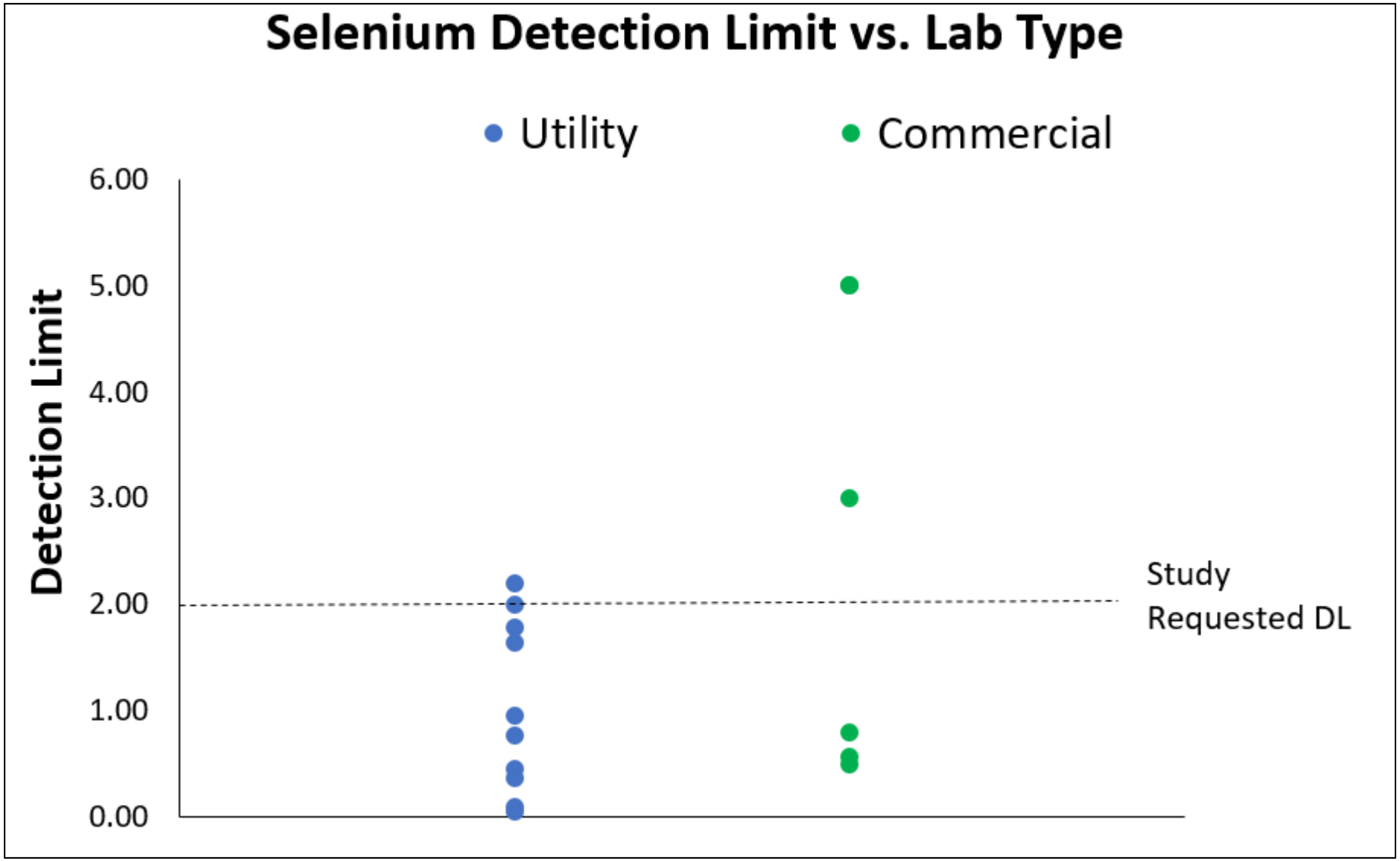
Reported Detection Limits - Selenium



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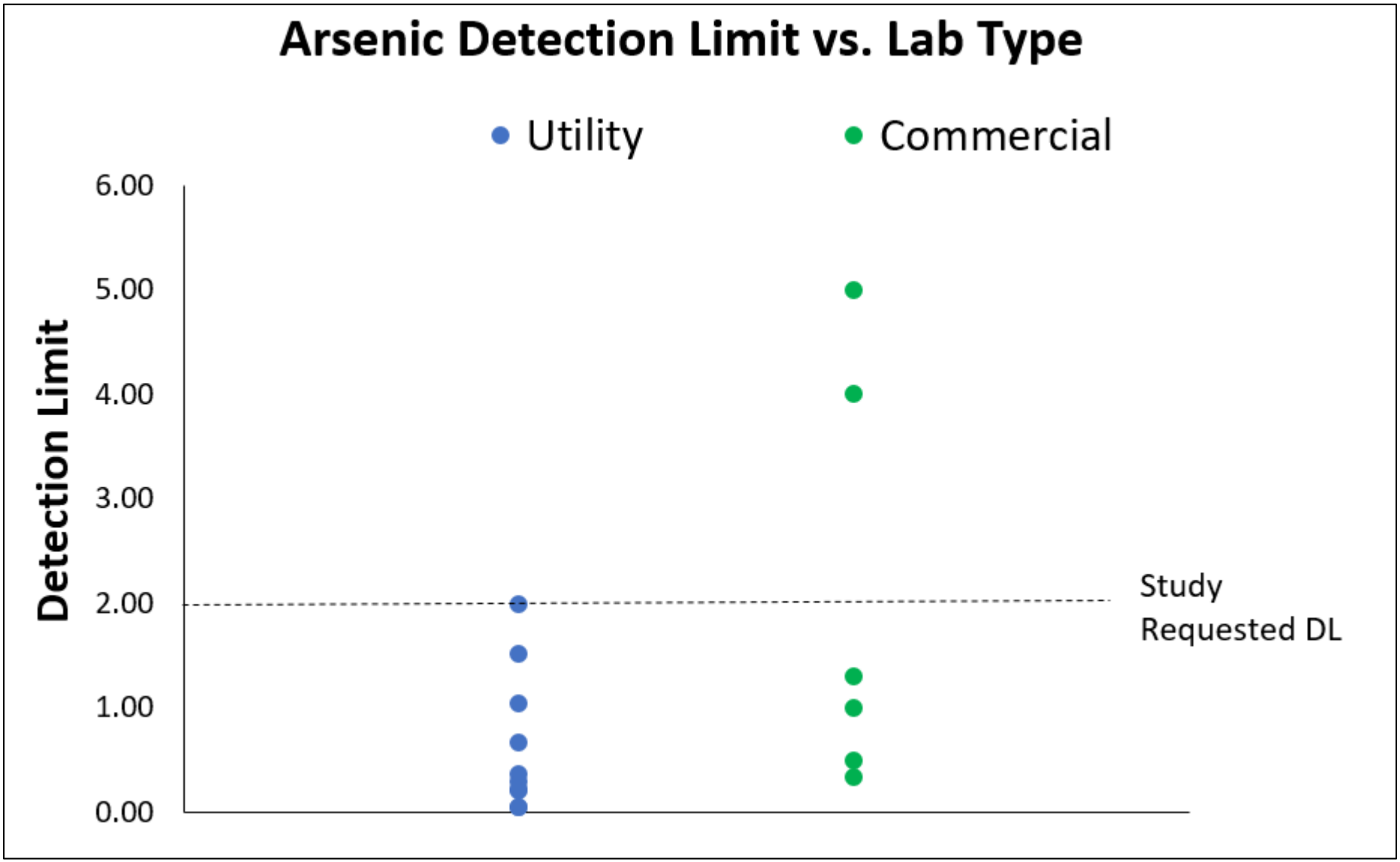
Reported Detection Limits - Arsenic



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Method Variability Conclusions

- No statistically significant impact on mean selenium or arsenic concentration for any instrument/method variant
  - CRC vs DRC vs QQQ
  - Cell gas type
  - Digestion type
- Outlier lab for Se – high bias
  - EPA 3015A microwave digestion with dual mode CRC/DRC ICP-MS
  - Reason for high bias under investigation
- Wide range of reported detection limits
  - Arsenic (0.05 to 5.0 µg/L)
  - Selenium (0.05 to 5.0 µg/L)

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Study Conclusions & Recommendations

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Study Conclusions

- Bottle type (HDPE vs. borosilicate glass) -- no significant differences for the study samples.
  - Selenocyanate (SeCN), adsorbs strongly to HDPE container walls. Where SeCN is known or suspected to be present, borosilicate glass should be used to minimize selenium loss to bottle walls.
- Preservation with nitric acid and peroxide and closed-vessel digestion minimizes negative selenium bias for some biologically treated FGD wastewaters.
- Reported detection limits from some non-specialty commercial labs are not adequate to measure accurately below ELG limits.

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Study Recommendations

- Use a closed vessel digestion approach to reduce loss of volatile selenium.
  - Significantly lower concentrations of selenium and low MS/MSD recoveries were observed for some samples using open vessel digestion.
- Consider using ICP-QQQ-MS if arsenic is near regulatory limits.
  - EPA has not evaluated a triple quadrupole instrument for use in CWA compliance monitoring; thus, acceptability as a modification to EPA Method 200.8 has not been determined for NPDES monitoring.
- Further evaluation of selenium digestion methods and arsenic instrumental methods is in progress.

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