An Evaluation of Rare Earth M^{2+} Interference Correction Approaches for Inclusion in the Update of EPA Method 200.8

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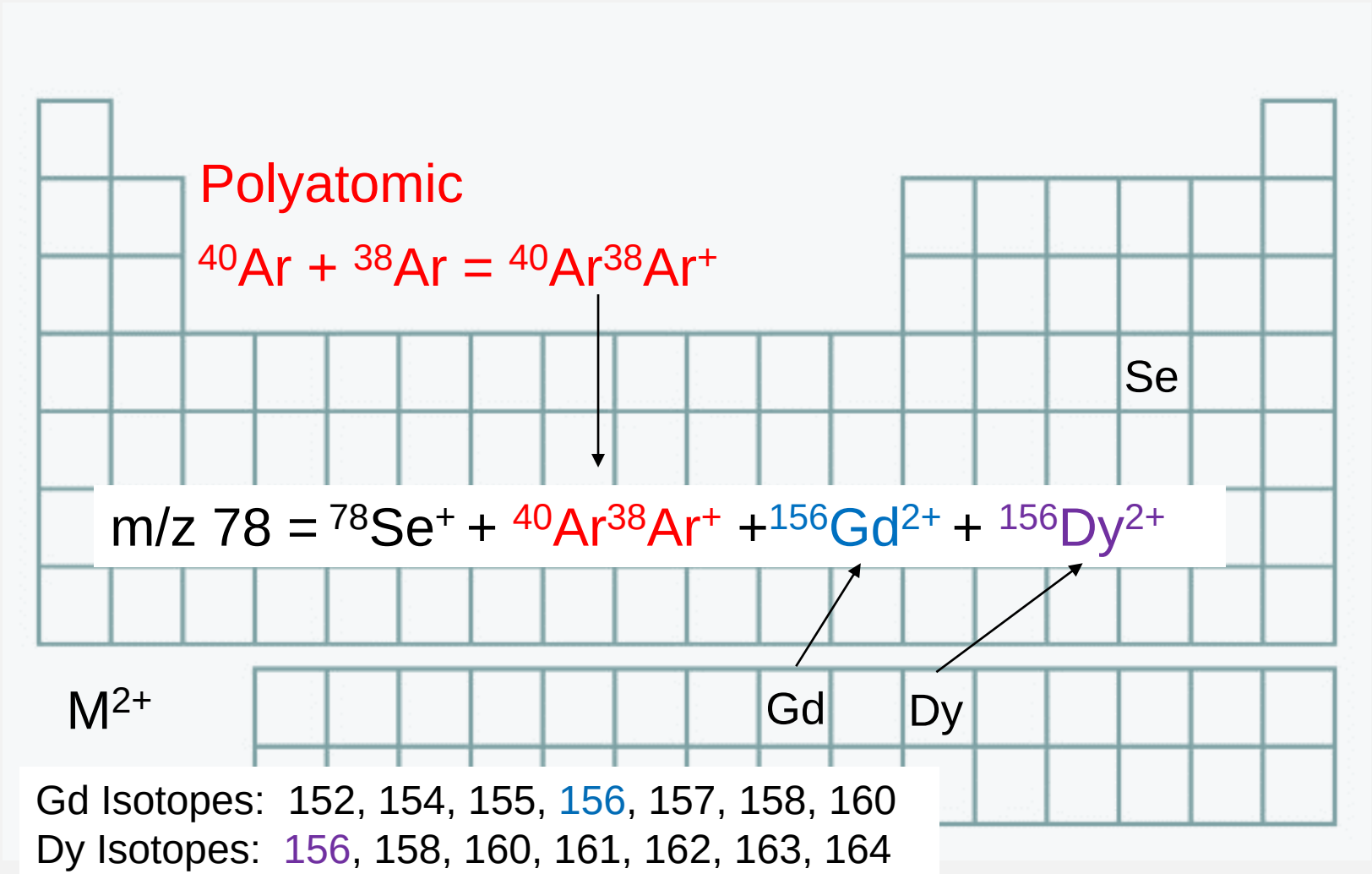
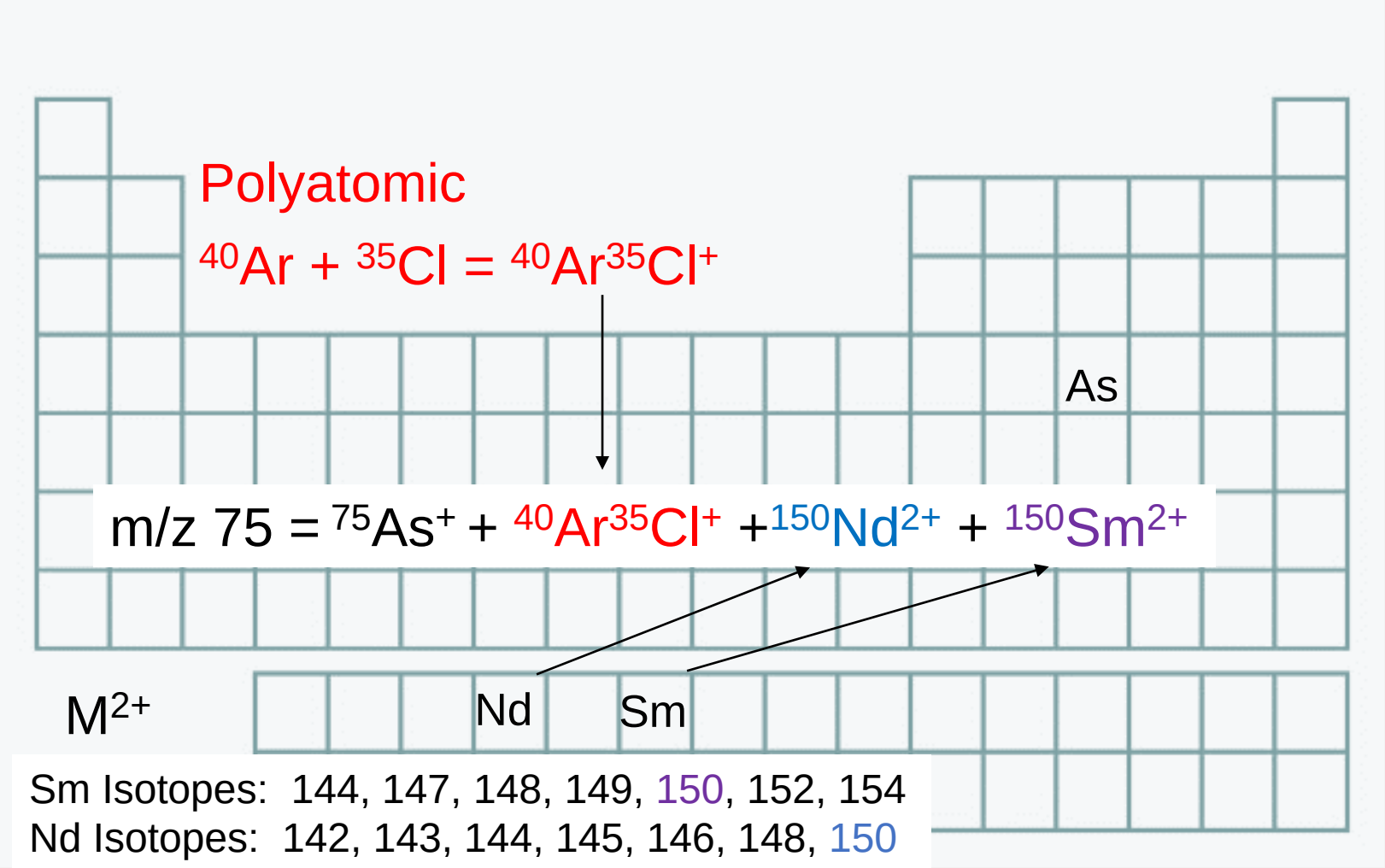
Isobaric Polyatomic and M^{2+} Interferences can Produce False Positive on Selenium



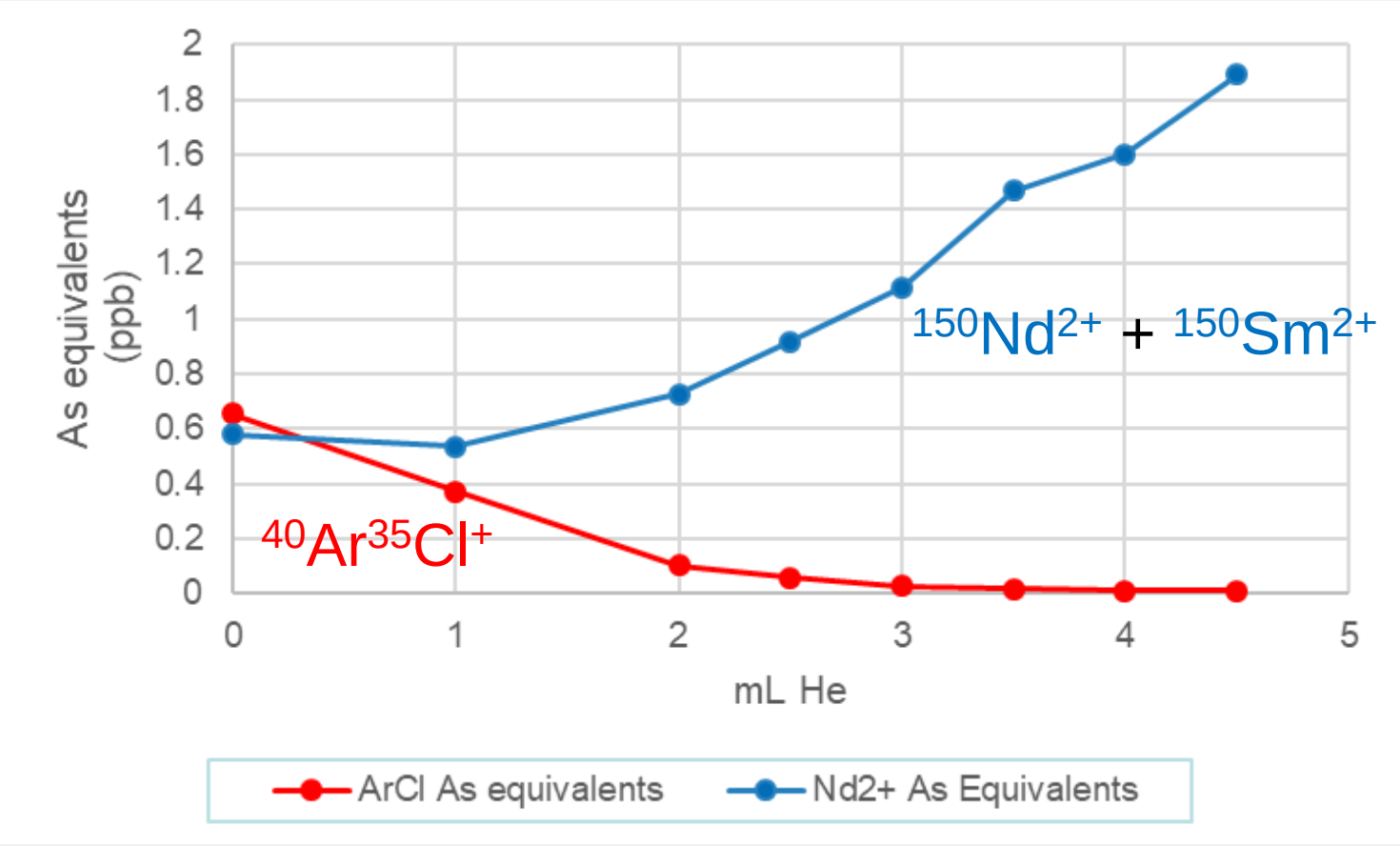
Gd Isotopes: 152, 154, 155, 156, 157, 158, 160
Dy Isotopes: 156, 158, 160, 161, 162, 163, 164

Isobaric Polyatomic and M^{2+} Interferences can Produce False Positive on Arsenic



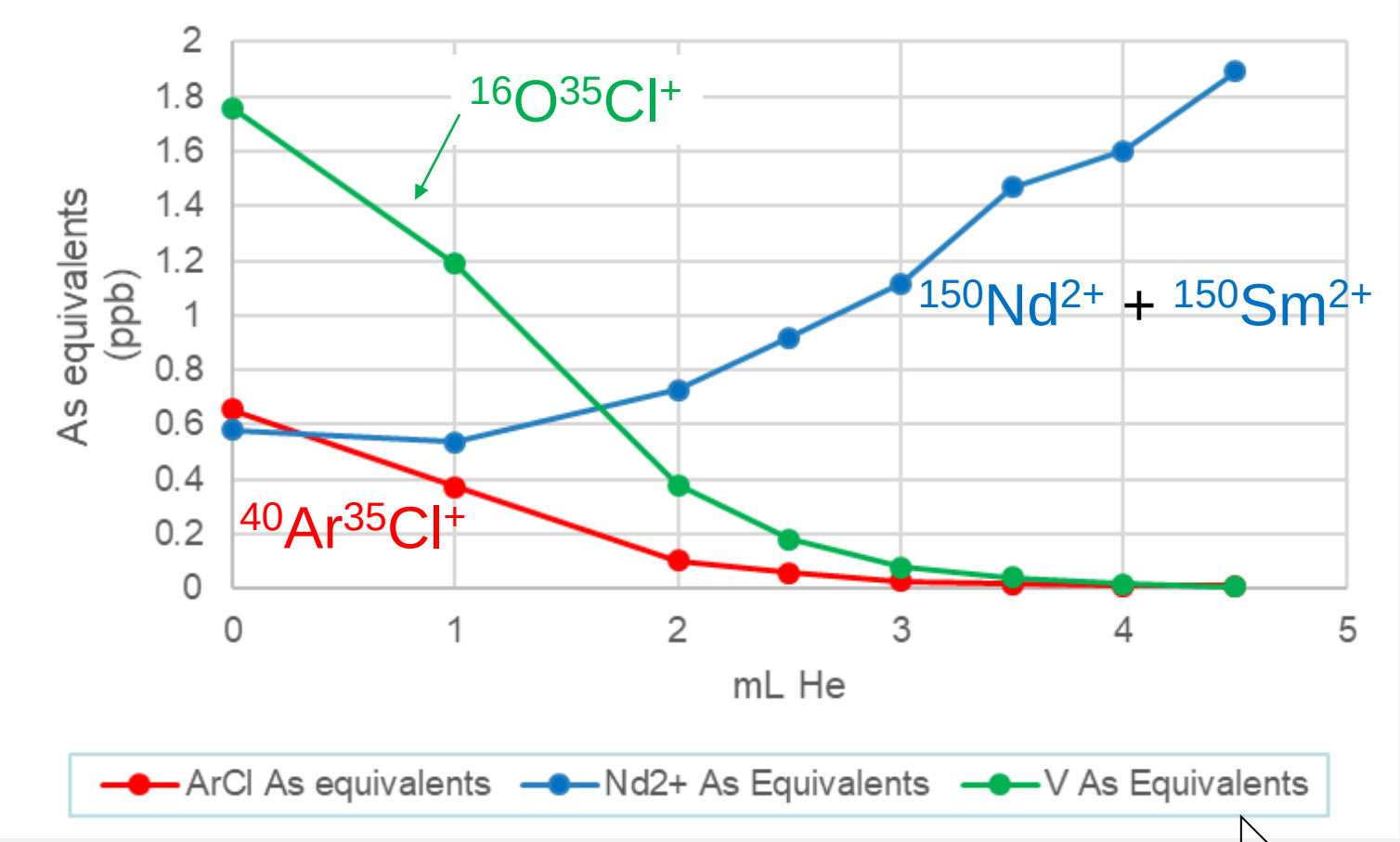
Trade Off between Polyatomic Reduction and Rare Earth False-Positive using a Single Tune

- m/z 75 = $^{75}As^{+}$ + $^{40}Ar^{35}Cl^{+}$ + $^{150}Nd^{2+}$ + $^{150}Sm^{2+}$



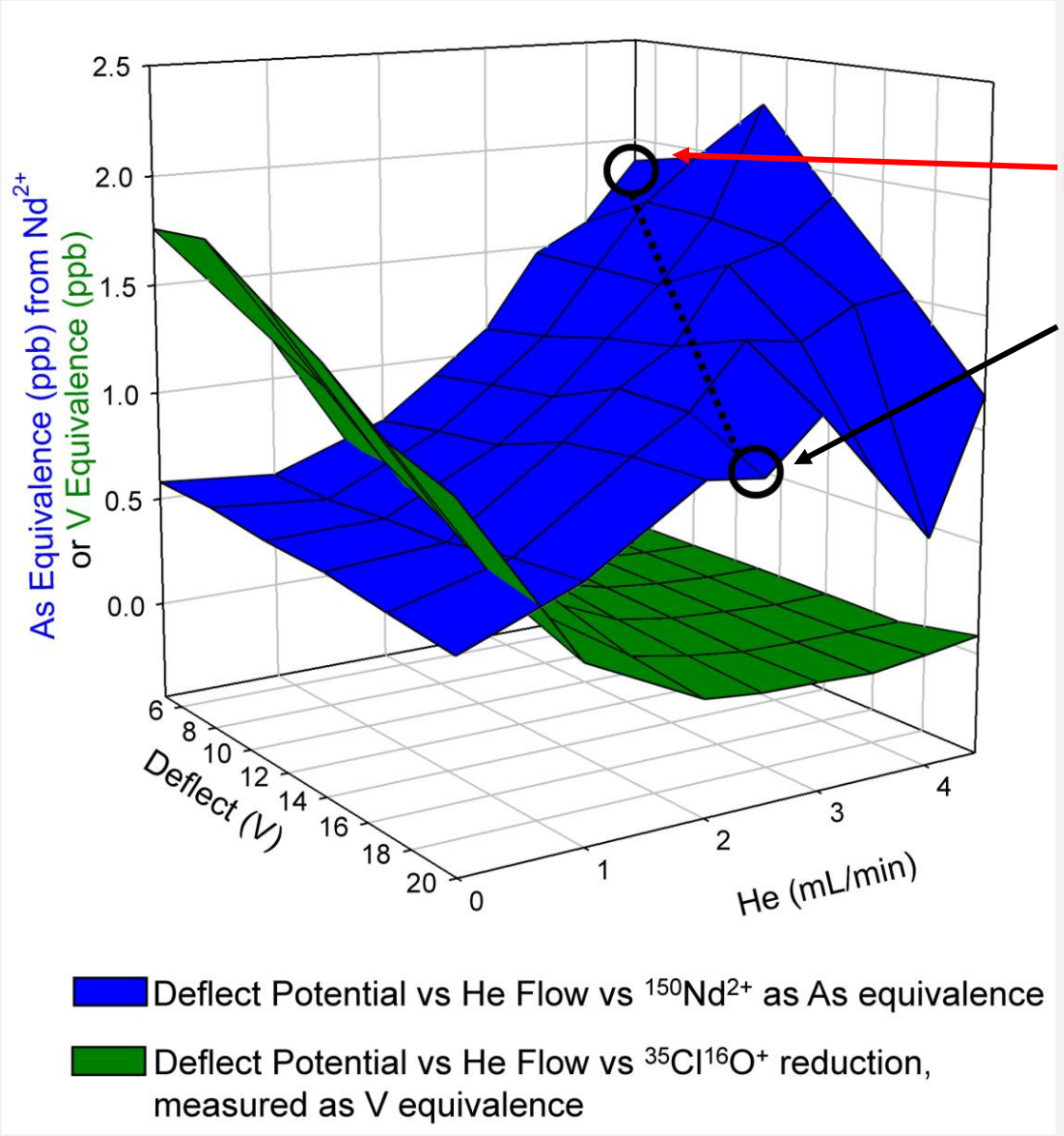
Trade off between Polyatomic Reduction and Rare Earth Positive using a Single Tune

- $^{150}Nd^{2+}$ + $^{150}Sm^{2+}$ versus $^{16}O^{35}Cl^{+}$ + $^{40}Ar^{35}Cl^{+}$



Decreasing cps / ppb

Trade Off between $^{16}O^{35}Cl^{+}$ and $^{150}Nd^{2+}$ across Instrument Tunes



High Helium Tune = HHe

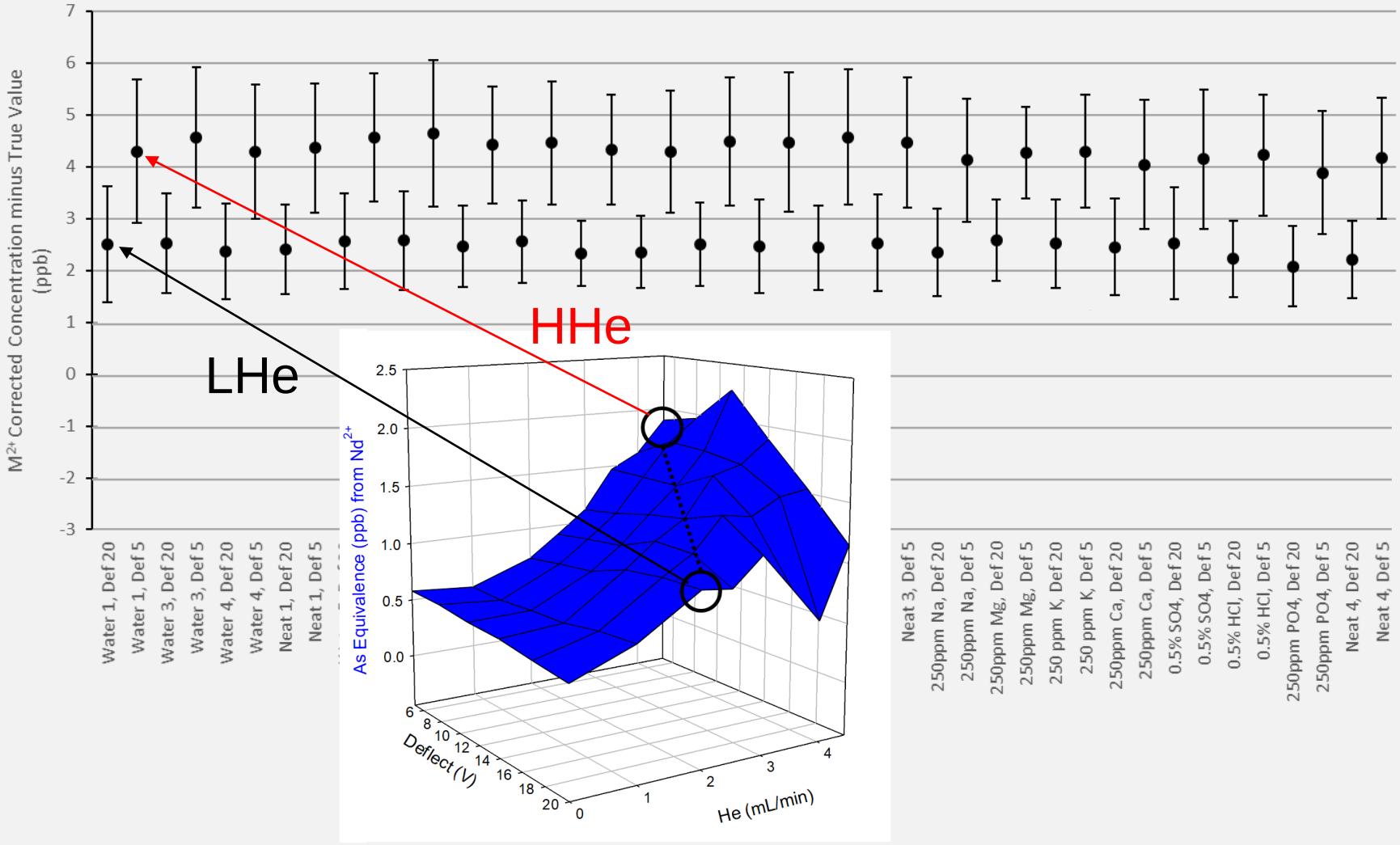
Low Helium Tune = LHe

What M^{2+} correction will minimize the difference across the two tunes and reduce the residual false positive?

M^{2+} Experimental Design : Performance Across Matrix-Analysis Day and Tune

1. Fortified 11 drinking waters and 7 matrices with rare earths
2. M^{2+} Analyte Standard - 100ppb Nd, Sm, Gd; 10ppb Be, Sc, Co, Y, In and Th; 20ppb Ho
3. Analyze fortified samples on 8 non-consecutive days over two months using ICP-MS with 0.4 AMU resolution
4. Measure M^{2+} using half masses (avoids elemental overlap)
5. Analyze fortified samples using ICP-QQQ and HR-ICP-MS to determine true As & Se values
6. Evaluate M^{2+} corrections for HHe and LHe tunes versus true value over study period

Mean and 95% Confidence Bound for As after True Value Subtraction (Samples Collected over 8 Days using HHe and LHe Tunes)



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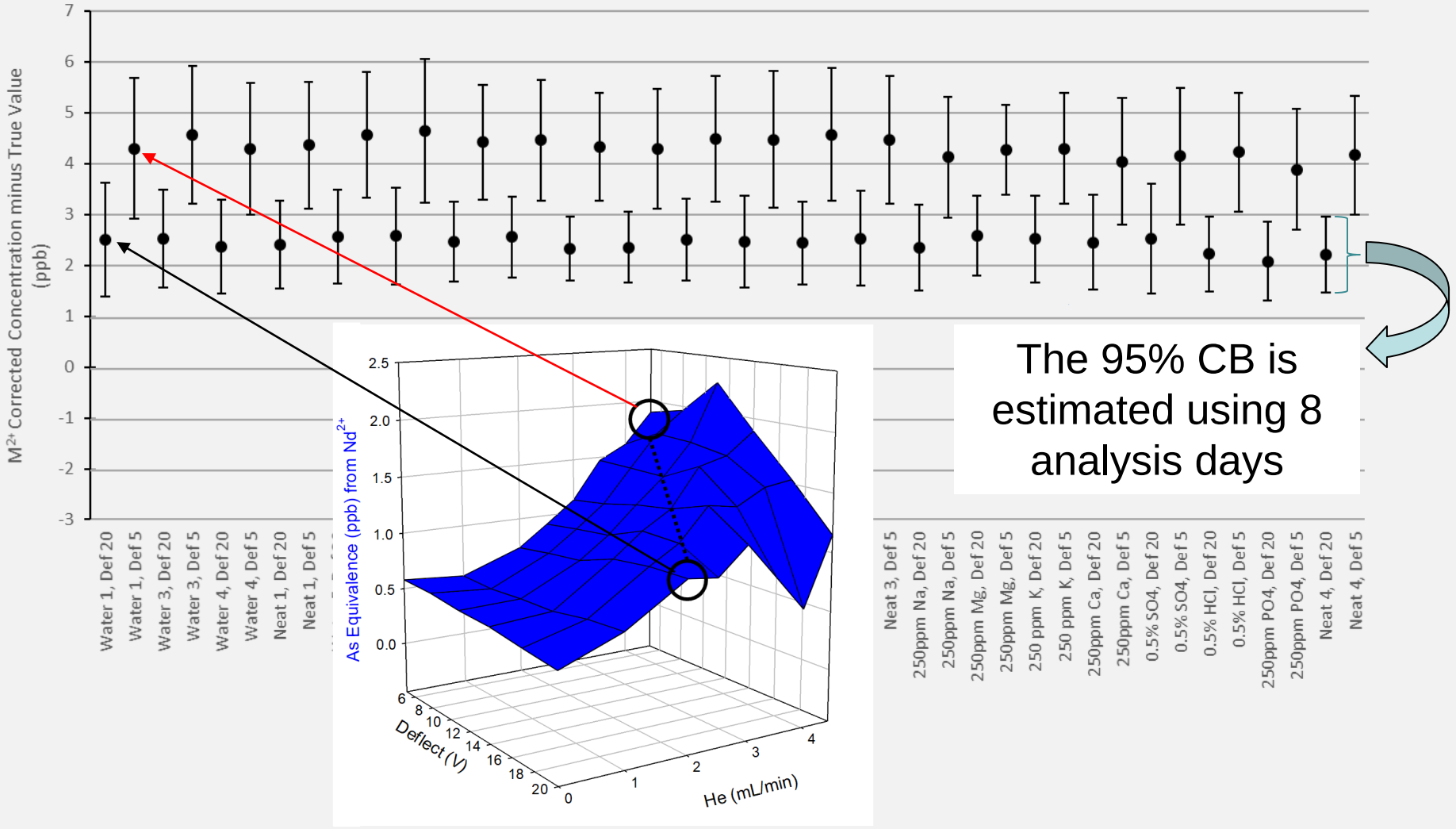
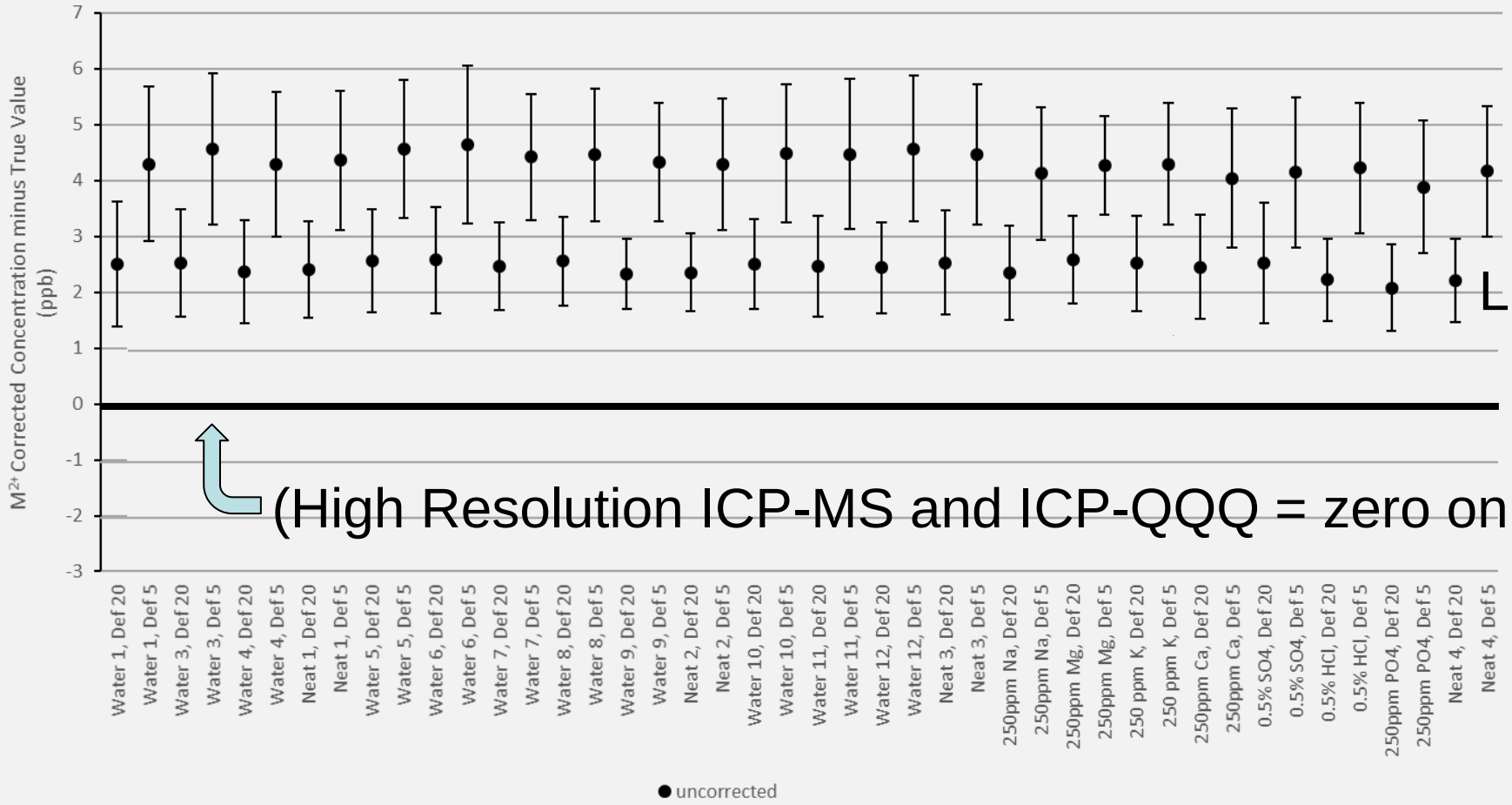


Any good M^{2+} approach would have all sample means close to zero ppb



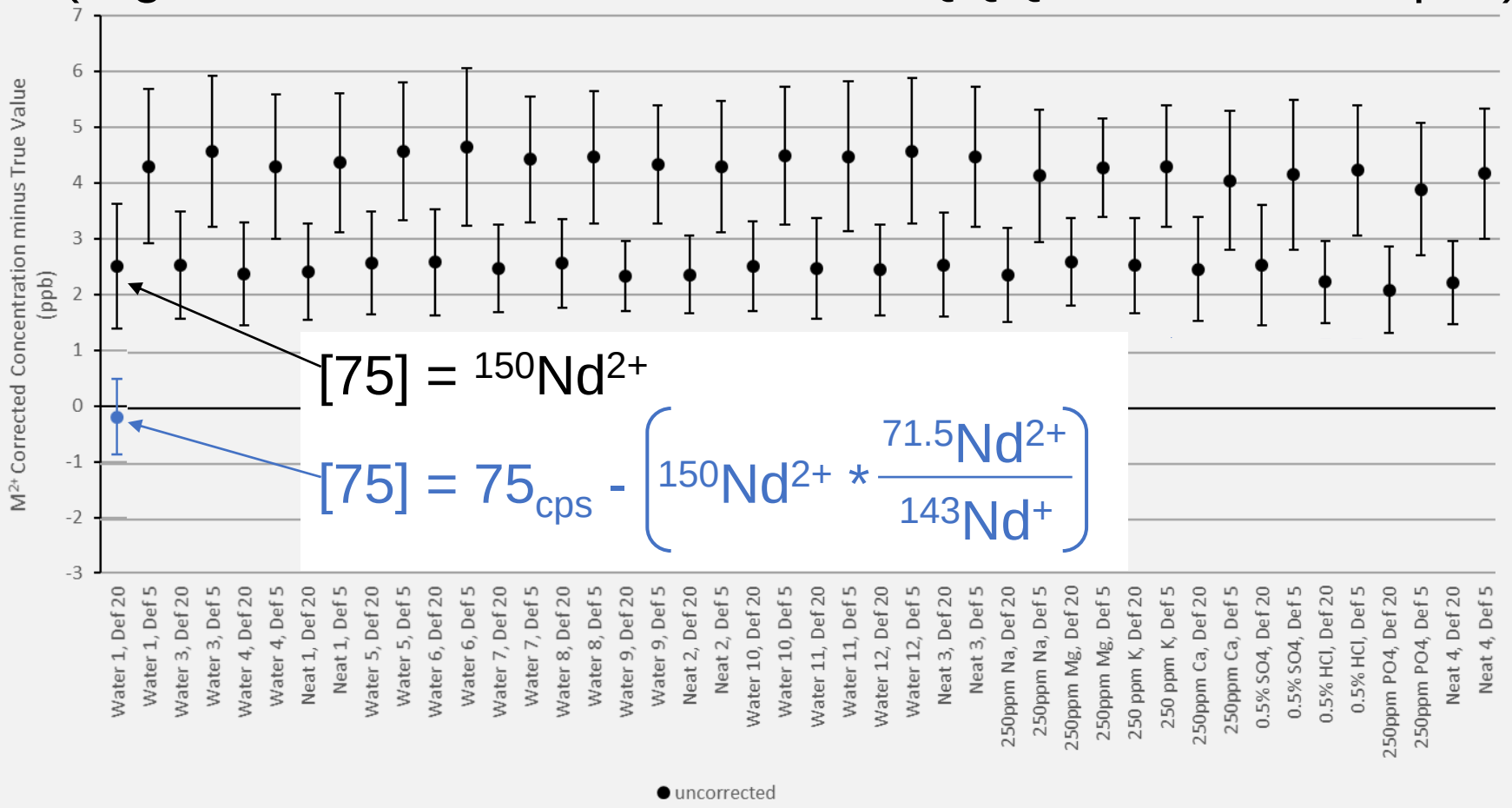
HHe

LHe

(High Resolution ICP-MS and ICP-QQQ = zero on this plot)

Applying a Fixed Factor Correction which is Estimated Once a Day using a Rare Earth QC Sample

(High Resolution ICP-MS and ICP-QQQ = zero on this plot)



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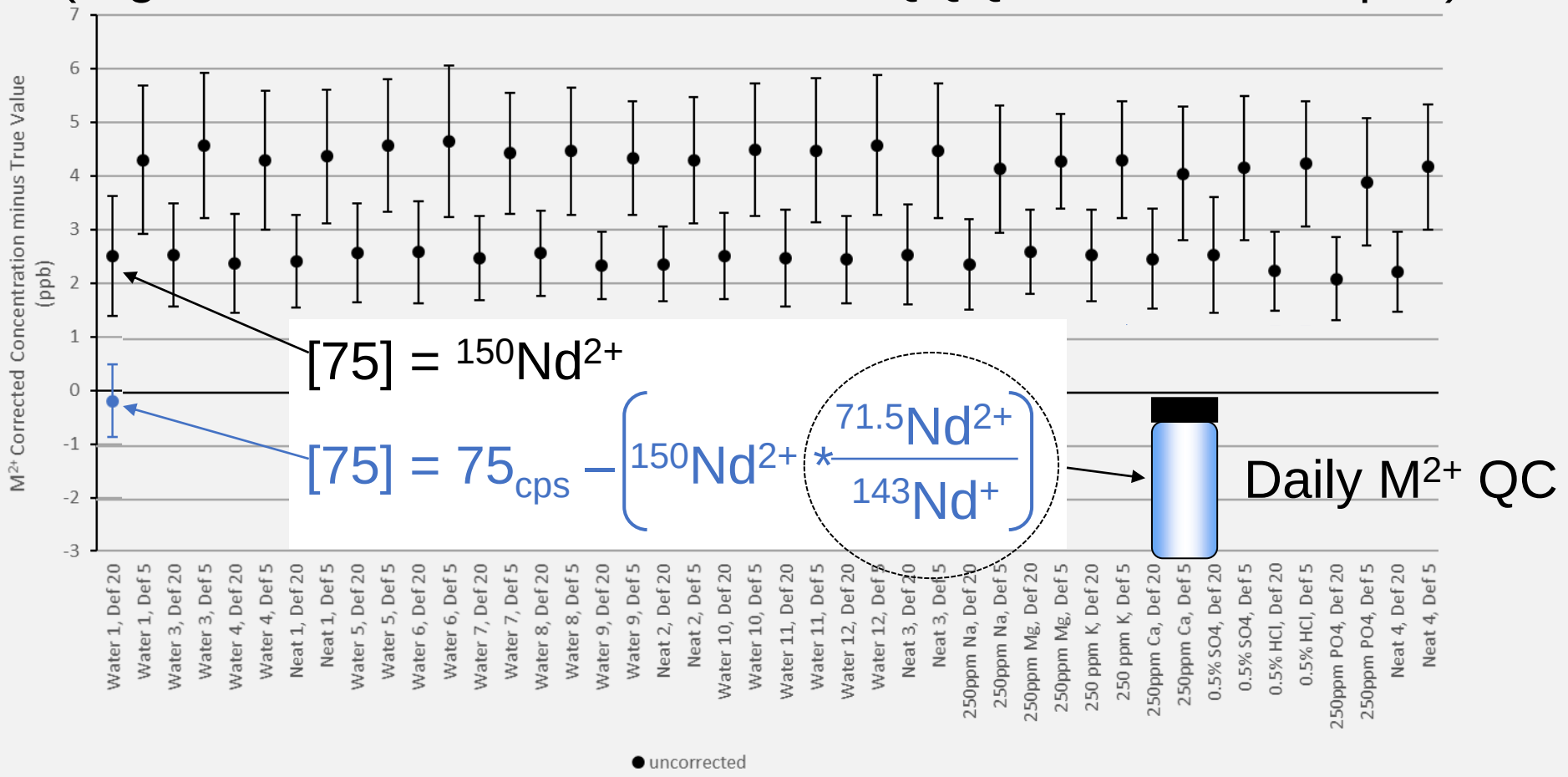

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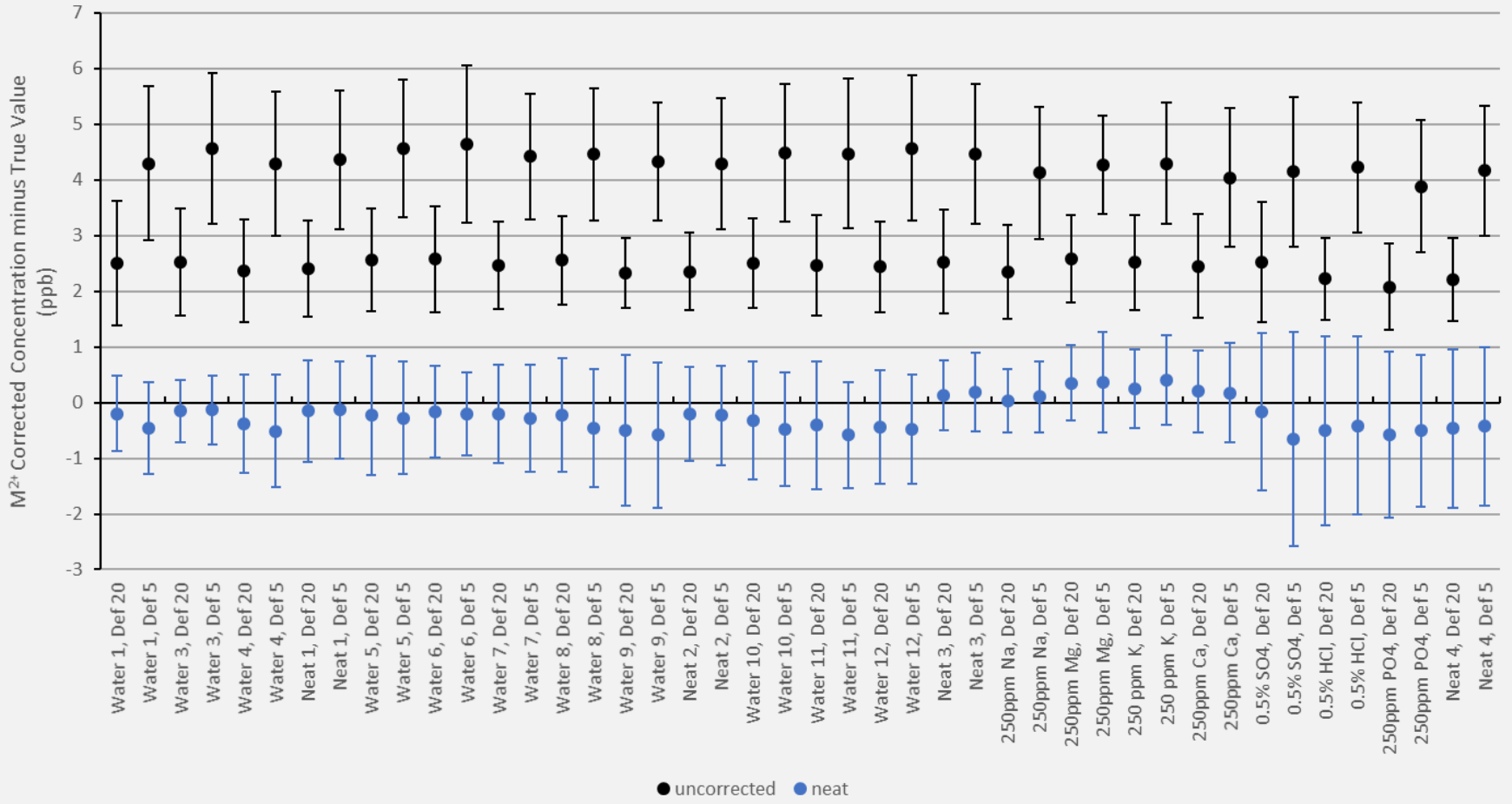
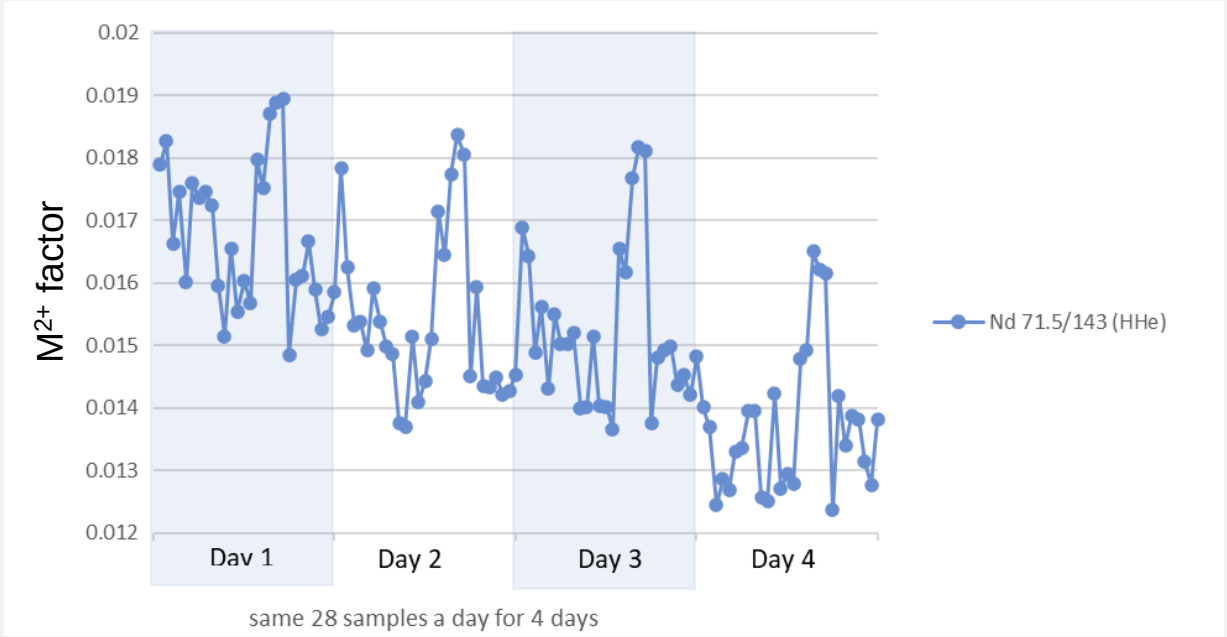
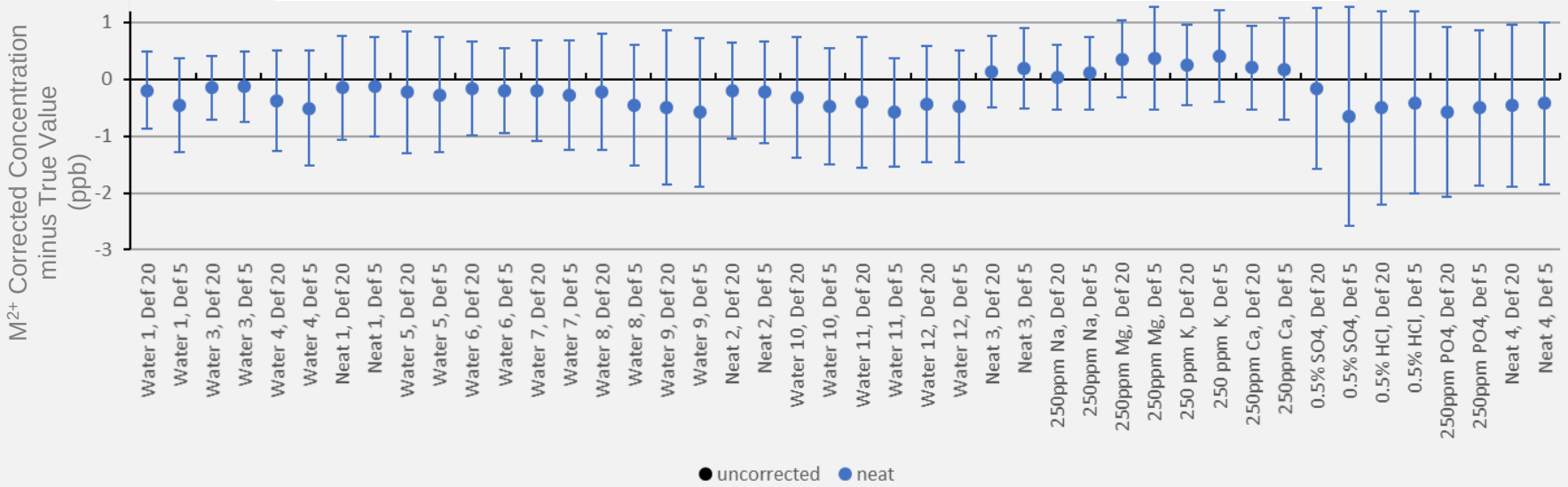


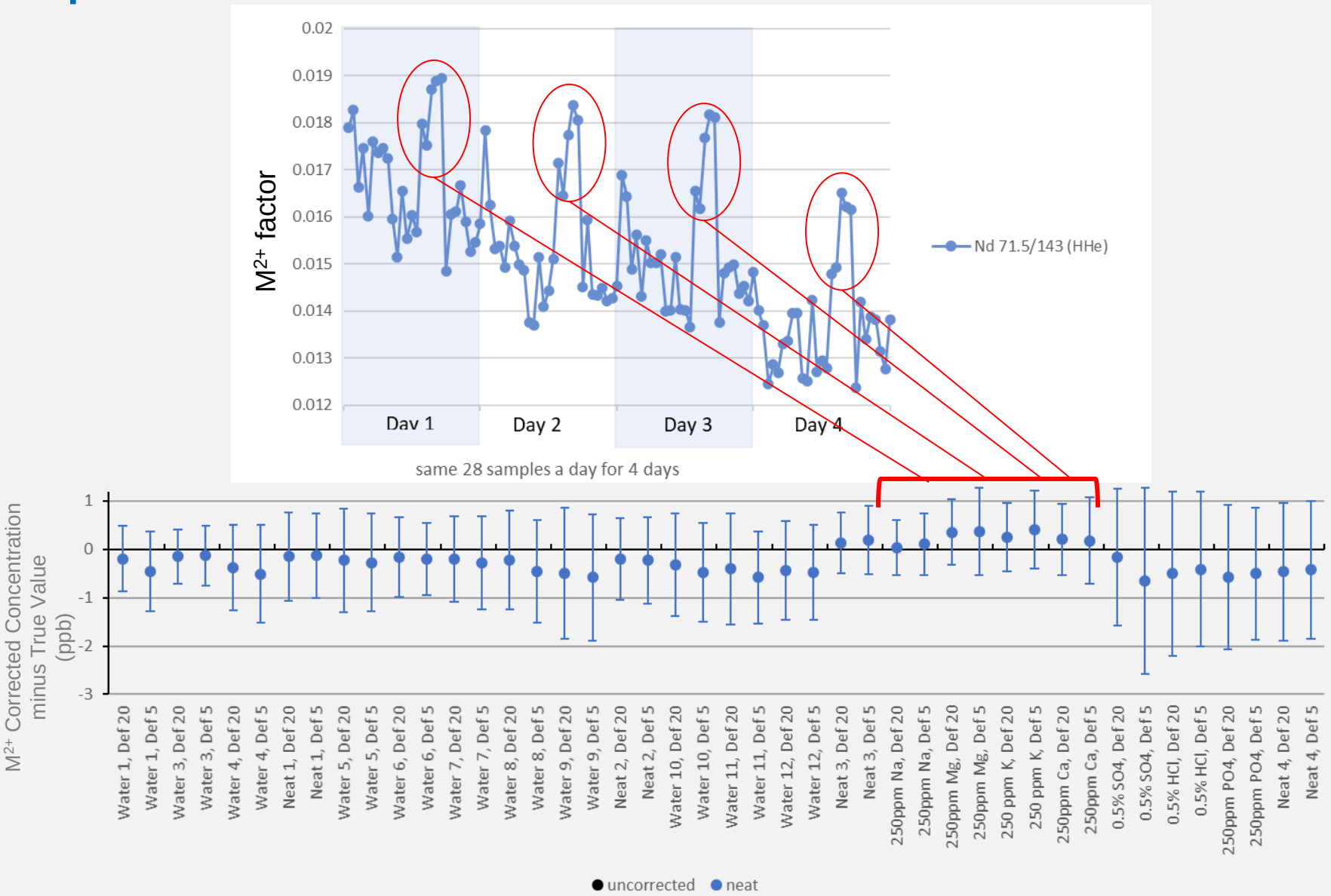
Is a Fixed M^{2+} Factor a good assumption?



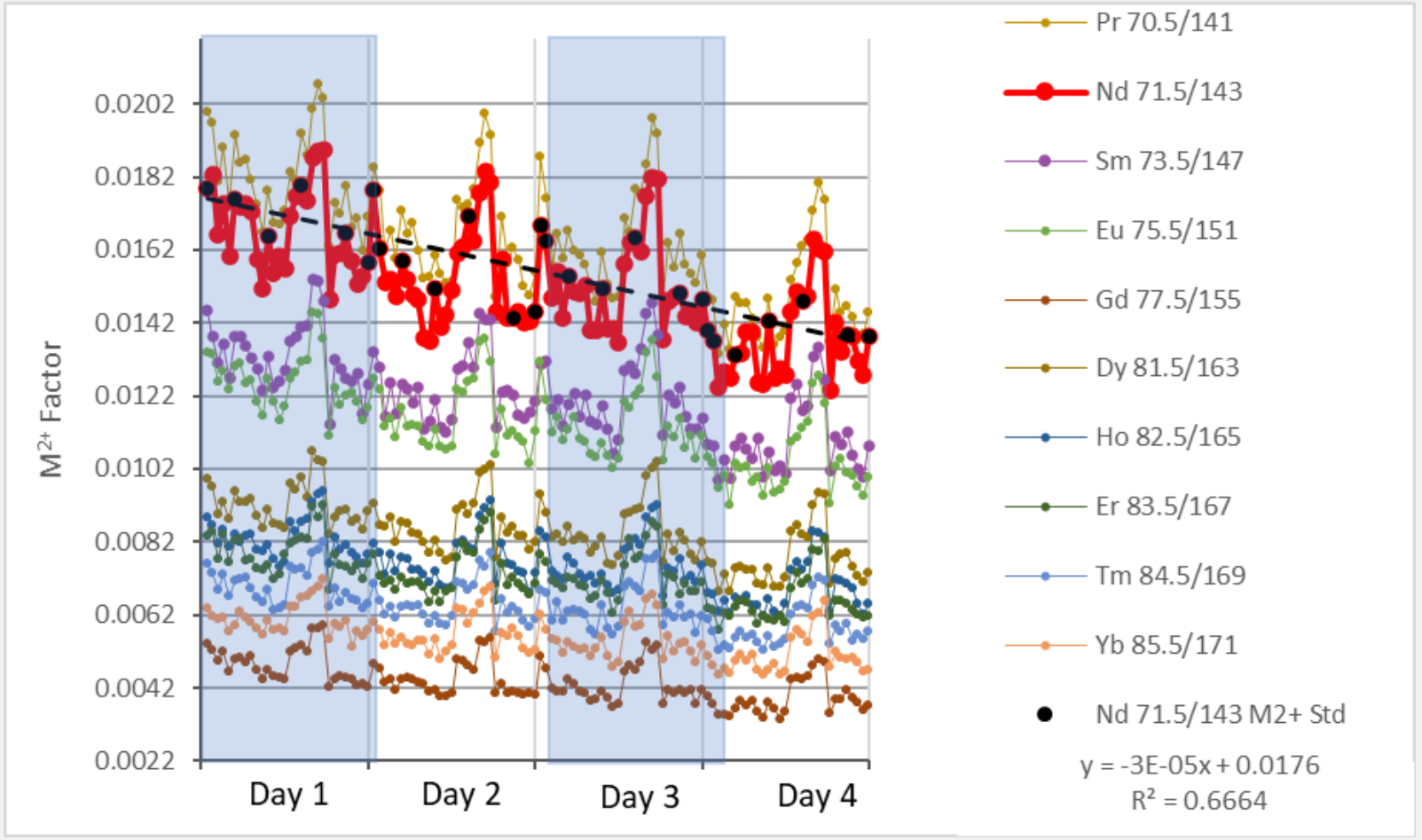
same 28 samples a day for 4 days



Matrix induced shifts in M^{2+} factor produces sample specific bias



Shift in M^{2+} Ratio with Matrix and Time is Consistent across All Rare Earths



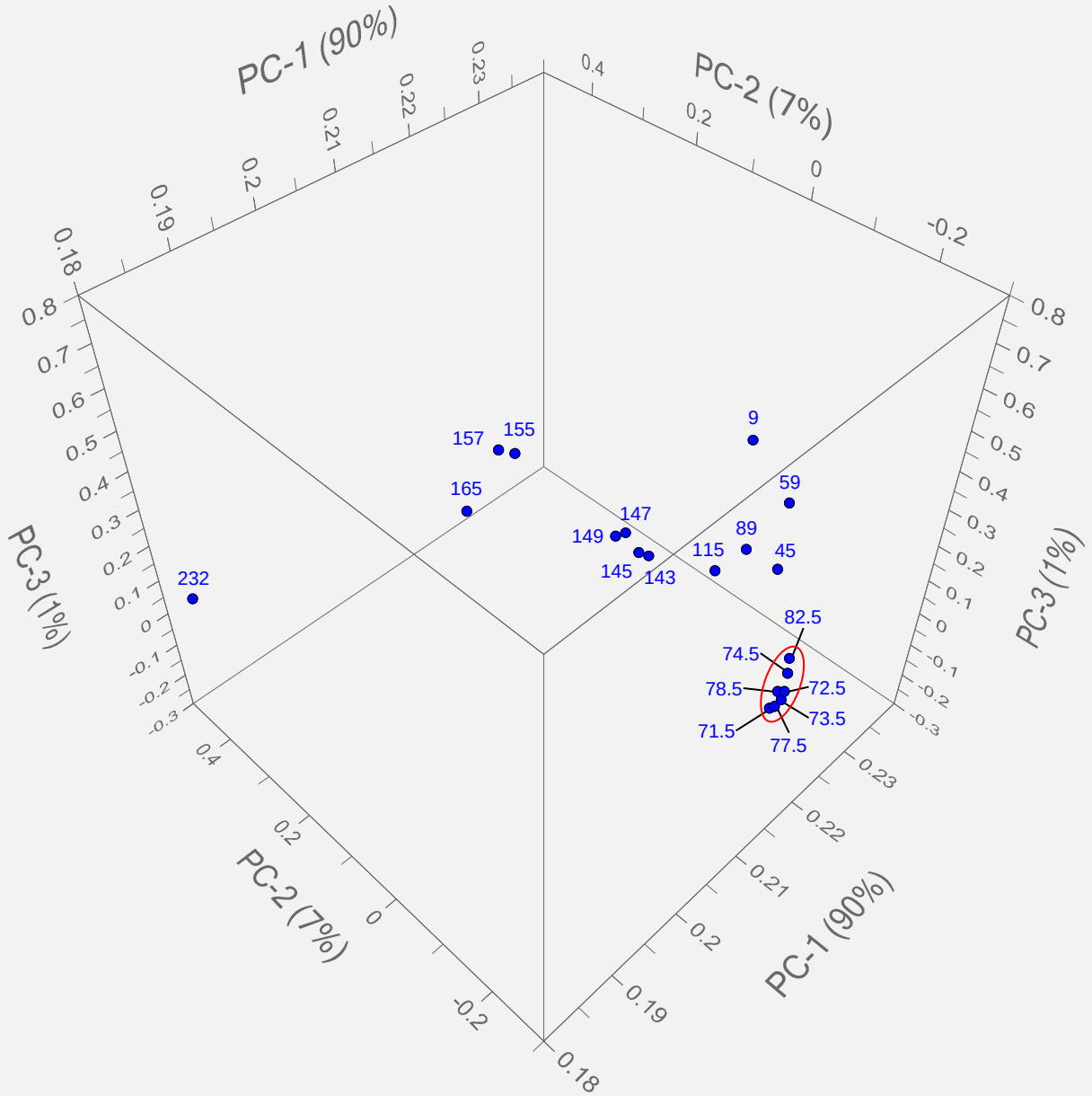
How to Select an Internal Standard that Corrects for M^{2+} Shifts Induced by Matrix and Instrument Drift

- Can we use internal standards to improve the M^{2+} correction relative to a fixed factor approach?

	QC sample				Sample 1 → n
M^{2+} Fixed Factor	0.02				0.02
Internal Standard	0.02	X	Sample specific internal standard factor	=	Sample Specific M^{2+} correction factor

What ions drift together with M^{2+} ions across matrix and day?

A Multiday PCA Loading Plot Based on the Day Specific Drift of M^{2+} and Other M^{1+} Internal Standard Ions



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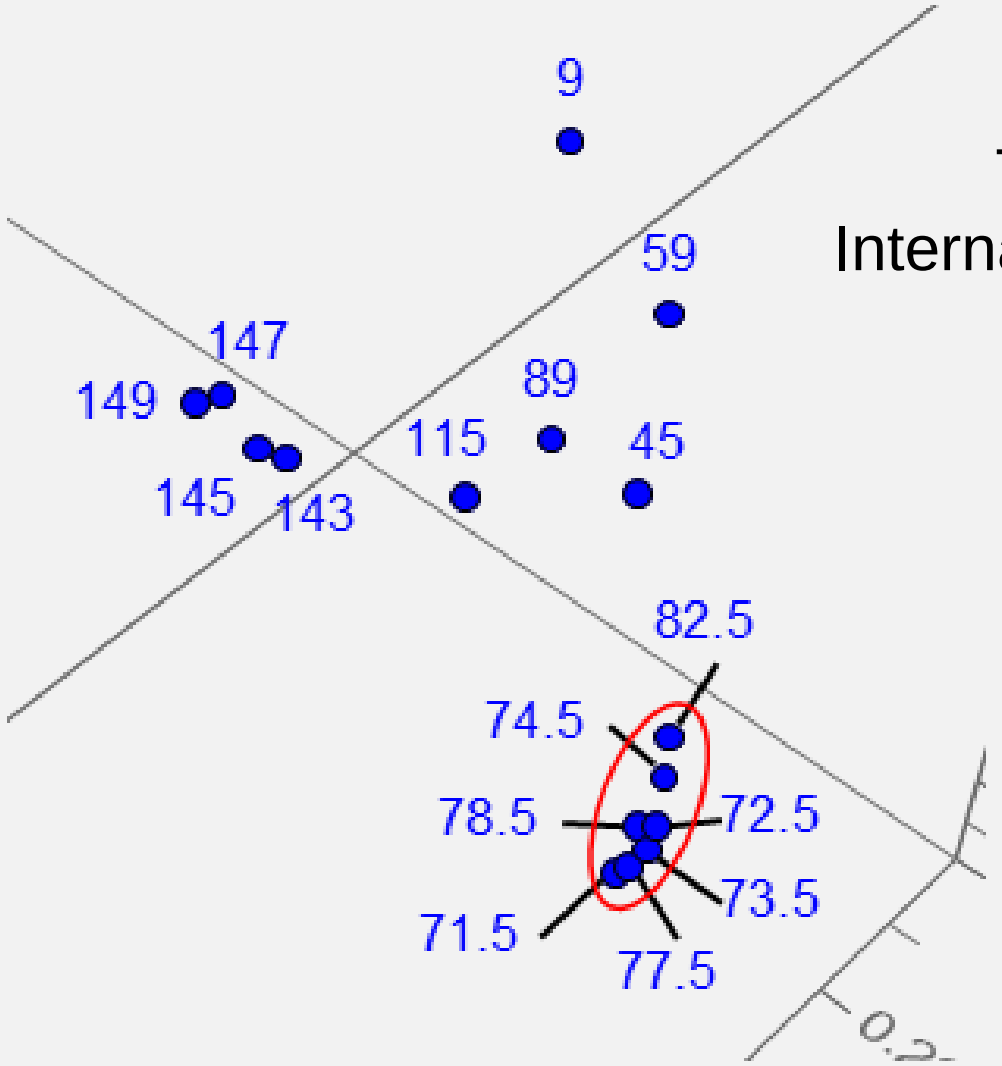
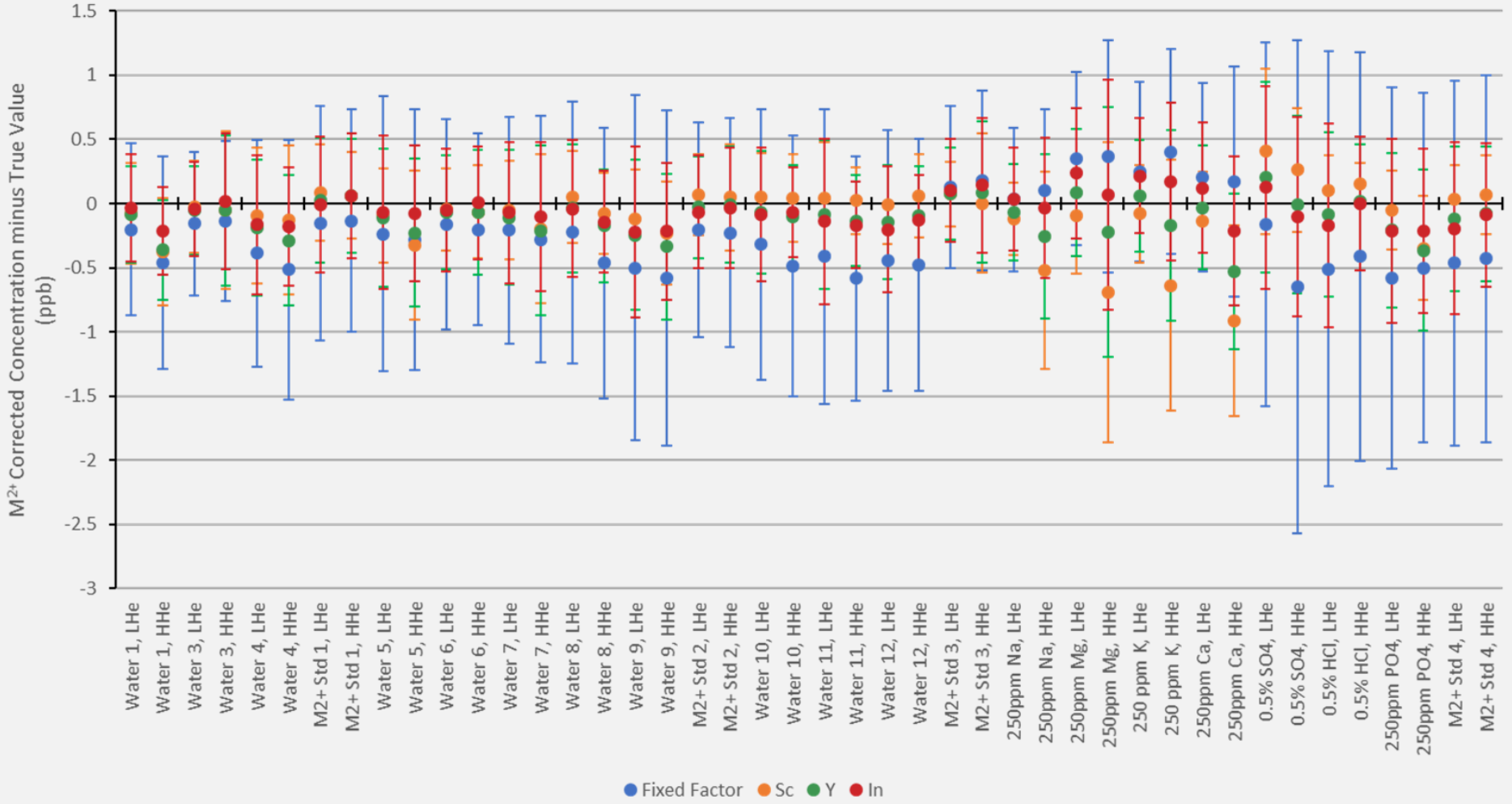


Typical
Internal Standards
45
89
115

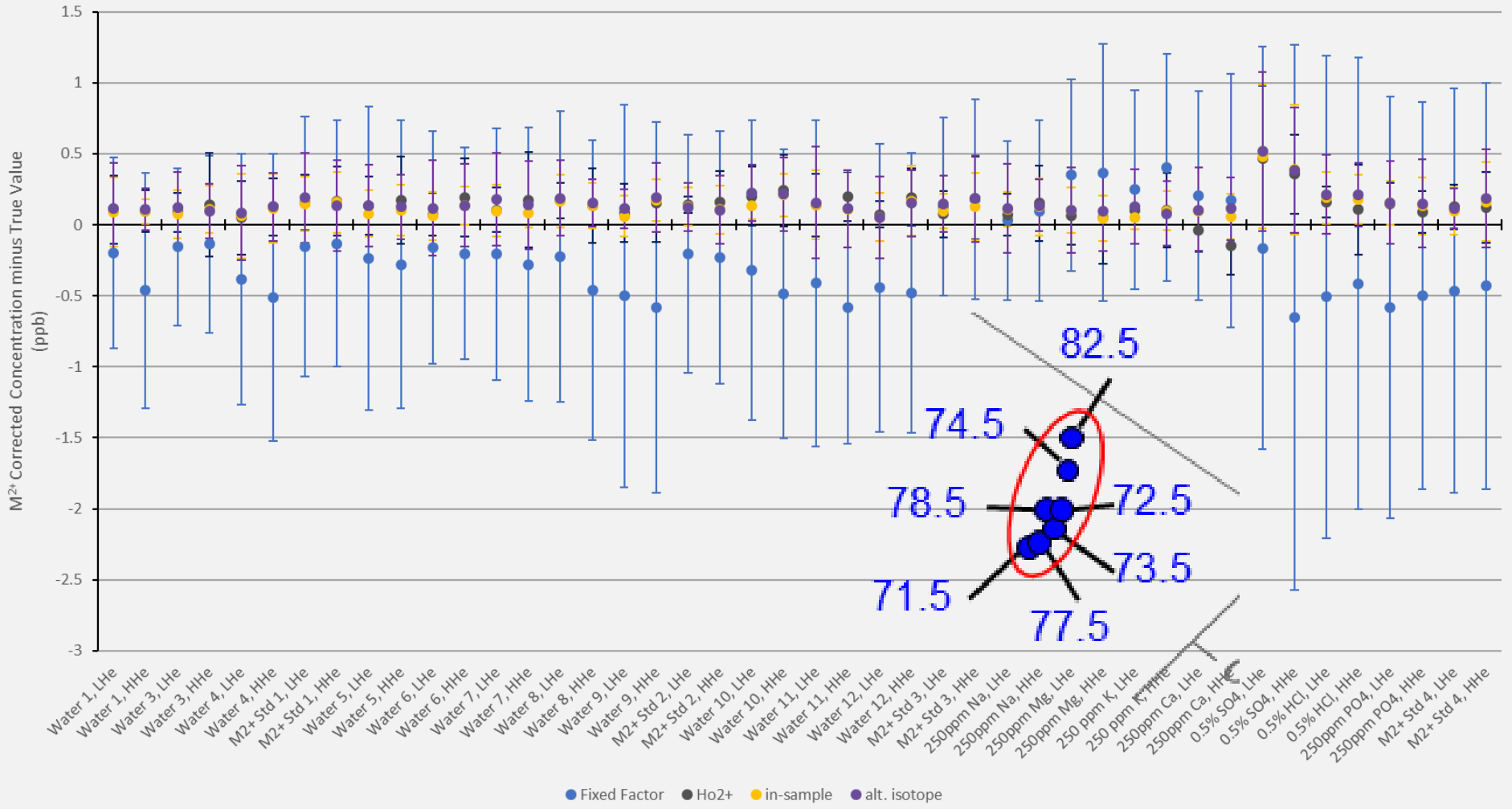
Can we use Internal Standards (Sc, Y or In) to Improve the M^{2+} Correction Relative to a Fixed Factor?

(High Resolution ICP-MS and ICP-QQQ = zero on this plot)

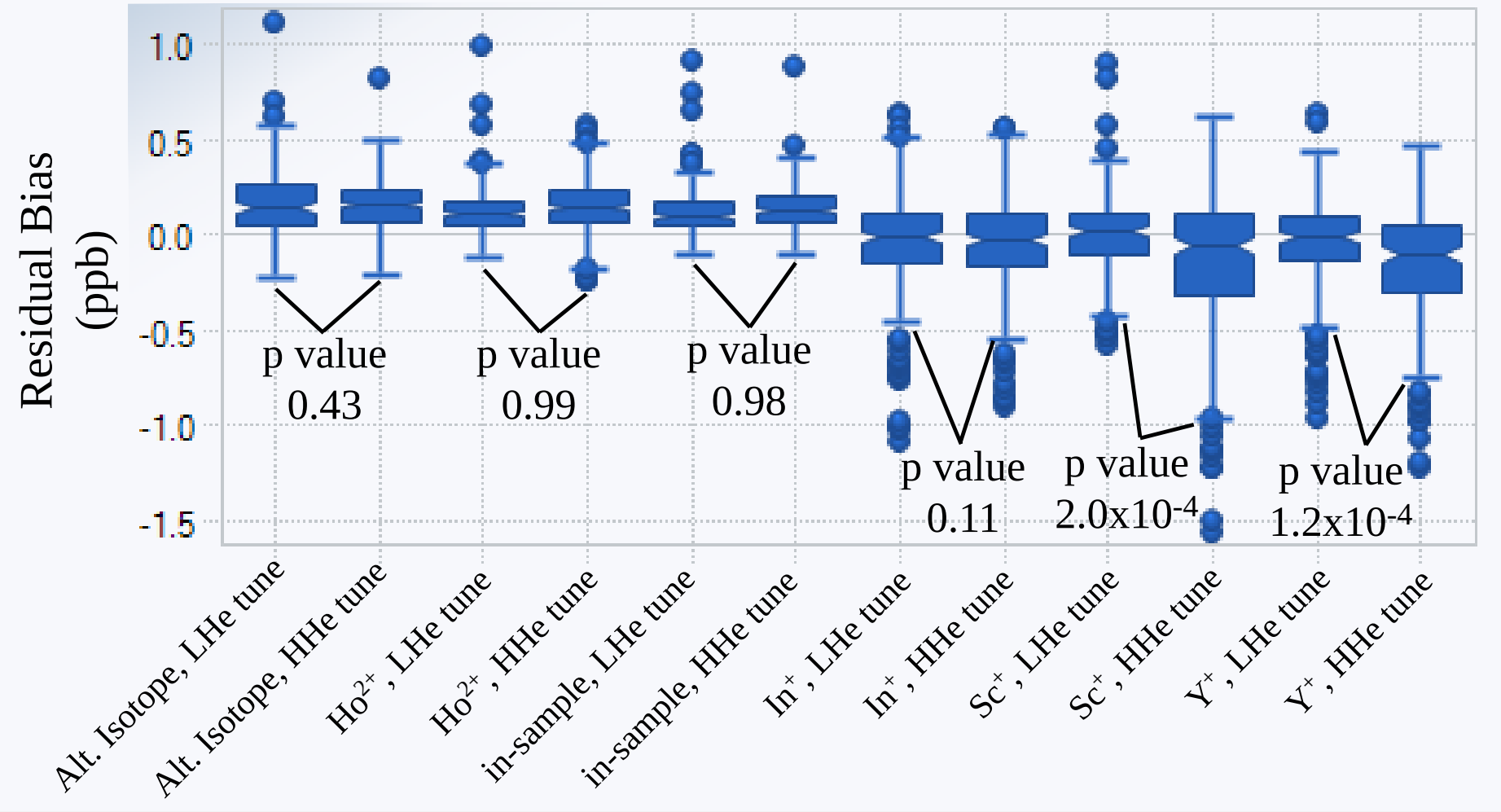


Can we use Internal Standards (Ho^{2+} or Nd^{2+}) to Improve the M^{2+} Correction Relative to a Fixed Factor?

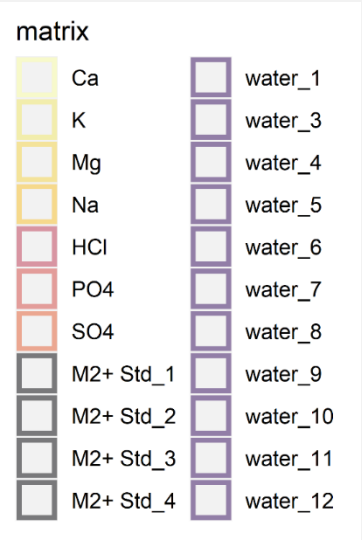
(High Resolution ICP-MS and ICP-QQQ = zero on this plot)



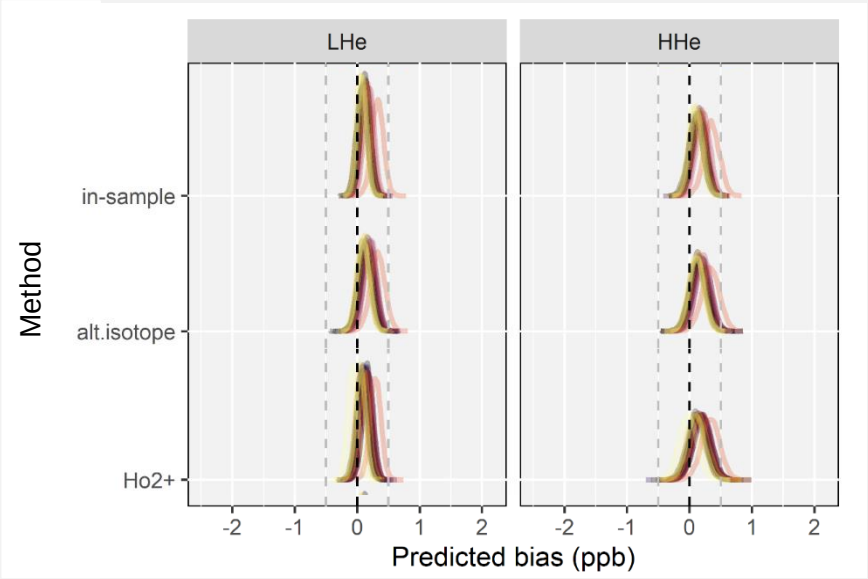
Statistical Comparison across Instrument Tunes (LHe and HHe) for Various Internal Standard Approaches



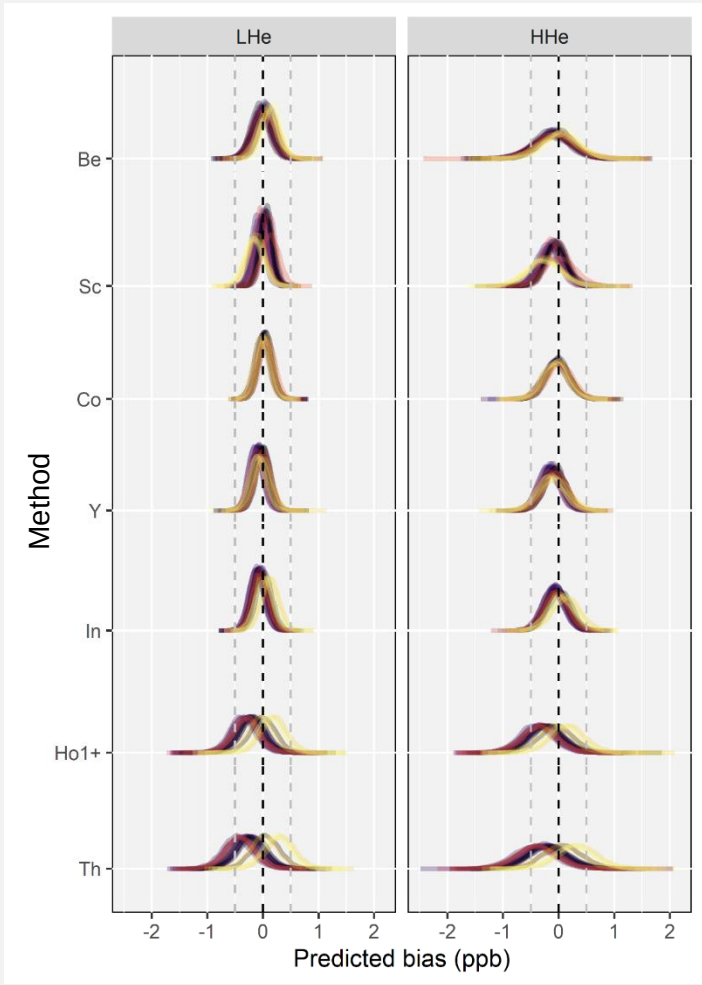
Matrix Specific Estimates of Bias using the Hierarchical Model



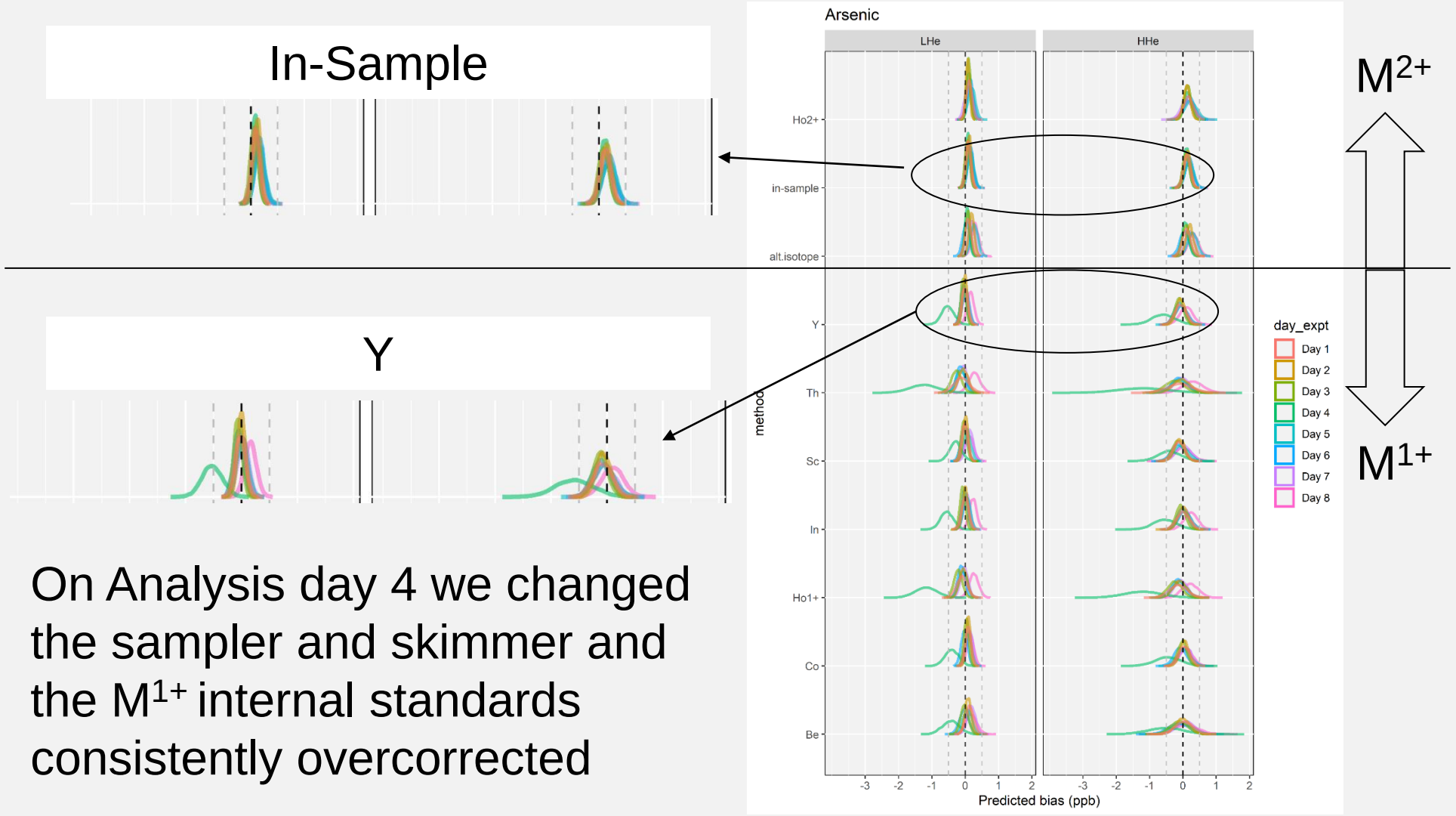
M^{2+} Internal Standards



M^{1+} Internal Standards



Day-Specific Estimates of Bias using the Hierarchical Model



On Analysis day 4 we changed the sampler and skimmer and the M^{1+} internal standards consistently overcorrected

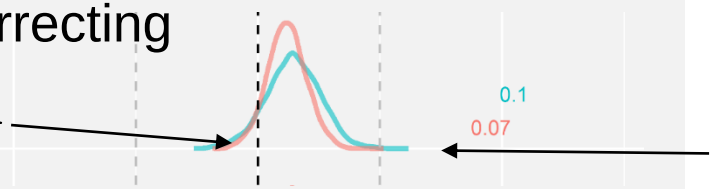
Bias Estimates for a New Day Across Matrix Using the Hierarchical Model

In-Sample

Probability of Overcorrecting

LHe = 10%

HHe = 7%

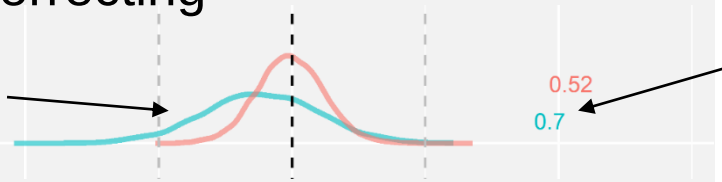


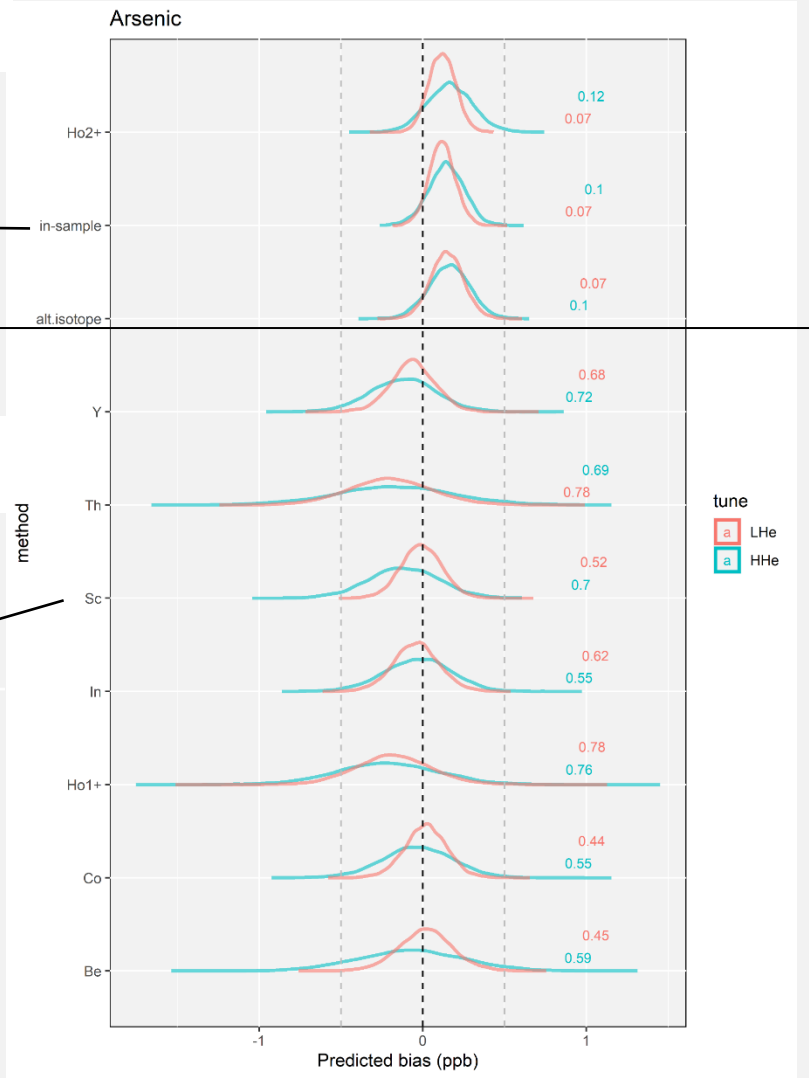
Sc

Probability of Overcorrecting

LHe = 52%

HHe = 70%





M^{2+}

M^{1+}

The spread increases the likelihood of overcorrecting

Conclusions

1.) A fixed factor approach is unable to compensate for matrix shifts and instrument drift.

2.) PCA graphs indicate Metal plus two ions tend to cluster together over matrix, analysis day and tune.

3.) M^{2+} internal standards tend to generate tighter distributions across matrix, day and tune relative to M^{1+} internal standards.

4.) Hierarchical modeling provides insight into distribution shifts as a function of day and matrix