

Evaluation of New XRF Instruments

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HYSLOP



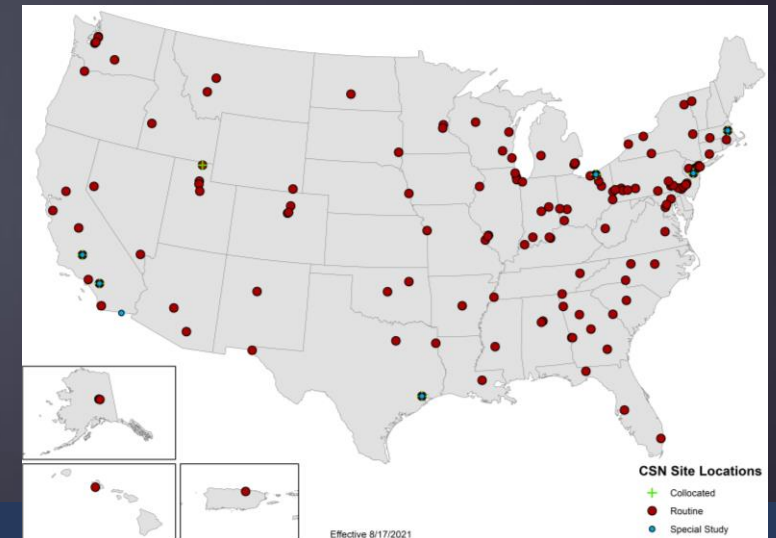
Timeline of CSN Elemental Analyses

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CSN

- ~140 monitoring sites across urban centers in the US
- Monitor 33 elements by XRF
- Generates ~1,250 samples for XRF analysis per month
- Data used to study correlations between fine PM and human health and monitor impact of clean air regulations



XRF Instrument Replacement

- Our 5 Panalytical Epsilon 5 XRF instruments are 8-13 years old
 - Currently used to analyze all CSN and IMPROVE samples
 - Manufacturer will end service in a few years
- 3 new Bruker Puma XRF instruments purchased in 2022 to analyze CSN samples
 - Development continues, getting close
 - Working on integrating Bruker instruments into lab operations

Bruker Puma S2 X-Ray Fluorescence Instruments

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Pros:

- Direct excitation
- Moderate (20) sample capacity
- Benchtop
- Higher energy flux, shorter analysis time



Cons:

- Need to develop 25 mm filter holders
- Manufacturer spectral processing software is inadequate for our thin-film samples
- Need to create custom software to optimize performance

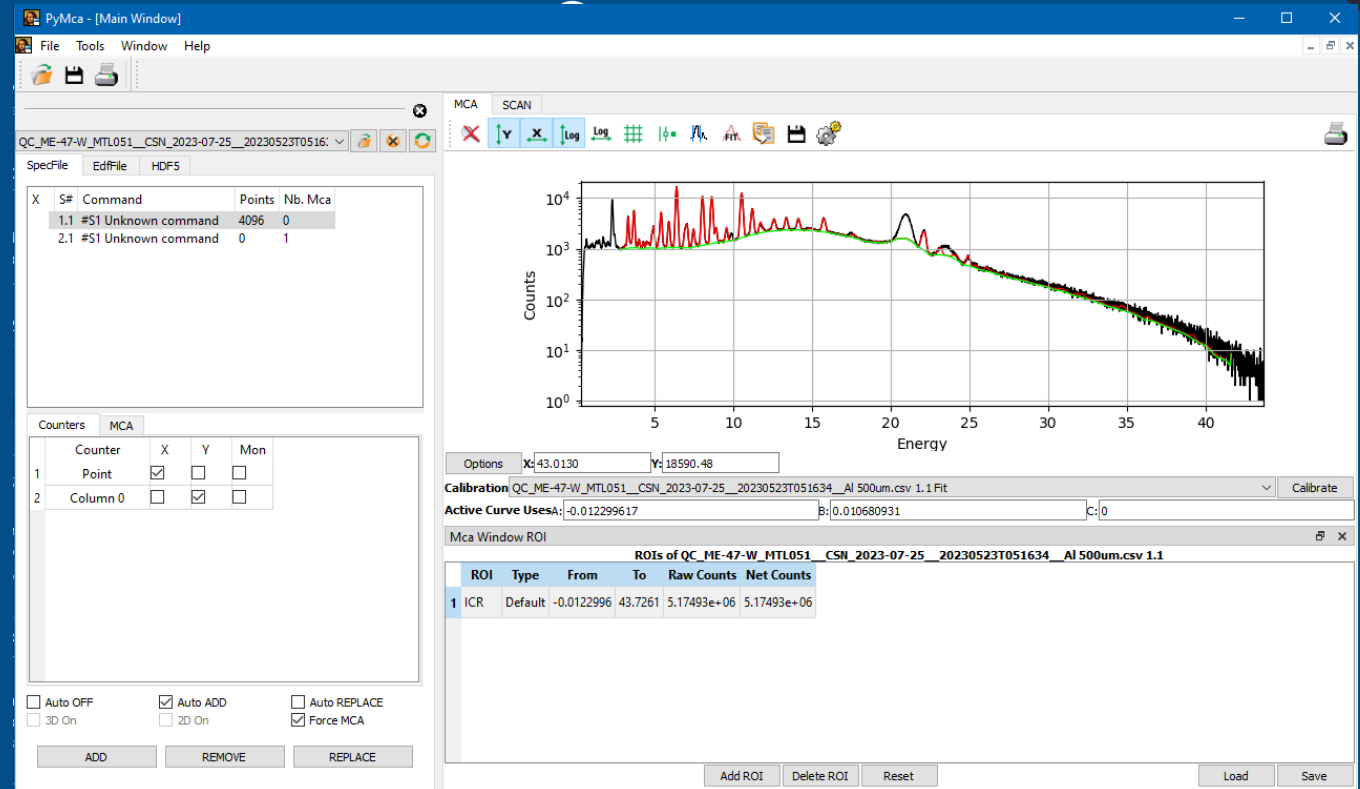


Bruker Puma S2 X-Ray Fluorescence Instruments

High quality, open source, XRF processing software is available and has been consistently improved by community feedback for > 10 years.

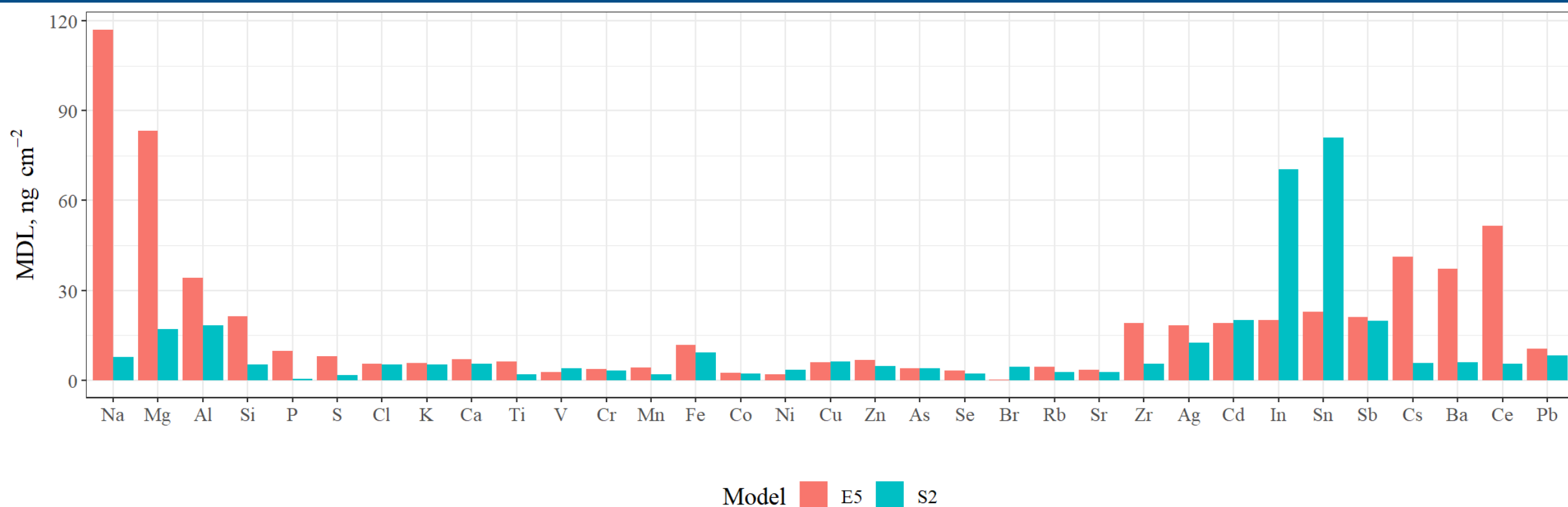
This increases control over assumptions otherwise imposed by commercial software.

Added complexity to the evaluation



V.A. Sole, E. Papillon, M. Cotte, Ph. Walter, J. Susini, A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra, Spectrochim. Acta Part B 62 (2007) 63-68.

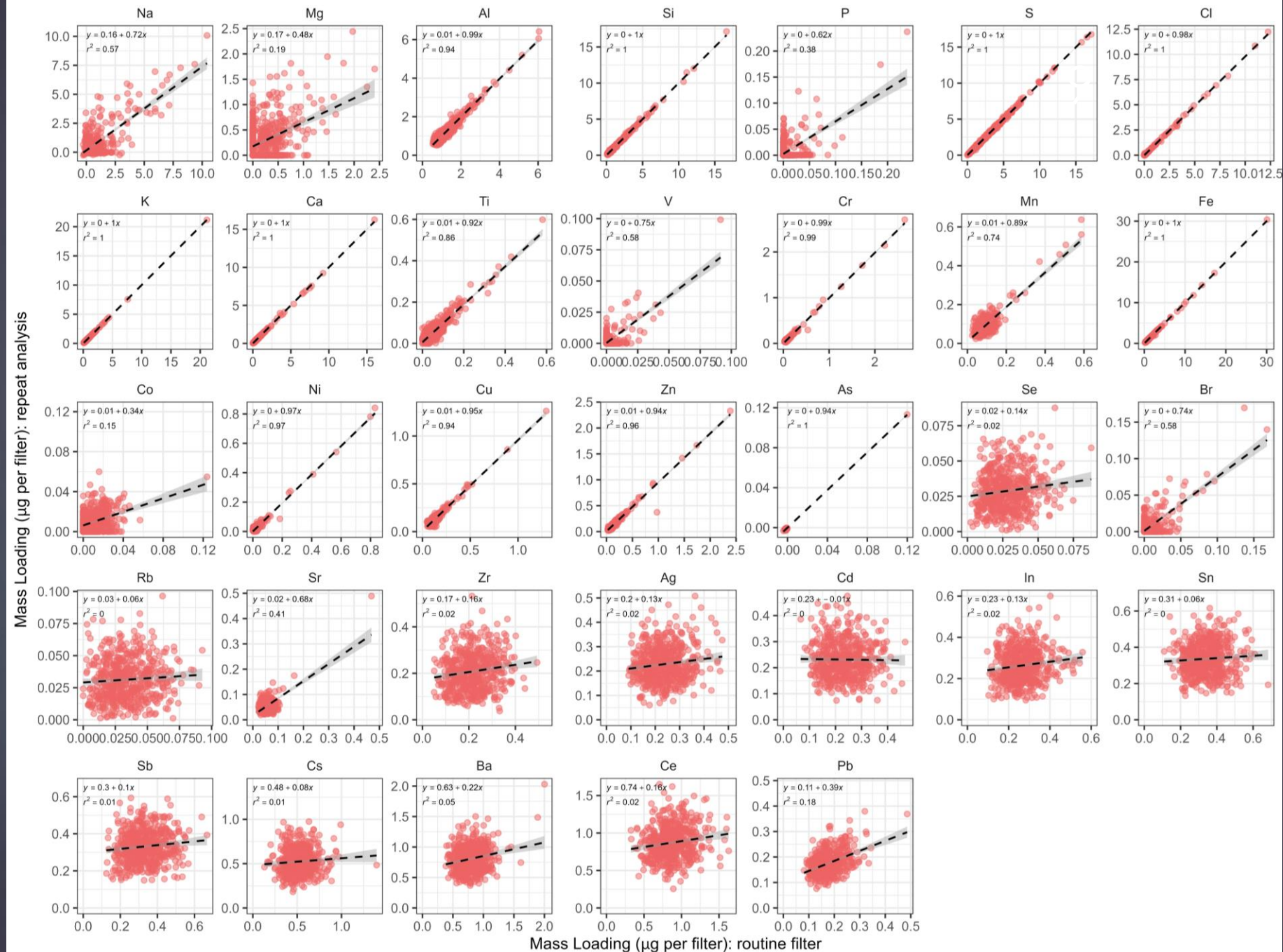
Method Detection Limit Estimates



MDL estimates based on new EPA method using higher standard deviation of blanks or lightly-loaded reference materials

XRF Replicates

- ▶ Best case scenario for CSN
- ▶ Samples analyzed in replicate on the same Panalytical E5 XRF instrument
- ▶ About half the elements are just noise
- ▶ 12 are regularly well-measured
- ▶ This makes the intercomparison difficult



XRF Inter-comparison

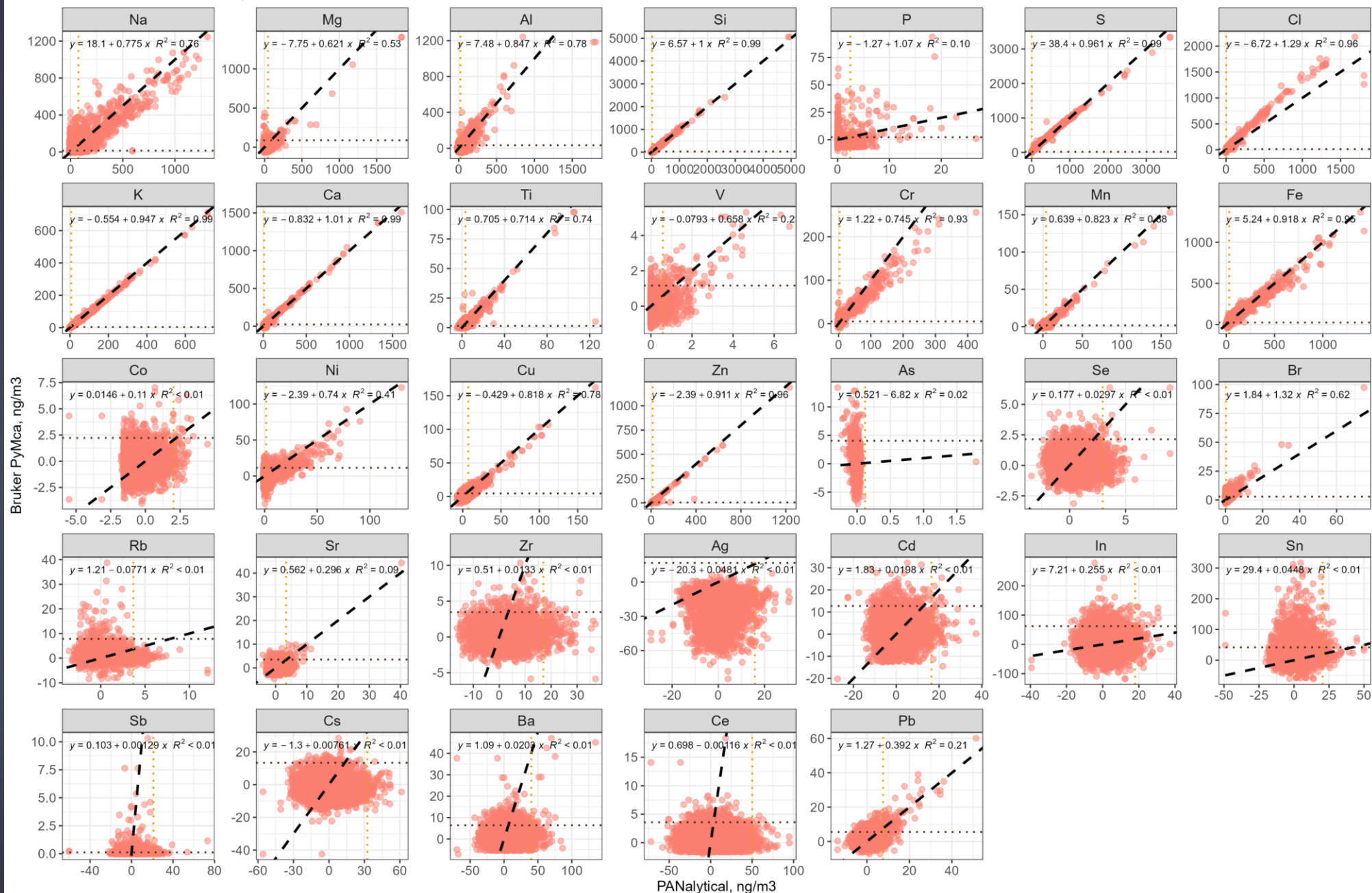
► Bruker S2 (3 instruments) versus Panalytical E5 (5 instruments)

► Elements that are precisely measured on the existing Panalytical instruments are also precisely measured on the Bruker instruments

► Some biases exist

Comparison of Bruker PyMca vs. PANalytical (2941 CSN samples from 2024 Feb~May)

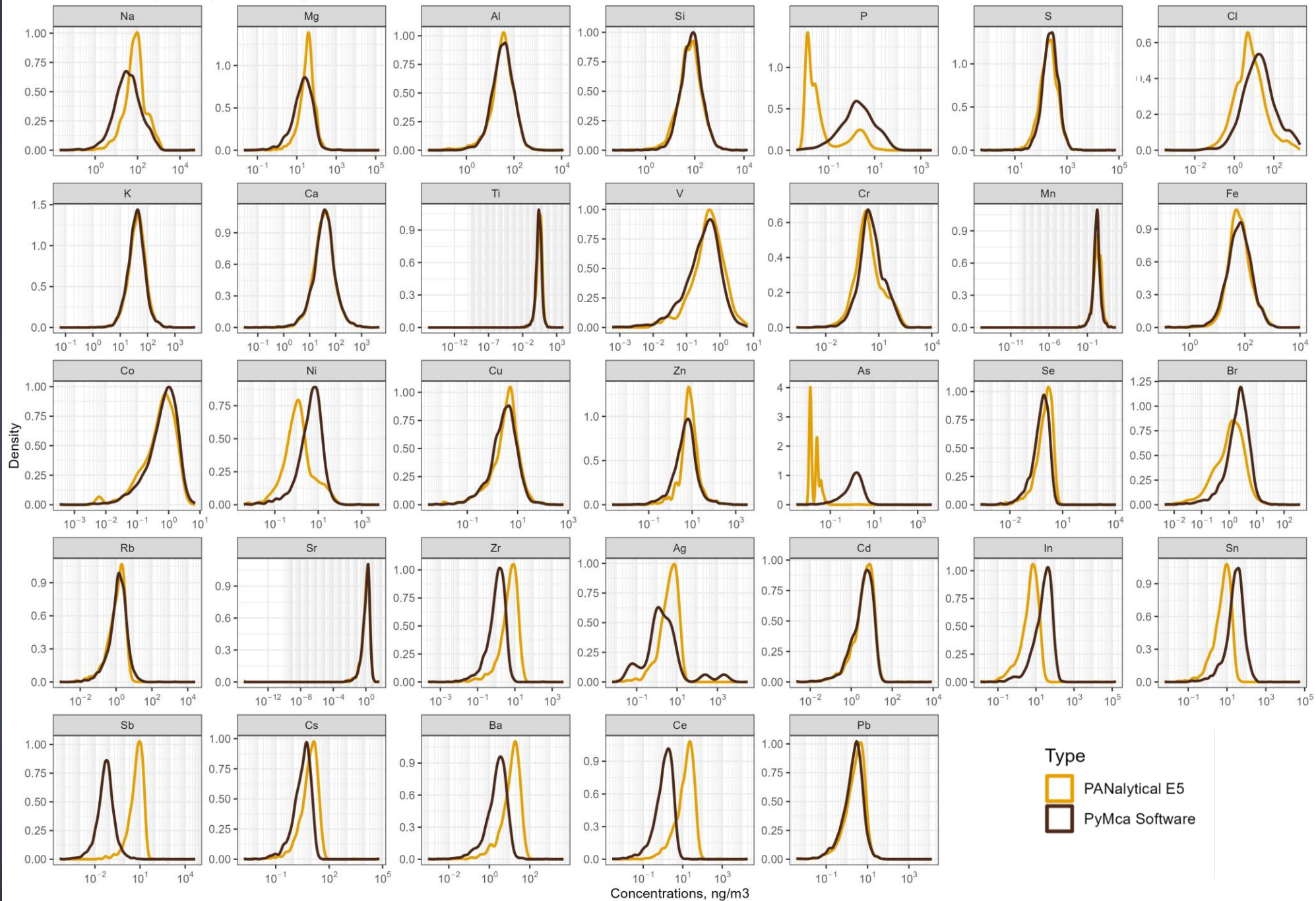
The black dash lines are 1:1, and the vertical and horizontal dot lines are MDLs



XRF Inter-comparison

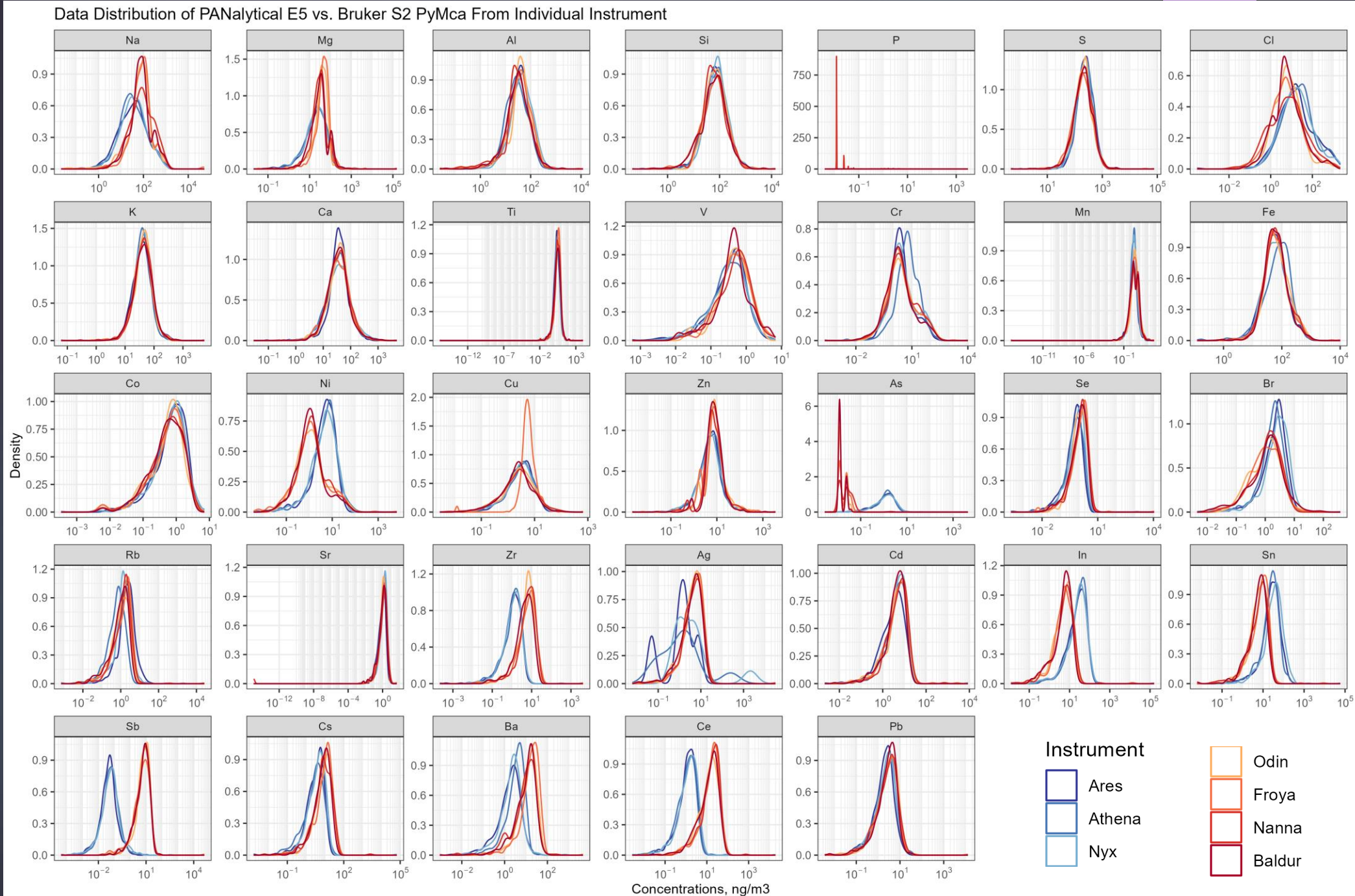
Same data,
different
view

Data Distribution of Panalytical E5 vs. Bruker S2 PyMca
- 2941 CSN samples sampled in Feb-May 2024



Same data, different view

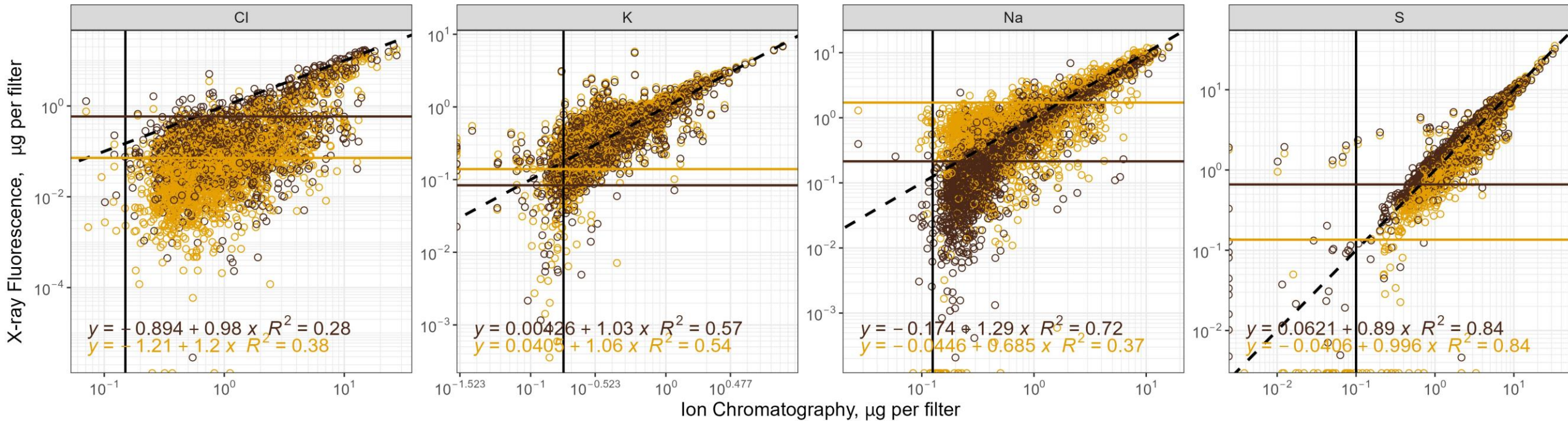
- ▶ Eliminated ≤ 0
- ▶ Individual Instruments identified
- ▶ Cool colors are Bruker instruments
- ▶ Warm colors are Panalytical instruments



XRF elements versus Ion Chromatograph ions

► Relationships are similar

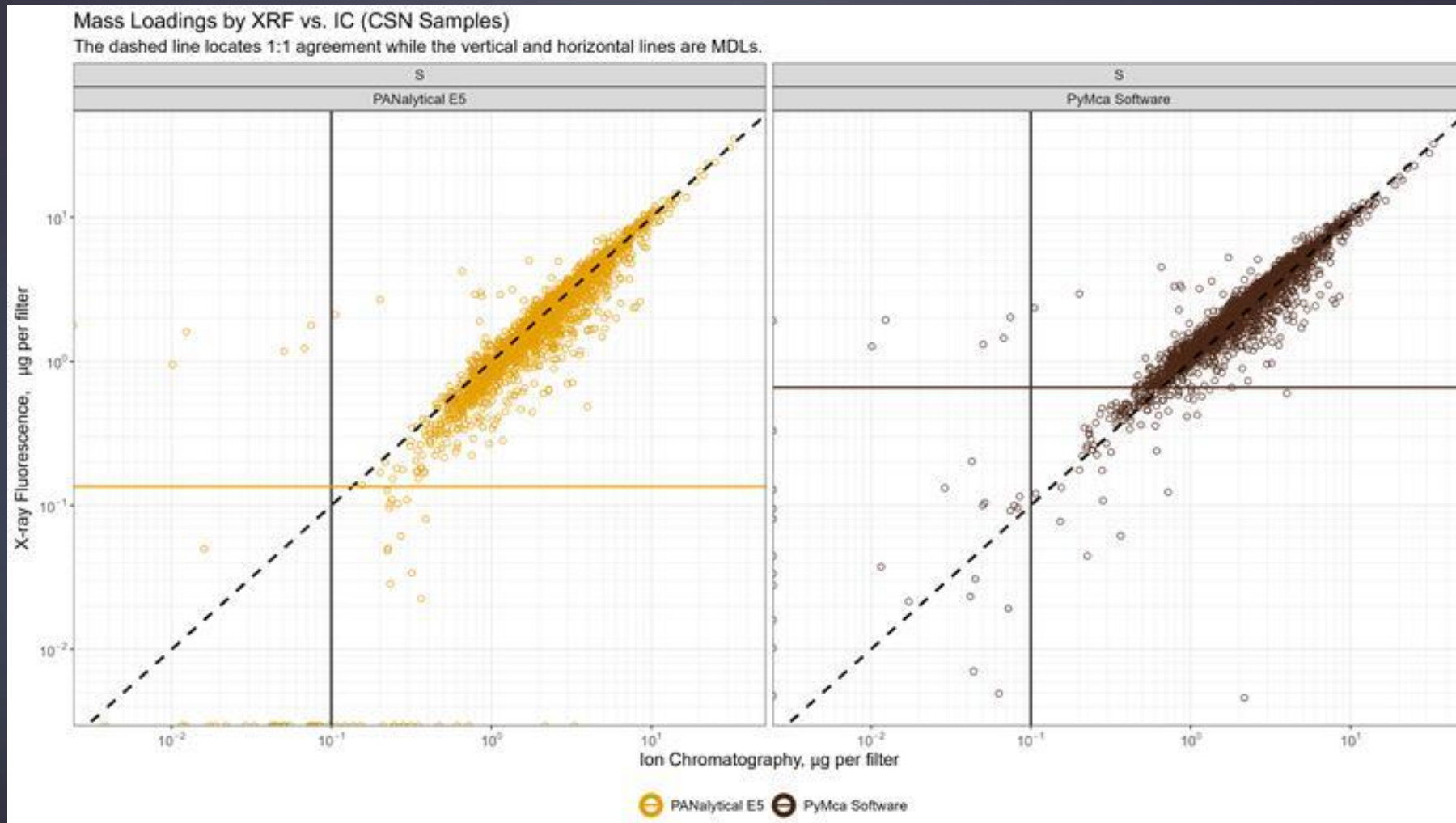
Mass Loadings by XRF vs. IC (2941 CSN Samples in Feb~May 2024)
The dashed line locates 1:1 agreement while the vertical and horizontal lines are MDLs.



Focusing in on Sulfur versus Sulfate

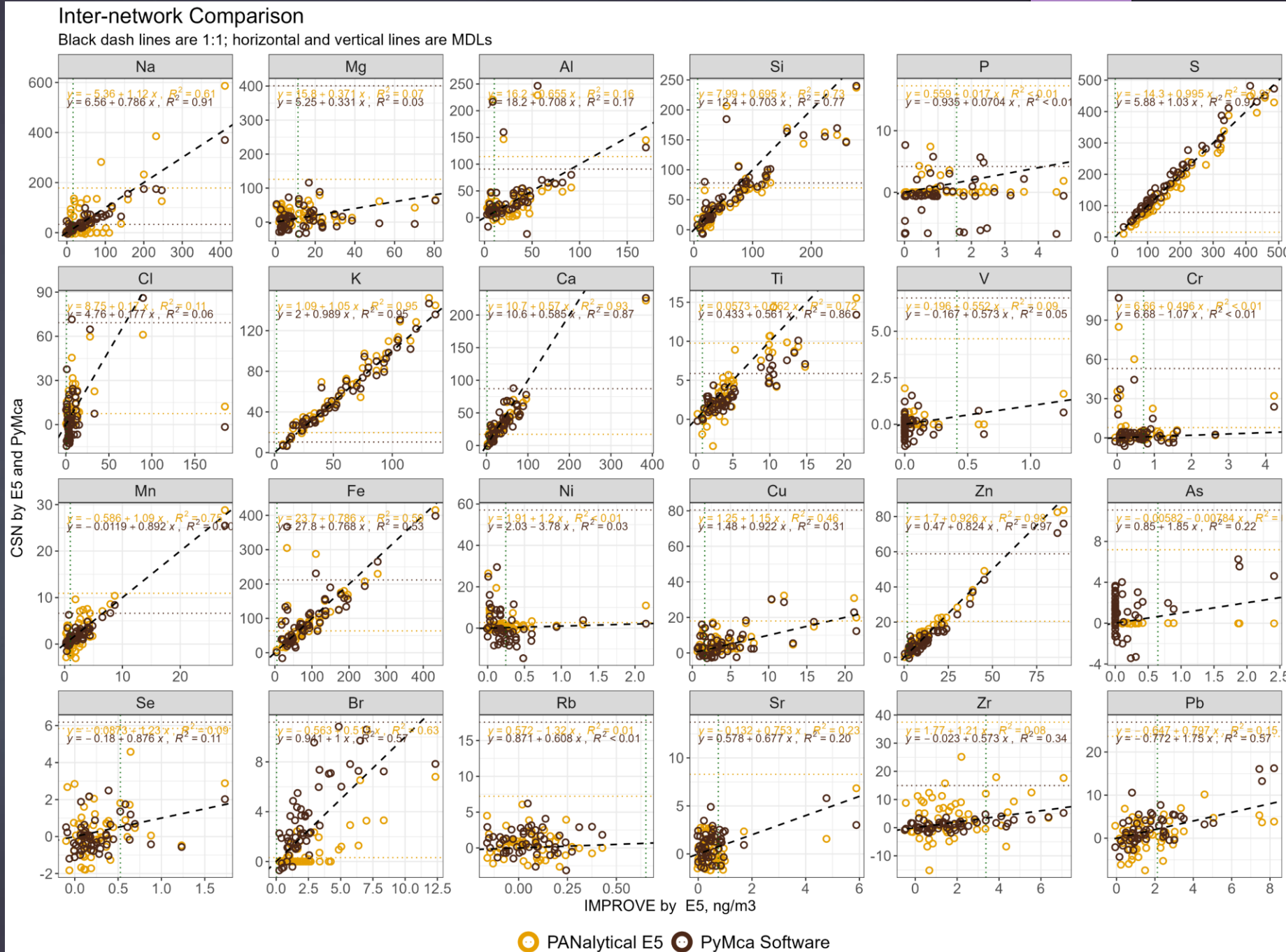
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- ▶ Panalytical E5 seems to be biased low at low concentrations



CSN vs IMPROVE

- ▶ Collocated IMPROVE and CSN samples from Feb, March, April, and May 2024
- ▶ IMPROVE samples only analyzed on Panalytical E5 instruments (x-axis)
- ▶ CSN samples analyzed on both Panalytical E5 (orange points) and Bruker instruments (black points)



To be continued...