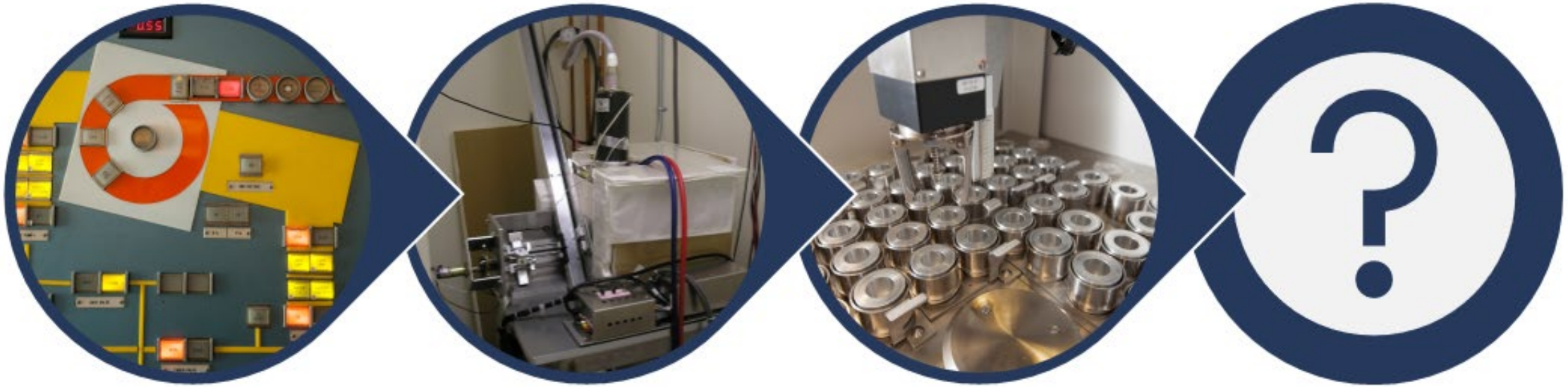
Next Generation Elemental Analyses in the Chemical Speciation Network: Investigation of Current X-ray Fluorescence Technology

- **Nicholas J Spada, Ph.D. njspada@ucdavis.edu**
- Jason Giacomo, Jiayuan Wang, Nicole Hyslop *Air Quality Research Center, University of California, Davis*

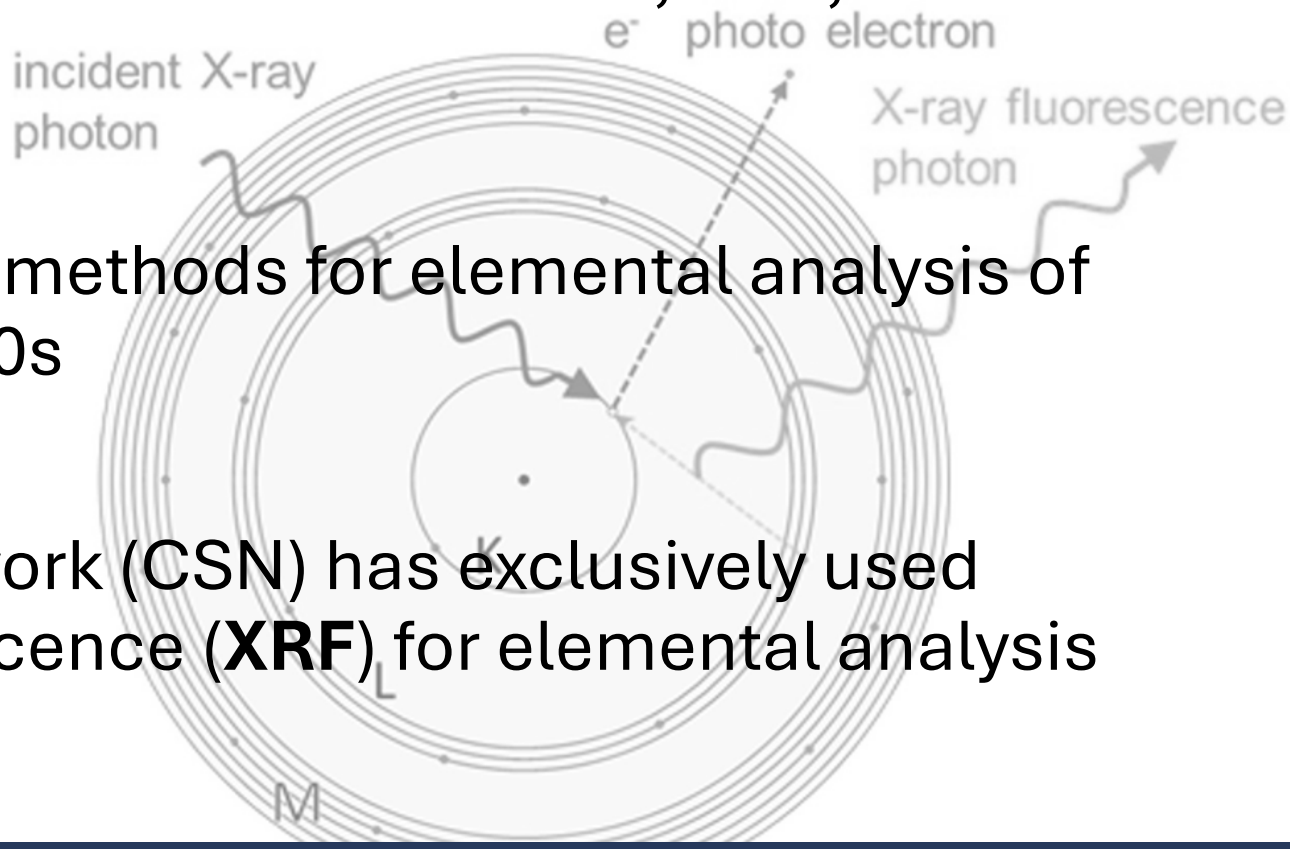


UCDAVIS
Air Quality Research Center

This work was supported by EPA contract 68HERH23D0004 with additional support from the California Cooperative Ecosystem Studies Unit (CESU) grant no. P21AC11294-03

Elemental Analysis for $PM_{2.5}$ Long-Term Trends

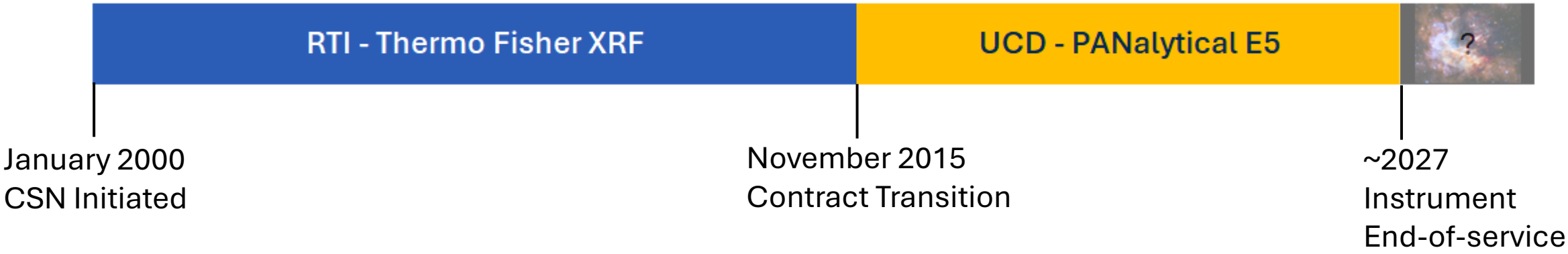
- *Speciation* of $PM_{2.5}$ includes detection of ***elements***, *ions*, and *carbon species*



- UC Davis has been developing methods for elemental analysis of PM samples since the late 1970s

- The Chemical Speciation Network (CSN) has exclusively used energy dispersive X-ray fluorescence (**XRF**) for elemental analysis

Timeline of CSN Elemental Analyses



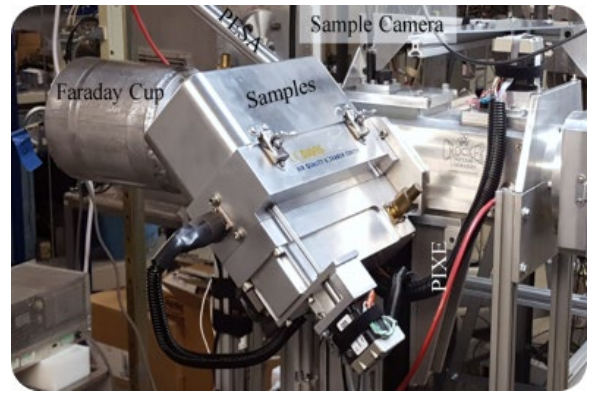
Paths of Exploration

Commercial Instrument
(this presentation)

Explore ICP-MS
(next presentation)

Update Existing Instruments

Ion Beam Analysis
(PIXE/PESA/RBS)



Replacement Instrument Selection Criteria

- Primary Considerations
  - Sample throughput
  - Detector resolution/background
  - Costs (per unit and operational)
  - Analytical Geometry (Cartesian or direct excitation)
- Secondary
  - Instrument components, e.g., temperature (electronic vs. nitrogen cool)
  - Customer support/service contracts
  - Reported user experiences

Instrument Comparison: E5 and S2

	PANalytical E5 (current)	Bruker S2 (evaluated)
Principle	EDXRF	EDXRF
Source	Sc/W anode X-ray tube	Ag anode X-ray tube
Detector	High-resolution PAN-32 solid state Ge detector	HighSense ™ XP (C – Am): Peltier cooled silicon drift detector
Atmosphere	Light Vacuum	Light Vacuum
Sample capacity	52	20
~Analysis Time, min	65	35

Determining Data Quality and Suitability

Comparison of:

Were the elements detected? – Sensitivity

- Method detection limits (MDL) by field blanks (and reference materials)

Are the measured data reliable? – Precision, Repeatability

- Real world samples (N = 1273, Feb – May 2023)
  - Inter-elemental comparison
  - XRF-IC comparison
  - Collocated comparison

Other factors considered but not presented:

- Safety, power consumption, staff logistics, maintainability

Determining Data Quality and Suitability

Comparison of:

Were the elements detected? – Sensitivity

- Method detection limits (MDL) by field blanks (and reference materials)

Are the measured data reliable? – Precision, Repeatability

- Real world samples (N = 1273, Feb – May 2023)
  - Inter-elemental comparison
  - XRF-IC comparison
  - Collocated comparison

Other factors considered but not presented:

- Safety, power consumption, staff logistics, maintainability

Determining Data Quality and Suitability

Comparison of:

Were the elements detected? – Sensitivity

- Method detection limits (MDL) by field blanks (and reference materials)

Are the measured data reliable? – Precision, Repeatability

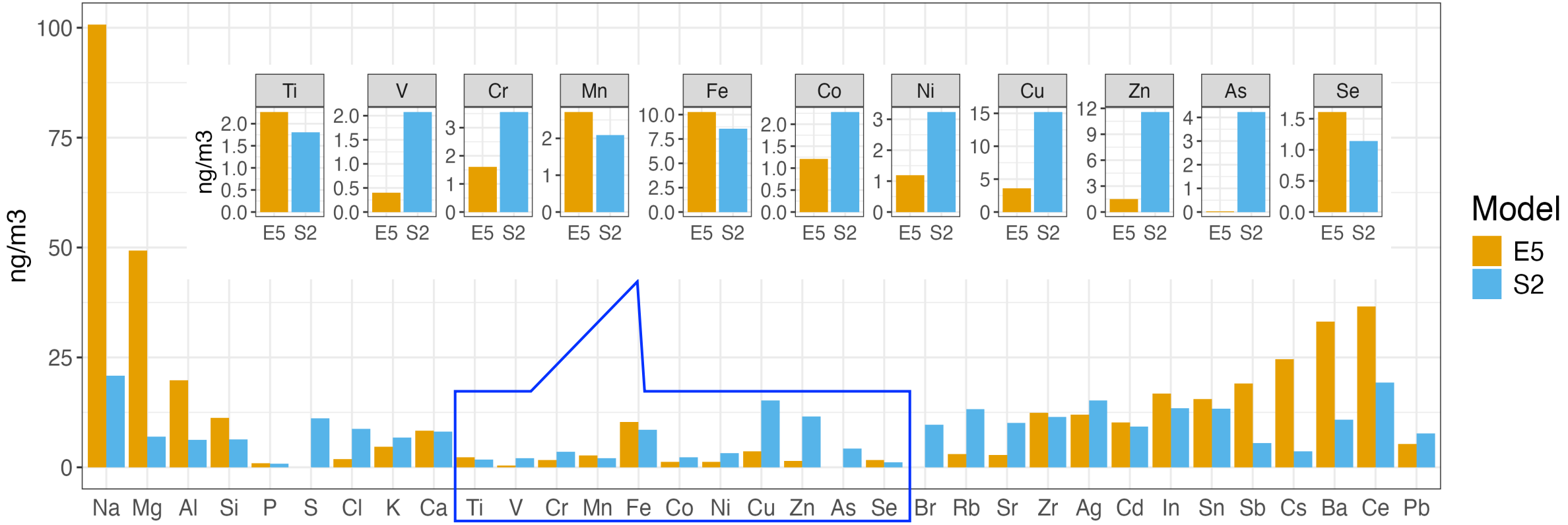
- Real world samples (N = 1273, Feb – May 2023)
  - Inter-elemental comparison
  - XRF-IC comparison
  - Collocated comparison

Other factors considered but not presented:

- Safety, power consumption, staff logistics, maintainability

Comparison of Sensitivity

Median MDL determined by field blanks



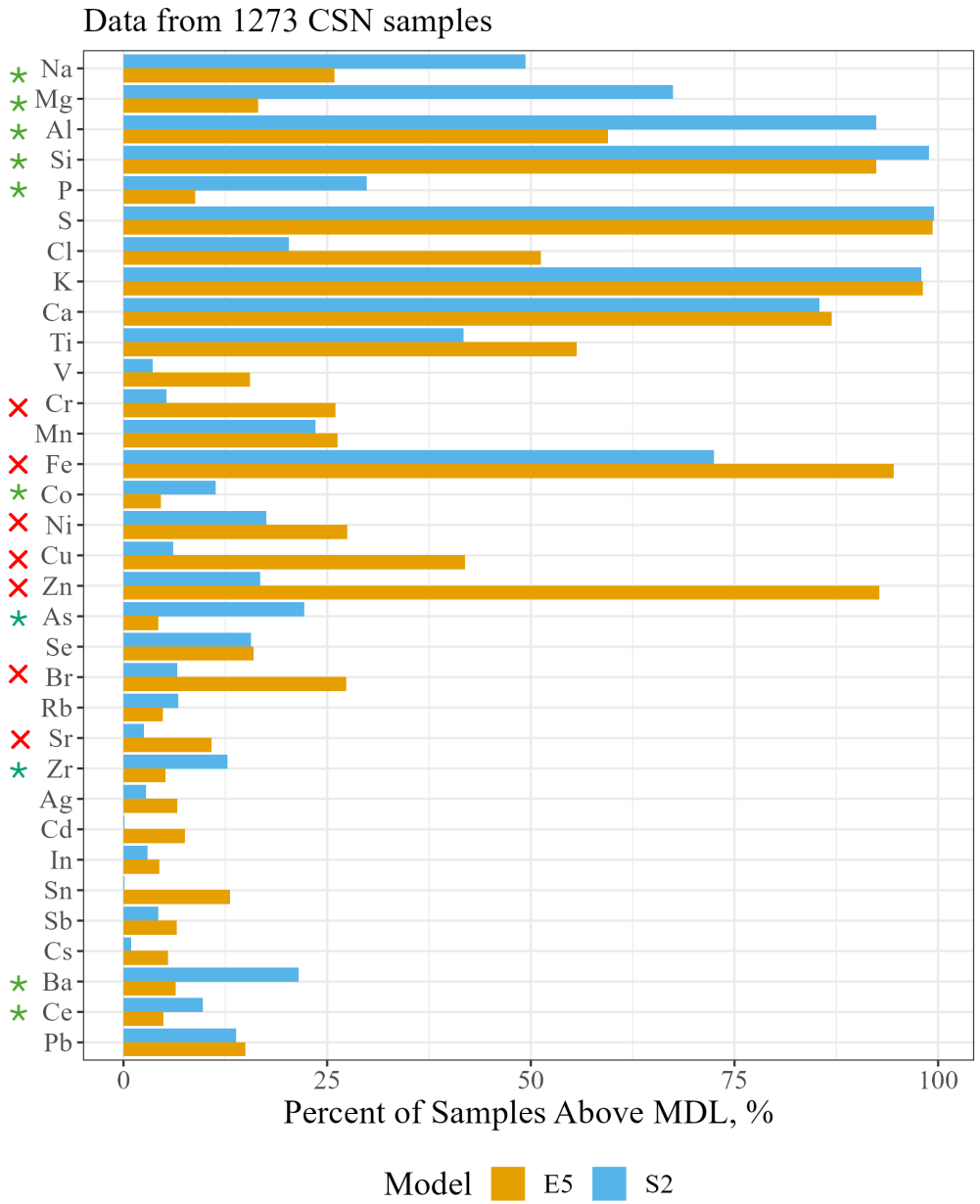
Note: performance of S2 improved when raw spectral data was processed using custom software. All data presented uses this dataset

Detection Rates

* S2 presented higher detection rates for Na, Mg, Al, Si, P, Co, As, Zr, Ba, Ce

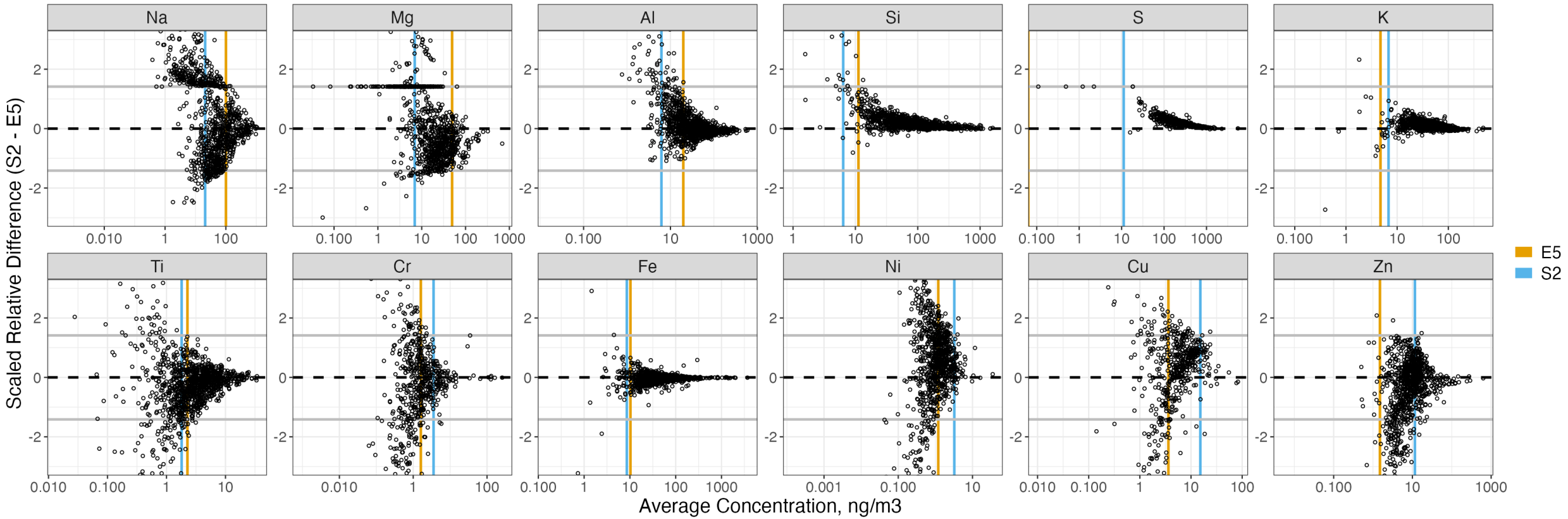
× S2 presented lower detection rates for Cr, Cu, Zn, Br, and Sr

Most elements routinely measured in CSN (> 50 %) still detectable



E5: PANalytical Epsilon 5 (current)
S2: Bruker Puma S2 (evaluated)

Statistical Agreement Between Instruments



The vertical lines are MDLs colored by instrument models;
The gray horizontal lines are $\pm\sqrt{2}$

Evaluating Accuracy

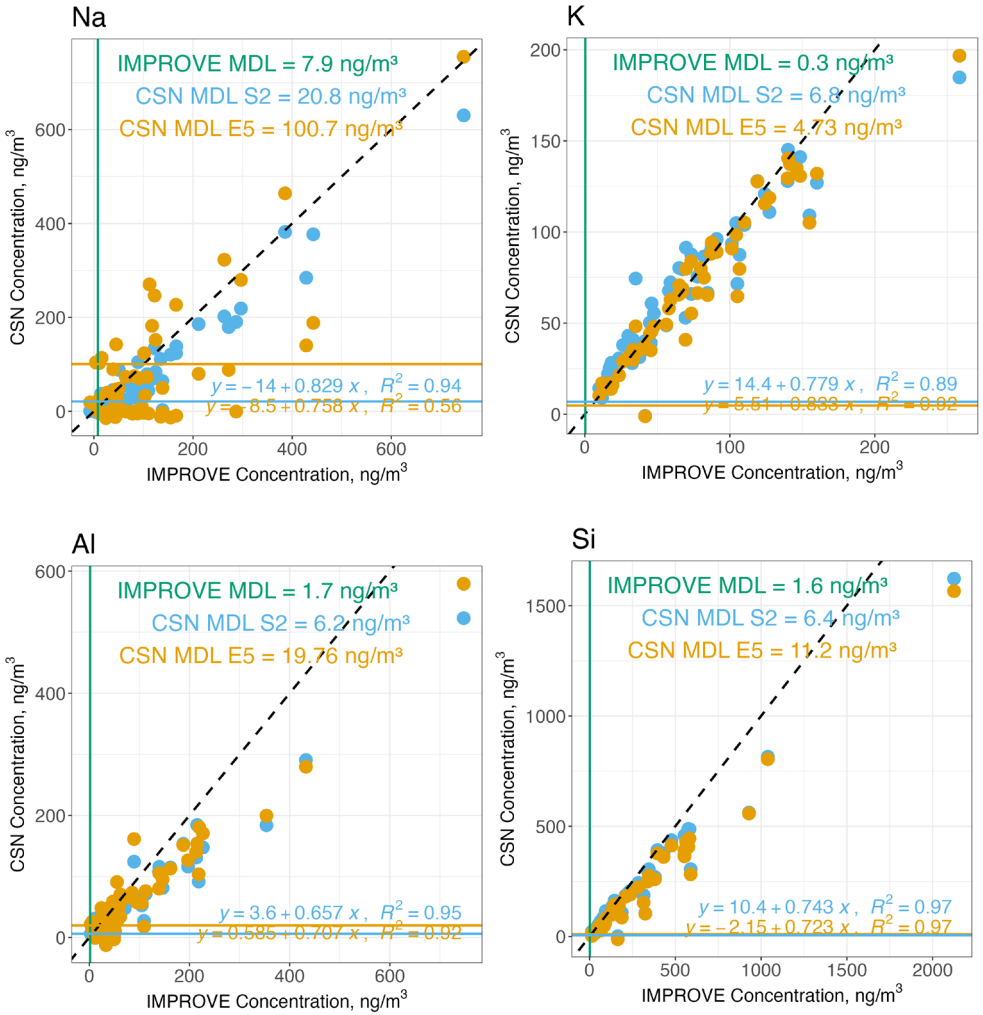
CSN-IMPROVE Collocated Comparisons

XRF vs. IC Comparisons (Na vs. Na^+, K vs. K^+, S vs. Sulfate, Cl vs. Cl^-)

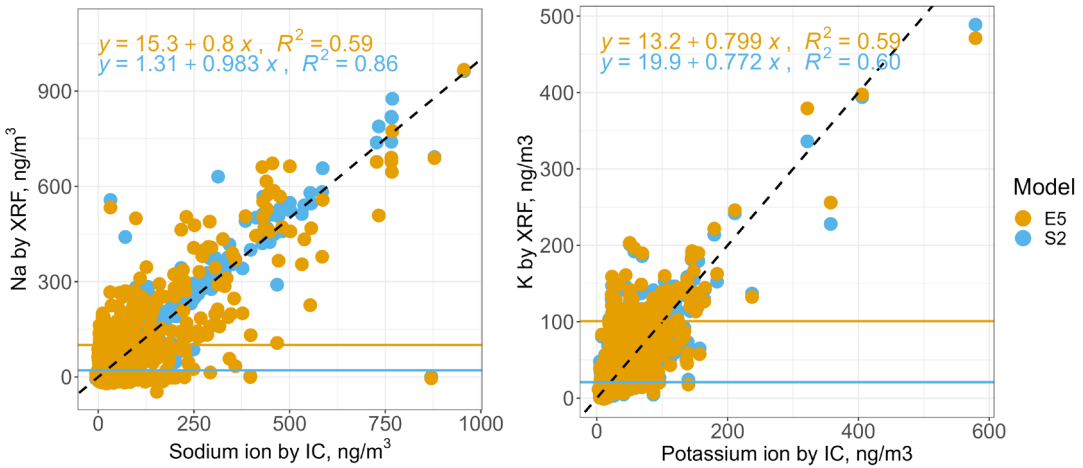
Inter-element Comparisons

Bruker S2 presented slightly tighter or comparable correlations for lower-Z elements

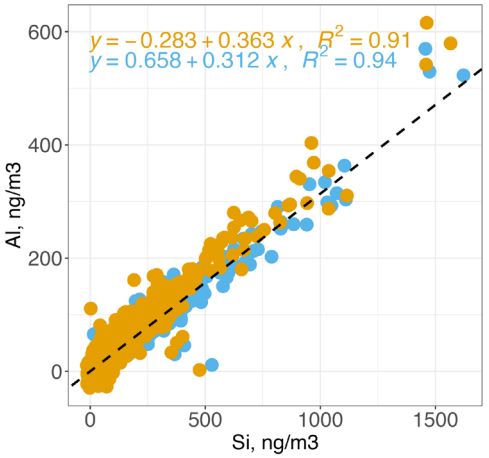
Collocated



XRF vs. IC



Inter-element

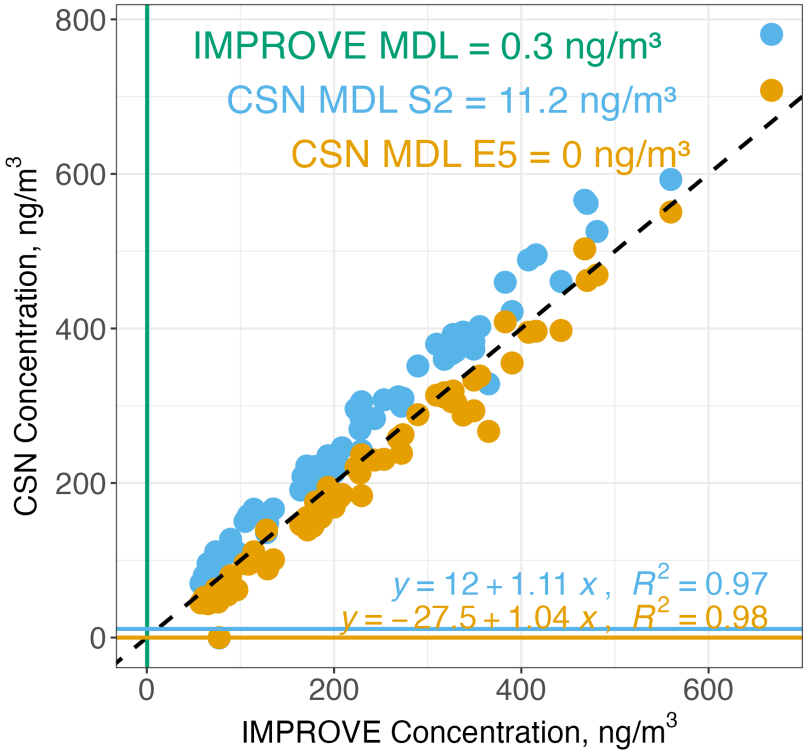


** Dash line is the bulk continental crust ratio of Al/Si (0.314) (Taylor and McLennan, 1995)*

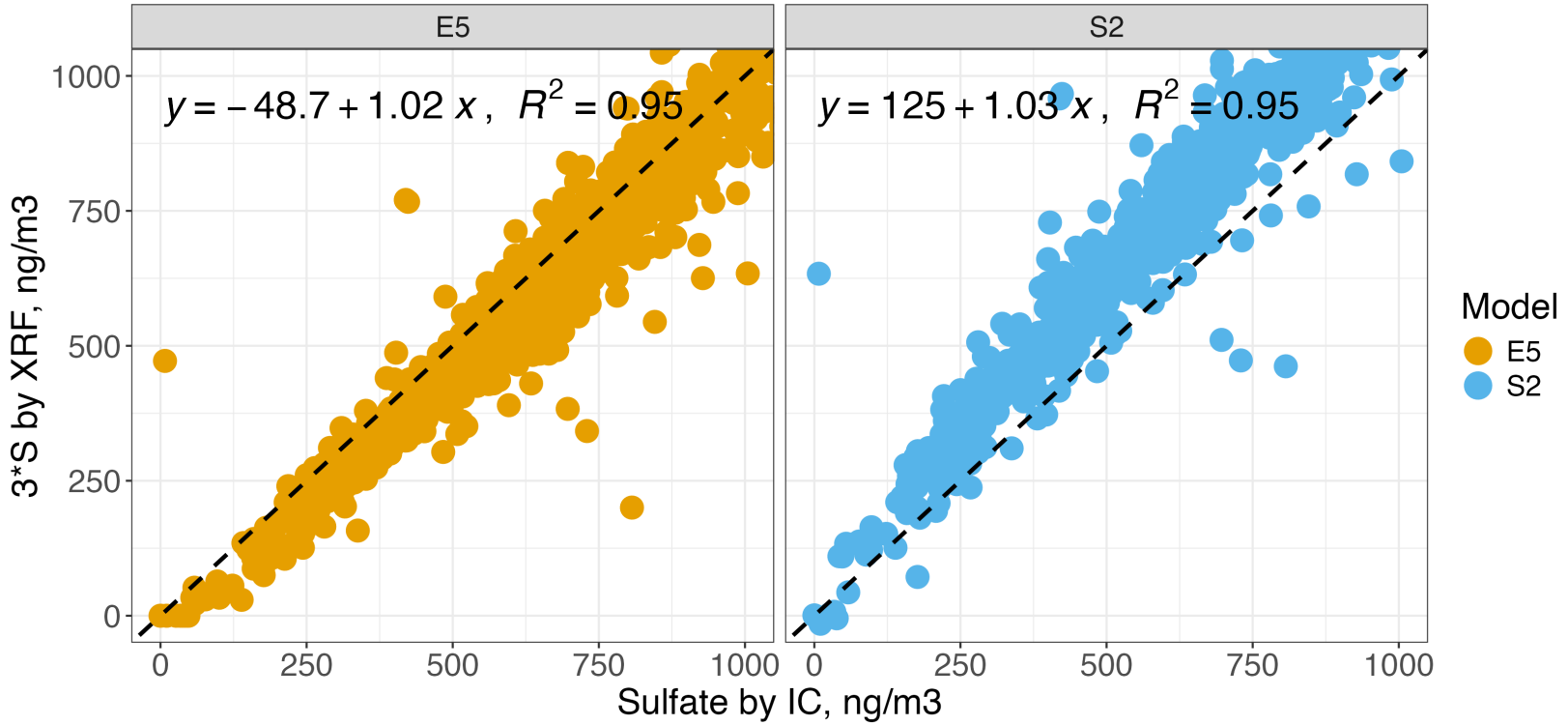
E5: PANalytical Epsilon 5 (current)
S2: Bruker Puma S2 (evaluated)
Colored lines in the co-located plots are MDLs; Black dash lines are 1:1

Success in Progress: Sulfur

Collocated

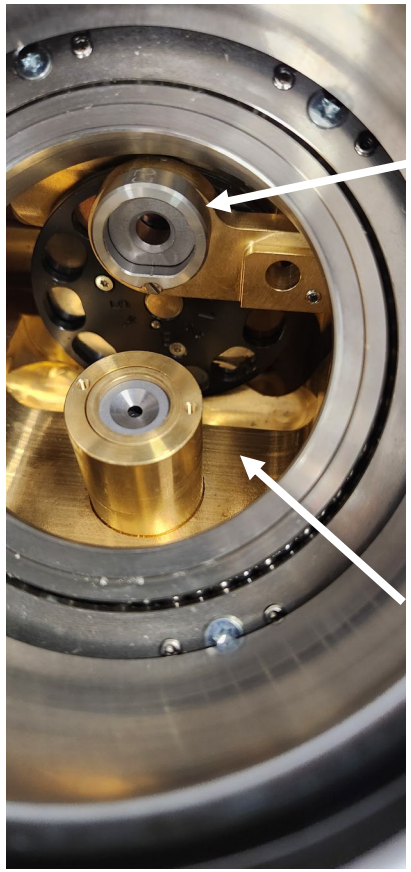


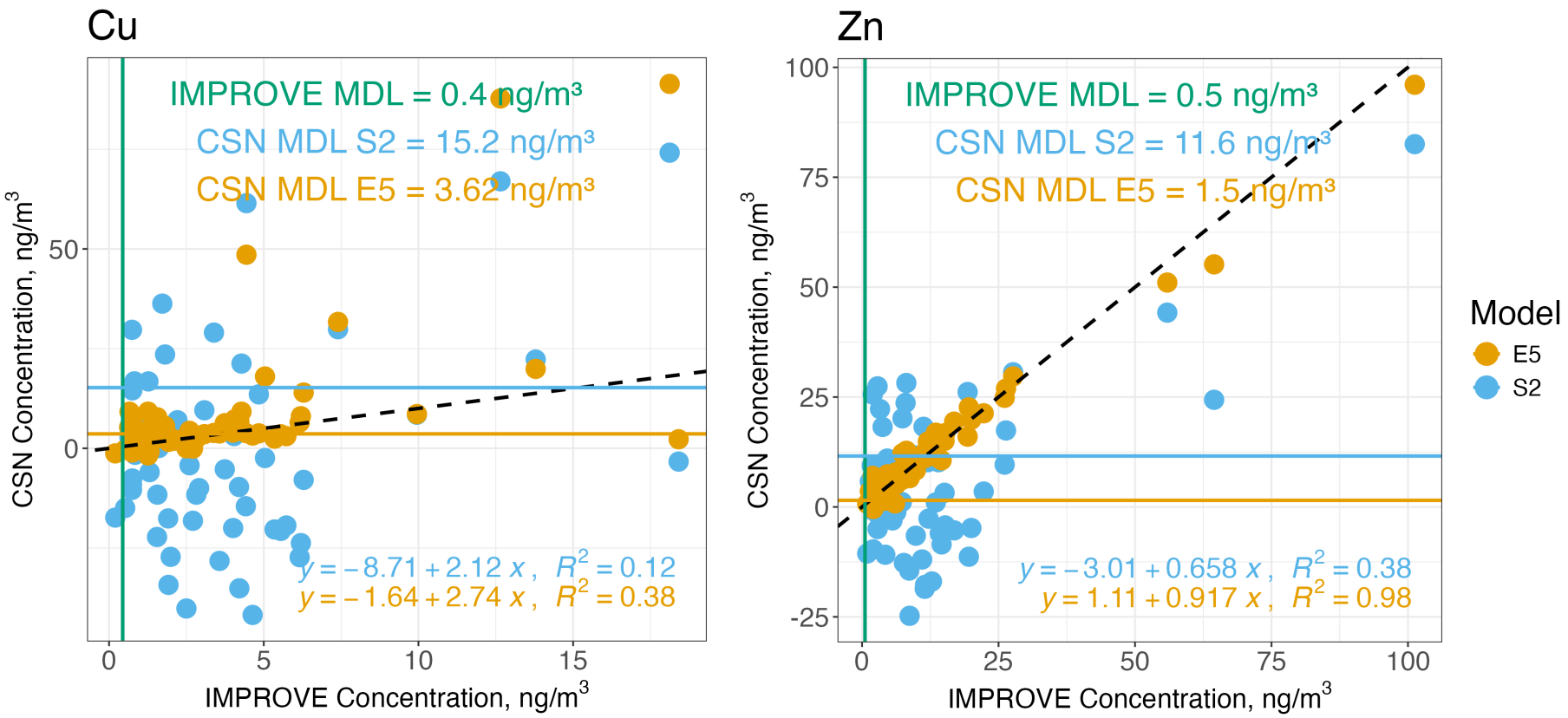
XRF vs. IC



* Dash lines are 1:1

Consequences of Instrument Design





Colored lines in the co-located plots are MDLs; Black dashed lines are 1:1

E5: PANalytical Epsilon 5 (current)
S2: Bruker Puma S2 (evaluated)

Current Findings

✓ Bruker Puma S2 presents better comparitive results than the PANalytical Epsilon 5 on several lighter elements (e.g., Na, Mg, and Al)

〰 MDLs and detection rates are comparable between E5 and S2 instruments when using custom software for processing raw data

❌ Due to the manufacturing design, Bruker S2 presents high backgrounds for important CSN elements Cu, Zn (brass) and Fe, Cr, Ni (stainless steel)

Additional testing is in progress to address shortcomings

Thank you for your time

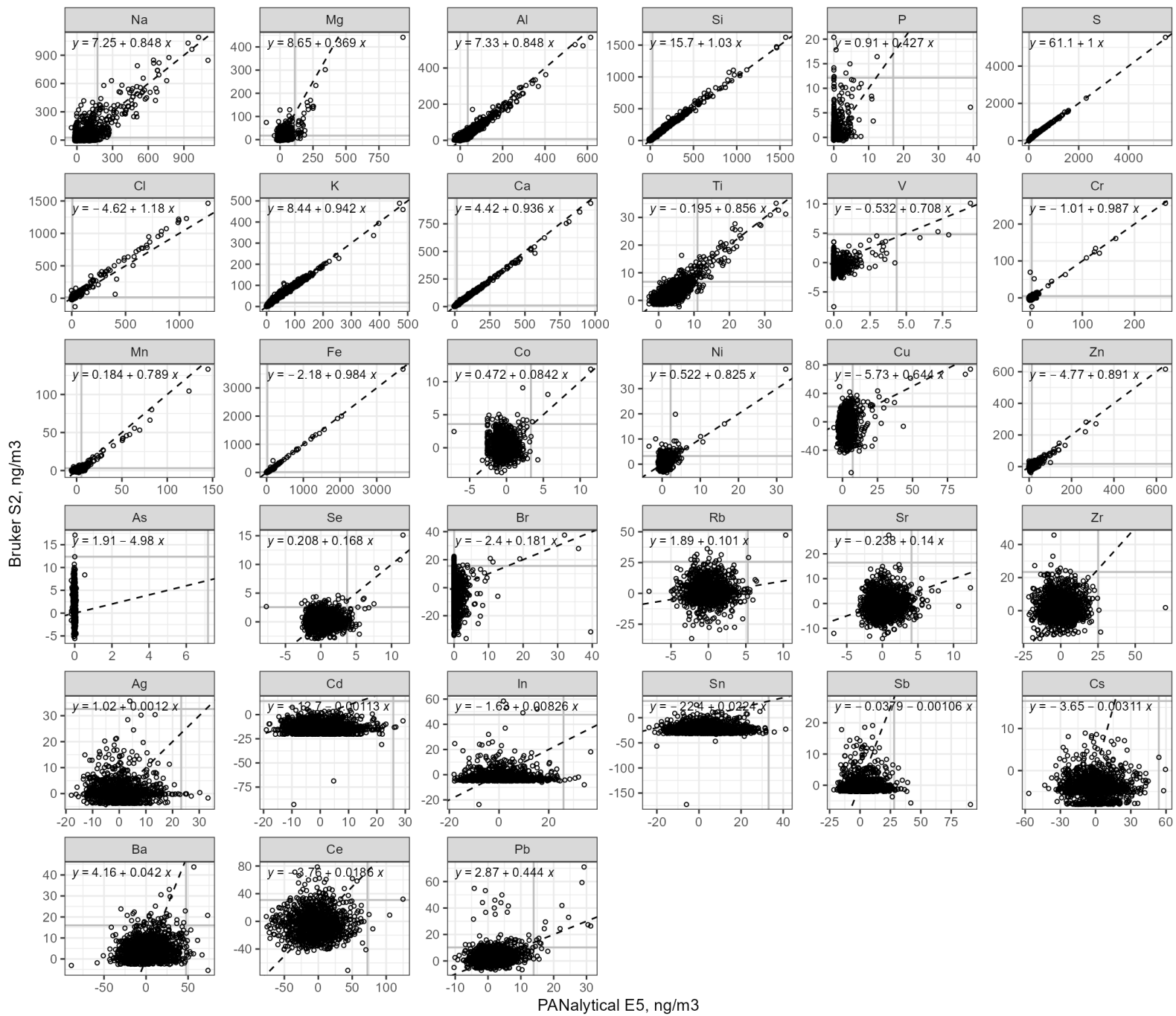
To be continued . . .

Upgrade the PANalytical E5?

Ion Beam Analysis?

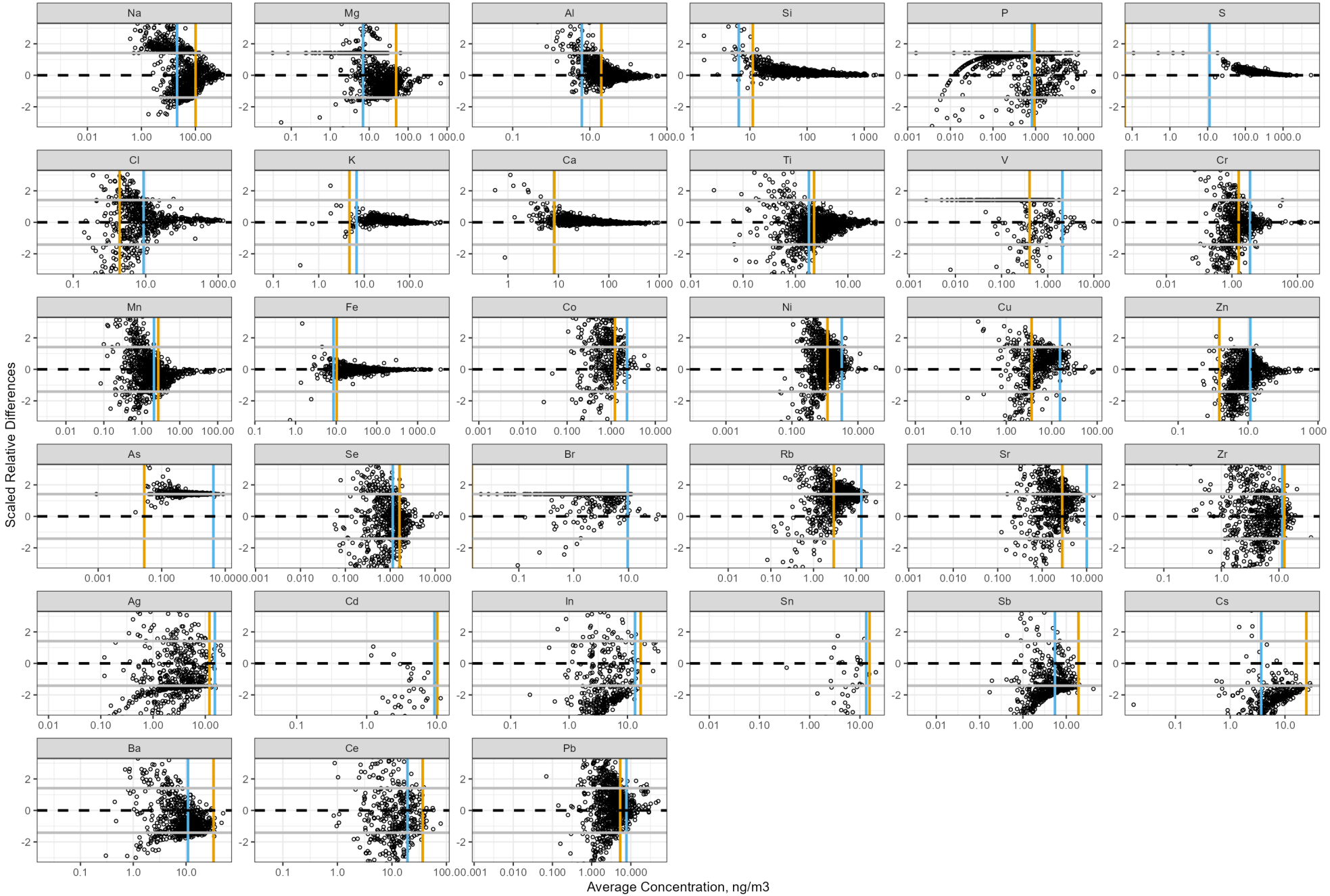
UCDAVIS
Air Quality Research Center

Nicholas J Spada, njspada@ucdavis.edu

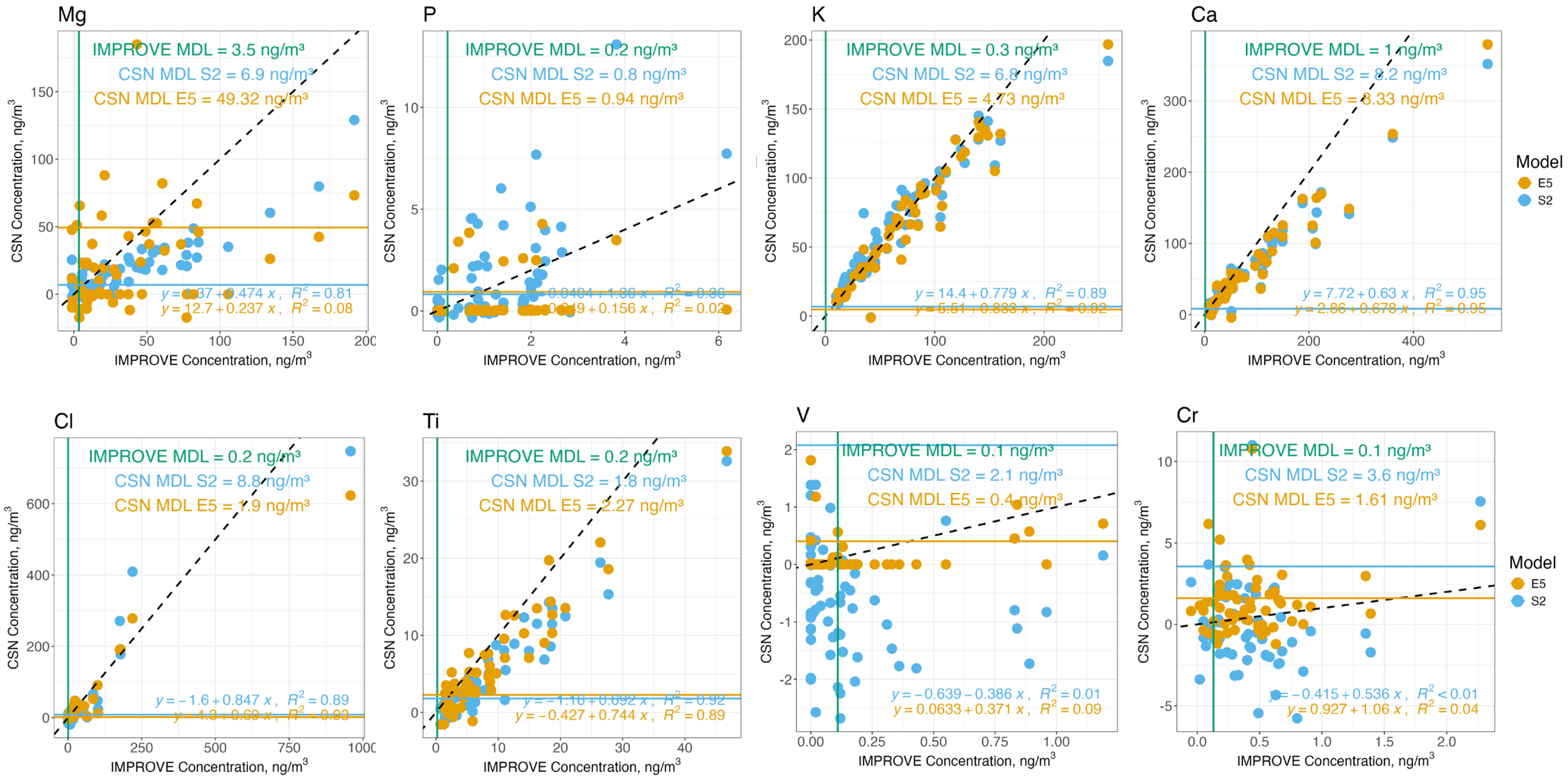

Bruker S2 vs. PANalytical E5
Dashed line is 1:1 ratio; dotted lines are median MDLs
Na
y = 7.25 + 0.848 x
Mg
y = 8.65 + 0.369 x
Al
y = 7.33 + 0.848 x
Si
y = 15.7 + 1.03 x
P
y = 0.91 + 0.427 x
S
y = 61.1 + 1 x
Cl
y = − 4.62 + 1.18 x
K
y = 8.44 + 0.942 x
Ca
y = 4.42 + 0.936 x
Ti
y = − 0.195 + 0.856 x
V
y = − 0.532 + 0.708 x
Cr
y = − 1.01 + 0.987 x
Mn
y = 0.184 + 0.789 x
Fe
y = − 2.18 + 0.984 x
Co
y = 0.472 + 0.0842 x
Ni
y = 0.522 + 0.825 x
Cu
y = − 5.73 + 0.644 x
Zn
y = − 4.77 + 0.891 x
As
y = 1.91 − 4.98 x
Se
y = 0.208 + 0.168 x
Br
y = − 2.4 + 0.181 x
Rb
y = 1.89 + 0.101 x
Sr
y = − 0.238 + 0.14 x
Zr
Ag
y = 1.02 + 0.0012 x
Cd
y = − 12.7 − 0.0113 x
In
y = − 1.63 + 0.00826 x
Sn
y = − 2.29 + 0.0224 x
Sb
y = − 0.0379 − 0.00106 x
Cs
y = − 3.65 − 0.00311 x
Ba
y = 4.16 + 0.042 x
Ce
y = − 3.76 + 0.0186 x
Pb
y = 2.87 + 0.444 x
Bruker S2, ng/m3
PANalytical E5, ng/m3

Scaled Relative Differences (SRD) vs. Average Conc of S2 and E5 (y axis limited -3 ~ 3)

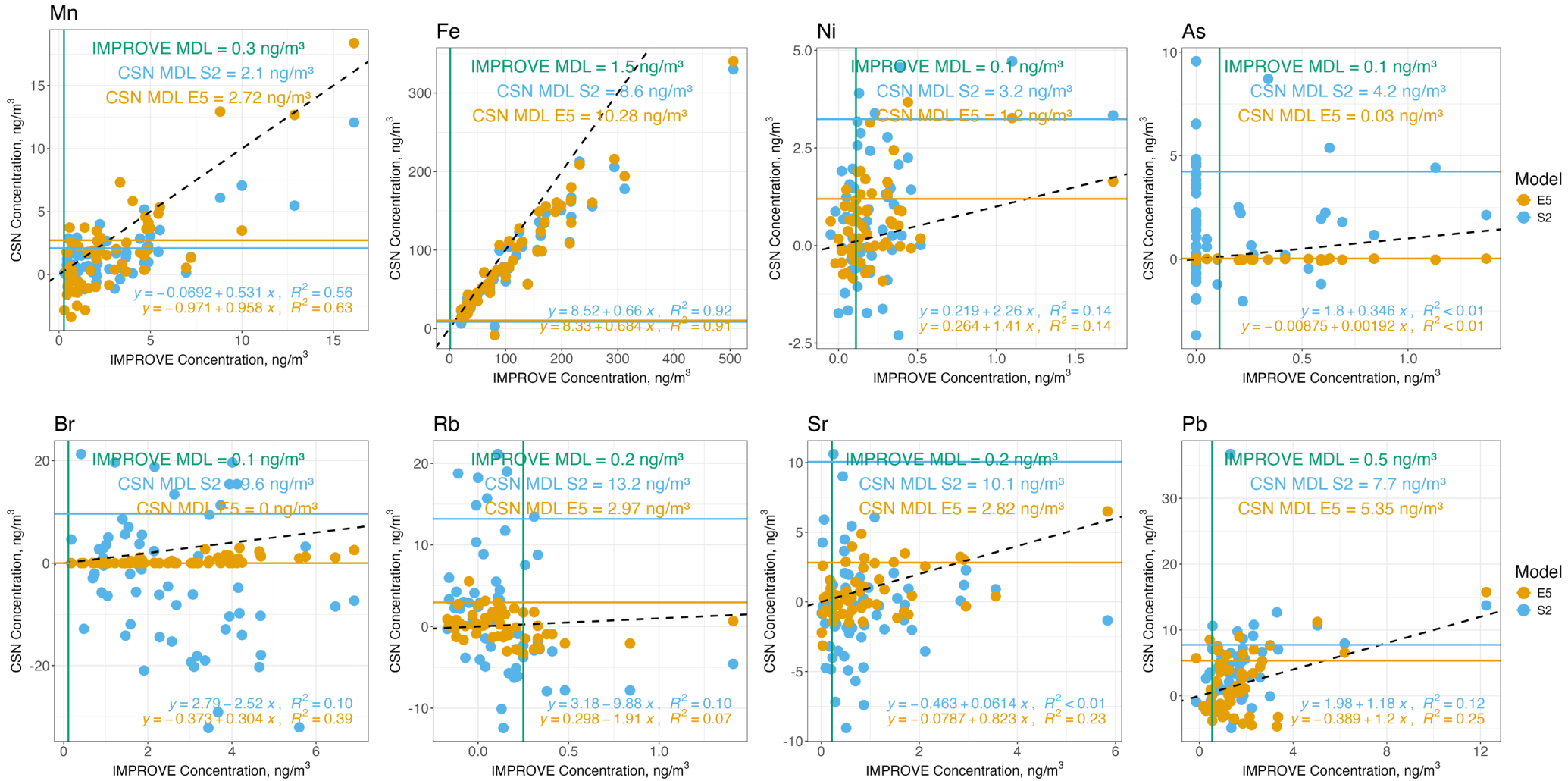
* Dashed lines are the median MDLs
* SAD = (S2-E5) / sqrt(2)
* Average Conc. = (S2 + E5) / 2



Co-located Comparison (lighter elements)



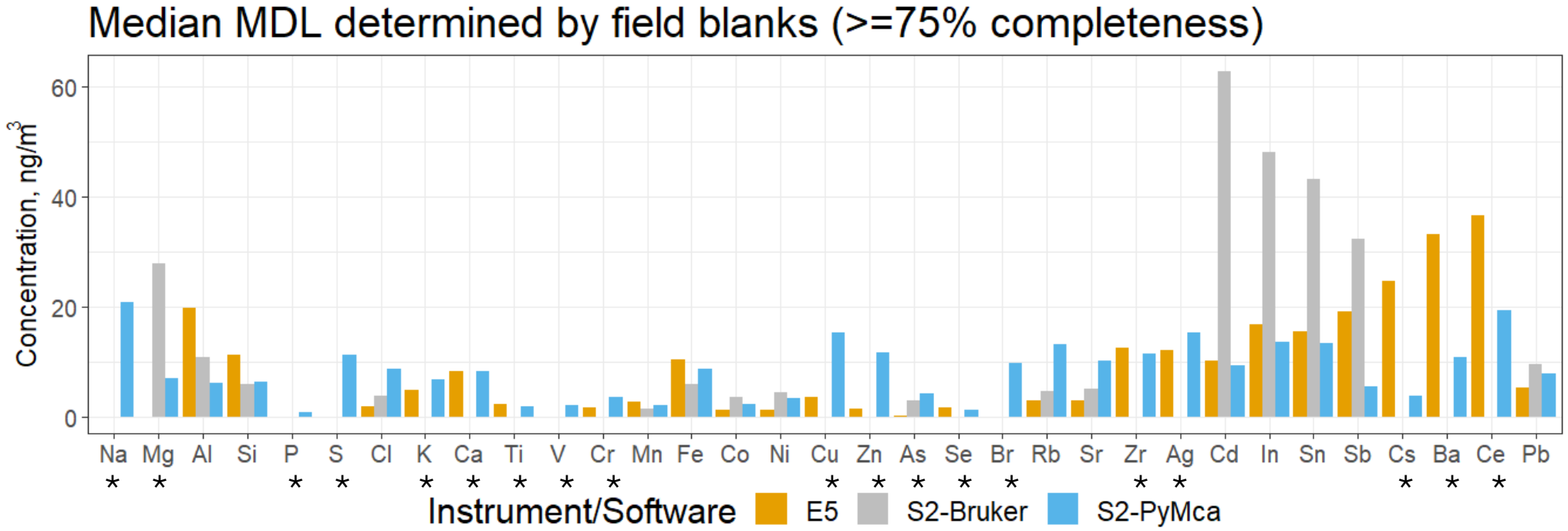
Co-located Comparison (heavier elements)



MDL Comparison – Bruker and E5 software report 0 for several elements

Zero list:

- Bruker fitting: Na, P, S, K, Ca, Ti, V, Cr, Cu, Zn Se Br Zr Ag Cs Ba Ce;
- E5 fitting: Na, Mg, P, S, V, Br
- PyMca fitting: None



E5: PANalytical Epsilon 5 (current)
S2: Bruker Puma S2 (evaluated)

Lead/Tin Comparison Between Instruments

The black, dashed line represents the upper continental crustal ratio. The gray points are from the Deer Park NATTS 2018 data set measured by ICP-MS. The gray line corresponds to the weak Deer Park trend (R2 = 0.007).