An interlaboratory comparison of elemental loadings on $PM_{2.5}$ samples via energy-dispersive XRF and single quadrupole ICP-MS

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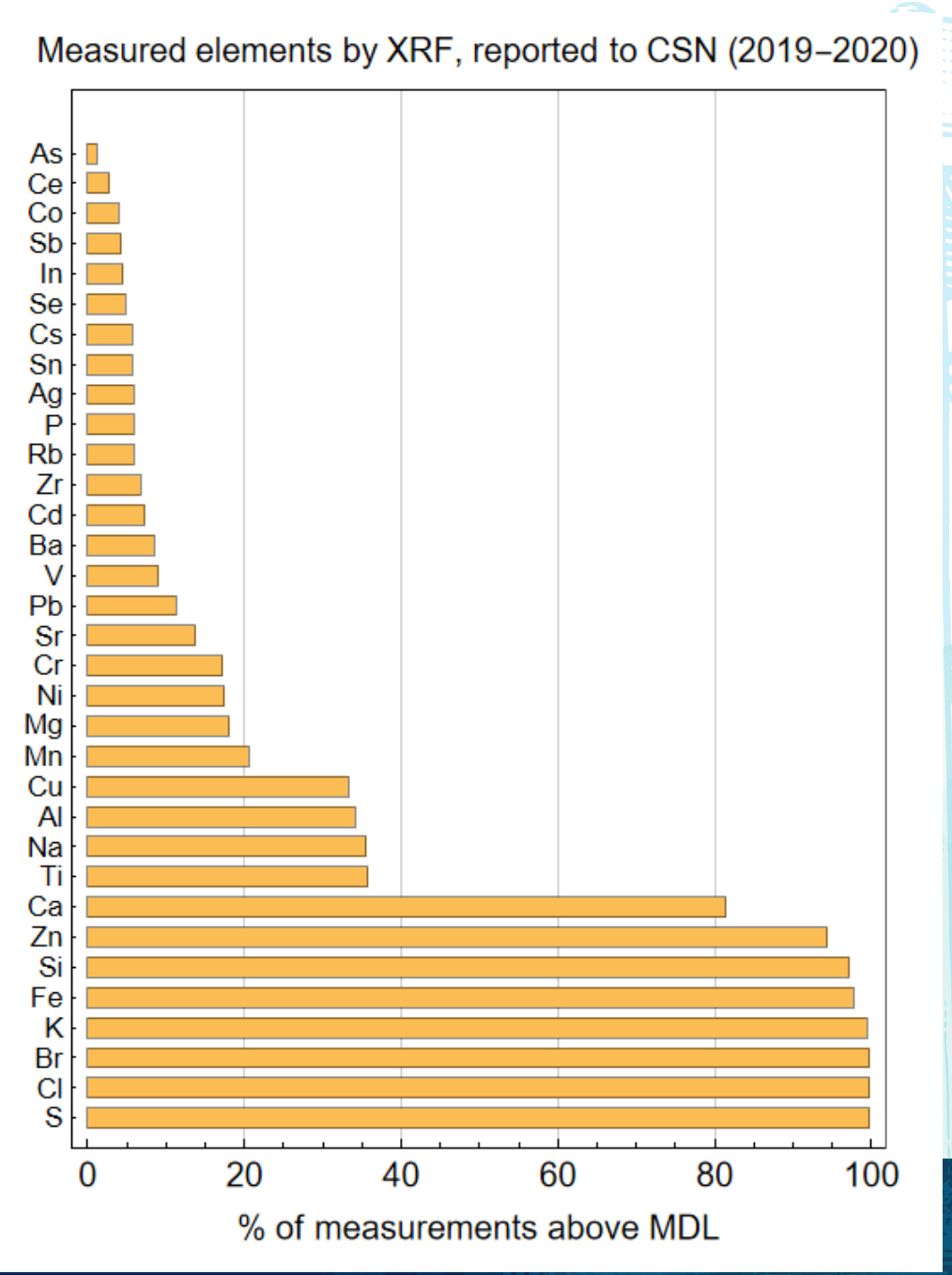
Outline

- Motivation
- XRF vs ICPMS
- Methodology
- Inter-instrumental comparison
- Internal checks: Intra-instrumental
  - Inter-elemental comparison
  - Precision: collocated
- Summary + Future steps

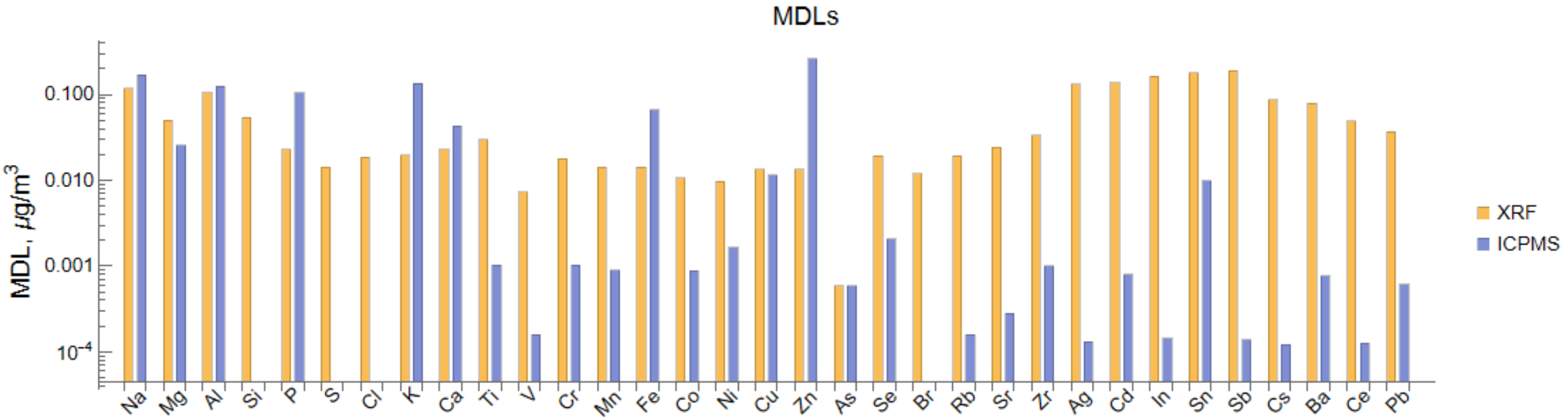
Motivation

Pollutant concentrations since inception of CSN have decreased

→ now many are at/below the lower limits of current analytical techniques



MDLs



- 4 elements measured by XRF cannot be measured using the applied ICPMS protocol (Si, S, Cl, Br)
- All elements regularly measured below MDL by XRF can be measured via ICPMS

Note: MDLs are calculated differently for XRF and ICPMS

XRF & ICPMS

Image from Thermo Fisher

	XRF	ICPMS
Sample Preparation	None	Acid digestion
Sample run time (multi-element)	~1 hour	10-15 minutes
Calibration Standards	Single or multi-element	Multi-elemental standard
Frequency of calibration	Yearly	Before every run
Sample Preservation	Nondestructive	Destructive

Sample Selection + Analyses

Archived CSN samples in UCD (analyzed via XRF): January 2019 – August 2020

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- Batch 1 (N=209): 33 elements (10th, 50th, and 90th percentile sample for each element)
- Batch 2 (N=146): Collocated samples from 3 sites
  - 18 from Rutgers, NJ; 38 from Dudley Square (Boston, MA); 20 from Rubidoux (Riverside, CA)
- Batch 3 (N=194) : Higher total elemental concentrations based on UCD XRF

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Sent to RTI

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XRF

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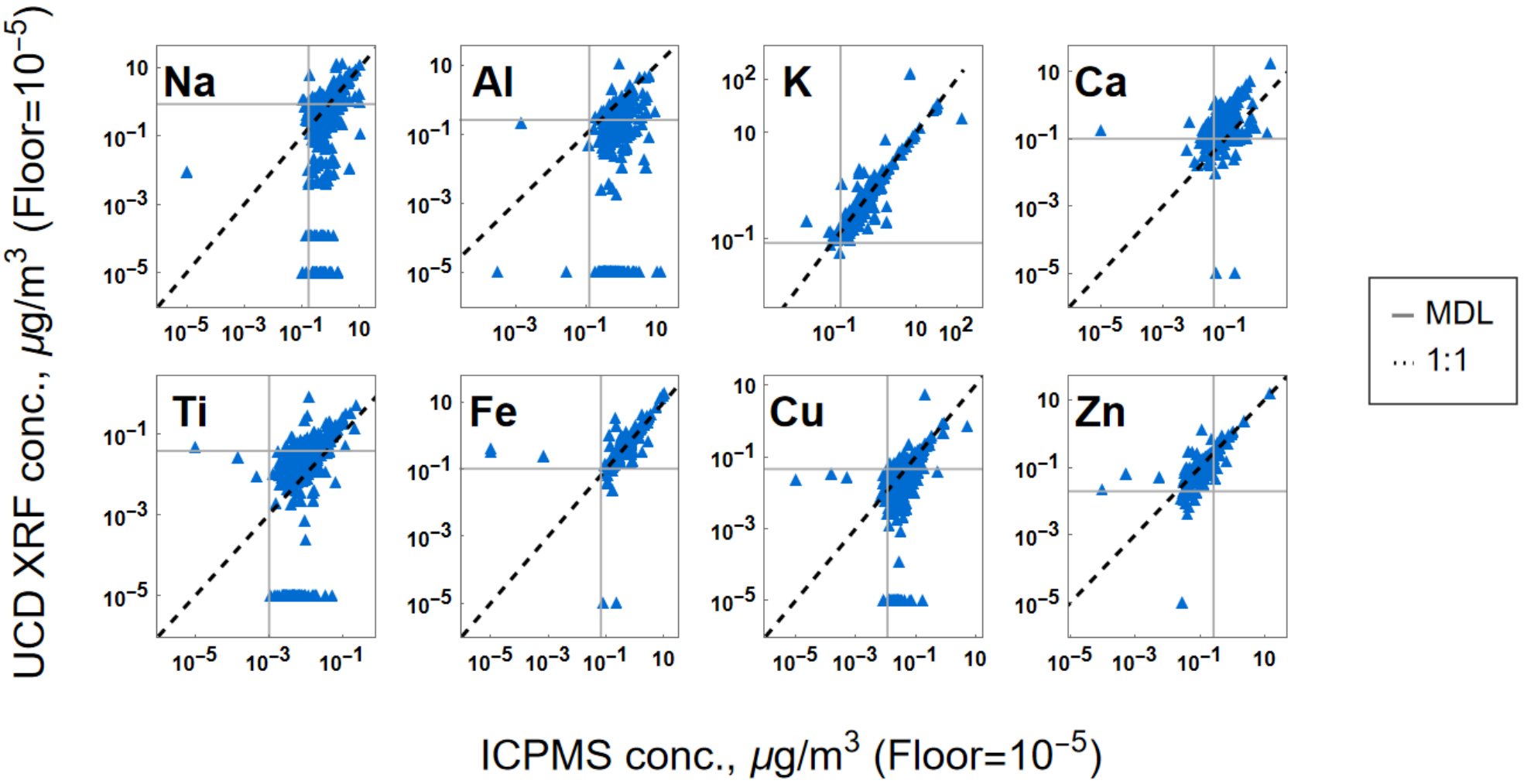
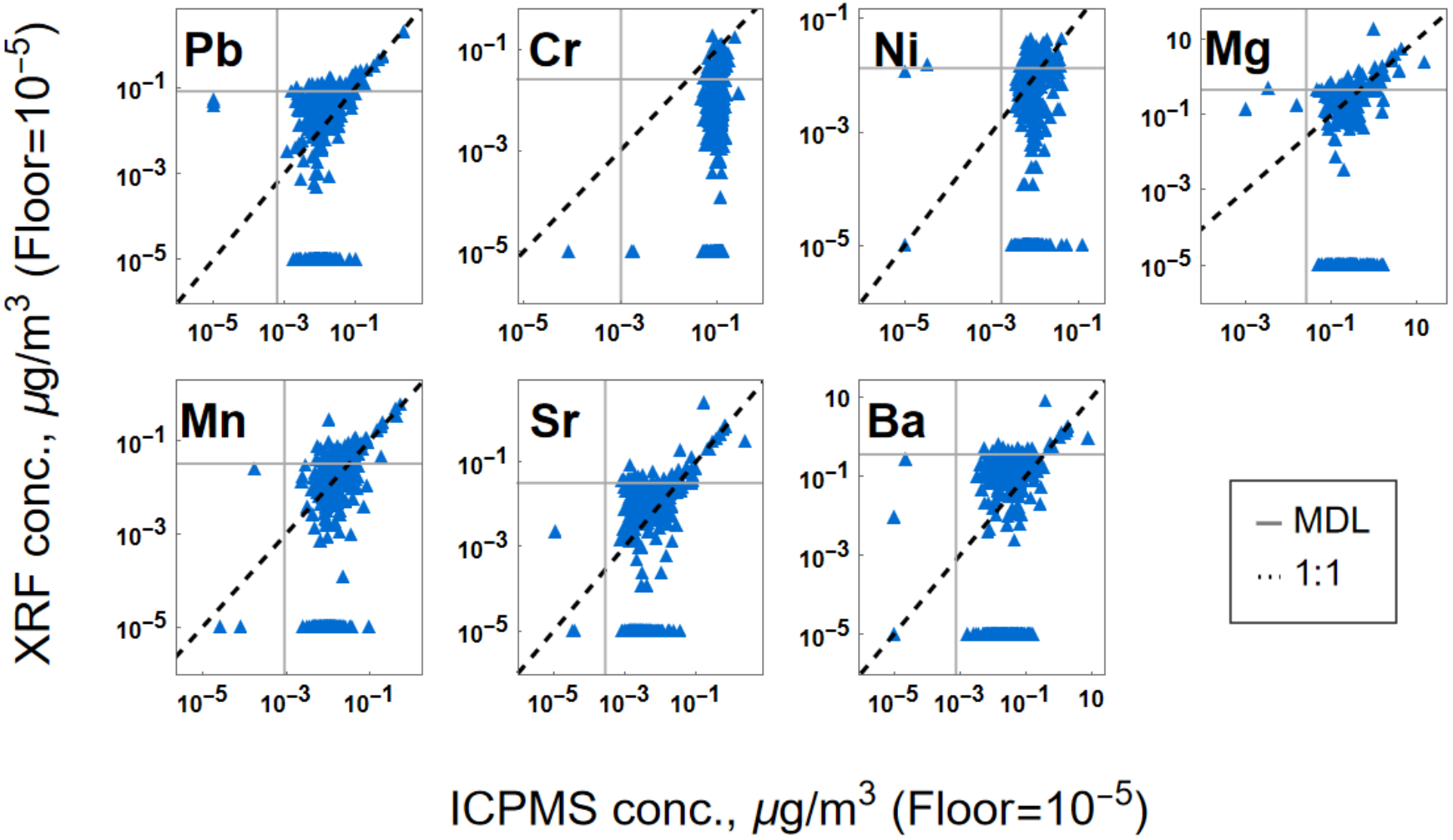
ICPMS

Inter-instrumental comparison
XRF vs ICPMS

Inter-instrumental comparison



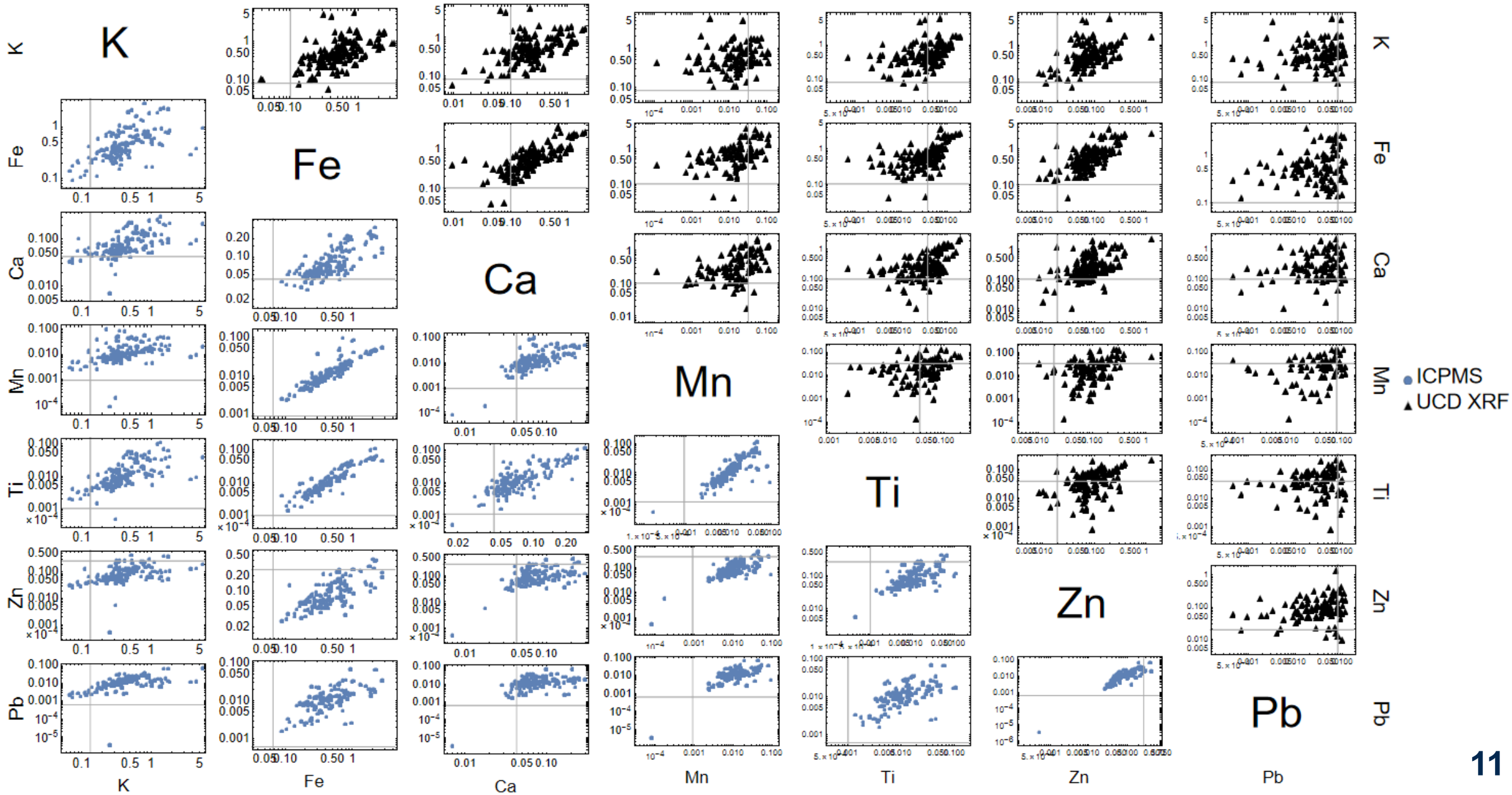
Inter-instrumental comparison



Checks for internal consistency

1. Inter-elemental plots
2. Collocated samples

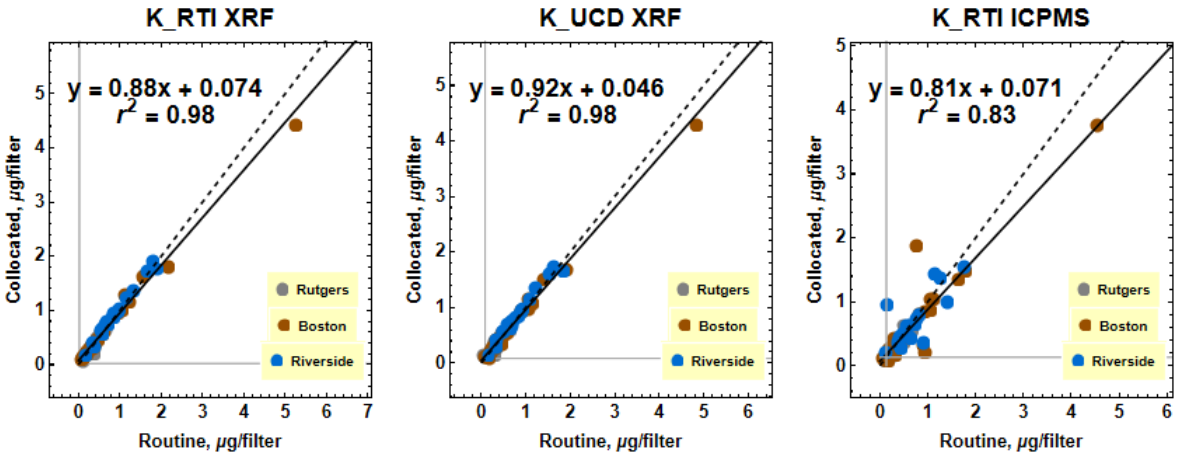
Inter-elemental correlation

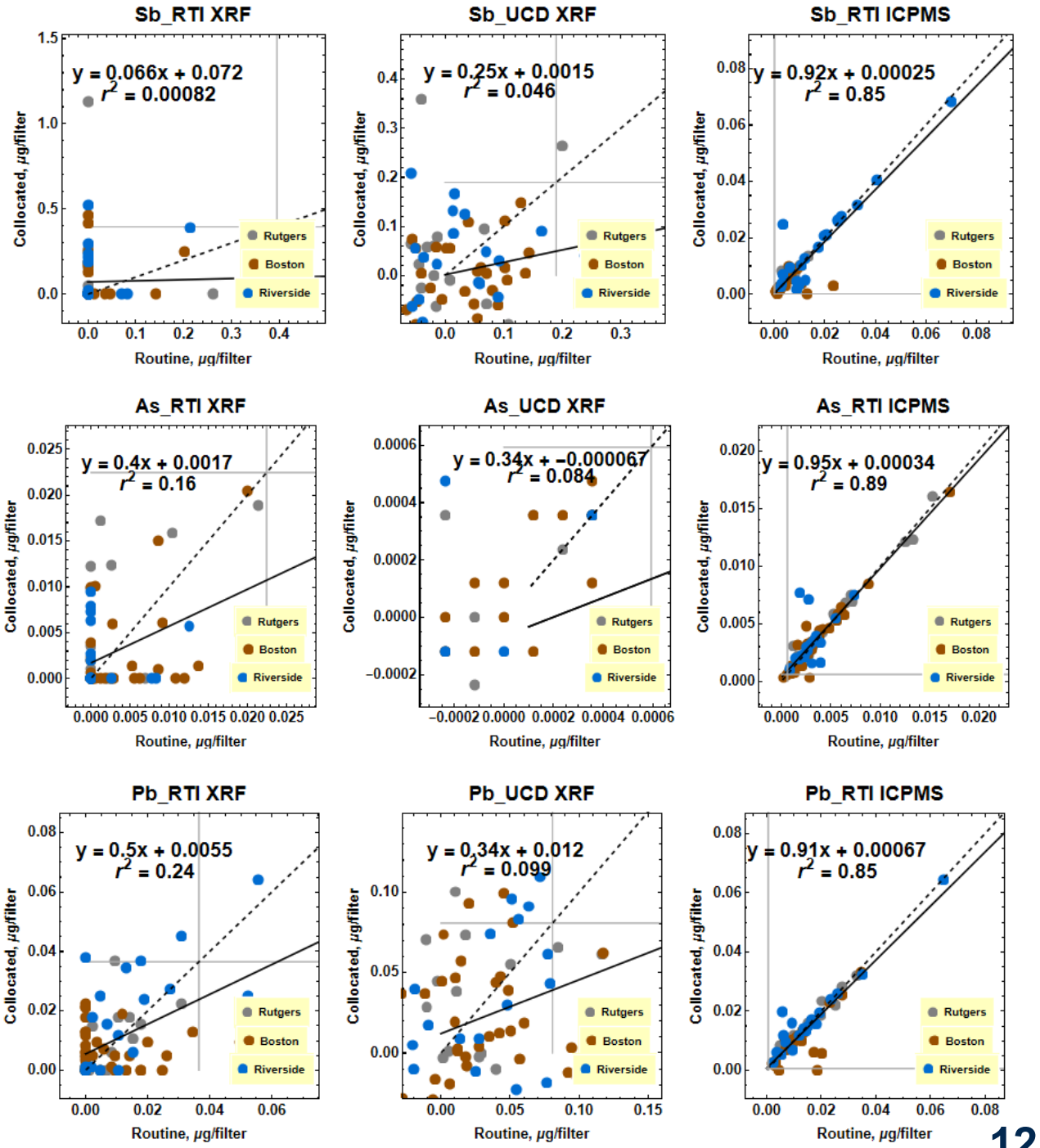


Collocated samples

— MDLs

Routine vs Collocated sampler comparisons provide benchmark for inter-instrument comparisons





Summary

- CSN Samples are too lightly loaded for XRF, most elements are below detection limits of XRF
- Inter-elemental correlations are better with ICPMS, suggesting that ICPMS is more precise than XRF
- Not all elements measured by XRF can be measured by selected ICPMS protocol
    - S, Si, Cl, Br cannot be measured via ICPMS but are well-measured via XRF

Future steps + Outstanding questions

- Statistical analysis (correlative analysis)
    - Batch 3 results recently obtained
- Reference materials to evaluate the extraction efficiency and accuracy of the measurements
    - XRF and ICPMS have no common reference materials and biases between measurements are common
- Ongoing project to concentrate CSN samples using smaller diameter filters would improve XRF detection rates

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