Advances in elemental characterization with the XRF

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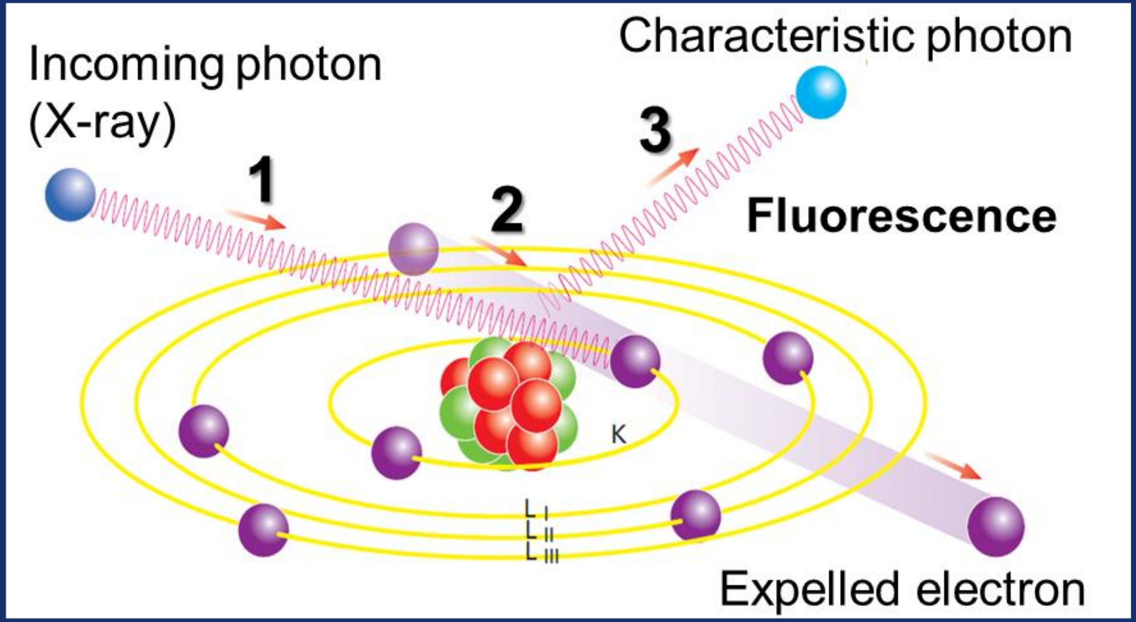
SPARTAN provides valuable information to estimate the exposure of dust and hazardous trace elements

X-ray fluorescence (XRF) is a non-destructive technique that requires no sample pretreatment

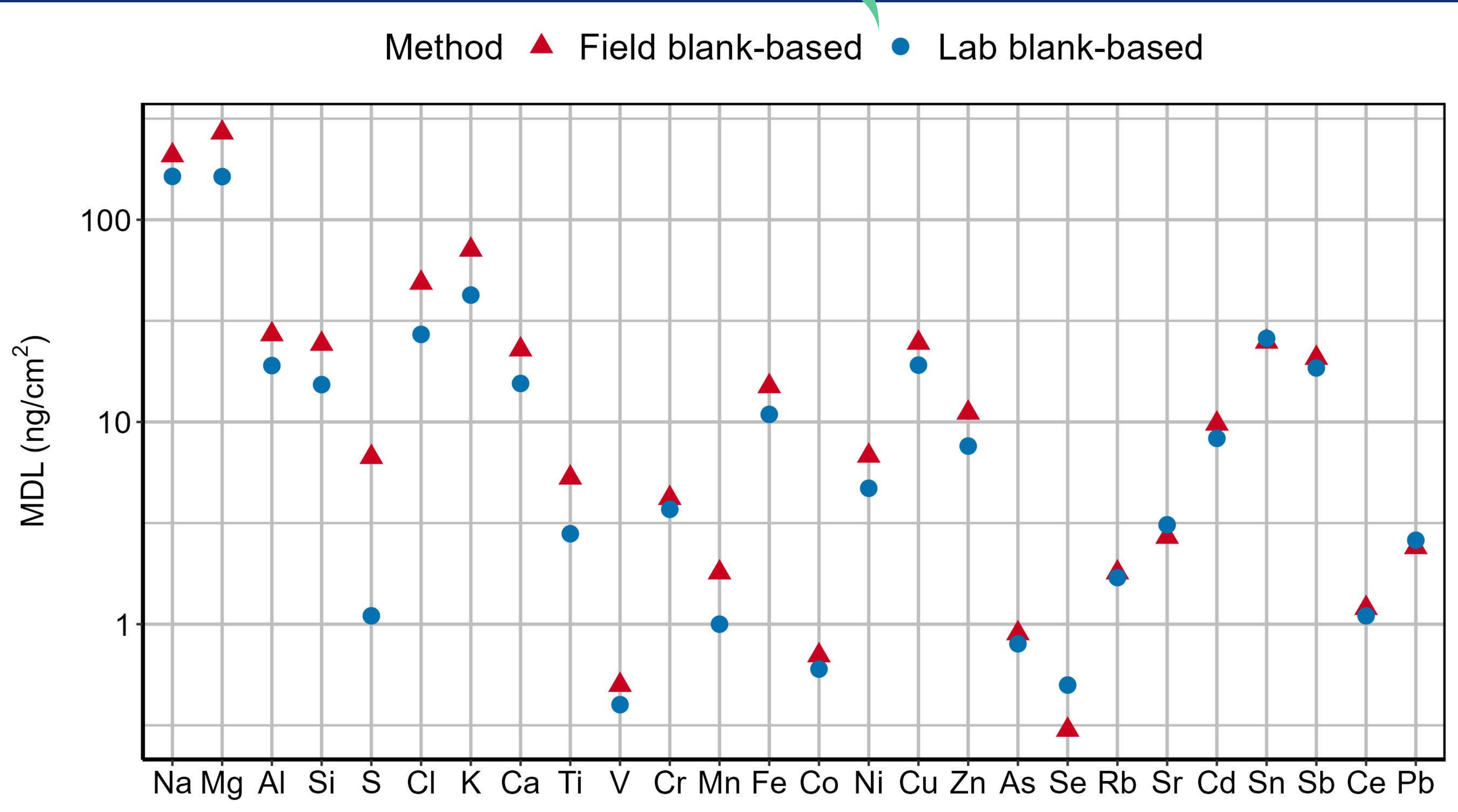
Epsilon 4 (Malvern PANalytical)



Reference materials (RMs)	Teflon filters?
Micromatter RMs	✗
NIST Standard RM	✗
UCD single compound RMs	✓
UCD multi-element RMs	✓

Method detection limit (MDL) estimates use both field and lab blanks

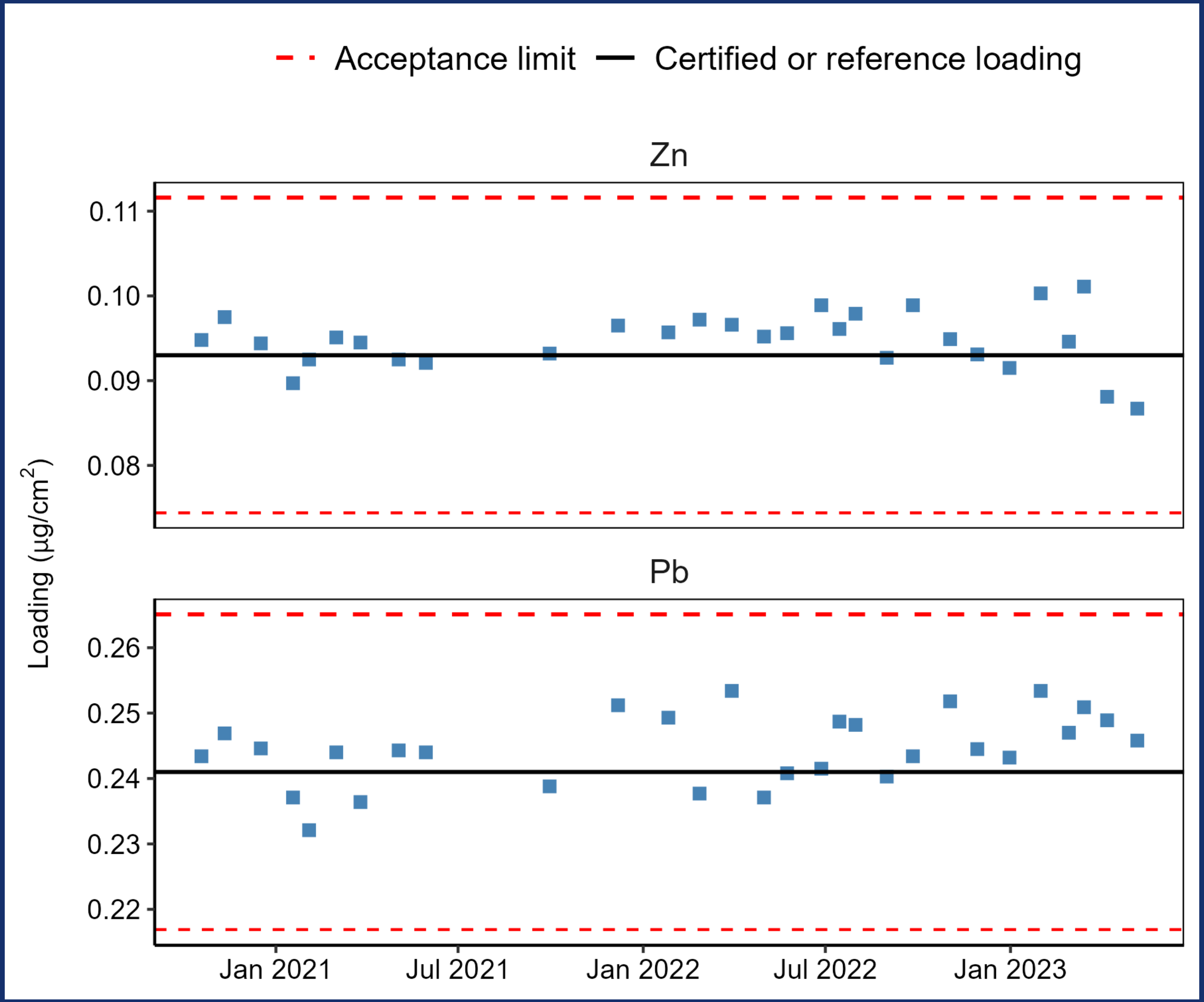
(*95%ile − median*) of 100 blanks



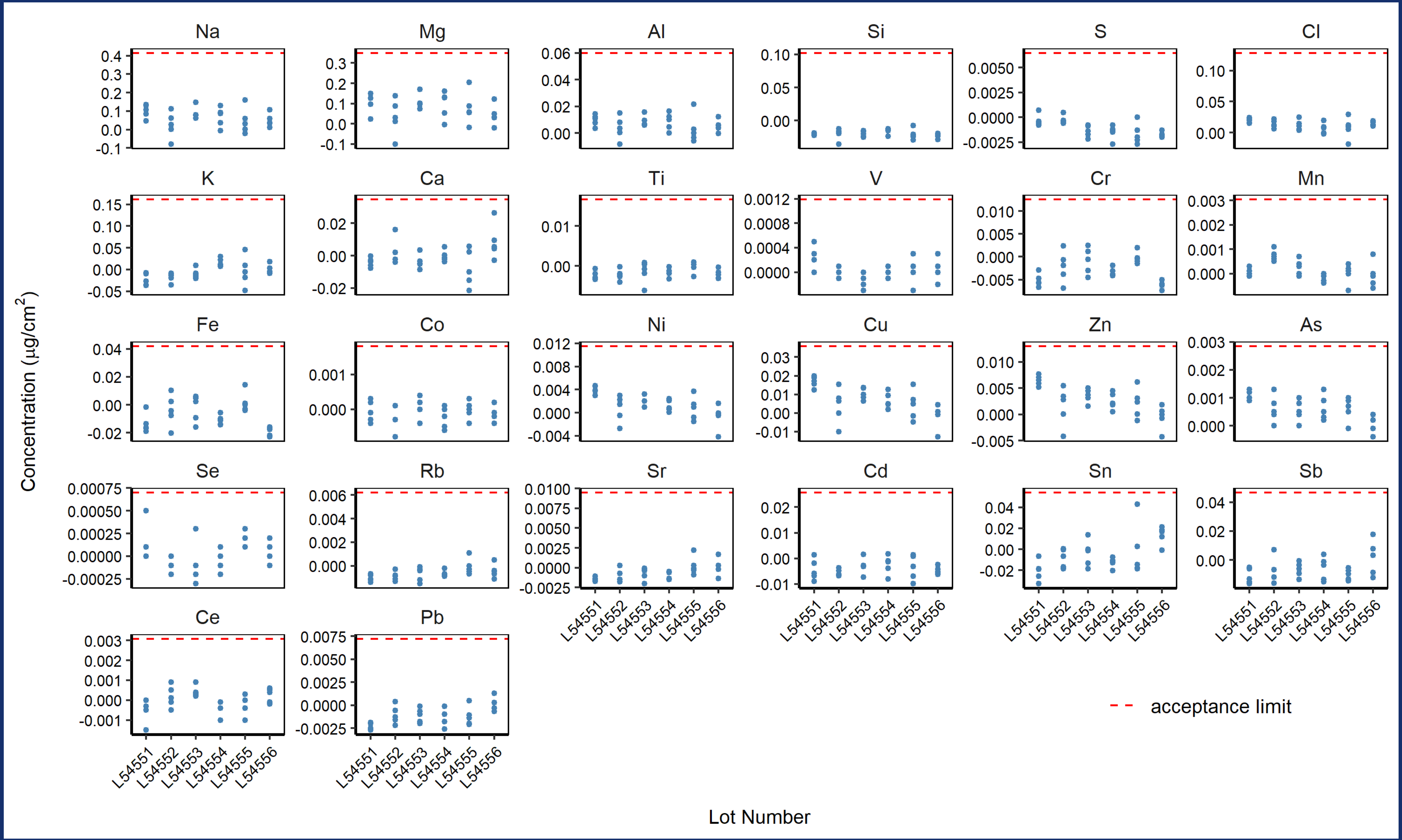
Element	MDL (ng/cm²)	% > MDL
Na	208	91
Mg	269	56
Al	27	99
Si	24	100
S	6.7	100
Cl	49	29
K	71	90
Ca	23	98
Ti	5.3	90
V	0.5	87
Cr	4.2	34
Mn	1.8	90
Fe	15	99
Co	0.7	40
Ni	6.8	16
Cu	25	14
Zn	11	81
As	0.9	85
Se	0.5	76
Rb	1.8	47
Sr	3.1	37
Cd	9.8	12
Sn	26	19
Sb	21	19
Ce	1.2	50
Pb	2.6	69

Routine quality control measures are conducted to monitor long-term stability of the instrument

Analysis	Frequency
Lab blank	Daily
UCD multi-element reference material	Monthly
NIST Standard reference material	Monthly
Representative SPARTAN samples	Monthly



Acceptance testing is performed to ensure filter quality by evaluating the contamination level of elements on new filters



Estimate uncertainty using the "bottom-up" approach

$$\sigma\ (\mathrm{ng/m^3}) = \sqrt{\left(\sigma_{additive} \times \frac{\mathrm{S}}{V}\right)^2 + \sigma_{proportion}^2 \times C^2}$$

additive uncertainty (ng/cm^2) — proportional uncertainty (%) — concentration (ng/m^3)

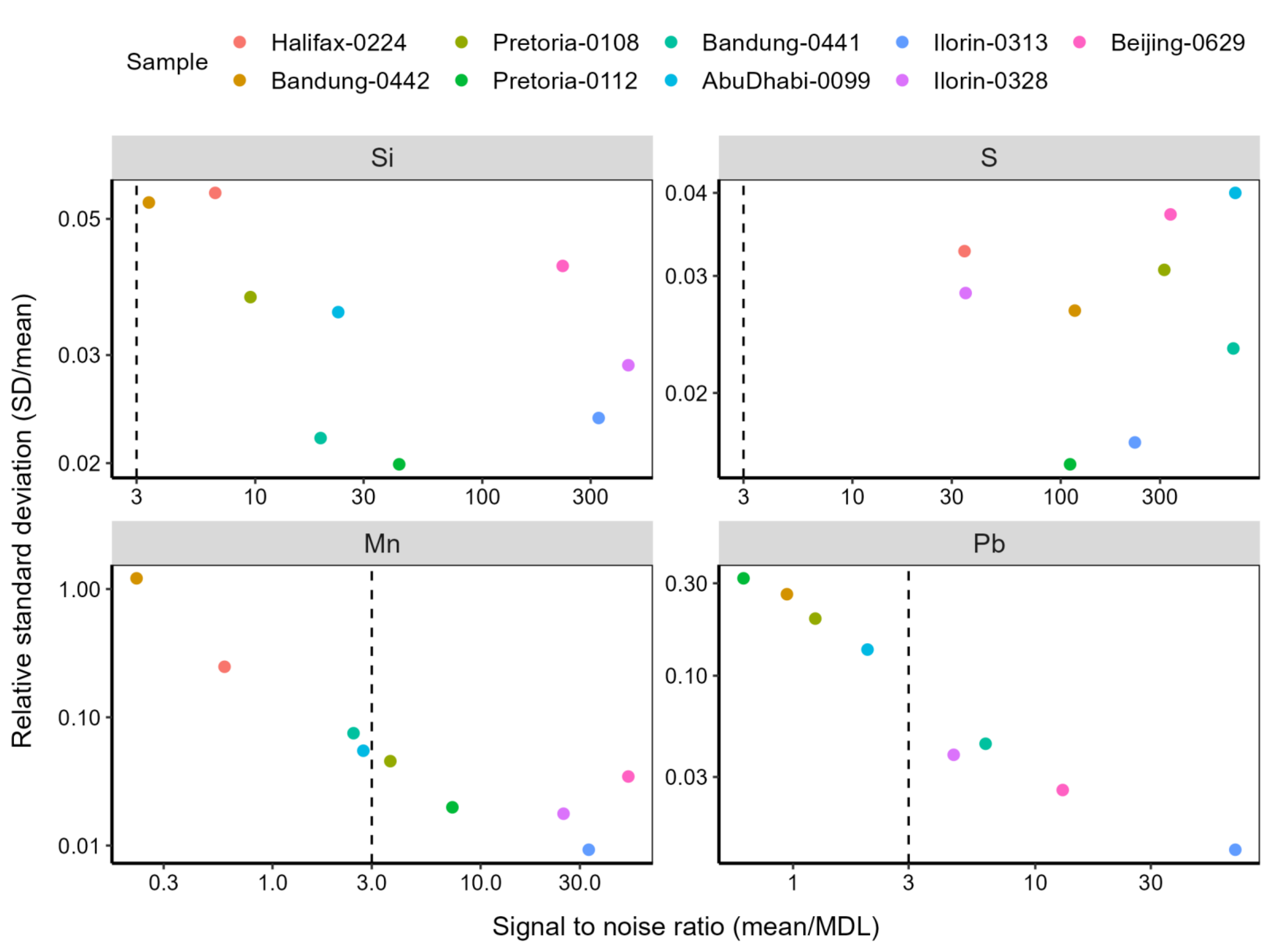
lab blanks / field blanks → additive uncertainty (ng/cm^2) —[deposit area, S (cm^2) / Volume, *V* (m^3)]→ additive uncertainty (ng/m^3)

$$\sigma_{proportion}^2 = \sigma_{mass}^2 + \sigma_{volume}^2$$

$$\sigma_{volume} = \sigma_{flow} = 3.5\%$$

re-analysis of field samples → proportional mass uncertainty (%) —[volume (flow rate)]→ total proportional uncertainty (%)

Proportional mass uncertainty is estimated as the mean of relative SD from monthly re-analysis measurements with mean > 3×MDL



Loading level	Representative samples
Low	Halifax-0224, Bandung-0442, Pretoria-0108
Moderate	Pretoria-0112, Bandung-0441, AbuDhabi-0099
High	Ilorin-0313, Ilorin-0328, Beijing-0629

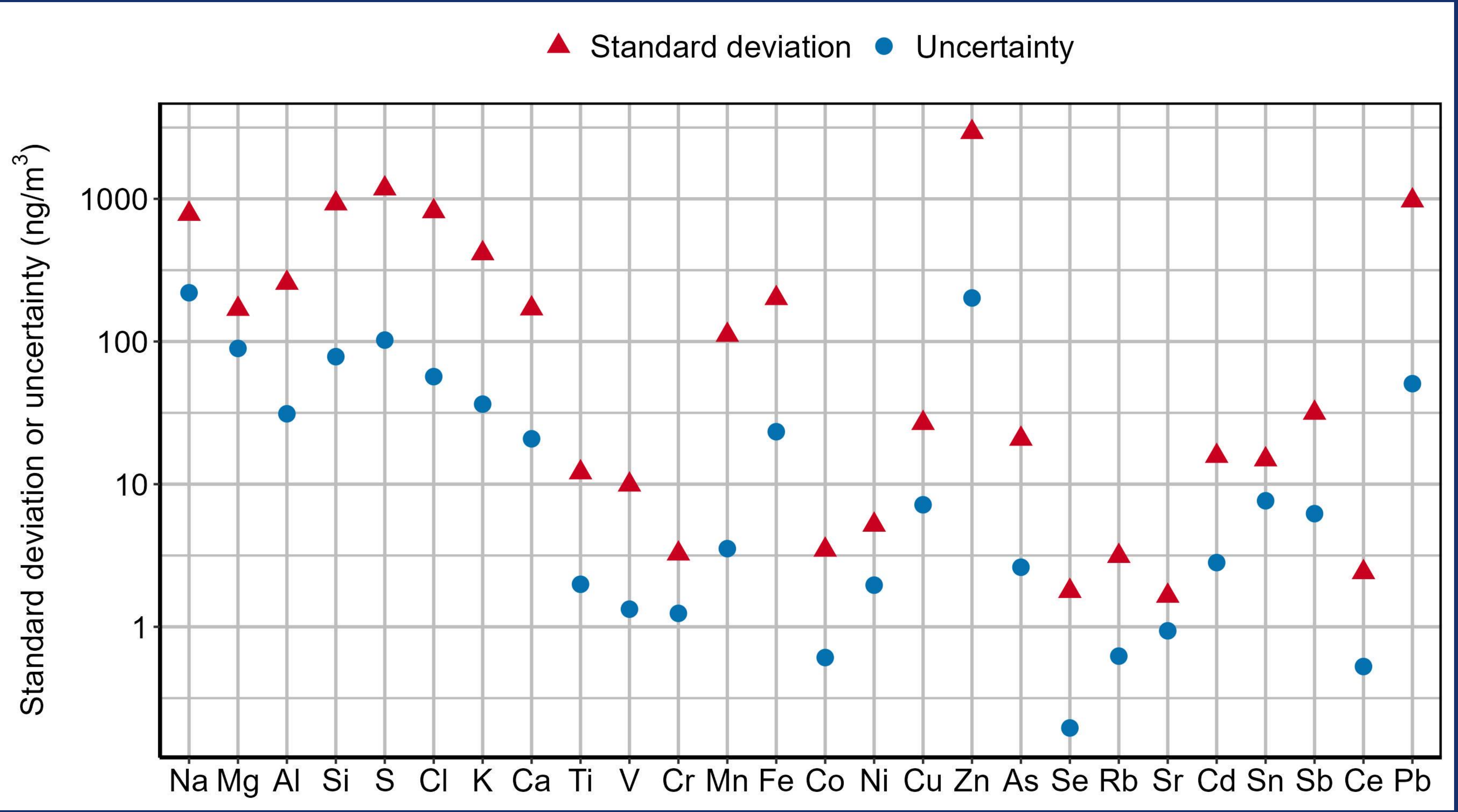
~20 measurements for each sample

Summary of uncertainty estimates

Element	# of samples with mean > 3×MDL	σ_{mass} (%)	$\sigma_{proportion}$ (%)	$\sigma_{additive}$ (ng/cm^2)
Na	8	11	12	126
Mg	3	8	9	164
Al	8	4	5	16
Si	9	4	5	15
S	9	3	4	4.1
Cl	2	6	7	30
K	7	3	5	43
Ca	7	5	6	14
Ti	5	4	5	3.2
V	6	9	9	0.3
Cr	0	–	–	2.6
Mn	5	3	4	1.1
Fe	8	5	6	9.1
Co	3	10	11	0.4
Ni	0	–	–	4.1
Cu	0	–	–	15
Zn	5	4	5	6.7
As	4	9	9	0.6
Se	1	5	6	0.3
Rb	3	5	6	1.1
Sr	2	5	6	1.9
Cd	0	–	–	5.9
Sn	0	–	–	16
Sb	0	–	–	13
Ce	3	10	11	0.7
Pb	4	3	5	1.6

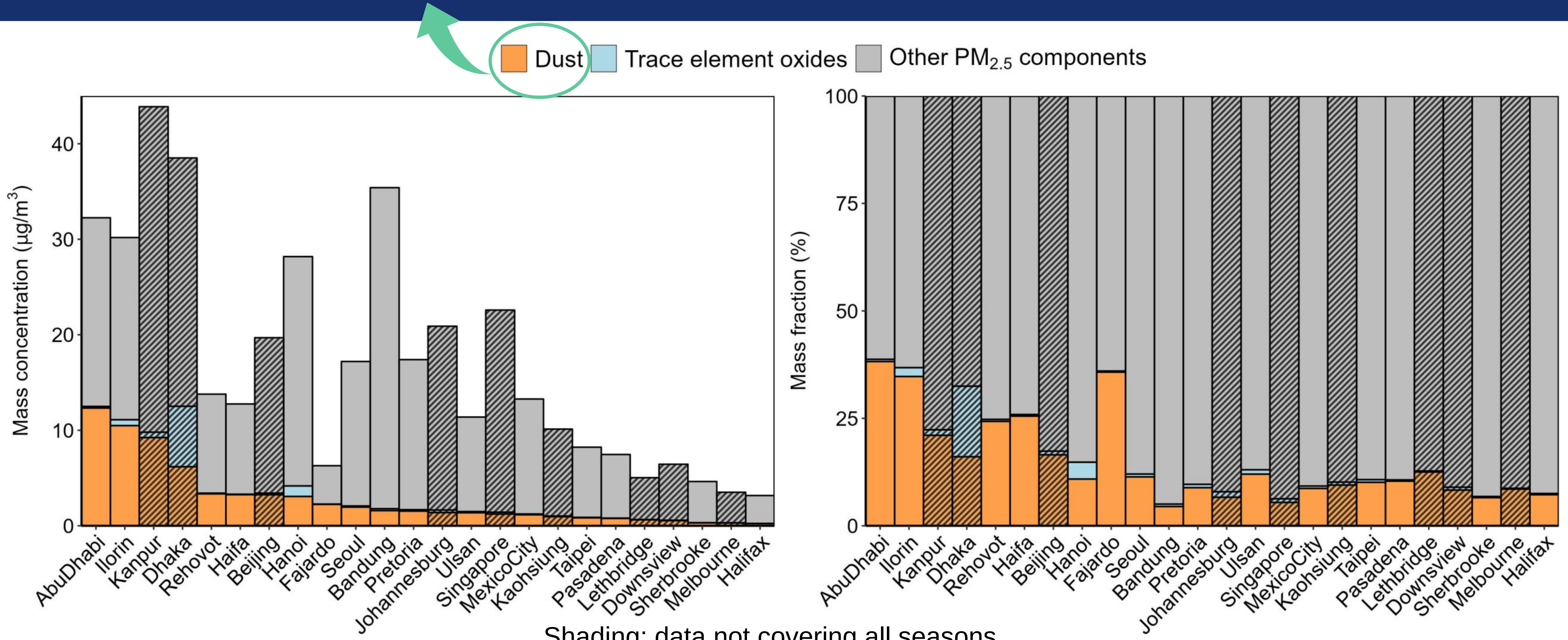
The measurement uncertainty is significantly lower than the SD of samples for most elements

Dhaka, Bangladesh



The consistent methodology and global dust equation enable us to estimate and compare dust and trace element oxides globally

Global dust equation (*Liu, Turner, Hand, Schichtel, & Martin, JGR, 2022*)



Shading: data not covering all seasons

A global dust equation with region-specific coefficients

Global equation: Dust = [1.89Al×(1+MAL)+2.14Si+1.40Ca+1.36Fe+1.67Ti]×CF

MAL: mineral-to-aluminum ratio

CF: correction factor

Type	Region	Regional MAL	Regional CF
source region	Crust	0.62	1.02
	Middle East	0.72	1.14
	Sahara	0.69	1.14
	Sahel	0.27	1.05
	Australia	0.24	1.05
	East Asia	0.59	1.11
	Southwest US	0.66	1.14
non-source region	South Europe & the Atlantic islands	0.48	1.10
	Korea & Japan	0.59	1.04

Anthropogenic Dust Type	MAL	CF
Paved road	0.62	1.12
Unpaved road	0.62	1.12
Agricultural soil	0.31	1.02

Summary

Measures are conducted to ensure data quality for elemental analysis of the SPARTAN network

Measurement uncertainty is generally significantly lower than standard deviation

This elemental dataset can help us estimate the level of dust and trace elements and examine their health impacts and emission sources globally

Washington University in St. Louis
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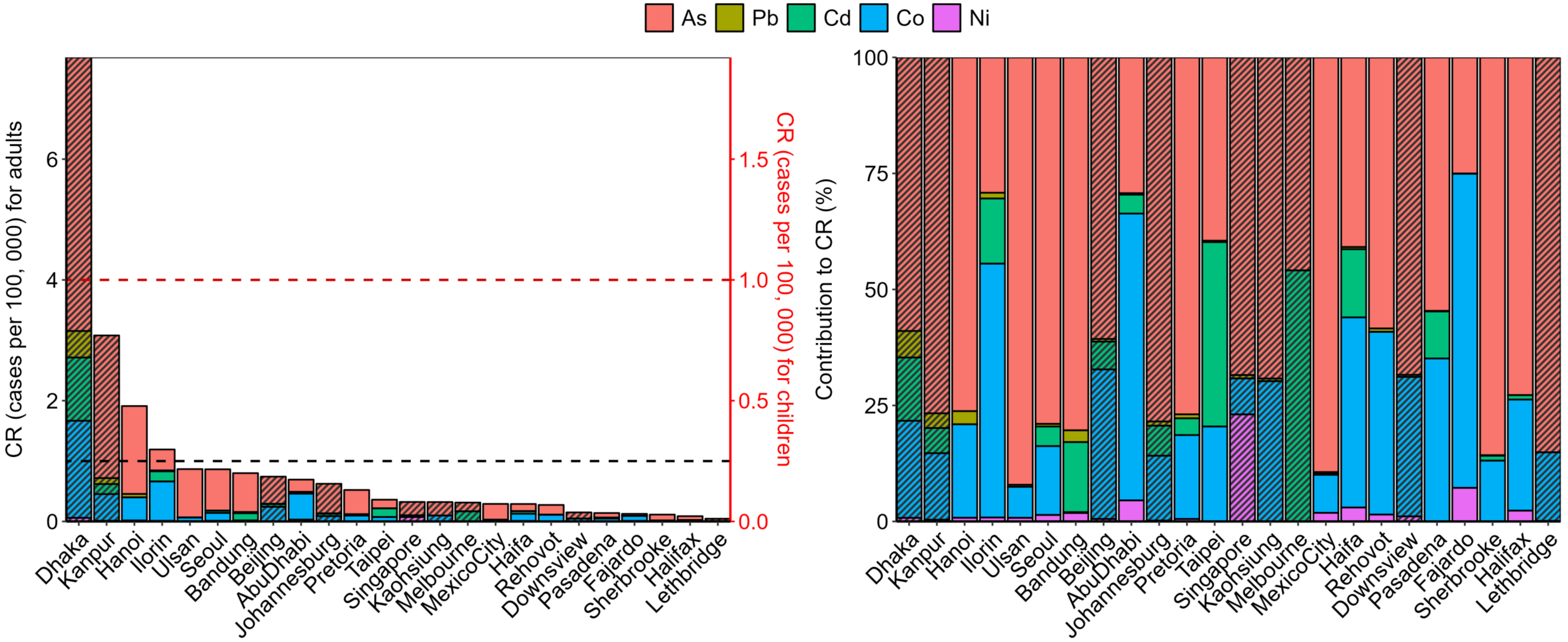
SPARTAN

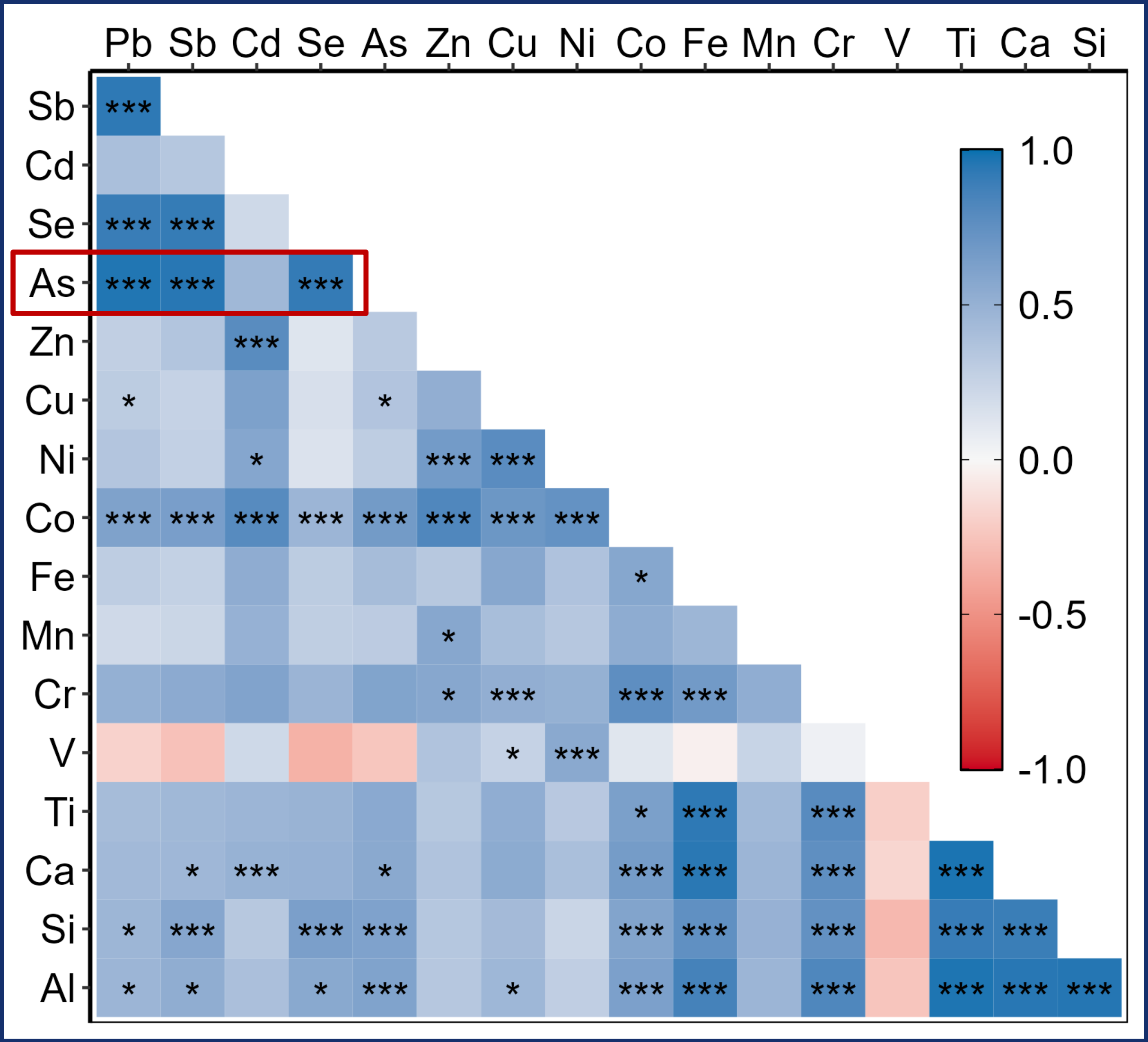
The consistent methodology enables us to assess and compare health risks caused by exposure to toxic trace elements globally

Carcinogenic risk (CR) = Exposure concentration × Inhalation unit risk



High level of As in $PM_{2.5}$ at Dhaka may mainly come from anthropogenic sources

Principal component analysis (PCA) for Dhaka (11/6/2019 - 8/18/2021)



Element	PC1	PC2	PC3	PC4
Pb	0.16	0.97	0.09	0.06
Sb	0.22	0.97	0.05	0.00
Cd	0.29	0.13	0.79	-0.05
Se	0.22	0.97	-0.02	0.00
As	0.23	0.96	0.10	0.06
Zn	0.15	-0.02	0.90	0.31
Cu	0.30	0.39	0.05	0.72
Ni	0.04	0.26	0.52	0.76
Co	0.36	0.52	0.69	0.30
Fe	0.94	0.00	0.15	0.20
Mn	0.20	-0.14	0.41	0.31
Cr	0.74	0.20	0.20	0.41
V	-0.18	-0.27	0.16	0.90
Ti	0.96	0.17	0.13	-0.03
Ca	0.89	0.24	0.27	-0.04
Si	0.79	0.41	0.23	-0.20
Al	0.92	0.34	0.16	0.05

PC1: dust
PC2: coal combustion, battery recycling
PC3: traffic
PC4: shipping

Health risk assessment

US EPA health risk assessment model

Exposure concentration (EC)

$$\mathrm{EC} = C \times \frac{ET \times EF \times ED}{AT}$$

Carcinogenic risk (CR)

$$\mathrm{CR} = \mathrm{EC} \times IUR$$

Non-carcinogenic risk: Hazard quotient (HQ)

$$\mathrm{HQ} = \mathrm{EC}/RfC$$

Hazard index (HI)

$$\mathrm{HI} = \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{HQ_i}$$

Parameter	Definition	Unit	Assumption
ET	exposure time	hours/day	24
EF	exposure frequency	days/year	350
ED	exposure duration	years	6 (children); 24 (adults)
AT	averaging time	hours	70×365×24 (carcinogens); ED×365×24 (non-carcinogens)
IUR	inhalation unit risk	$(\mu g/m^3)^{-1}$	
RfC	Chronic inhalation reference conc.	$\mu g/m^3$	

Develop a global dust equation with region-specific coefficients

IMPROVE equation: Dust = [1.89Al+2.14Si+1.40Ca+(1.36+**0.6**×1.20)Fe+1.67Ti]×**1.16**

Global equation: Dust = [1.89Al×(1+MAL)+2.14Si+1.40Ca+1.36Fe+1.67Ti]×CF

MAL → mineral-to-aluminum ratio

CF → correction factor

$$MAL = (K_2O+MgO+Na_2O)/Al_2O_3 = (1.21K/Al+1.66Mg/Al+1.35Na/Al)/1.89$$

Only use dust component (1.21K/Al+1.66Mg/Al+1.35Na/Al)

$$CF = \frac{100\ wt\%}{100\ wt\% - [1\ wt\% + CO_2(wt\%)]} \times WAF$$

1 wt% → $MnO+P_2O_5$+crystal H_2O

WAF → Water Adjustment Factor (for adsorbed water)

CO_2 (wt%) →

$$CO_2\ (total) = CO_2\ (CaCO_3)_{HWSD/USGS} \times \left[\frac{CO_2\ (total)}{CO_2\ (CaCO_3)}\right]_{literature}$$

HWSD: Harmonized World Soil Database
USGS: U.S. Geological Survey