



Supplement of

Xact625i vs. PX-375: a comparative study of online XRF ambient multi-metal monitors vs. ICP-MS

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Flow rate checks

Flow rate checks on the Xact625i and PX-375 were performed using a Gilibrator 2 air flow calibrator (Sensidyne, USA) once per month. When the flow rates varied by over 1% compared to the reference flow meter, a flow calibration was carried out. Average variation in flow rates over the campaign for both instruments was <1%.

Table S1. Overview of technical specifications for the two ED-XRF instruments.

Spec	Xact 625i (Cooper Environmental)	PX-375 (Horiba)
X-ray source	Rh anode tube, max 50 kV / 50 W	W tube (vacuum, Be window), 15 / 50 kV auto switch
Primary filters	3 (Al, Pd, Cu)	2 (none, Mo)
Detector	Silicon Drift Detector (SDD, ED-XRF)	Silicon Drift Detector (SDD, ED-XRF)
Sampling	Teflon filter tape, 16.7 L/min	PTFE filter tape, 16.7 L/min, β -ray attenuation + XRF, CMOS spot imaging
Elements measured	Up to 40+ (Al–Bi, configurable)	16 standard (Al–Cd), 25+ with extended calibration
Time resolution	15 min – 4 h selectable, analysis time identical to sampling time	0.5 – 24 h selectable (500–10000 s analysis time selectable)
Calibration / QA	Calibration with SRMs; Internal reference checked each sample; daily auto-drift	Factory calibration with SRM
Power	~2 kW, 120/220 VAC	~400 W, 100–240 VAC
Size / Weight	~48×51×76 cm / ~83 kg	~43×55×29 cm / ~40 kg
Distinguishing	Wide element coverage, EPA-validated	Dual PM mass + metals, compact, low power, CMOS dust-spot imaging

Table S2. XRF calibration check using the Xact625i single-element calibration standards. The XRF tests were carried out before, during, and after the campaign.

Elements	Analysis time (s)	Concentration (ng/m³)				
		Reference	measured (n = 3)			
			mean	std	Recovery rate	Relative Error
Al	4400	62143	61677	130.83	99.25%	-0.75%
Si	2700	50375	49728	133.45	98.72%	-1.28%
S	1200	17665	17337	91.80	98.14%	-1.86%
K	300	28098	27930	53.57	99.40%	-0.60%
Ca	120	30785	30414	182.13	98.79%	-1.21%
Ti	60	65171	64851	225.66	99.51%	-0.49%
V	60	61356	61015	100.11	99.44%	-0.56%
Cr	60	69430	69020	93.73	99.41%	-0.59%
Mn	60	62822	62104	412.49	98.86%	-1.14%
Fe	60	56768	56510	55.29	99.55%	-0.45%
Ni	70	53038	52418	135.37	98.83%	-1.17%
Cu	70	56612	56337	61.03	99.51%	-0.49%
Zn	120	19544	19400	9.49	99.26%	-0.74%
As	70	38473	37803	82.18	98.26%	-1.74%
Cd	2700	36632	36505	10.70	99.65%	-0.35%
Pb	70	62029	61385	216.13	98.96%	-1.04%

Table S3. XRF calibration check using the SRM2783 multi-element calibration standard (*cadmium single-element standard tested separately). The XRF tests were carried out before, during, and after the campaign.

Elements	Concentration (ng/m ³ , *ug/cm ²)				
	Reference	Analysis time = 500 s, measured (n = 3)		Recovery rate	Relative Error
		mean	std		
Al	2064.52	2142.18	134.16	104%	4%
Si	5395.52	5405.92	245.59	100%	0%
S	113.51	99.56	13.85	88%	-12%
K	490.33	495.41	10.60	101%	1%
Ca	1288.58	1282.07	17.93	99%	-1%
Ti	144.71	138.78	3.25	96%	-4%
V	5.43	5.21	1.29	96%	-4%
Cr	17.31	15.14	3.89	87%	-13%
Mn	27.55	30.97	1.42	112%	12%
Fe	2548.63	2530.52	4.51	99%	-1%
Ni	6.00	5.13	1.30	85%	-15%
Cu	43.57	32.85	6.54	75%	-25%
Zn	173.36	168.62	4.79	97%	-3%
As	1.10	0.84	0.31	76%	-24%
Cd*	11.20	10.87	0.15	97%	-3%
Pb	35.21	35.02	4.44	99%	-1%

Table S4. Repeat blank tape measurements for both instruments with concentrations in ng/m³. Analysis times were 120 min for the Xact625i and 500 s for the PX-375 to harmonise with field measurements.

Element	Xact625i (n = 6)			PX-375 (n = 10)		
	Mean	Mean unc	std	Mean	Mean unc	std
Al	24.48	60.54	75.14			
Si				1.15	0.05	1.44
S	0.54	1.42	2.23			
K				3.46	0.17	3.82
Ca				9.95	0.49	5.43
Ti	0.030	0.162	0.064	0.356	0.018	0.858
V	0.010	0.063	0.041			
Cr				0.303	0.015	0.232
Mn				0.019	0.001	0.053
Fe						
Ni				0.010	0.001	0.028
Cu						
Zn						
As	0.001	0.006	0.006			
Cd	0.174	0.573	1.166	1.885	0.094	2.339
Pb				0.018	0.001	0.042

Table S5. Instrumental Limit of Detections (LoDs) in ng/m³. For the PX-375: * 3 σ averages from literature values, ** 3 σ field blank measurements, and *** 2 σ manufacturer values.

Element	Xact625i (1 σ) interference-free LoD (doubled from manufacturer values)	PX-375 (mixed)
Al	122.57	40.10*
Si	21.72	4.32**
S	3.85	6.60***
K	1.43	11.46**
Ca	0.36	16.29**
Ti	0.19	5.00***
V	0.15	0.42*
Cr	0.14	0.50***
Mn	0.17	2.20***
Fe	0.21	2.49*
Ni	0.12	0.57*
Cu	0.1	0.93*
Zn	0.08	1.06*
As	0.08	2.01*
Pb	0.16	2.40***
Cd	3.08	10.40***

Table S6. Final data coverage after data treatment procedure. Starred elements omitted from analysis due to low coverage.

Element	Sample coverage (n samples)	
	PX-375	Xact625i
Al	1294 (68.6%)	189 (10.0%)
Si	1787 (94.6%)	1111 (58.9%)
S	1800 (95.3%)	1800 (95.3%)
K	1722 (91.2%)	1793 (94.9%)
Mn	1775 (94.0%)	1783 (94.4%)
Fe	888 (47.0%)	1780 (94.3%)
Ca	238 (12.6%)	405 (21.5%)
Ti	423 (22.4%)	595 (31.5%)
V	1025 (54.3%)	1515 (80.2%)
Cr	1751 (92.7%)	1787 (94.7%)
Zn	1764 (93.4%)	1747 (92.5%)
Pb	722 (38.3%)	890 (47.1%)
As*	3 (0.2%)	96 (5.1%)
Cu*	40 (2.1%)	1526 (80.9%)
Ni*	43 (2.3%)	18 (1.0%)
Cd*	18 (1.0%)	2 (0.1%)

Table S7. Descriptive data from campaign measurements of the 43 daily averaged samples with concentrations in ng/m³.

Element	Median concentration across field measurements (+/- uncertainty)		
	PX-375	Xact625i	ICP-MS
Al	272.08 (+/-) 40.11	63.81 (+/-) 416.21	134.83 (+/-) 21.98
Si	480.01 (+/-) 61.61	343.76 (+/-) 692.47	261.18 (+/-) 44.36
S	715.92 (+/-) 119.22	417.41 (+/-) 7.76	448.49 (+/-) 16.42
K	64.71 (+/-) 7.76	87.87 (+/-) 3.46	94.80 (+/-) 13.31
Ca	107.42 (+/-) 13.67	121.21 (+/-) 4.87	142.26 (+/-) 30.63
Ti	8.54 (+/-) 1.48	11.73 (+/-) 1.14	5.62 (+/-) 0.78
V	0.20 (+/-) 0.05	0.19 (+/-) 1.25	0.30 (+/-) 0.05
Cr	0.62 (+/-) 0.14	0.23 (+/-) 1.91	0.34 (+/-) 0.05
Mn	2.52 (+/-) 0.55	2.63 (+/-) 0.74	3.90 (+/-) 0.44
Fe	111.33 (+/-) 14.58	125.68 (+/-) 4.71	143.05 (+/-) 22.73
Zn	5.87 (+/-) 0.68	5.51 (+/-) 0.31	6.33 (+/-) 1.32
Pb	1.22 (+/-) 0.18	0.63 (+/-) 0.82	1.37 (+/-) 0.14
As*		0.79 (+/-) 0.17	0.40 (+/-) 0.06
Cu*		0.87 (+/-) 0.21	1.85 (+/-) 0.38
Total	1772	1182	1245

**Starred samples omitted due to too many samples <LoD for the PX-375 for As and Cu.*

Table S8. Deming regression results and Pearson correlation coefficients for ED-XRF vs ICP-MS i) forced through origin and ii) with intercept. Uncertainties ($\pm$) represent one standard error from 2000 bootstrap resamples; 95% confidence intervals $\approx$ estimate $\pm 1.96 \times$ SE.

Element	ED-XRF vs ICP-MS (Deming, forced through origin)		PX-375 vs ICP-MS (Deming with intercept)		Xact625i vs ICP-MS (Deming with intercept)		N samples
	PX375 slope (0,0)	Xact625i slope (0,0)	Slope	Intercept	Slope	Intercept	
Al	2.19 $\pm$ 0.14	0.38 $\pm$ 0.10	2.2 $\pm$ 0.46	-0.95 $\pm$ 26.73	0.26 $\pm$ 0.56	-2.55 $\pm$ 53.84	189
Si	1.89 $\pm$ 0.17	1.31 $\pm$ 0.08	1.89 $\pm$ 0.39	0.34 $\pm$ 34.95	1.53 $\pm$ 0.17	-45.52 $\pm$ 13.15	1111
S	1.57 $\pm$ 0.02	0.93 $\pm$ 0.01	1.67 $\pm$ 0.08	-33.22 $\pm$ 23.81	0.98 $\pm$ 0.04	-15.54 $\pm$ 13.05	1800
K	0.58 $\pm$ 0.03	0.93 $\pm$ 0.04	0.81 $\pm$ 0.15	-15.61 $\pm$ 9.35	1.17 $\pm$ 0.23	-18.75 $\pm$ 15.58	1722
Ca	0.76 $\pm$ 0.04	0.86 $\pm$ 0.02	0.69 $\pm$ 0.1	5.83 $\pm$ 6.21	0.93 $\pm$ 0.08	-5.4 $\pm$ 7.31	1775
Ti	0.86 $\pm$ 0.21	2.22 $\pm$ 0.11	0.93 $\pm$ 0.51	-0.13 $\pm$ 0.51	2.18 $\pm$ 0.32	0.13 $\pm$ 0.43	888
V	0.35 $\pm$ 0.06	0.63 $\pm$ 0.08	0.54 $\pm$ 0.12	-0.02 $\pm$ 0.01	0.84 $\pm$ 0.2	-0.08 $\pm$ 0.04	238
Cr	1.42 $\pm$ 0.16	0.56 $\pm$ 0.05	1.03 $\pm$ 0.25	0.12 $\pm$ 0.08	0.56 $\pm$ 0.1	-0.0 $\pm$ 0.02	423
Mn	0.52 $\pm$ 0.03	0.69 $\pm$ 0.03	0.6 $\pm$ 0.09	-0.19 $\pm$ 0.21	0.82 $\pm$ 0.12	-0.52 $\pm$ 0.27	1025
Fe	0.70 $\pm$ 0.04	0.90 $\pm$ 0.02	0.75 $\pm$ 0.11	-2.89 $\pm$ 3.97	0.93 $\pm$ 0.06	-2.07 $\pm$ 2.23	1751
Zn	0.89 $\pm$ 0.03	0.85 $\pm$ 0.02	1.0 $\pm$ 0.12	-0.5 $\pm$ 0.52	1.03 $\pm$ 0.07	-0.91 $\pm$ 0.41	1747
Pb	0.55 $\pm$ 0.06	0.42 $\pm$ 0.05	0.91 $\pm$ 0.19	-0.26 $\pm$ 0.15	0.73 $\pm$ 0.09	-0.37 $\pm$ 0.08	722
As*		1.85 $\pm$ 0.12			1.39 $\pm$ 0.14	0.23 $\pm$ 0.05	31
Cu**		0.53 $\pm$ 0.06			0.53 $\pm$ 0.16	0 $\pm$ 0.21	197
Ni*							18
Cd*							17
Average***	1.02 $\pm$ 0.11	0.89 $\pm$ 0.12	1.03 $\pm$ 0.24		0.95 $\pm$ 0.13		

*Omitted due to an excessive number of samples below LoD. **A number of outliers skew Cu results for the Xact625i; with 10 outliers removed, a slope of 0.5 and an r^2 value of 0.76 remains.

***Excluding Cu for the Xact625i.

Table S9. Deming regression results and Pearson correlation coefficients for ED-XRF vs ED-XRF using i) 2-hour data and ii) 24-hour averages. Uncertainties ($\pm$) represent one standard error from 2000 bootstrap resamples; 95% confidence intervals $\approx$ estimate $\pm 1.96 \times$ SE.

Element	Xact625i vs PX-375 (2-hour data)			Xact625i vs PX-375 (24-hour averages)		
	Slope	r ²	N samples	Slope	r ²	N samples
Al	1.09 $\pm$ 0.19	0.96	189	1.42 $\pm$ 0.4	0.47	58
Si	1.26 $\pm$ 0.16	0.96	1111	0.93 $\pm$ 0.12	0.84	143
S	0.59 $\pm$ 0.01	0.99	1800	0.60 $\pm$ 0.01	0.99	174
K	1.64 $\pm$ 0.13	0.97	1722	1.32 $\pm$ 0.11	0.89	174
Ca	1.15 $\pm$ 0.08	0.9	1775	0.86 $\pm$ 0.15	0.70	173
Ti	1.59 $\pm$ 0.13	0.98	888	1.05 $\pm$ 0.27	0.69	146
V	1.34 $\pm$ 0.16	0.98	238	0.66 $\pm$ 0.22	0.45	72
Cr	0.65 $\pm$ 0.1	0.94	423	0.34 $\pm$ 0.05	0.24	99
Mn	1.63 $\pm$ 0.12	0.98	1025	1.06 $\pm$ 0.26	0.35	165
Fe	1.37 $\pm$ 0.15	0.98	1751	1.14 $\pm$ 0.17	0.79	174
Zn	0.99 $\pm$ 0.05	0.88	1747	0.80 $\pm$ 0.12	0.90	174
Pb	0.65 $\pm$ 0.03	0.83	722	0.98 $\pm$ 0.06	0.74	134
Average	1.16 $\pm$ 0.11	0.95		0.93 $\pm$ 0.16	0.67	

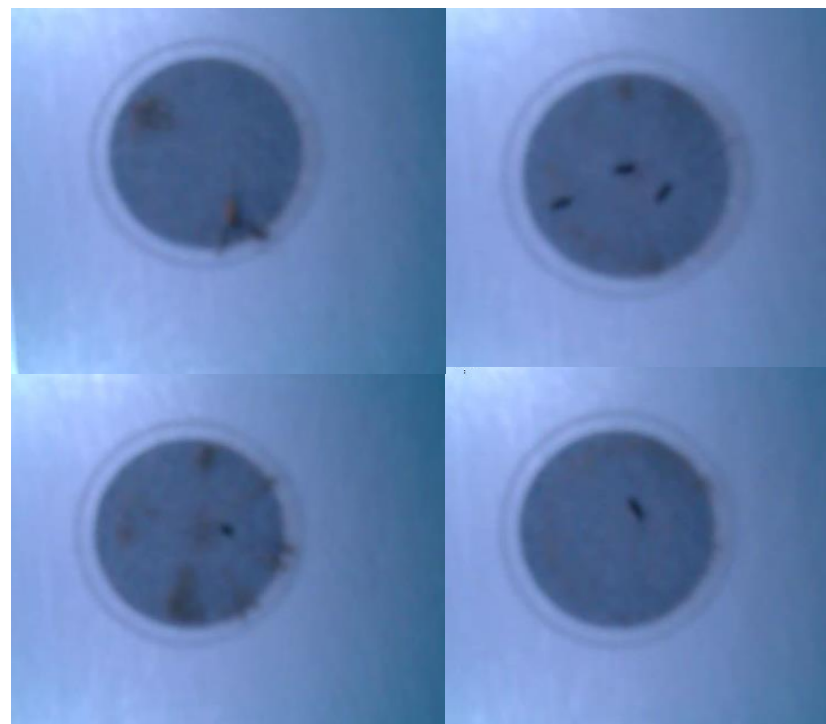


Figure S1. Insect and other debris in the sampling spot of the PX-375 in samples flagged as outliers due to high concentrations of crustal elements.

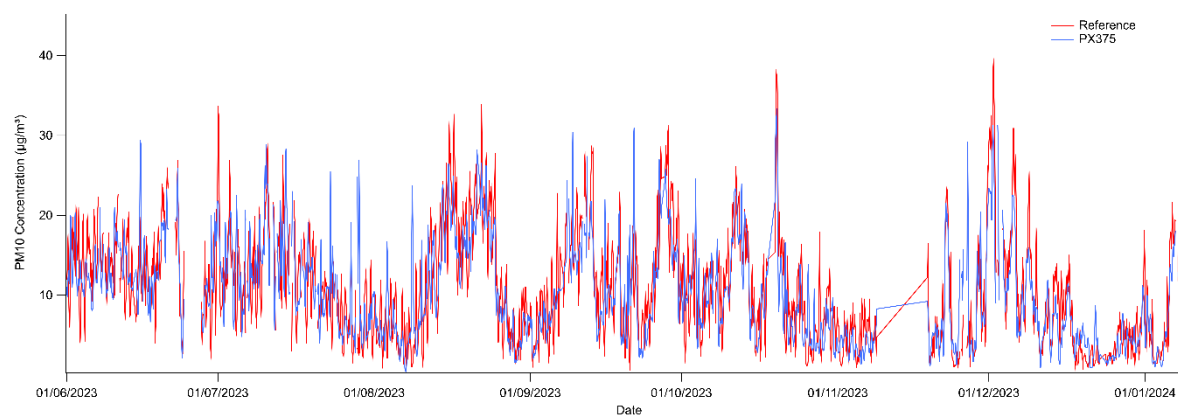


Figure S2. PM₁₀ two-hour time series for reference and PX-375 in-built gravimetric analyses.

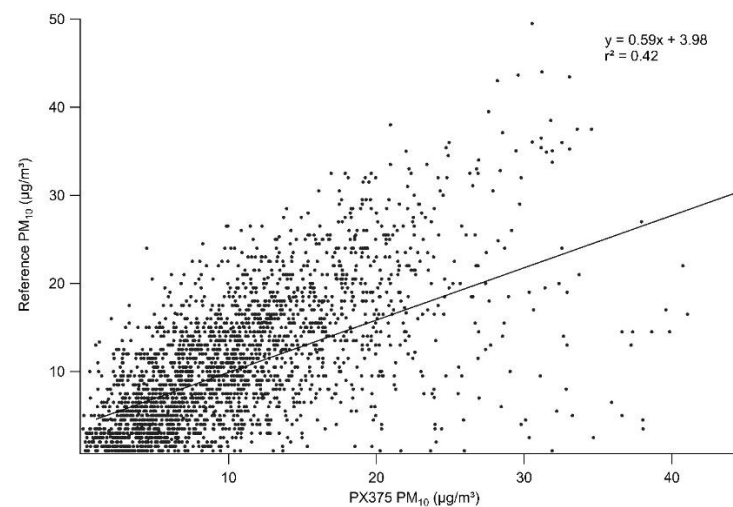


Figure S3. PM₁₀ two-hour linear regression scatter plot for reference and PX-375 in-built gravimetric analyses.

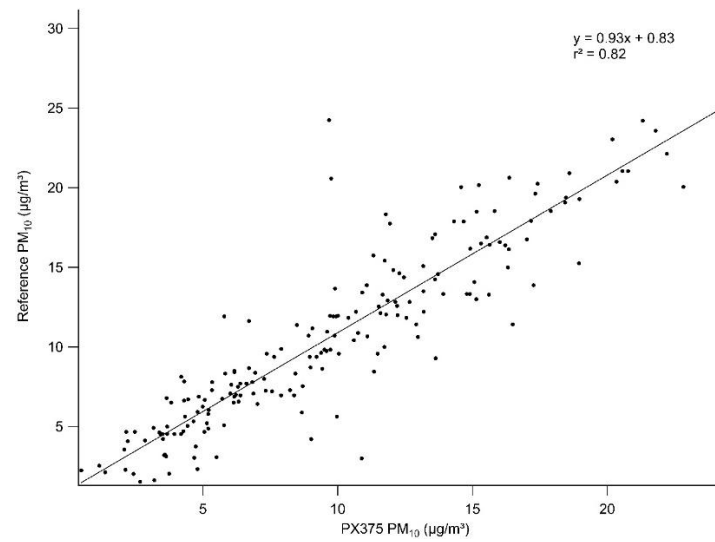
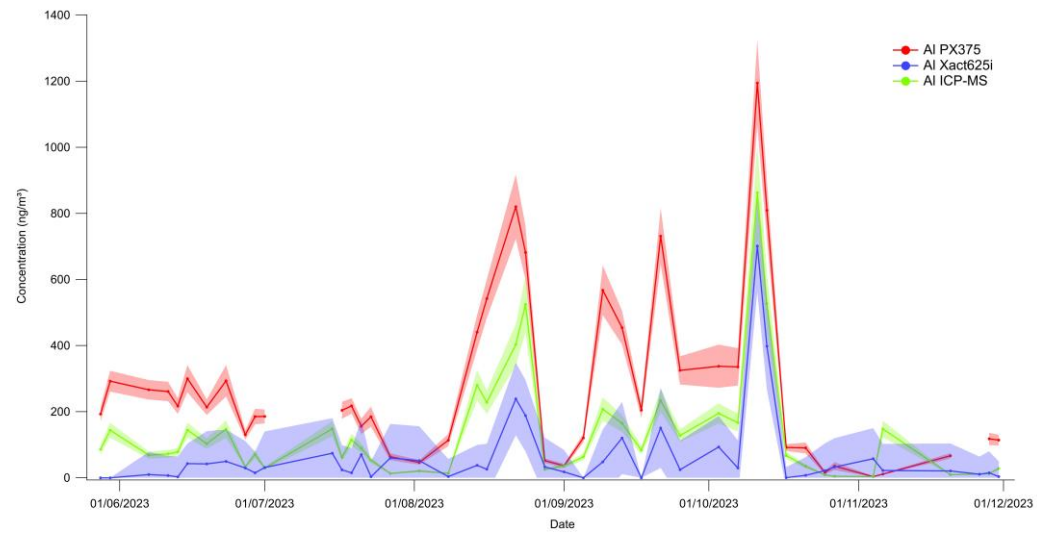
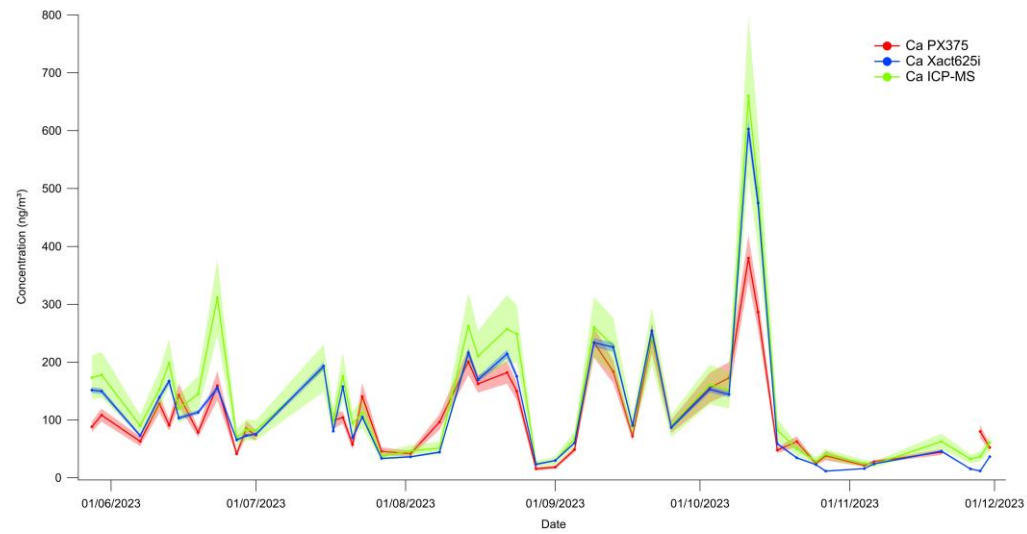
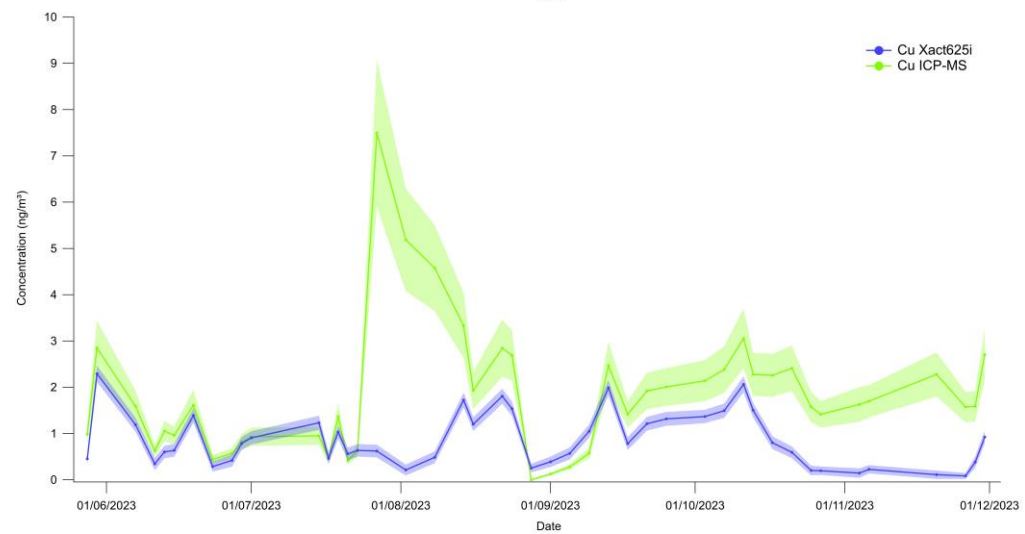
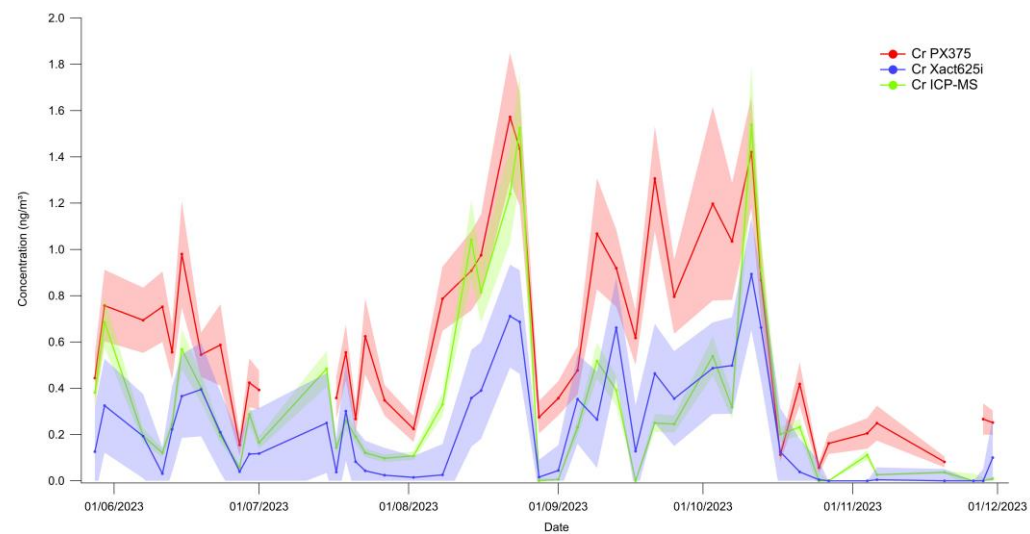
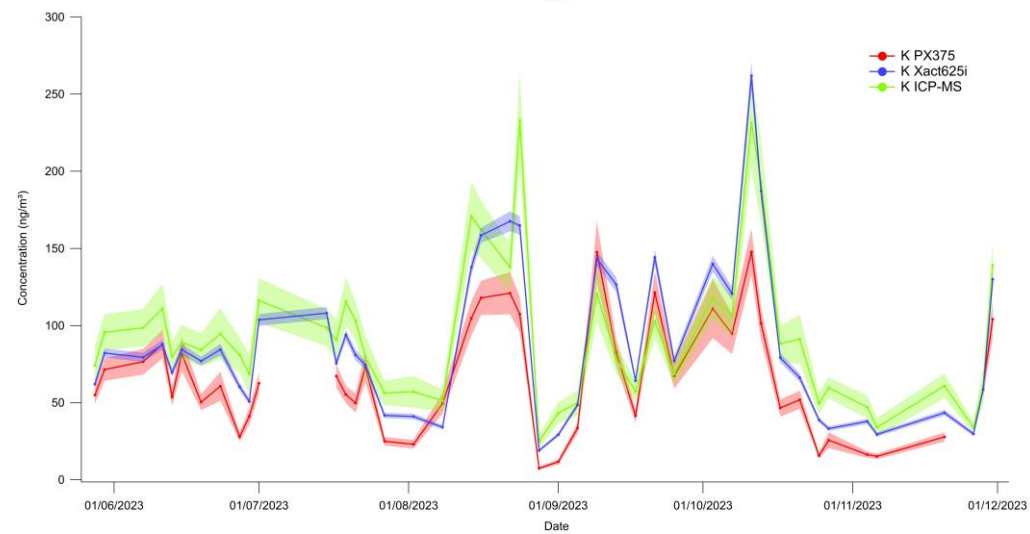
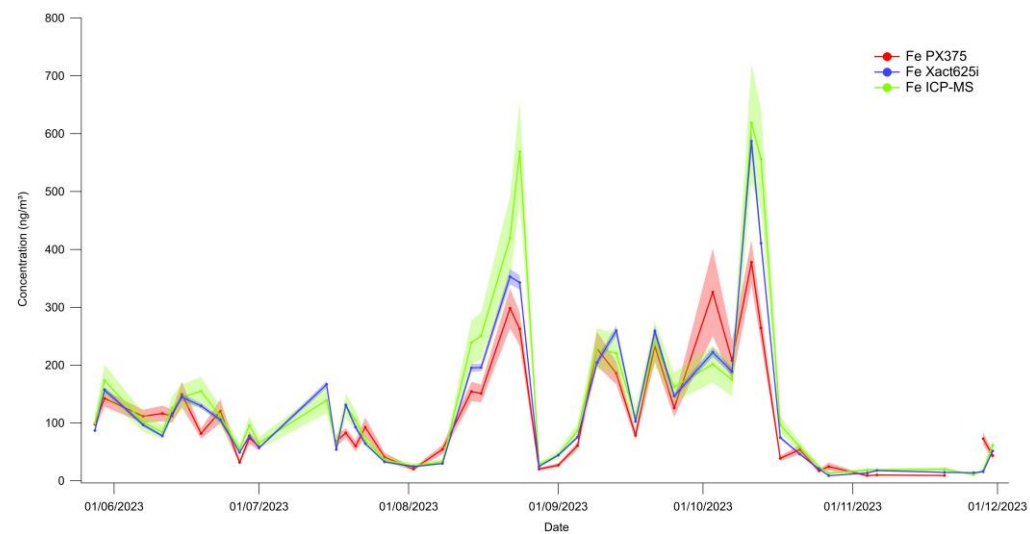
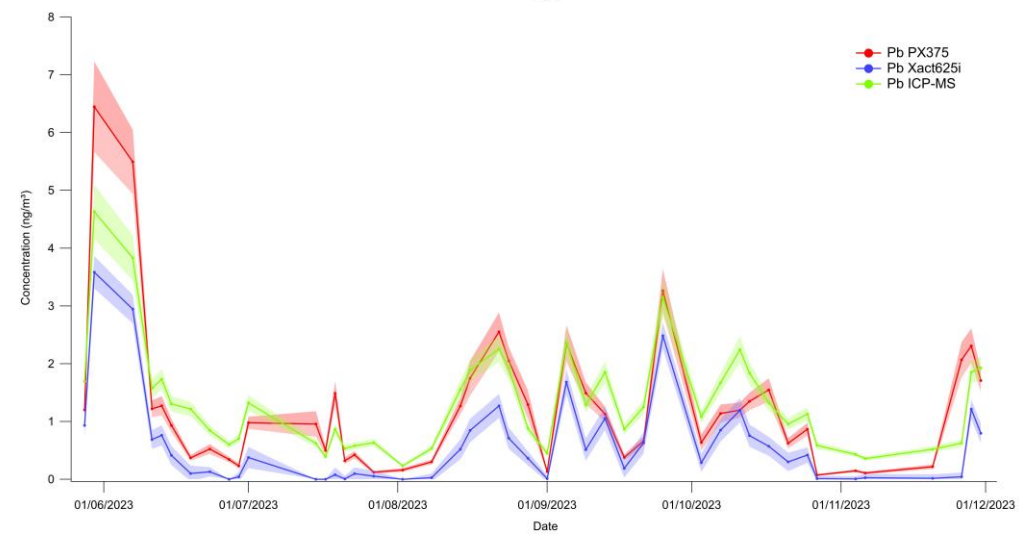
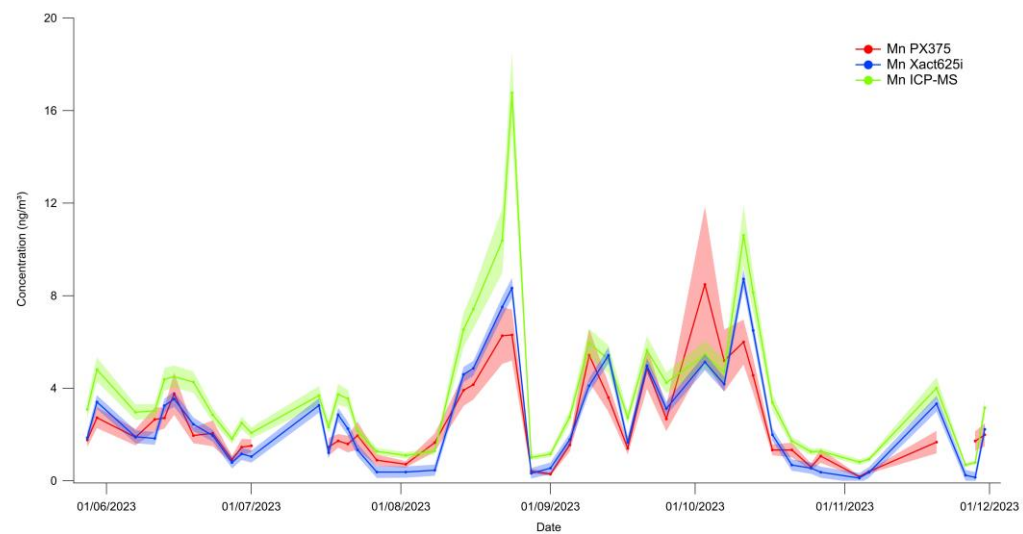


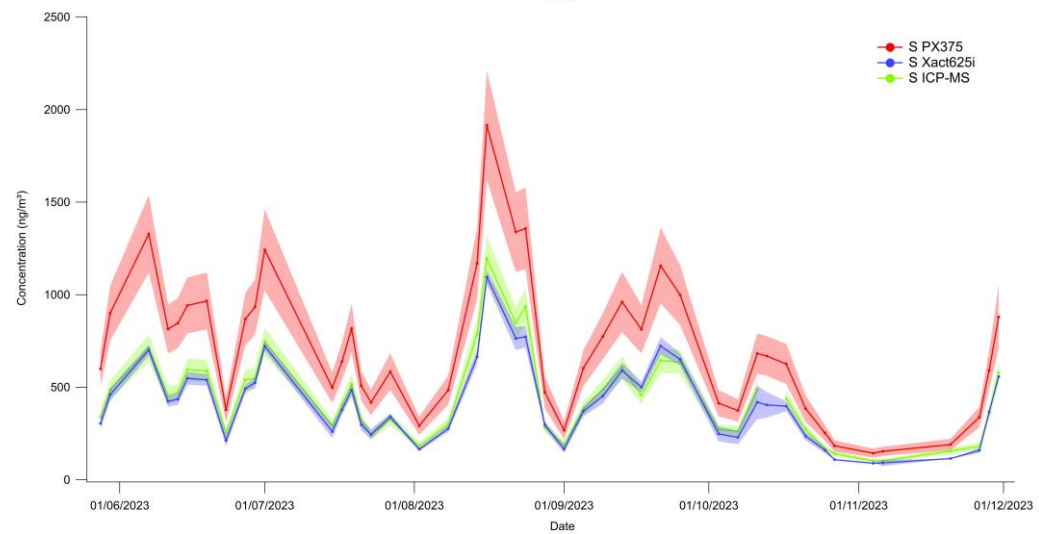
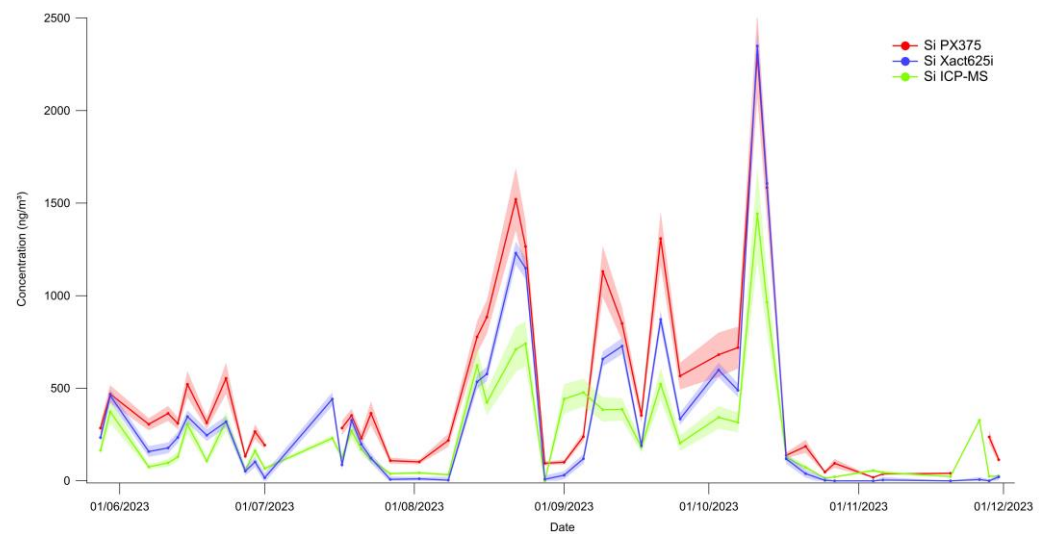
Figure S4. PM₁₀ daily-averaged linear regression scatter plot for reference and PX-375 in-built gravimetric analyses.

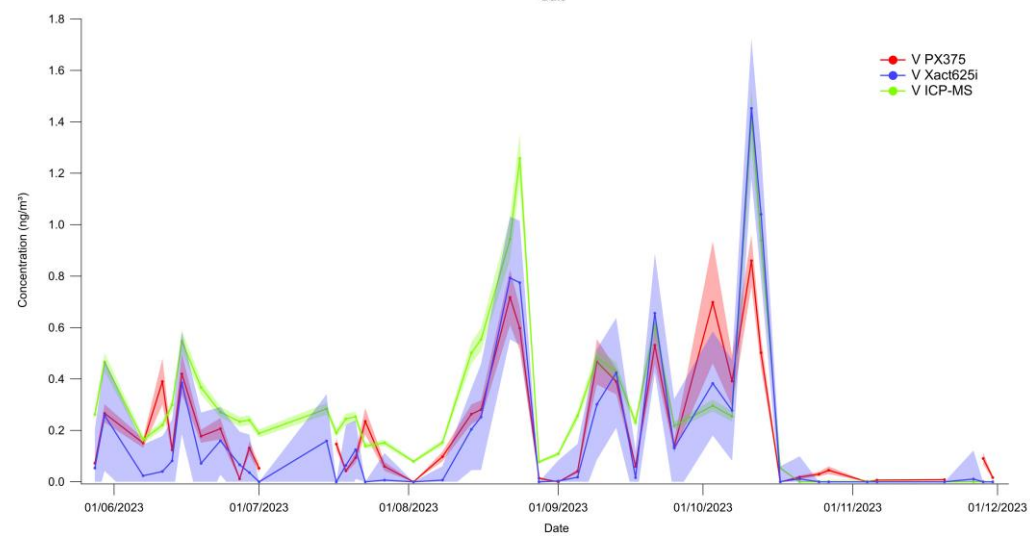
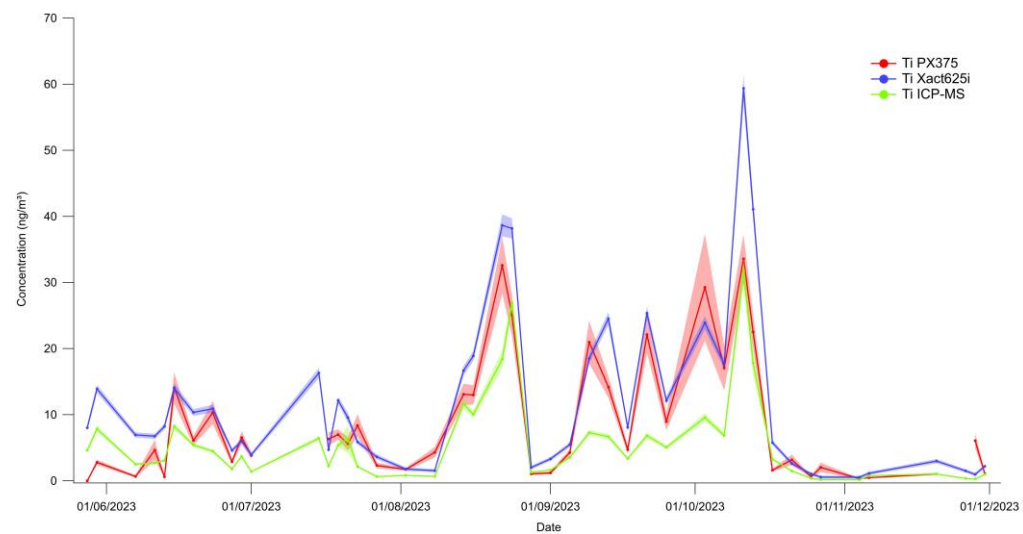












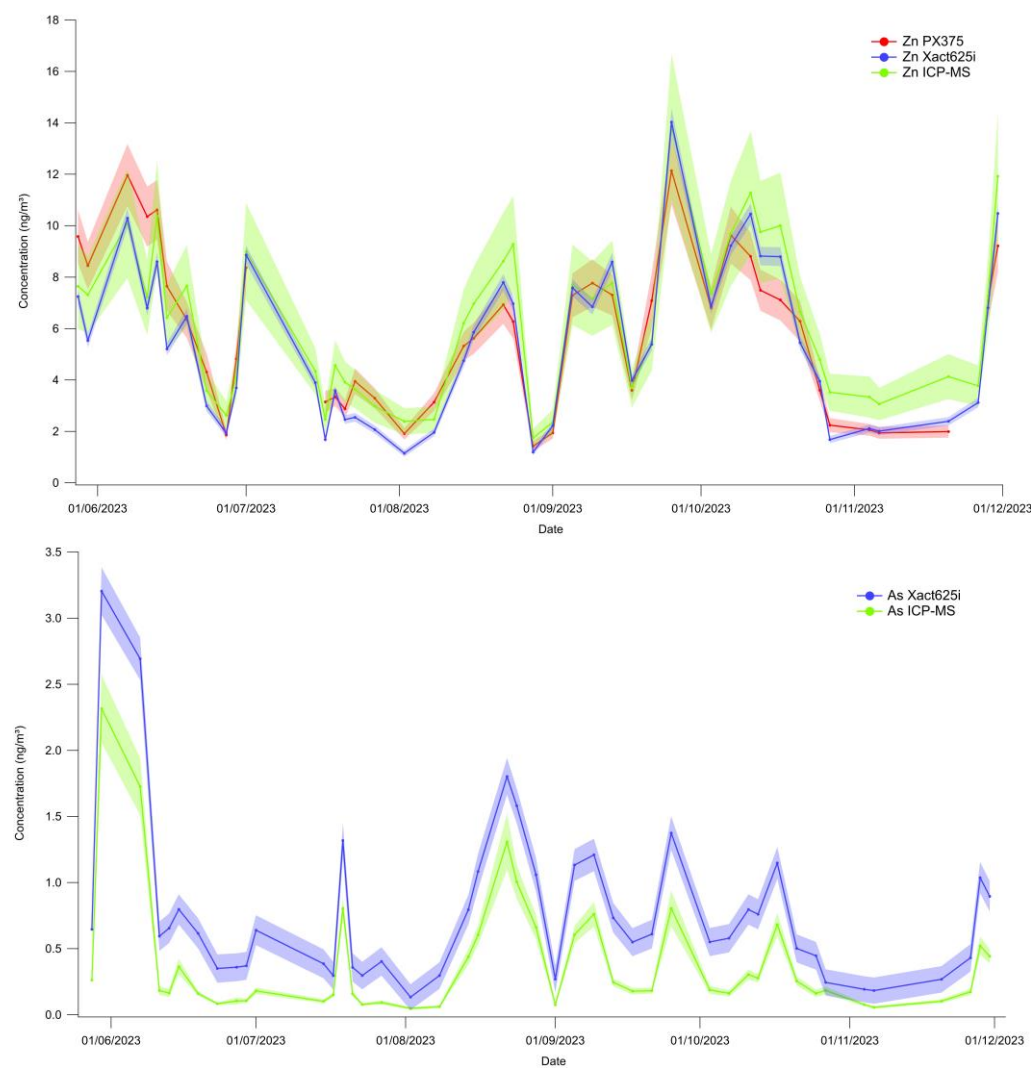
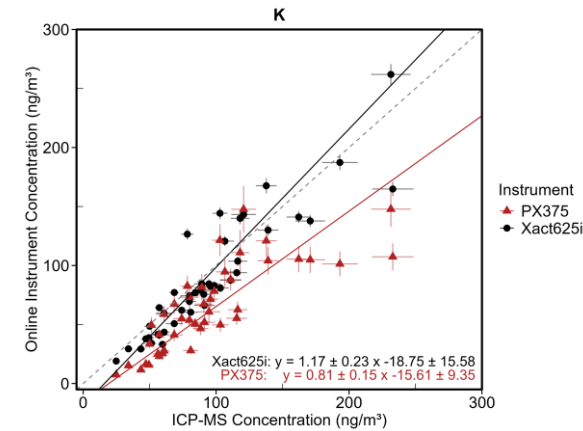
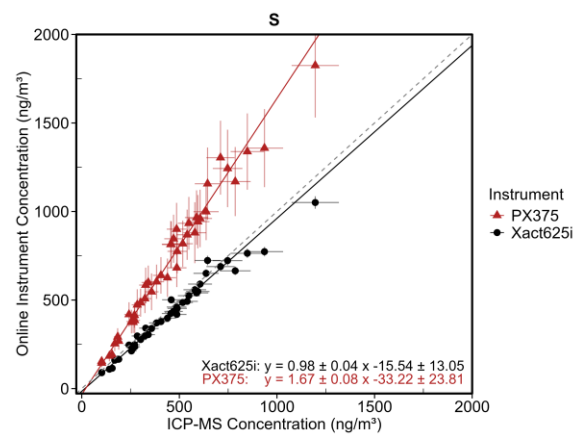
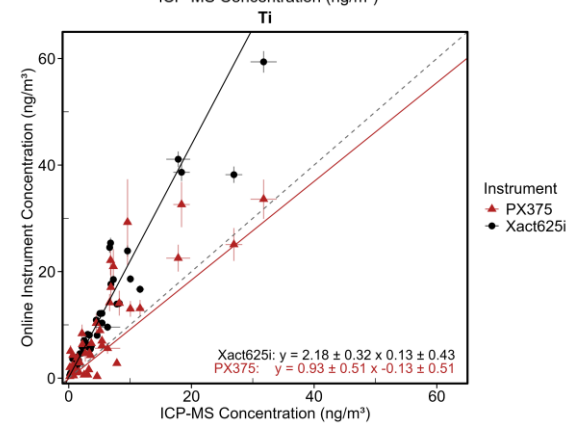
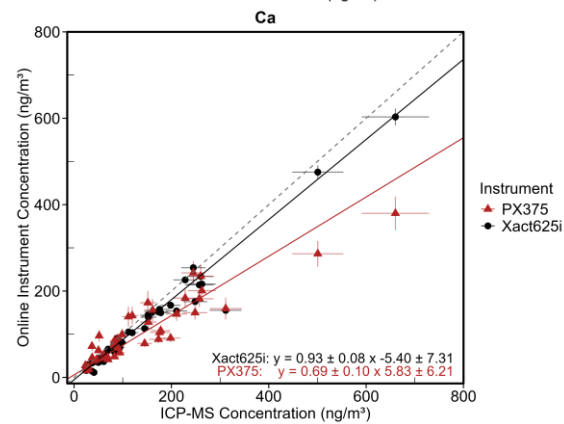
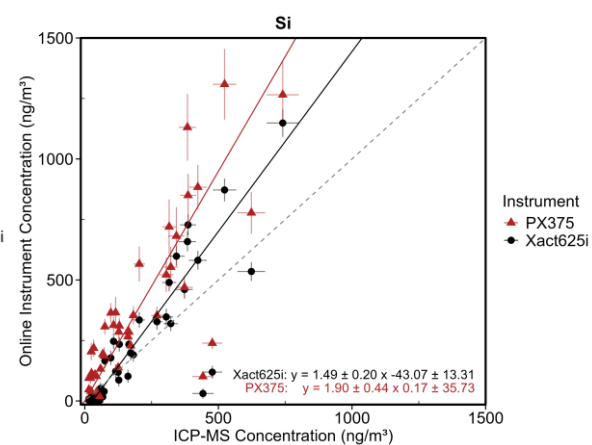
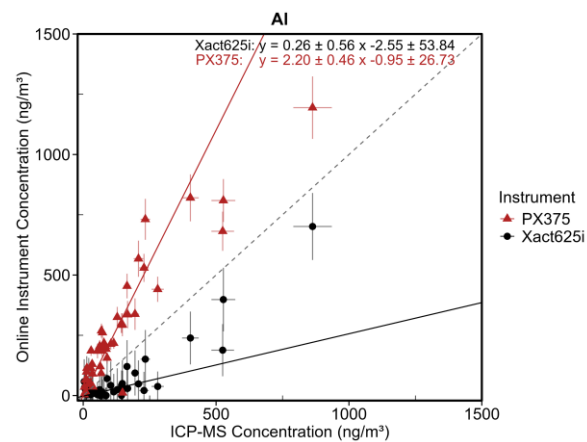
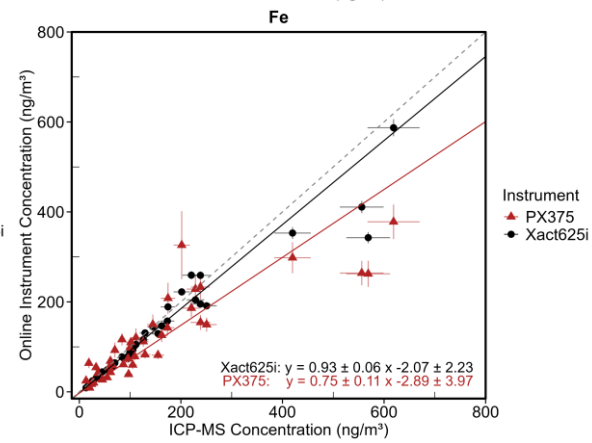
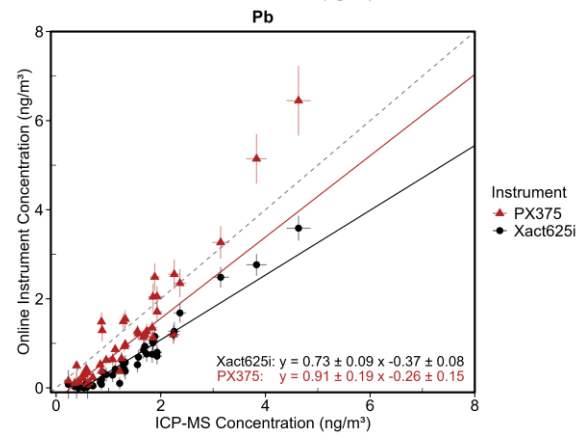
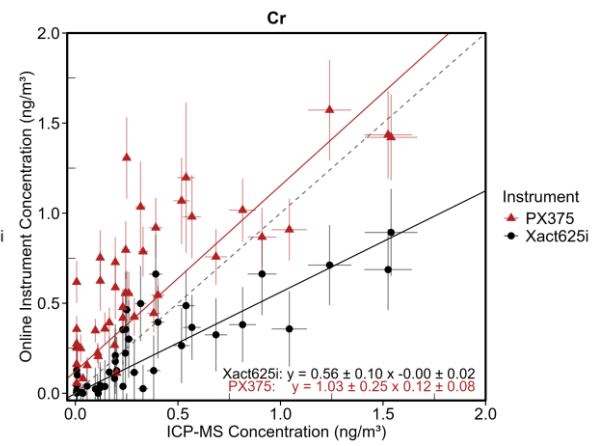
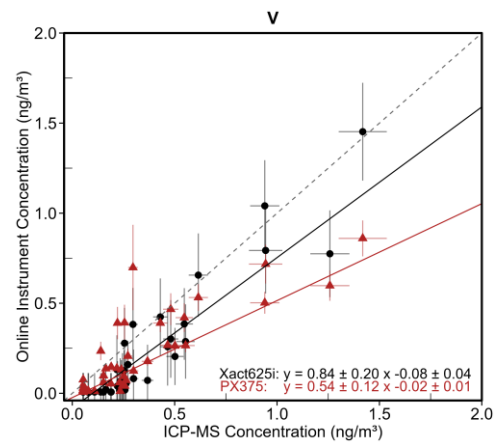


Figure S5. Elemental time series for the Xact625i and PX-375 against reference ICP-MS.





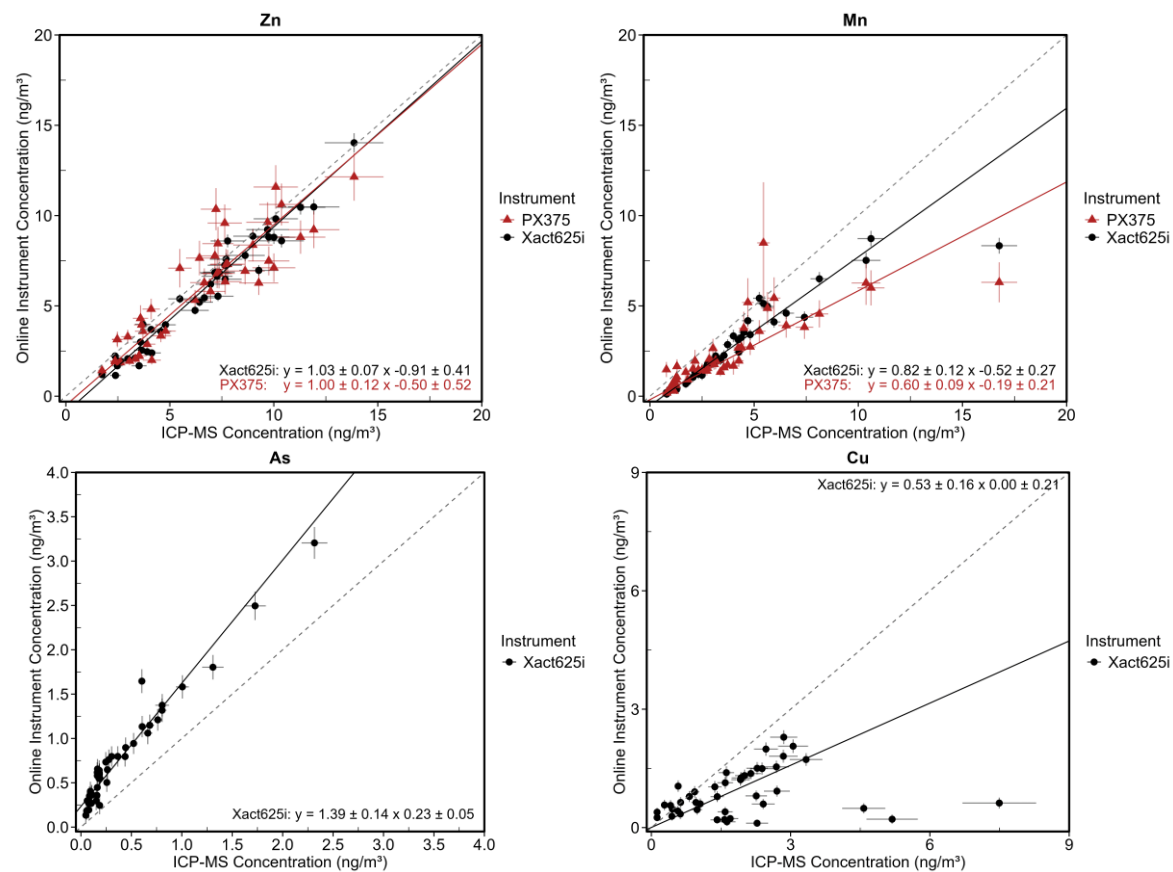


Figure S6. Deming regression charts for ED-XRF instruments against ICP-MS without forcing through origin.

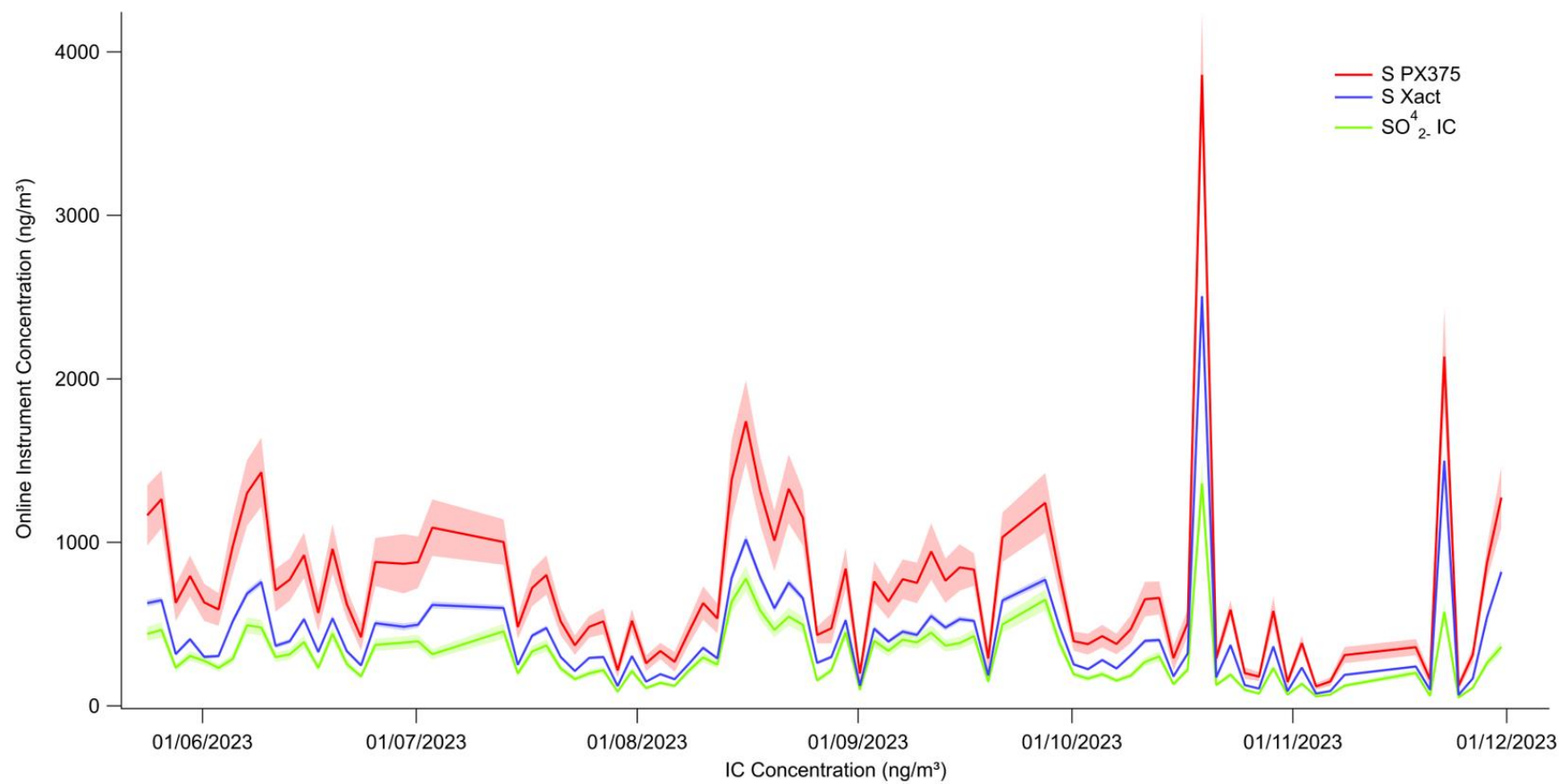


Figure S7. Time series of elemental sulphur by ED-XRF instruments and offline corrected sulphate by ion chromatography.

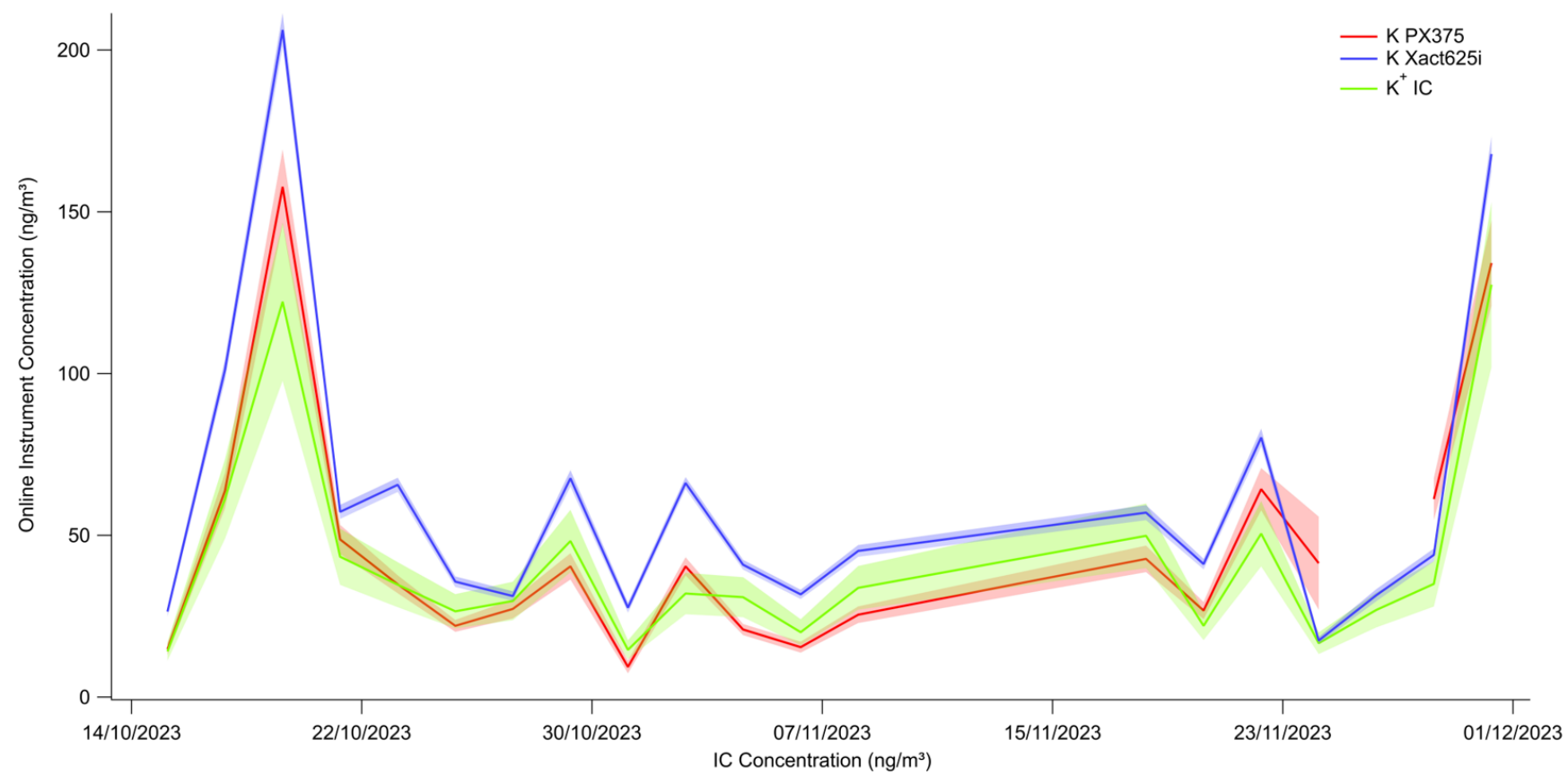


Figure S8. Time series of elemental potassium by ED-XRF instruments and offline potassium cation by ion chromatography.