

Supplement for: Xact625i vs PX-375: A Comparative Study of Online XRF Ambient Multi-Metal Monitors

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 – 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 S2 – 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 S3 – 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 S4. 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 S5. 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 S6 – 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.*

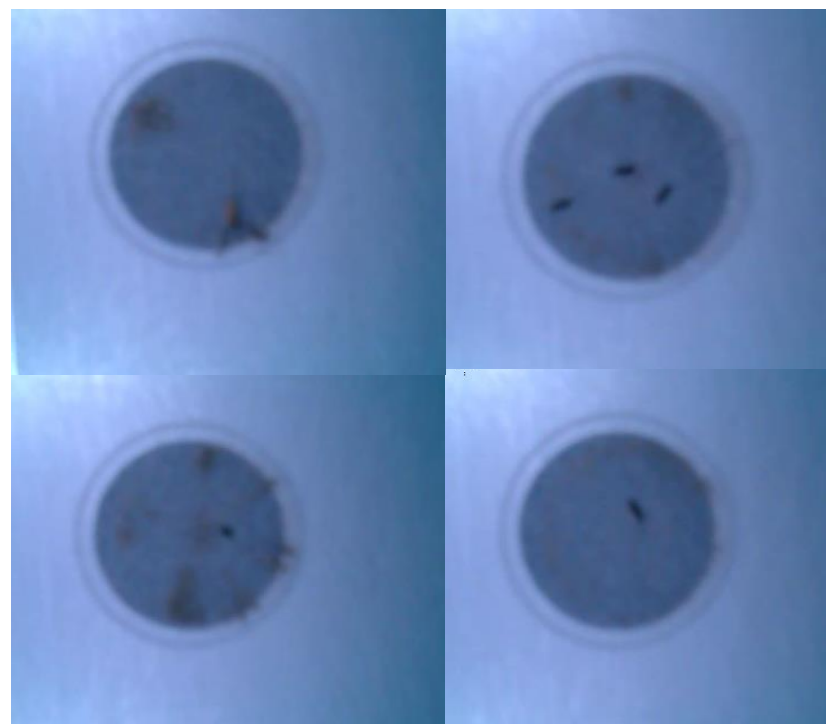


Figure S1. Insect and other debris in the sampling spot of the PX-375 in samples flagged as outliers due to high concentrations of crustal elements.

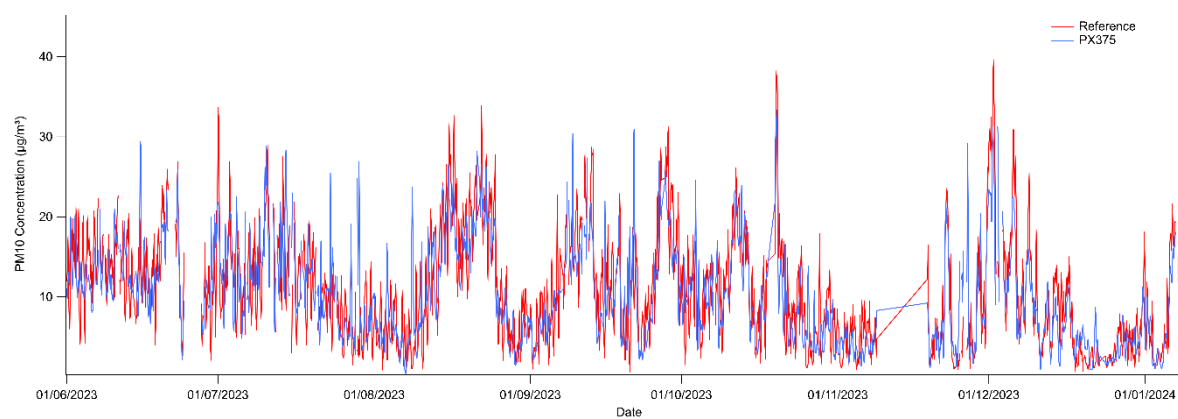


Figure S2. PM₁₀ two-hour time series for reference and PX-375 in-built gravimetric analyses.

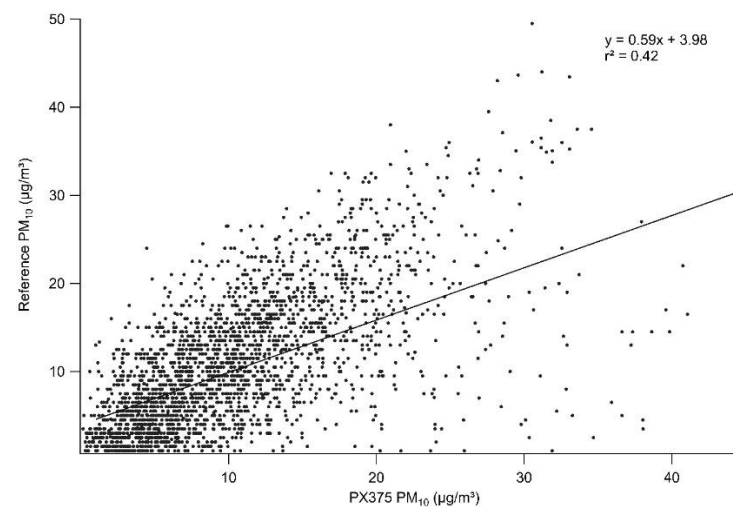


Figure S3. PM₁₀ two-hour linear regression scatter plot for reference and PX-375 in-built gravimetric analyses.

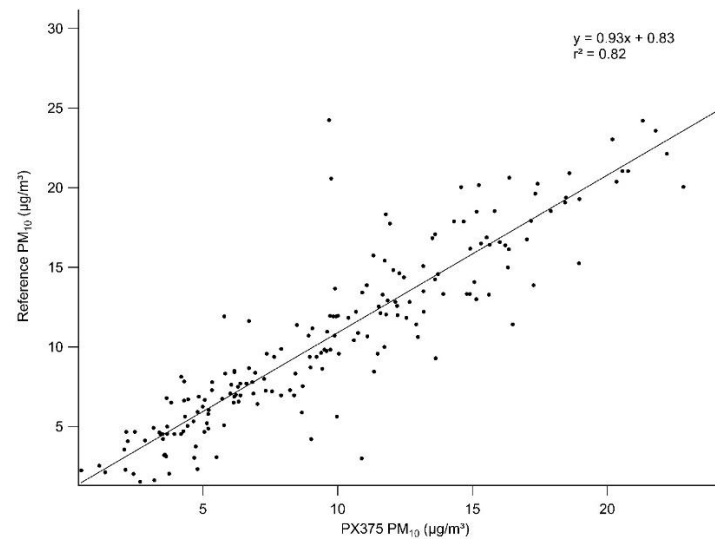
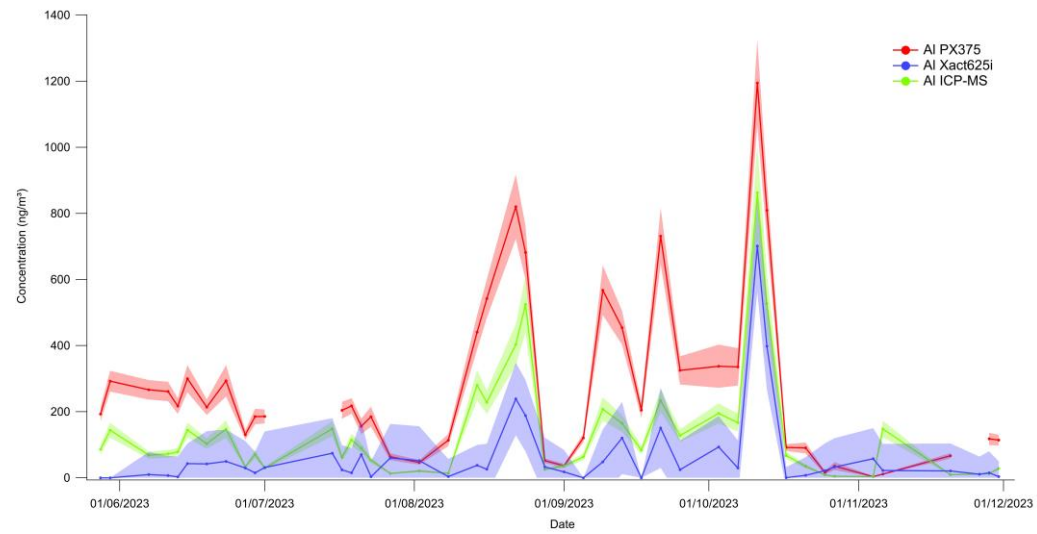
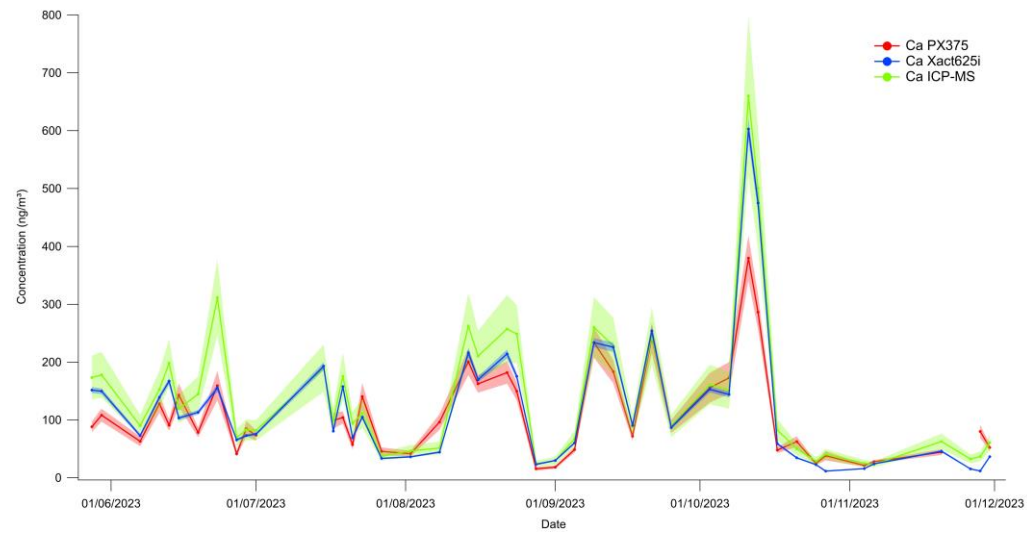
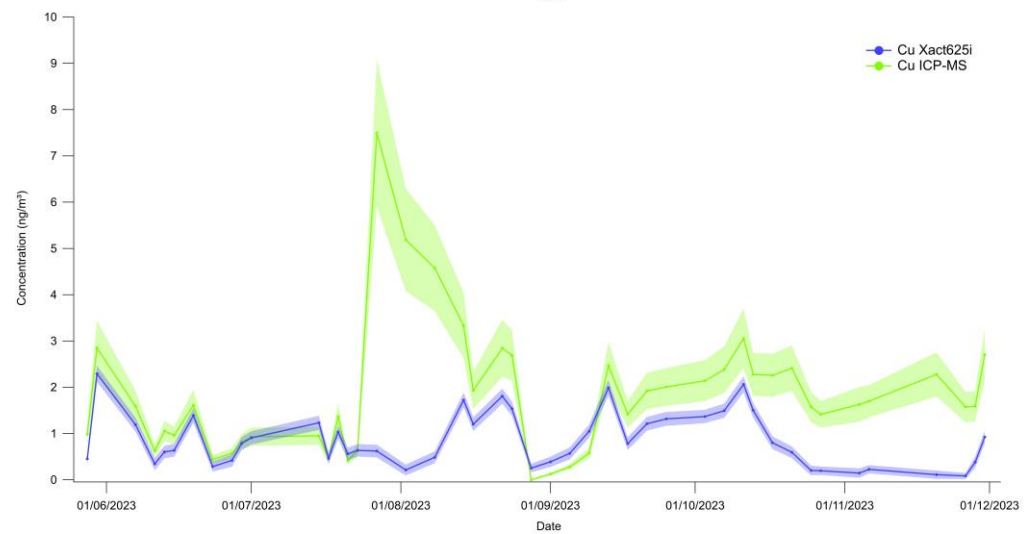
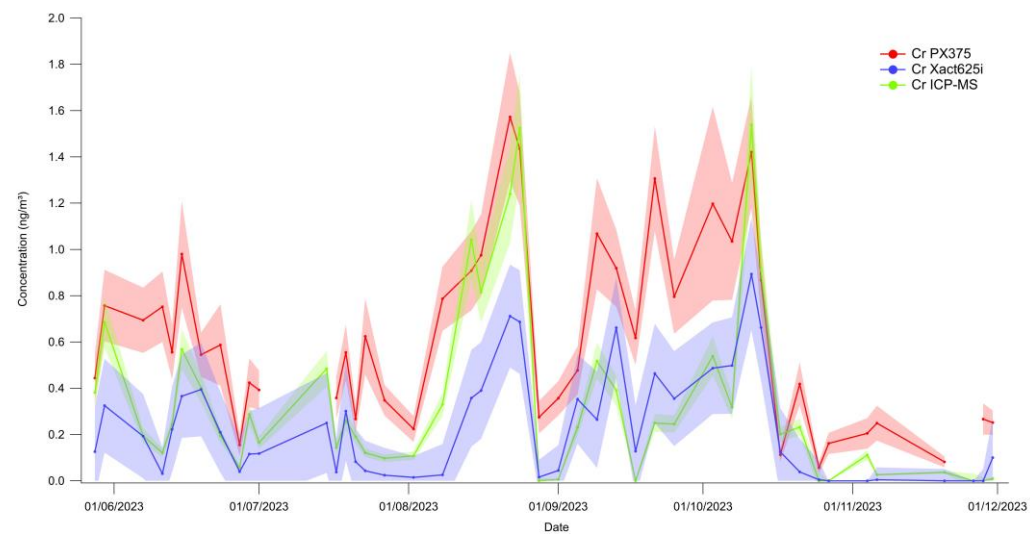
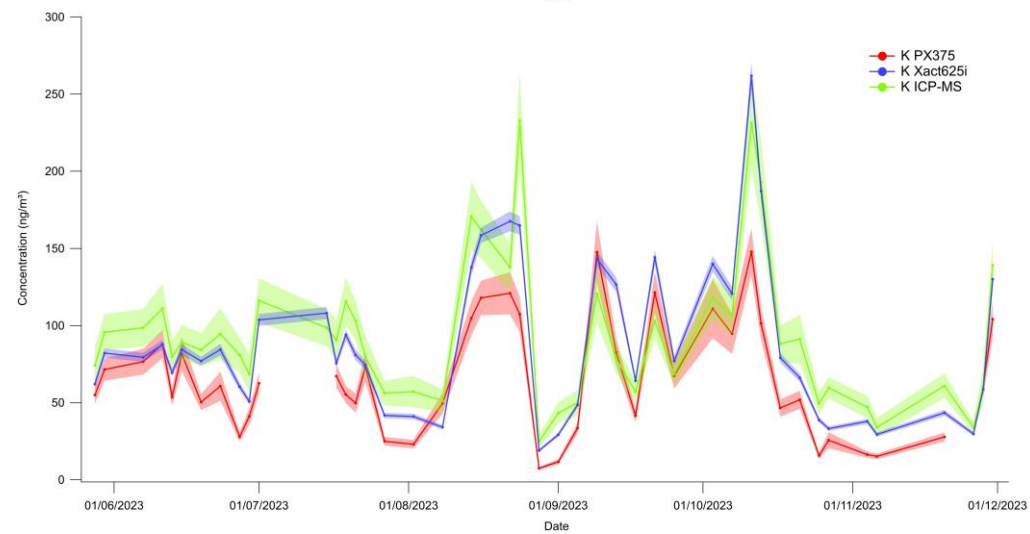
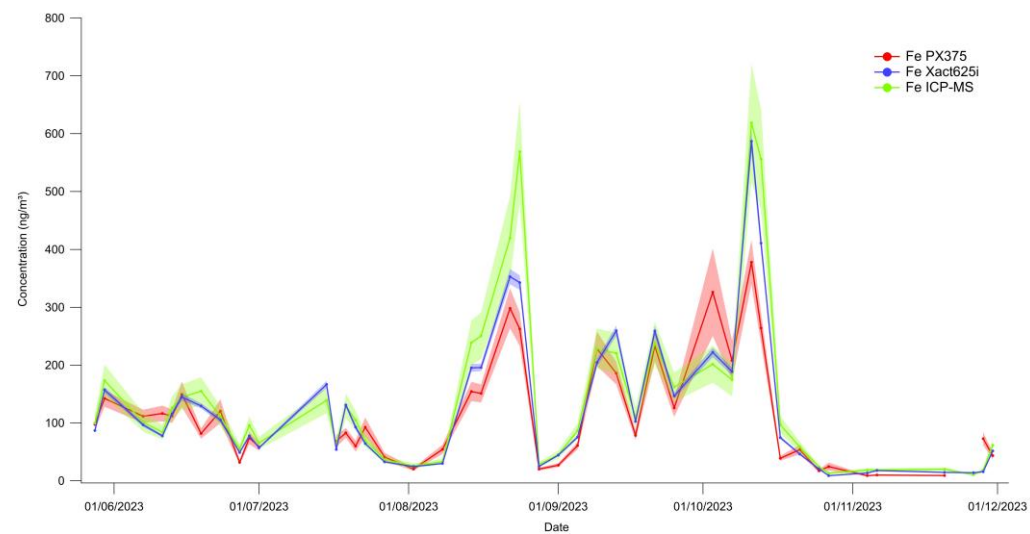
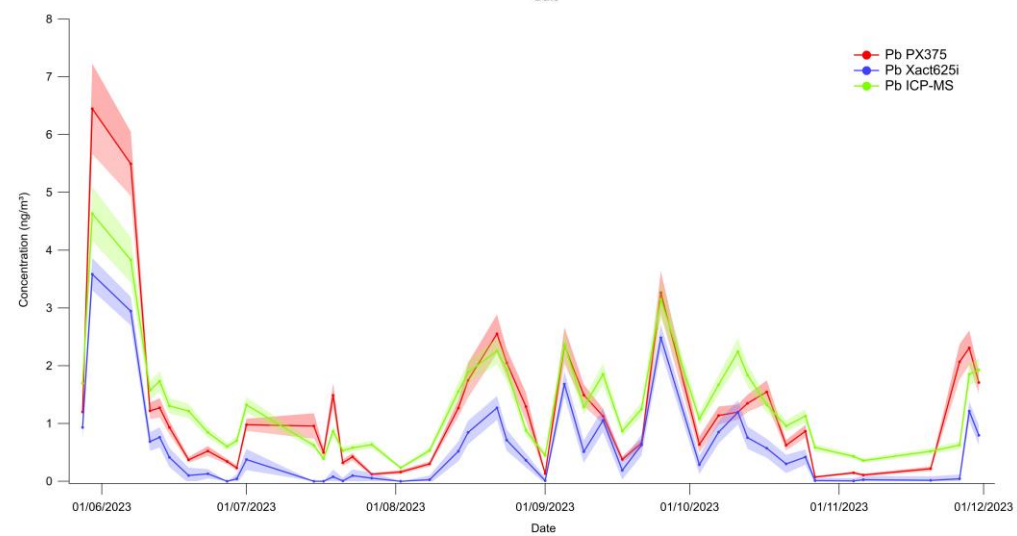
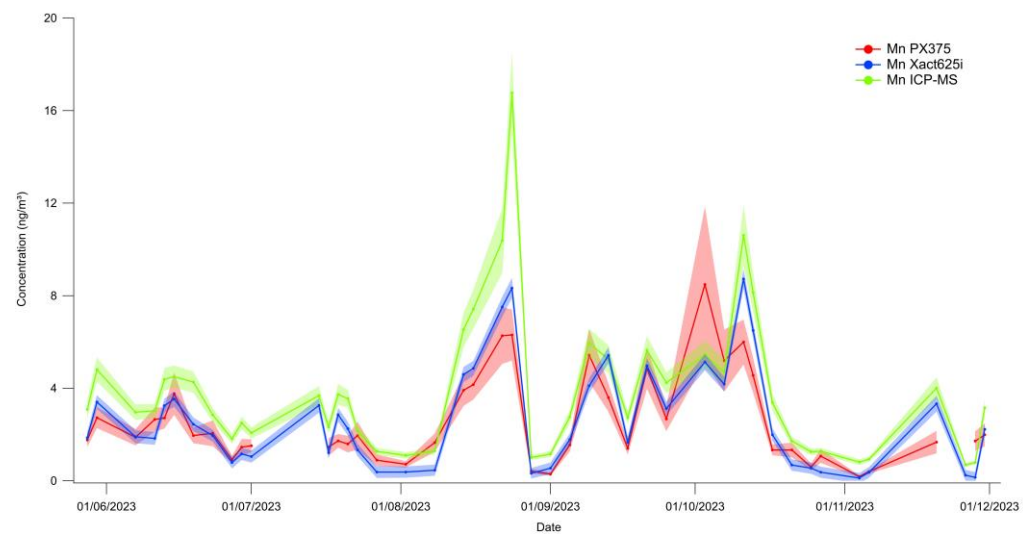


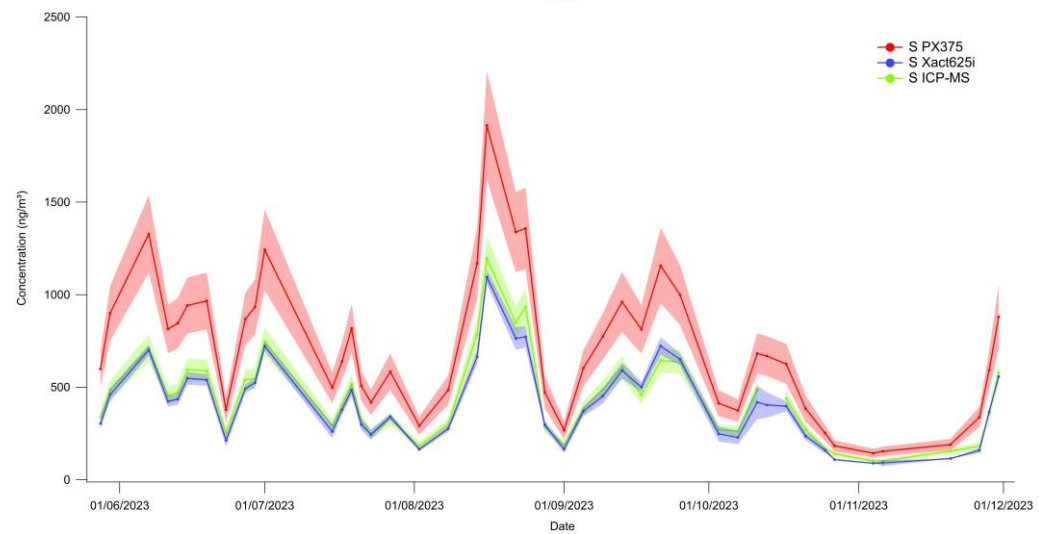
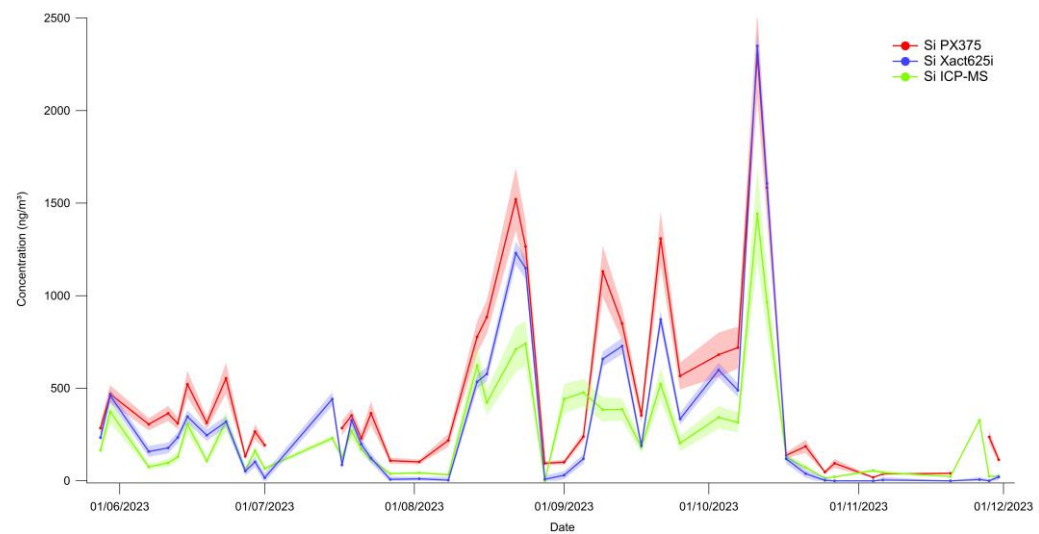
Figure S4. PM₁₀ daily-averaged linear regression scatter plot for reference and PX-375 in-built gravimetric analyses.

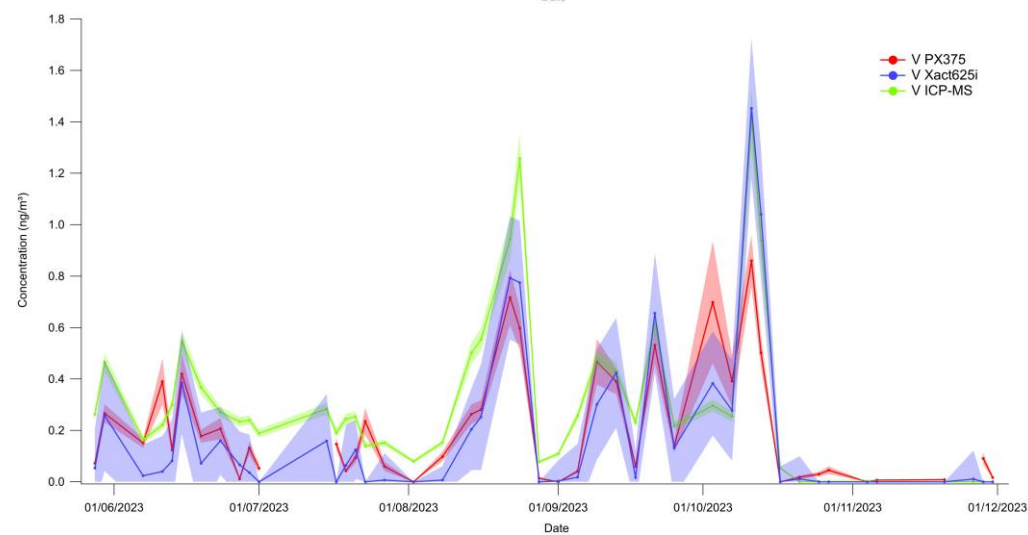
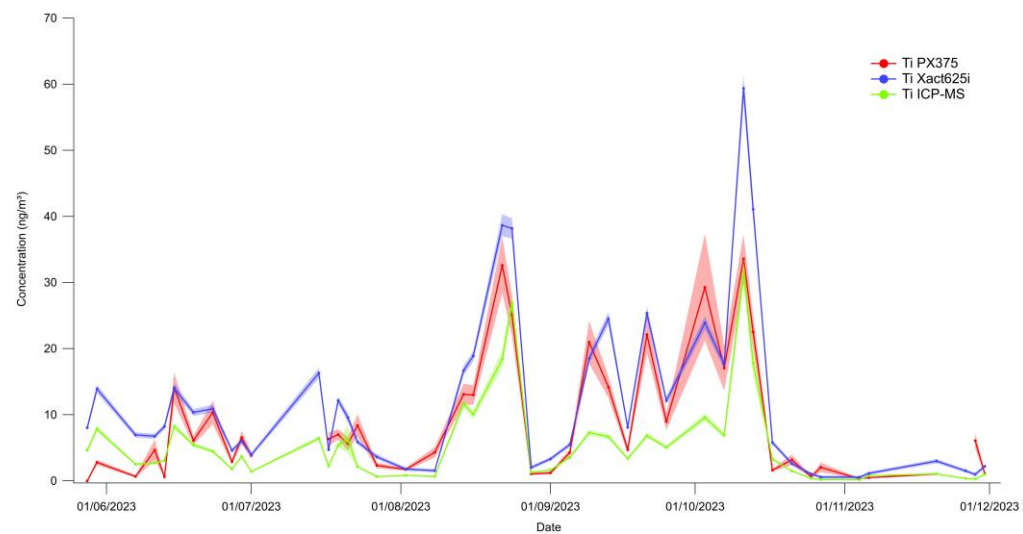












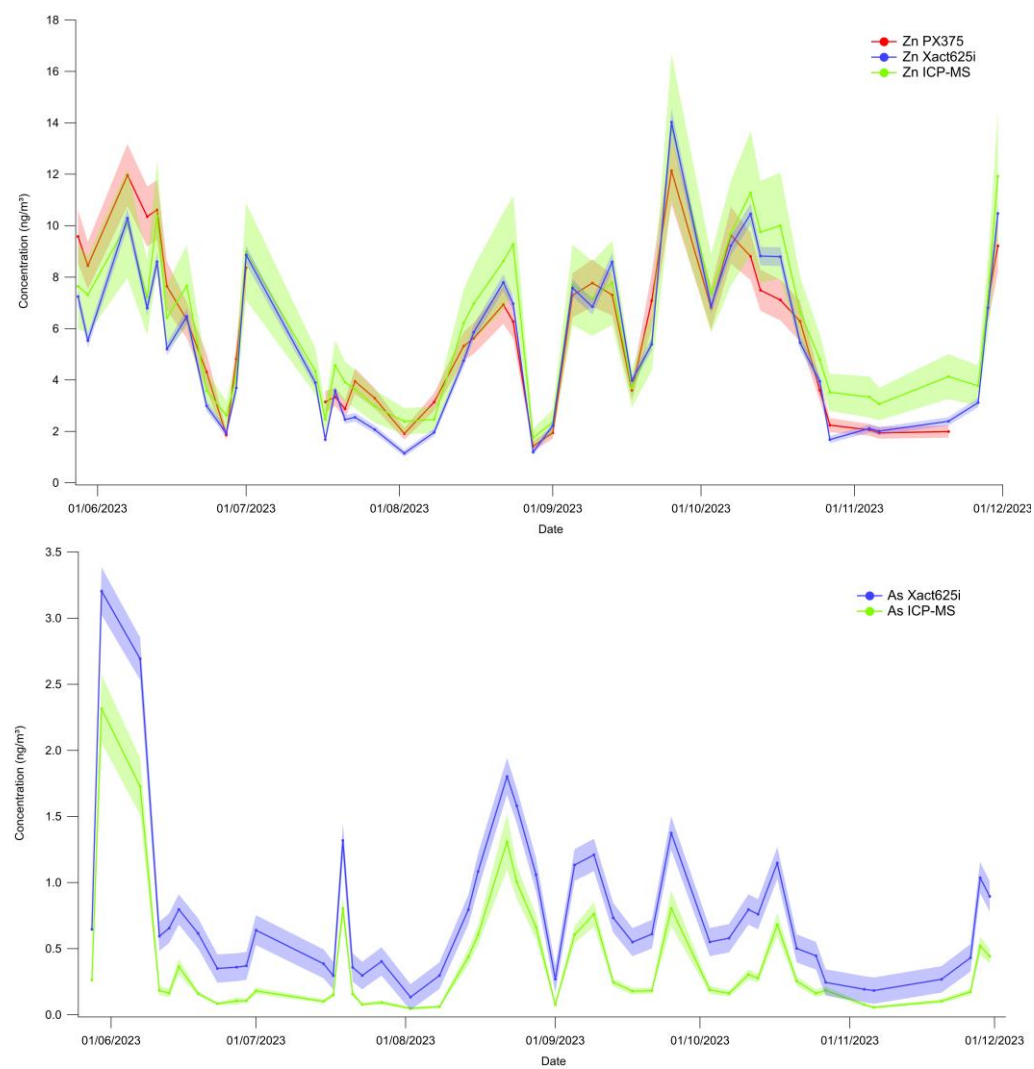


Figure S5. Elemental time series for the Xact625i and PX-375 against reference ICP-MS.

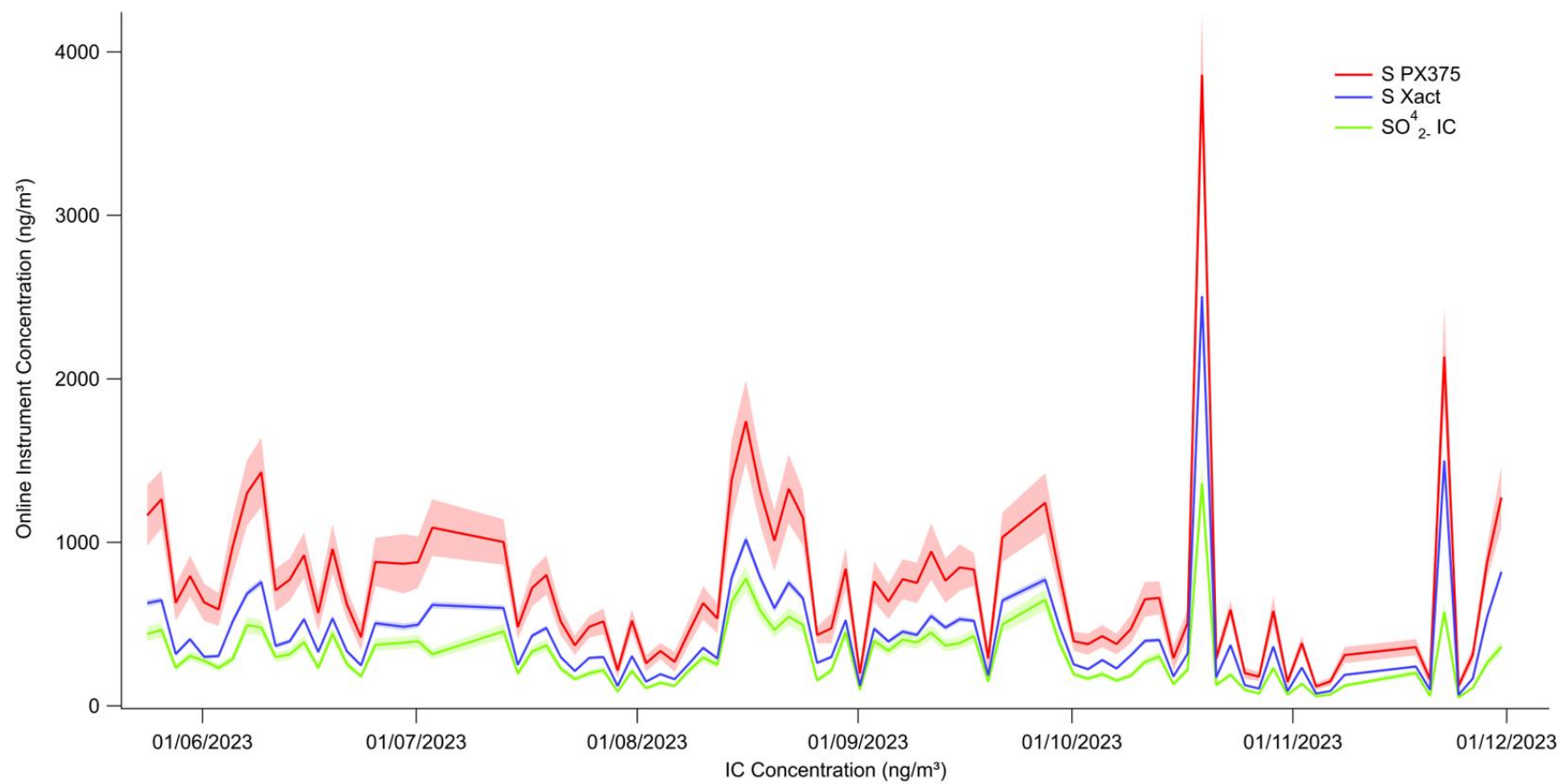


Figure S6. Time series of elemental sulphur by ED-XRF instruments and offline corrected sulphate by ion chromatography.

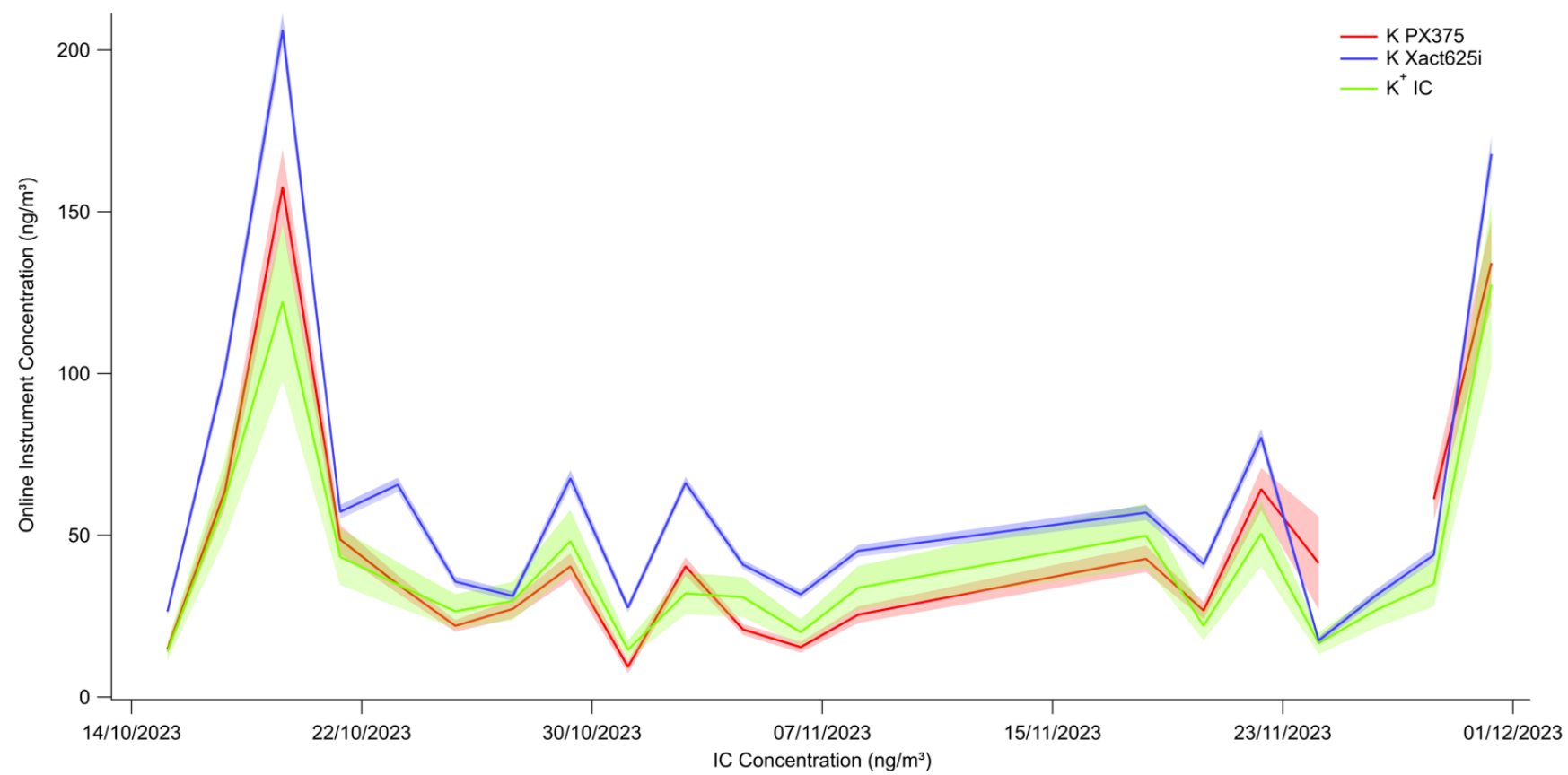


Figure S7. Time series of elemental potassium by ED-XRF instruments and offline potassium cation by ion chromatography.