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Authors	Papagiannis, Stefanos;Manousakas, Manousos I.;Anagnostopoulos, Dimitrios F.;Pikridas, Michael;Baalbaki, Rima;Sciare, Jean;O'Sullivan, Niall;Hellebust, Stig;Wenger, John;Fossum, Kirsten N.;Ovadnevaite, Jurgita;Tremper, Anja;Green, David;Eleftheriadis, Konstantinos;Diapouli, Evangelia
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Near real-time & benchtop XRF intercomparison for PM elemental analysis on quartz and teflon filters: a case study across three European cities

Stefanos Papagiannis et al.

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Table S1: Limits of Detection in ng m^{-3} for the benchtop ED-XRF spectrometer.

	ATH-DEM station	DUB-P station	CAO-NIC station
Element	**PTFE (ng m^{-3})**	**Quartz fiber (ng m^{-3})**	**Quartz fiber (ng m^{-3})**
Na	11.7	127.4	126.1
Mg	6.0	49.0	43.3
Al	4.1	56.7	50.9
Si	2.4	-	-
P	0.7	2.3	2.1
S	0.5	1.0	1.0
Cl	0.3	0.4	0.5
K	0.4	0.4	0.4
Ca	2.5	4.4	4.0
Ti	1.5	2.1	2.7
V	1.0	2.0	1.9
Cr	0.8	1.6	1.5
Mn	0.6	1.2	1.1
Fe	0.9	0.9	0.9
Co	0.4	0.9	0.6
Ni	0.3	0.7	0.6
Cu	0.7	0.8	0.7
Zn	0.3	0.8	0.7
Ga	0.3	0.7	0.6
Ge	0.3	0.6	0.6
As	0.4	1.1	1.0
Se	0.9	1.7	1.6
Br	0.4	1.1	0.8
Rb	0.5	0.8	0.8
Sr	0.7	1.3	1.1
Ag	4.5	6.8	6.2
Cd	6.0	5.9	7.3
Sn	9.7	11.8	10.8
Sb	13.1	15.2	14.0

Cs	40.7	51.2	47.0
Ba	44.5	55.8	51.4
Ce	54.8	69.4	64.4
Pt	1.6	3.4	3.1
Au	1.7	3.9	3.6
Hg	1.3	2.5	2.5
Pb	1.1	2.2	2.0

Table S2: Limits of Detection in ng m^{-3} for the Xact 625 and Xact 625i for 60-minute time resolution.

Element	Xact 625 60 min (ng m^{-3})	Xact 6252i 60min (ng m^{-3})
Al	-	170
Si	181	30.9
P	-	9
S	12.14	5.5
Cl	8.97	3
K	2.37	2
Ca	0.90	0.52
Ti	0.38	0.28
V	0.29	0.21
Cr	0.29	0.2
Mn	0.28	0.25
Fe	0.76	0.3
Co	-	0.24
Ni	0.23	0.17
Cu	0.27	0.14
Zn	0.23	0.12
Ga	-	0.1
Ge	-	0.1
As	0.11	0.11
Se	0.14	0.14
Br	-	0.18
Rb	-	0.33
Sr	0.45	0.38
Y	-	0.48
Zr	-	0.57
Mo	0.98	-

Cd	5.75	4.4
In	-	5.4
Sn	-	7.1
Sb	0.66	9
Ba	0.95	0.67
Ce	0.78	-
Pt	0.23	-
Hg	-	0.21
Tl	-	0.2
Pb	0.22	0.22
Bi	-	0.23

Table S3: Summary of the number of samples with measured elemental concentrations above the limit of quantification (>LOQ) relative to the total number of paired samples collected at the ATH-DEM, CAO-NIC, and DUB-P monitoring sites.

	Ath-DEM (21 pairs total)		**CAO NIC (256 pairs total)**		**DUB P (50 pairs total)**	
Element	Benchtop ED-XRF	Xact 625i	Benchtop ED-XRF	Xact 625i	Benchtop ED-XRF	Xact 625
Si	21	4	-	-	-	-
S	21	21	256	256	50	50
Cl	10	18	177	210	49	50
K	21	21	256	256	50	50
Ca	21	21	256	256	37	50
Ti	6	21	128	255	-	-
V	-	-	-	-	23	46
Mn	-	-	66	154	-	-
Fe	21	21	255	255	46	50
Ni	-	-	-	-	30	49
Cu	-	-	75	146	-	-
Zn	21	21	243	256	27	50
Sr	-	-	21	38	-	-
Pb	-	-	76	126	-	-

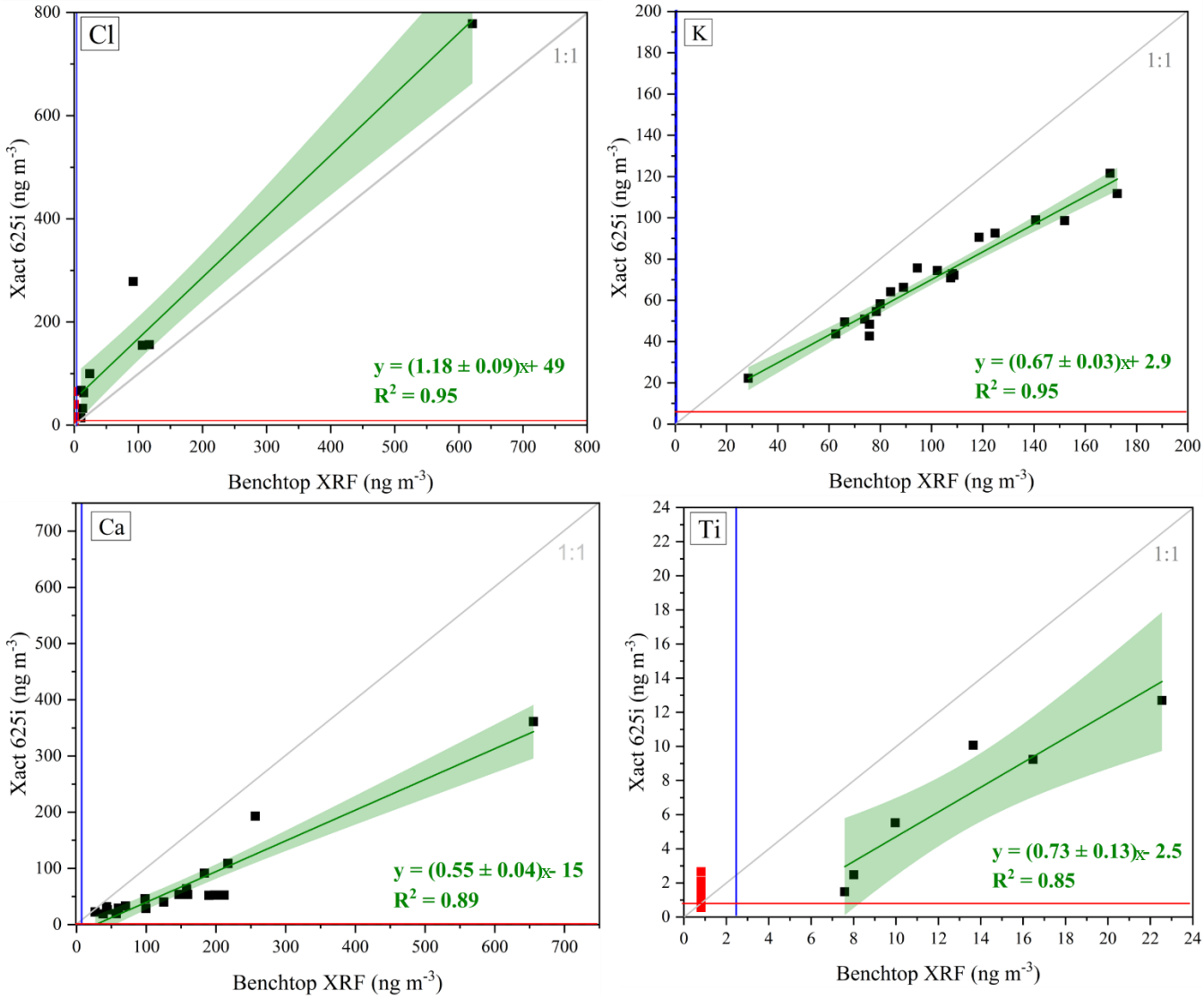


Figure S1: Comparison of elemental concentrations in ng m^{-3} for Si, K, Cl, Ti, Fe and Zn for the ATH-DEM station. The grey line represents the 1:1 reference line, while the green line represents the linear regression fit. The blue lines indicate the LOQ threshold for the benchtop XRF spectrometer, while the red lines represent the corresponding threshold for the Xact 625i continuous elemental monitor.

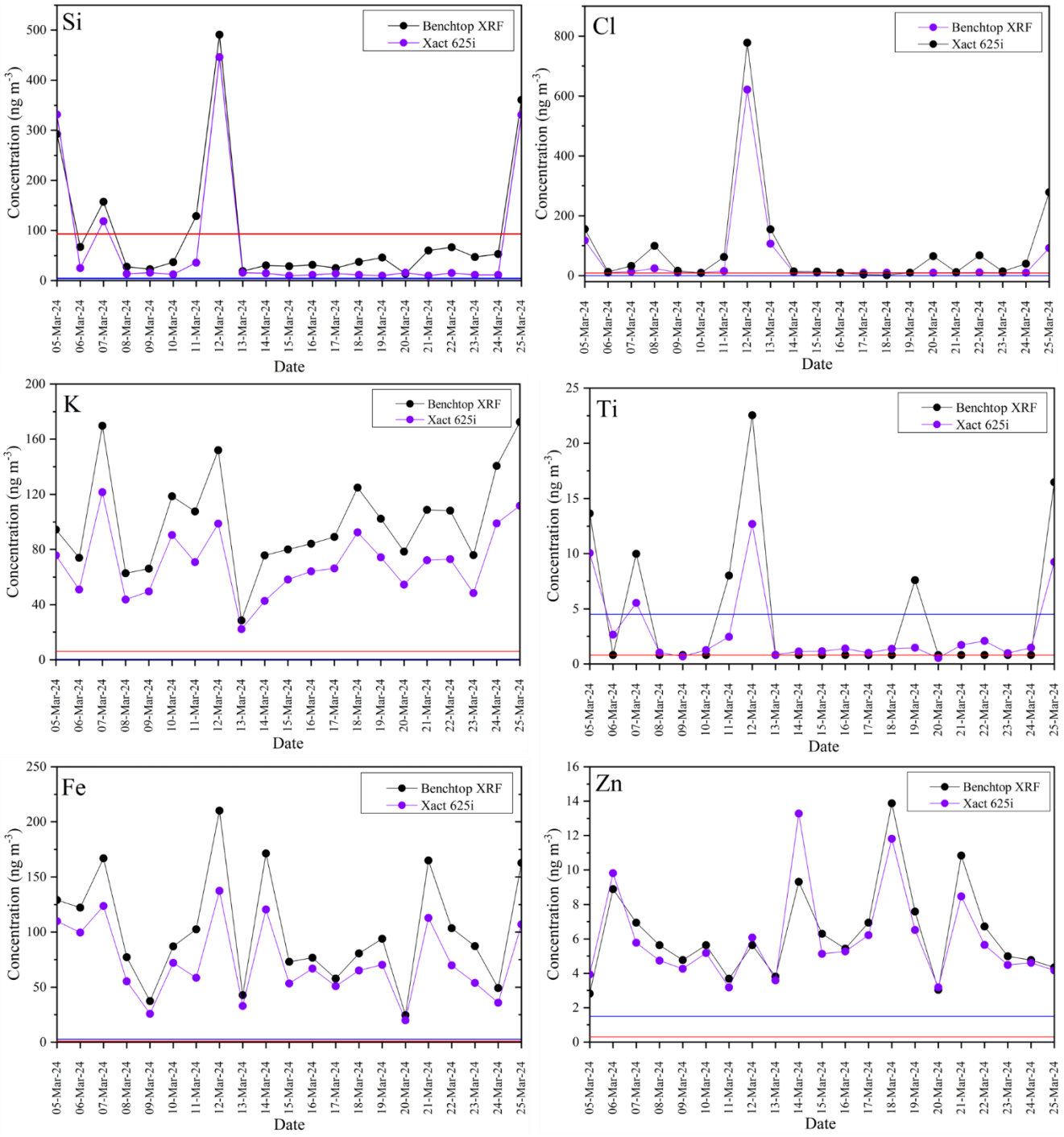


Figure S2: Time series graphs comparing Si, K, Cl, Ti Fe and Zn concentrations (ng m⁻³) from March 5 to 25, 2024 for the ATH-DEM station. The blue lines indicate the LOQ threshold for the benchtop XRF spectrometer, while the red lines represent the corresponding threshold for the Xact 625i continuous elemental monitor.

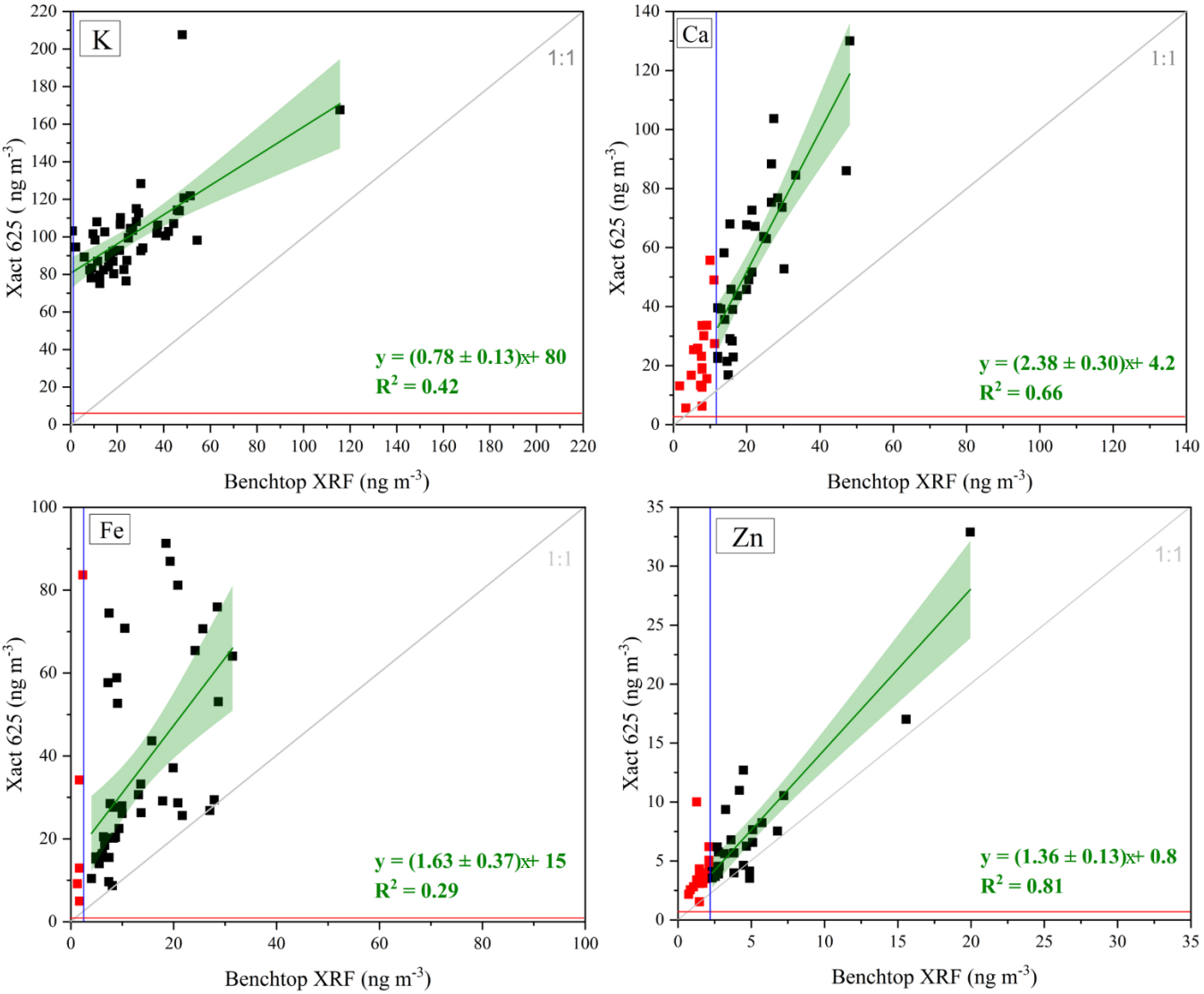


Figure S3: Comparison of elemental concentrations in ng m^{-3} for K, Ca, Fe and Zn for the DUB-P station. The grey line represents the 1:1 reference line, while the green line represents the linear regression fit. The blue lines indicate the LOQ thresholds for the benchtop XRF spectrometer, while the red lines represent the corresponding thresholds for the Xact 625 continuous elemental monitor.

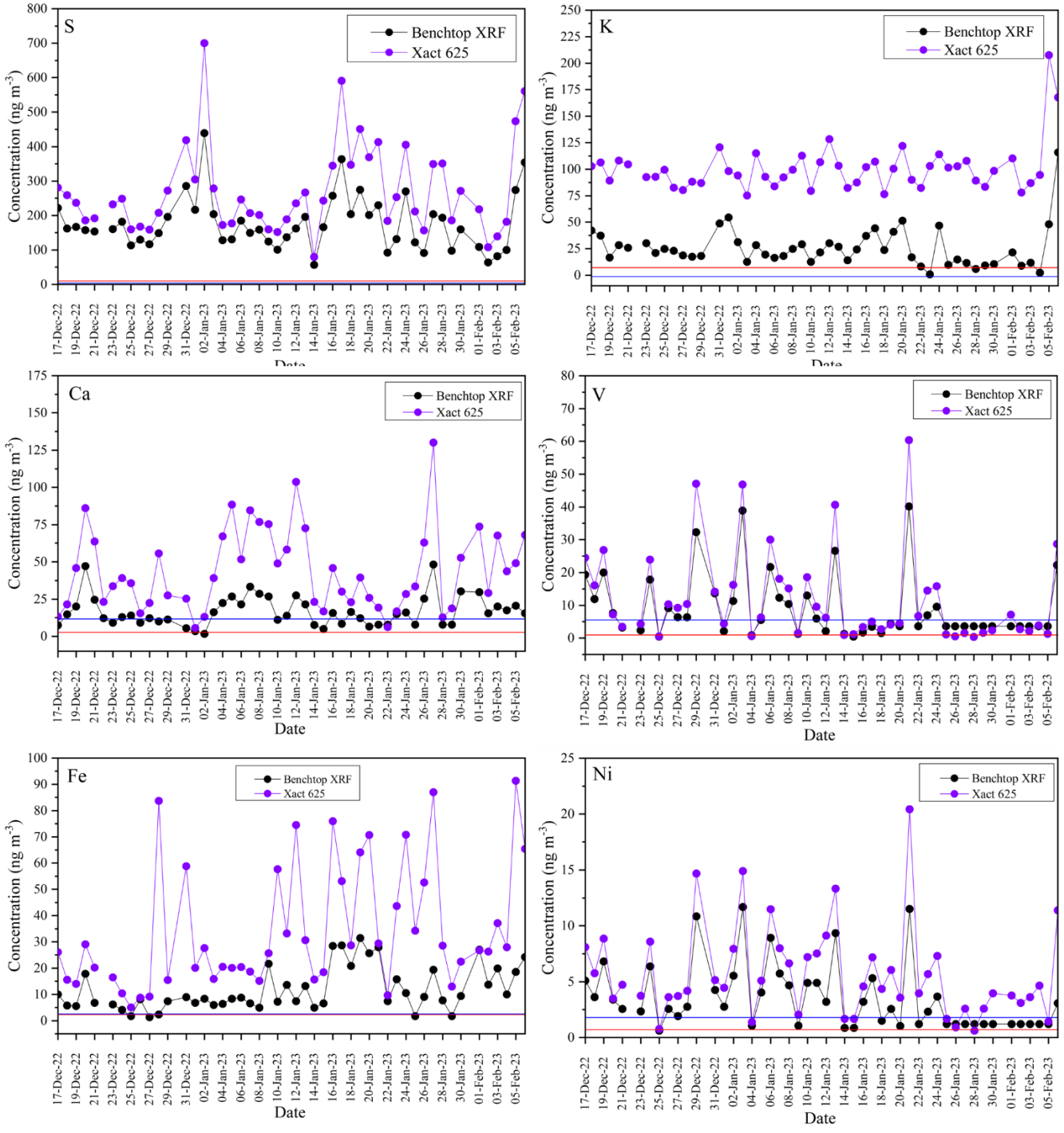
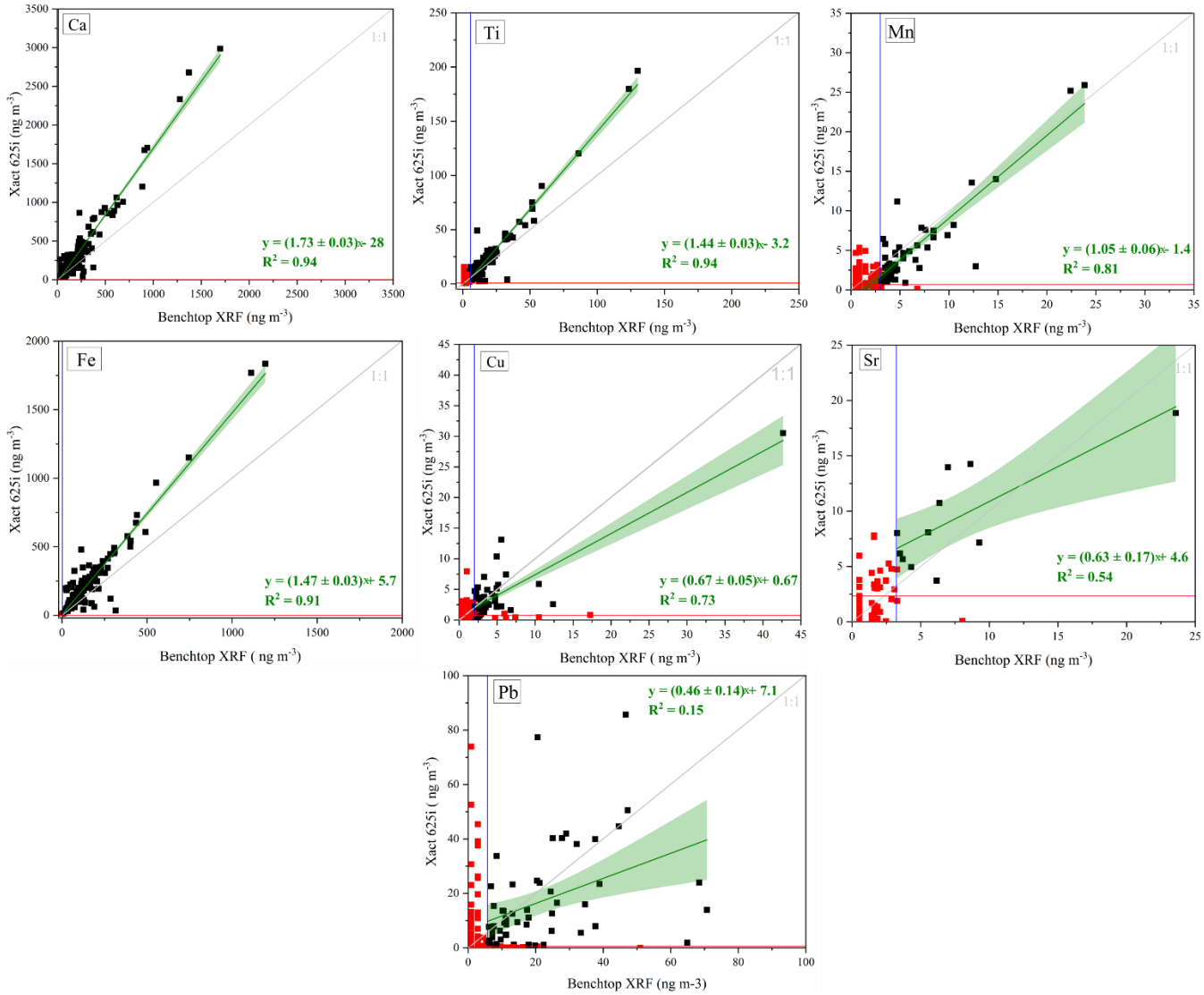


Figure S4: Time series graphs comparing S, K, Ca, V, Fe and Ni concentrations (ng m⁻³) from December 17, 2022 to February 06, 2023 for the for the DUB-P station. The blue lines indicate the LOQ threshold for the benchtop XRF spectrometer, while the red lines represent the corresponding threshold for the Xact 625i continuous elemental monitor. S and K concentrations are shown after quartz-filter correction.


Ca
y = (1.73 ± 0.03)x- 28
R² = 0.94
Ti
y = (1.44 ± 0.03)x- 3.2
R² = 0.94
Mn
y = (1.05 ± 0.06)x- 1.4
R² = 0.81
Fe
y = (1.47 ± 0.03)x+ 5.7
R² = 0.91
Cu
y = (0.67 ± 0.05)x+ 0.67
R² = 0.73
Sr
y = (0.63 ± 0.17)x+ 4.6
R² = 0.54
Pb
y = (0.46 ± 0.14)x+ 7.1
R² = 0.15
1:1
Xact 625i (ng m-3)
Benchtop XRF (ng m-3)
Benchtop XRF (ng m-3)
Benchtop XRF (ng m-3)
Benchtop XRF (ng m-3)
Benchtop XRF (ng m-3)
Xact 625i (ng m-3)
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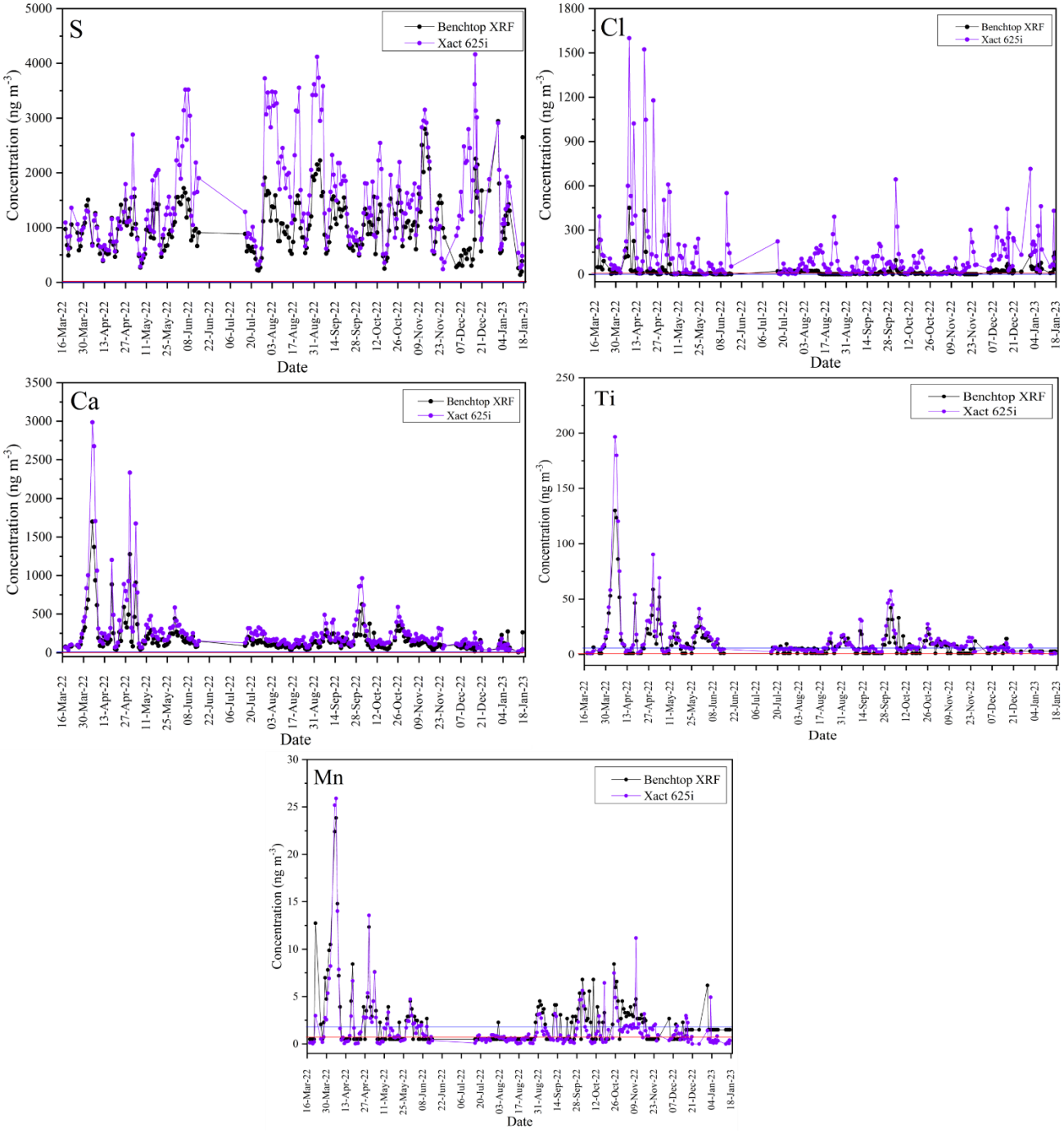


Figure S6: Time series graphs comparing S, Cl, Ca, Ti and Mn concentrations in ng m^{-3} from 18 March 2022 to 17 January 2023 for the CAO-NIC station. Concentrations for S and Cl are shown after applying the quartz-filter correction. The blue lines indicate the LOQ thresholds for the benchtop XRF spectrometer, while the red lines represent the corresponding thresholds for the Xact 625i continuous elemental monitor.

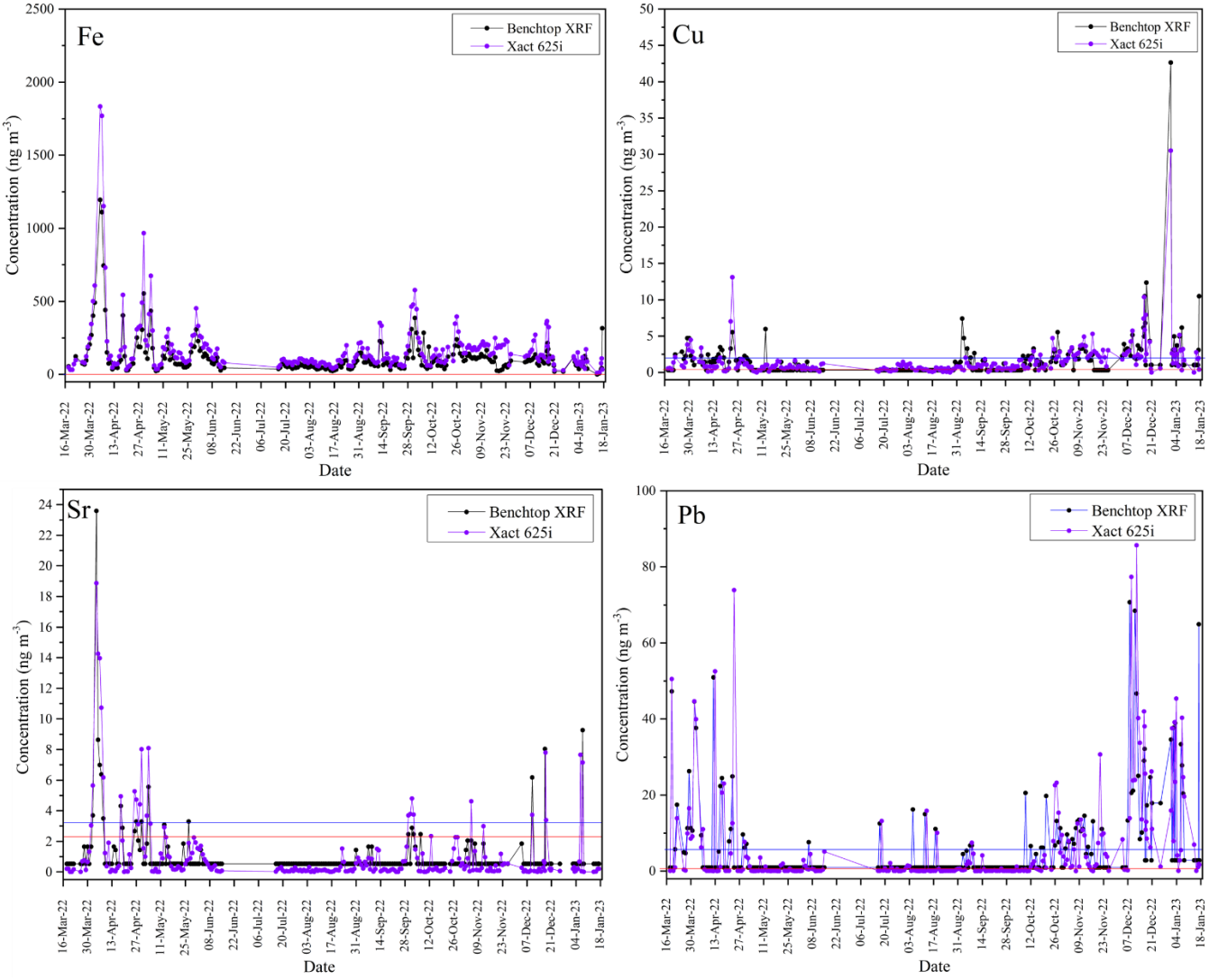


Figure S7: Time series graphs comparing Fe, Cu, Sr and Pb concentrations in ng m^{-3} from 18 March 2022 to 17 January 2023 for the CAO-NIC station. Concentrations for S and Cl are shown after applying the quartz-filter correction. The blue lines indicate the LOQ thresholds for the benchtop XRF spectrometer, while the red lines represent the corresponding thresholds for the Xact 625i continuous elemental monitor.