Supplementary Material

Intercomparison of online and offline XRF spectrometers for determining the elemental composition of ambient aerosol

Laura Cadeo[1], Beatrice Biffi[2], Benjamin Chazeau[3,4], Cristina Colombi[2], Rosario Cosenza[2], Eleonora Cuccia[2], Manousos-Ioannis Manousakas[3], Kaspar R. Daellenbach[3,*], André S. H. Prévôt[3], Roberta Vecchi[1,**]

[1]Department of Physics, Università degli Studi di Milano, Milan, 20133, Italy
[2]ARPA Lombardia, Milan, 20124, Italy
[3]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
[4]Aix Marseille Univ, LCE, Marseille, France

**Corresponding authors*: kaspar.daellenbach@psi.ch, roberta.vecchi@unimi.it

List of Tables

Table S1: XRF excitation conditions (voltage, current, tube filter, medium) for the measurements performed by Xact® 625i.

V [kV]	**I** [μA]	**Filter**	**Medium**	**Elements**
25	1300	Al	Air	Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Sn, Sb, Te, I, Cs, Ba
48	1000	Pd	Air	Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se Br, Nb, Pt, Au, Hg, Ti, Pb, Bi
48	1000	Cu	Air	Pd, Ag, Cd, In, Sn, Sb, Te

Table S2: Xact® 625i Minimum Detection Limits ($MDL_{1\sigma}$), provided by the manufacturer. Interference free one sigma detection limits at 68% Confidence Level ($C_{1\sigma}$) according to US EPA IO3.3 (1999) and Currie (1977).

$MDL_{1\sigma}$ [ng m^{-3}] for Xact® 625i							
Element	**Atomic number**	**Sampling/Analysis time (min)**					
		15	30	60	120	180	240
Al	13	840	290	100	35	19	12
Si	14	150	51	17.8	6.3	3.4	2.2
P	15	44	15	5.2	1.8	0.99	0.64
S	16	26	9.1	3.16	1.1	0.6	0.39
Cl	17	15	5	1.73	0.61	0.33	0.21
K	19	9.8	3.4	1.17	0.41	0.22	0.14
Ca	20	2.5	0.86	0.3	0.1	0.057	0.037
Ti	22	1.3	0.46	0.16	0.056	0.03	0.02
V	23	1	0.34	0.12	0.042	0.023	0.015
Cr	24	0.97	0.33	0.12	0.041	0.022	0.014
Mn	25	1.2	0.41	0.14	0.05	0.027	0.018
Fe	26	1.4	0.49	0.17	0.061	0.033	0.021
Co	27	1.1	0.39	0.14	0.049	0.026	0.017
Ni	28	0.78	0.27	0.1	0.034	0.018	0.012
Cu	29	0.65	0.23	0.079	0.028	0.015	0.01
Zn	30	0.55	0.19	0.067	0.023	0.013	0.008
Ga	31	0.48	0.17	0.059	0.021	0.011	0.007
Ge	32	0.46	0.16	0.056	0.02	0.011	0.007
As	33	0.52	0.18	0.063	0.022	0.012	0.008
Se	34	0.66	0.23	0.081	0.029	0.016	0.01
Br	35	0.85	0.3	0.1	0.037	0.02	0.013
Rb	37	1.6	0.55	0.19	0.068	0.037	0.024
Sr	38	1.8	0.62	0.22	0.076	0.041	0.027
Y	39	2.3	0.79	0.28	0.097	0.053	0.034
Zr	40	2.7	0.94	0.33	0.12	0.063	0.041
Cd	48	21	7.2	2.5	0.89	0.48	0.31
In	49	26	8.9	3.1	1.1	0.6	0.39
Sn	50	33	12	4.1	1.4	0.78	0.51
Sb	51	42	15	5.2	1.8	0.99	0.64
I	53	4.1	1.4	0.49	0.17	0.093	0.061
Ba	56	3.3	1.1	0.39	0.14	0.074	0.048
Hg	80	0.99	0.35	0.12	0.043	0.023	0.015
Tl	81	0.95	0.33	0.12	0.041	0.022	0.014
Pb	82	1	0.36	0.13	0.045	0.024	0.016
Bi	83	1.1	0.37	0.13	0.046	0.025	0.016

Table S3: XRF excitation conditions (voltage, current, tube filter, medium) for the measurements performed offline by ARPA Lombardia with the Epsilon 4 spectrometer.

V [kV]	**I** [μA]	**Filter**	**Medium**	**Elements**
9	1666	Ti	Helium	Al, Cl, P, S, Si
12	1250	Al 50 μm	Helium	Ca, K, Ti
50	300	Ag	Air	Cr, Mn, V
20	750	Al 200 μm	Air	Br, Cu, Fe, Ni, Pb, Rb, Sr, Zn

Table S4: Minimum Detection Limits ($MDL_{3\sigma}$) for the offline XRF analysis performed by ARPA Lombardia with the Epsilon 4 spectrometer and for online Xact® 625i (sampling/analysis time: 60 min)

Element	**$MDL_{3\sigma}$ [ng m^{-3}] for offline XRF**	**$MDL_{3\sigma}$ [ng m^{-3}] for online XRF**
Al	8.0	300
Si	4.0	53.4
P	2.0	15.6
S	13	9.48
Cl	25	5.19
K	3.0	3.51
Ca	6.0	0.9
Ti	5.0	0.48
V	0.3	0.36
Cr	2.0	0.36
Mn	0.5	0.42
Fe	3.0	0.51
Ni	0.3	0.3
Cu	1.0	0.24
Zn	0.4	0.20
Br	0.3	0.3
Rb	0.6	0.57
Sr	0.7	0.66
Pb	0.3	0.39

Table S5: Summary of the periods of interruption of the measurements lasting more than 12 hours. The start and end dates of the periods are given, together with the duration of the interruption, for both Xact® 625i hourly data and daily filters by ARPA Lombardia.

	Shutdown	Restart	Hours of stop
Xact® 625i	11/07/23 12:00	12/07/23 09:00	21
	16/07/23 15:00	17/07/23 10:00	19
	19/07/23 13:00	20/07/23 05:00	16
	26/07/23 13:00	27/07/23 09:00	20
	12/08/23 07:00	25/08/23 12:00	317
	13/09/23 07:00	14/09/23 14:00	31
	11/10/23 04:00	12/10/23 10:00	30
	14/10/23 07:00	16/10/23 09:00	50
	22/10/23 16:00	09/11/23 07:00	423
	05/12/23 22:00	12/12/23 08:00	154
	Shutdown	**Restart**	**Days of stop**
Daily filters	13/08/23	21/08/23	8
	15/10/23	16/10/23	1
	01/11/23	03/11/23	2

Table S6: Number of data points [%] with concentrations above MDL during the experimental campaign, for both Xact® 625i hourly measurements and daily filters measured by offline XRF.

Element	Xact	Offline XRF	Element	Xact	Offline XRF
	# data > MDL [%]	**# data > MDL** [%]		**# data > MDL** [%]	**# data > MDL** [%]
Al	64	100	As	98	-
Si	95	100	Se	64	-
P	0	100	Br	97	100
S	100	100	Rb	28	67
Cl	86	100	Sr	80	99
K	100	100	Y	1	-
Ca	100	100	Zr	56	-
Ti	100	93	Cd	0	-
V	24	95	In	0	-
Cr	99	83	Sn	7	-
Mn	99	100	Sb	0	-
Fe	100	100	I	0	-
Co	8	-	Ba	93	-
Ni	92	86	Hg	1	-
Cu	100	100	Tl	0	-
Zn	100	100	Pb	88	100
Ga	0	-	Bi	9	-
Ge	1	-			

Table S7: Overview of elemental concentrations detected by Xact® 625i and offline XRF (ng m^{-3}). Basic statistics (number of data; Mean, Standard Deviation, 25-50-75th percentile) of the collected data are reported separately for different periods.

Jul-Aug	**Xact® 625i** [ng m^{-3}]						**Offline XRF** [ng m^{-3}]					
Element	**N**	**Mean**	**SD**	**50th**	**25th**	**75th**	**N**	**Mean**	**SD**	**50th**	**25th**	**75th**
Al	491	555	337	454	368	619	49	275	232	180	117	363
Si	914	1031	1163	729	366	1225	49	836	612	588	384	1044
S	934	608	423	520	282	859	49	559	288	545	377	797
Cl	740	145	286	32	14	129	49	90	113	48	28	76
K	933	133	202	102	66	152	49	159	82	137	103	199
Ca	934	572	594	427	244	734	49	566	328	478	321	757
Ti	934	19	18	14	8.3	22	48	21	15	15	10	27
Cr	863	5.3	8.8	2.8	1.6	5.2	35	2.4	1.0	2.4	1.5	3.2
Mn	858	5.7	5.2	4.3	2.4	7.5	49	7.4	3.5	6.6	5.3	10
Fe	935	461	327	358	237	599	49	447	196	389	291	584
Ni	736	1.5	2.1	0.9	0.6	1.5	36	0.9	0.6	0.8	0.6	1.1
Cu	930	14	14	10	5.8	17	49	16	7.4	15	11	18
Zn	935	20	20	14	8.5	26	49	21	10	21	14	27
Br	892	3.5	2.6	3.1	2.0	4.5	49	3.9	1.5	4.2	3.0	4.9
Sr	740	2.7	2.6	2.1	1.3	3.3	49	2.9	1.5	2.5	1.7	4.0
Pb	688	5.7	11	2.4	1.1	6.2	49	5.5	4.0	4.3	2.6	7.3
Sept-Oct	**Xact® 625i** [ng m^{-3}]						**Offline XRF** [ng m^{-3}]					
Element	**N**	**Mean**	**SD**	**50th**	**25th**	**75th**	**N**	**Mean**	**SD**	**50th**	**25th**	**75th**
Al	836	822	645	610	438	949	59	363	318	278	106	527
Si	1076	2121	2538	1332	613	2580	60	1228	983	910	398	1906
S	1105	856	541	723	451	1175	60	699	410	610	353	942
Cl	927	149	244	54	24	174	60	166	126	118	98	172
K	1105	242	214	188	112	323	60	245	126	204	141	337
Ca	1106	792	582	692	347	1114	60	728	417	675	383	1061
Ti	1105	34	33	25	14	41	55	34	23	30	15	46
Cr	1105	10	11	6.3	3.8	11	49	6.7	3.7	5.3	4.0	9.6
Mn	1098	13	10	11	5.9	18	60	16	8.1	14	9.7	21
Fe	1106	1036	833	783	468	1328	60	998	509	1011	604	1231

Ni	1071	1.8	1.7	1.5	0.9	2.3	51	1.9	1.0	1.6	1.3	2.8
Cu	1105	35	49	19	11	37	60	39	21	35	24	48
Zn	1105	42	27	34	20	58	60	41	19	38	27	54
Br	1104	4.7	5.7	3.5	2.5	5.3	60	5.1	2.1	4.7	3.7	6.2
Sr	974	3.8	3.0	2.9	1.8	4.8	59	4.3	2.3	3.8	2.7	5.7
Pb	1053	14	21	6.8	3.0	16	60	16	11	14	7.3	21
Nov-Dec	**Xact® 625i** [ng m^{-3}]						**Offline XRF** [ng m^{-3}]					
Element	**N**	**Mean**	**SD**	**50th**	**25th**	**75th**	**N**	**Mean**	**SD**	**50th**	**25th**	**75th**
Al	390	593	298	512	379	688	40	125	82	98	63	191
Si	574	744	670	559	288	1019	40	531	333	423	278	811
S	653	455	460	336	185	567	40	423	294	339	221	584
Cl	646	302	330	203	83	418	40	177	116	145	104	215
K	652	287	235	260	149	382	40	295	160	260	186	358
Ca	653	537	486	389	195	742	40	496	281	453	260	731
Ti	653	17	13	13	7.4	23	35	20	12	18	10	27
Cr	651	10	10	7.5	4.0	13	37	9.7	7.5	7.2	5.2	12
Mn	648	12	9.1	9.9	5.3	17	40	15	8.3	13	9.0	20
Fe	653	976	793	752	457	1306	40	1015	608	819	565	1314
Ni	623	2.2	2.1	1.7	0.9	2.9	39	2.3	1.6	1.6	1.3	2.8
Cu	653	38	47	23	12	44	40	48	38	35	23	59
Zn	653	61	81	52	24	80	40	59	39	57	33	80
Br	612	5.4	8.0	3.8	2.1	6.4	40	5.8	6.5	4.4	3.1	7.4
Sr	450	4.1	24	2.3	1.4	3.6	40	3.7	4.1	2.8	2.0	4.2
Pb	622	12	14	8.4	3.9	14	40	14	9.1	12	7.1	22

Table S8: Mean relative uncertainties of both online measurements by Xact® 625i and offline XRF measurements by ARPA Lombardia.

Element	Uncertainty [%]	
	Xact® 625i	**Offline XRF**
Al	50	10
Si	30	10
S	10	10
Cl	30	30
K	10	10
Ca	10	10
Ti	20	20
Cr	30	30
Mn	30	10
Fe	10	10
Ni	50	30
Cu	10	10
Zn	10	10
Br	30	10
Sr	50	30
Pb	30	10

Figure List:

Figure S1: Timeline of the periods of interruption of the measurements, reported separately for different seasons, for both Xact® 625i hourly data and daily filters by ARPA Lombardia.

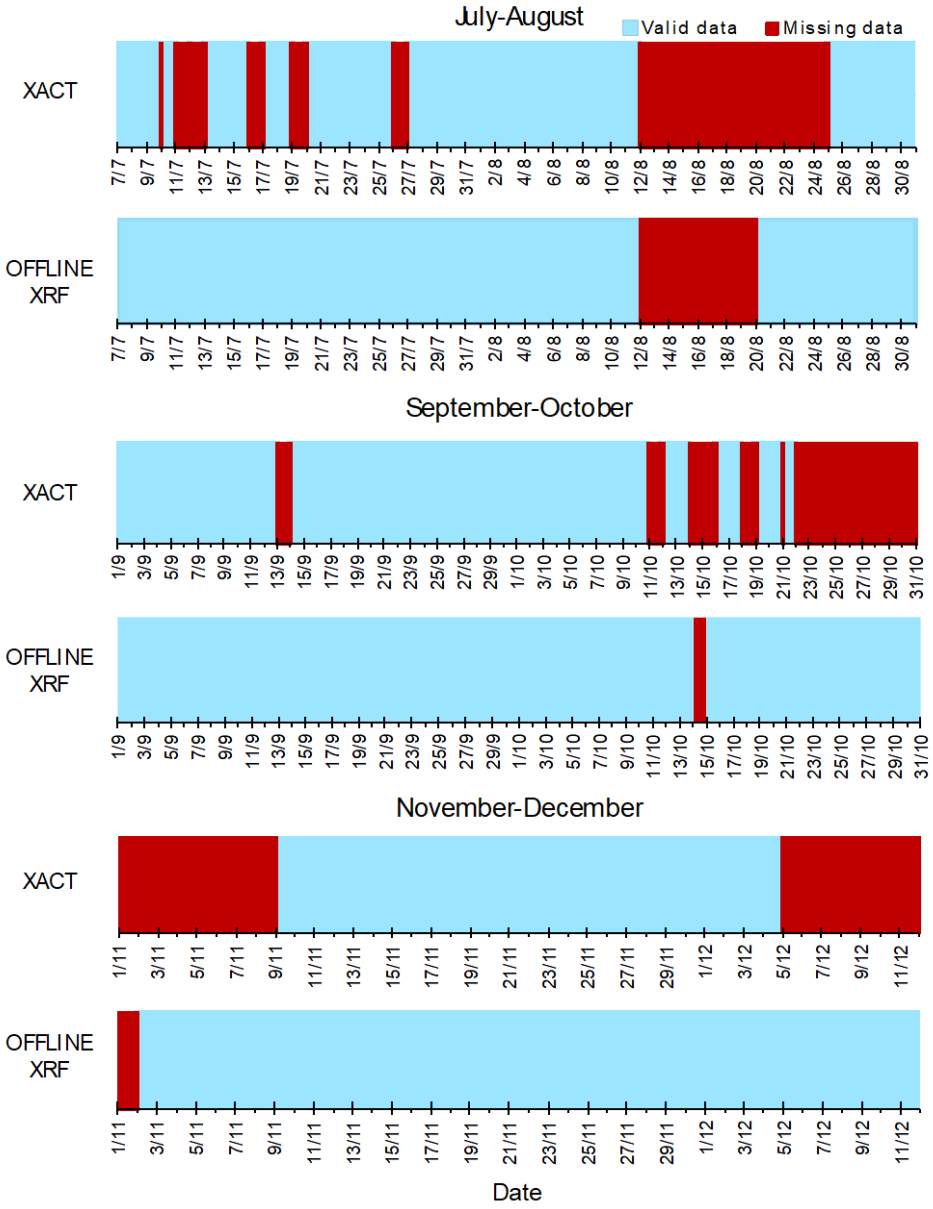


Figure S2: Scatterplots of the intercomparison between Xact® 625i data and offline XRF data for the elements V and Rb.

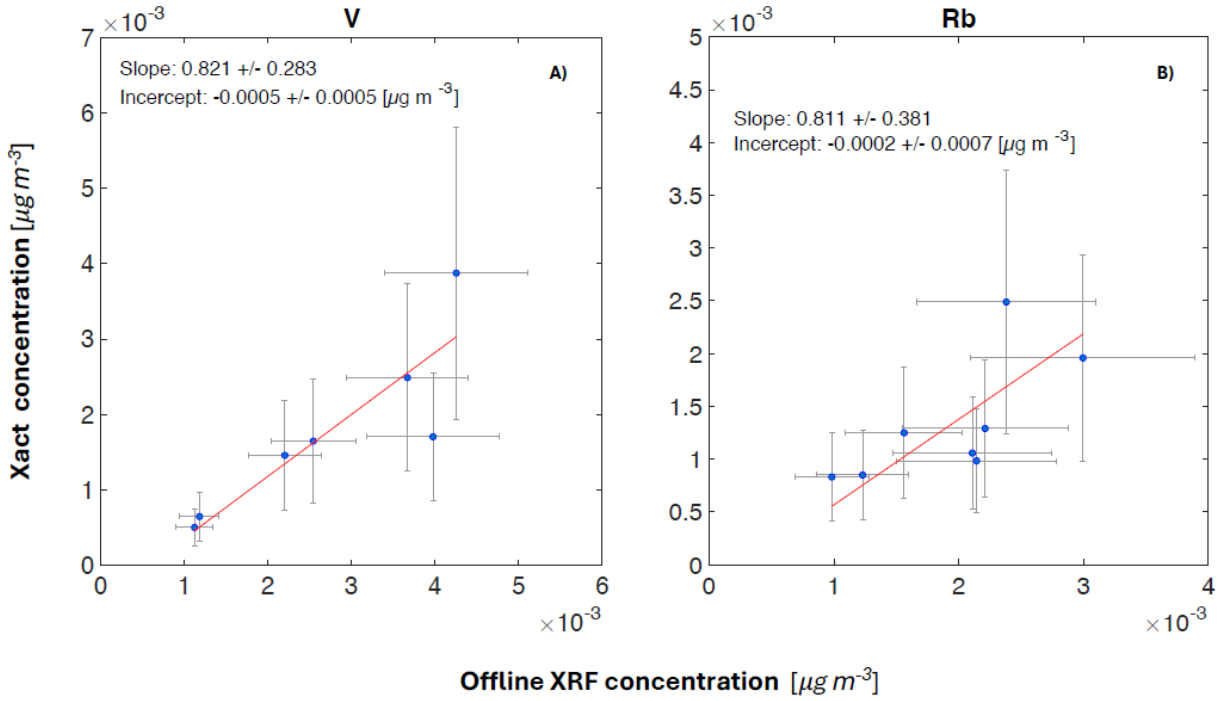


Figure S3: Time plots of the intercomparison between Xact® 625i data and offline XRF, Group A: K, Ca, Ti, Fe.

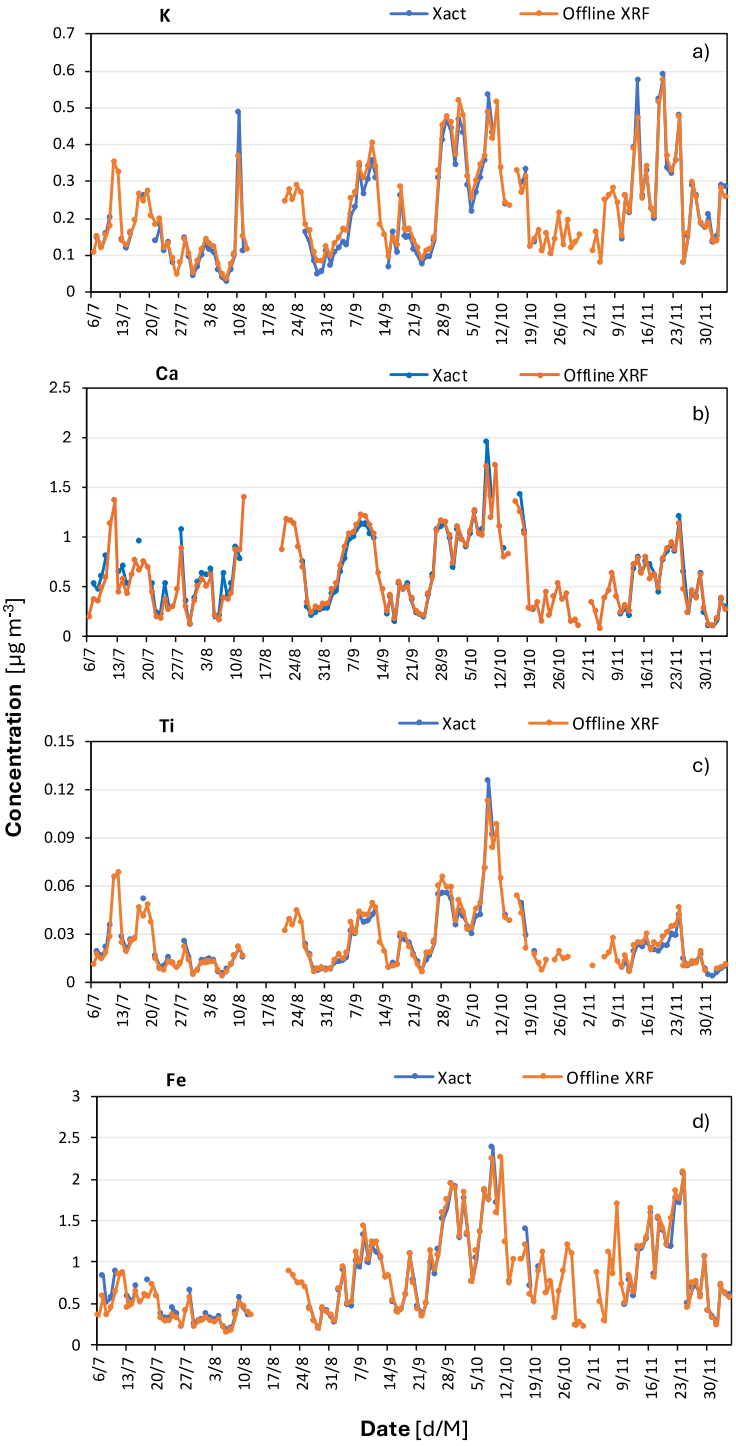


Figure S4: Time plots of the intercomparison between Xact® 625i data and offline XRF, Group A: Zn, Br, Sr, Pb.

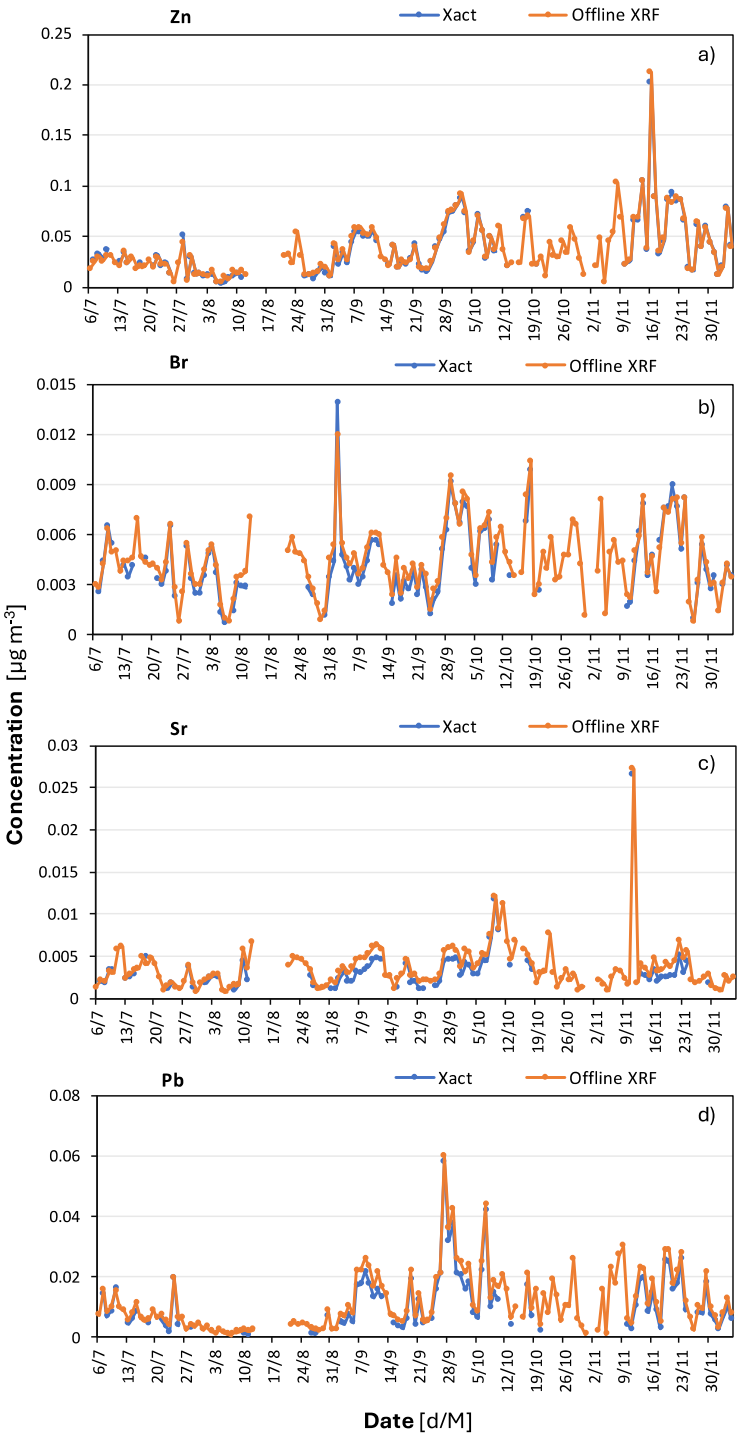
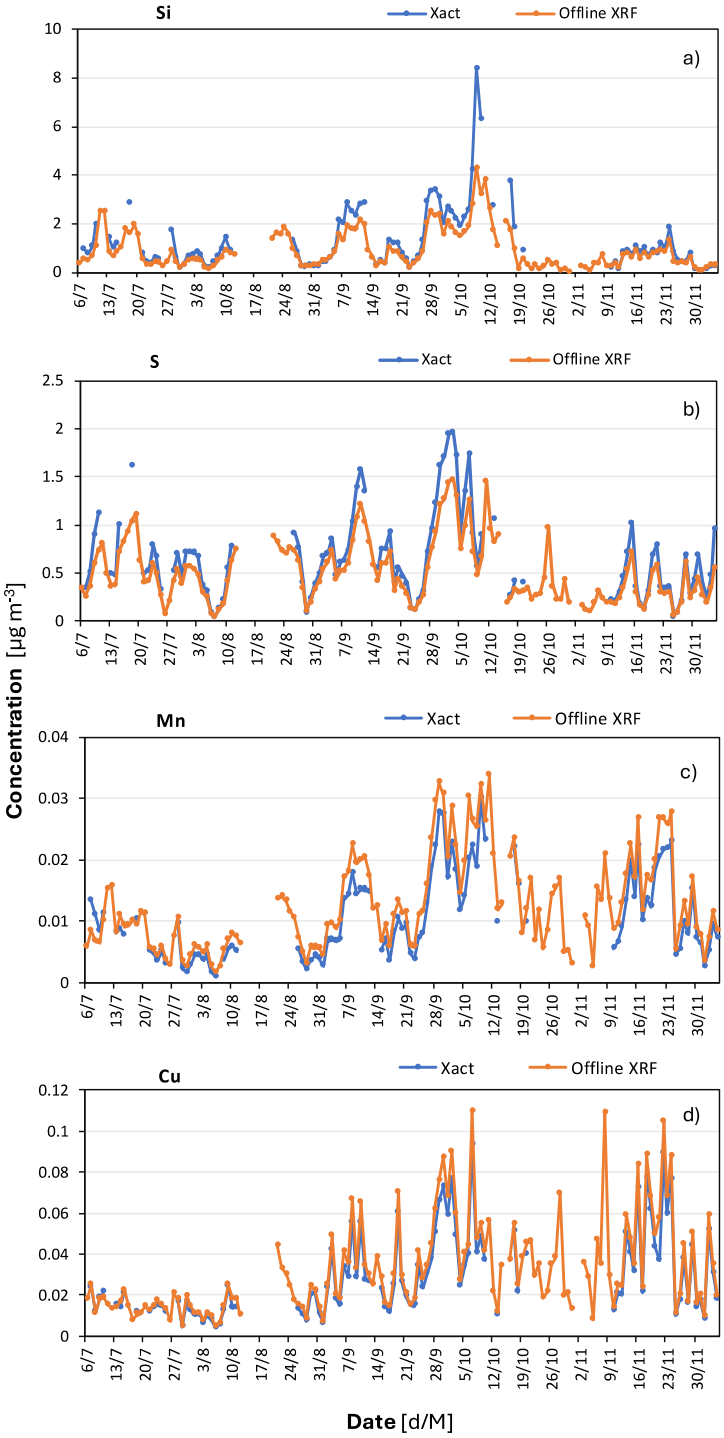
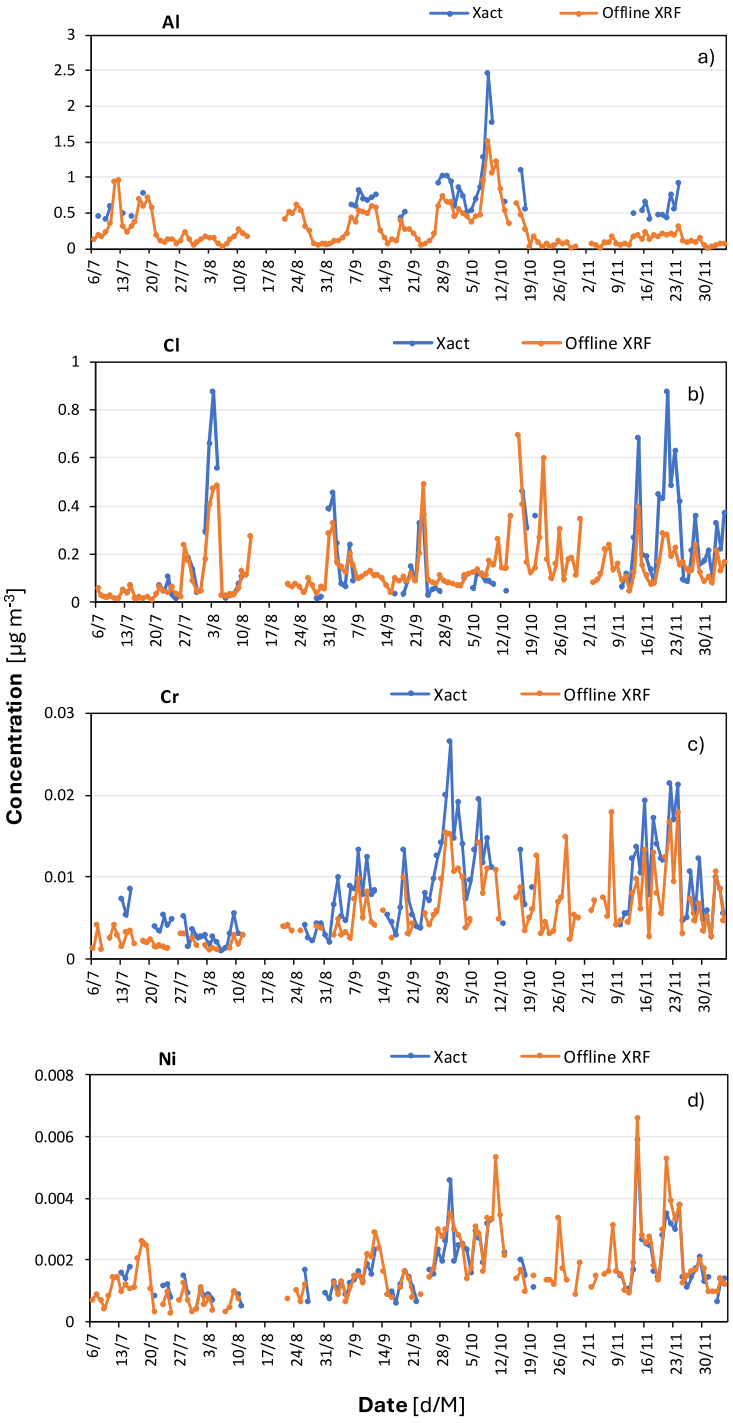


Figure S5: Time plots of the intercomparison between Xact® 625i data and offline XRF, Group B: Si, S, Mn, Cu.



124 **Figure S6**: Time plots of the intercomparison between Xact data and offline XRF, Group C: Al, Cl, Cr, Ni.



125

References

Currie, L.: Detection and quantification in X-ray fluorescence spectrometry. In: X-Ray fluorescence analysis of environmental samples, edited by: Dzubay, T. G., IX, Ann Arbor Science Publishers, 289–306, 1977.

U.S. EPA: Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, method IO-3.3, EPA/625/R-96/010a, https://www.epa.gov/sites/default/files/2019-11/documents/mthd-3-3.pdf, last access: June 1999.