S1. Ambient filter samples for method intercomparisons

A quarter each of three NABEL filters of the series analysed at IDAEA were also analysed with XRF at CES and with ICP-MS at ERG. This allows for an intercomparison between benchtop XRF and ICP-MS, between ICP-MS of two different laboratories, and between Xact XRF and benchtop XRF. The elements Zn, Sr, Cu, Pb, Fe, K, Ca, Mn, Se, and Ba were selected for this comparison. Benchtop XRF required no further sample preparation except punching a 47-mm piece of the original filter. IDAEA's digestion protocol is described in the main paper. Of three different filter blanks, blank 1 appeared contaminated and was not further considered, blanks 2 and 3 were averaged and subtracted from the analysis, but the values are not reported. ERG followed a protocol of the USEPA describing the multi-elemental determination of total metals by ICP-MS in ambient air samples collected on 47mm Teflon® filters following guidelines in EPA method IO-3.5 and EPA FEM Method "Standard Operating Procedure for the Determination of Lead in PM10 by Inductively Coupled Plasma Mass Spectrometry (ICPMS) with Hot Block Dilute Acid and Hydrogen Peroxide Filter Extraction" (EQL-0512-202). The filters were digested in a HotBlock™ for 2.5 hours using an extraction fluid containing 1.85% nitric acid (HNO_3), 0.5% hydrochloric acid (HCl), and 0.17% hydrofluoric acid (HF) with 0.33 mg/L of gold added for mercury stabilization. One aliquot of hydrogen peroxide (H_2O_2) was added after 1.5 hours of extraction and was allowed to effervesce. The extract was analyzed by ICP-MS and the data were collected using the manufacturer's software. The results are given in Table S1.

Table S1. Analyses of three ambient (NABEL) samples (1, 6 and 12 August 2015) from Härkingen. Comparisons of Xact and benchtop XRF (CES), benchtop XRF (CES) and ICP-MS (IDAEA and ERG), and ICP-MS at two laboratories (IDAEA and ERG). NR = not reported; BD = below limit of detection.

Sample	Element	Xact Daily Average (ng m^{-3})	CES XRF Results (ng m^{-3})	Background (ng cm^{-2})	IDAEA Results (ng m^{-3})	ERG Values (ng m^{-3})	Background (ng m^{-3})	% Difference							
								CES vs. IDAEA (CES - IDAEA) / IDAEA	Average CES vs. IDAEA	CES vs. ERG (CES - ERG) / ERG	Average CES vs. ERG	ERG vs. IDAEA (ERG - IDAEA) / IDAEA	Average ERG vs IDAEA	Xact vs. CES (Xact-CES)/CES	Average Xact vs. CES
Field_PSI_213	Zn	31.2	19.2	1.0	19.6	22.4	64.0	-1.9	-1.5	-14.2	-0.8	14.4	0.4	62.1	59.2
Field_PSI_218		25.4	16.5	1.0	15.8	15.9	64.0	4.2		3.5		0.7		53.9	
Field_PSI_224		30.4	18.8	1.0	20.2	17.4	64.0	-6.7		8.2		-13.7		61.4	
Field_PSI_213	Sr	NR	60.0	0.0	61.1	58.6	0.9	-1.9	-36.6	2.4	-32.5	-4.1	-8.3	NR	NR
Field_PSI_218		NR	1.5	0.0	2.0	1.9	0.9	-23.9		-18.4		-6.8		NR	
Field_PSI_224		NR	0.2	0.0	1.1	0.9	0.9	-84.0		-81.4		-14.0		NR	
Field_PSI_213	Cu	58.2	44.6	0.0	42.2	49.9	1.9	5.5	-0.1	-10.6	-15.2	18.0	17.8	30.5	50.6
Field_PSI_218		39.1	25.8	0.0	26.1	31.3	1.9	-1.3		-17.6		19.8		51.5	
Field_PSI_224		35.8	21.1	0.0	22.1	25.5	1.9	-4.5		-17.3		15.5		69.7	
Field_PSI_213	Pb	4.4	NR	0.0	4.4	4.5	8.7	NR	NR	NR	NR	2.2	-14.8	NR	NR
Field_PSI_218		4.3	NR	0.0	4.0	3.4	8.7	NR		NR		-15.5		NR	
Field_PSI_224		5.3	NR	0.0	4.6	3.2	8.7	NR		NR		-31.1		NR	
Field_PSI_213	Fe	757.1	529.7	33.6	465.5	479.4	74.9	13.8	12.4	10.5	9.7	3.0	2.5	42.9	35.6
Field_PSI_218		1021.1	805.4	32.8	685.4	732.4	74.9	17.5		10.0		6.9		26.8	
Field_PSI_224		906.6	661.6	32.9	624.7	609.7	74.9	5.9		8.5		-2.4		37.0	
Field_PSI_213	K	2640.7	2046.1	0.0	2263.0	2663.0	41.2	-9.6	9.7	-23.2	0.3	17.7	9.9	29.1	32.9
Field_PSI_218		225.8	194.2	0.0	143.0	156.4	41.2	35.8		24.2		9.4		16.3	
Field_PSI_224		209.5	136.7	0.0	133.0	136.7	41.2	2.8		0.0		2.8		53.2	
Field_PSI_213	Ca	213.5	172.1	12.9	160.6	795.5	190.0	7.2	4.7	-78.4	-27.6	395.4	135.6	24.1	38.6
Field_PSI_218		791.9	597.8	12.6	555.7	602.9	190.0	7.6		-0.9		8.5		32.5	
Field_PSI_224		517.9	324.9	12.7	327.2	336.9	190.0	-0.7		-3.6		3.0		59.4	
Field_PSI_213	Mn	7.3	8.3	0.1	4.3	5.8	1.4	94.7	57.5	42.3	25.5	36.9	24.6	-12.2	3.4
Field_PSI_218		12.3	11.9	0.1	8.1	9.7	1.4	46.9		22.8		19.6		3.1	
Field_PSI_224		11.1	9.3	0.1	7.1	8.4	1.4	30.9		11.5		17.3		19.3	
Field_PSI_213	Se	BD	BD	0.0	0.3	0.5	0.1	NR	168.8	NR	-13.3	64.0	105.1	NR	-25.5
Field_PSI_218		0.3	BD	0.0	0.4	0.5	0.1	NR		NR		41.3		NR	
Field_PSI_224		0.7	1.0	0.0	0.4	1.1	0.1	168.8		-13.3		210.0		-25.5	
Field_PSI_213	Ba	109.1	88.9	13.6	110.9	111.0	81.1	-19.8	-19.8	-19.9	-19.9	0.1	-33.2	22.7	22.7
Field_PSI_218		14.3	BD	13.3	10.7	8.5	81.1	NR		NR		-20.5		NR	
Field_PSI_224		9.2	BD	13.3	8.6	1.8	81.1	NR		NR		-79.0		NR	

The data shows a somewhat better comparison between offline XRF and ICP than between online XRF (Xact) and ICP, though the scatter in the relative differences (XRF-ICP/ICP) varied from -37 % (Sr) to +57 % (Mn), if Se and Ba, for which only one filter shows concentrations above the XRF detection limit, are not considered. Comparing the ICP-MS results between the two labs (ERG-IDAEA/IDAEA) shows a range from -33 % (Ba) to +25 % (Mn), when Se and Ca are not considered. Se concentrations are close to their ICP MDL and hence rather uncertain, while Ca shows a problem with one ERG measurement. If Ca and Se are excluded, the average relative difference between the two labs is -0.1 %, with a standard deviation of 19 %. The comparison of the daily averaged Xact values with the benchtop XRF values shows an average difference of 37 % (Xact-CES)/CES) for the elements Zn, Cu, Fe, K, Ca, and Mn, which is close to the observed mean difference to ICP. It is also consistent in the sense that all average differences Xact – CES for these elements are positive.

S2. Spiked filter samples for method intercomparisons

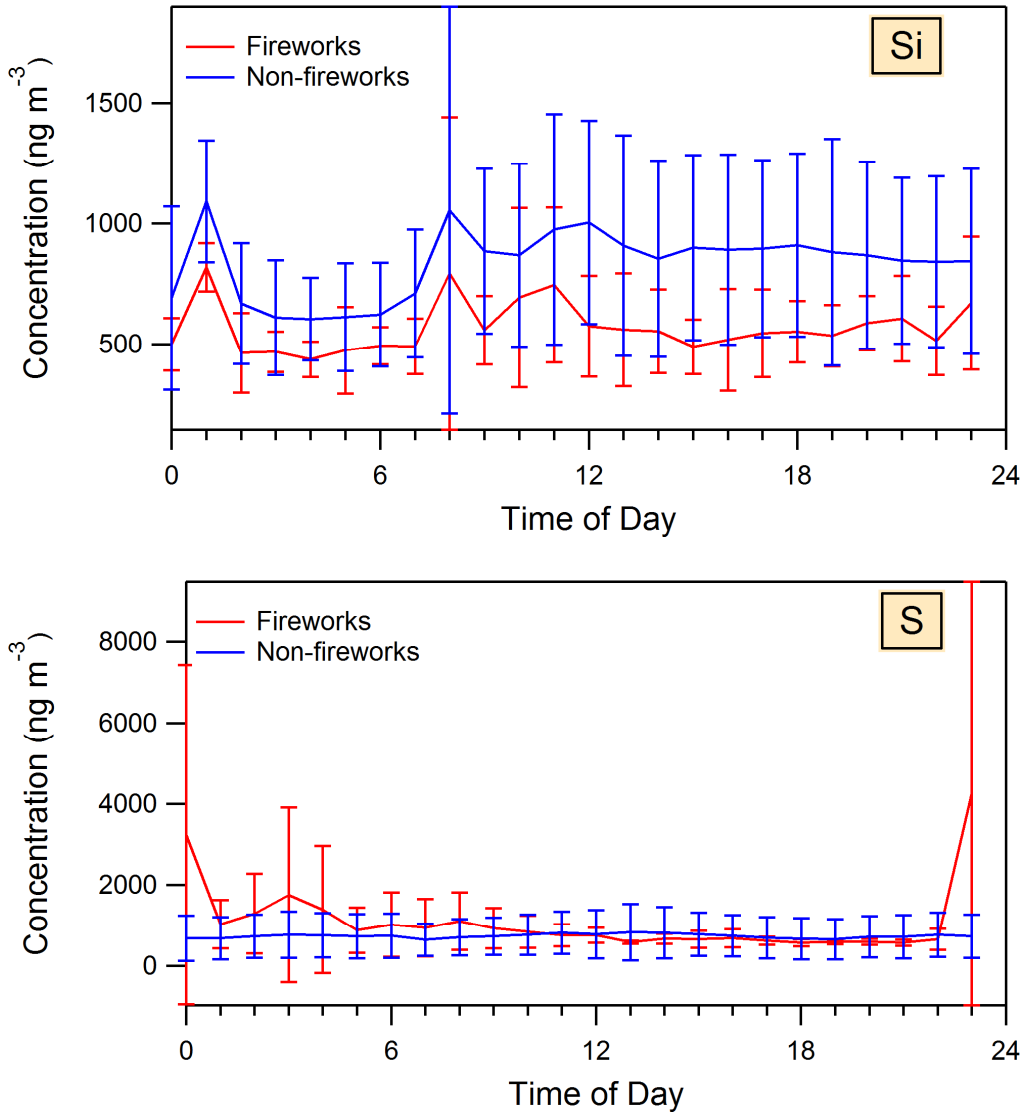
CES produced a set of six quartz filters coated with known amounts of the elements Zn, Sr, Cu, Pb, and Fe. These filters were analysed with a benchtop XRF instrument by CES, and three each of them were sent to IDAEA-CSIC, and ERG for analysis with ICP-MS. The results are presented in Table S2. Notice that Pb is not reported for XRF, because of large variations of the measured values for quartz filters. This indicates a problem with the XRF fitting routine for quartz filters, as the issue is not seen with Teflon filters.

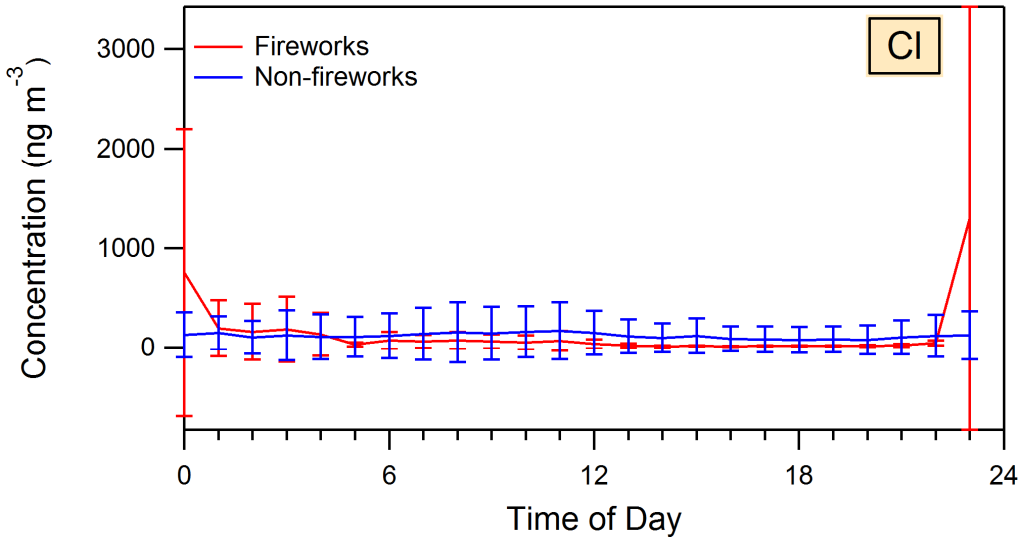
Table S2. Spiked filter analyses for five elements. Comparison between XRF and ICP-MS analyses performed at three independent laboratories.

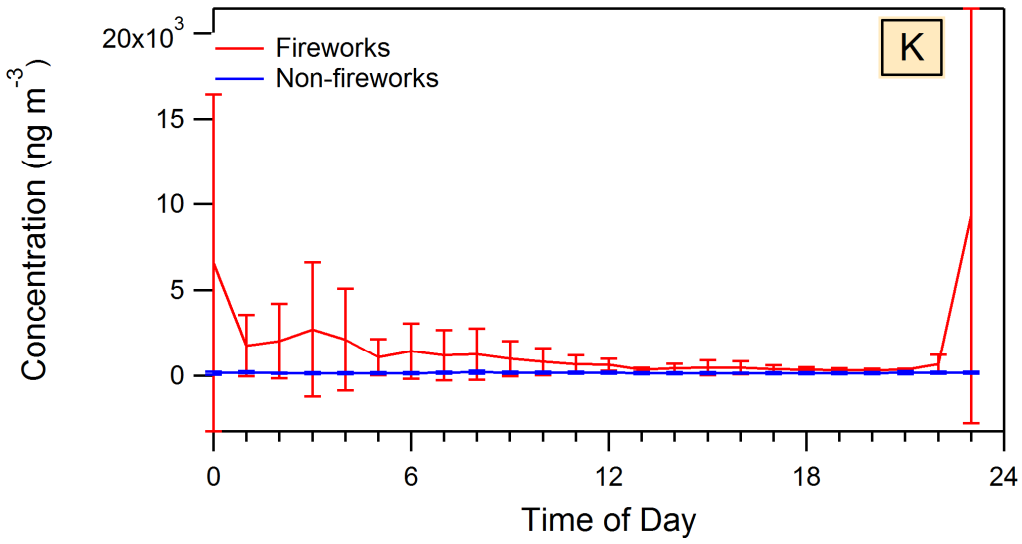
Sample Start Time	Sample	Element	CES			IDAEA	ERG		% Difference					Average Percent Difference				
			Spiked Conc. (ng cm^{-2})	XRF Conc. (ng cm^{-2})	Blank (ng cm^{-2})	Conc. (ng cm^{-2})	ERG Values (ng cm^{-2})	Blank (ng cm^{-2})	Spiked vs. CES (CES - spiked) / spiked	Spiked vs. IDAEA (IDAEA - spiked) / spiked	Spiked vs. ERG (ERG - spiked) / spiked	IDAEA vs. CES (CES - IDAEA) / IDAEA	ERG vs. CES (CES - ERG) / ERG	Spiked vs. CES (CES - spiked) / spiked	Spiked vs. IDAEA (IDAEA - spiked) / spiked	Spiked vs. ERG (ERG - spiked) / spiked	IDAEA vs. CES (CES - IDAEA) / IDAEA	ERG vs. CES (CES - ERG) / ERG
21.04.2016 11:50	PQ042116A	Zn	97.4	88.1	10.2	133.1			-9.6	36.6		-33.8		-9.7	32.0	22.4	-30.3	-24.6
21.04.2016 12:25	PQ042116B		97.4	89.2	10.2	155.0			-8.4	59.1		-42.4						
21.04.2016 13:00	PQ042116C		97.4	83.5	10.2	97.7			-14.3	0.3		-14.5						
21.04.2016 15:13	PQ042116D		97.4	88.3	10.2		104.1	30.7	-9.3		6.8		-15.1					
21.04.2016 15:46	PQ012116E		97.4	92.4	10.2		123.2	30.7	-5.1		26.4		-25.0					
21.04.2016 16:19	PQ042116F		101.5	90.2	10.2		136.0	30.7	-11.2		34.0		-33.7					
21.04.2016 11:50	PQ042116A	Sr	206.0	191.6		178.6			-7.0	-13.3		7.3		-6.2	-15.7	-7.0	12.7	0.8
21.04.2016 12:25	PQ042116B		206.0	194.0		194.5			-5.8	-5.6		-0.2						
21.04.2016 13:00	PQ042116C		206.0	193.9		147.8			-5.9	-28.2		31.1						
21.04.2016 15:13	PQ042116D		206.0	191.6			190.5	1.5	-7.0		-7.5		0.5					
21.04.2016 15:46	PQ012116E		206.0	194.0			189.8	1.5	-5.8		-7.9		2.2					
21.04.2016 16:19	PQ042116F		206.0	193.9			194.6	1.5	-5.9		-5.5		-0.3					
21.04.2016 11:50	PQ042116A	Cu	127.6	108.1		111.9			-15.3	-12.3		-3.4		-13.6	-17.0	5.8	5.9	-18.2
21.04.2016 12:25	PQ042116B		127.6	110.6		117.8			-13.3	-7.7		-6.1						
21.04.2016 13:00	PQ042116C		127.6	111.9		87.9			-12.3	-31.1		27.2						
21.04.2016 15:13	PQ042116D		127.6	108.1	0.8		131.2	1.3	-15.3		2.8		-17.6					
21.04.2016 15:46	PQ012116E		127.6	110.6	0.8		129.4	1.3	-13.3		1.4		-14.5					
21.04.2016 16:19	PQ042116F		127.6	111.9	0.8		144.3	1.3	-12.3		13.1		-22.5					
21.04.2016 11:50	PQ042116A	Pb	20.5	NR		22.6			NR	10.3		NR		NR	32.4	57.7	NR	NR
21.04.2016 12:25	PQ042116B		20.5	NR		37.9			NR	84.7		NR						
21.04.2016 13:00	PQ042116C		20.5	NR		20.9			NR	2.1		NR						
21.04.2016 15:13	PQ042116D		20.5	NR			27.1	1.1	NR		32.0		NR					
21.04.2016 15:46	PQ012116E		20.5	NR			29.1	1.1	NR		41.8		NR					
21.04.2016 16:19	PQ042116F		20.5	NR			40.9	1.1	NR		99.4		NR					
21.04.2016 11:50	PQ042116A	Fe	3024.6	2759.6		2827.6			-8.8	-6.5		-2.4		-8.1	-3.6	-0.8	-2.1	-7.2
21.04.2016 12:25	PQ042116B		3024.6	2795.5		3543.9			-7.6	17.2		-21.1						
21.04.2016 13:00	PQ042116C		3024.6	2786.4		2377.9			-7.9	-21.4		17.2						
21.04.2016 15:13	PQ042116D		3024.6	2759.6	154.5		2901.2	140.5	-8.8		-4.1		-4.9					
21.04.2016 15:46	PQ012116E		3024.6	2795.5	154.5		2901.2	140.5	-7.6		-4.1		-3.6					
21.04.2016 16:19	PQ042116F		3024.6	2786.4	154.5		3202.9	140.5	-7.9		5.9		-13.0					

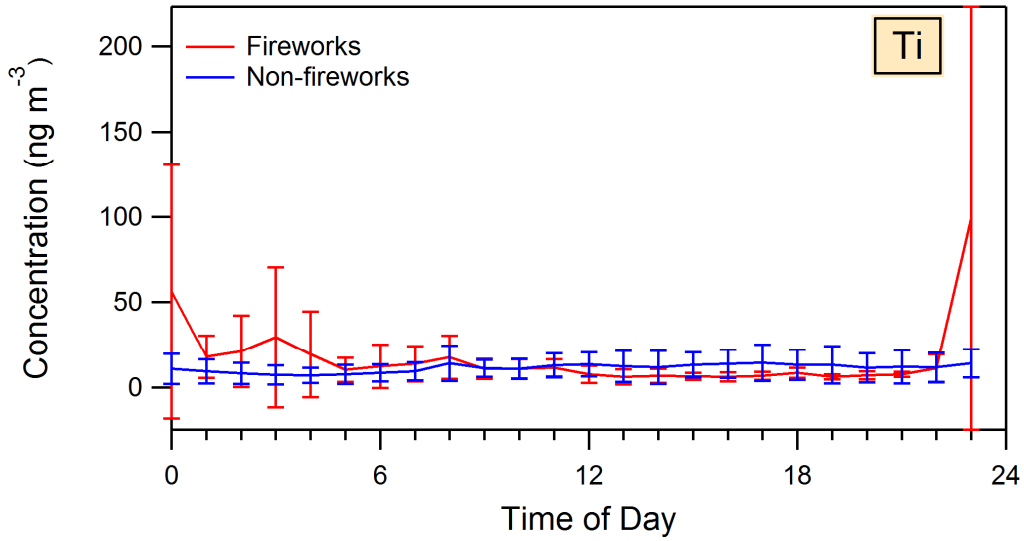
Tests with specifically produced reference samples of Fe, Cu, Zn, Sr, and Pb (Table S2) showed relative differences between the measured concentrations and the theoretically expected concentrations ranging from -6.2 % (Sr) to -13.6 % (Cu) for benchtop XRF, on average -9.4 % (without Pb). For all these elements, XRF underestimated the expected value, as expected for absorption of fluorescence radiation by the quartz fiber material (Tanner et al. 1974). ICP showed differences between -17 % and +32 % (average 5.6 %) for IDAEA-CSIC, and -7 % and +58 % (average 15.6 %) for ERG. The scatter is much larger than for the field samples, and differences can be positive or negative.

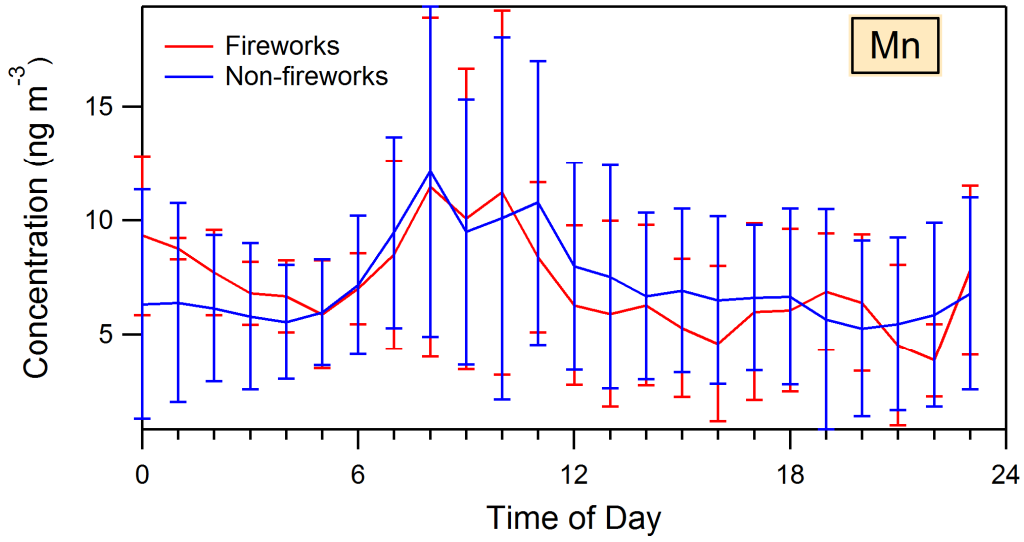
S3. Diurnal variations of elements for fireworks and non-fireworks periods

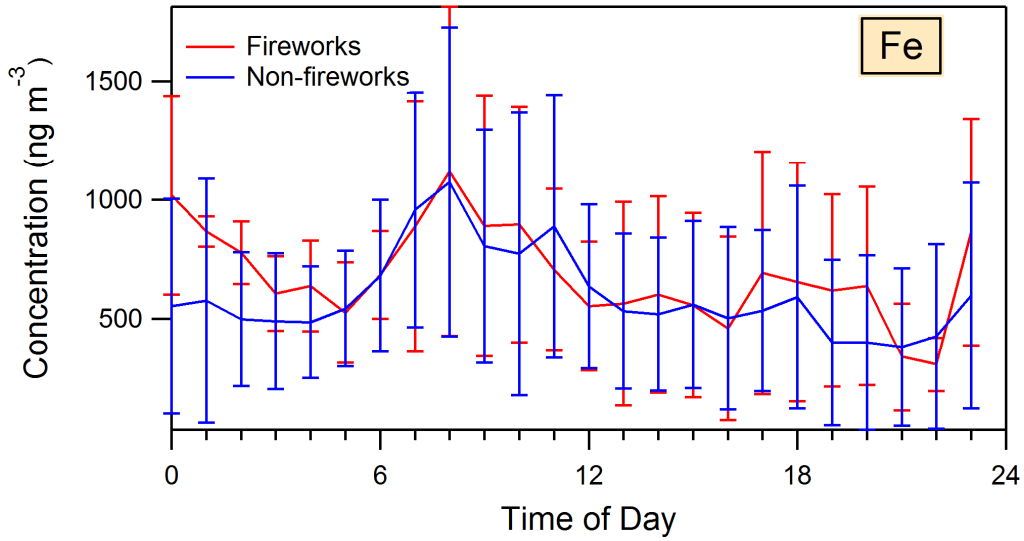


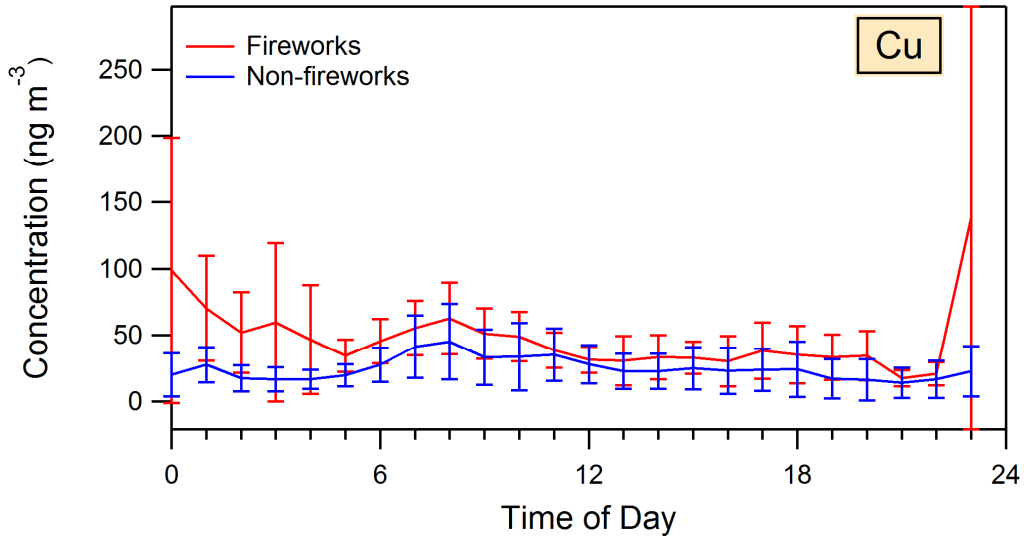

Cl
Fireworks
Non-fireworks
Concentration (ng m-3)
3000
2000
1000
0
0
6
12
18
24
Time of Day


K
Fireworks
Non-fireworks
Concentration (ng m-3)
20x10^3
15
10
5
0
0
6
12
18
24
Time of Day


Ti
Fireworks
Non-fireworks
Concentration (ng m-3)
200
150
100
50
0
0
6
12
18
24
Time of Day


Mn
Fireworks
Non-fireworks
Concentration (ng m-3)
15
10
5
0
6
12
18
24
Time of Day


Fe
Fireworks
Non-fireworks
Concentration (ng m-3)
1500
1000
500
0
6
12
18
24
Time of Day


Cu
Fireworks
Non-fireworks
Concentration (ng m-3)
250
200
150
100
50
0
0
6
12
18
24
Time of Day

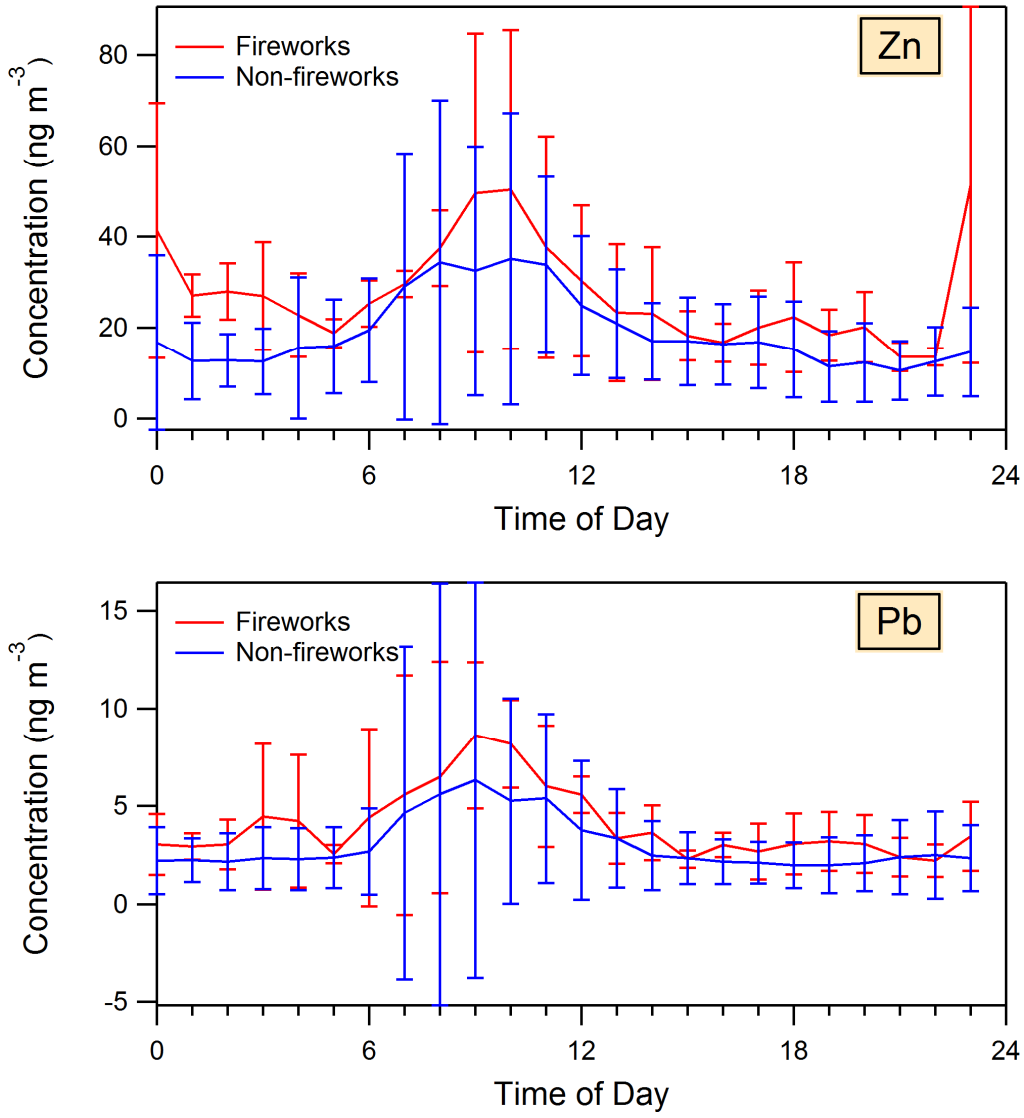
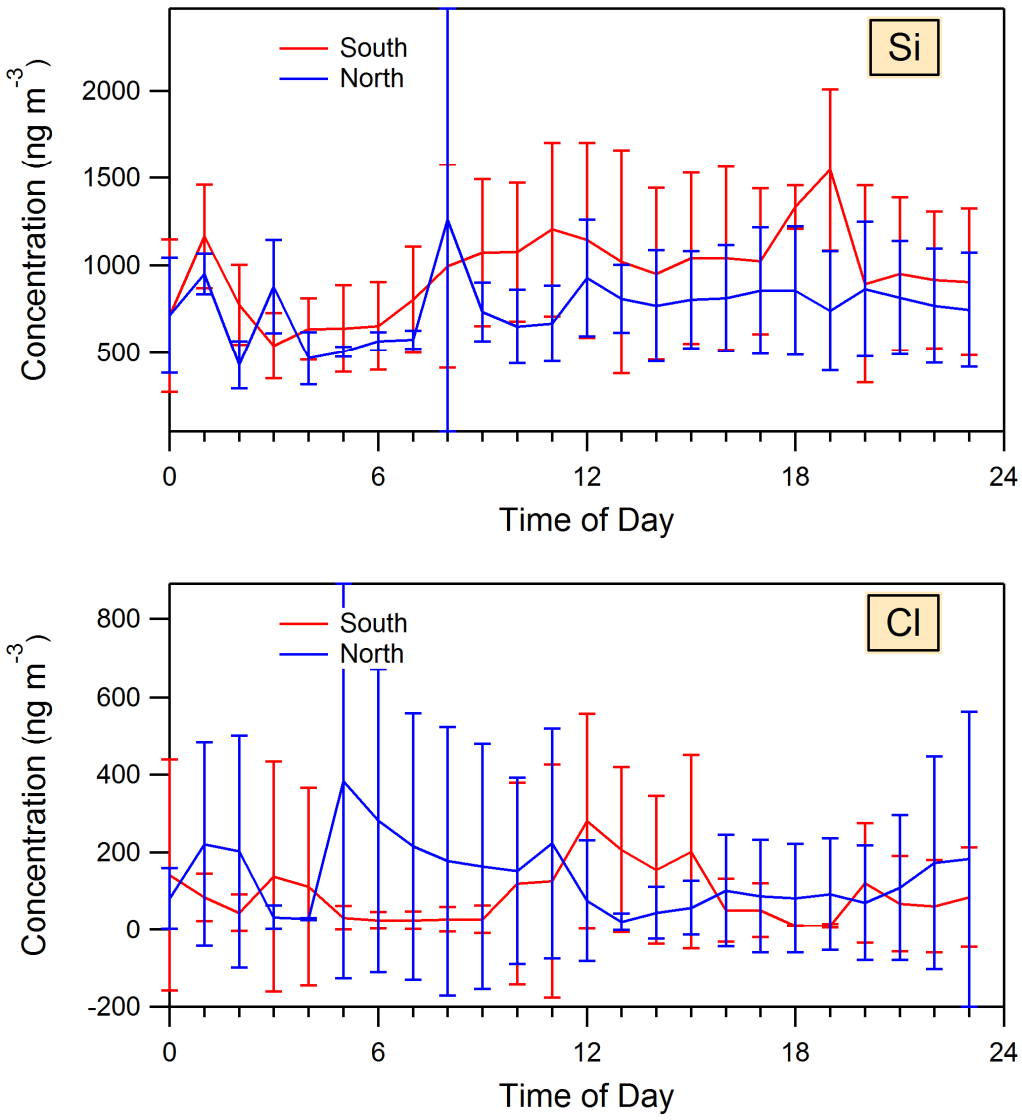
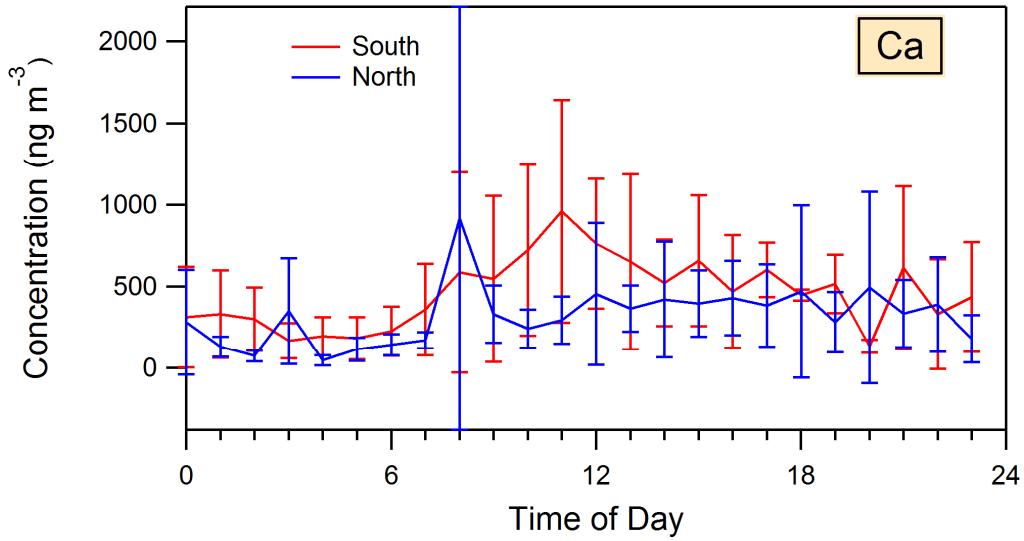
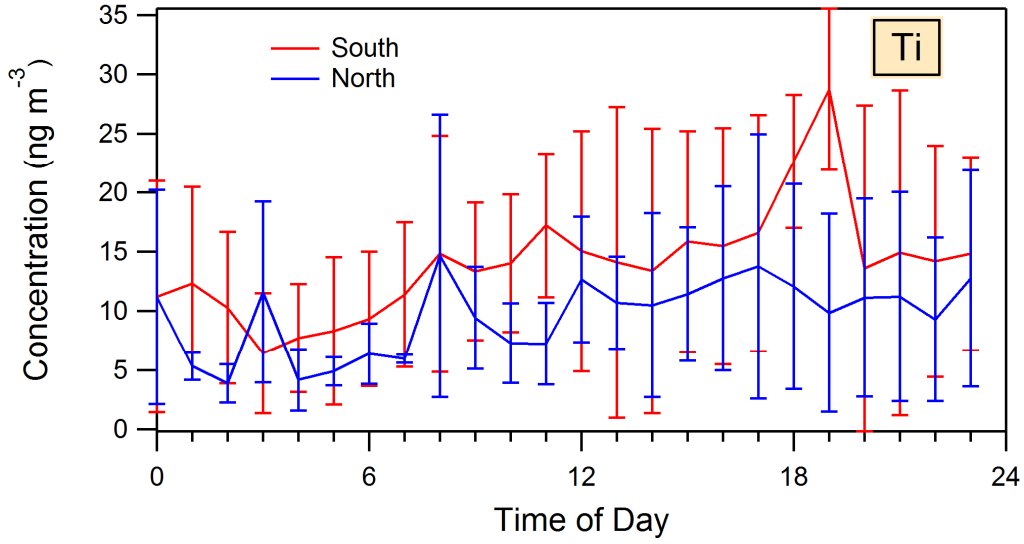


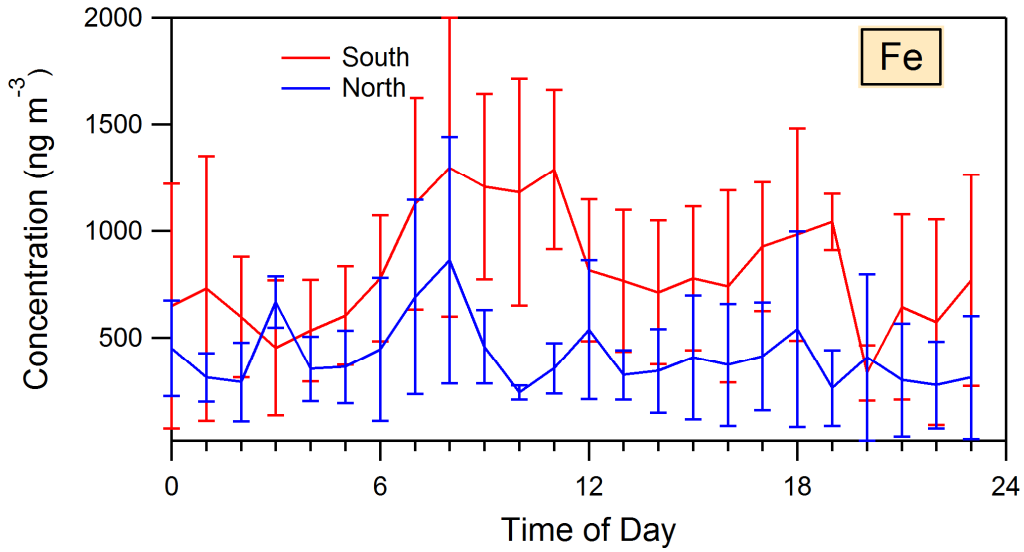
Figure S3: Diurnal variations of the Group A elements Si, S, Cl, K, Ti, Mn, Fe, Cu, Zn, and Pb. See Fig. 7.

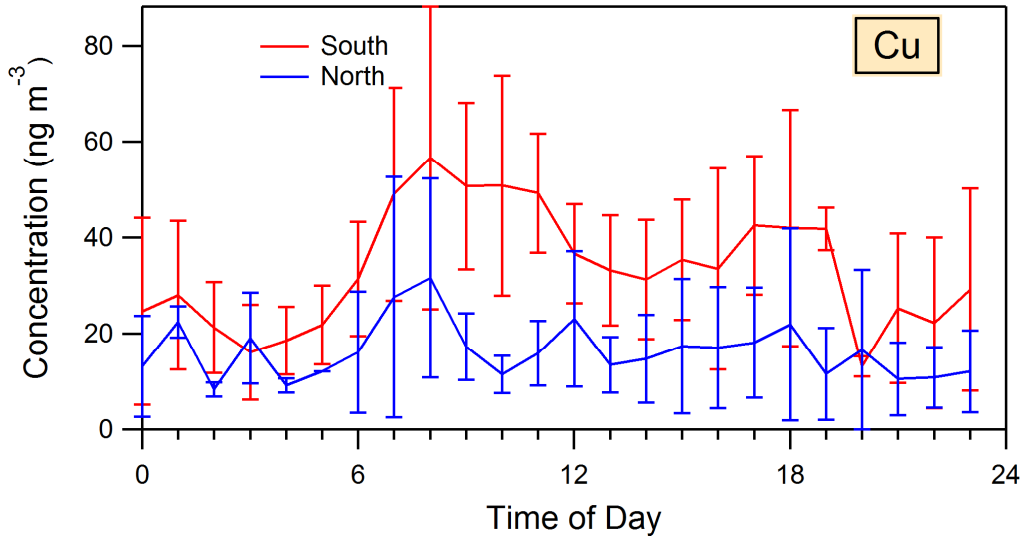
S4. Diurnal variations of elements for north and south wind sectors

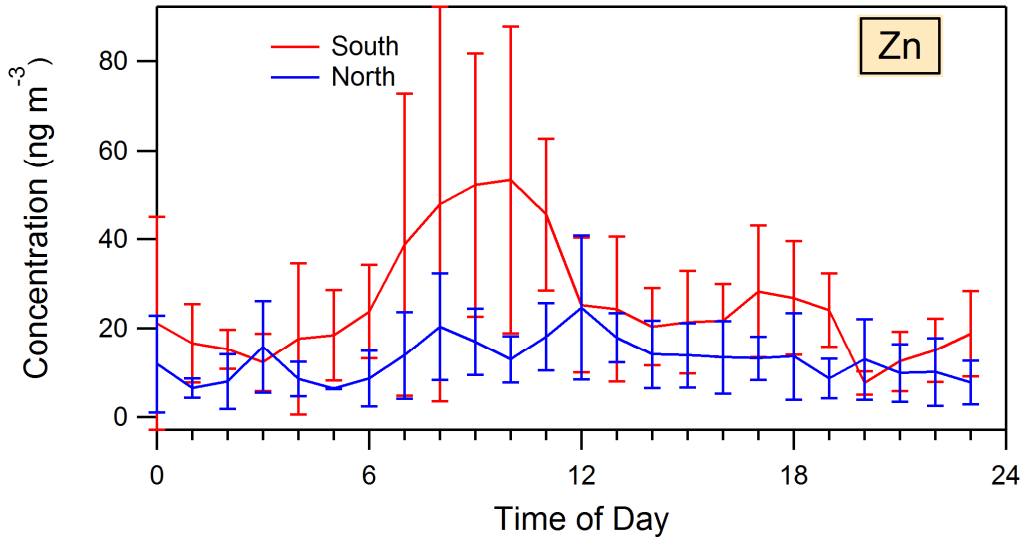


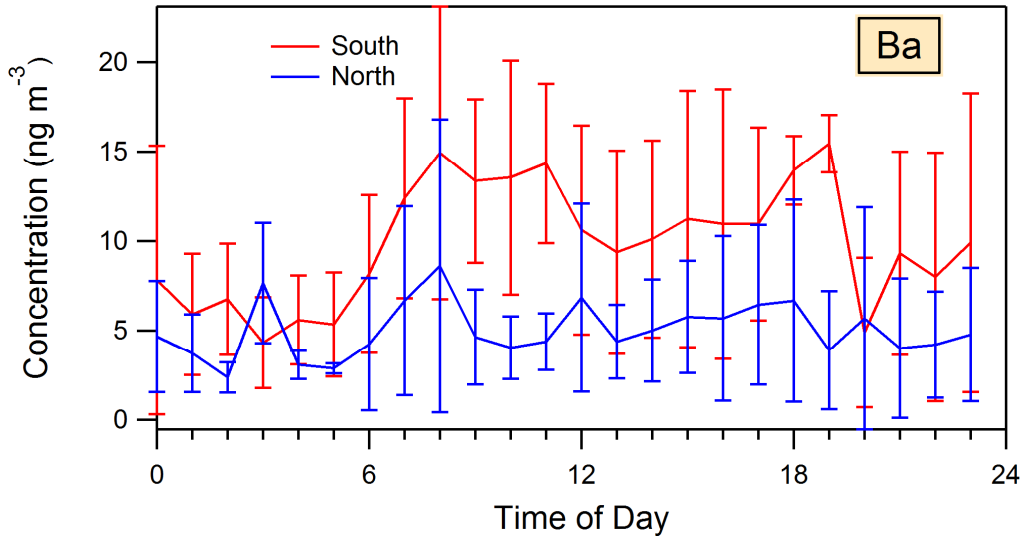

Ca
South
North
Concentration (ng m-3)
Time of Day
0
500
1000
1500
2000
0
6
12
18
24


Ti
South
North
Concentration (ng m-3)
Time of Day
0
5
10
15
20
25
30
35
0
6
12
18
24


Fe
South
North
Concentration (ng m-3)
2000
1500
1000
500
0
6
12
18
24
Time of Day


Cu
South
North
Concentration (ng m-3)
80
60
40
20
0
0
6
12
18
24
Time of Day


Zn
South
North
Concentration (ng m-3)
Time of Day
0
20
40
60
80
0
6
12
18
24


Ba
South
North
Concentration (ng m-3)
Time of Day
0
5
10
15
20
0
6
12
18
24

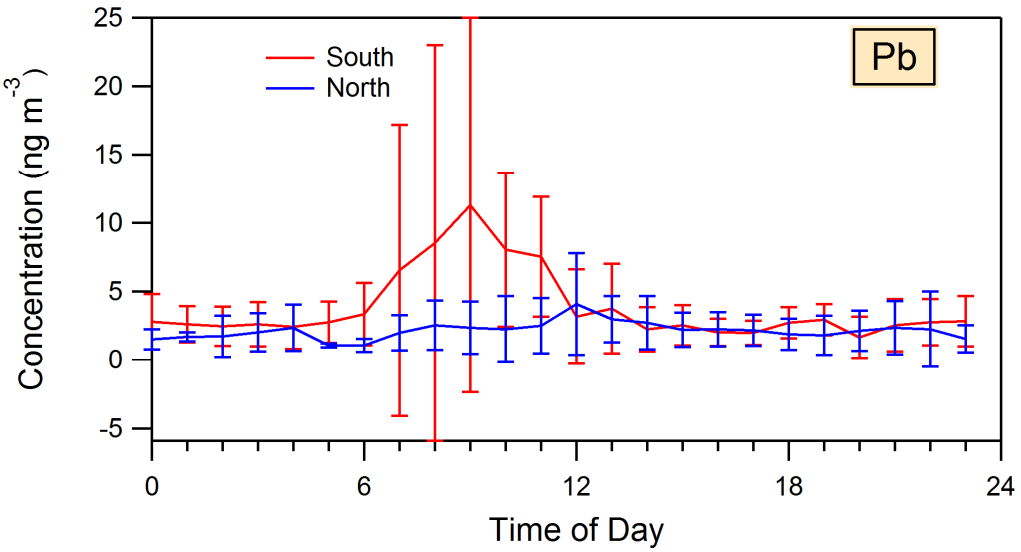


Figure S4: Diurnal variations of the Group A elements Si, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Ba, and Pb. South means a wind from the freeway towards the station. See Fig. 10.

Reference

Tanner, T. M., Young, J. A., and Cooper, J. A.: Multielement analysis of St. Louis aerosols by nondestructive techniques, Chemosphere, 3, 211-220, 1974.