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Elemental composition of ambient aerosols measured with high temporal resolution using an online XRF spectrometer

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S1. General statistics of Xact 625 data

Table S1: Data characteristics of Xact 625 measurements in Härkingen. Elements are sorted according to the groups in Table 1). Data were classified into fireworks and non-fireworks periods. The non-fireworks period was further classified into north (rural) and south (freeway) sectors according to the wind direction. Numbers in italics indicate cases where the daily averages were <MDL. The cases for the two wind sectors do not add up to the non-fireworks cases as wind data are missing for a total of 12 h (cf. Fig. 1).

	Non-Fireworks				Fireworks				South sector (non-fireworks)				North sector (non-fireworks)			
Element	avg	sdev	max	median	avg	sdev	max	median	avg	sdev	max	median	avg	sdev	max	median
	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}
# cases	370				86				173				185			
S	739	525	2508	602	1155	1667	12034	677	795	516	2254	660	712	537	2508	499
K	161	57	484	153	1661	3855	27349	494	176	61	395	169	151	50	484	145
Ca	391	385	3211	263	253	390	3109	141	474	476	3211	275	325	266	2254	253
Ti	11.4	8.1	43.4	8.8	18.3	36.2	282.2	8.0	13.1	8.9	39.6	11.1	10.3	7.2	43.4	8.2
Mn	7.1	4.6	27.0	5.7	7.3	3.9	22.2	7.0	9.5	5.1	27.0	8.6	5.0	2.8	21.0	4.7
Fe	587	429	2338	460	700	386	1909	700	852	453	2338	780	350	228	1309	304
Cu	24.1	17.7	109	20.1	49.3	48.7	372	38.9	35.5	18.3	109	30.7	13.5	8.5	49.0	9.9
Zn	18.7	16.8	143	14.3	28.6	18.9	104	23.4	26.1	20.8	143	20.7	12.3	8.0	66.1	10.7
Ba	7.1	5.5	25.3	5.3	75.4	169	1127	22.6	10.2	6.0	25.3	9.2	4.4	3.2	17.2	3.5
Pb	3.0	3.9	41.1	2.0	4.2	3.0	15.3	3.0	3.9	5.3	41.1	2.8	2.2	1.6	9.4	1.7
V	*0.06*	*0.15*	*1.22*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.07*	*0.18*	*1.22*	*0.00*	*0.05*	*0.13*	*0.89*	*0.00*
Cr	2.4	2.3	13	1.75	2.5	2.2	9.2	1.98	3.8	2.5	13	3.4	1.09	1.10	6.2	0.76
Co	*0.02*	*0.08*	*0.70*	*0.00*	*0.01*	*0.03*	*0.23*	*0.00*	*0.00*	*0.02*	*0.21*	*0.00*	*0.03*	*0.11*	*0.70*	*0.00*
Ni	0.62	0.65	10.3	0.54	0.56	0.35	1.95	0.51	0.64	0.45	4.0	0.59	0.61	0.81	10.3	0.50
As	*0.02*	*0.14*	*1.31*	*0.00*	*0.09*	*0.31*	*1.91*	*0.00*	*0.04*	*0.20*	*1.31*	*0.00*	*0.01*	*0.06*	*0.84*	*0.00*
Se	*0.27*	*0.32*	*4.4*	*0.20*	*0.16*	*0.13*	*0.44*	*0.14*	*0.30*	*0.41*	*4.4*	*0.24*	*0.24*	*0.22*	*0.90*	*0.17*
Cd	*6.8*	*3.6*	*23.6*	*6.2*	*6.5*	*3.1*	*21.3*	*6.1*	*6.9*	*3.7*	*19.1*	*6.3*	*6.7*	*3.6*	*23.6*	*6.2*
Sn	20.8	7.8	55.3	19.6	21.8	8.3	54.3	20.1	22.1	8.4	55.3	21.1	19.6	7.0	45.4	18.7
Sb	31.3	11.2	112	29.8	31.0	10.4	68.0	29.4	33.0	11.9	77.6	31.3	29.9	10.4	112	28.9
Hg	0.63	0.25	1.49	0.61	0.64	0.18	1.31	0.63	0.63	0.23	1.18	0.63	0.64	0.26	1.49	0.61
Bi	*0.07*	*0.12*	*0.70*	*0.00*	*1.27*	*3.8*	*23.5*	*0.15*	*0.09*	*0.13*	*0.50*	*0.00*	*0.04*	*0.10*	*0.70*	*0.00*
Si	839	398	3415	714	570	224	1758	532	925	469	3415	796	775	309	2052	682
Cl	114	200	970	26.4	153	578	4455	18.1	88.0	161	871	19.8	116	211	970	30.5
Pt	*0.05*	*0.11*	*0.66*	*0.00*	*0.03*	*0.07*	*0.34*	*0.00*	*0.04*	*0.10*	*0.66*	*0.00*	*0.06*	*0.11*	*0.64*	*0.00*

S2. 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 47 mm 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^{-1} 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 S2.

Table S2. 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	19.2	1.0	19.6	22	64	-1.9	-1.5	-14.2	-0.8	14.4	0.4	62	59
Field_PSI_218		25	16.5	1.0	15.8	15.9	64	4.2		3.5		0.7		54	
Field_PSI_224		30	18.8	1.0	20	17.4	64	-6.7		8.2		-13.7		61	
Field_PSI_213	Sr	NR	60	0.0	61	59	0.9	-1.9	-37	2.4	-32	-4.1	-8.3	NR	NR
Field_PSI_218		NR	1.5	0.0	2.0	1.9	0.9	-24		-18.4		-6.8		NR	
Field_PSI_224		NR	0.2	0.0	1.1	0.9	0.9	-84		-81		-14.0		NR	
Field_PSI_213	Cu	58	45	0.0	42	50	1.9	5.5	-0.1	-10.6	-15.2	18.0	18	31	51
Field_PSI_218		39	26	0.0	26	31	1.9	-1.3		-17.6		20		51	
Field_PSI_224		36	21	0.0	22	26	1.9	-4.5		-17.3		15.5		70	
Field_PSI_213	Pb	4.4	NR	0.0	4.4	4.5	8.7	NR	NR	NR	NR	2.2	-15	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		NR	
Field_PSI_213	Fe	757	530	34	465	479	75	13.8	12.4	10.5	9.7	3.0	2.5	43	36
Field_PSI_218		1021	805	33	685	732	75	17.5		10.0		6.9		27	
Field_PSI_224		907	662	33	625	610	75	5.9		8.5		-2.4		37	
Field_PSI_213	K	2641	2046	0.0	2263	2663	41	-9.6	9.7	-23	0.3	17.7	9.9	29	33
Field_PSI_218		226	194	0.0	143	156	41	36		24		9.4		16.3	
Field_PSI_224		210	137	0.0	133	137	41	2.8		0.0		2.8		53	
Field_PSI_213	Ca	214	172	12.9	161	796	190	7.2	4.7	-78	-28	395	136	24	39
Field_PSI_218		792	598	12.6	556	603	190	7.6		-0.9		8.5		32	
Field_PSI_224		518	325	12.7	327	337	190	-0.7		-3.6		3.0		59	
Field_PSI_213	Mn	7.3	8.3	0.1	4.3	5.8	1.4	95	57	42	26	37	25	-12.2	3.4
Field_PSI_218		12.3	11.9	0.1	8.1	9.7	1.4	47		23		19.6		3.1	
Field_PSI_224		11.1	9.3	0.1	7.1	8.4	1.4	31		12		17.3		19.3	
Field_PSI_213	Se	BD	BD	0.0	0.3	0.5	0.1	NR	169	NR	-13.3	64	105	NR	-25
Field_PSI_218		0.3	BD	0.0	0.4	0.5	0.1	NR		NR		41		NR	
Field_PSI_224		0.7	1.0	0.0	0.4	1.1	0.1	169		-13.3		210		-25	
Field_PSI_213	Ba	109	89	13.6	111	111	81	-19.8	-19.8	-19.9	-19.9	0.1	-33	23	23
Field_PSI_218		14.3	BD	13.3	10.7	8.5	81	NR		NR		-21		NR	
Field_PSI_224		9.2	BD	13.3	8.6	1.8	81	NR		NR		-79		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 %. Similarly the agreement between each of the labs and bench top XRF is good as well. If Se and Ca are excluded the average percent difference between XRF and IDEA is 5.4 % while the difference between XRF and ERG is -3.1 %. 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. The benchtop XRF and the Xact are typically within 5 % when analysing the same standard. Further both benchtop XRF and Xact use the same type of fitting routine (with minor differences in the determination of spectral background), hence the most likely explanation for the difference between the Xact and the labs is differences due to sampling or sampling location.

S3. 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 S3. 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 S3. Spiked filter analyses for five elements. Comparison between XRF and ICP-MS analyses performed at three independent laboratories.

			CES			IDAEA	ERG		% Difference					Average Percent Difference				
Sample Start Time	Sample	Element	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	88	10.2	133			-9.6	37		-34		-9.7	32	22	-30	-25
21.04.2016 12:25	PQ042116B		97	89	10.2	155			-8.4	59		-42						
21.04.2016 13:00	PQ042116C		97	84	10.2	98			-14	0.3		-14.5						
21.04.2016 15:13	PQ042116D		97	88	10.2		104	31	-9.3		6.8		-15.1					
21.04.2016 15:46	PQ012116E		97	92	10.2		123	31	-5.1		26		-25					
21.04.2016 16:19	PQ042116F		102	90	10.2		136	31	-11		34		-34					
21.04.2016 11:50	PQ042116A	Sr	206	192		179			-7.0	-13.3		7.3		-6.2	-15.7	-7.0	12.7	0.8
21.04.2016 12:25	PQ042116B		206	194		194			-5.8	-5.6		-0.2						
21.04.2016 13:00	PQ042116C		206	194		148			-5.9	-28		31						
21.04.2016 15:13	PQ042116D		206	192			191	1.5	-7.0		-7.5		0.5					
21.04.2016 15:46	PQ012116E		206	194			190	1.5	-5.8		-7.9		2.2					
21.04.2016 16:19	PQ042116F		206	194			195	1.5	-5.9		-5.5		-0.3					
21.04.2016 11:50	PQ042116A	Cu	128	108		112			-15.3	-12.3		-3.4		-13.6	-17.0	5.8	5.9	-18.2
21.04.2016 12:25	PQ042116B		128	111		118			-13.3	-7.7		-6.1						
21.04.2016 13:00	PQ042116C		128	112		88			-12.3	-31		27						
21.04.2016 15:13	PQ042116D		128	108	0.8		131	1.3	-15.3		2.8		-17.6					
21.04.2016 15:46	PQ012116E		128	111	0.8		129	1.3	-13.3		1.4		-14.5					
21.04.2016 16:19	PQ042116F		128	112	0.8		144	1.3	-12.3		13.1		-22					
21.04.2016 11:50	PQ042116A	Pb	21	NR		23			NR	10.3		NR		NR	32	58	NR	NR
21.04.2016 12:25	PQ042116B		21	NR		38			NR	85		NR						
21.04.2016 13:00	PQ042116C		21	NR		21			NR	2.1		NR						
21.04.2016 15:13	PQ042116D		21	NR			27	1.1	NR		32		NR					
21.04.2016 15:46	PQ012116E		21	NR			29	1.1	NR		42		NR					
21.04.2016 16:19	PQ042116F		21	NR			41	1.1	NR		99		NR					
21.04.2016 11:50	PQ042116A	Fe	3025	2760		2828			-8.8	-6.5		-2.4		-8.1	-3.6	-0.8	-2.1	-7.2
21.04.2016 12:25	PQ042116B		3025	2795		3544			-7.6	17.2		-21						
21.04.2016 13:00	PQ042116C		3025	2786		2378			-7.9	-21		17.2						
21.04.2016 15:13	PQ042116D		3025	2760	155		2901	141	-8.8		-4.1		-4.9					
21.04.2016 15:46	PQ012116E		3025	2795	155		2901	141	-7.6		-4.1		-3.6					
21.04.2016 16:19	PQ042116F		3025	2786	155		3203	141	-7.9		5.9		-13.0					

Tests with specifically produced reference samples of Fe, Cu, Zn, Sr, and Pb (Table S3) 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). Similarly spiked teflon filters (not shown) also showed underestimation of the expected concentrations, though not as much as for the quartz filters. A statistical analysis revealed that at the 99 % confidence level only Cu showed a significant difference between the two filter types. ICP showed differences between -17 % and +32 % (average 5.6 %) for IDAEA-CSIC, and -7 % and +58 % (average 15.6 %) for ERG for quartz filters. The scatter is much larger than for the field samples, and differences can be positive or negative.

S4. Diurnal variations of elements for fireworks and non-fireworks periods

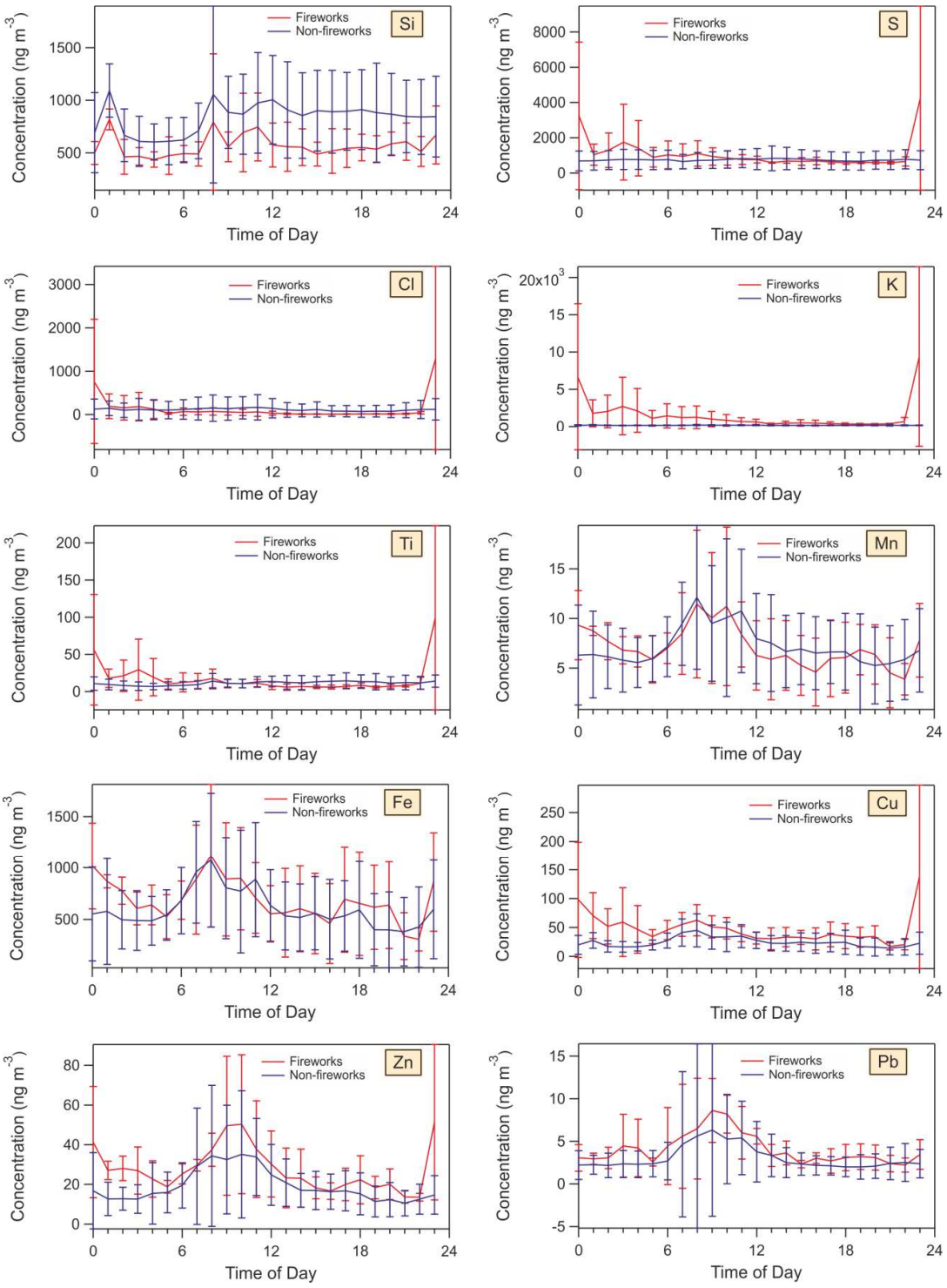

Figure S4: Diurnal variations of the Group A elements Si, S, Cl, K, Ti, Mn, Fe, Cu, Zn, and Pb. See Fig. 6.

S5. Diurnal variations of elements for north and south wind sectors

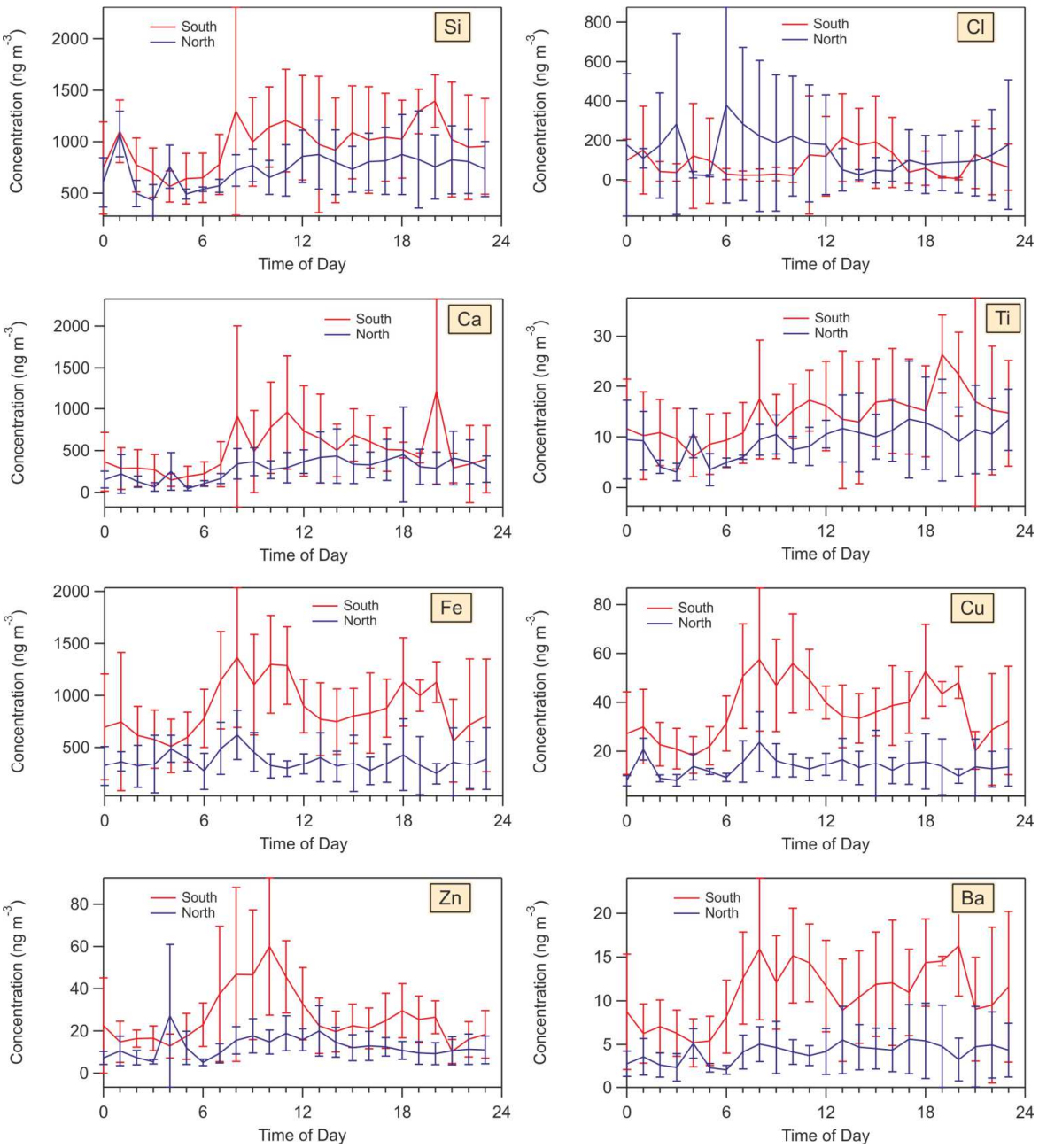

Figure S5: Diurnal variations of the Group A elements Si, Cl, Ca, Ti, Fe, Cu, Zn, and Ba. South means a wind from the freeway towards the station. See Fig. 8.

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.