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Atmospheric Measurement Techniques
Discussions
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Interactive comment on "Elemental composition of ambient aerosols measured with high temporal resolution using an online XRF spectrometer" *by* Markus Furger et al.

Markus Furger et al.

markus.furger@psi.ch

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(Referee's statements in italics)

The authors would like to thank the referee for thoughtful reading and critical commenting of the manuscript.

Issue 1: in the discussion of the level of agreement between the Xact 625 results with the other standard techniques, the Authors consider that some differences could be due the use of different sampling devices placed not exactly in the same position. My question is: why the substrates used in the Xact625 have not been analyzed off-line by other techniques? This would have removed any possible ambiguity related to

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different amount of sampled material...I have not found in the text any comment on this possibility. I consider a detailed discussion on this point absolutely necessary.

Good point. An offline analysis of the Xact sampling tape was not considered for two reasons: 1) Hourly samples do not collect sufficient mass for ICP analysis. 2) The samples collected are typically not amenable to post-sampling offline analysis due to potential for cross-contamination from sampled filter tape wound upon itself onto the filter wheel.

We added the following statement to the text in Section 2.3:

“While this approach is non-destructive, the samples collected are typically not amenable to offline analysis post-sampling due to potential for cross-contamination from sampled filter tape wound upon itself onto the filter wheel.”

Issue2: the Authors discuss quite in deep the differences in the PM composition in the two periods (with and without fireworks) of the campaign. I do not find in such discussion any new or general element which could deserve to stay in the text. I think that this falls outside the main focus of the paper and that most of this discussion should be moved to the on-line supplementary material (or maybe it should find space in some local report). On this point, see the punctual comments below.

Partly agreed. It was originally the goal to demonstrate the capabilities of the Xact in field research in Switzerland, and to show an application of Xact data for source apportionment. From all three reviewers’ comments we see that focussing on the first aspect was more desired than emphasizing the source apportionment. We therefore decided to shorten the source apportionment part, and to save part of the material for an upcoming publication. On the other hand, we elaborated the intercomparison part more deeply. This led to some re-writing of various parts of the manuscript, dropping two figures (Figs. 6 and 9), moving Table 1 to the supplementary material, and keeping the source apportionment part at a level demonstrating a few basic capabilities of the Xact data. We do, however, not agree with removing the whole Section 3.3 to the supplementary material, as it demonstrates important findings for operating the Xact. We instead condensed the section to the necessary, documenting the value of 1-h time resolution and the large dynamic range of the Xact (a concentration jump to 48 μg m^{-3} within an hour). A comparison of the Xact's and TEOM's peaks could demonstrate how closely the Xact elemental mass represents the total measured PM10 mass in this particular case. We consider this to be a significant finding of this study.

Punctual comments

Abstract, line 17: the wording "Xact PM10 mass" could be misleading since by ED-XRF just a small fraction of the elements presents in PM10 can be detected. I recommend to use "the total concentration of the elements detected by Xact in PM10"

Agreed. However, when condensing the abstract as suggested by Referee #1 this sentence was deleted from the abstract.

Abstract, line 19: Begin the statement with "Ten" instead of "10"

Done.

Introduction, line 38: replace "historically required" with "require"

Done.

Introduction, line 39: This is not true: there are well known methods (e.g.: streaker sampler + PIXE, DRUM impactor + SXRF) which provide hourly or even sub-hourly time resolution with very low MDL. The statement must be changed accordingly.

Agreed. We added the sentences and references at the appropriate place:

"For high time resolution, impactors are used where the sample is collected on a foil (e.g. a rotating drum impactor, Lundgren, 1967), or on a combination of an impactor plate and a filter, such as in a streaker sampler (e.g. Annegarn et al., 1992). These samples are then exposed to X-rays or a particle beam without further treatment, which provide quantitative data with low detection limits."

Page 2, line 3: replace "similar X ray facility" with "accelerator facilities"

Done.

Page 2, line 5: delete "overwhelming"

Done.

Page 2, line 10: the advantages offered by high time resolution have been discussed in literature well before the "older" reference given in the list. . .to my memory come some papers dating back to the eighties and I think that the Authors should be more precise on this point. Two reference papers are: Annegarn et al., Source profiles by unique ratios (SPUR) analysis: Determination of source profiles from receptor-site streaker samples. Atmos. Env. 26, 1992 D'Alessandro et al., Hourly elemental composition and sources identification of fine and coarse PM10 particulate matter in four Italian towns. JAS 34, 2002

Agreed. We added the two references and quoted them in the appropriate places in the introduction.

Page 3, line 37-38: a list of element detectable by Xact is reported with the explanation that the system sensitivity has been determined for each element by a reference sample. Actually, there are in the list couples of elements which interfere in a X-ray analysis (Fe-Co, Pb-As, Ba-Ti) and I really wonder that, for instance, Co and As can been safely detected in ambient aerosol (usually much richer in Fe and Pb). I have not found in the text any comment of this point. I think that the calibration procedure should be better described including a discussion on these possible interferences. This impacts on the data summarized in Table 1 too.

Very good point. We added some text discussing this point:

"Line interference is well-known for element couples like Fe-Co, Pb-As, Ba-Ti and makes detection of one element difficult if the other is abundant in the sample. The linear least squares reference deconvolution algorithm implemented in the Xact fits the measured sample spectrum with the library of pure element reference spectra to resolve concentrations of each calibrated element."

The last remark on the impact of line interference on the data in Table 1 concerns only the pair Ba-Ti, as for each other pair one element is below MDL. We found a high correlation between Ti and Ba for the fireworks (r2=0.94), where it is expected, and a different, but still good correlation (r2= 0.55) for the non-fireworks cases (see attached Figure), where both elements also show a different behaviour and different enhancement ratios (Fig. 7 in the manuscript). This is a hint towards a good element separation despite the potential Ba-Ti line interference. In addition, from Fig. 2 it can be seen that both Ba and Ti are highly correlated with their corresponding ICP-MS data, with the largest values corresponding to the fireworks cases. One would expect the Ti values of the fireworks to deviate more from the ICP data when Ba interference were not adequately considered.

We added the following sentences:

"Potential line interference between Ti and Ba can be largely exluded, because the element couple reveals two different regressions for fireworks and non-fireworks cases, as well as distinct diurnal variations in the non-fireworks cases."

"The element couples of Fe-Co and Pb-As do not show correlations within the couples, because most of their data points are below their respective MDLs, and no conclusion about the deconvolution of interfering lines can be drawn for these elements. Comparing the Xact values with the NABEL annual mean values (Table 2) shows differences smaller than 40 % for Cu, Pb, and Ni, while the differences are much larger for As and Cd. The latter two elements are below their respective MDL (Fig. 2)."

Page 4, first lines: the procedure to determine the MDL takes into account the spectrum collected in a blank portion of the filter. This ways the MDL get underestimated since, in each portion of the spectrum, the continuum is not due to the filter only but also to the tails of all the peaks due to the PM elements. Moreover, this method completely *not consider the interferences discussed above. More realistic MDL values should be given for each element and a given sampling/analysis time in a dedicated table but should be calculated as an average of PM samples.*

Partly agreed. The MDLs reported by the manufacturer are interference-free, 1-sigma confidence level, minimum detection limits determined for single element standards. They are clearly defined and well reproducible, and they are re-determined at regular intervals (1 to 3 months). They indicate the lowest possible detection limits under ideal conditions. While we agree that the table suggested by Referee #3 would be very helpful and probably more meaningful, its determination would require numerous experiments with different sample compositions and concentrations which is beyond the scope of the current study.

“Interference free MDLs, while true are idealized lower limits of detection of one single element. As with most analytical methods, matrix effects in ambient samples from interferences between different elements and analyte concentrations could potentially result in MDLs of ambient samples to be higher and vary across samples, which makes them difficult to generalize and report.”

Page 8, Par 3.3: the whole section with related figures should move to the supplementary material

Partly agreed, see issue 2, above. We condensed the Section 3.3 to the necessary, but want to keep it in place. We consider the Section relevant for the article.

We try to clarify this point with the following text sequence:

“Investigation of the highest peaks reveals the performance of the Xact under high load conditions, when sample thickness may become critical for XRF analysis. A comparison of the two instruments’ peaks could demonstrate how closely the Xact mass represents the total measured PM10 mass. Inspection of the different time series indicates that the TEOM peak is broader (3 h) and higher (59.6 μg m^{-3}), and its maximum concentration is reached 1 h later (at 2 Aug 2015 0000 LT), but its increase in concentration starts at the same time as the Xact (at 2200 LT). The delay in the maximum can be attributed to the time constant of the TEOM used for reducing measurement noise and to the averaging procedure. For a comparison of the two peaks their measured masses were integrated over the duration of the peaks, i.e. over 2 h for the Xact data and the ACSM data, and 3 h for the NABEL data..”

Pag. 11, line 9-14: the origin of possible discrepancy have not been clearly identified and the wording “are attributed” is not correct and should be replaced by “could be attributed”

Done.

Pag. 11 , line 25-31: these lines should be removed from the conclusions. . .they are of very local interest and more than a conclusion are just a summary of the findings

Agreed. Done.

Figure 1: the plot in the top panel should be shown in log. Scale: the present picture is not so informative

Not agreed. We want to emphasize the size of the fireworks peak in relation to the background concentrations, and this is best visible with a linear y-axis. Furthermore, on a logarithmic scale with stacked element concentration, the first element is shown with proportionally more area than the subsequent elements, yielding a distorted picture of its importance. Therefore, we prefer to leave the linear scale on the y-axis in the top panel as is.

Figure 2: the number of digits In the value of the a and b coeff. Is too high (i.e. show just significant digit). The values of the correlation coeff. Should be added in each plot.

Agreed. However, we redrew Fig. 2 completely and moved all the regression coefficients to (new) Table 1 (former Table 2), where all coefficients are given to 2 decimal digits. The new figure represents the elements in Group A with colours, while Group B and C elements are represented in black and white, indicating that their data has issues with MDLs and others. Still, we retain all data in the graph to present the complete picture – in accordance with referee #2. We have also reordered that data in Figs. 7 and 11 (new: 7 and 9) according to the groups, hence we consistently show good and bad data throughout the article.

Figure 3: In my opinion the right part of the picture (from V on) does not give any information and should be deleted

Partly agreed. We completely redrew Fig. 3, adding the MDLs for Xact and ICP, the regression slopes and intercept-to-average ratios for all elements. See also comment on Fig. 2, above.

Figure 5: the fit of the red points is more or less meaningless. please add the R2 values in the plot both for blue and red points

Agreed. Done.

Table 2: should be deleted by inserting the R2 values in the plot of fig. 2

The changes made to Figs. 2 and 3 and Table 2 make this suggestion obsolete.

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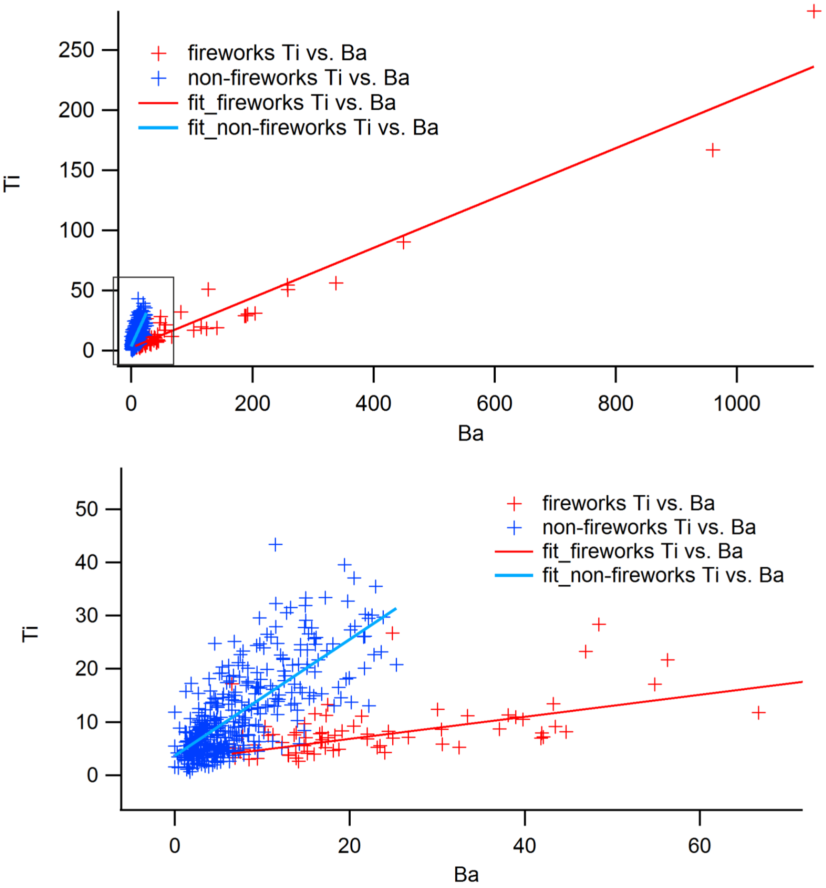

Fig. 1. Ba-Ti correlations. Top: full range. Bottom: zoomed area.

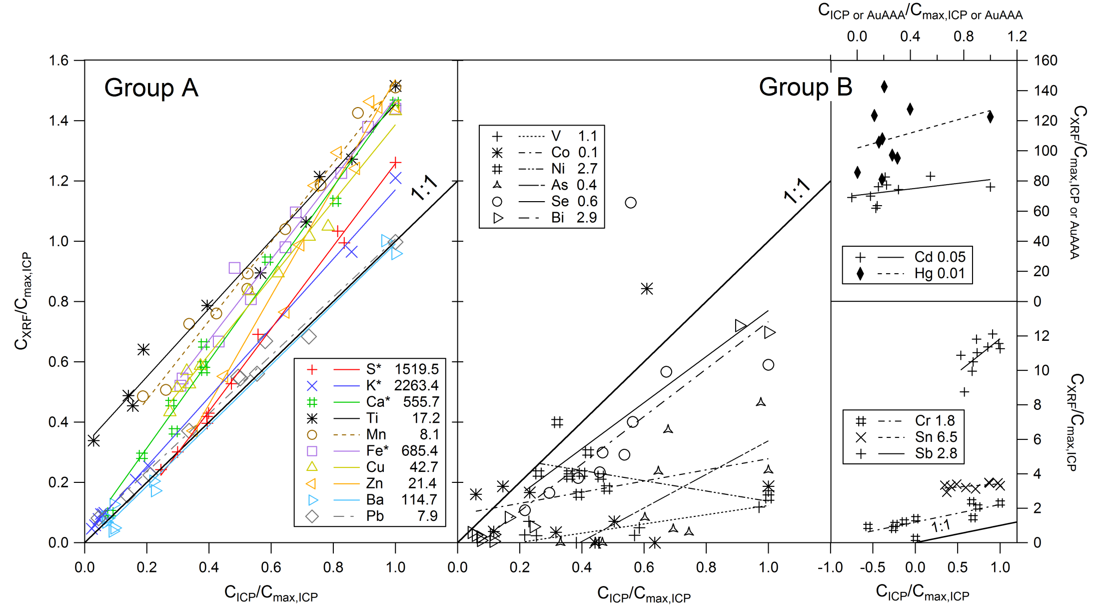

Fig. 2. New Figure 2.

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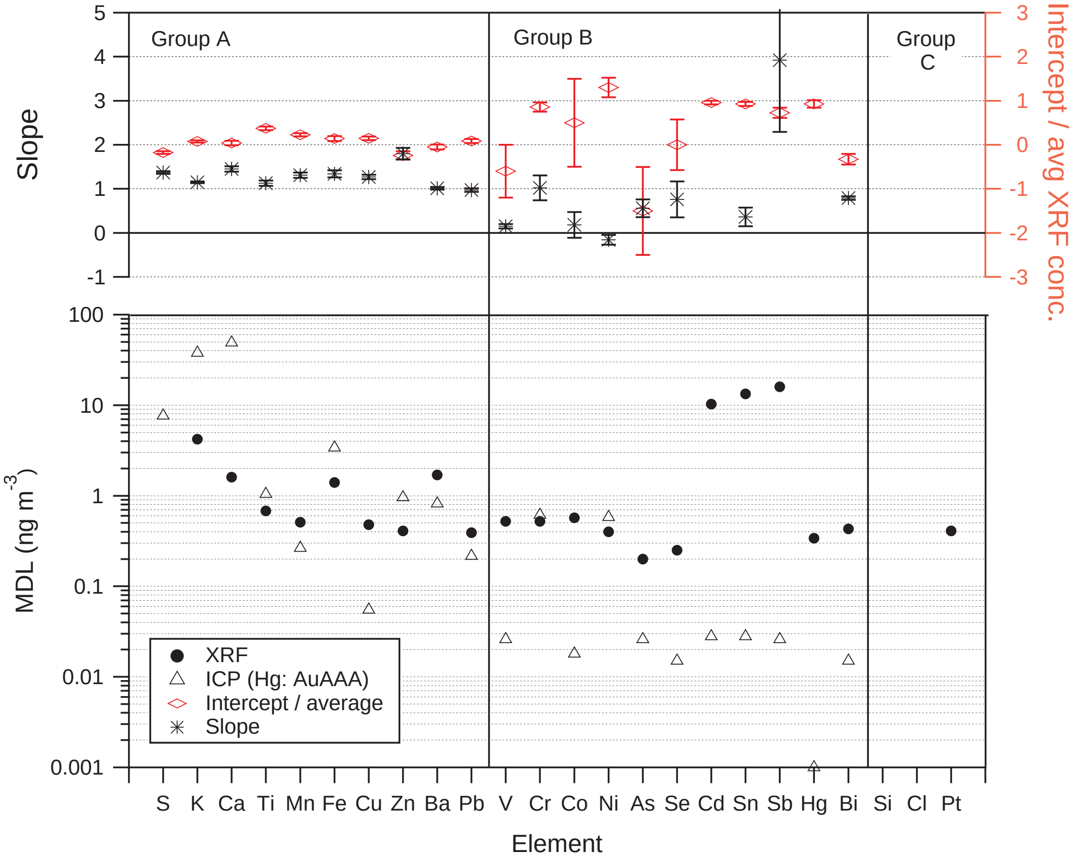

Fig. 3. New Figure 3.

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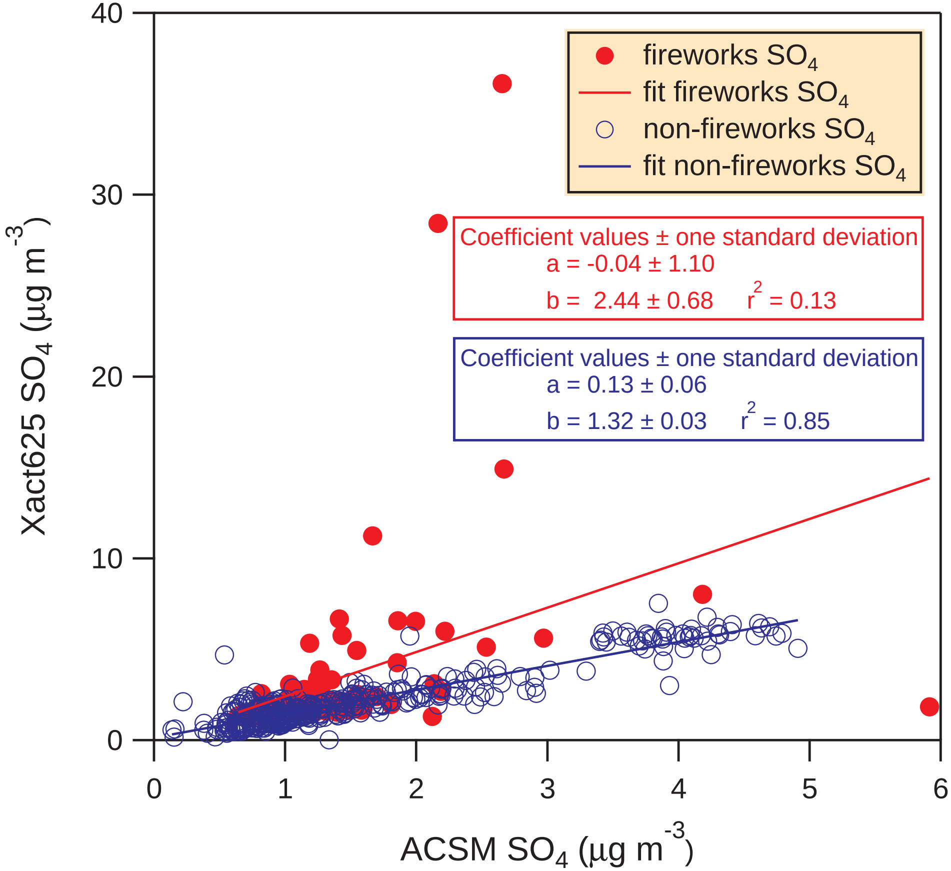

Fig. 4. Corrected Figure 5.

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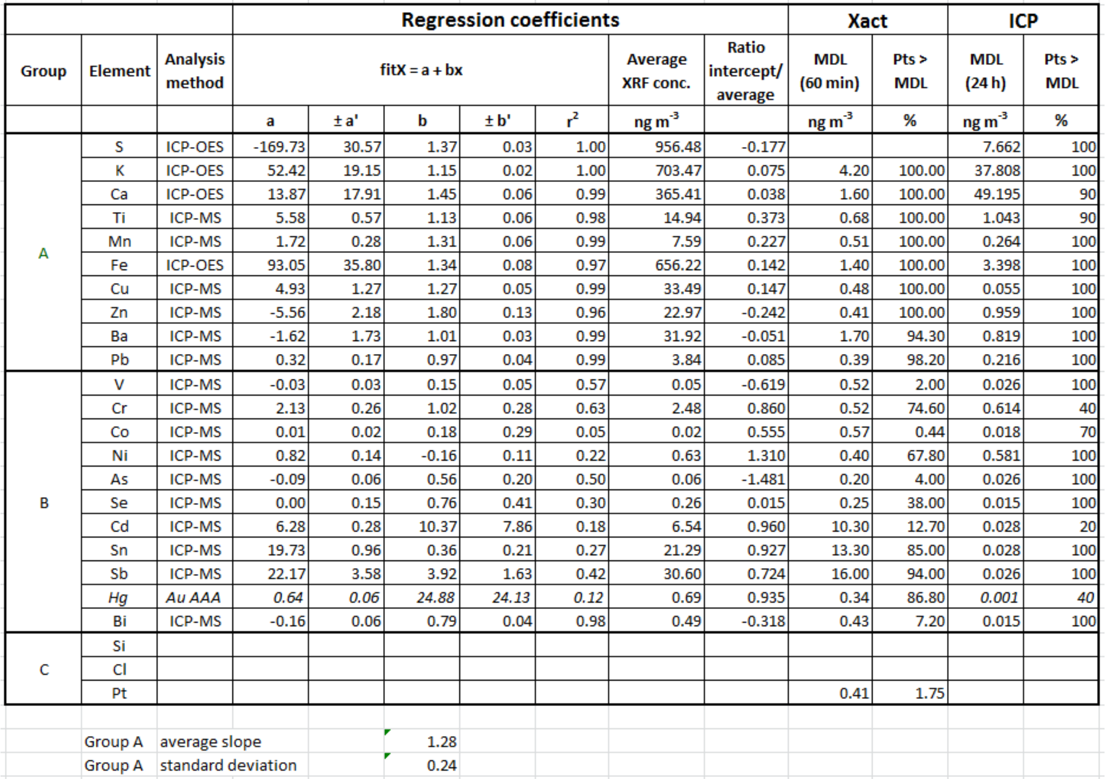

			Regression coefficients							Xact		ICP	
Group	Element	Analysis method	fitX = a + bx					Average XRF conc.	Ratio intercept/ average	MDL (60 min)	Pts > MDL	MDL (24 h)	Pts > MDL
			a	± a'	b	± b'	r^2	ng m^{-3}		ng m^{-3}	%	ng m^{-3}	%
A	S	ICP-OES	-169.73	30.57	1.37	0.03	1.00	956.48	-0.177			7.662	100
	K	ICP-OES	52.42	19.15	1.15	0.02	1.00	703.47	0.075	4.20	100.00	37.808	100
	Ca	ICP-OES	13.87	17.91	1.45	0.06	0.99	365.41	0.038	1.60	100.00	49.195	90
	Ti	ICP-MS	5.58	0.57	1.13	0.06	0.98	14.94	0.373	0.68	100.00	1.043	90
	Mn	ICP-MS	1.72	0.28	1.31	0.06	0.99	7.59	0.227	0.51	100.00	0.264	100
	Fe	ICP-OES	93.05	35.80	1.34	0.08	0.97	656.22	0.142	1.40	100.00	3.398	100
	Cu	ICP-MS	4.93	1.27	1.27	0.05	0.99	33.49	0.147	0.48	100.00	0.055	100
	Zn	ICP-MS	-5.56	2.18	1.80	0.13	0.96	22.97	-0.242	0.41	100.00	0.959	100
	Ba	ICP-MS	-1.62	1.73	1.01	0.03	0.99	31.92	-0.051	1.70	94.30	0.819	100
	Pb	ICP-MS	0.32	0.17	0.97	0.04	0.99	3.84	0.085	0.39	98.20	0.216	100
B	V	ICP-MS	-0.03	0.03	0.15	0.05	0.57	0.05	-0.619	0.52	2.00	0.026	100
	Cr	ICP-MS	2.13	0.26	1.02	0.28	0.63	2.48	0.860	0.52	74.60	0.614	40
	Co	ICP-MS	0.01	0.02	0.18	0.29	0.05	0.02	0.555	0.57	0.44	0.018	70
	Ni	ICP-MS	0.82	0.14	-0.16	0.11	0.22	0.63	1.310	0.40	67.80	0.581	100
	As	ICP-MS	-0.09	0.06	0.56	0.20	0.50	0.06	-1.481	0.20	4.00	0.026	100
	Se	ICP-MS	0.00	0.15	0.76	0.41	0.30	0.26	0.015	0.25	38.00	0.015	100
	Cd	ICP-MS	6.28	0.28	10.37	7.86	0.18	6.54	0.960	10.30	12.70	0.028	20
	Sn	ICP-MS	19.73	0.96	0.36	0.21	0.27	21.29	0.927	13.30	85.00	0.028	100
	Sb	ICP-MS	22.17	3.58	3.92	1.63	0.42	30.60	0.724	16.00	94.00	0.026	100
	Hg	*Au AAA*	*0.64*	*0.06*	*24.88*	*24.13*	*0.12*	0.69	0.935	0.34	86.80	*0.001*	*40*
	Bi	ICP-MS	-0.16	0.06	0.79	0.04	0.98	0.49	-0.318	0.43	7.20	0.015	100
C	Si												
	Cl												
	Pt									0.41	1.75		
	Group A	average slope			1.28								
	Group A	standard deviation			0.24								

Fig. 5. New Table 1 (previously Table 2).

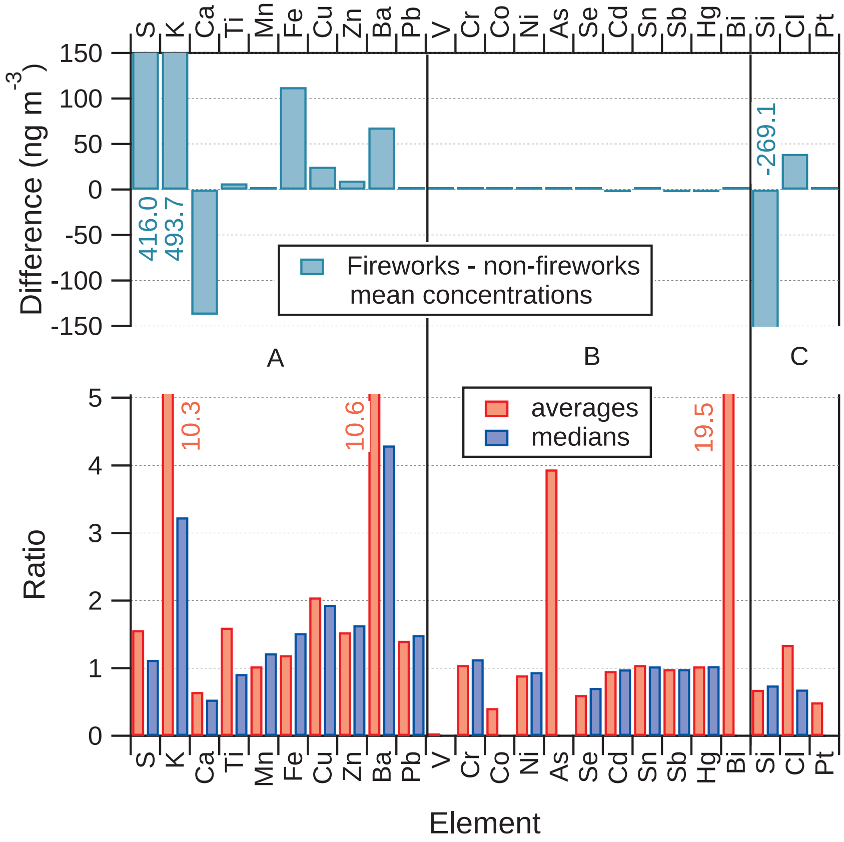

Fig. 6. New Figure 7.

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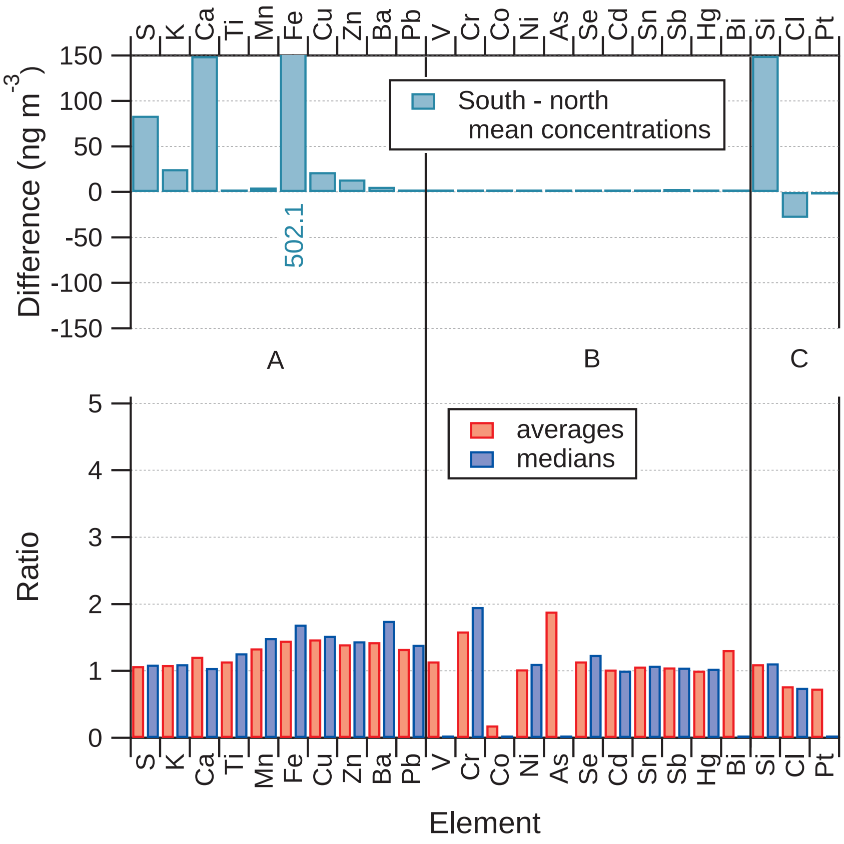

Fig. 7. New Figure 9.