Atmospheric Measurement Techniques Discussions

Interactive comment on "Quantitative sampling and analysis of trace elements in ambient air: impactor characterization and Synchrotron-XRF mass calibration" *by* A. Richard et al.

A. Richard et al.

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We thank Referee 2 very much for her/his comments, which will be of great benefit in the revision of our manuscript. In the following, we are referring to the comments one by one.

1. Comment: Compared with Sections 2 and 3, Section 4 is relatively weak. Although there is a paragraph describing Figure 10, more discussion and description could be given. For instance, the captions of Figure 10 only mention the percentage of PM10 mass. What about PM2.5 and PM1? How do they compare with simultaneous filter

measurements if available? Adding descriptions like these will improve the complete-ness of the dis- cussion.

Answer: Following the suggestion made by Referee 1 we already elaborated Section 4 further, see inserted section below. We included the discussion about the sample homogeneity as outlined in the previous short comment so that a deeper focus is given to the discrepancies of filter and RDI measurements:

INSERTED TEXT -> Some days (e.g. 9 December) show a higher variability than oth-ers which may be due to increased sample inhomogeneity or other unknown experi-mental issues. The sample inhomogeneity is a critical issue if only a fraction of the total sample area is analyzed using focused SR-XRF beams. The low number of sampled particles in the RDI (estimated to be around 10000 particles/analyzed area for stage 1 and 100 particles/analyzed area for stage 10, see Bukowiecki et al., 2008, 2009) raises the question of sufficient uniformity of the deposited material. In both beam line setups the respective possible maximum beam sizes were chosen. Due to the constraints given by the beamline optics as well as the geometry of the sample holder, it was never possible to match the beam cross section exactly to the RDI bars. In earlier work (Bukowiecki et al., 2009), specifically addressing the uniformity, a 2D-high resolution scan was performed with a considerably smaller micro-focus beam (beam size 4 μm^2, step width 7 μm) at the LUCIA beamline at SLS, PSI. There, it could be seen that some elements deposit in distinct spots. For a 1-h stage 10 RDI sample of urban ambient air, an average Fe particle-to-particle distance of about 70 μm was estimated, correspond-ing to a particle area density of 213 Fe-containing particles/mm^2. The FWHM of the area of Fe-containing particles on the film was found to be 1.4 mm, which is reasonably close to the nozzle width and thus RDI bar width of 1.52 mm. However, no sharp edges were found. For stage 2.5 a Fe particle-to-particle distance of about 30-40 μm and an overall particle-to-particle distance of less than 2 μm were estimated. These values lie within the dimensions of the beam sizes (100 $\times$ 200 μm and 70 $\times$ 140 μm).

Furthermore, TEM images were taken in that same study showing the uniformity of

sampled particles on the film. The total number of particles in the coarse size range was found to be around 800 particles/mm^2 for a 1-h aerosol sample. The density of particles is lowest for the coarse size fraction and increasingly higher for the smaller size ranges. On the basis of this information, it is assumed that the chosen beam sizes for analysis at the SLS X05DA beam line and the HASYLAB L beam line allow for an extrapolation from the measured to total sample area if an adequate uncertainty estimate is assigned to the values. As mentioned above, the RDI bar area contributes an error of $\pm 20\%$ to the uncertainty calculation.

In the case of the filter analysis, outliers due to sample inhomogeneity are rather improbable since the percentage of analyzed area from total sample area amounts to 12.5% (1/8 of the filter) and is thus significantly larger than for the RDI analysis. Since inhomogeneities in the distribution of the material on the filters are a function of the distance to the center, portions of the filter were taken like pieces of a round pie to avoid this influence (Brown et al., 2009).

But, since 12 RDI values are averaged to be compared to one filter value, it is difficult to find an explanation for the discrepancy in just one of the two methods. Also, correlations of RDI values versus filter values show no clear trend towards a general over- or under-estimation by the RDI analysis and thus it is assumed that deviations lie within the uncertainties of both methods and atmospheric variability. <- END OF INSERTED TEXT

Concerning Fig. 10 the percentage of trace elements of total PM$_{10}$ is given, since this is approximately the sum of all shown size ranges in the pie charts (we compare the sum of PM$_{10-2.5}$ + PM$_{2.5-1}$ + PM$_{1-0.1}$ to total PM$_{10}$). We only mention PM10, because it was quasi-continuously monitored (every 10 min), while PM$_1$ was not. Following the suggestions by Referee 2, we added also the comparison to daily PM$_{2.5}$ measurements in the manuscript text, changed the Figure caption and added a table with more detailed values to the supplementary material:

INSERTED TEXT -> The trace element percentage of the average PM$_{10}$ mass concentration during the campaign is obtained by the sum of PM$_{10-2.5}$ + PM$_{2.5-1}$ + PM$_{1-0.1}$, and similarly for PM$_{2.5}$. The average mass contributed by all detected elements (Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Zr, Mo, Cd, Sn, Sb, Ba and Pb) to the average PM$_{10}$ mass concentration of 24.6 µg m^{-3} quasi-continuously monitored (every 10 min) by a tapered element oscillating microbalance (TEOM 8500) amounts to 4.6 µg m^{-3}, thus to about 20%. The average mass concentration of PM$_{2.5}$ was retrieved from daily filters of high-volume samplers (Digitel AG, Aerosol Sampler DHA-80) to be 21 µg m^{-3} and detected elements summed up to 3 µg m^{-3}, corresponding to about 15% of the total PM$_{2.5}$ mass concentration. Again, the period during New Year's Eve is excluded, for more details see Table 1 in the supplementary material. <- END OF INSERTED TEXT

We also added a comparison of the total averaged mass measured with filter and RDI, for both PM$_1$ and PM$_{10}$:

INSERTED TEXT -> Averaged concentrations of elements detected by both methods for days of simultaneous measurements compared very well: the average concentration of PM$_1$ filter data was equal to 0.64 µg m^{-3} while the average concentration of PM$_{1-0.1}$ RDI data summed up to 0.68 µg m^{-3} (this comparison includes the following elements: Al, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Zr, Cd, Sn, Sb, Ba and Pb). Average concentrations of PM$_{10}$ filter data amounted to 2.7 µg m^{-3} and the average concentration of PM$_{10-0.1}$ RDI data was equal to 2.55 µg m^{-3}, including the same elements as for PM$_1$ as well as Cl and Mo. For more details see Table 1 in the supplementary material. <- END OF INSERTED TEXT

However, compared to Sections 2 and 3, Section 4 is not as detailed, since the full analysis of these data (Positive Matrix Factorization) will be shown in an upcoming publication. We simply aimed at underlining and supporting the findings of Section 2, which is the information gained by the size segregation, as shown in Fig. 10. Secondly, we wanted to demonstrate the application of the mass calibration described in Section

3, which was evaluated by a comparison to an independent complementary method, namely the filter measurements.

2. Comment: Figure 11 provides some interesting comparisons of RDI and filter data. Like reviewer 1, I feel more could be said about the discrepancy. With the modified Figure in your reply to reviewer 1, 2 hr data are added. They are useful to illustrate the agreement of general trend of the two measurements. One needs to add legend for the 2hr data if this is going to replace Figure 11. Retaining this Figure is fine, because the comparison is quite useful to illustrate the capability of RDI against the conventional filter approach. I would suggest adding scattering plot panels to compare the averaged RDI data vs. filter data for the species compared. Because this will help illustrate the similarity or dissimilarity of these data points and promote more discussion of why such discrepancy is observed. Another comment is the error bars, how do you calculate the propagated errors? Are you showing them in Figure 11 with $\pm$ 1ï ?AÂÿs? It is somewhat strange when the 2 hr data points are well spread at several points in the new Figure 1 that the error bars do not seem to include the deviation of these data points. Also, the captions of new Figure 1 need to be revised to reflect the changes or additions.

Answer: We included more explanations about the discrepancies in the final manuscript; see new version and text above. We would like to stress the point that deviations from the "true" value (which is unknown) cannot by attributed to one method alone. The RDI method has the advantage of the higher time resolution, so that 12 values are averaged to be compared to one filter value reducing the probability that the reason of deviation is only due to RDI values. On the other hand, sample inhomogeneities are much more improbable for the filter analysis since a much larger portion of the filter is analyzed (a fraction of 12.5% or 1/8 of the total filter). Therefore the conclusion is that deviations might originate from sample inhomogeneities of RDI samples but eventually both methods are subject to certain variability, which is reflected in varying deviations of the measured values. Certain variability can be observed for the

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RDI data, which is due to diurnal cycles of emissions.

Concerning the error calculation: as mentioned in the manuscript, the errors were calculated based on the propagation described in Section 3.4 in the manuscript and were then propagated for the calculation of the mean value. We agree that another option would be to calculate the standard deviation (do you mean σ?, there seems to be a formatting error in your comment), which will increase the error and thus be in accordance with the variability (i.e. diurnal cycles) of RDI values. By doing so, we would actually show two different kinds of errors in one plot: for the filter data it is the actual measurement uncertainty, while for RDI data we would show the standard deviation of all 12 binned values. Since we added the 12 single values, which do effectively represent the standard deviation, we decided to stay with the real measurement error. We modified Figure 11 once more, adding barplots for filter values and dots for RDI values, see below. The legend and caption is replaced in the final version.

Scatter plots are added to the supplementary material, see below and attached document.

Specific editorial comments 1. p2481, line 12, (Digital), is this a vendor? Adding model number can help clarify.

Answer: Yes, Digitel is a vendor, we added the model number in the final manuscript (DPM10/2,3/01).

2. p2482, line 22, ELPI, needs to be defined first, electrical low-pressure impactor?

Answer: Yes, we are sorry for this missing part and added the definition.

3. p2496, line 20, two outlier days (7 and 9 December), it is a bit confusing using the current time format on the x-axis. Minimally, the time format should be explained in the captions to reduce confusion. It may be useful to drop the month and just use the day of the month to simplify the presentation.

Answer: Yes, we dropped the month on the axis and change to "day of the month".

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4. p2497, line 11, ". . . properly matched the requirements", what requirements? These were not clearly specified.

Answer: Here, the above mentioned (Sect. 3) requirements are addressed (similar elemental composition, particle size, sample homogeneity and substrate thickness for ambient aerosol analysis on PP films). We agree and we repeated them in the conclusions.

5. p2497, line 27, show a good agreement, delete "a".

Yes.

6. References, as mentioned above, many extra numbers at the end of each reference.

Answer: They were inserted by the Copernicus typesetting office, and by clicking on it the reader will be guided to the page of the manuscript where the respective reference was cited.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/3/C1323/2010/amtd-3-C1323-2010-supplement.pdf

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 2477, 2010.

Table 1. Comparison of average mass concentrations: the first two columns present mean values of elements measured by PM_1 and PM_{10} high-volume filters compared to the same elements measured with the RDI. PM_1 daily filter samples were taken every day in the period from 30 November 2008 till 17 December 2008 and analyzed for the following elements (a): Al, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Zr, Cd, Sn, Sb, Ba and Pb. PM_{10} daily filter samples were taken every second day in the period from 1 till 17 December 2008 and analyzed for the following elements (b): Al, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Zr, Mo, Cd, Sn, Sb, Ba and Pb. In addition, average values for all data points throughout the whole campaign as well as the same period excluding New Year's Eve (NYE, 31 December 2008 15:00 LT to 1 January 2009 05:00 LT) are shown. The third column lists the average values for the whole range of elements, which can be detected by the RDI-SR-XRF method (c): Al, Si, P, S Cl, K Ca, Ti, Cr Mn, Fe, Co, Ni, Cu, Zn, Sr, Zr, Mo, Cd, Sn, Sb, Ba and Pb. The last two columns give averaged values for quasi-continuously monitored PM_{10} mass concentrations as well as averaged $PM_{2.5}$ and PM_{10} mass concentrations from daily filter analysis. Values marked with an asterisk (*) are averaged only for days in 2008 (28 November till 31 December).

PM_1	Filter (a)	RDI (a)	all RDI elements (c)	PM_1 cont.	PM_1 daily
Filter period	0.64	0.68	0.69	-	-
Whole camp.	-	1.99	2.02	-	-
Period w/o NYE	-	1.67	1.68	-	-
$PM_{2.5}$	Filter (NA)	RDI (NA)	all RDI elements (c)	$PM_{2.5}$ cont.	$PM_{2.5}$ daily
Whole camp.	-	-	3.52	-	-
Period w/o NYE	-	-	3.08	-	21.19*
PM_{10}	Filter (b)	RDI (b)	all RDI elements (c)	PM_{10} cont.	PM_{10} daily
Filter period	2.7	2.55	2.78	20.56	20.61
Whole camp.	-	5.09	5.3	25.23	-
Period w/o NYE	-	4.58	4.79	24.64	24.96*

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Fig. 1.

Fig. 2.

Fig. 3.