**Atmospheric
Measurement
Techniques
Discussions**

Interactive
Comment

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.

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Dear Referee, Thank you very much for your comments and suggestions, which will help in improving our paper!

1. My only remark/question is on the homogeneity of the aerosol deposition inside each "bar" (see fig. 1) of the impaction stages: this is particularly important since I understand that just a very small portion of each "bar" is actually analyzed and this could create problems. In other similar cases (such as the IBA analysis of streaker samples described in one of the referenced papers: D'Alessandro et al. 2003) this problem was acknowledged and faced scanning the whole deposit with the incident

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beam.

Answer: This is in fact an issue that we faced using focused SR-XRF beams during our analysis. The low number of sampled particles (estimated to be around 10000 particles/analyzed area for stage 1 and 100 particles/analyzed area for stage 10) raises the question of uniformity of the deposited material. In the beam line setups we used, we chose the maximum beam sizes possible. Due to the constraints given by the beamline optics, it unfortunately was never possible to match the beam cross section exactly to the RDI bars. Since we are scanning the wheels in an automated procedure, we could not increase the beam size significantly, since we would have irradiated blank areas next to the bars for the fine size range, stage 1, where the bar width is 0.3 mm. In earlier work (Bukowiecki et al, 2008, 2009), where we specifically addressed the uniformity, we performed several so called homogeneity scans. We decreased the automated movement of the goniomenter down to 0.1 degrees and obtained a fine scan of the distribution of sampled material on the film. The result was that the material is distributed reasonably homogenous on the film. Due to the nature of analyzed materials (trace elements in aerosol particles) it is of course not perfectly homogeneous, which could be seen from another 2D-fine scan, which we performed with a considerably smaller micro-focus beam (beam size 4 μm^2, step width 7 μm) at the Line for Ultimate Characterisation by Imaging and Absorption (LUCIA) at SLS (see Bukowiecki et al, 2009). Here, we could clearly see that some elements deposit in distinct spots. For a 1-h RDI sample of stage 10 in urban ambient air, an average Fe particle-to-particle distance of about 70 μm was estimated, corresponding 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 the same study showing the uniformity of sampled particles on the film. The total

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number of particles in the coarse size range was found to be around 800 particles/mm^2 for a 1h aerosol sample. The density of particles is lowest for the coarse size fraction and significantly higher for the smaller size ranges. On the basis of this information, we believe that the chosen beam size for analysis at the optics and Hasylab beam lines allow for an extrapolation from the measured to total sample area. In our current calculations, we account for this systematic uncertainty with an error of 20% of the area (in contradiction with the 10% we mention in the draft manuscript; we will adapt the value in the final version). We will include an elaboration about the sample homogeneity in the final manuscript.

2. The agreement between HVS and RDI data is not completely satisfying and the few reported data present significative discrepancies (in some cases, see fig. 11), which could alter significantly the output of the upcoming PMF analysis quoted in the last statement of the text. May be the origin of such discrepancies related to inhomogeneity of the RDI samples? The last statement of sec. 4 (the overall comparison of 24h...etc) is very qualitative and, to me, is not completely supported by the data shown in fig. 11).

Answer: Yes. As we mention above and in the manuscript, the deviations of HVS and RDI data are most likely due to sample inhomogeneities. Neither the RDI films nor the HVS filters are analyzed completely, in both cases it is a fraction of the total area. This introduces a certain uncertainty, which is included in the uncertainty calculation. If the measurement is performed on a "hot spot" with an agglomeration of sample materials, outliers might occur for one or the other method. Given the fact, that 12 RDI values are averaged to compare a single filter value, the "outlier" has to be attributed most probably to the filter value. We argue that the comparison is reasonable enough, since the time trends of both methods agree well and there is no general over- or underestimation in the measurements. Therefore we assume that the observed deviations are within the limits of atmospheric analyses.

3. I would suggest to include as supplementary material the time series of the elemental concentration values measured in the three stages during the Zurich experiment:

this could help in understanding possible artifacts due to samples inhomogeneity.

Answer: Thanks for this suggestion; we will take it into account.

4. I would also suggest to change the title a little bit since the focus of the manuscript is on the performance of the sampler+analytical techniques. I would prefer: Quantitative sampling and analysis of trace elements in atmospheric aerosols: impactor characterization and Synchrotron-XRF mass calibration.

Answer: Thanks also for this suggestion, on which we agree as well.

References:

Bukowiecki, N., Lienemann, P., Zwicky, C. N., Furger, M., Richard, A., Falkenberg, G., Rickers, K., Grolimund, D., Borca, C., Hill, M., Gehrig, R., and Baltensperger, U.: X-ray fluorescence spectrometry or high throughput analysis of atmospheric aerosol samples: the benefits of synchrotron X-rays, Spectrochim. Acta B, 63, 929–938, 2008. Bukowiecki, N., Richard, A., Furger, M., Weingartner, E., Aguirre, M., Huthwelker, T., Lienemann, P., Gehrig, R., and Baltensperger, U.: Deposition uniformity and particle size distribution of ambient aerosol collected with a rotating drum impactor, Aerosol Sci. Tech., 43(9), 891–901, 2009.

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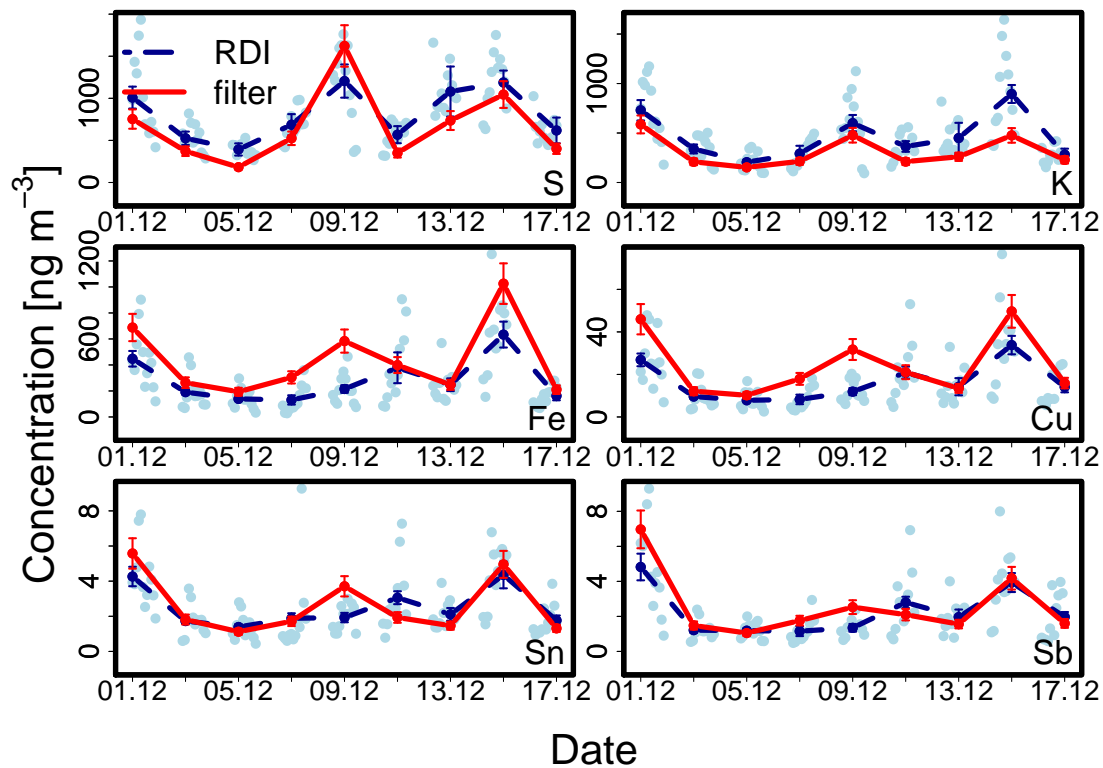Printer-friendly Version

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Fig. 1. Time series of RDI and filters with 2-h data of RDI.