

# Highly time and size-resolved trace elemental composition of aerosols analyzed with Synchrotron Radiation induced X-Ray Fluorescence Spectrometry

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Size-resolved measurements of trace elemental composition provide a highly specific technique for the identification of primary aerosol sources in the ambient atmosphere. The utility of such measurements is improved by sampling with a high time resolution in the order of hours, and coordination with other aerosol composition measurements. A high time resolution makes it possible to detect diurnal variations in elemental concentrations caused by certain strongly time dependent emission sources, like traffic or shipping. However, a highly sensitive detection method is required to quantify the few  $\mu\text{g}$  collected during a sampling interval. Synchrotron Radiation induced X-Ray Fluorescence Spectrometry (SR-XRF) is able to quantify the ambient elemental concentrations with a detection limit for single element masses on the order of a few pg.

During two beam times in 2011 at the HASYLAB Beamline L a broad range of elements (Mn, Fe, Co, Ni, Cu, Zn, Br, Sr, Zr, Cd, Sn, Sb, Ba) was measured. This significantly extended the data set measured at the Swiss Light Source (SLS) at the Paul Scherrer Institute, Switzerland (elements Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni). The few elements measured at both facilities facilitate to crosscheck the quantification of the data. At HASYLAB, measurements were done with a polychromatic beam with a continuous energy range from 5 to 80 keV. The beam spot size was set to  $100 \times 400 \mu\text{m}$ , providing a sufficient photon flux for the required detection limit [1, 2]. If the photon flux resulted in dead time and saturation effects, the spot size was reduced by narrowing the exit slits in the beam path. A Si(Li) detector with a large active volume (crystal area  $80 \text{ mm}^2$ , crystal depth 4 mm) and a  $12.5 \mu\text{m}$  beryllium window enabled the measurement of heavier elements up to the Ba  $K\alpha$  line at 32 keV (nitrogen cooled Sirius 80, Gresham). Aluminium absorbers of different thicknesses allowed changes in the shape of the continuous spectrum.

In 2010 and 2011 several field campaigns took place, among others CalNex-LA in Los Angeles (USA), MEGAPOLI in Paris (France) and APICE in Marseille (France). Sampling took place with a 3-stage Rotating Drum Impactor (RDI) with a 2-h time resolution, compared to more common 24-h filter measurements. The RDI stages enable particle size segregation in the ranges  $10\text{-}2.5 \mu\text{m}$ ,

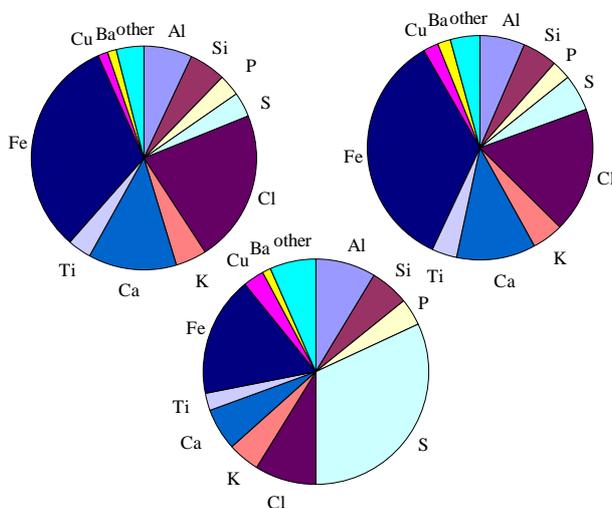


Figure 1: Relative contribution of elements to PM<sub>10-2.5</sub> (left), PM<sub>2.5-1.0</sub> (right) and PM<sub>1.0-0.1</sub> (center) identified by RDI-SR-XRF during CalNex-LA 2010.

2.5-1.0  $\mu\text{m}$  and 1.0-0.1  $\mu\text{m}$ . Measurements of trace elements are important from a health effect point of view, but even more so for source apportionment. Especially in addition to organic aerosol measurements, many local and regional sources can be identified from highly time and size-resolved trace elemental analysis [3, 4].

Figure 1 shows an example of the relative elemental contribution to the three stages averaged over the CalNex-LA campaign. Fe and Cl make up a large fraction of the two largest stages. The main source of Fe in the coarse fraction is typically mineral dust, while Cl can indicate sea spray. The extreme S fraction, a known marker for secondary sulphate in  $\text{PM}_{1.0-0.1}$ , points to secondary and aged aerosol transported from Los Angeles to the sampling site in Pasadena.

An RDI from a U.S. group was operated parallel to the PSI sampler during CalNex-LA. The RDI from an U.S. group had eight stages compared to PSI's 3-stage RDI. SR-XRF analysis was done independent of each other (the U.S. group used the Advanced Synchrotron facility (ALS) in Berkeley, California), creating a perfect opportunity to compare the data quantification. Figure 2 reveals the results for Fe  $\text{PM}_{10}$ , thus by adding the concentrations for all stages per time step. The red curve, the result of a 2010 beam time at Beamline L, and the green curve, the data from the U.S. are not identical. Therefore, we re-measured our data set in a 2011 beam time, and the result is the blue curve. The 2011 beam time gives about ten percent higher values than the 2010 beam time, caused by a slightly different calibration. However, these two beam times are very well comparable, showing clear reproducibility at Beamline L. The lower values in the first part of the campaign, compared to the U.S. data, presumably come from problems during sampling with our RDI. However, the more variable values seen in both the 2010 and 2011 beam time are a result of the high 2-h time resolution. A clear diurnal pattern is visible, while the USA data cannot produce this. The USA-RDI collects elements by continuously rotating the sample drums, which result in smoothed concentrations relative to our well-defined 2-h time resolution.

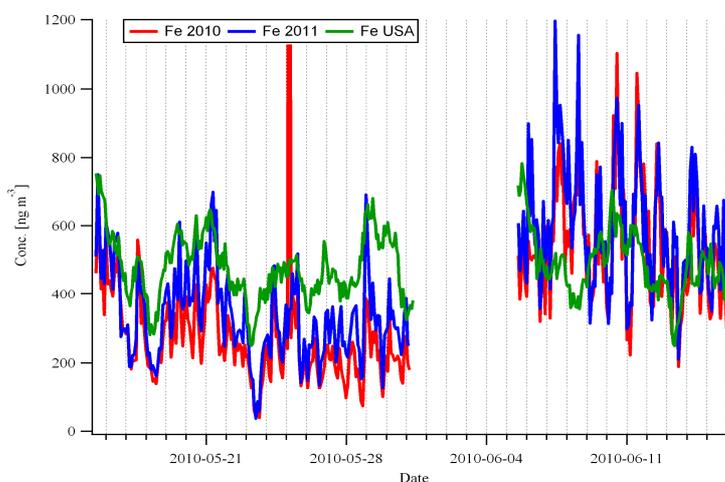


Figure 2: Time series of size-segregated 2-h Fe concentrations analysed in two beam times at HASYLAB Beamline L (red, blue) and results from RDI-SR-XRF analysis from an U.S. group (green).

Source apportionment for the different campaigns will reveal specific local and regional sources, and geographical influences. A larger fraction of sea spray e.g. is expected in Los Angeles and in Marseille compared to Paris. Urban regions exhibit stronger traffic influences, while rural sites can be affected by secondary and aged aerosol transported from urban areas. The identification of heavier elements, possible at HASYLAB Beamline L, significantly improves the apportionment of emission sources.

## References

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