Elemental composition of ambient aerosols measured in high temporal resolution with an online x-ray fluorescence spectrometer

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Trace elements are important markers for emissions sources, and certain metals have been linked to detrimental health effects. A variety of techniques exist to quantify these elements in ambient air, including inductively-coupled plasma mass spectrometry (ICP-MS), inductively-coupled atomic emissions spectroscopy (ICP-AES), X-ray fluorescence (XRF), and proton-induced X-ray emission spectrometry (PIXE). However, most applications of these techniques require sample collection and storage, followed by analysis in the laboratory. This can be very laborious and/or require access to special facilities such as synchrotrons, making impractical the routine analysis of large datasets. Thus there is an urgent need for online methods capable of ambient trace element analysis.

The Xact 625 Ambient Metals Monitor (Xact, Cooper Environmental Services) provides real-time, online measurements of trace element concentrations in ambient aerosol with a time resolution of 15 to 240 min. Ambient air is continuously pulled through a Teflon filter tape, where particles are collected. After the designated collection interval, the filter tape is moved into the analysis area, where it is analysed by XRF. In the present study, the Xact collected PM_{10} samples with 1-hr time resolution from 23 July 2015 to 13 August 2015 in Härkingen, Switzerland. The site is located in a rural area, adjacent to a freeway and several small villages. The sampling period included Swiss National Day, which was celebrated with fireworks in the nearby villages.

The Xact measurements were compared with 24-hr PM_{10} filters analysed by ICP-MS and ICP-AES. Approximately 20% of the total mass is measured by the Xact, and consists primarily of Si, S, Ca, and Fe. Strong correlations (R^2 > 0.9) between Xact and HiVol filter measurements are observed for S, K, Ca, Ti, Fe, Mn, Cu, Zn, Ba, Pb, and Bi. The mean slope (Xact vs. filter) for these elements is 1.35, indicating that the Xact tends to estimate a higher mass concentration than the ICP systems. This difference may be due in part to different inlet transmission curves for large particles. Most other elements with concentrations were above detection limits exhibited R^2 values between 0.25 and 0.9.

Data were classified into fireworks and non-fireworks periods based on the concentration of K. The ratio of trace element concentrations measured by the Xact for these two periods is shown in Fig. 1. Strong enhancements in K, Ba, Bi, Cu and As are observed, with lesser enhancements in S, Cl, Ti, Zn, and Pb. These enhancements are consistent with previous measurements of fireworks composition (Kong *et al*, 2015). This analysis can be used to derive source signatures suitable for source apportionment.

Classification of the non-fireworks data according to south (highway-influenced) and north (not highway-influenced) can be used to identify the effect of traffic emissions on trace element composition. Highway emissions lead to enhancements in Ba, Cr, Cu, Fe, and Mn during the day. Interestingly, no enhancement is observed for Sb, which is used as a tracer for vehicle brake wear. This likely reflects the local traffic patterns, as the free traffic flow and flat topology results in minimal braking on this section of highway. Highway traffic also contributed to resuspended dust, primarily observed in the morning and early afternoon. Finally, enhanced Cl contributions during the first half of the campaign could be attributed to transported sea salt.

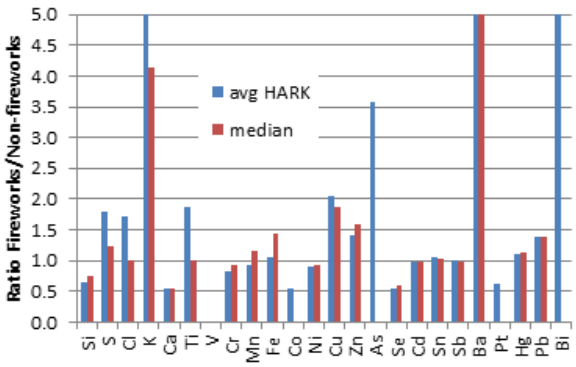

Figure 1. Ratio of trace element concentrations for fireworks/non-fireworks periods (1 = no enhancement).

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