Chemical composition and source apportionment of PM10 at different Swiss locations, 2008/2009 compared to 1998/1999

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During a one year period (from August 2008 to July 2009) PM10 samples from different locations in Switzerland (urban kerbside, urban background, suburban and rural) were collected and analysed for inorganic ions, trace elements and the carbonaceous fraction. In addition, a detailed speciation of organic compounds was performed for selected PM10 samples. The data from the 2008/2009 provided a detailed picture of the variation of the chemical composition of PM10 between different site types, regions and seasons.

Ten years earlier, from January 1998 to March 1999, a similar study has been performed. As in the recent study, the data provided a detailed picture of the PM10 chemical composition at different Swiss sites (Hueglin et al., 2005) and allowed the identification and characterisation of the main emission sources.

During the last decades, the concentrations of atmospheric PM10 steadily decreased in Switzerland (Barmpadimos et al., 2011). PM10 concentrations measured in 1998/1999 and 2008/2009 reflect this trend (Fig. 1). Between the two studies the most noticeable change in major PM10 constituents was observed for sulphate: at all sites average annual concentrations decreased between 1.1 and 1.5µg/m^3 (Fig, 1). Decreasing concentrations were also observed for elemental carbon (EC), ammonium and the sum of trace elements. Decreasing trace element concentrations were especially pronounced at the urban kerbside site, indicating declining trace element emissions from road traffic. Organic matter (OM) showed only decreasing concentrations at the urban kerbside site, the nitrate concentrations were slightly increasing at all sites. The average concentration of natural mineral dust as calculated from the concentrations of Al and Mg as well as from estimates of the geogenic fractions of total measured Fe, K and Ca slightly decreased at the urban kerbside site, while remained constant at the other sites.
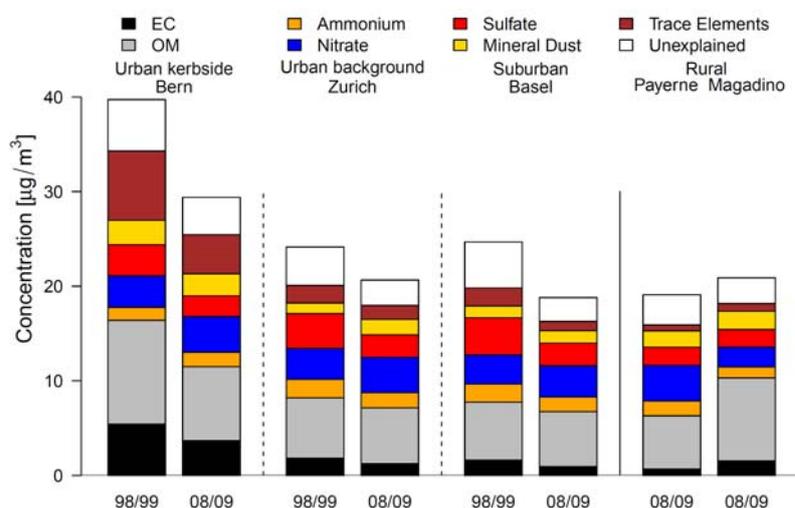
Figure 1: Chemical composition of atmospheric PM10 at urban kerbside, urban background ad suburban sites in 1998/1999 and 2008/2009 and at two rural sites in 2008/2009.

In order to identify and quantify PM10 sources and components, receptor modelling by positive matrix factorisation (PMF) was performed on the five chemical composition datasets from the 2008/2009 study. For the urban kerbside site 7 PM10 sources and components were identified, while at the other sites 6 factors were resolved.

Three factors interpreted as mineral dust, sulphate-rich secondary aerosols and nitrate-rich secondary aerosols were common at all sites. Road dust, road traffic exhaust emissions and de-icing road salt were factors

specific to the urban kerbside site, while at the other four sites two factors identified as road traffic and sodium (Na) and magnesium (Mg) rich aerosols were modelled.

The differences in PM10 source apportionment between the urban background, the suburban and the rural site north of the Alps (ZUE, BAS and PAY) are rather small: secondary aerosols (NSA and SSA) constitute with 48-52% of the PM10 mass (9.3-10 μg/m^3), the largest fraction of atmospheric PM10 at all these sites. Road traffic and wood combustion have similar annual mean contributions, accounting for 15-18% (2.8-3.7μg/m^3) and for 13-15% (2.6-2.8μg/m^3) of PM10, respectively. The remaining PM10 mass fraction is about equally divided into mineral dust (8-13%) and Na-Mg-rich particulate matter (8-10%). The slightly higher annual mean PM10 concentrations at the urban background site ZUE compared to the suburban and rural sites BAS and PAY (20.7 μg/m^3 compared to 18.8-19.1μg/m^3) are due to higher contributions from mineral dust and road traffic (+0.7 and +1.0μg/m^3 respectively, see Fig. 2).

The PM10 source apportionment results for the rural site south of the Alps (MAG) are strongly different from the results found at PAY, BAS and ZUE (see Fig. 2). On the one hand wood combustion and road traffic accounted at MAG for a larger fraction of average PM10 (31% and 24%), and on the other hand secondary aerosols only constituted 29% of PM10, with much lower contribution of NSA at MAG compared to the other sites (8% of PM10 compared to 22-32%). The high contributions of wood combustion and road traffic emissions to atmospheric PM10 at MAG are not surprising, because concentrations of OC and EC are during the cold season much higher than at PAY, BAS and ZUE (see Fig. 1).

At the urban kerbside site (BER) contributions from road traffic (sum of exhaust emissions and resuspension of road dust, 8.7μg/m^3) were found to be much higher than at the urban background site (ZUE). Slightly higher contributions were also observed for mineral dust (3.7μg/m^3) and NSA (6.7μg/m^3), while deicing road salt accounted on average for 3.0μg/m^3 of PM10. The clearly higher average PM10 level at BER (29.4μg/m^3) compared to the urban background (20.7μg/m^3) results mainly from higher contribution of these four PM10 components and sources (see Fig. 2).
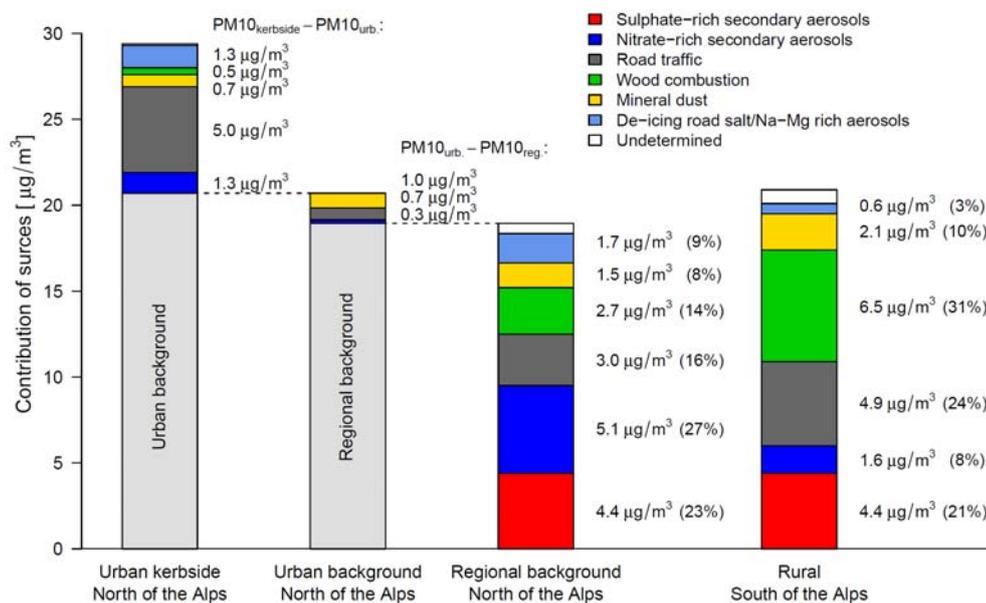
Figure 2: Summary of PM10 source apportionment for the samples collected in 2008/2009. Source contributions at the rural site south of the Alps (MAG, right), and for the regional background PM10 north of the Alps represented by the average source contributions at PAY and BAS (middle right). In addition, source contributions to the urban increment (PM10$_{urb}$-PM10$_{reg}$, as deduced from the urban background site ZUE - middle left), and to the urban kerbside increment (PM10$_{kerbside}$-PM10$_{urb}$, as estimated from the source apportionment results at BER - left) are shown.

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Hueglin, C., Gehrig, R., Gysel, M., Baltensperger, U., Monn, C., Vonmont, H., 2005. Chemical characterisation of PM10 and PM2.5 at urban, near-city and rural sites in Switzerland. Atmos. Environ. 39, 637-651.

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Introduction

During a one year period (from August 2008 to July 2009) PM10 samples from different locations in Switzerland (see Figure 1) were collected and analysed for inorganic ions, trace elements and the carbonaceous fraction. In addition, a detailed speciation of organic compounds was performed for selected PM10 samples. The data provide a detailed picture of the variation of the PM10 chemical composition between different site types, regions and seasons.

10 years earlier, from January 1998 to March 1999, a similar study had been performed [1].

Figure 1: Map of Switzerland with the sampling locations. Basel (suburban, 1998-99 and 2008-09), Bern (urban kerbside, 1998-99 and 2008-09), Magadino (rural, 2008-09), Payerne (rural, 2008-09), Zurich (urban background, 1998-99 and 2008-09).

Chemical Analysis

Water soluble inorganic ions were analysed by ion chromatography (IC), inductively coupled plasma mass spectrometry (ICP MS) was used for measurement of element concentrations. Elemental and organic carbon (EC and OC) were determined by the thermal-optical transmission method [2]. Levoglucosan was analyzed by GC-MS after an organic solvent extraction with an Accelerated Solvent Extractor.

PM Mass Closure and Source Apportionment

Organic matter (OM) was calculated as 1.6·OC to account for non-C atoms in particulate organics. Mineral dust was calculated from measured concentrations of Al and Mg as well as from estimates of the crustal fractions of total measured Fe, K and Ca. Trace elements represent the sum of the remaining element concentrations.
PM10 sources and components were identified by Positive Matrix Factorization (PMF).

Results

PM10 chemical composition

Figure 2: PM10 chemical composition for 2008/2009: regional background site south of the Alps (right, rural site) and regional background sites north of the Alps (middle right, summary of a rural site and a suburban site). Composition of the PM10 urban increment (middle left) and of the PM10 roadside increment (left) north of the Alps.

PM10 source apportionment

Figure 3: PM10 source apportionment for 2008/2009: regional background site south of the Alps (right, rural site), and regional background sites north of the Alps (middle right, summary of a rural site and a suburban site). Sources of the PM10 urban increment (middle left) and of the PM10 roadside increment (left) north of the Alps.
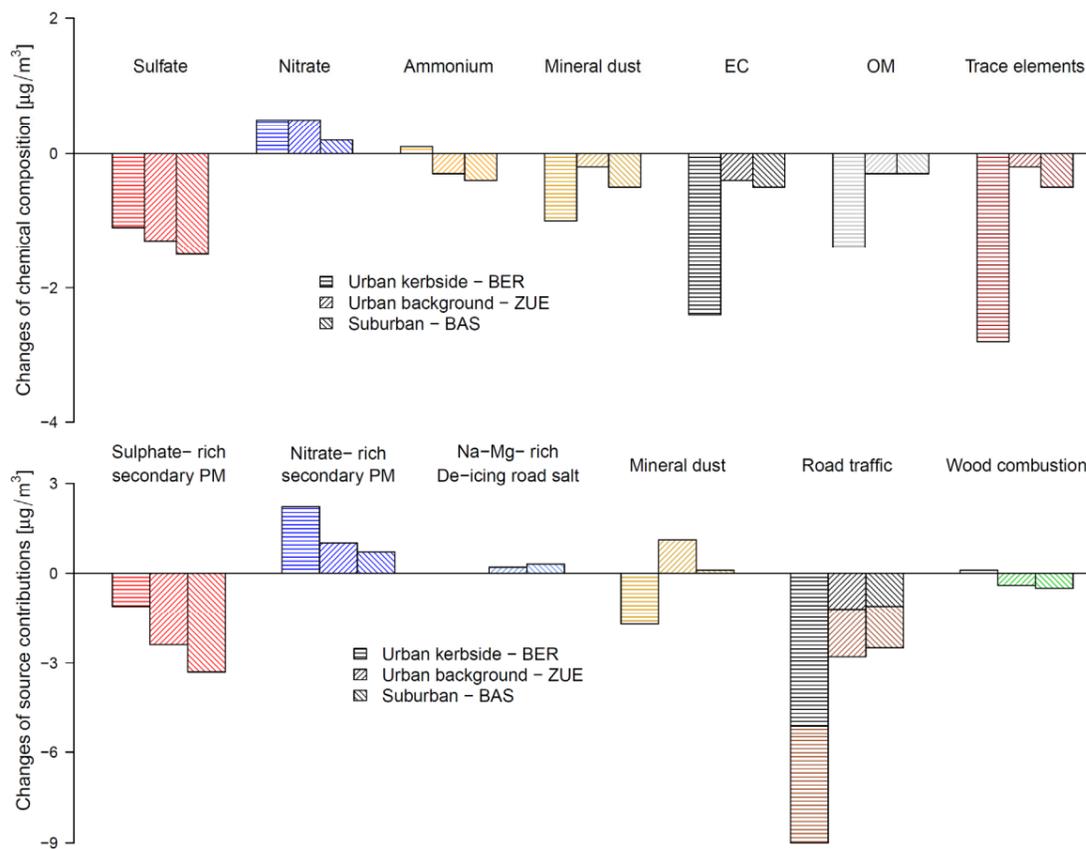
Figure 4: Changes of PM10 chemical composition between 1998/1999 and 2008/2009 at the urban kerbside site (BER), at the urban background site (ZUE) and the suburban site (BAS).

Figure 5: Changes of contributions to atmospheric PM10 between 1998/1999 and 2008/2009 at the urban kerbside site (BER), at the urban background site (ZUE) and at the suburban site (BAS).

In 1998/1999 instead of a wood combustion factor, a mixed anthropogenic factor was identified. Contributions of wood combustion were determined through measured K^+ concentrations and of wood burning/K^+ ratio as determined in 2008/09. The contribution of wood combustion was subtracted from the contribution of the mixed anthropogenic factor, the resulting mass concentration was included in the road traffic budget (brown bars in Fig. 2).
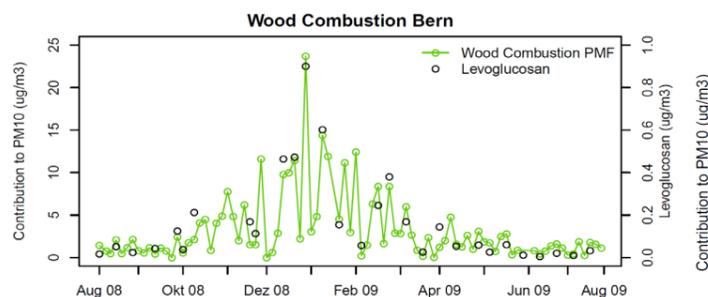
Figure 6: Modelled contribution of wood combustion and measured concentrations of levoglucosan in PM10 at an urban kerbside (Bern).
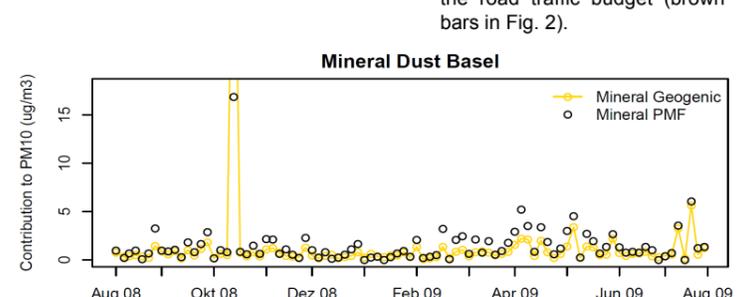
Figure 7: Contribution of mineral dust (PMF) and concentrations of geogenic mineral dust as calculated from element concentrations at Basel (suburban site).

Conclusions

■ Chemical composition of PM10 at regional background sites north of the Alps clearly differs from chemical composition at the regional background site south of the Alps.

■ The urban and the roadside PM10 increments consist mainly of EC, trace elements and OM.

■ The most pronounced changes in PM10 composition for the two measuring periods are:
-decrease of sulphate concentrations at all sites,
-slightly increase of nitrate concentrations,
-decrease of EC and trace elements, in particular at urban kerbside site.

■ PM10 source apportionment in 2008/2009 indicates that wood combustion is an important source of PM10.

■ Variations in PM10 source apportionment between 1998/1999 and 2008/2009 confirm the decrease of sulphate-rich secondary PM and indicates a strong decrease of road traffic contributions to ambient PM10.

■ In 2008/2009, contributions of wood combustion was highly correlated with levoglucosan concentrations. Similarly mineral dust (PMF) was correlated with geogenic mineral dust (calculated from the element concentrations).

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References:
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[2] Cavalli, F. et al., *Atmos. Meas. Tech.*, 3, 79-89, (2010)