Chemical composition and source apportionment of atmospheric PM10 in Switzerland

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Chemical composition and source apportionment of atmospheric PM10 in Switzerland

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presented by
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2012
## Contents

Abstract  

Riassunto  

1 Introduction  
1.1 Impact on human health  
1.2 Impact on climate  
1.3 Variability of chemical composition  
1.4 Thesis motivation and overview  

2 Source Apportionment of Atmospheric Aerosols  
2.1 The Lenschow approach  
2.2 Quantification and source apportionment of specific PM fractions  
2.2.1 Quantification of mineral dust  
2.2.2 Fossil vs. non fossil contribution to carbonaceous matter  
2.3 Receptor models  
2.3.1 Chemical Mass Balance - CMB  
2.3.2 Positive Matrix Factorisation - PMF  

3.1 Introduction  
3.2 Methodology  
3.2.1 Sampling sites  
3.2.2 PM10 sampling and chemical characterisation  
3.2.3 Determination of mineral dust  
3.2.4 Representation of concentration gradients and temporal changes  
3.3 Results and discussion  
3.3.1 Levels of PM10 and major constituents
3.3.2 Trend of PM10 and influence of meteorology

3.3.3 Trend of major chemical constituents in PM10

3.3.4 Dependence of element concentrations on site type

3.3.5 Temporal trend of elements in PM10

3.4 Conclusions


4.1 Introduction

4.2 Methods

4.2.1 Sampling sites

4.2.2 Sampling methods and chemical analysis

4.2.3 Receptor modelling

4.2.4 Determination of the number of sources

4.3 Results and discussion

4.3.1 PM10 sources for 2008/2009

4.3.2 PM10 sources for 1998/1999

4.3.3 Changes in source contributions from 1998/1999 to 2008/2009

4.4 Conclusions

5 Source Apportionment of PM10, Organic Carbon and Elemental Carbon at Swiss Sites: An Intercomparison of Different Approaches

5.1 Introduction

5.2 Methods

5.2.1 Sampling sites, sampling methods, and instrumentation

5.2.2 Chemical analysis

5.2.3 Chemical Mass Balance (CMB) model

5.2.4 Positive Matrix Factorisation (PMF)

5.2.5 Aethalometer model (AeM)

5.3 Results and discussion

5.3.1 Intercomparison of OC apportionment (CMB vs. PMF)

5.3.2 Intercomparison of EC apportionment (CMB, PMF, and AeM)

5.3.3 Intercomparison of PM10 apportionment (CMB vs. PMF)

5.4 Conclusions

6 Summary and Outlook

6.1 Summary and conclusions
6.2 Outlook ........................................... 75

A Supplement to ”Comparative Source Apportionment of PM10 in Switzerland for 2008/2009 and 1998/1999 by Positive Matrix Factorisation” - Chapter 4 77
A.1 Definition of signal to noise ratio (S/N) ........................................... 77
A.2 Source profiles and source contributions for the 2008/2009 datasets ........... 80
A.3 Backward air parcel trajectories ...................................................... 90
A.4 Source profiles and source contributions for the 1998/1999 datasets ........... 92
A.5 Relative contribution of PMF factors to selected chemical species ............ 98
A.6 Scatter plot of wood combustion contributions to PM10 and measured K+ ... 99

B Supplement to ”Source Apportionment of PM10, Organic Carbon and Elemental Carbon at Swiss Sites: An Intercomparison of Different Approaches” - Chapter 5 101

References ........................................... 105

Curriculum vitae ................................. 119

Acknowledgements .............................. 121
Abstract

Atmospheric particulate matter (PM) plays an important role in atmospheric processes, modifying the radiative budget and thus impacting the climate of the Earth. Several studies have demonstrated that airborne PM has negative effects on human health (increasing mortality and morbidity) and ecosystems (causing acidification, nitrification and eutrophication). In order to reduce the negative impact on human health and ecosystems, authorities have adopted air quality standards and developed several mitigation strategies aiming to reduce ambient PM concentrations. The achievement of detailed knowledge on the composition and sources of atmospheric PM is of crucial importance for the formulation of new, efficient, and effective mitigation strategies.

The goal of this thesis has been to infer information on the chemical composition and sources of airborne PM10 (PM with a diameter less than 10μm) at different site types in Switzerland, and to assess the evolution of the chemical composition and sources during the past decade. To achieve this goal, chemical composition datasets from different site types (urban roadside, urban background, suburban, and rural sites) and time periods (from 2008/2009 and 1998/1999) were analysed.

The analysis of chemical speciation data has shown that at most sites north of the Alps (i.e. urban background, suburban, and rural sites), secondary inorganic PM (nitrate, sulphate, and ammonium) constituted the largest PM10 mass fraction, followed by carbonaceous matter (sum of organic matter (OM) and elemental carbon (EC)). A different situation was found at a rural site south of the Alps, where the concentrations of secondary inorganic components were much lower, and the concentrations of OM and EC were clearly higher than north of the Alps. Enhanced concentrations of EC, trace elements (as Cu, Fe, Mo, Sb, and Ba), and to a lesser extent OM and mineral dust, were found at an urban roadside site. The comparison of present-day chemical speciation data with data collected in 1998/1999 displayed consistent decreases in sulphate (relative decrease 35%), EC (relative decrease between 24-39%, with maximum absolute decrease of 2.4 μg/m³ at the urban roadside site), and many trace elements (e.g. heavy metals such as Pb, Ni, V, and Cd). In contrast, the concentration of nitrate increased slightly at all of the study sites (absolute increases of 0.2 - 0.5 μg/m³, relative increases of 6-15%).

Sources of airborne PM10 were identified and quantified through receptor modelling using Positive Matrix Factorisation (PMF). Modelling of today’s chemical speciation data revealed that secondary aerosols (sulphate- and nitrate-rich secondary aerosols (SSA and NSA)) were the most abundant components of PM10 at sites north of the Alps. As expected, at the urban roadside site, road traffic represented the most relevant primary source of PM10 (40% of PM10, including road salt), while at the other sites north of the Alps, contributions from road traffic and wood combustion were similar (17% and 14%, respectively). At the rural site south of the Alps, the most relevant source of atmospheric PM was wood combustion (31% of PM), while secondary aerosols and road traffic accounted for 29% and 24% of PM, respectively.
Comparing PM10 source apportionment for the two time periods (1998/1999 and 2008/2009) revealed decreasing average contributions to PM10 from road traffic and SSA (decrease of 43-51% and 20-37%, respectively), slight increasing contributions from NSA (+17-37%) and constant contributions from wood combustion.

A major result of this study was to demonstrate that the measures implemented in Switzerland and neighbouring countries to reduce road traffic (in particular EC) and sulphate precursor emissions have been successful, while further significant reductions in NO\textsubscript{x} emissions are certainly necessary for lowering the nitrate concentration in PM10. Furthermore, it was shown that PMF can be a useful tool for the assessment of long-term changes in source contributions to ambient particulate matter.

In the last part of this work, source apportionment of PM10 and important PM10 constituents (i.e. organic carbon (OC) and elemental carbon) as obtained by PMF modelling was compared with results from other source apportionment approaches (i.e. molecular marker chemical mass balance (MM-CMB) and the Aethalometer model (AeM)). On the one hand, this comparison was used for a mutual validation of model outputs. On the other hand, the intercomparison was helpful to identify the strengths and the weaknesses of the different approaches. In particular, this intercomparison underlined that highly correlated emission patterns represents an obstacle for a correct identification and quantification of PM sources when applying PMF. A similar situation prevails when the PM variability is predominantly driven by meteorology rather than by variability of the emissions of the PM sources. In both situations, the identified factors can represent mixtures of different emission sources rather than single emission sources.
Riassunto

Le polveri sottili (PM) giocano un ruolo importante nei processi atmosferici, modificando il budget radiativo della terra e quindi influenzando il suo clima. Molti studi hanno inoltre dimostrato che le PM sospese nell’aria hanno effetti negativi sulla salute umana (causando l’aumento della mortalità e dei casi di malattia) e sugli ecosistemi (portando alla loro acidificazione, nitrificazione ed eutrofizzazione). Alfine di ridurre il loro impatto negativo sulla salute umana e sugli ecosistemi, in molti stati sono stati introdotti standard per la qualità dell’aria e sono state sviluppate ed attuate diverse strategie che puntano alla riduzione delle concentrazioni di PM nell’atmosfera. Per la formulazione di nuove, efficienti ed effettive strategie di riduzione, il raggiungimento di una dettagliata conoscenza della composizione e delle fonti di PM è di cruciale importanza.

Lo scopo di questa tesi è stato quello di ottenere informazioni sulla composizione chimica e sulle fonti di PM10 (PM con un diametro inferiore a 10\(\mu m\)) presso differenti tipologie di siti in Svizzera, e di studiare l’evoluzione della composizione chimica e delle fonti di PM10 durante lo scorso decennio. Per raggiungere tale scopo, dati sulla composizione chimica raccolti presso differenti tipologie di siti (urbano stradale, urbano di sottofondo, suburbano e rurale) e durante differenti intervalli temporali (2008/2009 e 1998/1999) sono stati analizzati.

L’analisi dei dati inerenti la composizione chimica ha mostrato che presso la maggior parte dei siti posti a nord delle Alpi (urbano di sottofondo, suburbano e rurale) i composti secondari inorganici (nitrato, solfato ed ammonio) costituiscono la frazione più rilevante di PM10, seguiti dal materiale carbonaceo (somma del materiale organico (OM) e del carbone elementare (EC)). Una situazione differente è stata riscontrata presso il sito rurale posto a sud delle Alpi, dove le concentrazioni delle componenti secondarie inorganiche sono molto inferiori, e le concentrazioni del materiale carbonaceo sono chiaramente superiori a quelle misurate a nord delle Alpi. Elevate concentrazioni di EC, elementi in traccia (come Cu, Fe, Mo, Sb e Ba), ed in minor parte di OM e di polvere minerale sono state osservate presso il sito stradale urbano. Il confronto della composizione chimica odierna con quella del periodo 1998/1999 mostra una consistente diminuzione del solfato (diminuzione del 35%), di EC (diminuzione relativa del 24-39%, con una diminuzione assoluta massima di 2.4 \(\mu g/m^3\) presso il sito urbano stradale), e di diversi elementi in traccia (ad esempio di metalli pesanti come Pb, Ni, V a Cd). Al contrario le concentrazioni di nitrato sono leggermente aumentate presso tutti i siti inclusi in questo studio (aumento assoluto di 0.2 - 0.5 \(\mu g/m^3\), aumento relativo del 6-15%).

Le fonti di PM10 sono state identificate e quantificate per mezzo di un modello a recettori, utilizzando Positive Matrix Factorisation (PMF). La modellizzazione della composizione odierna ha rilevato che gli aerosol secondari (aerosol secondari ricchi di solfato e quelli ricchi di nitrato, rispettivamente SSA e NSA) rappresentano la componente più abbondante di PM10 presso i siti posti a nord delle Alpi. Come da previsione, il traffico stradale è la più importante fonte presso il sito stradale urbano (includendo il sale stradale antigelo, questa fonte emette il
40% delle PM10 misurate), mentre presso gli altri siti a nord delle Alpi la contribuzione del traffico stradale e della combustione di legna si equivalgono (17% e 14%). A sud delle Alpi la più importante fonte di PM10 è la combustione di legna (31%), mentre gli aerosol secondari ed il traffico stradale sono responsabili rispettivamente del 29% e del 24% di PM10.


Uno dei risultati più rilevanti di questo studio è stato di dimostrare che le misure implementate in Svizzera e nei paesi confinanti per ridurre le emissioni del traffico stradale (in particolare di EC) come dei precursori di solfato hanno avuto successo. Al contrario, un’ulteriore significante riduzione delle emissioni di NOx è necessaria per diminuire le concentrazioni di nitrato nelle PM10. In aggiunta è stato possibile mostrare che PMF è un tool adatto per lo studio dei cambiamenti su lungo periodo delle fonti di particolato.

Nell’ultima parte di questo lavoro, i risultati nell’apporzionamento delle fonti di PM10 e di importanti costituenti di PM10 (ovvero il carbone organico (OC) ed il carbone elementare) ottenuti tramite PMF sono stati comparati con gli outputs di altri modelli di apporzionamento (ovvero molecular marker chemical mass balance (MM-CMB) ed Aethalometer model (AeM)). Da un lato questa comparazione è stata utilizzata per ottenere una validazione mutuale dei risultati dei differenti modelli. Dall’altro lato essa è stata utile per identificare i punti forti ed i punti deboli dei differenti approcci. In particolare, questa comparazione ha sottolineato che una forte correlazione temporale nelle emissioni delle differenti fonti rappresenta un ostacolo per una corretta identificazione e quantificazione delle fonti di PM tramite PMF. Una simile situazione è riscontrabile quando la variabilità delle concentrazioni di particolato è dominata dalle condizioni meteorologiche piuttosto che dalla variabilità delle emissioni delle fonti. In entrambe le situazioni i fattori identificati possono rappresentare l’unione di differenti fonti di emissione anziché singole fonti di emissione.
Chapter 1

Introduction

Atmospheric aerosols are defined as suspensions of solid, liquid, or mixed phase particles in the atmosphere. These particles can be emitted directly to the atmosphere (primary particles) or formed in the atmosphere through chemical reactions and/or gas to particle conversions of gaseous precursors (secondary particles). The origin of atmospheric aerosols can be natural or anthropogenic: sea salt, pollen and geogenic mineral dust are examples of natural atmospheric aerosols, while anthropogenic aerosols can be emitted by fossil fuel and wood/biomass combustion or by industrial activities, and resuspended by mechanical processes, e.g. from agricultural activities, road traffic and construction works. Atmospheric aerosols have been found to have an impact on both human health (Section 1.1) and climate (Section 1.2). Moreover, they are known to have significant effects on ecosystems, causing acidification and eutrophication (Grantz et al., 2003; UNECE, 2004). For these reasons, atmospheric particles have been, and still are, the focus of numerous research activities.

1.1 Impact on human health

The impact of atmospheric aerosols on human health has been assessed by a large number of epidemiological and laboratory studies. Long-term exposure to elevated particulate matter (PM) levels has been associated with a general increase in mortality (Pope, 2007; Pope and Dockery, 2006), with particular evidence pointing to an increase in cardiovascular (Brook et al., 2004; COMEAP, 2006) and respiratory diseases (Pope and Dockery, 1992).

Together with the mass concentration, further aerosol characteristics may have an influence on the toxicity of atmospheric particulate matter. In particular, parameters such as size and chemical composition appear to have an impact on human health.

Numerous studies (see e.g. Peters et al. (1997)) have identified the smallest size fractions, in particular the particles with aerodynamic diameter smaller than 1 µm (PM1) and the ultrafine particles (particles with aerodynamic diameter smaller than 0.1 µm), as the most dangerous size fractions. These particles have the most negative impact on human health because they present the largest surface area and can penetrate deeper into lung tissue than coarse particles (Nel, 2005).

Recent studies have however showed that the impact of the coarse fraction (particles with aerodynamic diameter between 2.5 and 10 µm) on human health is not negligible. In particular studies of chronic obstructive pulmonary disease, asthma and respiratory admissions have shown...
Figure 1.1: Size and deposition of PM in the human respiratory tract (figure adapted from: UGZ (2004))

that coarse PM has a stronger or as strong short-term effect as fine PM (PM2.5, with aerodynamic diameter <2.5 μm), suggesting that coarse PM may lead to adverse responses in the lungs triggering processes leading to hospital admissions (Brunekreef and Forsberg, 2005).

Figure 1.1 illustrates the deposition zone of the particles as a function of their size: only particles with aerodynamic diameter smaller than 10 μm (PM10) are capable of penetrating into the nasopharyngeal region; the fine particles (PM2.5) can penetrate up to the bronchia and bronchioles, while as previously noted, only the smallest particles (PM1 and the ultrafine particles) can penetrate deeper into the respiratory tract, reaching the alveoli.

While the associations between PM exposure and the occurrence of chronic and acute respiratory and cardiovascular diseases are portrayed by several epidemiological studies, the biological mechanisms behind these associations are not fully understood (de Kok et al., 2006). A mechanism suggested to explain part of the toxic effects of inhaled PM is the oxidative stress arising from interaction of the particles with inflammatory cells, as alveolar macrophages (Li et al., 2003; Mazzoli-Rocha et al., 2010). As underlined by Mazzoli-Rocha et al. (2010), the ability of PM to cause oxidative stress probably underlies the association between increased exposure to PM and the exacerbation of lung diseases.

With respect to the chemical composition, there is increasing evidence that pro-oxidative organic hydrocarbons, such as polycyclic aromatic hydrocarbons (PAH), and transition metals such as copper (Cu), vanadium (V), nickel (Ni), and iron (Fe) induce pulmonary inflammation through the generation of oxidative stress (Nel, 2005). Similarly, de Kok et al. (2006) reported that smaller particles generally contain higher concentrations of PAHs and transition metals have a higher radical generating capacity and higher toxicological effects (mutagenicity, cytotoxicity and DNA-reactivity) than coarse particles.

Together with toxicological studies, some epidemiological studies also showed that specific pollutants have negative impacts on human health. An example is elemental carbon (EC), which has been associated with deficits in lung functions in children (Gauderman et al., 2004).
Air quality standards for PM and PM constituents

In order to reduce the negative effects of particulate matter on the environment and on the human health, authorities in many countries promulgated air quality standards and adopted various measures to reduce ambient PM concentrations. On the basis of current scientific findings, the World Health Organisation (WHO) sets the following guidelines for PM10 and PM2.5: mean annual PM10 concentrations should not exceed 20 µg/m³ (10 µg/m³ for PM2.5) and daily averages should not exceed 50 µg/m³ more than once a year (25 µg/m³ for PM2.5) (WHO, 2006).

In Switzerland, the standards for PM10 are in agreement with those recommended by the WHO (Swiss Federal Council, 2010), while no standards for PM2.5 are prescribed. In addition to the above-mentioned limit for PM10, Swiss legislation also includes standards for concentrations of cadmium (Cd) and lead (Pb), two heavy metals recognised to have negative impacts on human health and the environment (Skerfving et al., 1998; Thompson and Bannigan, 2008). Mean annual concentrations of Pb in PM10 should not exceed 500 ng/m³, while the mean annual value for Cd should not exceed 1.5 ng/m³.

In the European Union, the threshold values for PM10 as fixed by legislation are higher than the limits recommended by the WHO: mean annual PM10 concentrations should not exceed 40 µg/m³ and daily averages should not exceed 50 µg/m³ more than 35 times per year. At the moment, no PM2.5 standards are operative in the European Union. However, a target value that should be met by January 2010 has been defined (target value of 25 µg/m³), and a limit value will become operative by 2015 (25 µg/m³, reduced to 20 µg/m³ by 2020). In addition to the mentioned PM2.5 standards, national exposure reduction targets for the period 2018-2020 based on PM concentrations measured at urban background sites in the period 2008-2010 have been fixed (EU-Commission, 2008).

In contrast to the EU and Switzerland, PM2.5 standards in the USA are in force: the mean annual PM2.5 concentrations should not exceed 15 µg/m³ (annual mean, averaged over 3 years), while daily concentrations should not exceed 35 µg/m³ (more precisely, the 3-year average of the 98th percentile of 24-hour exposure should be less than 35 µg/m³) (EPA, 2006). For PM10 only maximal daily concentrations are prescribed (i.e. daily PM10 concentrations should not exceed 150 µg/m³ more than once per year).

1.2 Impact on climate

Greenhouse gases and aerosols affect climate by altering incoming solar radiation and outgoing infrared (thermal) radiation that are part of Earth’s energy balance. Changing the atmospheric abundance or properties of these gases and particles can lead to a warming or cooling of the climate system (IPCC, 2007). The increase of atmospheric concentrations of carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and halocarbons from anthropogenic emissions since the pre-industrial times (i.e. since 1750) have led to a positive radiative forcing (i.e. to a heating of the climate system), while for anthropogenic aerosols a net negative radiative forcing has been quantified (Figure 1.2).

Atmospheric aerosols influence the radiative budget of the Earth system in two ways: through the direct effect (scattering and absorbing solar and thermal infrared radiation - see e.g. Haywood and Boucher, 2000) for details) and through the indirect effect (aerosols acting as cloud condensation nuclei and ice nuclei, which modifies the radiative properties and lifetime of clouds - see e.g. Lohmann and Feichter, 2005) for details).
Chapter 1. Introduction

Figure 1.2: Principal components of the radiative forcing of climate change since 1790. Positive forcings lead to climate warming and negative forcings lead to a net cooling; black error bars represent the range of uncertainty for the respective values (figure from: IPCC (2007)).

The total direct aerosol effect was estimated to have a radiative forcing of $-0.5 \pm 0.4 \text{ W/m}^2$ (see Figure 1.2), while that of the cloud albedo effect (also referred as first indirect effect) was estimated as $-0.7 \text{ W/m}^2$ (ranging between $-0.3$ and $-1.8 \text{ W/m}^2$). Note that the radiative forcing caused by long-lived greenhouse gases has been well documented and has a high level of scientific understanding. On the contrary the level of scientific understanding of the total direct and cloud albedo effect is still low (IPCC 2007).

The chemical composition of atmospheric aerosols plays an important role in determining their optical properties and thus their influence on the Earth’s radiation budget (Pilinis et al. 1995; Yu et al. 2006). Aerosol constituents such as sulphate and nitrate are reported to have a negative direct radiative forcing, while other compounds such as black carbon (BC) have a positive direct radiative forcing (see Table 1.1). In addition, the impact of atmospheric particles on the Earth’s radiative budget does not always finish with their deposition at the surface: BC deposited in or on snow or sea ice reduces its albedo, increasing absorption of solar radiation to the ground (Jacobson 2010). The radiative forcing of this process was estimated as $+0.10 \pm 0.10 \text{ W/m}^2$ (see Table 1.1).

Furthermore, chemical composition is an important parameter influencing the ability of aerosols to act as cloud condensation nuclei (CCN) or ice nuclei (IN) (Gorbunov et al. 2001; Juranyi et al. 2010). As outlined by Lohmann and Feichter (2005), changes in CCN and IN concentration can impact cloud lifetime and optical properties, thus modifying the Earth’s radiation budget and hydrological cycle.
Table 1.1: Estimates of aerosol direct radiative forcing and radiative forcing by surface albedo change for different chemical species and aerosol sources (IPCC, 2007).

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Direct radiative forcing ($\pm$ 90% confidence interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>-0.40 W/m$^2$ ($\pm$ 0.20 W/m$^2$)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>-0.10 W/m$^2$ ($\pm$ 0.10 W/m$^2$)</td>
</tr>
<tr>
<td>Fossil fuel OC</td>
<td>-0.05 W/m$^2$ ($\pm$ 0.05 W/m$^2$)</td>
</tr>
<tr>
<td>Fossil fuel BC</td>
<td>+0.20 W/m$^2$ ($\pm$ 0.15 W/m$^2$)</td>
</tr>
<tr>
<td>Biomass burning aerosol</td>
<td>+0.03 W/m$^2$ ($\pm$ 0.12 W/m$^2$)</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>+0.10 W/m$^2$ ($\pm$ 0.20 W/m$^2$)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Surface albedo change ($\pm$ 90% confidence interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC on ice and snow</td>
<td>+0.10 W/m$^2$ ($\pm$ 0.10 W/m$^2$)</td>
</tr>
</tbody>
</table>

1.3 Variability of chemical composition

As discussed in Sections 1.1 and 1.2, the chemical composition appears to be an important variable that, among others, governs the impact of atmospheric aerosols on climate and on human health. Atmospheric aerosols consist of a complex mixture of organic matter (OM), elemental/black carbon (EC or BC), sulphate, nitrate, ammonium, crustal matter, trace elements, and water. Composition of tropospheric bulk aerosols can be strongly influenced by numerous factors, such as meteorological conditions and the strength of the local natural or anthropogenic aerosol sources. These conditions influence the levels and proportions in which the individual aerosol components are present.

The location of a site has an important influence on the chemical composition of PM. Concentrations of BC/EC, OM, and crustal matter are elevated at urban roadside sites compared to remote, rural, and near-city sites (Putaud et al., 2004a). Causes of these differences are direct vehicular emissions and the resuspension of dust by road traffic. For secondary inorganic PM constituents (i.e. sulphate, nitrate, and ammonium) the differences between the different types of sites are much smaller (see Figure 1.3).

Another important variable that can influence the chemical composition is the geographic location of the site where PM10 is characterised. Putaud et al. (2010) divided the European continent into three geographic regions: North-western, Southern, and Central Europe, and showed that monitoring sites belonging to the same site typology can differ in chemical composition depending on their geographic locations. In particular, they found that sites in Southern Europe are characterised by higher concentrations of mineral dust compared to the other geographic zones (see Figure 1.4). This is likely due to the presence of windblown dust from semi-arid soils of this region and to the frequent Saharan dust events observed in this region (Rodriguez et al., 2001). On the other hand, the sites located in central Europe are characterised by higher concentrations of EC and total carbon (TC), along with lower concentrations of sea salt (see also Manders et al., 2010).
Chapter 1. Introduction

Figure 1.3: Mean annual chemical composition of PM10 at remote, rural, near-city, urban, and kerbside sites in Europe (adapted from Putaud et al. (2004a)).

Figure 1.4: Relative mean annual chemical composition of PM10 in different European regions (North-western, Southern, and Central Europe) and at different types of monitoring sites (indicated by the colours of site name, green: rural background, gold: near-city, gray: urban background, black: kerbside) (adapted from Putaud et al. (2010)).
1.4 Thesis motivation and overview

As underlined in the previous chapters, atmospheric aerosols have a relevant impact on human health, the Earth’s radiative budget, and the environment. A reduction of aerosol concentrations is thus indispensable to decrease these negative effects. To plan and implement adequate and effective PM abatement strategies, a detailed knowledge of the PM chemical composition and of the PM emission sources is required. In addition, for evaluating the efficiency of the implemented abatement strategies, information concerning the long-term evolution of both PM constituents and PM sources is of great interest. Despite their importance, only limited information on these topics is available in Switzerland. In this thesis, the present day chemical composition and sources of PM10 at different site typologies representing typical environmental conditions characteristic of Switzerland are investigated and discussed. Further, the evolution of PM constituents and most important PM10 sources observed during the last decade is presented. Below an overview of the 6 chapters that together with the Introduction (Chapter 1) compose this thesis is provided:

Chapter 2 (Source apportionment of atmospheric aerosols) introduces the source apportionment methods applied in this work. In particular this chapter focuses on a site-to-site comparison approach (Lenschow approach - roadside and urban enrichment), on quantification and source apportionment of specific PM components (e.g. mineral dust and carbonaceous matter), and finally on receptor models (e.g. Positive Matrix Factorisation - PMF, and Chemical Mass Balance - CMB) applied to determine PM emission sources and components at receptor sites.

Chapter 3 (Publication I) presents the chemical composition of PM10 at different site types in Switzerland, and discusses its evolution comparing the present-day data with those collected a decade earlier. By application of a simple site-to-site comparison approach, the fractions of PM and PM constituents emitted by local road traffic, by the urban environment, and the fraction constituting the regional PM background are quantified. The evolution of the chemical composition of PM10 is discussed in the light of the different abatement measures implemented to reduce ambient PM10 concentrations.

Chapter 4 (Publication II) exposes the sources and components contributing to ambient PM10 as identified by a factor analytical receptor model at the sites and for the time periods presented in Chapter 3. The potential of receptor modelling for identification of PM sources and their long-term evolution is discussed.

Chapter 5 (Publication III) is devoted to the comparison of the results of receptor modelling presented in Chapter 4 with those of two complementary source apportionment approaches. The first being a molecular markers-based source apportionment approach, and the second being based on aerosol light absorption for apportionment of sources of EC/BC. The weaknesses and strengths of the different source apportionment approaches are identified and discussed.

Finally, Chapter 6 (Summary and Outlook) summarises the results presented in chapter 3, 4 and 5 and provides an outlook on the strategies that could be applied to obtain more reliable information on the evolution of PM composition and more precise PM source apportionment.
Chapter 2
Source Apportionment of Atmospheric Aerosols

A large number of methods has been developed in order to apportion atmospheric aerosols to their emission sources. These methods range from approaches based on the comparison of PM chemical composition at different site types (e.g. the Lenschow approach, see Section 2.1), to approaches developed to quantify and apportion single PM fractions (e.g. mineral dust and carbonaceous matter), up to more sophisticated statistical modelling of chemical composition speciation data of PM at a receptor site (called receptor modelling, see Section 2.3).

In the following Sections we present the methods for source apportionment of atmospheric PM applied in this thesis (see Chapters 3, 4 and 5), and we introduce some approaches often used to validate results of source apportionment studies (e.g. $^{14}$C analysis).

2.1 The Lenschow approach

The Lenschow approach is a method developed to quantify the combined contributions of the different PM sources within an agglomeration (Lenschow et al., 2001). In particular it allows to apportion PM (and its constituents) to local road traffic related PM, PM emitted in the urban environment and regional PM (see Figure 2.1).

This approach is based on the assumptions that monitoring sites representing typical environmental conditions as urban roadside, urban background and regional/rural background environments can be identified, and that each single site belonging to a given category is representative for all the sites belonging to this group. Furthermore it is assumed that the increment in PM concentration and the differences in PM chemical composition between the urban background site and the roadside site are due to the emissions of the road traffic adjacent to the roadside site. Similarly, the differences in PM concentration and chemical composition at urban background sites compared to rural background sites are due to PM emitted in the urban environment. And finally, that the PM concentrations observed at the rural background site are due to regional sources with negligible contributions from the urban environment. The last assumption is violated when the chemical composition at rural background sites is strongly affected by urban emissions as during persistent anticyclonic episodes.
Chapter 2. Source Apportionment

1. Urban roadside site
2. Urban background site
3. Regional background site

Figure 2.1: Schematic of the PM concentration at an urban agglomeration (adapted from Lenschow et al. (2007)).

The roadside and the urban enrichment

The concept developed by Lenschow et al. (2001) has been revisited by Oliveira et al. (2010) and successively by Amato et al. (2011) by introducing the concept of roadside impact or roadside enrichment (RE). The RE of a given chemical component represents the mass fraction of the chemical component that results from the emissions in the immediate vicinity of the roadside site, and is defined as the fractional difference between the concentration at a roadside site (RS) and an urban background site (UB) (Oliveira et al., 2010):

\[
RE_i = \left( \frac{X_{RS,i} - X_{UB,i}}{X_{RS,i}} \right) \times 100
\]  \hspace{1cm} (2.1)

where \(i\) is the given chemical component, and \(X_{RS}\) and \(X_{UB}\) its concentrations at a roadside site and an urban background site.

Following the concept introduced by Lenschow et al. (2001) and the definition of RE, the urban enrichment (UE) can be defined. The UE represents the mass fraction of a chemical component measured at an urban background site that results from the emissions of the urban environment, and it is expressed as:

\[
UE_i = \left( \frac{X_{UB,i} - X_{RB,i}}{X_{UB,i}} \right) \times 100
\]  \hspace{1cm} (2.2)

where \(i\) is the given chemical component and \(X_{RB}\) its concentration at a regional background site.
2.2 Quantification and source apportionment of specific PM fractions

2.2.1 Quantification of mineral dust

Concentrations of mineral dust (often referred as crustal material) can be derived by the measured concentrations of elements that constitute the Earth’s crustal material.

According to Wedepohl (1995), most of the mass fraction of the continental earth crust is constituted by oxides of Si, Al, Fe and Ca. Oxides of Mg and K present lower concentrations compared to the above mentioned major constituents, but their contribution is not negligible.

Concentrations of mineral dust can thus be derived from the measured concentrations of Si, Al, Fe, Ca, Mg and K; and as these elements are mainly present as oxides, measured elemental concentrations are usually scaled by multiplication factors to account for the unmeasured oxygen mass fractions (Chow et al., 1994; Hueglin et al., 2005; Solomon et al., 1989). The equation introduced by Solomon et al. (1989) and subsequently revised by Hueglin et al. (2005) to quantify the mineral dust contribution to ambient PM is:

\[ \text{Mineral dust} = 2.14 \text{Si} + 1.89 \text{Al} + 1.66 \text{Mg} + 1.40 \text{Ca} + 1.21 \text{K} + 1.43 \text{Fe} \]  \hspace{1cm} (2.3)

Other equations often applied to quantify mineral dust contributions were compiled by Putaud et al. (2010). Application of these formulas depends on the availability of the different tracers. Some of these equations are listed below:

\[ \text{Mineral dust} = 2.9 \text{Si} + 2.1 \text{Al} + 2.1 \text{Mg} + 1.40 \text{Ca} + 1.55 \text{K} + 1.43 \text{Fe} \]

\[ \text{Mineral dust} = 2.5 \text{Si} + 2.2 \text{Al} + 1.6 \text{Ca} + 2.4 \text{Fe} + 1.9 \text{Ti} \]

\[ \text{Mineral dust} = 4.5 \text{Ca}^{2+} \]

Equivalence of these equations was tested by comparing the different approaches at different site types and for different European regions. This analysis showed that although correlations are good over a year, uncertainty of mineral dust concentrations can reach ± 150% (Putaud et al., 2010).

A limitation of the described approach is the impossibility to quantify the anthropogenic and natural or geogenic fraction of mineral dust. This topic will be investigated in Chapter 3 of this thesis, where a method for the quantification of natural mineral dust is presented.
2.2.2 Fossil vs. non fossil contribution to carbonaceous matter

**Radiocarbon - $^{14}\text{C}$**

Carbon-14 ($^{14}\text{C}$) concentration measurements are one of the most widespread source apportionment approaches of carbonaceous matter. The physical principle at the basis of this apportionment method is the fact that $^{14}\text{C}$, with a half-life of 5730 years, has completely decayed in fossil fuel and thus emissions by fossil-fuel combustion are free of $^{14}\text{C}$. Assuming that biomass combustion and biogenic emission contain modern $^{14}\text{C}$ fractions (assumed to be known) it is possible to quantify contemporary and fossil carbon in atmospheric carbonaceous aerosols, and consequently to distinguish between fossil fuel combustion and biogenic or wood combustion emissions (Currie, 2000).

As an extension of the original radiocarbon approach, separated analyses of $^{14}\text{C}$ in EC and OC (Szidat et al., 2004) or in PAHs (Reddy et al., 2002) are possible. Combustion generated compounds like EC and PAHs are attributed to two sources: fossil fuel combustion and wood/biomass combustion. For OC, separation of contributions from wood/biomass combustion and biogenic emissions is not possible. The $^{14}\text{C}$ method allows the determination of the combined contribution of these two sources as well as the determination of the contribution of fossil fuel combustion to total OC.

**The Aethalometer model**

Together with $^{14}\text{C}$ concentrations also aerosol optical properties are exploited to infer information on the sources of carbonaceous aerosols. In particular source apportionment of carbonaceous matter based on the different optical properties of fossil-fuel and wood/biomass combustion emitted carbonaceous aerosols have been proposed (Aethalometer model - see Sandradewi et al. (2008b)). The physical principle on which the apportionment of carbonaceous matter is based on, is that fossil-fuel combustion and wood/biomass burning aerosols can be distinguished on the basis of different wavelength dependencies in light absorption. Absorption of fossil fuel combustion aerosols exhibit a relatively weak wavelength dependence, while absorption of brown carbon-rich biomass smoke aerosols has a much more pronounced wavelength dependence (Kirchstetter et al., 2004).

The Aethalometer model has been applied to total carbonaceous matter for data from short-term field campaigns (Favez et al., 2010; Sandradewi et al., 2008a) and to the apportionment of BC measured during an extended time period (Herich et al., 2011).
2.3 Receptor models

Receptor models are methods applied to obtain information about the sources of air pollutants (e.g. PM and volatile organic compounds - VOC) from measured concentrations of the air pollutant constituents at a receptor point (Hopke and Allan, 2009). The application of receptor models is based on a simple mass conservation argument: if interactions with other chemical compounds and removal from the atmosphere are negligible, the measured concentration of a chemical compound \( x_j \) at a receptor site is the sum of the contributions of the \( p \) individual emission sources (Henry et al., 1984):

\[
x_j = \sum_{k=1}^{p} z_{kj},
\]

(2.4)

where \( z_{kj} \) is the contribution of the source \( k \) to the single compound \( j \).

Receptor models imply furthermore that contributions \( (z_{kj}) \) of an emission source \( k \) to a single chemical compound \( j \) can be expressed as the product of the total contribution of the source \( k \) \( (g_k, \text{ e.g. total PM contribution}) \) and the mass fraction of the chemical compound \( j \) in the total emission of source \( k \) \( (f_{kj}) \). This means that the source contributions can be expressed as:

\[
z_{kj} = g_k \cdot f_{kj},
\]

(2.5)

where the term \( f_{kj} \) is nothing more than the chemical emission profile of source \( k \).

Finally by assuming that emission profiles of each source remain constant over time (a central assumption in receptor models), the contribution to the chemical compound \( j \) at the time \( i \) \( (x_{ij}) \) is:

\[
x_{ij} = \sum_{k=1}^{p} g_{ik} \cdot f_{kj} + e_{ij},
\]

(2.6)

where \( g_{ik} \) are the total contribution of the source \( k \) at time \( i \). The model error \( e_{ij} \) is the error that can arise from measurement uncertainties and violations of model assumptions, e.g. occurrence of atmospheric or transformation processes and temporal variation of the chemical profile of source emissions.

The basic equation in matrix form can be written as:

\[
X = GF + E,
\]

(2.7)

where the \( X, G, F \) and \( E \) are the data matrices (the \( nxm \)-matrix of the \( m \) measured chemical species in \( n \) samples), the score matrix (a \( nxp \)-matrix which columns represent the contributions of the \( p \) sources), the factor matrix (a \( pxm \)-matrix which rows represent the profiles of \( p \) sources), and the residual matrix.
Chapter 2. Source Apportionment

Different concepts and methods for determination of the contribution of sources of atmospheric pollutants have been developed in the past. Figure 2.2 shows specific receptor models and more general modeling concepts in relation to the a priori knowledge about the emission sources that is required for application of the corresponding approach. The approaches range from Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) where only qualitative a priori information about the number and the chemical profiles of the sources are needed, up to the Chemical Mass Balance (CMB) model where detailed knowledge of the chemical profiles of all of the important sources is required. In the following, CMB and PMF, which are two of the most frequently applied receptor models, are described in more detail.

Figure 2.2: Receptor model approaches for estimation of source contributions (taken from Viana et al., 2008a). Shown are more general concepts as well as specific receptor models (in italic, dotted arrows). The methods are ordered depending on the required a priori knowledge about the emission sources.

2.3.1 Chemical Mass Balance - CMB

The application of CMB models requires the quantitative a priori knowledge of the source number and of the chemical profile of the source emissions (i.e. of $p$ and $f_{kj}$ in equation 2.6), while the only unknown is the mass contribution of the different $p$ sources to each sample (i.e. $g_{ik}$). In CMB equation 2.6 is usually solved using effective-variance least-square approach, where both the uncertainty of the measurement at the receptor and the uncertainty of the source profile are considered for model error weighting (Watson et al., 1984).

Main disadvantages of CMB are the inability to model unknown sources and the difficulty to quantify contribution of secondary aerosol components (Viana et al., 2008b). In addition before application of CMB it is necessary to experimentally determine local emission source profiles.
This implies an intensive work before data modelling. CMB gives however the possibility to perform receptor modelling on a low number of samples and no error can happen in the identification of the source (sources are a priori known).

### 2.3.2 Positive Matrix Factorisation - PMF

Positive Matrix Factorisation (PMF) is a factor analytical receptor model that solves the mass balance equation 2.7 by minimising the Frobenius norm of the residual matrix $E$ divided by the measurement uncertainty matrix $S$, with the constrains that all the elements of $G$ and $F$ have to be non-negative (Paatero, 1997; Paatero and Tapper, 1994).

In other words, the residuals $e_{ij}$ of mass balance equation 2.6 are weighted by error estimates $s_{ij}$ of measured data $x_{ij}$, and the sum of the square of scaled residual $Q(E)$ defined as:

$$Q(E) = \sum_{i=1}^{n} \sum_{j=1}^{m} \left( \frac{e_{ij}}{s_{ij}} \right)^2 = \sum_{i=1}^{n} \sum_{j=1}^{m} \left( \frac{x_{ij} - \sum_{p} g_{ip} f_{pj}}{s_{ij}} \right)^2$$  

has to be minimised under constrains that $f_{ij}$ and $g_{ij}$ have to be non-negative.

The advantage of the element-by-element weighing procedure applied in PMF model is that low concentration samples presenting low measurement uncertainties have similar weight as high concentration samples affected by high measurement uncertainties. The element-by-element weighing approach is different from the procedure applied by other widely applied receptor models (e.g. Principal Component Analysis (PCA)), where only the sum of the squares of the un-weighted residual is minimised, and where high concentration samples tend to dominate the analysis (Lee et al., 1999).

Non-negativity of the $F$ and $G$ matrix is a central point of PMF: source can not have a negative elemental concentration and similarly source contributions to atmospheric pollution can not emit negative mass. Negative source profiles (rows of $F$) and source contributions (columns of $G$) are physically impossible and these factors are thus not meaningful.

To ensure non-negativity, a new objective function $\bar{Q}(E,F,G)$ called enhanced object function $Q$ is defined. The new objective function originates form the sum of the original objective function $Q(E)$ (see equation 2.8) with four additional terms:

$$\bar{Q}(E,F,G) = Q(E) + P(F) + P(G) + R(F) + R(G)$$

$$= \sum_{i=1}^{n} \sum_{j=1}^{m} \left( \frac{e_{ij}}{s_{ij}} \right)^2 - \alpha \sum_{i=1}^{n} \sum_{h=1}^{p} \log G_{ih} - \beta \sum_{h=1}^{p} \sum_{j=1}^{m} \log F_{hj}$$

$$+ \gamma \sum_{i=1}^{n} \sum_{h=1}^{p} G_{ih}^2 + \delta \sum_{h=1}^{p} \sum_{j=1}^{m} F_{hj}^2.$$  

(2.9)

where $P(F)$ and $P(G)$ are the two penalty terms preventing that $G$ and $F$ become negative, $R(G)$ and $R(F)$ are the regularisation terms reducing rotational freedom (rotational freedom referred
There is the possibility to identify pairs of matrices $\mathbf{G}$ and $\mathbf{F}$ resulting by linear transformation of the original $\mathbf{G}$ and $\mathbf{F}$ matrices, i.e. $\mathbf{G} = \mathbf{GT}$ and $\mathbf{F} = \mathbf{T}^{-1}\mathbf{F}$, where $\mathbf{TT}^{-1} = \mathbf{I}$, and $\alpha$, $\beta$, $\gamma$ and $\delta$ are the coefficients that control the strength of the penalty terms and the regularisation terms. These coefficients are given smaller values during the iteration so that their final values are negligible but not zero (Paatero, 1997).

The application of Positive Matrix Factorisation (PMF) does not require quantitative a priori information on the number of emission sources and on their chemical composition (see also Figure 2.2). Receptor modelling by PMF requires however qualitative or semi quantitative \textit{a posteriori} information on source chemical profiles and on time variability of source contributions. This information is of high importance for determination of the correct number of sources and for interpretation of the identified sources.

While on the one hand the low required a priori knowledge of the number and chemical profile of emission sources can be an advantage (lower sampling and chemical characterisation efforts), on the other hand it can also become a problem. When less information on the emission sources is available, a misinterpretation of the emission sources cannot be excluded.

Furthermore, if chemical profiles of different emission sources are co-linear, or if emission patterns are highly correlated (co-variability of sources emissions) or if the PM variability is predominantly driven by meteorological conditions rather than by the variability of the emission sources, the ability of PMF to properly resolve sources and correctly predict their contributions deteriorates (Habre et al., 2011). The identified factors can represent mixtures of different emission sources rather than single emission sources.

In order to minimise problems arising by highly correlated emissions from different sources, the chemical characterisation and the subsequent modelling of a large number of samples from a receptor site is recommended. In this way the probability to collect PM samples in periods when source emissions do not co-vary or when PM variability is not driven by meteorological conditions increases. In addition, as underlined in Chapter 4, the analysis of data from multiple sites and different time periods might help for the correct interpretation of identified emission sources. In any case, it is advisable to use auxiliary data (e.g. measurements of specific tracers like levoglucosan) and other available information for independent tests for plausibility of the obtained results.

The intercomparison of the results from different source apportionment approaches is a further option that can be exploited for reciprocal validation of modelling findings. This topic is addressed in Chapter 5 where the results of three different source apportionment approaches (PMF, CMB and the Aethalometer model) are compared and discussed.
Chapter 3


The content of the following chapter is adopted from:


Abstract

In this study, the chemical composition of PM10 at various sites in Switzerland during a one year period in 2008/2009 and changes since the time of a similar characterisation campaign in 1998/1999 are investigated. The concentrations of main components of PM10 were found to be similar at different site types north of the Alps (i.e. urban background, suburban and rural sites). Secondary inorganic PM10 components (nitrate, sulphate and ammonium) constituted the largest PM10 mass fraction, followed by carbonaceous matter (OM and EC), while the abundance of mineral dust and trace elements was small (both <10\%). At a rural site south of the Alps the concentrations of secondary inorganic components were much lower and the concentrations of OM and EC clearly higher than north of the Alps. Enhanced concentrations of EC, trace elements and to a lesser extent of OM and mineral dust were found at an urban roadside site. At this site, typical traffic related trace elements like Cu, Fe, Mo, Sb and Ba were highly enriched.

This paper indicates clear positive effects of emission reduction measures for PM10 and precursors implemented during the past ten and more years. The concentrations of sulphate and EC declined during the considered time period, EC reductions were especially strong at the urban roadside site (-2.4 µg/m\(^3\), -39\%). In contrast, the concentration of nitrate slightly increased at all of the considered sites (absolute increase of 0.2 - 0.5 µg/m\(^3\), relative increase of 6-15\%). Large reductions in the concentrations of many trace elements in PM10 during the past ten

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years are evident. As an example, the observed relative decrease of Pb is about -80%, which is a success of the ban of leaded gasoline in Switzerland and in the EU.

### 3.1 Introduction

Atmospheric particulate matter (PM) has raised severe concerns in many aspects. Elevated PM levels have been associated with an increase of respiratory and cardiovascular diseases (Pope and Dockery, 2006) and allergies (Monn, 2001), with the reduction of visibility (Horvath, 1993) and with acidification and eutrophication of ecosystems (UNECE, 2004). It was further recognized that atmospheric PM plays an important role in the climate system (IPCC, 2007), and it has been shown that the elemental composition of PM has a strong influence on its effects on human health and on the environmental behaviour (de Kok et al., 2006; Harrison and Yin, 2000; Heeb et al., 2008; Lighty et al., 2000; Mueller et al., 2010).

In order to reduce the concentration of atmospheric PM and its impact on human health and the environment, air quality standards have been promulgated and various measures have been implemented in Europe during the last decades. An example is the ban of leaded gasoline, which became effective at 1st January 2000 in Switzerland (Swiss Federal Council, 1999) as well as in the EU (EU-Commission, 1998b). As a result, the emissions of PM and precursors of PM have continuously declined in Europe (Monks et al., 2009). Consequently, ambient PM10 concentrations decreased during the last decades in Switzerland (Barmpadimos et al., 2011), leading to improvements for the public health (Bayer-Oglesby et al., 2005; Schindler et al., 2009). Despite of these positive trends, the air quality standards for PM10 are still regularly exceeded in large parts of Switzerland (BAFU, 2010) and in various European regions (Putaud et al., 2010). For assessment of the effect of implemented reduction measures and planning of further air pollution abatement strategies, a detailed knowledge of PM10 chemical composition and temporal trends in PM10 composition is of high importance.

During the last years several PM chemical characterisation studies have been performed across Europe, improving the knowledge on the chemical composition of atmospheric PM at different European regions (Putaud et al., 2004a, 2010; Querol et al., 2004a). However, detailed PM chemical speciation studies in Europe were mostly focused on short term campaigns (Putaud et al., 2010), not providing information on long term trends of PM composition. This study is focusing on the investigation of the chemical composition of PM10 collected during a one-year period (August 2008 - July 2009) at five Swiss sites, and on the comparison with the results from a previous campaign from April 1998 to March 1999 (Hueglin et al., 2005). The comparison of the PM10 composition during these two campaigns is used for an assessment of the effects of PM10 reduction measures implemented during the last decade.

### 3.2 Methodology

#### 3.2.1 Sampling sites

PM10 samples were collected from August 2008 to July 2009 at five sites of the Swiss National Air Pollution Monitoring Network (NABEL). The selected sites represent different air quality situations: an urban roadside site in Bern (BER), an urban background site in Zurich (ZUE), a
3.2. Methodology

Figure 3.1: Map of Switzerland with the location of the sampling sites.

suburban site in Basel (BAS), a rural site north of the Alps in Payerne (PAY), and a rural site south of the Alps in the Magadino plane (MAG). Fig. 3.1 shows the location of the sampling sites, more details are given in Table 3.1.

Three of these sites (BAS, BER, and ZUE) were already included in an earlier campaign performed from April 1998 to March 1999 (Hueglin et al., 2005). Note that at the urban roadside site BER, the numbers of vehicles per day on the road nearby the site decreased during the time between the two campaigns by 29% (Table 3.1), the absolute numbers of heavy duty vehicles remained about constant (2’100 vehicles per day in 1998/1999 and 2’000 vehicles per day in 2008/2009). The evolution of the traffic density at the urban roadside site BER is due to changes in the local traffic management, and is not representing a general trend for urban roadside sites in Switzerland. Note moreover that the pavement of the road nearby BER has been renewed immediately before the start of the 2008/2009 campaign.

3.2.2 PM10 sampling and chemical characterisation

For a direct comparison of the PM10 chemical composition data from 2008/2009 with those from the previous study, PM10 sampling and chemical analysis were mainly identical or only slightly modified to those described in Hueglin et al. (2005).

PM10 samples were collected using high-volume samplers (Digitel DA-80H, 30 m$^3$h$^{-1}$ flow rate) equipped with PM10 inlets meeting the requirements of EN 12341 (CEN, 1998). Particles were collected during 24h on quartz fibre filters (Pallflex Tissuquartz QAT-2500-UP, Ø=150mm). PM10 sampling was performed on every 4th day during the sampling period (Table 3.1). After sampling the filters were stored in a freezer at -18°C until analysis. In addition to the PM10 samples, a total of 24 field blank filters were taken and used for investigation of possible contaminations during sampling and analysis (Ulrich and Wichser, 2003) and thus for determination of the analytical detection limits. PM10 mass concentration was determined by means of an automatic PM10 monitor (TEOM 1400AB/FDMS 8500, Thermo Scientific Fisher).
Chapter 3. Chemical composition of PM10 in Switzerland

Table 3.1: Characteristics of the sampling sites and periods of comparison. Traffic density were measured at urban roadside site only. The fraction of heavy duty vehicles was 6.7% in 1998/1999 and 8.9% in 2008/2009.

<table>
<thead>
<tr>
<th>Site</th>
<th>Altitude (m a.s.l.)</th>
<th>Site type</th>
<th>Traffic density (vehicle/day)</th>
<th>Period of comparison</th>
<th>Number of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bern</td>
<td>536</td>
<td>Urban roadside</td>
<td>31500</td>
<td>1 Apr. 98 - 31 Mar. 99</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22500</td>
<td>4 Aug. 08 - 30 Jul. 09</td>
<td></td>
</tr>
<tr>
<td>Zurich</td>
<td>410</td>
<td>Urban background</td>
<td>1 Apr. 98 - 31 Mar. 99</td>
<td>4 Aug. 08 - 30 Jul. 09</td>
<td>103</td>
</tr>
<tr>
<td>Basel</td>
<td>317</td>
<td>Suburban</td>
<td>1 Apr. 98 - 31 Mar. 99</td>
<td>4 Aug. 08 - 30 Jul. 09</td>
<td>103</td>
</tr>
<tr>
<td>Magadino</td>
<td>204</td>
<td>Rural south of the Alps</td>
<td>4 Aug. 08 - 30 Jul. 09</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>Payerne</td>
<td>489</td>
<td>Rural north of the Alps</td>
<td>4 Aug. 08 - 30 Jul. 09</td>
<td>91</td>
<td></td>
</tr>
</tbody>
</table>

Sampling of particulate matter on inert filters such as the quartz fibre filters used in this work is prone to sampling artefacts. As outlined e.g. in Putaud et al. (2004a), substantial losses of ammonium nitrate can occur at temperatures above 10°C (Hering and Cass, 1999). Adsorption and volatilization of semi-volatile organics can cause both positive and negative artefacts for particulate organics (Eatough et al., 1993). However, these artefacts do not considerably affect the conclusions drawn from this study.

The concentration of water soluble inorganic ions (Na\(^+\), NH\(_4\)^+, Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Cl\(^-\), NO\(_3\)^-, SO\(_4^{2-}\)) was determined by ion chromatography (Dionex IC 3000) after extraction from the filters in 40ml of water during 24h.

Inductively coupled plasma mass spectrometry (ICP-MS) was applied after microwave digestion in HNO\(_3\) - H\(_2\)O\(_2\), to determine the concentration of 28 trace elements. Filter punches of 3 cm diameter were cut for subsequent acid digestions in a MLS START 1500 microwave system. Each filter punch was posed in a digestion vessel and an acid solution of 3 ml nitric acid (HNO\(_3\)) and 1 ml hydrogen peroxide (H\(_2\)O\(_2\)) was added. As discussed by Hueglin et al. (2005), the relatively mild extraction method was selected because a HNO\(_3\) - HF digestion of the filter samples lead to clearly higher detection limits for some of the elements due to contamination from the filter material. After digestion the solution was filled to an end volume of 10 ml. To minimize contamination due to sample preparation, all digestion vessels were prequalified before use. The digested filter segments were characterised for Na, Mg, Al, K, Ti, Mn, Ni, Cu, Zn, Ga, Rh, Sr, Y, Mo, Cd, Sb, Ba, La, Ce, Nd, Pb and Bi using a quadrupole-ICP-MS (Q-ICP-MS, Perkin-Elmer/Sciex Elan 600); Ca, V, Cr, Fe, As and Se were determined with a high-resolution magnetic sector field-ICP-MS (Finnigan ELEMENT 2). From each PM10 sample, two filter punches were analysed separately in order to determine the measurement uncertainty of the element concentrations including the contribution from inhomogeneous deposition of PM10 on the quartz fibre filter. As the applied analytical method was similar to the method used in the earlier study, the recovery rates of the measured elements can be assumed to be similar to the ones in Hueglin et al. (2005).
For calculation of the mass concentrations of mineral dust and the sum of trace elements (Section 3.2.3), the measured element concentrations have been multiplied with the corresponding recovery rates determined by comparing the selected extraction method to a HNO$_3$ - HF digestion using PM10 samples collected on teflon filters and also by analysis of a certified reference material (see Hueglin et al. (2005) for details). The element concentrations reported in Table 3.4 are however the measured values, because recovery rates are unknown for several elements.

Elemental and organic carbon (EC and OC) were determined by the thermal-optical transmission method (TOT, OCEC Analyzer Sunset Laboratory Inc.) using the EUSAAR-2 temperature protocol (Cavalli et al., 2010). The TOT method utilizes the detection of the light transmission through the filter sample for correction of charring of OC that might occur during analysis (Birch and Cary, 1996). In the earlier study the VDI2465/1 method was used for measurement of total carbon (TC) and EC, OC was then calculated by subtracting the measured EC concentration from the measured TC concentration (VDI, 1996). Due to the fact that different analytical methods can lead to large differences in OC and EC concentrations as indicated by Schmid et al. (2001), the PM10 filter samples from BER and ZUE collected during the earlier study were re-analysed using the TOT/EUSAAR-2 method.

Quantitative re-analysis of the old PM10 filter samples was possible for EC, whereas OC and TC mass concentrations increased due to uptake of semi-volatile organic compounds during the storage for several years at room temperature. However, parallel measurements of TC proved that the VDI2465/1 method agreed very well with TOT/EUSAAR-2. It is only the split between EC and OC that depends strongly on the applied analytical method. Consequently, OC was re-calculated from the difference of originally measured TC and re-analysed EC. Unfortunately, five of the PM10 samples from 1998/1999 collected at BER and one sample from ZUE got lost and could not be re-analysed. The EC concentrations of these missing samples were estimated from the linear relationships between TOT/EUSAAR-2 and VDI2465/1 determined at both sites individually.

Also the PM10 samples collected during 1998/1999 in BAS were not available for re-analysis. EC at BAS from the 1998/1999 study was therefore corrected by applying a linear relationship between TOT/EUSAAR-2 and VDI2465/1 as obtained from re-analysis of the PM10 samples from 1998/1999 at ZUE and PAY (note that PAY 1998/1999 data are not presented here), two sites with similar PM10 composition as BAS. The OC concentrations were then calculated as described above for BER and ZUE. The re-analysis of EC and recalculation of OC in PM10 from 1998/1999 eliminates the influence of methodical differences for a comparison of EC and OC during the two campaigns. The applied correction for BAS increases the uncertainty for daily EC and OC concentrations, the additional uncertainty is however negligible for aggregated values such as seasonal and annual mean concentrations.

The concentration of organic matter (OM) was calculated from OC by multiplication with a factor of 1.6 to account for the mass of oxygen and other unmeasured elements in non-carbon organic matter (Turpin and Lim, 2001). However, Turpin and Lim (2001) pointed out that OM/OC ratios can be higher at non-urban sites and vary with location, season and daytime. The use of a constant factor of 1.6 at all sites (urban and non-urban) must therefore be considered as an approximate and conservative estimation of OM mass.
3.2.3 Determination of mineral dust

The contribution of crustal material (mineral dust) is often determined from the measured concentrations of main elements in rock-forming minerals, i.e. Si, Al, Fe, Mg, Ca and K, assuming that these elements are present as oxides (Chow et al., 1994). However, Fe, Ca and K have significant emissions from anthropogenic sources, and cannot be considered to be only of geogenic origin. This can be seen from scatter plots of the measured concentrations of these elements at the different sites versus the concentration of aluminium (Fig. 3.2), which is assumed to have negligible contributions from other sources (Lough et al., 2005). The Fe/Al and Ca\(^{2+}/\)Al ratios show clear gradients from the urban to the rural sites, implying anthropogenic sources of Fe in the urban environment (e.g. non-exhaust road traffic emissions due to abrasion of brake wear). Note that the water-soluble fraction of Ca (Ca\(^{2+}\)) instead of total Ca was used here because of implausible low concentrations of total Ca (Table 3.4). On the other hand, the K/Al ratio does not show a dependence on site type but a high variability, indicating a frequent impact of other sources than resuspension of crustal material, for K most likely wood and biomass combustion (Godoy et al., 2005; Khalil and Rasmussen, 2003).

The concentration of the geogenic fraction of Fe, Ca\(^{2+}\), and K (Fe\(^{geo}\), Ca\(^{2+geo}\) and K\(^{geo}\)) was determined from the 10% of the total measurements from all sites with the lowest Fe/Al, Ca\(^{2+}/\)Al and K/Al (see Fig. 3.2). The slopes of linear regressions of these 10% of all measurements against Al (β\(_{Fe}\), β\(_{Ca}\), and β\(_{K}\)) were determined and considered as representative for the average Fe/Al, Ca\(^{2+}/\)Al and K/Al of crustal material in Switzerland. At the rural site MAG a lower Ca\(^{2+}/\)Al was found compared to the sites north of the Alps. These differences can be expected from the geology of Switzerland: The Swiss plateau north of the Alps is a molasse basin composed of sediment such as conglomerate and sandstone, whereas in southern Switzerland crystalline rocks such as gneiss predominate. Therefore a site-specific β\(_{Ca}\) (β\(_{Ca-MAG}\)) was determined. The geogenic fractions of Al, Ca\(^{2+}\) and K were then calculated as follows:

\[
\begin{align*}
F_{e}e^{geo} &= \beta_{Fe}Al, & \beta_{Fe} &= 1.13 (\pm 0.05) \\
Ca^{2+geo} &= \beta_{Ca}Al, & \beta_{Ca} &= 1.15 (\pm 0.07) & \beta_{Ca-MAG} &= 0.70 (\pm 0.07) \\
K^{geo} &= \beta_{K}Al, & \beta_{K} &= 0.61 (\pm 0.05)
\end{align*}
\]

(3.1)

The concentration of the mineral anthropogenic or non-geogenic dust fractions of Fe, Ca\(^{2+}\), and K were then determined from the differences of the measured total element concentrations and the corresponding geogenic fractions. Determination of silicon in PM10 is not possible from samples collected on quartz fiber filters. Therefore, Si concentrations were estimated from the average ratio of Si and Al in the earth crust as Si=3.62 Al (Wedepohl, 1995). The concentration of mineral dust was then calculated according to Hueglin et al. (2005):

\[
Mineral\ dust = 2.14Si + 1.89Al + 1.66Mg + 1.40Ca^{2+geo} + 1.21K^{geo} + 1.43Fe^{geo}
\]

(3.2)

It should be noticed, that mineral dust as defined by equation (3.2) includes natural geogenic dust, but can also include contributions from anthropogenic activities with similar chemical profile than crustal material (e.g. resuspension of road dust, emission from construction work).

Finally, the concentrations of all other measured elements and the anthropogenic fractions of Fe, Ca\(^{2+}\), and K were added to a PM10 fraction denoted as “trace elements”. The fact that Ca\(^{2+}\) was used instead of total Ca means that the derived concentrations of calcium in mineral dust and trace elements are underestimating the true values.
3.2. Methodology

Figure 3.2: Scatter plot of the measured concentration of Fe (left), K (middle) and $Ca^{2+}$ (right) vs. the measured concentration of Al (element concentrations scaled by corresponding recovery rates). The lines show the estimated average Fe/Al, K/Al and $Ca^{2+}$/Al ratios of crustal material in Switzerland. For $Ca^{2+}$ different ratios were estimated depending on the sampling site location (dashed line: south of the Alps MAG, solid line: north of the Alps). Note that the Saharan dust event on 15 Oct. 2008 was excluded from the analysis: composition of crustal materials in these samples was not representative for the composition of crustal materials in Switzerland.

3.2.4 Representation of concentration gradients and temporal changes

Relative differences in concentrations of PM10, the main constituents of PM10 and individual trace elements between the roadside site BER and the urban background site ZUE are expressed as average roadside enrichment (RE):

$$RE_i = \left( \frac{X_{BER,i} - X_{ZUE,i}}{X_{BER,i}} \right) \times 100$$  \hspace{1cm} (3.3)

where $X_{BER,i}$ and $X_{ZUE,i}$ are the annual average concentrations of a measured component [Amato et al., 2011]. The roadside enrichments can be interpreted as the fraction of the measured component that results from the emissions in the immediate vicinity of the roadside site BER. Annual average concentrations were used in equation 3.3 instead of daily values as by [Amato et al., 2011] because of the rather large distance between the two sites (approx. 100km). Roadside enrichments calculated on a daily basis for a pair of distant sites have a larger variability than for a pair of nearby urban roadside and urban background sites because of the more pronounced differences in local influencing factors other than traffic (e.g. meteorology). For annual average concentrations, however, the assumption of similar urban background concentrations at BER and ZUE is certainly reasonable.

Similarly, the urban enrichment (UE) was calculated as the relative difference between the mean annual concentration at the urban background site ZUE and at the suburban site BAS. The suburban site was used instead of the rural site PAY because the first was included in both 2008/2009 and 1998/1999 studies and because BAS and PAY have similar PM10 levels and composition.

Calculation of the relative changes in PM10 mass concentration and chemical composition during the ten years between the studies were performed using an equation similar to equation 3.3. Relative changes were calculated from the difference of the determined average concentrations in 2008/2009 and 1998/1999 divided by the average concentration in 1998/1999. The obtained values represent the percentage change of PM10 or of its constituents during the considered ten year period.
### Chapter 3. Chemical composition of PM10 in Switzerland

#### 3.3 Results and discussion

##### 3.3.1 Levels of PM10 and major constituents

The annual mean mass concentrations of PM10 and of its major constituents for the time period from August 2008 to July 2009 are given in Table 3.2. In Table 3.3, the corresponding data from the earlier campaign (April 1998 to March 1999) are listed for the three sites that were included in both campaigns. Note that the values in Table 3.3 can differ from the numbers in Hueglin et al. (2005), because of the differences in the analytical methods and data treatment as described in Section 3.2. Fig. 3.3 gives an overview of the seasonal variation of the chemical composition of PM10 in 2008/2009. Annual average concentrations for the 2008/2009 period indicate a very weak gradient in PM10 from rural to urban background sites (Table 3.2, Fig. 3.4), from 18.8 to only 20.9 µg/m³. Clearly higher PM10 concentrations were measured at the urban roadside site (29.4 µg/m³) corresponding to a roadside enrichment for PM10 of 29.9% (see Section 3.2.4 for definition). This means that about 30% of PM10 at the urban roadside site is generated by local road traffic emissions and shows that this emission source is important for the total PM10 level at this site. An overview of the urban and roadside enrichment of the species considered in this section is given in Fig. 3.5.

Secondary inorganic aerosols (nitrate, sulphate and ammonium) are rather homogeneously distributed north of the Alps: concentrations of these compounds vary only between 7.2 and 7.8 µg/m³ at PAY, BAS, ZUE and BER. They represent with 38% the largest fraction of PM10 at PAY, BAS and ZUE, at BER their relative contribution is lower (25.4%). Concerning the carbonaceous fraction, similar average concentrations of OM were measured at BAS, PAY and

#### Table 3.2: Annual mean concentrations of PM10 and major constituents of PM10 at different site types in Switzerland, for the time period from August 2008 to July 2009. The mineral dust concentration is strongly influenced by a single Saharan dust event at 15 Oct. 2008. If this event is excluded, average mineral dust concentrations at Bern, Zurich, Basel, Payerne, and Magadino reduce to 1.7 µg/m³, 1.0 µg/m³, 0.8 µg/m³, 0.9 µg/m³, and 1.7 µg/m³, respectively.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Urban roadside</th>
<th>Urban background</th>
<th>Suburban</th>
<th>Rural</th>
<th>Rural</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>Bern µg/m³</td>
<td>Zurich µg/m³</td>
<td>Basel µg/m³</td>
<td>Payerne µg/m³</td>
<td>Magadino µg/m³</td>
</tr>
<tr>
<td>PM10</td>
<td>29.4 100</td>
<td>20.7 100</td>
<td>18.8 100</td>
<td>19.1 100</td>
<td>20.9 100</td>
</tr>
<tr>
<td>EC</td>
<td>3.7 12.6</td>
<td>1.3 6.1</td>
<td>0.9 5.0</td>
<td>0.7 3.5</td>
<td>1.5 7.3</td>
</tr>
<tr>
<td>OM</td>
<td>7.8 26.5</td>
<td>5.9 28.5</td>
<td>5.8 30.9</td>
<td>5.6 29.5</td>
<td>8.8 42.0</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>3.8 12.8</td>
<td>3.8 18.2</td>
<td>3.3 17.5</td>
<td>3.8 19.8</td>
<td>2.1 10.0</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>1.5 5.2</td>
<td>1.6 7.7</td>
<td>1.5 8.2</td>
<td>1.6 8.1</td>
<td>1.2 5.6</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2.2 7.4</td>
<td>2.4 11.5</td>
<td>2.4 12.8</td>
<td>1.9 10.1</td>
<td>1.9 9.0</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>2.4 8.2</td>
<td>1.7 8.1</td>
<td>1.4 7.2</td>
<td>1.8 9.3</td>
<td>1.9 9.1</td>
</tr>
<tr>
<td>Trace elements</td>
<td>4.0 13.8</td>
<td>1.4 6.9</td>
<td>0.9 5.0</td>
<td>0.6 3.0</td>
<td>0.8 4.0</td>
</tr>
<tr>
<td>Unknown</td>
<td>3.9 13.4</td>
<td>2.7 13.0</td>
<td>2.5 13.4</td>
<td>3.2 16.7</td>
<td>2.7 13.0</td>
</tr>
</tbody>
</table>
ZUE (5.6-5.9 µg/m³), while at BER significantly higher average concentrations were measured (7.8 µg/m³). On the other hand EC showed a clearly increasing concentration gradient when moving from rural to urban roadside sites (from 0.7 to 3.7 µg/m³), indicating that EC, and to a lesser extent also OM, have significant emission sources in the urban environment.

**Table 3.3:** Annual mean concentrations of PM10 and major constituents of PM10 at different site types in Switzerland, for the time period from April 1998 to March 1999. In contrast to 2008/2009, no significant impact of Saharan dust was observed during this time period.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Bern µg/m³</th>
<th>%</th>
<th>Zurich µg/m³</th>
<th>%</th>
<th>Basel µg/m³</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM10</td>
<td>39.7</td>
<td>100.0</td>
<td>24.1</td>
<td>100.0</td>
<td>24.7</td>
<td>100.0</td>
</tr>
<tr>
<td>EC</td>
<td>6.1</td>
<td>15.4</td>
<td>1.7</td>
<td>7.0</td>
<td>1.4</td>
<td>5.6</td>
</tr>
<tr>
<td>OM</td>
<td>9.2</td>
<td>23.1</td>
<td>6.2</td>
<td>25.7</td>
<td>6.1</td>
<td>24.9</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>3.3</td>
<td>8.4</td>
<td>3.3</td>
<td>13.6</td>
<td>3.1</td>
<td>12.5</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>1.4</td>
<td>3.5</td>
<td>1.9</td>
<td>8.1</td>
<td>1.9</td>
<td>7.8</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3.3</td>
<td>8.3</td>
<td>3.7</td>
<td>15.3</td>
<td>3.9</td>
<td>15.9</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>2.7</td>
<td>6.7</td>
<td>1.2</td>
<td>4.8</td>
<td>1.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Trace elements</td>
<td>6.8</td>
<td>17.2</td>
<td>1.6</td>
<td>6.5</td>
<td>1.4</td>
<td>5.7</td>
</tr>
<tr>
<td>Unknown</td>
<td>6.9</td>
<td>17.5</td>
<td>4.6</td>
<td>19.1</td>
<td>5.5</td>
<td>22.4</td>
</tr>
</tbody>
</table>

**Figure 3.3:** Mean relative chemical composition of PM10 at the urban roadside site (Bern), the urban background site (Zurich), the suburban site (Basel) and at the two rural site (Payerne - north of the Alps and Magadino - south of the Alps) for the different seasons based on daily measurements between August 2008 and July 2009.
At the rural site south of the Alps (MAG) the average concentrations of OM, EC and secondary aerosols strongly differ from the concentrations measured at the rural site north of the Alps. Secondary inorganic aerosols only constitute 24.6% of PM10 (5.2 $\mu\text{g/}m^3$) while carbonaceous matter sums up to 49.3% of average PM10 mass (EC: 1.5 $\mu\text{g/}m^3$, OM: 8.8 $\mu\text{g/}m^3$), representing the largest PM10 fraction. The enrichment of PM10 and its major constituents at the rural sites south of the Alps compared to the suburban, rural and urban background sites north of the Alps are shown in Fig. 3.6.

The high fraction of carbonaceous matter at MAG is mainly the result of high concentrations during autumn and winter (Fig. 3.3), when emissions from residential wood combustion have a strong impact at this site (Gianini et al., 2012b). The lower contribution of secondary inorganic aerosols is mainly due to the much lower concentrations of particulate ammonium nitrate at MAG. It is known from measurements using denuder systems, that the concentrations of total ammonium ($\text{NH}_3+\text{NH}_4^+$) and total nitrate ($\text{HNO}_3+\text{NO}_3^-$) are similar at MAG and PAY: In 2009, total ammonium concentrations at MAG and PAY were 5.2 $\mu\text{g/}m^3$ and 4.8 $\mu\text{g/}m^3$, total nitrate concentrations at these two sites were 5.1 $\mu\text{g/}m^3$ and 5.5 $\mu\text{g/}m^3$, respectively (BAFU, 2010). It is assumed that the lower ammonium nitrate concentration south of the Alps at MAG is the result of higher average ambient temperatures and lower relative humidity. Mean temperatures in 2009 in MAG and PAY were 12.2 °C and 9.9°C, the average relative humidity at these two sites were 73.7% and 77.8%, respectively. The difference in relative humidity is even more pronounced at dryer conditions (25-percentiles were 56.3% and 66.4%). The higher temperature and lower relative humidity in MAG probably leads to a shift of the ammonia-nitric acid-water system towards the gas phase (Seinfeld and Pandis, 1998).
3.3. Results and discussion

![Graph showing urban enrichment versus roadside enrichment for PM10 and major constituents of PM10, for the 2008/2009 campaign (Saharan dust event on 15 Oct 2008 excluded). The centre of each text indicates the location of the enrichment percentages (TE: trace elements, MD: mineral dust). The dashed lines represent the one-to-one line and the 35% urban and roadside enrichment lines.](image)

Figure 3.5: Urban enrichment versus roadside enrichment for PM10 and major constituents of PM10, for the 2008/2009 campaign (Saharan dust event on 15 Oct 2008 excluded). The centre of each text indicates the location of the enrichment percentages (TE: trace elements, MD: mineral dust). The dashed lines represent the one-to-one line and the 35% urban and roadside enrichment lines.

The average mineral dust concentrations for the 2008/2009 study are strongly influenced by a single Saharan dust event on 15 October 2008. If this event is excluded, the average mineral dust concentrations are clearly reduced (see legend of Table 3.2). The Saharan dust corrected mineral dust concentration at the urban roadside site BER amounts to 1.7 µg/m³ and is therefore higher than at the other sites north of the Alps (0.8-1.0 µg/m³). This is likely due to anthropogenic contributions, e.g. from resuspension of pavement wear and other deposited mineral dust by traffic which is typical for roadside sites (Bukowiecki et al., 2010). At the rural site south of the Alps (MAG), average mineral dust concentrations are 1.7 µg/m³ and thus considerably higher than north of the Alps (except BER). This difference is likely to reflect the increased resuspension of soil in the drier climatic conditions south of the Alps. Note that at the site south of the Alps the impact of the Saharan dust event on mineral dust concentration is lower compared to the other sites. The MAG site was probably impacted earlier by the transport event. Due to the fact that samples were collected at every 4th day this event was only partially observed at this site.

The average mass concentration of trace elements shows a clearly decreasing gradient from urban roadside to rural sites (from 4.0 to 0.6 µg/m³). The high concentration at the urban roadside site BER is mainly caused by elevated concentrations of Fe, Ca²⁺, Na and Cl⁻ (Table 3.4), elements that can be attributed to non-exhaust particle emissions (brake abrasion, road dust and road salt) from road traffic (Bukowiecki et al., 2010). A detailed discussion on the abundance and trends of these elements is given in Section 3.3.4.
Finally, 2.5 µg/m³-3.9 µg/m³ (13.0-16.7%) of the average PM10 mass concentration remained unaccounted. This range is typical for chemical PM characterisation studies (Putaud et al., 2004a, 2010) and result from possible underestimation of some PM constituents (e.g. OM, mineral dust and trace elements) as well as the undetermined amount of aerosol-bound water.

As a summary of the chemical characterisation of PM10 during the 2008/2009 campaign, Fig. 3.4 provides estimates of the average composition of the regional PM10 background in Switzerland north of the Alps (represented by PAY and BAS) as well as south of the Alps (represented by MAG). In addition, following the approach of (Lenschow et al., 2001) and (Querol et al., 2004b), the chemical characteristics of the urban PM10 increment (PM10\text{urbanbackground} - PM10\text{regionalbackground}) and the roadside PM10 increment (PM10\text{urbanroadside} - PM10\text{urbanbackground}) are given. As mentioned above, the average urban PM10 increment in Switzerland is small (approx. 2 µg/m³) and mainly composed of trace elements, mineral dust and EC. For these three PM10 components the urban enrichment ranges between 15-30% (Fig. 3.5). The increment from an urban background to a heavily trafficked urban roadside site is much larger (approx. 9 µg/m³). This surplus of PM10 at the roadside site is mainly composed of trace elements, EC, OM, mineral dust and unexplained PM10, and is generated by high contributions from road traffic related sources as exhaust emissions, re-suspension of mineral and road dust and emissions of de-icing road salt (Gianini et al., 2012b). The highest relative roadside enrichment was found for EC and the trace elements (>60%, see Fig. 3.5), followed by mineral dust and OM.

Figure 3.6: Enrichment of PM10 and PM10 main components at the rural sites south of the Alps (MAG) relative to the urban background site (ZUE), the suburban site (BAS) and the rural site (PAY) north of the Alps. The south-north enrichment was calculated using equation 3.3; positive (negative) percentages indicate higher (lower) concentrations at the rural site south of the Alps. The impact of the Saharan dust event on 15 Oct. 2008 was excluded, because this single event had a strong impact on average mineral dust concentrations north of the Alps.
3.3.2 Trend of PM10 and influence of meteorology

The PM10 concentrations at the Swiss sites during the 2008/2009 study were clearly lower than during the earlier study in 1998/1999. It is difficult to deduce a general trend from two yearly measurement campaigns because of the influence of meteorology on PM10 concentrations. However, the observed PM10 concentrations are in line with the negative trend of PM10 in Switzerland as determined by Barmpadimos et al. (2011). They applied statistical models for estimation of the influence of meteorology on PM10 at various Swiss sites (including the sites considered in this work) and calculated meteorologically adjusted trends of PM10 for the time from 1991 to 2008, determining that the average annual trends of PM10 at BER, ZUE and BAS are -1.2 $\mu g/m^3 yr^{-1}$, -0.55 $\mu g/m^3 yr^{-1}$ and -0.61 $\mu g/m^3 yr^{-1}$, respectively. These results are in reasonable agreement with the measured difference in PM10 concentration for the 2008/2009 and 1998/1999 campaigns at BER, ZUE and BAS (-10.3 $\mu g/m^3$, -3.4 $\mu g/m^3$ and -5.9 $\mu g/m^3$, respectively, see Table 3.2 and 3.3).

Moreover, the application of a meteorological adjustment of PM10 at BER, ZUE and BAS similar to the approach by Barmpadimos et al. (2011) shows that the meteorology during the two study periods was not exceptional and the difference in the meteorologically adjusted PM10 concentrations remained about constant. It is therefore justified to assume that the change in PM10 concentrations observed during the studies in 1998/1999 and 2008/2009 can be regarded as representative for the general trend of PM10 at these sites during the considered ten year period.

3.3.3 Trend of major chemical constituents in PM10

Fig. 3.7 shows the differences of the concentration of PM10 and of its major constituents in 1998/1999 and 2008/2009 at the urban roadside site BER, at the urban background site ZUE and at the suburban site BAS. The most evident change is the decreasing concentration of sulphate from 3.3-3.9 $\mu g/m^3$ in 1998/1999 to 2.2-2.4 $\mu g/m^3$ in 2008/2009 (meaning a relative decrease of about 35%), which is certainly a result of continuing reductions of SO$_2$ emissions in Europe (Monks et al., 2009; Vestreng et al., 2007). In contrast, nitrate concentrations in PM10 showed a slight increase during the past ten years, although the emissions of nitrogen oxides declined in Switzerland and most of the neighbouring countries (Vestreng et al., 2009). The ratio of nitrate to sulphate consequently increased at BER, ZUE and BAS from 0.8-1.0 in 1998/1999 to 1.4-1.7 in 2008/2009. Negative trends of sulphate and constant nitrate concentrations were also reported by Putaud et al. (2004a) for six sites of the EMEP (European Monitoring and Evaluation Programme; including Payerne) for the 1991-2001 period.

A possible explanation is the competition between sulphate and nitrate for available ammonia. Decreasing sulphate concentrations leave increasing amounts of ammonia to react with nitric acid to form aerosol nitrate (Seinfeld and Pandis, 1998). However, long-term measurements of total ammonia and total sulphate at Payerne within EMEP indicate that an ammonia-rich regime prevails at this site and likely also in large parts of Switzerland. The molar ratio of total ammonia (NH$_3$ + NH$_4^+$) to sulphate increased at Payerne from 10.8 in 1998/1999 to 12.9 in 2008/2009, therefore high excess of ammonia was available for both time periods.

OM showed a relevant decrease at the urban roadside site (relative 15%, absolute 1.4 $\mu g/m^3$), while EC decreased at all the sites, with relative reductions ranging between 24% and 39% and a maximum absolute decrease at the urban roadside site (2.4 $\mu g/m^3$). The decreasing EC
concentrations reflect the success of various reduction measures implemented in Switzerland and in the EU, as the promotion or imposition of diesel particulate filter for buses (Swiss Federal Council, 2008b) and construction machinery (Swiss Federal Council, 2008a), as well as the introduction of tighter emission standards for heavy duty vehicles and passenger cars (European Commission, 1998a; Swiss Federal Council, 2010). The strongest decrease of EC at the urban roadside site (-39%) can be explained by an additional effect of the reduced traffic density in the immediate vicinity of the site (-29%, see Section 3.2.1). Similarly, the reduction of OM at the urban roadside site might be attributed to decreasing primary OC emitted by road traffic. It has been shown by (Heeb et al., 2010) that the above mentioned implemented reduction measures have a positive effect on OC emissions.

At the urban roadside site BER clearly lower concentrations of trace elements were observed during the study in 2008/2009 (4.0 µg/m³) compared to the study in 1998/1999 (6.8 µg/m³), corresponding to a relative decrease of more than 40%. Similarly, the average mineral dust concentration for 2008/2009 (Saharan dust corrected, 1.7 µg/m³) is considerably lower than in the earlier study (2.7 µg/m³). Again, the reduction of traffic density at BER most likely contributed to the decreasing trace element and mineral dust concentrations. It is, however, also likely that these reductions are in addition due to the renewal of the road surface nearby the site a few months before PM10 sampling for the 2008/2009 study was started. As shown by (Gehrig et al., 2010), modern porous pavements in good condition show reduced emissions from abrasion and resuspension of PM10.

Similar to BER, declining concentrations of mineral dust and trace elements were also observed at the urban background (ZUE) and the suburban site (BAS). The concentrations of mineral dust (corrected for the single Saharan dust event on 15 October 2008) have decreased by 17% and 38%, respectively, while the trace elements concentrations have decreased by 13% at ZUE and 36% at BAS. Interpretation of the temporal trends of individual trace elements follows in Section 3.3.5.

<table>
<thead>
<tr>
<th>Component</th>
<th>Urban roadside – BER</th>
<th>Urban background – ZUE</th>
<th>Suburban – BAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>-1 µg/m³</td>
<td>-0.5 µg/m³</td>
<td>-0.3 µg/m³</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0 µg/m³</td>
<td>0.5 µg/m³</td>
<td>0 µg/m³</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0 µg/m³</td>
<td>-0.5 µg/m³</td>
<td>0 µg/m³</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>-1 µg/m³</td>
<td>-0.5 µg/m³</td>
<td>-0.3 µg/m³</td>
</tr>
<tr>
<td>EC</td>
<td>-2 µg/m³</td>
<td>-1 µg/m³</td>
<td>-0.5 µg/m³</td>
</tr>
<tr>
<td>OM</td>
<td>0 µg/m³</td>
<td>-0.5 µg/m³</td>
<td>0 µg/m³</td>
</tr>
<tr>
<td>Trace elements</td>
<td>-1 µg/m³</td>
<td>-0.5 µg/m³</td>
<td>-0.3 µg/m³</td>
</tr>
</tbody>
</table>

Figure 3.7: Differences of the annual average concentration of PM10 and its major components between the 1998/1999 and the 2008/2009 periods, at the urban roadside site BER, the urban background site ZUE and at the suburban site BAS (Saharan dust event on 15 Oct 2008 excluded).
3.3.4 Dependence of element concentrations on site type

The average annual concentrations of trace elements measured in PM10 during 2008/2009 are shown in Table 3.4. Similar to the findings for the 1998/1999 study (Hueglin et al., 2005), the concentrations of many elements show a strong dependence on site type. This dependence can be represented by the enrichments defined by equation 3.3 and used to structure the abundance of trace elements in PM10. Thus, the measured elements are arranged into following different groups:

- **Group I** includes all elements with high enrichments (>35%) at the roadside site and the urban background site (Ba, Bi, Cr, Cu, Fe, Mo, Sb and the water soluble fraction of Ca, Fig. 3.8). These elements (except Bi) are associated with non-exhaust road traffic emissions due to abrasion of brake wear (Ba, Cr, Cu, Mo, Sb and Fe) and resuspension of road dust (Fe and Ca$^{2+}$; Amato et al., 2011; Bukowiecki et al., 2010; Thorpe and Harrison, 2008).

- Elements with strong roadside enrichments (> 35%) but moderate or insignificant urban and suburban enrichments (Al, Ti, Y, Nd, Ce, La, Sr, Mn, Zn, Ni, Ga and V) belong to **Group II**. These elements are mainly associated with mineral dust (as Al, Ti, Y, Nd and La), road dust (as Mn and Zn; Thorpe and Harrison, 2008) or with heavy oil combustion and petrochemical plants emissions (Ni and V; Lee et al., 1994; Querol et al., 2007), and seem to have significant sources in cities like the elements of **Group I**.

- Sodium (Na) and water soluble Chlorine (Cl$^{-}$) are considered as an own **Group III**, both elements are highly enriched at the urban roadside site due to application of de-icing salt during the cold season. At sites that are not in the near vicinity of road traffic long-range transport of sea salt can significantly contribute to average ambient levels of Na (Gianini et al., 2012b).

- Finally, **Group IV** includes all elements and ions that have similar concentrations at the different site types (As, Cd, Pb, K$^{+}$, Mg, Rb, Se). The absence of a concentration gradient between different site types indicates that these elements and ions have either spatially uniform sources or are dominated by long-range transport to Switzerland. Examples for spatially uniform emission sources are K$^{+}$ and Rb as indicators for emissions from biomass and wood combustion (Currie et al., 1994; Godoy et al., 2005). Examples for dominating long-range transport are As and Se emitted from coal and heavy oil combustion appliances (Lee et al., 1994), emissions sources that are not common in Switzerland. Interestingly, the gradually decreasing concentrations of Pb in PM10 from urban traffic sites to urban background, suburban and rural sites as observed in the 1998/1999 study (Hueglin et al., 2005) has vanished, so that Pb is assigned to **Group IV** (see also Section 3.3.5).

Concerning the two rural sites, concentration of trace elements belonging to **Group I** show higher concentrations at MAG than at PAY (see Table 3.4), suggesting that the rural site south of the Alps is more influenced by road traffic emissions than the site north of the Alps, a presumption that is confirmed by Gianini et al. (2012b). Similarly, clearly higher concentrations
of mineral dust related trace elements (belonging to \textit{Group II}) were measured at the rural site south of the Alps, indicating that resuspension of mineral dust is more important at MAG than at PAY.

### 3.3.5 Temporal trend of elements in PM10

Fig. 3.9 shows the relative changes of the element concentrations at BER, ZUE and BAS during the two sampling periods (2008/2009 and 1998/1999) as defined in Section 3.2.4. The largest decrease was observed for lead (decrease between -75% and -87%). The negative concentration gradient of Pb from urban roadside to suburban sites as observed in 1998/1999 almost disappeared (see Section 3.3.4), indicating that after the ban of leaded gasoline (EU-Commission 1998b, Swiss Federal Council 1999) road traffic is no longer a dominating emission source of Pb. Also the concentrations of other heavy metals markedly declined during the last decade: Ni and V decreased at all sites (largest reduction at BAS), reductions of Cd concentrations are at all sites about 50%, and As shows clearly lower concentrations at BER and BAS. It is evident that the decrease of the concentrations of several heavy metals observed already since the mid-1980s in Switzerland (Hueglin et al. 2005) has continued during the last decade.
Table 3.4: Mean annual concentrations (ng/m$^3$) of water soluble compounds and trace elements at different site types in Switzerland (PM10 samples from August 2008 to July 2009). The detection limits (ng/m$^3$) were calculated as two times the standard deviation of concentrations in n=24 field blank filters.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Urban roadside</th>
<th>Urban background</th>
<th>Suburban</th>
<th>Rural</th>
<th>Rural</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>Bern</td>
<td>Zurich</td>
<td>Basel</td>
<td>Payerne</td>
<td>Magadino</td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>669</td>
<td>71</td>
<td>86</td>
<td>30</td>
<td>45</td>
<td>19</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>486</td>
<td>152</td>
<td>184</td>
<td>126</td>
<td>73</td>
<td>7</td>
</tr>
<tr>
<td>K$^+$</td>
<td>240</td>
<td>201</td>
<td>225</td>
<td>172</td>
<td>195</td>
<td>5</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>36</td>
<td>31</td>
<td>26</td>
<td>23</td>
<td>21</td>
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<tr>
<td>Ca$^{2+}$</td>
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<td>343</td>
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</tr>
<tr>
<td>Na</td>
<td>519</td>
<td>141</td>
<td>167</td>
<td>122</td>
<td>68</td>
<td>13</td>
</tr>
<tr>
<td>K</td>
<td>303</td>
<td>258</td>
<td>274</td>
<td>240</td>
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<tr>
<td>Mg</td>
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<td>162</td>
<td>186</td>
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<tr>
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<td>125</td>
<td>86</td>
<td>70</td>
<td>92</td>
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<td>2.3</td>
<td>1.8</td>
<td>2.2</td>
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</tr>
<tr>
<td>V</td>
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<td>0.7</td>
<td>0.5</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Cr</td>
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<td>2.0</td>
<td>0.9</td>
<td>0.7</td>
<td>1.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Mn</td>
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<td>3.7</td>
<td>2.9</td>
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<td>0.4</td>
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<tr>
<td>Fe</td>
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<td>420</td>
<td>181</td>
<td>119</td>
<td>315</td>
<td>10</td>
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<tr>
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<td>Zn</td>
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<td>19.4</td>
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<td>0.14</td>
<td>0.07</td>
<td>0.11</td>
<td>0.01</td>
</tr>
<tr>
<td>As</td>
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<td>0.52</td>
<td>0.39</td>
<td>0.51</td>
<td>0.66</td>
<td>0.13</td>
</tr>
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</tr>
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<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Mo</td>
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<td>1.16</td>
<td>0.53</td>
<td>0.25</td>
<td>0.85</td>
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</tr>
<tr>
<td>Cd</td>
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<td>0.12</td>
<td>0.17</td>
<td>0.09</td>
<td>0.14</td>
<td>0.02</td>
</tr>
<tr>
<td>Sb</td>
<td>6.64</td>
<td>2.24</td>
<td>0.97</td>
<td>0.59</td>
<td>1.00</td>
<td>0.04</td>
</tr>
<tr>
<td>Ba</td>
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<td>3.7</td>
<td>2.2</td>
<td>1.7</td>
<td>3.1</td>
<td>0.7</td>
</tr>
<tr>
<td>La</td>
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<td>0.07</td>
<td>0.07</td>
<td>0.05</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>Ce</td>
<td>0.40</td>
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<td>0.11</td>
<td>0.10</td>
<td>0.12</td>
<td>0.01</td>
</tr>
<tr>
<td>Nd</td>
<td>0.07</td>
<td>0.05</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>6.2</td>
<td>5.2</td>
<td>5.0</td>
<td>3.7</td>
<td>4.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Bi</td>
<td>0.30</td>
<td>0.17</td>
<td>0.09</td>
<td>0.07</td>
<td>0.08</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Chapter 3. Chemical composition of PM10 in Switzerland

Figure 3.9: Relative change of mean annual element concentration between the 1998/1999 and the 2008/2009 periods, at the urban roadside site BER, the urban background site ZUE and at the suburban site BAS. Positive (negative) percentages indicate increasing (decreasing) concentrations. The impact of the Saharan dust event on 15 Oct. 2008 was excluded, because this single event had a strong impact on average mineral dust concentrations in the 2008/2009 period. Note: Ga at roadside site and urban background site is truncated, the relative changes are 264% and 210%, respectively.

The concentrations of most of the elements associated with mineral dust or road dust (belonging to Group II) declined at all three sites (largest reduction at BER followed by BAS and ZUE). The reason for the temporal trend of this class of elements remains unknown. At BER, it is likely that both the decreasing traffic density and the renewal of the pavement immediately before the start of PM10 sampling for the 2008/2009 campaign (see Section 3.3.3) strongly contributed to the generally observed decline of these elements.

Concerning the elements of Group I, the concentrations of Fe and Ca\(^{2+}\) mainly followed the trend showed by the mineral dust and road dust elements of Group II. As for these last elements the decrease of Fe and Ca\(^{2+}\) concentrations can partially be explained by reduced resuspension of road dust. Moreover the widespread use of corrosion resistant materials for cars may have an positive effect on traffic related Fe emissions. Elements reported to be emitted by abrasion of brake and tyre wear as Mo, Sb, Cu, Ba and Zn do not show univocal trends: Sb concentrations have strongly increased, whereas Mo slightly decreased at all sites. The concentrations of Cu, Zn and Ba show different temporal changes at the different site types.

Concentrations of K\(^+\) remained constant at BAS and ZUE and slightly increased at BER, indicating that wood combustion emissions might not have changed significantly during the last decade. Noticeable changes can be observed for Ga, the concentrations markedly increased at all three sites. This might be related to the widespread use of Ga in the electronic products, e.g. LEDs and photovoltaic cells (Moskalyk 2003). It is, however, unclear how and to what extent Ga can be released from these products to contribute to ambient PM10.
3.4 Conclusions

This paper provides a detailed update of the chemical composition of PM10 at different site types in Switzerland. It is evident from this work that the emission reduction strategies for PM10 and precursors of secondary PM10 that have been implemented during the past ten and more years led to a clear improvement of ambient PM10 levels. The most noticeable changes are the decreasing concentrations of sulphate, EC, and many trace elements (e.g. heavy metals as Pb, Ni, V, Cd). The decreasing concentrations of EC (which has also been found in the Netherlands; Keuken et al. 2011) indicate that significant reductions of exhaust emissions from road traffic have been achieved. This indication has been confirmed by analyses of the datasets from 2008/2009 and 1998/1999 for source contributions by use of positive matrix factorization (PMF), which is discussed in detail in a closely related paper by Gianini et al. (2012b). In view of the reduced NOx emissions and slightly decreasing ambient NO2 concentrations during the past ten years in Switzerland and in neighbouring countries, the observed increase in nitrate is remarkable but currently not fully understood. It can be assumed that the temporal evolution of nitrate is related to the decreasing sulphate concentrations. Another hypothesis is, that the increasing average ozone concentrations in Switzerland and other European countries (increase of mean annual concentrations, most probably due to the reduced effect of the ozone titration by NO as a consequence of the decreased emissions of NO during the past two decades, see e.g. Ordonez et al. (2005) and BAFU (2010)) might enhance the formation of nitric acid during the night (see e.g. Seinfeld and Pandis (1998) for associated reactions) and thus the formation of nitrate. The increasing fraction of NO2 in NOx from road traffic exhaust emissions (Grice et al. 2009) might also contribute to increasing average ozone as indicated by Jenkin et al. (2008) and therefore favours the above mentioned mechanism. However, an atmospheric chemical modelling study that includes all relevant processes is required for clarification of the observed trend of particulate nitrate. Nevertheless, further significant reductions in NOx emissions are certainly necessary for lowering the nitrate concentration in PM10 in Switzerland.

Acknowledgements

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Chapter 4


The content of the following chapter is adopted from:


Abstract

PM10 speciation data from various sites in Switzerland for two time periods (January 1998 - March 1999 and August 2008 - July 2009) have been analysed for major sources by receptor modelling using Positive Matrix Factorisation (PMF). For the 2008/2009 period, it was found that secondary aerosols (sulphate- and nitrate-rich secondary aerosols, SSA and NSA) are the most abundant components of PM10 at sites north of the Alps. Road traffic and wood combustion were found to be the largest sources of PM10 at these sites. Except at the urban roadside site where road traffic is dominating (40% of PM10 - including road salt), the annual average contribution of these two sources are of similar importance (17% and 14% of PM10 , respectively). At a rural site south of the Alps wood combustion and road traffic contributions to PM10 were higher (31% and 24%, respectively), and the fraction of secondary aerosols lower (29%) than at similar site types north of the Alps.

Comparison of PMF analyses for the two time periods (1998/1999 and 2008/2009) revealed decreasing average contributions of road traffic and SSA to PM10 at all sites. This indicates that the measures that were implemented in Switzerland and in neighbouring countries to reduce emissions of sulphur dioxide and PM10 from road traffic were successful. On the other hand, contributions of wood combustion did not change during this ten year period, and the

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contribution of nitrate-rich secondary aerosols has even increased. It is shown that PMF can be a helpful tool for the assessment of long-term changes of source contributions to ambient particulate matter.

4.1 Introduction

Atmospheric particular matter (PM) has been found to have several adverse effects on human health and the environment. PM has been associated with an increase of respiratory and cardiovascular diseases (Pope and Dockery, 2006), acidification and eutrophication of ecosystems (UNECE, 2004), reduction of visibility (Horvath, 1993) and was found to play an important role in climate change (IPCC, 2007). For these reasons authorities in many countries promulgated air quality standards and adopted various measures to reduce ambient PM concentrations. In Switzerland mean annual PM10 concentrations should not exceed 20 $\mu g/m^3$ and daily averages should not exceed 50 $\mu g/m^3$ more than once a year (Swiss Federal Council, 2010). These standards are in agreement with the recommendations of the World Health Organisation, WHO (WHO, 2006).

During the last decades, PM10 concentrations in Switzerland have continuously decreased (Barmpadimos et al., 2011). However the air quality standards are still regularly exceeded in large parts of the country (BAFU, 2010). For planning and implementation of further air pollution abatement strategies a detailed and quantitative knowledge of the sources of PM10 is of high importance.

In a recent study, the chemical composition of daily PM10 samples collected during a one year period (from August 2008 to July 2009) at five Swiss sites was determined. The measured data provide a detailed picture of the variation of the PM10 chemical composition between different site types, regions and seasons in Switzerland (Gianini et al., 2012a). This characterisation study was the follow-up of a similar survey performed ten years earlier (from January 1998 to March 1999, see Hueglin et al., 2005).

Receptor modelling applied to chemical speciation data is an often used approach for identification of the main sources of atmospheric PM and for estimation of the corresponding source contributions at a specific measurement site. Positive Matrix Factorisation (PMF; Paatero, 1997; Paatero and Tapper, 1994) is one of different available receptor models that has been successfully used in the past (Heo et al., 2009; Kim et al., 2003; Lee et al., 1999; Polissar et al., 2001; Yuan et al., 2006). The principal advantages of PMF compared to other receptor models are that only qualitative knowledge about PM sources are required and that the solution space is restricted to non-negative source contributions and source profiles (Viana et al., 2008b).

In this paper, PMF has been applied to the chemical speciation data for PM10 collected at several Swiss locations during the two campaigns in 1998/1999 and 2008/2009. The sources and their contributions to PM10 at an urban roadside site, an urban background site, a suburban site and two rural sites as determined from the 2008/2009 data are presented. Three of the sites considered in the 2008/2009 campaign were already included in the earlier study from 1998/1999. The potential of receptor modelling for estimation of trends of source contributions is highlighted and the determined changes of source impacts during the past ten years are discussed.
4.2 Methods

4.2.1 Sampling sites

For the recent study PM10 was collected at five sites of the Swiss National Air Pollution Monitoring Network (NABEL). The selected sites represent different site types: an urban roadside site - Bern (BER), an urban background site - Zurich (ZUE), a suburban site - Basel (BAS), a rural site north of the Alps near Payerne (PAY), and a rural site south of the Alps near Cadenazzo in the Magadino plane (MAG). Fig. 4.1 shows a map of Switzerland with the location of the sampling sites, more details about the sites can be found in Gianini et al. (2012a). Three of the sites (BAS, BER, and ZUE) were already included in the earlier study from 1998/1999 (Hueglin et al., 2005).

![Map of Switzerland with sampling sites](image)

**Figure 4.1:** Map of Switzerland with the location of the sampling sites.

4.2.2 Sampling methods and chemical analysis

The sampling procedure and the performed chemical analyses are described in detail by Gianini et al. (2012a) and Hueglin et al. (2005). Briefly, PM10 sampling and chemical analyses were performed as follows: During both sampling campaigns (August 2008 - July 2009 and January 1998 - March 1999) PM10 was collected during 24h using high-volume samplers (Digitel DA-80, 30m3h-1 flow rate) equipped with PM10 inlets. Particles were collected at every 4th day using quartz fibre filters (Pallflex Tissuquartz QAT-2500-UP - Ø=150mm in 2008/2009, Schleicher und Schuell QF20 - Ø=150mm in 1998/1999).

The concentrations of trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) and water soluble inorganic ions were characterised by ion chromatography (IC). In the 2008/2009 study elemental and organic carbon (EC and OC) were determined by the thermo-optical method using the EUSAAR-2 temperature protocol (Cavalli et al., 2010), while in the earlier study the VDI 2465/1 method (VDI, 1996) was used. PM10 mass con-
centration was measured in 2008/2009 with hourly temporal resolution by an automated PM10
monitor (TEOM 1400AB/FDMS 8500, Thermo Scientific). In 1998/1999 PM10 mass concentra-
tion was obtained from gravimetric determination of the mass of the quartz fibre filters before
and after PM10 sampling for 24 hours.

For the recent 2008/2009 study, a selection of the PM10 samples collected at the urban road-
side site (BER), the urban background site (ZUE) and at the two rural stations (PAY and MAG)
were analysed for levoglucosan concentrations using gas chromatography mass spectrometry
(GC/MS), following the procedures as described by [Piot et al.] (2012). Briefly, sample were ex-
tracted with a dichloromethane/acetone mixture using an Accelerated Solvent Extractor (ASE
200, Dionex) and reduced to a volume of 1mL. For organic polar compounds, 100 µL extract
fraction was derivatized with 100 µL of N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA +
1%TMCS) for two hours at 50°C. Levoglucosan was then quantified by GC-MS.

4.2.3 Receptor modelling

The basic principle of receptor modelling is that mass conservation can be assumed and a mass
balance analysis can be used to identify and apportion sources of airborne particulate matter in
the atmosphere [Hopke 2003]. Positive Matrix Factorisation (PMF) is a receptor model based
on a weighted least squares fit, where the weights are derived from the analytical uncertainties

In PMF, the mass balance equation

\[ X = GF + E \]

(4.1)

is solved. The data matrix \( X \) (the nxm-matrix of the m measured chemical species in n samples)
is factorised into two matrices: \( F \), a pxm-matrix which rows represent the profiles of p sources,
and \( G \), an nxp-matrix which columns represent the contributions of the p sources. The matrix \( E \)
is the residual matrix. In PMF the factorisation problem is solved by minimizing the residuals,
\( E \), weighted by measurement uncertainty matrix, \( S \).

Thus minimising the object function \( Q(E) \) defined as

\[ Q(E) = \sum_i \sum_j \left( \frac{e_{ij}}{s_{ij}} \right)^2 = \sum_i \sum_j \left( \frac{x_{ij} - \sum_p g_{ip} f_{pj}}{s_{ij}} \right)^2 \]

(4.2)

with the constraint that each of the elements of \( G \) and \( F \) is to be non negative, and where \( e_{ij}, s_{ij}, x_{ij}, g_{ip} \) and \( g_{pj} \) are the elements of the matrices \( E, S, X, G \) and \( F \). The elements of the
measurement uncertainty matrix are calculated using following equation that was adapted from
the formula in Anttila et al. (1995):

\[ s_{ij} = \sqrt{(DL_j)^2 + (CV_j x_{ij})^2 + (a x_{ij})^2} \]

(4.3)

where \( DL_j \) is the detection limit for compound \( j \) (\( DL_j \) was calculated as twice the standard de-
viation of the field blanks), \( CV_j \) is the coefficient of variation for the compound \( j \) (calculated as
the standard deviation of repeated analyses divided by the mean value of the repeated analyses),
and \( a \) is a factor (\( a=0.03 \)) applied to account for additional sources of uncertainty.
The datasets from the different measurement sites and campaigns have been analysed separately. Samples for which PM10 mass concentration was not available were excluded. Double counting of pairs of elemental and ionic species (S and SO$_4^{2-}$, Na and Na$^+$, K and K$^+$, Ca and Ca$^{2+}$, Mg and Mg$^{2+}$) were avoided by excluding the species having higher coefficients of variation (S, Na, K, Ca, and Mg). Concerning the 2008/2009 data sets, chemical species with a large fraction (>50%) of values below detection limit (BDL) or with a signal to noise ratio (S/N; Paatero and Hopke 2003, see supplementary material for definition) lower than 1.0 were not included in the analyses (Cl$^-$, Ni, Br, Se, Rh, Pd and Pt, see Table A.1). Moreover chemical species that are not indicative of any sources expected to significantly contribute to PM10 are discarded from PMF analyses (Tl and Bi). The concentration measurements of levoglucosan were also not included in the PMF analysis but used as auxiliary data for validating the PMF results.

Chemical species discarded from the 2008/2009 datasets were generally not included in the 1998/1999 datasets, only exceptions were Cl$^-$ (at urban roadside site) and Se (at all sites). In 1998/1999 Se had small fractions of BDL data (BDL $<$ 30%, see Table A.2) and high S/N values at all sites, similarly Cl$^-$ had at BER high signal to noise ratio.

The mass balance equation (equation 4.1) was solved using the program PMF2 (version 4.2) in the robust mode to reduce the influence of extreme values on the PMF solution (Paatero, 1997). For this purpose $\alpha=4$ was chosen as the value for the outlier threshold distance.

The PM10 mass concentration was included as an independent variable in PMF modelling to directly obtain the source contributions to the daily mass concentrations; the estimated uncertainties of the mass concentrations were set at 4 times their values so that the large uncertainties decreased their weight in the model fit (Kim et al. 2003).

### 4.2.4 Determination of the number of sources

Determination of the number of sources in PMF is a critical step. PMF was run with different numbers of sources in order to identify the solution with the physically most reasonable solution. In this study source identification was performed comparing the obtained source profiles with source profiles from literature, looking at the contribution time series and taking into account the explained variation (EV) of the sources (Lee et al. 1999).

After fixing the number of sources, the PMF solutions were analysed for rotational ambiguity by varying the Fpeak parameter (Paatero et al. 2002). Solutions with Fpeak values between -1 and +1 were investigated in order to find Fpeak-intervals where the objective function $Q(E)$ value remains relatively constant (Paatero et al. 2002). These intervals were successively explored as proposed by (Paatero et al. 2005). The procedure called G space plotting was applied, statistical dependence between source contributions caused by unrealistic rotations were investigated.

The seven-source model provided the most reasonable solution for the urban roadside datasets (BER 1998/1999 and 2008/2009). For all other data sets solutions with six sources were found to be optimal. Increasing the number of sources led to the split of interpretable source profiles into two unrealistic ones. Solutions with Fpeak values between -0.3 and +0.3 showed relatively constant $Q(E)$ values for each datasets. Based on G space plotting, Fpeak=0 was chosen.

At BER a model with a larger number of sources compared to the other sites was selected. This was due to the fact that the seven-source model better describes the variability of the measured
Chapter 4. Comparative Source Apportionment of PM10

4.3 Results and discussion

4.3.1 PM10 sources for 2008/2009

PM10 sources and components that were identified at all of the sites were: sulphate-rich secondary aerosols (SSA), nitrate-rich secondary aerosols (NSA), wood combustion and mineral dust. At the urban roadside site (BER) three additional factors were identified: de-icing road salt, vehicle wear and road traffic exhaust emissions. Road traffic and a Na-Mg-rich factor were further identified at the other four sites (BAS, MAG, PAY, ZUE). The source profiles and their contributions at the different sites are presented in the supplementary material (Figs. A.1-A.10). The relative contributions of the PMF factors to the measured species in PM10 are resumed in Table 4.1. The obtained PMF factors were interpreted as sources and components based on the following characteristics:

- The NSA profiles are dominated by NO$_3^-$ and NH$_4^+$. More than 81% of the NO$_3^-$ mass and 44-70% of NH$_4^+$ mass is explained by this factor. The calculated molar ratio of ammonium to nitrate ranges between 0.9 and 1, suggesting that secondary ammonium nitrate dominates in NSA. Contributions to PM10 show strong seasonal variations with highest values in winter.

- The SSA profiles are characterised by high concentrations of SO$_4^{2-}$ and NH$_4^+$. The calculated molar ratio of ammonium to sulphate ranges between 2.0 and 2.2, suggesting that secondary ammonium sulphate plays an important role in SSA. Moreover a relevant fraction of measured OC (16-38%) is also explained by the SSA factors; secondary OC is expected to be in receptor modelling studies largely associated with the secondary SO$_4^{2-}$ because of similar temporal variation of these constituents of atmospheric PM (Kim et al., 2003). Relatively high contents of OC in secondary sulfate factors have been attributed to the condensation of semi-volatile compounds on the high specific surface area of ammonium sulphate (Amato et al., 2009).

- The mineral dust profiles are dominated by Ca$^{2+}$, Fe, Al and Mg$^{2+}$, representing the main components of crustal matter (Wedepohl, 1995). The mineral dust factors account moreover for a large mass fraction (> 45%) of crustal elements such as Ti, Sr, Y, La, Ce and Nd. At all sites the largest contribution of mineral dust was found for 15 October 2008, a day with clear influence of Saharan dust transported to Switzerland (Fig. A.11). The mineral dust contributions estimated by PMF show strong correlations with mineral dust as calculated from the chemical composition of PM10 (Gianini et al., 2012a, R$^2$ > 0.69, see Fig. 4.2).

- The wood combustion profiles are characterised by high concentrations of OC, EC and K$^+$ (Fine et al., 2002; Schmidl et al., 2008; Watson et al., 2001). These factors also explain a relevant mass fraction (49-63%) of Rb, an element related to biomass combustion emissions (Godoy et al., 2005). The EC to OC ratios in the wood combustion profiles varied between 0.18 and 0.23 and are in good agreement with values reported in literature and referenced by Szidat et al. (2006). The estimated contributions of wood combustion
to PM10 show strong seasonal variations with highest values in winter. Moreover, estimated PM10 contributions from wood combustion are highly correlated with measured levoglucosan concentrations ($R^2 > 0.63$, see Fig. 4.3), the content of levoglucosan in wood combustion related PM10 is 7.9% at MAG and higher than at the sites north of the Alps (3.8 to 6.5%).

- The de-icing road salt factor (only present at the urban roadside site BER) contributes to 93% of the measured $\text{Na}^+$ mass. Noticeable contributions to PM10 were only observed during the cold season between November and March.

- The Na-Mg-rich factors contribute to an high fractions of $\text{Na}^+$ (78-87%). In contrast to the de-icing road salt factor identified at BER, the Na-Mg-rich factors account also for a high fraction of $\text{Mg}$ (31-69%). Moreover the contributions of the Na-Mg-rich factors do not show this clear annual cycle with elevated values during winter. The highest contributions of the Na-Mg factors were observed at 16 March 2009. Back-trajectory analysis suggests that these high contributions are caused by long-range transport of sea spray aerosol particles (Fig. A.12).

- The vehicle wear factor found at the urban roadside site BER accounted for major mass fractions of several elements such as $\text{Mo}$, $\text{Sb}$, $\text{Cu}$, $\text{Zn}$, $\text{Fe}$, $\text{Cr}$, $\text{Mn}$ and $\text{Ba}$. These elements are known to be emitted from road traffic abrasion processes (e.g. abrasion of brake pads) or are important constituents of road dust [Amato et al., 2010; Bukowiecki et al., 2009; Harrison et al., 2003].

- The road traffic exhaust emission profile at the urban roadside site BER was dominated by EC and OC.

- The road traffic factors identified at the urban background site, at the suburban site and at the two rural sites combine the characteristics of the two road traffic factors obtained at BER (road traffic exhaust emission factor and vehicle wear factor). This source profile explains large fractions of EC, OC and the above mentioned road traffic related elements.

In Table 4.2, the average contributions of the identified sources and components to annual PM10 for the 2008/2009 study are given. It can be seen that the estimated source contributions to PM10 show clear similarities at the urban background site, the suburban site and the rural site north of the Alps (ZUE, BAS and PAY). About 48-52% of PM10 ($9.3-10 \, \mu \text{g/m}^3$) is attributed to secondary aerosols (NSA and SSA), NSA and SSA constitute the most important fraction of atmospheric PM10 at all of these sites. Annual mean contributions of road traffic and wood combustion are similar at these three sites, road traffic is found to account for 15-18% of PM10 ($2.8-3.7 \, \mu \text{g/m}^3$) while the contribution of wood combustion emissions is 13-15% ($2.6-2.8 \, \mu \text{g/m}^3$). Note that road traffic and wood combustion emissions are in addition contributing to NSA and SSA through emissions of gaseous precursors of secondary aerosols. However, determination of source contributions to secondary aerosol mass concentration is not possible with the applied method and is currently one of the most challenging problem in aerosol science.

The average contributions of mineral dust and Na-Mg-rich PM are about similar at ZUE, BAS and PAY: mineral dust contributes to 8-13% of PM10 mass (8-11% when excluding the Sahara dust event on 15 Oct. 2008), while Na-Mg-rich PM contributes to 8-10% of PM10. The slightly higher mean annual PM10 concentrations at the urban background site ZUE compared to the suburban and rural sites BAS and PAY ($20.7 \, \mu \text{g/m}^3$ compared to 18.8-19.1 $\mu \text{g/m}^3$) are due to
Table 4.1: Relative contribution of PMF factors to the measured chemical species. Elements with factor contributions < 0.30 are not always included.

<table>
<thead>
<tr>
<th>Site</th>
<th>Bern</th>
<th>Zurich</th>
<th>Basel</th>
<th>Payerne</th>
<th>Magadino</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSA</td>
<td>NO$_3^-$ 0.81</td>
<td>NO$_3^-$ 0.90</td>
<td>NO$_3^-$ 0.92</td>
<td>NO$_3^-$ 0.94</td>
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<td></td>
<td>NH$_4^+$ 0.62</td>
<td>NH$_4^+$ 0.66</td>
<td>NH$_4^+$ 0.62</td>
<td>NH$_4^+$ 0.70</td>
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<tr>
<td></td>
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<td>SO$_2^-$ 0.15</td>
<td>SO$_2^-$ 0.21</td>
<td></td>
</tr>
<tr>
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<td>SO$_4^{2-}$ 0.55</td>
<td>SO$_4^{2-}$ 0.63</td>
<td>SO$_4^{2-}$ 0.56</td>
<td>SO$_4^{2-}$ 0.73</td>
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<tr>
<td></td>
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<td>NH$_4^+$ 0.28</td>
<td>NH$_4^+$ 0.45</td>
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<tr>
<td></td>
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<td>OC 0.38</td>
<td>OC 0.19</td>
<td>OC 0.16</td>
</tr>
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<td>Na$^+$ 0.93</td>
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<td>Na$^+$ 0.84</td>
<td>Na$^+$ 0.87</td>
<td>Na$^+$ 0.78</td>
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<tr>
<td></td>
<td>Mg$^{2+}$ 0.31</td>
<td>Mg$^{2+}$ 0.69</td>
<td>Mg$^{2+}$ 0.53</td>
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<td>Mg$^{2+}$ 0.32</td>
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<td>K$^+$ 0.70</td>
<td>K$^+$ 0.63</td>
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</tr>
<tr>
<td></td>
<td>Rb 0.50</td>
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<td>Rb 0.57</td>
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<tr>
<td></td>
<td>OC 0.26</td>
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<td>OC 0.52</td>
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<tr>
<td></td>
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</tr>
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<td>Y 0.79</td>
<td>Y 0.93</td>
<td>Y 0.81</td>
</tr>
<tr>
<td></td>
<td>Sr 0.66</td>
<td>Sr 0.81</td>
<td>Ce 0.63</td>
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<tr>
<td></td>
<td>Ca$^{2+}$ 0.64</td>
<td>Ca$^{2+}$ 0.71</td>
<td>Nd 0.61</td>
<td>La 0.80</td>
<td>Nd 0.72</td>
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</tr>
<tr>
<td></td>
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<td>Ti 0.56</td>
<td>Sr 0.70</td>
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<tr>
<td></td>
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<td>Nd 0.60</td>
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<td>Ti 0.64</td>
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</tr>
<tr>
<td></td>
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<td>La 0.48</td>
<td>Al 0.54</td>
<td>Sr 0.58</td>
</tr>
<tr>
<td></td>
<td>Al 0.45</td>
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<td>Fe 0.53</td>
<td>Gd 0.42</td>
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<tr>
<td></td>
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<td>Manganese 0.42</td>
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<td>Mg$^{2+}$ 0.36</td>
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<tr>
<td></td>
<td>Mn 0.32</td>
<td>Ga 0.32</td>
<td>Ga 0.35</td>
<td>Mg$^{2+}$ 0.23</td>
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<tr>
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<td>Fe 0.30</td>
<td>OC 0.21</td>
<td>Fe 0.26</td>
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</tr>
<tr>
<td>Vehicle wear (BER) / Road traffic</td>
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<td>Sn 0.61</td>
<td>EC 0.54</td>
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<td>Mo 0.60</td>
</tr>
<tr>
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<td>EC 0.61</td>
<td>Mo 0.41</td>
<td>Cr 0.50</td>
<td>Sn 0.56</td>
</tr>
<tr>
<td></td>
<td>Cu 0.51</td>
<td>Cu 0.58</td>
<td>Cr 0.39</td>
<td>Sb 0.48</td>
<td>EC 0.56</td>
</tr>
<tr>
<td></td>
<td>Cr 0.49</td>
<td>Sn 0.56</td>
<td>Cu 0.36</td>
<td>EC 0.47</td>
<td>Cu 0.54</td>
</tr>
<tr>
<td></td>
<td>Fe 0.48</td>
<td>Sn 0.41</td>
<td>Sn 0.44</td>
<td>Cu 0.53</td>
<td>Fe 0.47</td>
</tr>
<tr>
<td></td>
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<td>Zn 0.32</td>
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<td>Zn 0.47</td>
</tr>
<tr>
<td></td>
<td>Mn 0.38</td>
<td>Mn 0.28</td>
<td>Mn 0.27</td>
<td>Mn 0.41</td>
<td>Mn 0.38</td>
</tr>
<tr>
<td></td>
<td>Ba 0.36</td>
<td>Ba 0.37</td>
<td>Mn 0.28</td>
<td>Mn 0.41</td>
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</tr>
<tr>
<td></td>
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<td>Ga 0.34</td>
<td>OC 0.21</td>
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<td>Cd 0.32</td>
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<tr>
<td></td>
<td>OC 0.26</td>
<td></td>
<td></td>
<td></td>
<td>OC 0.25</td>
</tr>
<tr>
<td>Exhaust emissions (BER)</td>
<td>EC 0.67</td>
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<td></td>
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<tr>
<td></td>
<td>OC 0.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3. Results and discussion

higher contributions from mineral dust and road traffic (+0.7 and +1.0 µg/m³, respectively; see Fig. 4.4).

Figure 4.2: Scatter plot of mineral dust as quantified by PMF and mineral dust calculated directly from the measured PM10 composition (Gianini et al., 2012a). The Saharan dust event observed north of the Alps (15 October 2008) was excluded from the regression calculation. All plots include one-to-one lines (dashed lines), regression lines (red lines) and equations of the regression lines.

At the rural site south of the Alps (MAG), the average contributions of the identified sources and components are clearly different from the values found for PAY, BAS and ZUE (see Fig. 4.4). On one hand the absolute and relative contribution of wood combustion and road traffic to PM10 is higher (relative contribution 31% and 24%, respectively), and on the other hand secondary aerosols only constitute 29% of PM10, with much lower contribution of NSA at MAG compared to the other sites (8% of PM10 compared to 22-32%). During winter, the concentrations of OC and EC are clearly higher than at PAY, BAS and ZUE (Gianini et al., 2012a), which is already an indication of a stronger impact of combustion related PM10. PMF analysis shows that at MAG most of the OC is related to wood combustion emissions (52%) followed by road traffic emissions (25%, see Fig. 4.5). Only in summer, a relevant fraction of OC is explained by the SSA factor.

At the sites north of the Alps (PAY, ZUE and BAS) the contribution of wood combustion to OC is smaller than at MAG. In contrast, the fraction of OC that is attributed to secondary PM10 (SSA and NSA) is much larger (33-46%; see Fig. 4.5). The content of water soluble potassium (K⁺) in wood combustion related PM10 varies at the sites north of the Alps (BER, ZUE, BAS, PAY) between 5.4% and 7.1% and is much lower at the rural site south of the Alps (MAG, 2.4%) (inverse of slopes in Table 4.3). In addition the K⁺/OC ratio in the wood combustion profiles is much lower at MAG (0.04) than at the other sites (between 0.12 and 0.18). The lower K⁺/OC in the wood combustion profile could indicate that MAG is stronger impacted by
Table 4.2: Mean annual source contributions (µg/m³) and relative contributions (%) to PM10 as determined by PMF for the samples from 01.08.2008-31.07.2009. The road traffic contribution at the urban roadside site results from the sum of vehicle wear (3.1µg/m³ - 11%) and exhaust emissions (5.6µg/m³ - 19%). Mean annual contributions of mineral dust at the sites north of the Alps were strongly influenced by a Saharan dust event at 15 October 2008. Excluding this event, average mineral dust contributions to PM10 are 3.1µg/m³ at the urban roadside site, 2.3µg/m³ at the urban background site, 1.3 µg/m³ at the suburban site, 1.6µg/m³ at the rural site north of the Alps and 2.1µg/m³ at the rural site south of the Alps.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Urban roadside</th>
<th>Urban background</th>
<th>Suburban</th>
<th>Rural</th>
<th>Rural</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>Bern</td>
<td>Zurich</td>
<td>Basel</td>
<td>Payerne</td>
<td>Magadino</td>
</tr>
<tr>
<td>PM10</td>
<td>29.4 100</td>
<td>20.7 100</td>
<td>18.8 100</td>
<td>19.1 100</td>
<td>20.9 100</td>
</tr>
<tr>
<td>NSA</td>
<td>6.7 23</td>
<td>5.5 26</td>
<td>4.1 22</td>
<td>6.1 32</td>
<td>1.6 8</td>
</tr>
<tr>
<td>SSA</td>
<td>4.3 15</td>
<td>4.5 22</td>
<td>5.6 30</td>
<td>3.2 17</td>
<td>4.4 21</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>3.4 11</td>
<td>2.7 13</td>
<td>1.4 8</td>
<td>2.1 11</td>
<td>2.2 10</td>
</tr>
<tr>
<td>Wood combustion</td>
<td>3.2 11</td>
<td>2.7 13</td>
<td>2.6 14</td>
<td>2.8 15</td>
<td>6.5 31</td>
</tr>
<tr>
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<td>1.9 10</td>
<td>1.5 8</td>
<td>0.6 3</td>
</tr>
<tr>
<td>Na-Mg-rich</td>
<td>8.7 30</td>
<td>3.7 18</td>
<td>2.8 15</td>
<td>3.2 17</td>
<td>4.9 24</td>
</tr>
<tr>
<td>Road traffic</td>
<td>0.1 0</td>
<td>0.0 0</td>
<td>0.3 2</td>
<td>0.2 1</td>
<td>0.6 3</td>
</tr>
</tbody>
</table>

Figure 4.3: Scatter plot of wood combustion contribution to PM10 as quantified by PMF and measured levoglucosan concentrations. All plots include regression lines and the corresponding equations. Note that no levoglucosan measurements are available from BAS.
4.3. Results and discussion

Figure 4.4: Summary of PM10 source apportionment for 2008/2009. The estimated mean annual source contributions at MAG are considered to be representative for rural sites south of the Alps, the regional background north of the Alps is represented as the average source contributions at the suburban site (BAS) and the rural site north of the Alps (PAY). The urban background is derived from source apportionment of PM10 at ZUE.

![Graph showing source contributions for MAG and PAY](image)

**Magadino, rural south of the Alps**

**Payerne, rural north of the Alps**

Figure 4.5: Time series of the sources of OC as obtained with PMF for 2008/2009: MAG, rural site south of the Alps (top panel) and PAY, rural site north of the Alps (bottom panel).
Table 4.3: Number of observations, coefficient of determination ($R^2$), as well as slope and intercept of a linear regression of estimated contribution of wood combustion emissions to PM10 against measured K$^+$ for 2008/2009.

<table>
<thead>
<tr>
<th>Site</th>
<th>Bern</th>
<th>Zurich</th>
<th>Basel</th>
<th>Payerne</th>
<th>Magadino</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of observations</td>
<td>88</td>
<td>91</td>
<td>91</td>
<td>90</td>
<td>91</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.94</td>
<td>0.94</td>
<td>0.96</td>
<td>0.93</td>
<td>0.90</td>
</tr>
<tr>
<td>Slope</td>
<td>16.0 ($\pm$0.8)</td>
<td>16.2 ($\pm$0.9)</td>
<td>14.1 ($\pm$0.6)</td>
<td>18.7 ($\pm$1.1)</td>
<td>41.8 ($\pm$3.0)</td>
</tr>
<tr>
<td>Intercept</td>
<td>-0.6 ($\pm$0.3)</td>
<td>-0.5 ($\pm$0.2)</td>
<td>-0.5 ($\pm$0.2)</td>
<td>-0.4 ($\pm$0.3)</td>
<td>-1.6 ($\pm$0.8)</td>
</tr>
</tbody>
</table>

emissions from incomplete wood combustion (Khalil and Rasmussen, 2003). At the southern parts of Switzerland, many houses use open fireplaces as a supplementary heating system. We assume that these types of wood combustion appliances are often not operated in an optimal way and consequently causing high emissions of organic matter. This hypothesis is supported by the results of various studies performed in Roveredo, an alpine village close (22 km northwest) to MAG. In Roveredo, wood combustion was found to be the dominating source of OM during winter (Lanz et al., 2010; Sandradewi et al., 2008a; Szidat et al., 2008).

It is not surprising that clearly higher contributions from road traffic (sum of exhaust emissions and vehicle wear, 8.7 $\mu g/m^3$) were found at the urban roadside site (BER) than at the urban background site (ZUE). Slightly higher contributions were also observed for mineral dust (3.4 $\mu g/m^3$) and NSA (6.7 $\mu g/m^3$), while the de-icing road salt factor accounted on annual average for 3.0 $\mu g/m^3$ of PM10. The much higher average PM10 concentration at BER (29.4 $\mu g/m^3$) compared to the urban background (20.7 $\mu g/m^3$) results mainly from the higher contributions of these four PM10 sources and components (see Fig. 4.4).

The gradually decreasing concentration of mineral dust from the urban roadside site, the urban background site and the rural and suburban sites north of the Alps (see Fig. 4.4), indicates an impact of human activities on mineral dust concentrations (e.g. resuspension by road traffic and construction activities). As shown in Fig. 4.2, mineral dust as retrieved by PMF results in higher concentrations than by calculation of mineral dust based on the measured concentration of crustal elements (Gianini et al., 2012a). The largest differences are found at the urban roadside site (BER), the urban background site (ZUE) and the rural site (PAY), while differences are lower at the suburban site (BAS) and the rural site (MAG). The discrepancy at BER and ZUE could indicate that the mineral dust as estimated by PMF contains not only natural crustal material but also a fraction of mineral dust like material of anthropogenic origin. However, this hypothesis can not explain the difference between the mineral dust concentration at PAY as estimated from the chemical composition (Gianini et al., 2012a) and by PMF.

4.3.2 PM10 sources for 1998/1999

Sources and components of PM10

PMF analysis of the data from 1998/1999 resulted in the same number of factors and the same interpretation of the factor profiles (loadings) than for 2008/2009 (six factors at BAS and ZUE,
4.3. Results and discussion

Figure 4.6: Relative contribution of PMF factors to selected chemical species at the urban background site (ZUE): apportionment of the chemical species for the 2008-2009 period (top), and for the 1998-1999 period (bottom).

seven factors at BER) except one difference: Instead of the well unmixed wood combustion emission factors for 2008/2009, obviously mixed factors including wood combustion emissions and contributions from road traffic were found for 1998/1999 in BER, ZUE, and BAS (see below). These factors are denoted as mixed anthropogenic factors and are characterised by profiles with high loadings of OC, EC, SO\(_4^{2-}\), K\(^+\) and Fe, and by high percentages of explained mass fractions of Rb, Zn, Cu and Pb. The appearance of a mixed factor might be due to the higher correlation between road traffic related elements (e.g. Fe and Mo) and wood combustion tracers (K\(^+\) and Rb) found in the 1998/1999 data compared to the 2008/2009 data.

Fig. 4.6 shows the percentages of the mass of the measured elements and compounds that is explained by the PMF factors obtained for 1998/1999 and 2008/2009 at the urban background site in Zurich. The corresponding graphs for the other measurement sites are given in the supplementary material (Appendix A, Fig. A.19). The attribution of many of the measured compounds and elements (e.g. NO\(_3^-\), NH\(_4^+\), SO\(_4^{2-}\), Na\(^+\), Al, Y, Nd, La, OC, K\(^+\) and Rb) is very similar for the data from 1998/1999 and 2008/2009, indicating a high robustness of the factors obtained with PMF. However, there are also obvious differences: Clearly higher fractions of Mg\(^{2+}\),Ca\(^{2+}\) and to a smaller extent Fe are attributed to mineral dust in 2008/2009, which is due to a single Saharan dust occurring in the 2008/2009 period (Section 4.3.1). Another apparent difference is the higher fraction of explained mass of Fe, Cu, Zn, Mo, and EC in the factor denoted as mixed anthropogenic factor in the 1998/1999 data compared to the wood
combustion factor in 2008/2009. The presence of the latter elements and EC and the high explained mass of $K^+$, Rb and OC is a strong indication that the anthropogenic mixed factor retrieved from the 1998/1999 data is representing wood combustion emissions and contributions from road traffic during the cold season. The factor profiles and the time series of the scores for 1998/1999 are given in the supplementary material (Figs. A.13[A.18]).

**PM10 source contributions for 1998/1999**

The estimated contributions of the identified sources and components of PM10 for the 1998/1999 study are given in Table 4.4. At the urban background and the suburban sites (ZUE and BAS) secondary aerosols (NSA and SSA) accounted for the largest fraction of PM10 (47-50%), the mixed anthropogenic factor and road traffic emissions accounted for another 18-19% (4.5-4.7 $\mu g/m^3$) and 16-20% (3.9-4.9 $\mu g/m^3$) of PM10, respectively. Mineral dust and Na-Mg-rich PM explained only minor fractions of PM10 (5% and 6-7%, respectively). At the urban roadside site (BER) contributions from road traffic (35%, 13.8 $\mu g/m^3$) and from mineral dust (12%, 4.8 $\mu g/m^3$) were clearly enhanced, while secondary aerosols (NSA and SSA) were of lower importance (25% of PM10). The mixed anthropogenic factor and de-icing road salt accounted for 18% (7.0 $\mu g/m^3$) and 7% (3.0 $\mu g/m^3$) of PM10, respectively.

For comparison of the changes of the mean contributions of sources and components between the two measurement periods (Section 4.3.3), the mixed anthropogenic factor in 1998/1999 is unsatisfactory. In order to divide the contribution of the anthropogenic mixed factor into the fraction resulting from wood combustion and from road traffic emissions, an ad-hoc approach based on the measured $K^+$ concentration in PM10 during the 1998/1999 period was applied. The average content of $K^+$ in wood combustion emissions has been calculated for all five sites of the 2008/2009 study from linear regression of wood combustion related PM10 as determined with PMF for 2008/2009 against the corresponding measured concentration of $K^+$. Table 4.3

**Table 4.4:** Mean annual source contributions ($\mu g/m^3$) and relative contributions (%) to PM10 as determined by PMF for the samples from 01.04.1998 to 31.03.1999. The total road traffic contributions at the urban roadside site is calculated as the sum of vehicle wear (4.8 $\mu g/m^3$ - 12%) and exhaust emissions (9.0 $\mu g/m^3$ - 23%).

<table>
<thead>
<tr>
<th>Site type</th>
<th>Urban roadside</th>
<th>Urban background</th>
<th>Suburban</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>Bern $\mu g/m^3$</td>
<td>%</td>
<td>Zurich $\mu g/m^3$</td>
</tr>
<tr>
<td>PM10</td>
<td>39.7</td>
<td>100</td>
<td>24.1</td>
</tr>
<tr>
<td>NSA</td>
<td>4.5</td>
<td>11</td>
<td>4.4</td>
</tr>
<tr>
<td>SSA</td>
<td>5.4</td>
<td>14</td>
<td>6.9</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>4.8</td>
<td>12</td>
<td>1.2</td>
</tr>
<tr>
<td>Mixed anthropogenic</td>
<td>7.0</td>
<td>18</td>
<td>4.7</td>
</tr>
<tr>
<td>De-icing road salt /</td>
<td>3.0</td>
<td>7</td>
<td>1.5</td>
</tr>
<tr>
<td>Na-Mg-rich</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Road traffic</td>
<td>13.8</td>
<td>35</td>
<td>4.9</td>
</tr>
<tr>
<td>Unknown</td>
<td>1.2</td>
<td>3</td>
<td>0.4</td>
</tr>
</tbody>
</table>
lists the coefficients of determination and the estimated parameters of the linear regression lines (see also Fig. A.20).

As mentioned in Section 4.3.1, similar contents of water soluble potassium in wood combustion related PM10 were found at the four sites north of the Alps. The slopes of the lines from linear regression of PM10 from wood combustion against K⁺ were found to be between 14.1 and 18.7 (Table 4.3). On the basis of these relationships and assuming the content of K⁺ in wood combustion emissions did not change during the past decade, the contributions of wood combustion to atmospheric PM10 for the 1998/1999 period were calculated as:

\[
\text{Wood combustion}_{BER}^{98/99} = \beta_{BER}^{98/99} K^+_{BER}^{98/99}, \quad \beta_{BER}^{08/09} = 16.0 (\pm 0.8)
\]

\[
\text{Wood combustion}_{ZUE}^{98/99} = \beta_{ZUE}^{98/99} K^+_{ZUE}^{98/99}, \quad \beta_{ZUE}^{08/09} = 16.2 (\pm 0.9) \quad (4.4)
\]

\[
\text{Wood combustion}_{BAS}^{98/99} = \beta_{BAS}^{98/99} K^+_{BAS}^{98/99}, \quad \beta_{BAS}^{08/09} = 14.1 (\pm 0.6)
\]

By applying this parameterisation, the contributions of wood combustion to PM10 for 1998/1999 are 3.1 µg/m³ at the urban roadside site (BER), 3.1 µg/m³ at the urban background site (ZUE) and also 3.1 µg/m³ at the suburban site (BAS). The difference of total contribution by the mixed anthropogenic factor and the derived fraction due to wood combustion emissions is taken to belong to road traffic emissions (3.9 µg/m³ at BER, 1.6 µg/m³ at ZUE and 1.4 µg/m³ at BAS). Consequently, the total contributions of road traffic to PM10 in 1998/1999 are: 17.7 µg/m³ at BER, 6.5 µg/m³ at ZUE and 5.3 µg/m³ at BAS.

### 4.3.3 Changes in source contributions from 1998/1999 to 2008/2009

Comparison of the source apportionment of PM10 at BER, ZUE and BAS for 2008/2009 and 1998/1999 gives a clear and consistent picture about the annual average changes during the considered ten year period (see Fig. 4.7). The contributions of sulphate-rich secondary aerosols declined by -1.1 to -3.3 µg/m³, while the contributions of nitrate-rich secondary aerosols remained about constant or were even slightly increasing, the observed changes are 0.6 to 2.2 µg/m³. These temporal developments agree with the measured decrease of SO₄²⁻ and increase of NO₃⁻ concentrations in PM10 (Gianini et al., 2012a).

Mean annual contributions of de-icing road salt and Na-Mg rich aerosols stayed about constant, the changes in mineral dust contributions are different at the three sites, probably reflecting the heterogeneity and temporal variability of sources of mineral dust-like aerosols (e.g. construction work). At the urban roadside site BER the mineral dust concentration decreased (-1.4 µg/m³), whereas at the urban background site ZUE mineral dust concentration increased (1.5 µg/m³). Finally, the modelled mineral dust concentration remained about constant at the suburban site BAS.

The changes of road traffic and wood contribution emissions of PM10 are clear: At the urban roadside site the contribution of road traffic to PM10 strongly decreased between the two measurement campaigns in 1998/1999 and 2008/2009 (-9.0 µg/m³). This obtained change in average road traffic contribution closely matches the difference in measured annual PM10 (-10.3 g/m³). However, it is important to note that due to changes in the local traffic management the total number of vehicles passing nearby the BER site declined during the time between the two measurement campaigns by 29% (number of heavy duty vehicles remained constant, see
Chapter 4. Comparative Source Apportionment of PM10

Figure 4.7: Evolution of source contributions between 1998/1999 and 2008/2009 for the urban roadside site BER, urban background site ZUE and for the suburban site BAS. Negative concentrations indicate decrease of source contributions from 1998/1999 to 2008/2009. Mineral dust contributions in 2008/2009 were calculated excluding the Sahara dust event. Changes in PM10 contributions from road traffic are given in stacked black and brown bars. Note that for BER the black bar represents contributions from two road traffic related factors (road traffic and vehicle wear). The brown bars account for the contributions of road traffic from the mixed anthropogenic factor in 1998/1999.

Gianini et al. (2012a). In addition, the pavement of the road nearby BER has been renewed immediately before the start of the 2008/2009 campaign. These changes certainly have an impact on road traffic contributions at the BER site, it is however not possible to quantify their effect. Nevertheless, negative temporal trends in road traffic contribution to PM10 can also clearly be seen at the urban background site (-2.8 \( \mu g/m^3 \)) and the suburban site (-2.5 \( \mu g/m^3 \)). In contrast to road traffic, the contributions of wood combustion emissions to PM10 remained constant (determined changes smaller than ± 0.5 \( \mu g/m^3 \)).

4.4 Conclusions

Receptor modelling of chemical speciation data of PM10 collected during a one year period in 2008/2009 showed that road traffic and wood combustion are the largest sources of primary PM10 in Switzerland. Except at the urban roadside site where road traffic is the dominating emission source, the annual average contributions of these two sources to PM10 are of similar importance. At the rural site south of the Alps, the contribution of wood combustion is on annual average even exceeding the contribution from road traffic. At this site, high contents of OC and levoglucosan and low contents of K⁺ in wood combustion related PM10 indicate a potential for optimising the operation of wood combustion appliances in order to improve air quality.

The changes in source contributions during the time from 1998/1999 to 2008/2009 show clearly decreasing contributions from road traffic. Within this study, it was not possible to quantify to what extent these changes can be attributed to reductions of exhaust and non-exhaust emissions.
However, the measures for reduction of PM10 emissions from road traffic that have been implemented during the past decade in Switzerland were mainly targeting at exhaust emissions (e.g. tighter limit values for exhaust gas emission of heavy duty vehicles, construction machineries and passenger cars). It can therefore be assumed that the observed decline is mainly due to reduced contributions from exhaust emissions. As for road traffic contributions, also sulphate-rich secondary aerosols decreased during the last decade, indicating that the strategies implemented in Switzerland and in Europe to reduce emissions of sulphate precursors were successful, too. On the other hand, no changes in source contributions have been observed for wood combustion emissions, while nitrate-rich secondary aerosols have increased.

PMF has shown to be a useful tool for the assessment of long-term changes of the contributions of main sources and components to PM10 and thus for assessment of the effect of measures taken to reduce the concentration of ambient particulate matter. However, quantification of source impacts can be difficult, misleading, or impossible when resulting PMF factors represent mixed source profiles. There are no general rules for identification and interpretation of factors that represent mixed sources, in some cases the analysis of data from multiple sites and different time periods might (like in this study) help. In any case, it is advisable to use auxiliary data (e.g. measurements of specific tracers like levoglucosan) and other available information for independent tests for plausibility of the obtained results.

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Chapter 5

Source Apportionment of PM10, Organic Carbon and Elemental Carbon at Swiss Sites: An Intercomparison of Different Approaches

The content of the following chapter is adopted from:

Matthias F.D. Gianini¹, Christine Piot²,³, Hanna Herich¹, Jean-Luc Besombes², Jean-Luc Jaffrezo³, Christoph Hueglin¹: Source Apportionment of PM10, Organic Carbon and Elemental Carbon at Swiss Sites: An Intercomparison of Different Approaches. Accepted for a publication in Science of the Total Environment.

Abstract

In this study, the results of source apportionment of particulate matter (PM10), organic carbon (OC), and elemental carbon (EC) - as obtained through different approaches at different types of sites (urban background, urban roadside, and two rural sites in Switzerland) - are compared. The methods included in this intercomparison are Positive Matrix Factorisation modelling (PMF, applied to chemical composition data including trace elements, inorganic ions, OC, and EC), molecular marker chemical mass balance modelling (MM-CMB), and the aethalometer model (AeM).

At all sites, the agreement of the obtained source contributions was reasonable for OC, EC, and PM10. Based on an annual average, and at most of the considered sites, secondary organic carbon (SOC) is the component with the largest contribution to total OC; the most important primary source of OC is wood combustion, followed by road traffic. Secondary aerosols predominate in PM10. All considered techniques identified road traffic as the dominant source of EC, while wood combustion emissions are of minor importance for this constituent.

The intercomparison of different source apportionment approaches is helpful to identify the strengths and the weaknesses of the different methods. Application of PMF has limitations

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when source emissions have a strong temporal correlation, or when meteorology has a strong impact on PM variability. In these cases, the use of PMF can result in mixed source profiles and consequently in the under- or overestimation of the real-world sources. The application of CMB models can be hampered by the unavailability of source profiles and the non-representativeness of the available profiles for local source emissions. This study also underlines that chemical transformations of molecular markers in the atmosphere can lead to the underestimation of contributions from primary sources, in particular during the summer period or when emission sources are far away from the receptor sites.

5.1 Introduction

Atmospheric particular matter (PM) has significant negative effects on the environment and on human health. It was recognised that atmospheric aerosols play an important role in the radiative balance of the Earth (IPCC, 2007), reduce visibility (Horvath, 1993), and cause acidification and eutrophication of ecosystems (UNECE, 2004). Moreover, elevated PM levels have been associated with an increase in respiratory and cardiovascular diseases (Nel, 2005) and allergies (Monn, 2001). In order to reduce the concentration of atmospheric PM, a detailed and quantitative knowledge of the sources of PM is required. For these reasons, source apportionment of atmospheric PM, and important PM constituents such as organic carbon (OC) and elemental carbon (EC), is an important research field in the atmospheric sciences.

Source apportionment by receptor modelling is a well established technique that is being increasingly applied in aerosol science (Viana et al., 2008a). The results of source apportionment studies are used for the development of effective and efficient air quality management plans (Hopke, 2008). Among the wide range of receptor models based on different statistical approaches, chemical mass balance (CMB) (Friedlander, 1973) and positive matrix factorisation (PMF) (Paatero and Tapper, 1994) belong to the most commonly applied techniques (Viana et al., 2008b). The choice between CMB and PMF depends primarily on the available information about the main sources of PM. While CMB models require detailed a priori knowledge of the emission sources and of their emission profiles, PMF only requires qualitative or semi-quantitative a posteriori information about the source emission profiles. PMF and CMB models have been applied in numerous source apportionment studies based on different types of tracers. CMB models based on organic (e.g. Schauer et al. (1996) and El Haddad et al. (2011)) or elemental tracers (e.g. Watson et al. (1994) and Pandolfi et al. (2008)) have been successfully applied in the past. Similarly, PMF has been successfully applied using both elemental (e.g. Lee et al. (1999)) and organic tracers (Jaegckels et al., 2007; Zhang et al., 2009), with further developments to highly time-resolved aerosol mass spectra in order to identify sources and components of organic aerosols (Lanz et al., 2007).

In addition to these well-established receptor models, another source apportionment method for carbonaceous matter (CM) has been recently developed (Sandradewi et al., 2008b). This model, referred as the Aethalometer model (AeM), takes advantage of the different optical properties of CM from wood and fossil fuel combustions for the estimation of the respective contributions of these two specific sources to CM. The AeM was applied successfully in various short-term source apportionment studies (Favez et al., 2009, 2010; Sandradewi et al., 2008a), and has also been adapted for long-term source apportionment studies for the apportionment of black carbon (BC) (Herich et al., 2011).
5.2 Methods

In the past, several intercomparison studies have been performed to evaluate the performances of different source apportionment methods. These studies were primarily focused on the modelling of the same dataset by different receptor models (Bullock et al., 2008; Hopke et al., 2006; Lee et al., 2008; Pandolfi et al., 2008; Rizzo and Scheff, 2007; Viana et al., 2008b), while only few intercomparison studies were based on the analysis of complementary datasets (e.g. parallel measurements of trace elements and organic molecular markers) (see e.g. Ke et al. (2008) and Shrivastava et al. (2007)). Recently, Favez et al. (2010) performed an intercomparison of different methods for the determination of the contribution of wood combustion to organic matter (OM) during the winter season. The authors investigated the optical properties of atmospheric aerosols using an aethalometer, characterised aerosol chemical composition with an Aerosol Mass Spectrometer (AMS), and determined the concentration of selected organic markers. The collected data were successively modelled using three source apportionment models (AeM, CMB, and PMF). This study demonstrated the limitations of the different approaches, but was limited to a two-week campaign performed at an urban site in winter.

In the present study, we compare source apportionment results for PM10, OC, and EC - as achieved through the application of the Aethalometer model, CMB based on organic tracers, and PMF based on elemental tracers - for extensive data sets collected at different types of sites during a one-year time period (from August 2008 to July 2009). On the one hand, the possibility to compare results from different types of sites and different seasons is exploited to gain additional information on the performances of the different models under different ambient conditions. Specifically, the difference between rural and urban sites and between the winter and summer seasons are investigated, while aiming to identify the weaknesses and strengths of the source apportionment methods for different site types and seasons. On the other hand, the model intercomparisons are used for a mutual validation of the model outputs. This last point is of particular interest when considering that a critical point of source apportionment methods is that the uncertainty of the resulting source contribution estimates is unknown and that the results need to be verified through comparison with other methods or auxiliary data.

5.2 Methods

5.2.1 Sampling sites, sampling methods, and instrumentation

Detailed description of the sampling sites, sampling, and measurement procedures can be found in Gianini et al. (2012a) and Herich et al. (2011), and will only be briefly presented here. PM10 sampling and Aethalometer measurements were performed at three sites of the Swiss National Air Pollution Monitoring Network (NABEL), representing different environmental conditions: urban background (Zurich-Kaserne, ZUE), rural north of the Alps (Payerne, PAY), and rural south of the Alps (in the Magadino plain near Cadenazzo, MAG). In addition to the aforementioned sites, PM10 samples were also collected at an urban roadside site (Bern, BER). PM10 was collected on a 24-hour basis using high-volume samplers (Digitel DA-80H, 30m$^3$h$^{-1}$ flow rate) equipped with PM10 inlets. Particles were collected every fourth day using quartz fibre filters (Pallflex Tissuquartz QAT-2500-UP, ø=150mm) from August 2008 to July 2009. The PM10 mass concentration was simultaneously measured with an automated PM10 monitor (TEOM 1400AB/FDMS 8500, Thermo Scientific).

BC measurements were performed using multiple-wavelength aethalometers (Magee Scientific, USA, model AE31) equipped with PM2.5 inlets. The measurement methods and peri-
Chapter 5. Intercomparison of Source Apportionment Methods

ods, the data handling, and the results concerning the AeM for MAG, PAY, and ZUE have been previously described by [Herich et al.] (2011). Briefly, the aethalometer continuously detects the aerosol attenuation coefficient $b_{ATN}(\lambda)$ of the collected aerosol particles at seven wavelengths $\lambda (370 – 950 nm)$. The aerosol absorption coefficients $b_{abs}(\lambda)$ are subsequently calculated from $b_{ATN}$ according to the data correction procedure presented by [Weingartner et al.] (2003). BC mass concentrations are calculated by dividing $b_{abs}(\lambda)$ by site-specific and wavelength-dependent aerosol light absorption cross sections $\sigma_{abs}(\lambda)$ derived from parallel measurements of $b_{abs}(\lambda)$ and elemental carbon in PM2.5 using the thermal-optical transmission method (see Section 5.2.2).

5.2.2 Chemical analysis

The chemical analyses of the collected PM10 samples for trace elements, inorganic ions, and the carbonaceous fraction are described in detail by [Gianini et al.] (2012a). Briefly, the concentrations of trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS), water soluble inorganic ions were characterised by ion chromatography (IC), while elemental and organic carbon (EC and OC) were determined by the thermal-optical transmission method using the EUSAAR-2 temperature protocol (Cavalli et al., 2010). Analysis of organic compounds was performed through GC-MS and HPLC-Fluorescence as described in [El Haddad et al.] (2009) and [Pavez et al.] (2010). Punches of the PM10 filter samples were extracted with a dichloromethane/acetone mix (1:1 v/v) using an Accelerated Solvent Extractor (ASE 200, Dionex) and reduced to a volume of 1 mL. This extract was then split into three fractions: a fraction directly injected into the GC-MS for the quantification of linear alkanes and hopanes, a fraction analysed by HPLC-Fluorescence for the quantification of polycyclic aromatic hydrocarbons (PAHs), while a third fraction of 100 $\mu$L was trimethylsilylated with 100 $\mu$L of N,0-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) for 2 h at 50$^\circ$C before GC-MS analysis for the quantification of anhydride sugars. Quantification through GC-MS was performed using selected ion current peak areas and calibration curves were established with authentic standards and a deuterated internal standard (checked every 10 samples and performed with 8 levels of concentration between 2 and 400 mgL$^{-1}$). Analysis of organic compounds was carried out for about 1/3 of the PM10 samples (approximately one measurement every 12 days). Mean concentrations of the analysed organic compounds are provided in the supplementary material (Table B.1).

5.2.3 Chemical Mass Balance (CMB) model

The Chemical Mass Balance (CMB) model developed by the US-EPA [EPA 1987] allows the statistical determination of the contribution of primary sources to OC, EC, and PM at a receptor site. The model version EPA-CMB 8.2 was used in this study. In CMB, the measured concentration of compound $i$ at the receptor site $k$ ($C_{ik}$) is represented by a linear combination of relative chemical compositions of sources and expressed with the following linear equation:

$$C_{ik} = \sum_{j=1}^{m} f_{ijk}a_{ij}s_{jk},$$

(5.1)

where $m$ is the total number of emission sources, $a_{ij}$ is the relative concentration of chemical species $i$ in emissions from the source $j$ (so-called source profile), $s_{jk}$ is the contribution at the
receptor site $k$ originating from source $j$, and $f_{ijk}$ is the coefficient of fractionation during the transport set to 1 (corresponding to the use of tracers considered as non-volatile and stable in the atmosphere, see Ke et al. (2007) and Sheesley et al. (2007)).

CMB is commonly applied to organic speciation and sensitive issues of this source apportionment method are the choices of chemical markers and source profiles. Chemical markers and source profiles used in the present study are the same as those used for studies conducted in Grenoble (France) during winter (Favez et al. 2010). Specific adaptations of chemical markers and source profiles to the Swiss sites and to the different seasons are discussed in Piot (2011). Finally, the same chemical markers and source profiles are used for all sites and seasons. Chemical markers used are: elemental carbon (EC), three hopanes (17α(H),21β(H)-Norhopane, 17α(H),21β(H)-Hopane (H30) and 17α(H),21β(H)-22S-Homohopane), 5 n-alkanes (containing 27 to 31 carbons), 3 PAHs (Benzo[e]pyrene, Benzo[ghi]perylene and Indeno[1,2,3-cd]pyrene) and levoglucosan. The selected source profiles are available from the literature and are: an American hardwood combustion profile (Fine et al., 2004), a French vehicular emission profile measured in a tunnel (El Haddad et al., 2009), a vegetative detritus emission profile (Rogge et al., 1993a), and a natural gas combustion profile (Rogge et al., 1993b). Secondary organic carbon (SOC) is calculated as the difference of measured OC and the sum of OC explained by all primary sources included in the CMB model.

The contributions of primary sources to PM10 are determined following the procedure presented by El Haddad et al. (2011). Briefly, OM mass associated with each source is calculated by applying an OC-to-OM conversion factor specific for each source. Source contributions to EC, sulphate, nitrate, and ammonium are determined combining OC source apportionment and emission profiles of the modelled sources. Secondary inorganic aerosols (secondary IA, i.e. secondary fractions of sulphate, nitrate, and ammonium) are calculated as the difference of measured IA concentrations and estimated IA from primary emissions. The results concerning OC and PM10 source apportionment by CMB are discussed in detail in Piot (2011).

Monotracer approach

Complementary monotracer approaches are used to estimate the contributions of two inorganic sources to PM. Sea salt emissions are estimated by multiplying the measured concentration of Na$^+$ by a factor of 2.54, as in Chan et al. (1997). Non-sea-salt mineral dust emissions are estimated following the procedure presented by Putaud et al. (2004b), i.e. mineral dust = \( 5.6 \times \text{nssCa}^{2+} \), where nssCa$^{2+}$ is the non-sea salt fraction of Ca$^{2+}$ that is determined by the equation \( \text{nssCa}^{2+} = \text{Ca}^{2+} - \text{Na}^+ / 26 \). Non-sea salt mineral dust concentrations are determined here based on Ca$^{2+}$ concentrations. Note that soil compositions differing from the relation given above (e.g. silicon-rich or carbonate-rich minerals) lead to biased concentrations of mineral dust.

5.2.4 Positive Matrix Factorisation (PMF)

Positive Matrix Factorisation (PMF) is a widely applied receptor model based on a weighted least squares fit (Paatero, 1997; Paatero and Tapper, 1994). The principle is to solve the mass balance equation \( \mathbf{X} = \mathbf{GF} + \mathbf{E} \); the data matrix \( \mathbf{X} \) (the nxm-matrix of the m measured chemical species in n samples) is factorised into two matrices: \( \mathbf{F} \), a pnxm-matrix whose rows represent the emission profiles of p factors, and \( \mathbf{G} \), an nxp-matrix whose columns represent the scores of
Chapter 5. Intercomparison of Source Apportionment Methods

the $p$ factors. Based on the chemical emission profile of the factors and the variability of the scores, the factors are attributed to emission sources, while the scores represent their activities. The matrix $E$ is the residual matrix. The factorisation problem is solved by minimising the sum of the square of the residuals weighted by the uncertainty of each individual data point (i.e. of each element of matrix $X$), under the constraint that each of the elements of $G$ and $F$ is to be non-negative. The version 4.2 of the programme PMF2 was used in this study.

The results of the PMF modelling for the four Swiss sites (BER, MAG, PAY, and ZUE) are discussed in detail in Gianini et al. (2012b). The main PM10 sources and components identified at the different sites were: sulphate-rich secondary aerosols (SSA), nitrate-rich secondary aerosols (NSA), wood combustion, mineral dust, de-icing road salt (at BER only), a Na-Mg-rich factor (at MAG, PAY, and ZUE), road traffic (at MAG, PAY, and ZUE), and vehicle wear and road traffic exhaust emissions (at BER only).

5.2.5 Aethalometer model (AeM)

The Aethalometer model (AeM) takes advantage of the different optical properties of carbonaceous particles emitted by fossil fuel (FF) combustion and wood burning (WB) (Sandradewi et al., 2008b). This approach relies on the assumptions that WB and FF combustion are the only relevant sources of BC and that light absorption from particles other than carbonaceous particles is negligible. Consequently, the measured aerosol absorption coefficient $b_{abs}(\lambda)$ can be expressed as:

$$b_{abs}(\lambda) = b_{absFF}(\lambda) + b_{absWB}(\lambda), \quad (5.2)$$

where $b_{absFF}(\lambda)$ and $b_{absWB}(\lambda)$ are the wavelength-dependent aerosol absorption coefficients of BC from FF combustion and WB emissions, respectively.

Applying the Beer-Lambert’s Law, the following equations can be obtained:

$$\frac{b_{absFF}(\lambda_1)}{b_{absFF}(\lambda_2)} = \left(\frac{\lambda_1}{\lambda_2}\right)^{\alpha_{FF}} \quad \text{and} \quad \frac{b_{absWB}(\lambda_1)}{b_{absWB}(\lambda_2)} = \left(\frac{\lambda_1}{\lambda_2}\right)^{\alpha_{WB}}, \quad (5.3)$$

where $\alpha_{WB}$ and $\alpha_{FF}$ are the Angstrom exponents for WB and FF BC ($\alpha_{WB} = 1.9$ and $\alpha_{FF} = 0.9$, see Herich et al. (2011) for details).

Solving the equations 5.2 and 5.3 for $\lambda_1=470$nm and $\lambda_2=880$nm, the values of $b_{absFF}(880\text{nm})$ and $b_{absWB}(470\text{nm})$ are determined. The contributions of FF and WB to total BC ($BC_{FF}$ and $BC_{WB}$) are calculated by the equations:

$$BC_{FF} = \frac{b_{absFF}(880\text{nm})}{\sigma_{absFF}(880\text{nm})} \quad \text{and} \quad BC_{WB} = \frac{b_{absWB}(470\text{nm})}{\sigma_{absWB}(470\text{nm})}, \quad (5.4)$$

where $\sigma_{absFF}(\lambda)$ and $\sigma_{absWB}(\lambda)$ are the wavelength-dependent aerosol light absorption cross sections for FF combustion and WB. Starting from the assumption that $\sigma_{absFF}(\lambda)$ and $\sigma_{absWB}(\lambda)$ can be represented by the average site-specific $\sigma_{abs}(\lambda)$, Herich et al. (2011) calculated this as the ratio between measured $b_{abs}(\lambda)$ and the corresponding measured EC concentration. The approach was applied for determination of BC from fossil fuel combustion and BC from wood combustion at MAG, PAY, and ZUE (see Herich et al. (2011) for details).
5.3 Results and discussion

5.3.1 Intercomparison of OC apportionment (CMB vs. PMF)

Source contributions to OC estimated by PMF and CMB at the four sites are presented in Fig. 5.1 and in Table B.2 of the supplementary material. As discussed in Sections 5.2.3 and 5.2.4, the sources identified by means of PMF are not always the same as the sources assumed within CMB. In order to compare source estimations by the two models, four source categories are defined (see Table 5.1): wood combustion, vehicular emissions, other primary sources / components, and secondary components. Wood combustion corresponds to the same sources in CMB and PMF. The category “vehicular emissions” obtained by CMB only includes direct exhaust emissions, while the PMF results also include non-exhaust traffic emissions (e.g. emissions from tyre wear, abrasion of brake pads and resuspension of road dust), see Gianini et al. (2012b) for details. At the roadside site BER, the PMF analysis found a small fraction of OC in the road salt factor (OC_{RS}), likely a result of the high correlation of de-icing road salt emissions and exhaust emissions of road traffic for days with significant impact of de-icing road salt emissions. Consequently, OC_{RS} was added to the category “vehicular emissions”. The category “other primary sources” includes primary sources / components for which no intercomparison is possible: vegetative detritus and natural gas combustion for CMB, and mineral dust and Na-Mg rich factor for PMF. With respect to the secondary components, secondary organic carbon (SOC) is quantified in PMF as the fraction of OC explained by the sulphate- and nitrate-rich factors, while in CMB, SOC is calculated as the difference of measured OC and the sum of OC explained by all primary sources (see Section 5.2.3). The source categories defined here are also partially used in Sections 5.3.2 and 5.3.3.

Table 5.1: Source categories that have been defined based on the applied CMB profiles and the identified PMF factors.

<table>
<thead>
<tr>
<th>Source category</th>
<th>PMF factors</th>
<th>CMB sources and components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood combustion</td>
<td>Wood combustion</td>
<td>Wood combustion</td>
</tr>
<tr>
<td>Vehicular emissions</td>
<td>Road traffic,</td>
<td>Direct exhaust vehicular emissions</td>
</tr>
<tr>
<td></td>
<td>Road salt (BER)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vehicle wear (BER)</td>
<td></td>
</tr>
<tr>
<td>Other primary sources</td>
<td>Mineral dust,</td>
<td>Vegetative detritus,</td>
</tr>
<tr>
<td></td>
<td>Na-Mg rich</td>
<td>Natural gas combustion</td>
</tr>
<tr>
<td>Secondary components</td>
<td>Nitrate-rich secondary aerosols,</td>
<td>Secondary organic carbon</td>
</tr>
<tr>
<td></td>
<td>Sulphate-rich secondary aerosols</td>
<td>(indirectly estimated)</td>
</tr>
</tbody>
</table>
Figure 5.1: Annual, winter and summer contributions of wood combustion, road traffic, secondary OC, and other minor sources to OC, as obtained by PMF and CMB at BER, ZUE, PAY, and MAG. Circles indicate mean measured OC concentrations, the numbers in brackets indicate the number of samples per year and season. Note that average contributions are calculated from days where results from both receptors models (PMF and CMB) were available.

Close to the detection limit) in this season, explained by the lower biomass combustion emissions and possibly to some extent by the degradation of this compound (Hennigan et al., 2010). On the other hand, the wood combustion contribution obtained with PMF might be biased high because during summer contributions from other sources (e.g., resuspension of mineral dust) to the considered wood combustion tracers (e.g., K⁺ and Rb) are dominating. Since the capabilities of PMF to resolve the impact of different sources depend on differences in the temporal source activities and on differences in the source emission profiles, highly correlated emission patterns represent an important obstacle for the correct source identification and quantification by PMF.
The application of the CMB method appears to be problematic during winter at the MAG site. Although the choice of the wood combustion profile was based on the type of wood burned at this site (the ratio of soft and hard wood was estimated from the levoglucosan/mannosan ratio, see [Piot (2011)]) and the different profiles were tested as detailed in [Favez et al. (2010)], the profiles available from the literature do not appear to be representative of the wood combustion emissions at this site during the cold season. This results in an incorrect estimation (i.e. overestimation) of $OC_{WC}$ and total OC obtained by CMB compared with the measured OC. Incorrect estimation of $OC_{WC}$ is observed in some other alpine valley sites largely impacted by biomass combustion emissions (Piot, 2011), indicating that the wood combustion emission profiles from the literature are inappropriate for this type of site. The inadequacy of the profiles could be related to the different meteorological conditions (for example, temperature) occurring in alpine valleys compared to those prevalent when the source profiles were established, resulting in a different repartition of the organic matter and tracers between the gas and particulate phases. The identification of source profiles that are representative for local sources is a central and complex exercise in CMB, and can limit the application of this source apportionment method.

Contributions of vehicular emissions estimated by CMB and PMF agree well at the traffic site and the urban background site during winter. At the other sites clear differences with lower road traffic contributions estimated by CMB than by PMF are observed. Several reasons might explain this finding. First of all, vehicular emissions by PMF also include other emission processes, e.g. non-exhaust emissions, which are not included in the CMB analysis. This difference between CMB and PMF can lead to a general underestimation of vehicular emissions by CMB compared to PMF. As underlined by [Amato et al.] (2009) and [Thorpe and Harrison] (2008), the contribution of the non-exhaust traffic emissions to OC cannot be neglected, at least at urban sites. However, the differences between the two methods are more important at the rural sites, with larger differences in summer. In summer and for the rural sites, concentrations of organic tracers of vehicular emissions are very low (near analytical detection limits). Photochemical degradation of organic tracers can lead to a complete removal of these compounds from the atmosphere, especially when air masses are transported over long distance (El Haddad et al., 2011; Robinson et al., 2006). Therefore, estimations of this contribution by receptor models based on these tracers are more difficult in this season and can lead to an underestimation of direct vehicular exhaust emissions. Degradation of organic tracers can be a limiting factor for the application of receptor models based on molecular markers (see also [Piot (2011)]).

A larger number of primary sources of OC are included in CMB modelling than delineated by PMF, including natural gas combustion and vegetative detritus emissions. Conversely, two further PM components are identified by PMF: a Na-Mg-rich factor and mineral dust, both having negligible contributions to OC (<10% of total measured OC). For all these sources/components, intercomparison between the two models was not possible.

Despite the fundamental differences of methods in the quantification of SOC (see above), the contributions estimated by the two methods are mostly similar, especially in winter. In summer, when SOC is present at higher concentrations, the differences between the two approaches are larger with lower contributions estimated by PMF (on average by 50-70%) compared to CMB. Several hypotheses can be raised to explain these differences. First, emissions of SOC precursors can be correlated with primary emissions and PMF would tend to associate some of the SOC with sources of primary OC, leading to an underestimation of the corresponding secondary factors. Second, CMB analysis can underestimate some primary sources in this season, due to some extent by the enhanced reactivity of tracers, and therefore attribute OC not explained by primary sources to secondary sources. However, it must be noted that the meth-
ods applied here to quantify SOC concentrations are only indicative. The absence of specific SOC tracers in element-based PMF and the possibility that in CMB OC emitted from unknown primary sources could be erroneously attributed to secondary OC make the quantification of SOC only a rough estimate. Moreover, the low time resolution of the sampling (24 h) is not really appropriate to correctly capture the formation of SOC in the atmosphere. In all cases, estimation of secondary sources remains a challenging and complicated task.

5.3.2 Intercomparison of EC apportionment (CMB, PMF, and AeM)

First, intercomparison of EC source apportionment by AeM, PMF, and CMB is complicated because these models are applied to data from different PM size fractions (PM2.5 for AeM and PM10 for PMF and CMB). Hueglin et al. (2005) showed that at the receptor sites included in this study, most of the EC mass concentration in PM10 is already found in PM2.5 (70-80%, based on an annual basis in 1998). Similar or even higher fractions were measured in more recent campaigns performed in the alpine area (Jaffrezo et al., 2005). These data could indicate that the use of either PM2.5 or PM10 size fraction only moderately influences the source apportionment of EC.

Second, the sources identified by means, or included in the different models, are in principle not the same. However in practice, the AeM method differentiates between fossil fuel and wood combustion, CMB assigns the predominant fraction of EC to direct vehicular exhaust emissions and wood combustion, while contributions of other sources are negligible.

Finally, the most important sources of EC as determined by PMF are also road traffic and wood combustion, while only lower fractions of EC are apportioned to PM10 components such as mineral dust, nitrate-rich secondary aerosols, or non-exhaust vehicular emissions. Therefore, direct comparisons can be performed in this study for wood combustion (present for all approaches), and direct vehicular exhaust emissions (CMB), road traffic (PMF), and fossil fuel combustion (AeM), under the assumption that EC emissions from non-road-traffic FF combustion are negligible. Note that the optical BC measurements with the aethalometer are consistent with the thermal-optical EC measurements used for CMB and PMF because the site-dependent optical mass absorption coefficients have been derived from comparison of optical absorption coefficient and thermal-optical EC (see Sections 5.2.1 and 5.2.5).

Mean annual and seasonal contributions of wood combustion and road traffic (or FF combustion), as determined by AeM, PMF, and CMB, are shown in Fig. 5.2 (see also Table B.3). On an annual basis, at all sites and for all source apportionment approaches, road traffic (or FF combustion) represents the most important source of atmospheric EC. Wood combustion becomes more important during the cold season (winter and partially in fall and spring).

Concerning contribution of wood combustion to EC (EC_{WC}), a good agreement between AeM and PMF is observed, especially at PAY and ZUE. The only discrepancies between the two models are observed at MAG, where EC_{WC} as obtained by PMF is much larger than the contribution found by AeM. In contrast to AeM and PMF, it is evident that the CMB model applied in this study is not capable to correctly estimate the contribution of wood combustion to the total ambient EC concentration. At all considered sites, EC is almost exclusively apportioned to road traffic emissions. At MAG, where the contribution from wood combustion to OC and PM10 is highest, less than 50% of total EC can be apportioned by CMB (Table 5.2). It is very likely that the fraction of EC in the used wood combustion emission profile is too low.
Figure 5.2: Contributions to EC from wood combustion and road traffic or FF combustion as obtained by PMF, CMB, and AeM. Upper panels: annual, winter, and summer contributions from the three models at Magadino (left) and Payerne (right). Lower panels: contributions in spring and summer at Zurich (left); annual, winter, and summer contributions from PMF and CMB at Zurich (middle) and Bern (right). Note that average contributions are calculated from days where results from all source apportionment approaches were available.

Another aspect that probably is of minor importance here is the fact that the fractions of EC and OC in the emission profiles can be strongly dependent on the analytical method applied to quantify the EC and OC concentrations. In the present study, EC/OC measurements were performed by the thermal-optical transmission (TOT) method with the EUSAAR-2 temperature protocol, while the emission profile was determined by TOT using the NIOSH temperature programme Fine et al. (2004). The NIOSH temperature programme has a higher peak temperature in the helium-mode of the analytical cycle than EUSAAR-2, leading to premature EC evolution in the helium-mode and thus to lower EC concentrations Subramanian et al. (2006). Parallel measurements performed on ambient PM samples using both the EUSAAR-2 and NIOSH temperature programmes showed that EUSAAR-2 overestimates EC concentrations compared to NIOSH (overestimates ranging between of 19 and 33%, see Piazzalunga et al. (2011)). The fact that EC in the wood combustion profile used in CMB was determined by using a NIOSH temperature protocol can partly explain the above-mentioned fraction of EC being too low in this emission profile.

In addition to the differences introduced by the analytical methods, the fraction of EC in the emission profiles depends on the combusted wood types and the combustion conditions. This leads to additional uncertainties in the apportionment of EC by CMB. Note however, that the chemical profiles proposed by Fine et al. (2004) lead to reasonable results for the source contributions to OC at the considered sites (see Section 5.3.1) as already shown for other European sites by Favez et al. (2010) and Piot (2011). This includes the excellent agreement with independent measurements of \(^{14}\)C in the FORMES field campaign in Grenoble Favez et al. (2010).
**Table 5.2:** Coefficient of determination ($R^2$), number of observations, slope, and intercept of a linear regression of EC$_{WC}$ and EC$_{TR}$ from PMF against EC$_{WC}$ and EC$_{TR}$ from AeM (upper part of table), and similarly for CMB against AeM (lower part of table). Numbers in this table can be slightly different from those in Herich et al. (2011) due to updates in PMF and AeM modelling results.

<table>
<thead>
<tr>
<th>Site</th>
<th>MAG</th>
<th>PAY</th>
<th>ZUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sources</td>
<td>Wood comb.</td>
<td>Road traffic or FF</td>
<td>Wood comb.</td>
</tr>
<tr>
<td>Sources PMF vs. AeM</td>
<td>R$^2$</td>
<td>0.77</td>
<td>0.74</td>
</tr>
<tr>
<td>Slope</td>
<td>1.58</td>
<td>1.19</td>
<td>0.81</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.08</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Observations</td>
<td>82</td>
<td>86</td>
<td>31</td>
</tr>
<tr>
<td>Sources CMB vs. AeM</td>
<td>R$^2$</td>
<td>0.78</td>
<td>0.36</td>
</tr>
<tr>
<td>Slope</td>
<td>0.83</td>
<td>1.06</td>
<td>0.17</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.01</td>
<td>0.05</td>
<td>-0.01</td>
</tr>
<tr>
<td>Observations</td>
<td>15</td>
<td>29</td>
<td>10</td>
</tr>
</tbody>
</table>

The overestimation of EC$_{WC}$ by PMF at MAG can be seen in the context of a general overestimation of wood combustion contribution to PM10 during winter: long periods of temperature inversions occurred at MAG during the considered time period, and corresponding accumulation of PM10 was primarily assigned to high contributions from wood combustion emissions. When the PM variability is predominantly driven by meteorological conditions rather than the variability of source activities, the identification and correct quantification of PM sources are hampered in PMF. Comparing the wood combustion profile estimated by PMF at MAG with the wood combustion profiles found at the other sites, higher fractions of OC and EC were found at MAG (Gianini et al., 2012b). This might on one hand be explained by an impact of additional sources, meaning that the obtained profile represents emissions from multiple sources rather than from wood combustion only. On the other hand, higher fractions of OC and EC at MAG could indicate a different source profile at this site due to e.g. the use of different wood types or different combustion conditions. This latter reason is supported by the fact that the EC/OC ratio in the wood combustion profile at MAG is in good agreement with values reported in the literature for wood combustion emissions (see discussion in Gianini et al. (2012b)).

A reasonable agreement between the contributions from road traffic or FF combustion (EC$_{TR}$) to EC was observed for AeM, PMF, and CMB. The correlations between AeM and PMF are mostly higher than those between AeM and CMB (see Table 5.2), with the lowest correlation at the rural site PAY. In general, mean annual EC$_{TR}$ determined by PMF is slightly lower than that given by AeM and CMB, with larger differences (both relative and absolute) in winter. Differences are also present in summer at the two rural sites (PAY and MAG), with EC$_{TR}$ determined by CMB being significantly lower than that given by PMF or AeM. Again, the source
5.3. Results and discussion

apportionment based on organic tracers seems to be problematic during summer, in particular for sites far away from the emission sources (e.g. rural sites as PAY and MAG).

5.3.3 Intercomparison of PM10 apportionment (CMB vs. PMF)

As pointed out in Sections 5.3.1 and 5.3.2, the sources determined by PMF are not always the same as the sources included in the CMB model. Thus the direct comparison of OC and EC source apportionment by the two methods can be difficult. This problem becomes even more relevant when considering the sources of PM10. As discussed in Section 5.2.4, six PM10 sources (at PAY, ZUE, and MAG) or seven PM10 sources (at BER) were identified by PMF, while for CMB combined with the monotracer approach, the contributions to PM10 from seven sources were estimated. For some sources, contributions to the PM10 estimated by both methods can be directly compared (e.g. wood combustion and mineral dust), while for other sources (e.g. road traffic from PMF and the direct vehicular exhaust emissions from CMB), a direct comparison is not possible.

In addition to the difference in PM sources, another difference between PMF and CMB makes the comparison difficult: the measured PM10 concentrations are directly included as one of the PMF variables, leading to the apportionment of the total measured PM10 mass. This is not the case for the CMB method, where the contribution of each source is estimated starting from the measured concentrations of the relevant chemical species. As in a mass closure approach (Hueglin et al., 2005), this leads to a general underestimation of apportioned PM mass compared to the measured PM concentrations.

Despite these differences between the two approaches, some systematic features in the PM10 apportionments can be identified for all sites. First, concentrations of secondary aerosols (SA) as estimated by PMF are in good agreement with the SA concentrations by CMB (see Fig. 5.3 and Table B.4). Although CMB seems to find systematic lower concentrations of SA at days with peak concentrations of secondary aerosol, the SA time series are at all sites highly correlated ($R^2 > 0.85$, Fig. 5.4). Second, contributions of wood combustion to PM10 ($PM10_{WC}$), as determined by CMB, are generally lower than the contributions found by PMF. However, the two fractions are well correlated for all sites ($R^2 > 0.60$, with the exception of MAG where $R^2=0.43$ only, see Table 5.3).

Finally, the contributions of mineral dust by PMF and mineral dust by the CMB/monotracer approach are well-correlated ($R^2 > 0.65$, see Table 5.3). High time correlations ($R^2 > 0.80$) were also observed between Na-Mg-rich/road salt (from PMF) and sea salt (from CMB/monotracer approach). For both of these PM10 components, the differences between PMF and the CMB/monotracer approach are lower at the urban roadside site and increase when shifting to the two rural sites (see Fig. 5.3). Concerning mineral dust, the same behaviour was observed when comparing results of the mass closure approach (Giannini et al., 2012a) with PMF, and could indicate an overestimation of the mineral dust contribution to PM10 by PMF. Similarly, the fraction of PM10 apportioned by PMF to Na-Mg-rich/road salt components is generally higher than the measured concentrations of $Na^+$, $Cl^-$ and $Mg^{2+}$. Due to the correlated temporal pattern of road salt and road traffic emissions, the road salt factor probably includes a fraction of OC and EC emitted by road traffic. Likewise, the Na-Mg-rich factor likely also contains fractions of secondary aerosols that are transported within the oceanic air mass or that are added when passing over the European continent.
Chapter 5. Intercomparison of Source Apportionment Methods

Figure 5.3: Annual, winter, and summer contributions to PM10 as obtained by PMF and CMB / monotracer approaches at BER, ZUE, PAY, and MAG. Circles indicate mean measured PM10 concentrations. Numbers in brackets indicate the number of samples per year and season. Note that average contributions are calculated from days where results from both receptors models (PMF and CMB) were available.

In contrast to the other PM10 sources or components, the contributions of road traffic as modelled by PMF are not correlated with the contributions of the direct vehicular exhaust emissions as quantified by CMB. The most relevant differences between the two approaches are for the summer season, when contributions to road traffic by CMB are low, as already discussed in Sections 5.3.1 and 5.3.2. In addition, it is important to remember that at all sites except for BER, road traffic contributions by PMF also include resuspended road dust, while vehicular emissions from CMB only include exhaust emissions. This can partially enhance the differences between the two models concerning road traffic contributions.
Figure 5.4: Scatter plot of secondary aerosol concentrations as quantified by PMF and CMB. All plots include one-to-one lines (dashed lines), regression lines (solid lines), equations of the regression lines, and coefficient of correlation.
Table 5.3: Coefficient of determination ($R^2$), number of observations, slope, and intercept of a linear regression of PM10 sources contributions as obtained by CMB/monotracer approaches against PM10 source contributions as obtained by PMF. Linear regression parameters are shown for secondary aerosols (CMB vs. PMF), wood combustion (CMB vs. PMF), mineral dust (monotracer approach vs. PMF), sea salt (monotracer approach) vs. road salt/Na-Mg rich (PMF) and vehicular exhaust emissions (CMB) vs. road traffic (PMF)

<table>
<thead>
<tr>
<th>Site</th>
<th>Parameter</th>
<th>Secondary aerosols</th>
<th>Wood combustion</th>
<th>Mineral dust</th>
<th>Road salt/Na-Mg rich</th>
<th>Road traffic</th>
</tr>
</thead>
<tbody>
<tr>
<td>BER</td>
<td>$R^2$</td>
<td>0.92</td>
<td>0.93</td>
<td>0.81</td>
<td>0.80</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>Slope</td>
<td>0.70 ($\pm$ 0.08)</td>
<td>0.50 ($\pm$ 0.06)</td>
<td>0.81 ($\pm$ 0.16)</td>
<td>0.43 ($\pm$ 0.09)</td>
<td>0.37 ($\pm$ 0.28)</td>
</tr>
<tr>
<td></td>
<td>Intercept</td>
<td>2.4 ($\pm$ 1.5)</td>
<td>0.1 ($\pm$ 0.4)</td>
<td>0.6 ($\pm$ 0.8)</td>
<td>0.5 ($\pm$ 0.6)</td>
<td>3.4 ($\pm$ 1.8)</td>
</tr>
<tr>
<td></td>
<td>Observations</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>ZUE</td>
<td>$R^2$</td>
<td>0.97</td>
<td>0.84</td>
<td>0.68</td>
<td>0.92</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>Slope</td>
<td>0.81 ($\pm$ 0.06)</td>
<td>0.61 ($\pm$ 0.10)</td>
<td>0.56 ($\pm$ 0.15)</td>
<td>0.28 ($\pm$ 0.03)</td>
<td>0.15 ($\pm$ 0.10)</td>
</tr>
<tr>
<td></td>
<td>Intercept</td>
<td>2.3 ($\pm$ 0.9)</td>
<td>-0.2 ($\pm$ 0.4)</td>
<td>0.3 ($\pm$ 0.5)</td>
<td>0.0 ($\pm$ 0.1)</td>
<td>1.4 ($\pm$ 0.5)</td>
</tr>
<tr>
<td></td>
<td>Observations</td>
<td>29</td>
<td>29</td>
<td>29</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>PAY</td>
<td>$R^2$</td>
<td>0.85</td>
<td>0.60</td>
<td>0.77</td>
<td>0.98</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>Slope</td>
<td>0.74 ($\pm$ 0.12)</td>
<td>0.51 ($\pm$ 0.16)</td>
<td>0.33 ($\pm$ 0.07)</td>
<td>0.22 ($\pm$ 0.01)</td>
<td>0.22 ($\pm$ 0.13)</td>
</tr>
<tr>
<td></td>
<td>Intercept</td>
<td>2.6 ($\pm$ 1.1)</td>
<td>0.0 ($\pm$ 0.5)</td>
<td>0.3 ($\pm$ 0.2)</td>
<td>0.1 ($\pm$ 0.0)</td>
<td>0.1 ($\pm$ 0.5)</td>
</tr>
<tr>
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<td>Observations</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
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</tr>
<tr>
<td>MAG</td>
<td>$R^2$</td>
<td>0.87</td>
<td>0.43</td>
<td>0.65</td>
<td>0.90</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>Slope</td>
<td>1.00 ($\pm$ 0.19)</td>
<td>0.96 ($\pm$ 0.55)</td>
<td>0.21 ($\pm$ 0.08)</td>
<td>0.31 ($\pm$ 0.05)</td>
<td>0.19 ($\pm$ 0.16)</td>
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<tr>
<td></td>
<td>Intercept</td>
<td>1.3 ($\pm$ 1.8)</td>
<td>1.9 ($\pm$ 6.3)</td>
<td>0.3 ($\pm$ 0.2)</td>
<td>0.0 ($\pm$ 0.1)</td>
<td>0.0 ($\pm$ 1.0)</td>
</tr>
<tr>
<td></td>
<td>Observations</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

5.4 Conclusions

Intercomparison of source apportionment of EC, OC, and PM10 as obtained by PMF, CMB, and AeM approaches has been performed. At all sites, the agreement between source contributions estimated with the different source apportionment approaches was better for OC than for EC and PM10.

On the basis of the results presented in the study, some general conclusions on the weakness of these different source apportionment methods can be drawn:

- The identification of source profiles that are representative for local sources is a central and complex exercise when applying CMB, and can limit the application of this source apportionment method.

- Due to possible degradation of molecular tracers, use of organic tracers within receptor modelling in summer and at rural sites can be problematic and can lead to an underestimation of primary OC and PM sources.

- The capability of PMF to resolve the main sources is based on differences in the activities of the various sources. Highly correlated emission patterns represent an obstacle for the
correct identification and quantification of PM source contributions when applying PMF. Specifically, when the PM variability is predominantly driven by meteorological conditions rather than by the impact of the variability of the emission sources, the identification of mixed source factors instead of unmixed sources cannot be excluded.

This work underlines that the source apportionment of single chemical constituents that are incorporated as variables in the receptor model can be achieved by CMB and PMF. Furthermore, source apportionment of single chemical constituents (e.g. EC) achieved by CMB and PMF can be used for validation of results from other source apportionment methods (e.g. from AeM).

The intercomparison of the different source apportionment methods is considered as being of crucial importance for the validation of model results and for the identification of weaknesses in the different methods. Validation of source apportionment results by cross-checking with independent methods is advisable for every source apportionment study.

**Acknowledgements**

This study was supported by the Swiss Federal Office for Environment (FOEN) and was associated with the IMBALANCE project of the Competence Centre Environment and Sustainability of the ETH Domain (CCES). The authors are grateful to the NABEL team at Empa for technical support and assistance and to Julie Cozic (LGGE) for helpful discussions. C. Piot thanks the Region Rhône-Alpes for her PhD grant.
Chapter 6

Summary and Outlook

6.1 Summary and conclusions

In this thesis, the chemical composition and sources of atmospheric aerosols at various Swiss sites with differing environmental conditions have been investigated. In particular, the focus was put on the analysis of present-day PM10 composition, on the identification and quantification of present-day PM10 sources, and on the analysis of the evolution of both PM10 chemical composition and sources during the past decade. The results presented in this work are useful to better understand the changes in PM10 concentrations observed during the past years, to assess the efficiency of the strategies implemented to abate atmospheric PM concentrations and to plan further effective PM abatement strategies.

Finally, the results of different source apportionment methods applied to quantify source contributions to PM10 and important PM10 constituents (i.e. organic carbon and elemental carbon) were intercompared. This allowed on the one hand a reciprocal validation of the results obtained by the single individual apportionment methods, and on the other hand permitted the identification and discussion of the strengths and weaknesses of the different methods.

As presented in Chapter 3, the combined analysis of PM chemical characterisation data from different site types is a powerful method to study PM emissions from urban road traffic and the urban environment. In particular, it was found that urban background, suburban and rural sites located north of the Alps present mostly homogeneous PM10 chemical composition. As expected, at the urban roadside site enhanced concentrations of EC and several traffic-related trace elements were measured. At the rural site located south of the Alps, much higher concentrations of carbonaceous PM components (OM and EC) and lower secondary inorganic aerosols (nitrate, sulphate and ammonium) than at similar site types located north of the Alps were observed.

From the results presented in Chapter 3, it is evident that the emission reduction strategies for PM and precursors of secondary PM that have been implemented during the past ten years have led to a clear improvement in ambient PM10 levels. Remarkable are the decreasing concentrations of sulphate, EC, and many trace elements (e.g. heavy metals such as Pb, Ni, V and Cd). In contrast to the above-mentioned species, nitrate concentrations have increased at the investigated sites for the period 2008/2009 compared to levels in 1998/1999. The slight increase observed in nitrate is remarkable, particularly when considering the reduced NOx emissions and slight decrease in ambient NO2 concentrations observed during the past ten years in Switzerland and in neighbouring countries. Possible mechanisms that can explain these trends include:
decreasing sulphate concentrations that leave increasing amounts of ammonia to react with nitric acid to form aerosol nitrate, and the increasing average ozone concentrations in Switzerland and other European countries that might enhance the formation of nitric acid at night. In all cases, the nitrate trend underlines the fact that further significant reductions in NO\textsubscript{x} emissions are certainly necessary to lower the nitrate concentration in PM\textsubscript{10}.

In a further step, PM\textsubscript{10} speciation data presented in Chapter 3 have been analysed for major sources by receptor modelling using Positive Matrix Factorisation (PMF) (see Chapter 4). Receptor modelling of data collected in 2008/2009 showed that road traffic and wood combustion are the largest sources of primary PM\textsubscript{10} in Switzerland. At the sites located north of the Alps, the average annual contributions of these two sources to PM\textsubscript{10} are of similar importance, with the only exception at the urban roadside site where road traffic is the dominating emission source. At the rural site south of the Alps, the contributions of wood combustion were much higher than those modelled north of the Alps. On annual average, wood combustion contributions even exceeded the contribution from road traffic. The high contents of OC and levoglucosan and low contents of K\textsuperscript{+} in wood combustion related PM\textsubscript{10} suggest the potential for optimising the operation of wood combustion appliances in order to improve air quality south of the Alps.

From the results presented in Chapter 4, it is evident that road traffic contributions to PM\textsubscript{10} have decreased at all of the sites during the period from 1998/1999 to 2008/2009. This is a clear sign that the numerous measures implemented during the past years for reduction of PM\textsubscript{10} emissions from road traffic (mainly targeting exhaust emissions) have been successful. The temporal developments of sulphate-rich secondary aerosols (SSA) and nitrate-rich secondary aerosols (NSA) agree with the measured decrease in sulphate and increase in nitrate concentrations in PM\textsubscript{10} (see discussion in Chapter 3). Finally, no changes in source contributions have been observed for wood combustion emissions.

As underlined for the chemical composition analysis, the comparison of results for source apportionment from different site types is a powerful method to study PM emissions from urban road traffic and the urban environment. PMF has been shown to be a useful tool for the assessment of site-to-site differences in source contribution. Moreover, PMF displayed its strength in the identification of long-term changes in the contributions of main sources and components to PM\textsubscript{10}, and thus for assessment of the effect of measures taken to reduce the concentrations of ambient particulate matter.

In Chapter 4, it was however pointed out that the quantification of source impacts can be difficult, misleading, or impossible when resulting PMF factors represent mixed source profiles. In some cases, the analysis of data from multiple sites and different time periods might help in the interpretation of factors that represent mixed sources. In any case, it is advisable to use auxiliary data (e.g. measurements of specific tracers like levoglucosan) and other available information (e.g. results from different source apportionment methods) for independent plausibility tests of the obtained results.

Some of the limitations of PMF discussed in Chapter 4 have been thoroughly examined in Chapter 5. Here the results of PMF modelling were intercompared with the results of two additional source apportionment methods (molecular markers Chemical Mass Balance (CMB) and the Aethalometer model (AeM)). The intercomparison allowed on the one hand a reciprocal validation of the results obtained through the individual source apportionment methods, while on the other hand permitted the identification and discussion of the strengths and weaknesses of the different methods. In particular the limitations of the application of CMB and PMF were outlined in this part of the thesis.
The intercomparison underlined that it can be difficult to assess if sources identified by PMF are well unmixed. Temporal correlation of source emissions is still a relevant problem and can hinder PMF analysis. Moreover, elements on which the modelling is based are rarely emitted by a single emission source; this can lead to a further difficulty in an ideal separation and identification of the emission sources. When applying CMB, temporal correlation in source emissions does not have negative impact on the quantification of source contribution. On the other hand, CMB presents other evident limitations: Detailed quantitative a priori information on the number and chemical profile of the emission sources must be known, implying a time-intensive source characterisation before model application. Alternatively, when the chemical profile used in the modelling is chosen from the literature, it must be clarified that this profile is representative for local emission sources. A further problematic point of CMB modelling is the impossibility of apportioning secondary aerosol components, and in the case of molecular markers based CMB the reactivity of the molecular tracers can in many cases lead to an underestimation of primary source contributions.

6.2 Outlook

As demonstrated in this study long-term chemical characterisation measurements (e.g. over one year) are useful to determine trends in PM composition and source contributions. However, it was also highlighted that it can be difficult to deduce a general trend from only two measurement campaigns over a year, due to the influence of meteorology on PM concentrations and composition.

To better identify and assess trends in PM composition, it would be worthwhile to introduce a continuous monitoring programme, following the approach implemented in the Chemical Speciation Network (CSN) by the US Environmental Protection Agency (EPA). Source apportionment by PMF could also benefit from continuous PM chemical speciation: a larger number of observations (e.g. over several years) might in fact allow for a better separation and identification of PM sources. In the absence of such long-term data it would be worth the effort to chemically characterise emissions from local sources. The incorporation of local source profiles in hybrid receptor models, such as the Multilinear Engine (ME2 - Paatero (1999)) or the Constrained Physical Receptor Model (COPREM - Wahlin (2003)) that integrate the advantage of CMB models and non-negative factor analysis, could thus lead to more precise and reliable PM source apportionment.
Appendix A

Supplement to ”Comparative Source Apportionment of PM10 in Switzerland for 2008/2009 and 1998/1999 by Positive Matrix Factorisation” - Chapter 4

The content of the following appendix is adopted from the supplementary material of:

Matthias F.D. Gianini¹, Andrea Fischer¹, Robert Gehrig¹, Andrea Ulrich², Adrian Wichser², Christine Piot³, Jean-Luc Besombes³, Christoph Hueglin¹: Comparative Source Apportionment of PM10 in Switzerland for 2008/2009 and 1998/1999 by Positive Matrix Factorisation., Atmospheric Environment, 54, 149–158, 2012.

A.1 Definition of signal to noise ratio (S/N)

The S/N of the specie i was calculated as:

\[
\frac{S}{N_i} = \left( \sum_j \frac{\text{abs}(x_{ij})}{s_{ij}} \right) / n_i
\]  

(A.1)

where \(x_{ij}\) and \(s_{ij}\) are the elements of the data matrix \(X\) and of the measurement uncertainty matrix \(S\), and \(n_i\) the number of observations of the chemical species \(i\).

The signal to noise ratios (S/N) calculated following equation [A.1] and the fraction of data below detection limit (BDL) are summarised in Table [A.1] (for the 2008/2009 period) and in Table [A.2] (for the 1998/1999 period).

¹Air Pollution/Environmental Technology Laboratory, Empa, Duebendorf, Switzerland
²Laboratory for Analytical Chemistry, Empa, Duebendorf, Switzerland
³LCME, Université de Savoie, Le Bourget du lac, France
⁴CNRS-LGGE-UMR, Université Joseph Fourier, Grenoble, France
Table A.1: Summary of fraction of data below the limit of detection (BDL) and of signal to noise ratio (S/N) for 2008/2009. (BDL>50% and S/N<1.0 are given in bold).

<table>
<thead>
<tr>
<th>Species</th>
<th>Bern BDL S/N</th>
<th>Zurich BDL S/N</th>
<th>Basel BDL S/N</th>
<th>Payené BDL S/N</th>
<th>Magadino BDL S/N</th>
<th>% of S/N</th>
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</thead>
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<td>0% 12.0</td>
<td>0% 12.1</td>
<td>0% 14.3</td>
<td></td>
</tr>
<tr>
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<td>0% 19.9</td>
<td>0% 19.9</td>
<td>0% 19.9</td>
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<td>1% 8.3</td>
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<td>0% 23.8</td>
<td>0% 23.2</td>
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<td></td>
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<tr>
<td>Na⁺</td>
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<td>NH₄⁺</td>
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<td>0% 18.2</td>
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</tr>
<tr>
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<td>33% 1.7</td>
<td>24% 1.8</td>
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<tr>
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<td>0% 7.6</td>
<td>1% 5.6</td>
<td>6% 4.8</td>
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<tr>
<td>As</td>
<td>9% 1.8</td>
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<td>26% 1.7</td>
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<tr>
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</table>
**Table A.2:** Summary of fraction of data below the limit of detection (BDL) and of signal to noise ratio (S/N) for 1998/1999. (BDL>50% and S/N<1.0 are given in bold).

<table>
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<th>Species</th>
<th>Bern BDL</th>
<th>Bern S/N</th>
<th>Zurich BDL</th>
<th>Zurich S/N</th>
<th>Basel BDL</th>
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</thead>
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<td>1%</td>
<td>8.2</td>
<td>1%</td>
<td>7.7</td>
</tr>
<tr>
<td>Cl⁻</td>
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<td>62%</td>
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</tr>
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<td>3.5</td>
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<td>17%</td>
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<td>13%</td>
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<td>7%</td>
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<td>4.3</td>
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<td>0%</td>
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</tr>
<tr>
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<td>9%</td>
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</tr>
<tr>
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</tr>
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<td>12%</td>
<td>3.9</td>
</tr>
<tr>
<td>Sb</td>
<td>0%</td>
<td>5.7</td>
<td>3%</td>
<td>4.1</td>
<td>11%</td>
<td>2.8</td>
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<tr>
<td>Ba</td>
<td>0%</td>
<td>4.7</td>
<td>45%</td>
<td>1.5</td>
<td>81%</td>
<td>0.6</td>
</tr>
<tr>
<td>La</td>
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<td>1.9</td>
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<td>1.8</td>
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<td>Ce</td>
<td>0%</td>
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<td>29%</td>
<td>1.7</td>
<td>34%</td>
<td>1.7</td>
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<tr>
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<td>0%</td>
<td>3.9</td>
<td>14%</td>
<td>2.3</td>
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<td>Tl</td>
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<td>16.4</td>
</tr>
<tr>
<td>Pb</td>
<td>0%</td>
<td>16.6</td>
<td>0%</td>
<td>13.1</td>
<td>0%</td>
<td>12.8</td>
</tr>
</tbody>
</table>
A.2 Source profiles and source contributions for the 2008/2009 datasets

The chemical profiles of the PM10 sources and components identified at the four sites in the 2008/2009 period are given in Figure A.1, A.3, A.5, A.7 and A.9. Figures A.2, A.4, A.6, A.8 and A.10 show the contributions of the modelled PM10 sources and components.

Figure A.1: PM10 source profiles (solid bars, left y-axis) and explained variation (blue squares, right y-axis) at the urban roadside site BER for the 2008/2009 dataset.
Figure A.2: PM10 source contributions at the urban roadside site BER for the 2008/2009 dataset.
Figure A.3: PM10 source profiles (solid bars, left y-axis) and explained variation (blue squares, right y-axis) at the urban background site ZUE for the 2008/2009 dataset.
Figure A.4: PM10 source contributions at the urban background site ZUE for the 2008/2009 dataset.
## Appendix A. Comparative Source Apportionment of PM10 (supplement)

| OC | EC | NO$_3^-$ | SO$_4^{2-}$ | Na$^+$ | NH$_4^+$ | K$^+$ | Mg$^{2+}$ | Ca$^{2+}$ | Al | Ti | V | Cr | Mn | Fe | Cu | Zn | Ga | As | Rb | Sr | Y | Mo | Cd | Sb | Ba | La | Ce | Nd | Pb |
|----|----|----------|-------------|--------|---------|-------|---------|---------|----|----|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|

### Nitrate–rich secondary aerosol

### Sulphate–rich secondary aerosol

### Mineral dust

### Wood combustion

### Sodium–magnesium–rich aerosol

### Road traffic

<table>
<thead>
<tr>
<th>Concentration [µg/µg]</th>
<th>Explained variation</th>
</tr>
</thead>
</table>

**Figure A.5:** PM10 source profiles (solid bars, left y-axis) and explained variation (blue squares, right y-axis) at the suburban site BAS for the 2008/2009 dataset.
A.2. Source profiles and source contributions for the 2008/2009 datasets

Figure A.6: PM10 source contributions at the suburban site BAS for the 2008/2009 dataset.
Figure A.7: PM10 source profiles (solid bars, left y-axis) and explained variation (blue squares, right y-axis) at the rural site north of the Alps PAY for the 2008/2009 dataset.
Figure A.8: PM10 source contributions at the rural site north of the Alps PAY for the 2008/2009 dataset.
Figure A.9: PM10 source profiles (solid bars, left y-axis) and explained variation (blue squares, right y-axis) at the rural site south of the Alps MAG for the 2008/2009 dataset.
Figure A.10: PM10 source contributions at the rural site south of the Alps MAG for the 2008/2009 dataset.
A.3 Backward air parcel trajectories

Back-trajecotry analysis support the hypothesis that the high concentrations of mineral dust observed at 15 October 2008 in Switzerland are due to the transport of dust from the Sahara region (Figure A.11).

Figure A.11: Backward air parcel trajectories based on analyses of the COSMO-7 numerical weather forecast model of MeteoSwiss for the 15. October 2008 - 00 UTC. These trajectories support the hypothesis that the high mineral dust contribution modelled on this day were related to a Sahara dust transport event.
Similarly to what observed at 15 October 2008, back-trajectory analysis suggests that the high contributions of the Na-Mg factors observed at 16 March 2009 are caused by long-range transport of sea spray aerosol particles (Figure A.12).

Figure A.12: Backward air parcel trajectories based on analyses of the COSMO-7 numerical weather forecast model of MeteoSwiss for the 16. March 2009 - 12 UTC. Air masses come from north Atlantic.
A.4 Source profiles and source contributions for the 1998/1999 datasets

The chemical profiles of the PM10 sources and components identified at the three sites in the 1998/1999 period are given in Figure A.13, A.15 and A.17. Figure A.14, A.16 and A.18 show the contributions of the modelled PM10 sources and components.

Figure A.13: PM10 source profiles (solid bars, left y-axis) and explained variation (blue squares, right y-axis) at the urban roadside site BER for the 1998/1999 dataset.
Figure A.14: PM10 source contributions at the urban roadside site BER for the 1998/1999 dataset. Represented is the period 1 April 1998 - 31 March 1999.
Figure A.15: PM10 source profiles (solid bars, left y-axis) and explained variation (blue squares, right y-axis) at the urban background site ZUE for the 1998/1999 dataset.
Figure A.16: PM10 source contributions at the urban background site ZUE for the 1998/1999 dataset. Represented is the period 1 April 1998 - 31 March 1999.
Figure A.17: PM10 source profiles (solid bars, left y-axis) and explained variation (blue squares, right y-axis) at the suburban site BAS for the 1998/1999 dataset.
Figure A.18: PM10 source contributions at the suburban site BAS for the 1998/1999 dataset. Represented is the period 1 April 1998 - 31 March 1999.
A.5 Relative contribution of PMF factors to selected chemical species

Figure A.19: Relative contribution of PMF factors to selected chemical species at the suburban (BAS, left panels) and the urban roadside site (BER, right panels): apportionment of the chemical species for the 2008/2009 period (top), for the 1998/1999 period (down).
A.6 Scatter plot of wood combustion contributions to PM10 and measured $K^+$

Figure A.20 show the scatter plot of wood combustion contributions to PM10 as quantified by PMF and measured $K^+$ concentrations in PM10. Note that at the rural site south of the Alps the slope of the regression line is much higher than at the sites north of the Alps.

---

Figure A.20: Scatter plot of wood combustion contributions to PM10 as quantified by PMF and measured $K^+$ concentrations in PM10. All plots include regression lines (red lines) and equations of the regression lines.
Appendix B

Supplement to ”Source Apportionment of PM10, Organic Carbon and Elemental Carbon at Swiss Sites: An Intercomparison of Different Approaches” - Chapter 5

The content of the following appendix is adopted from the supplementary material of:

Matthias F.D. Gianini\textsuperscript{1}, Christine Piot\textsuperscript{2,3}, Hanna Herich\textsuperscript{1}, Jean-Luc Besombes\textsuperscript{2}, Jean-Luc Jaffrezo\textsuperscript{3}, Christoph Hueglin\textsuperscript{1}: Source Apportionment of PM10, Organic Carbon and Elemental Carbon at Swiss Sites: An Intercomparison of Different Approaches. Accepted for a publication in Science of the Total Environment.

\textsuperscript{1}Air Pollution/Environmental Technology Laboratory, Empa, Duebendorf, Switzerland
\textsuperscript{2}LCME, Université de Savoie, Le Bourget du lac, France
\textsuperscript{3}CNRS-LGGE-UMR, Université Joseph Fourier, Grenoble, France
Table B.1: Mean concentrations (ng/m$^3$) of organic markers in PM10.

<table>
<thead>
<tr>
<th>Organic marker</th>
<th>BER</th>
<th>ZUE</th>
<th>PAY</th>
<th>MAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mannosan</td>
<td>21.3</td>
<td>16.0</td>
<td>10.2</td>
<td>40.6</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>161.5</td>
<td>122.4</td>
<td>89.9</td>
<td>471.5</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>1.11</td>
<td>0.50</td>
<td>0.37</td>
<td>1.76</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>0.61</td>
<td>0.34</td>
<td>0.20</td>
<td>0.74</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>0.52</td>
<td>0.33</td>
<td>0.26</td>
<td>0.67</td>
</tr>
<tr>
<td>n-heptacosane (C27)</td>
<td>5.17</td>
<td>3.80</td>
<td>3.90</td>
<td>4.18</td>
</tr>
<tr>
<td>n-octacosane (C28)</td>
<td>2.16</td>
<td>1.39</td>
<td>1.82</td>
<td>0.90</td>
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<tr>
<td>n-nonacosane (C29)</td>
<td>6.35</td>
<td>4.05</td>
<td>5.19</td>
<td>4.21</td>
</tr>
<tr>
<td>n-triacontane (C30)</td>
<td>1.80</td>
<td>1.07</td>
<td>1.09</td>
<td>1.16</td>
</tr>
<tr>
<td>n-hentriacontane (C31)</td>
<td>7.90</td>
<td>4.10</td>
<td>3.32</td>
<td>2.43</td>
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<tr>
<td>17α(H),21β(H)-Norhopane</td>
<td>0.41</td>
<td>0.12</td>
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<td>0.06</td>
</tr>
<tr>
<td>17α(H),21β(H)-Hopane</td>
<td>0.46</td>
<td>0.12</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>17α(H),21β(H)-22S-Homohopane</td>
<td>0.24</td>
<td>0.06</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table B.2: Mean source contributions ($\mu$m/m$^3$) and relative contributions (%) to OC as determined by PMF and CMB. Source categories are: wood combustion (WC), vehicular emissions (VE), secondary organic carbon (SOC), and other primary sources (other PS), see Table 5.1 for definitions. Note that average contributions are calculated only from days where results from both source apportionment approaches were available.

<table>
<thead>
<tr>
<th>Site</th>
<th>Model</th>
<th>WC $\mu$m/m$^3$</th>
<th>VE $\mu$m/m$^3$</th>
<th>other PS $\mu$m/m$^3$</th>
<th>SOC $\mu$m/m$^3$</th>
<th>Measured $\mu$m/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PMF</td>
<td>1.7</td>
<td>1.8</td>
<td>0.1</td>
<td>1.9</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td>1.4</td>
<td>1.7</td>
<td>0.6</td>
<td>2.0</td>
<td>5.7</td>
</tr>
<tr>
<td>BER</td>
<td>PMF</td>
<td>1.1</td>
<td>1.0</td>
<td>0.4</td>
<td>1.5</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td>0.9</td>
<td>0.6</td>
<td>0.3</td>
<td>2.1</td>
<td>4.0</td>
</tr>
<tr>
<td>ZUE</td>
<td>PMF</td>
<td>0.7</td>
<td>1.0</td>
<td>0.3</td>
<td>1.0</td>
<td>3.1</td>
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<td>0.6</td>
<td>1.8</td>
<td>3.1</td>
</tr>
<tr>
<td>PAY</td>
<td>PMF</td>
<td>3.2</td>
<td>1.4</td>
<td>0.3</td>
<td>1.2</td>
<td>6.1</td>
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<tr>
<td></td>
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<td>5.0</td>
<td>0.3</td>
<td>0.2</td>
<td>2.2</td>
<td>6.1</td>
</tr>
<tr>
<td>MAG</td>
<td>PMF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
Table B.3: Mean source contributions (µm/m³) and relative contributions (%) to EC as determined by PMF, AeM and CMB. Note that average contributions are calculated only from days where results from all source apportionment approaches were available.

<table>
<thead>
<tr>
<th>Site</th>
<th>Model</th>
<th>Wood combustion</th>
<th>Vehicular emissions</th>
<th>Measured</th>
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<tr>
<td>ZUE</td>
<td>PMF</td>
<td>0.11 12%</td>
<td>0.57 60%</td>
<td>0.95</td>
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<tr>
<td></td>
<td>AeM</td>
<td>0.12 12%</td>
<td>0.81 85%</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td>0.01 1%</td>
<td>0.98 103%</td>
<td>0.95</td>
</tr>
<tr>
<td>PAY</td>
<td>PMF</td>
<td>0.13 22%</td>
<td>0.33 58%</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>AeM</td>
<td>0.12 20%</td>
<td>0.46 81%</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td>0.02 4%</td>
<td>0.44 77%</td>
<td>0.57</td>
</tr>
<tr>
<td>MAG</td>
<td>PMF</td>
<td>0.66 42%</td>
<td>0.80 52%</td>
<td>1.55</td>
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<tr>
<td></td>
<td>AeM</td>
<td>0.30 19%</td>
<td>1.08 69%</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td>0.15 10%</td>
<td>0.49 31%</td>
<td>1.55</td>
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</table>
### Table B.4: Mean source contributions (µm$^2$/m$^3$) and relative contributions (%) to PM10 as determined by PMF and CMB/monotracer approach.

<table>
<thead>
<tr>
<th>Site</th>
<th>Model</th>
<th>WC</th>
<th>VE</th>
<th>MD</th>
<th>Na-Mg</th>
<th>SA</th>
<th>other PS</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>BER</td>
<td>PMF</td>
<td>8.3%</td>
<td>38%</td>
<td>6.0%</td>
<td>42%</td>
<td>7.7%</td>
<td>5.7%</td>
<td>3.3%</td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td>8.9%</td>
<td>38%</td>
<td>6.0%</td>
<td>42%</td>
<td>7.7%</td>
<td>5.7%</td>
<td>3.3%</td>
</tr>
<tr>
<td>ZUE</td>
<td>PMF</td>
<td>3.8%</td>
<td>18%</td>
<td>0.6%</td>
<td>9%</td>
<td>1.3%</td>
<td>7%</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td>3.9%</td>
<td>18%</td>
<td>0.6%</td>
<td>9%</td>
<td>1.3%</td>
<td>7%</td>
<td>2%</td>
</tr>
<tr>
<td>PAY</td>
<td>PMF</td>
<td>2.1%</td>
<td>13%</td>
<td>0.2%</td>
<td>5%</td>
<td>1.1%</td>
<td>8%</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td>2.1%</td>
<td>13%</td>
<td>0.2%</td>
<td>5%</td>
<td>1.1%</td>
<td>8%</td>
<td>1%</td>
</tr>
<tr>
<td>MAG</td>
<td>PMF</td>
<td>1.2%</td>
<td>6%</td>
<td>0.4%</td>
<td>2%</td>
<td>7%</td>
<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>CMB</td>
<td>1.5%</td>
<td>6%</td>
<td>0.4%</td>
<td>2%</td>
<td>7%</td>
<td>1%</td>
<td>2%</td>
</tr>
</tbody>
</table>

Note: The concentrations in this table are different from those in (Gianini et al., 2012b). Reason: The average contributions are calculated only from days where results from both source apportionment approaches were available, for this secondary aerosol (SA) and other primary sources (other PS - BEER PMF: vehicle wear; CMB: natural gas combustion and vegetation detritus). Source categories are: wood combustion (WC); vehicular emissions (VE); marine dust (MD); Na-Mg-rich PM; road salt/SOS salt (Na-Mg).
Bibliography


BIBLIOGRAPHY


Curriculum vitae

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PUBLICATIONS
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