Doctoral Thesis

Investigation of the chemical composition and sources of PM2.5 and relevant trace gases at multiple urban sites using mobile and stationary measurements

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Investigation of the chemical composition and sources of PM$_{2.5}$ and relevant trace gases at multiple urban sites using mobile and stationary measurements

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

(Dr. sc. ETH Zurich)

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Summary

Atmospheric aerosols comprise particles with a wide variety of sizes, chemical composition and physical properties. Such particles affect the Earth’s climate by scattering and absorbing sunlight, and modifying cloud characteristics. Moreover, exposure to PM$_{2.5}$ has been linked to 3.15 million premature deaths worldwide in 2010. Due to higher population density and increased emissions, the negative health effects of aerosols are enhanced in urban areas, especially in newly industrialized countries like China and India. In order to develop effective strategies for the prevention, control and abatement of particulate pollution, the major emission sources and processes leading to aerosol formation in the atmosphere need to be identified and characterized.

The major aerosol components in urban areas include organic aerosol (OA), inorganic aerosol (IA) and black carbon (BC). Aside from direct emissions of particles from anthropogenic and natural sources (primary emissions), aerosol is also formed in the atmosphere via gas to particle conversion processes (secondary formation). BC is a primary product of incomplete combustion processes, OA can originate from both primary emissions (e.g. combustion processes or biological emissions) and secondary aerosol formation (condensation of volatile organics), while most of the IA in the fine fraction have secondary origin (reaction and subsequent condensation of precursor gases, such as nitrogen oxides, sulfur dioxide, and ammonia). As secondary aerosol typically represent a large fraction of the PM$_{2.5}$ mass, a detailed knowledge of gaseous atmospheric chemistry and gas-particle interactions is also required to fully understand the formation and evolution processes of aerosol particles.

In this work, we studied the sources of air pollution in five cities with contrasted emissions: Xi’an (China), Beijing (China), Tartu (Estonia), Tallinn (Estonia), and Zurich (Switzerland). An aerosol mass spectrometer (AMS) was deployed to measure the chemical composition of the non-refractory aerosol (including OA and IA), and an Aethalometer was used to determine the equivalent black carbon (eBC) concentrations. The AMS was equipped with a newly-developed lens which extends the measured aerosol size to the full PM$_{2.5}$ fraction. Some of the most important gas-phase pollutants, including carbon dioxide (CO$_2$), carbon monoxide (CO), methane (CH$_4$) and ammonia (NH$_3$), were also measured during the mobile measurements in Estonia and Switzerland. A new measurement set-up was developed to decrease the adsorption of NH$_3$ on the inlet lines and reduce the associated measurement delay, which was required for the identification of point sources with the mobile laboratory. Moreover, a deconvolution algorithm was applied to correct for the remaining time-delays. Improved source apportionment approaches were applied to identify and characterize the major sources of organic aerosols (positive matrix factorization and multilinear engine) and of black carbon (aethalometer model). The use of the mobile laboratory in Estonia and Switzerland allowed for the identification of particular source areas within the cities. Moreover, the inclusion of background locations in the measurement route in Tartu permitted the determination of regional background concentrations and urban increments of the individual compounds and their sources in this city.
Extremely high concentrations of PM$_{2.5}$ were recorded during severe haze events in Xi’an (537 µg m$^{-3}$, on average) and Beijing (243 µg m$^{-3}$, on average). The extreme haze events were caused by a combination of primary emissions of OA (strongest contribution from wood burning in Xi’an and coal combustion in Beijing) and generation of secondary aerosol (i.e. ammonium nitrate, ammonium sulfate and oxygenated organic aerosol) during stagnant meteorological conditions. Much lower concentrations were recorded during the mobile measurements in Tartu (9.1 µg m$^{-3}$, on average), Tallinn (15.6 µg m$^{-3}$, on average) and Zurich (17.8 µg m$^{-3}$, on average). OA was found to be the major PM$_{2.5}$ component in these three European cities, dominated by primary emissions from traffic, wood burning and residential emissions during day-time, and by oxygenated organic aerosols during night-time. The analysis of the spatial distributions showed that the primary OA sources are strongly enhanced in particular areas of the cities, while the secondary components are homogeneously distributed over the measurement areas. In Tartu, the PM$_{2.5}$ showed an average increment in the city of 6.0 µg m$^{-3}$ over an average regional background concentration of 4.0 µg m$^{-3}$. This urban increment was strongly related to enhanced traffic emissions within the city. Traffic was also found to be the dominant source of NH$_3$ in urban areas (in terms of increases over the regional background concentrations). The mobile measurements (including also tunnel measurements in Zurich), allowed for the determination of traffic emission factors (EF) of the various related pollutants (including NH$_3$, eBC and HOA) for Tartu, Tallinn and Zurich. The estimated EFs showed a high variability (characteristic for real world EFs), but clearly higher EFs were obtained for the two Estonian cities (especially for eBC and HOA in Tartu) compared to Zurich. Such differences were attributed to the older vehicle fleet in Estonia.
Il particolato atmosferico è costituito da particelle di varie dimensioni, composizione chimica e proprietà fisiche. Tali particelle hanno un impatto sul clima, sia attraverso la dispersione e l’assorbimento della luce solare, sia influenzando le caratteristiche delle nuvole. Inoltre, l’esposizione al PM$_{2.5}$ è stata collegata a 3.15 milioni di morti premature in tutto il mondo nel 2010. A causa della maggiore densità di popolazione e delle incrementate emissioni, gli effetti negativi dell’aerosol sulla salute umana sono più rilevanti in aree urbane, soprattutto in paesi di recente industrializzazione come Cina e India. Al fine di sviluppare strategie efficaci per la prevenzione, il controllo e la riduzione dell’inquinamento da particolato, le principali sorgenti di emissione e i processi che portano alla formazione di aerosol secondario devono essere identificati e ben caratterizzati.

I principali costituenti dell’aerosol in aree urbane sono l’aerosol organico (OA), l’aerosol inorganico (IA) e il black carbon (BC). In aggiunta alle emissioni dirette di particelle provenienti da sorgenti antropiche e naturali (emissioni primarie), l’aerosol può anche essere formato in atmosfera tramite processi di conversione gas-particella (aerosol secondario). Il BC è un prodotto primario dei processi di combustione incompleta mentre l’OA può derivare da emissioni primarie (e.g. processi di combustione o emissioni biologiche) o dalla formazione di aerosol secondario (condensazione di composti organici volatili). La maggior parte dell’IA nella frazione fine ha invece origine secondaria (reazione di gas precursori come gli ossidi di azoto, il biossido di zolfo e l’ammoniaca e successiva condensazione). Siccome l’aerosol secondario tipicamente rappresenta una significativa frazione della massa di PM$_{2.5}$, è necessaria un’approfondita conoscenza della chimica atmosferica dei gas e delle interazioni gas-particella per la completa comprensione dei processi di formazione ed evoluzione dell’ aerosol.

Questo lavoro è incentrato sullo studio delle sorgenti d’inquinamento dell’aria in cinque città con emissioni variabili: Xi’an (Cina), Pechino (Cina), Tartu (Estonia), Tallinn (Estonia) e Zurigo (Svizzera). Un aerosol mass spectrometer (AMS) è stato utilizzato per discriminare la composizione chimica dell’aerosol non refrattario (compresi OA e IA), e un Aethalometer è stato utilizzato per determinare le concentrazioni di black carbon equivalente (eBC). L’AMS è stato implementato con una lente di recente sviluppo che ampie il range dimensionale misurato alla frazione PM$_{2.5}$. Alcuni dei gas inquinanti più rilevanti, tra cui il biossido di carbonio (CO$_2$), il monossido di carbonio (CO), il metano (CH$_4$) e l’ammoniaca (NH$_3$), sono stati inoltre misurati nelle misure con il laboratorio mobile in Estonia e in Svizzera. Un nuovo settaggio è stato sviluppato per ridurre l’adsorbimento di NH$_3$ sulle superfici dell’inlet dello strumento al fine di ridurre l’associato ritardo nella misurazione, requisito necessario per l’identificazione di sorgenti puntiformi con il laboratorio mobile. Ulteriormente, un algoritmo di deconvoluzione è stato applicato per correggere il ritardo rimanente. Perfezionate tecniche di source apportionment sono state applicate per identificare e caratterizzare le principali sorgenti di aerosol organico (positive matrix factorization e multilinear engine) e black carbon (l’Aethalometer model). L’uso del laboratorio mobile in Estonia e Svizzera ha reso possibile l’individuazione di aree di sorgenti all’interno delle città. L’inserimento di siti di background nel
percorsì di misura in Tartu ha permesso la determinazione delle concentrazioni regionali di fondo e la misura degli incrementi dei singoli composti e le loro sorgenti in questa città.

Concentrazioni particolarmente alte di PM$_{2.5}$ sono state registrate durante gli episodi di extreme haze a Xi’an (537 µg m$^{-3}$, in media) e Pechino (243 µg m$^{-3}$, in media). Gli eventi di extreme haze sono stati causati dalla combinazione di emissioni primarie di OA (provenienti principalmente dalla combustione di biomassa a Xi’an e dalla combustione di carbone a Pechino) e la generazione di aerosol secondario (nitrato di ammonio, solfato di ammonio e aerosol organico ossigenato) durante una condizione meteorologica stagnante. Concentrazioni notevolmente inferiori sono state registrate durante le misurazioni mobili a Tartu (9.1 µg m$^{-3}$, in media), Tallinn (15.6 µg m$^{-3}$, in media) e Zurigo (17.8 µg m$^{-3}$, in media). In queste tre città europee, l’OA rappresenta il principale componente del PM$_{2.5}$ ed è dominato dalle emissioni primarie del traffico, della combustione di biomassa e di altre emissioni residenziali durante il giorno e dall’aerosol organico ossidato durante la notte. L’analisi delle distribuzioni spaziali ha dimostrato che le sorgenti di OA primarie sono intensificate in certe aree delle città, mentre le componenti secondarie sono omogeneamente distribuite sulle aree di misurazione. In Tartu, il PM$_{2.5}$ mostra un incremento medio nella città di 6.0 µg m$^{-3}$ su una concentrazione regionale di fondo media di 4.0 µg m$^{-3}$. Questo incremento urbano è strettamente correlato all’incremento delle emissioni da traffico all’interno della città. Il traffico è anche stato la principale fonte di NH$_3$ nelle aree urbane (in termini di aumenti oltre le concentrazioni regionali di fondo). Le misurazioni mobili (includendo anche misurazioni all’interno di sottopassi a Zurigo), hanno permesso di determinare fattori di emissione (EF) dei vari inquinanti legati al traffico (NH$_3$, eBC e HOA) per Tartu, Tallinn e Zurigo. Gli EFs stimati mostrano un’elevata variabilità (caratteristica degli EFs del mondo reale), ma EFs chiaramente più alti sono risultati per le due città estoni (in particolare per eBC e HOA a Tartu) rispetto a Zurigo. Tali differenze sono state attribuite a un parco auto più vecchio in Estonia rispetto alla Svizzera.
1.1 Atmospheric aerosols

1.1.1 Definition and main physical properties

Atmospheric aerosols (or particulate matter, PM) are liquid or solid particles suspended in the air (Baron and Willeke, 2001). Aerosol particles are ubiquitous and vary greatly in composition, size and shape depending on their origin and the atmospheric processing. On a global scale, the dominant fraction of aerosols is of natural origin, including dust, sea salt, and emissions from wild fires, volcanic eruptions and plants. However, anthropogenic aerosols, arising primarily from combustion processes (e.g. traffic or biomass burning), can dominate in highly populated and industrialized areas. According to their formation processes, atmospheric aerosols can be further classified as primary or secondary aerosols. Primary aerosols are directly emitted in the atmosphere in particle-phase, while secondary aerosols are formed in the atmosphere by gas-to-particle conversion processes, such as nucleation, condensation of gas phase precursors and heterogeneous chemical reactions (Finlayson-Pitts and Pitts, 2000). Aerosol particles can then grow by condensation of gaseous species on the surface of preexisting particles and by particle coagulation to sizes where they are large enough to act as cloud condensation nuclei. The main removal processes for aerosols are wet deposition (rainout and washout) and dry deposition (sedimentation).

A typical size distribution resulting from these processes is shown in Fig. 1.1. The diameters of atmospheric aerosols range over about four orders of magnitude, from a few nanometers and up to about 100 micrometers. Several modes can be distinguished:

- **Nuclei and Aitken modes:** Although some previous works have combined them (e.g. Whitby et al., 1978), two modes can be distinguished below 0.1 µm: the nuclei mode (or
ultrafine particles) and the Aitken mode. The nuclei mode is formed by particles smaller than 0.01 µm that originate from gas-to-particle conversion processes, while the Aitken mode comprises particles in the size range 0.01 to 0.1 µm that can be formed by gas-to-particle conversion as well as by condensation of hot vapors on primary particles during combustion processes (e.g. from traffic). The nuclei and Aitken mode often account for the majority of particles by number, but due to their small size these particles represent only a few percent of the total aerosol mass. Particles in this mode rapidly grow by coagulation into the accumulation mode.

- **Accumulation mode**: Particles with diameters between 0.1 and 2.5 µm, resulting from primary emissions or from the growth of smaller particles by coagulation and condensation processes. Sometimes two peaks are observed in the accumulation mode, as shown by the dashed lines. The accumulation mode accounts for most of the aerosol surface area and a large fraction of the aerosol mass. As particle removal mechanisms are least efficient in this regime (i.e. the particles are too small to sediment at significant rates), particles tend to accumulate in this size fraction and are removed from the atmosphere mainly by scavenging by cloud droplets and subsequent rainout or washout. The nuclei and accumulation modes are commonly grouped in the “fine mode”, which includes all particles with diameter below 2.5 µm (PM\(_{2.5}\)). Note that a size cut-off of 1 µm (PM\(_{1}\)) is often also applied depending on the measurement technique (e.g. in aerosol mass spectrometry).

- **Coarse mode**: Particles with a diameter greater than 2.5 µm, produced mainly from mechanical processes including particles from natural sources (e.g. dust, sea salt, volcanic emissions, biological particles…) and anthropogenic sources (e.g. resuspension of dust, break wear…). Due to their high mass, these particles are removed by sedimentation in rather short time.

### 1.1.2 Chemical composition and sources of atmospheric aerosols

The chemical composition of atmospheric aerosols is highly variable in space and time and strongly depends on the emission sources (local and regional), as well as temperature and meteorological conditions. As an example, Fig. 1.2 illustrates the variability in the mass concentration and chemical composition of the PM\(_{2.5}\) fraction in 14 European sites classified in terms of the distance to large pollution source as natural, rural, near-city, urban or kerbside (Putaud et al., 2004). A clear increasing trend is observed for the aerosol average mass concentration with the proximity to the emission sources. In terms of relative contributions, the major fractions in the PM\(_{2.5}\) are the inorganic aerosol (including non-sea salt sulfate (nssSO\(_{4}^{2-}\)), nitrate (NO\(_{3}^{-}\)), ammonium (NH\(_{4}^{+}\))), the organic aerosol (OA, or organic matter (OM)) and black carbon (BC). Mineral dust and sea salt, which are dominant fractions in the coarse particles, contribute only with a few percent to the fine aerosol. The unaccounted fraction (i.e. the difference between quantified and gravimetrically determined mass) contains different species for the various locations, including water and other compounds that are reported in the legend but were not measured at all sites. Uncertainties associated to the estimation of organic matter (OM = 1.4*OC) and mineral dust concentrations (directly determined, or estimated based on measurements of tracers such as Al or nss-Ca\(^{2+}\)) may affect the
unaccounted mass. BC (from incomplete combustion processes), mineral dust and sea salt are emitted as primary particles to the atmosphere, the inorganic species (besides sea salt) are mostly formed in the atmosphere by secondary aerosol formation processes, while OM can be both primary as well as secondary and will be discussed in detail in Sect. 1.1.2.1. The influence from anthropogenic sources within the cities is reflected by increased BC, OM and nitrate contributions, whereas the fractional contribution from sea salt is higher at remote sites. The nssSO₄ shows the largest relative contributions at the remote and rural locations, but the absolute concentrations do not present very large spatial variations, in agreement with the formation of sulfate from SO₂ oxidation at large scales.

Figure 1.1: Schematic of the distribution of particle surface area of atmospheric aerosols (Finlayson-Pitts and Pitts, 2000). Principal modes, sources and particle formation and removal processes are described.
Chapter 1 Introduction

1.1.2.1 Organic aerosol

The OA represents a complex mixture of thousands of individual compounds (Hamilton et al., 2004), which still remain mostly unknown. The identification and quantification of such compounds is of great importance for the study of the influence of the chemical composition on climate change and aerosol health effects.

The aerosol mass spectrometer (AMS) is a widely used instrument for the investigation of the chemical composition and the size of submicron particles (Canagaratna et al., 2007). A detailed description of the instrument is provided in Sect. 2.2.1. An overview of the PM$_1$ aerosol composition from AMS measurements in the Northern Hemisphere is shown in Fig. 1.3 (Jimenez et al., 2009). In most cases OA has the largest average contribution to the PM$_1$ aerosol mass (18 to 70 %; average 45 %), followed by SO$_4$ (10 to 67 %; average 32 %), NH$_4$ (6.9 to 19 %; average 13 %) and NO$_3$ (1.2 to 28 %; average 10 %) (Zhang et al., 2007). Indeed, NO$_3$ contributions exceed the NH$_4$ at sites where the contribution of SO4 is low (e.g. during winter).

The OA can be classified in primary organic aerosol (POA), which is directly emitted as particles into the atmosphere, and secondary organic aerosol (SOA), which is formed in the atmosphere through the oxidation and subsequent condensation of gaseous organic precursors. Recent studies have demonstrated the importance of other SOA formation pathways, including the aging of POA (i.e. evaporation, oxidation and recondensation of POA...
to create oxidized POA (OPOA) and of intermediate-volatility organic compounds (IVOCs) (Zhao et al., 2016 and references therein). Although the AMS mass spectrum represents the bulk properties of the non-refractory (NR)-OA, the application of source apportionment techniques (see Sect. 2.3) allows identifying and quantifying the major emission sources. Traffic (hydrocarbon-like OA, HOA) and biomass burning (BBOA) are commonly identified as POA sources in urban areas (Jimenez et al, 2009). Recent studies have also reported primary emissions from coal combustion (CCOA) (e.g. dall’Osto et al., 2013; Sun et al., 2013; Zhang et al., 2014) and cooking (COA) (e.g. Sun et al., 2011; Mohr et al., 2012; Crippa et al., 2013). In certain locations, a large fraction of the OA is oxygenated OA (OOA) related to SOA formation. In summertime, the OOA can often be separated into a semi-volatile and a low-volatility component (SV-OOA and LV-OOA, respectively) based on the degree of oxygenation.

1.1.2.2 Precursors of secondary aerosols: focus on NH$_3$

As shown in Fig. 1.3, at many locations a large portion of the aerosol is of secondary origin, i.e. it is formed in the atmosphere through chemical transformations of precursor gases. The major precursor gases include volatile organic compounds (VOCs), nitrogen oxides (NO$_x$), sulfur dioxide (SO$_2$) and ammonia (NH$_3$). Such compounds, which can be emitted from both natural and anthropogenic sources, react in the atmosphere to form SOA (from oxidation of VOCs) and secondary inorganic aerosol (via heterogeneous or homogeneous reactions of NO$_x$, SO$_2$ and NH$_3$). Therefore, a detailed knowledge of the gaseous precursors and their interactions with the aerosol particles is required to understand the aerosol formation and aging processes.

Atmospheric NH$_3$ has long been known to play a key role in atmospheric chemical processes. Its importance derives from the rapid reaction with sulfuric and nitric acids to form ammonium salts (mostly (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$ and NH$_4$NO$_3$), and from the enhanced nucleation rates (and therefore increased number of cloud condensation nuclei (CCN)) observed in the presence of NH$_3$ (Kirkby et al., 2011), among others. Current evaluations of global NH$_3$ emissions are characterized by a high degree of uncertainty, with estimates varying between 35 and 65 Tg N year$^{-1}$ (Bouwman et al., 1997; Sutton et al., 2013). Natural sources of NH$_3$ include emissions from oceans, biomass burning, plant decomposition and natural soils. Among the anthropogenic sources, agriculture represents the largest source of NH$_3$ around the globe, where livestock and the use of fertilizers are the agricultural processes with higher emissions. Additional anthropogenic sources of NH$_3$ are present in urban areas, including road traffic, industries, residential biomass burning, sewage and waste management among others. In the following we focus on the vehicular emissions of NH$_3$, due to the probable increase in these emissions in the near-future.
Vehicular emissions of NH$_3$ derive mostly from the use of the three-way catalyst (TWC) in gasoline light duty vehicles (LDV). The TWC was introduced in the 1980s in the gasoline vehicles to convert CO and NO$_x$ into CO$_2$, N$_2$ and O$_2$ through chemical reactions that take place on a solid catalyst. However, some unwanted side reactions in the TWC might lead to the formation of molecular hydrogen (H$_2$) which can react with NO to form NH$_3$ (Suarez-Bertoa et al., 2015):

\begin{align*}
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \\
2\text{NO} + 2\text{CO} + 3\text{H}_2 & \rightarrow 2\text{NH}_3 + 2\text{CO}_2 \\
2\text{NO} + 5\text{H}_2 & \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}
\end{align*}

NH$_3$ vehicular emissions have also been linked to the more recent introduction of the selective catalytic reduction system (SCR) for the control of NO$_x$ emissions in heavy duty vehicles (HDV). The SCR system is based on the reduction of NO and NO$_2$ by NH$_3$ on a catalyst surface. The NH$_3$ is formed by the catalytic reaction of injected urea, and thus any over-doping of urea and/or catalyst degradation leads to undesired NH$_3$ emissions (Suarez-Bertoa et al., 2016). Thus, the NH$_3$ emission from road traffic strongly depends on the car fleet and the driving conditions, and can vary widely among different locations.
1.1.3 Major impacts of atmospheric aerosols

1.1.3.1 Climate effects

Atmospheric aerosols play a central role in the assessment and prediction of climate change. The effect of a certain compound on climate is usually described in terms of “radiative forcing” (RF). The term RF refers to the change in the earth's radiation balance of incoming and outgoing energy due to an imposed perturbation, with positive RF leading to a warming and negative RF to a cooling (Stocker et al., 2014).

The main effects of aerosols on irradiance changes are shown in Fig. 1.4. The aerosol-radiation interactions comprise the scattering and absorption of short-wavelength solar radiation by aerosol particles. Different aerosols scatter or absorb sunlight to varying degrees, depending on their physical properties (e.g. size, scattering albedo...). The aerosol-cloud interactions are related to the influence of aerosol particles on the cloud cover, reflectance and lifetime. High concentrations of aerosols particles that can act as cloud condensation nuclei (CCN) result in a larger amount of smaller droplets, leading to brighter clouds that scatter solar radiation back to the space more efficiently (“Twomey effect”). Moreover, the presence of smaller droplets with a longer lifetime inside the clouds prevents precipitation and thus the cloud lifetime is increased. Aside from these effects, rapid adjustments that come into play at shorter timescales are also considered in the effective radiative forcing values (ERF). These adjustments include all changes in clouds (cloud fraction, precipitation efficiency, lifetime, water content of clouds...) caused by the impact of the radiative heating on convective or larger-scale atmospheric circulations.

![Image of aerosol-radiation and aerosol-cloud interactions](Stocker et al., 2014)

Figure 1.4: Schematic of the aerosol-radiation and aerosol-cloud interactions (adapted from Stocker et al., 2014). The blue and the grey arrows symbolize solar radiation terrestrial radiation, respectively.

Figure 1.5 summarizes the RF estimated from the change between 1750 and 2011 by emitted components. The greenhouse gases (including CO₂, CH₄, N₂O and halo-carbons) show a clear net positive forcing (warming). Long-wavelength terrestrial radiation is absorbed by these gases and can be partially radiated back. Due to the aerosol-radiation interactions, emissions from SO₂, organic carbon and ammonia cause a negative forcing, while emissions of
Chapter 1 Introduction

black carbon lead to positive forcing. Mineral dust, aerosol-cloud interactions and the rapid adjustments also have a negative RF. Aerosols have a net cooling effect, but the uncertainty in the aerosol radiative forcing is very high. Reducing these uncertainties is required in order to obtain more accurate climate predictions.

Figure 1.5: Radiative forcing (RF) to climate change by emitted components from 1750 to 2011. The horizontal bars indicate the overall uncertainty, while the vertical bars are for the individual components (vertical bar lengths proportional to the relative uncertainty, with a total length equal to the bar width for a ± 50% uncertainty) (Stocker et al., 2014).

1.1.3.2 Health effects

In addition to its climate impact, epidemiologic and laboratory exposure studies have shown that particulate air pollution adversely affect human health. However the impact of size and chemical composition of the particles on human health is not yet clearly established.

Particles can be deposited in different regions of the respiratory tract as presented Fig. 1.6. Due to their inertia, large particles (\(d_p > 1 \mu\text{m}\)) will mostly sediment or impact in the upper airways. At small diameters (\(d_p < 0.1 \mu\text{m}\)), the particles can penetrate deep into the lungs and deposit in the large lung surface area in the alveolar region due to Brownian diffusion. Particles smaller than some tens of nm have a very high diffusion coefficient and are therefore already removed by diffusion in the upper airway. The combination of these two deposition mechanisms leads to a minimum in total deposition probability for particles with diameter in the range 0.1 to 1 \(\mu\text{m}\) (Maynard and Kuempel, 2005).
1.1 Atmospheric aerosols

Figure 1.6: Modeled total particle deposition probability in the human respiratory tract, and deposition probability in the alveolar region (Maynard and Kuempel, 2005).

Long-term exposure to moderate PM concentrations have been associated with increased mortality and increased risk of cardiopulmonary diseases and lung cancer (e.g. Dockery et al., 1993; Pope and Dockery, 2006; Brook et al., 2008; Beelen et al., 2014). Furthermore, a linear relationship has been observed between chronic exposure to PM$_{2.5}$ concentrations and mortality, also at concentrations as low as 8 $\mu$g m$^{-3}$ (Laden et al., 2006). In the same work, an increase of 10 $\mu$g m$^{-3}$ in the PM$_{2.5}$ concentrations was associated with a 16% increase in mortality risk. A recent modelling study by Lelieveld et al. (2015) estimated 3.15 million deaths in 2010 related to outdoor air pollution (PM$_{2.5}$ and ozone). Figure 1.7 shows the geographic distribution of the mortality linked to air pollution. China (with 1.36 million deaths a year) and India (with 0.65 million deaths a year) show the highest premature mortality as a combination of a high per capita mortality and high population density.

Figure 1.7: Modeled mortality (deaths per area of 100 km$^2$) linked to outdoor pollution in 2010 (Lelieveld et al., 2015).
Due to the severe health effects related to particulate pollution, the world health organization (WHO) recommends exposure limits for PM$_{2.5}$ of 10 μg m$^{-3}$ annual mean (25 μg m$^{-3}$ 24-hour mean) and for PM$_{10}$ of 20 μg m$^{-3}$ annual mean (50 μg m$^{-3}$ 24-hour mean).

1.2 Motivation and thesis outline

Particulate matter is of special concern in urban areas, where a higher number of emission sources leads to enhanced pollution levels compared to the surrounding areas. Although anthropogenic aerosols account only for 2 to 3 % of the PM mass emitted globally in the atmosphere (Gieré and Querol, 2010), such emissions strongly influence human health in areas with a high population density. As the sources and processes governing the aerosol composition and concentration in a city are highly complex and inhomogeneous, their characterization and the assessment of their impact on human health require their knowledge on a small scale (e.g. street level, or city level). Furthermore, as a significant portion of aerosols is formed in the atmosphere through chemical transformations of gaseous precursors (nitrogen oxides, sulfur dioxide, volatile organics or ammonia) a detailed knowledge of gaseous atmospheric chemistry and gas-particle interactions is required to fully understand aerosol formation and their evolution processes.

The overall aim of this PhD project is a detailed characterization of the aerosol chemical composition and sources in urban areas. For this purpose mobile and stationary measurements were conducted in contrasted urban locations with different emission sources: Xi’an (China), Beijing (China), Tartu (Estonia), Tallinn (Estonia) and Zurich (Switzerland). The major particle and gas-phase pollutants were measured in wintertime for 1-3 weeks at each location using state-of-the-art techniques. The sources of organic aerosols were then identified and characterized using advanced source apportionment methods. The use of a mobile platform (in Estonia and Switzerland) allowed mapping the distributions of the measured compounds and their sources and determining their regional background concentrations and urban increments. The mobile measurements were also used to further characterize the traffic emissions in Tartu, Tallinn and Zurich and to determine NH$_3$, equivalent BC (eBC) and HOA traffic EFs for the three locations.

Unlike previous ambient measurements using the AMS where only particles with $d_{\text{aero}} < 1 \mu m$ could be measured, in this work we deployed a recently developed aerodynamic lens (Williams et al., 2013) that permits the transmission of larger particles for direct measurements of the NR-PM$_{2.5}$ fraction.

An accurate study of the major gas-phase precursors is required for a comprehensive understanding of the processes leading to secondary aerosol formation in the atmosphere. Ammonia is an important precursor for secondary inorganic aerosols (mostly ammonium nitrate and ammonium sulfate), but the characterization of ambient concentrations and sources of NH$_3$ in European urban areas remains uncertain. One of the major challenges in measuring NH$_3$ is the high response and recovery times caused by the adsorption of NH$_3$ on the walls of the inlet line. In this work we have characterized and deployed a heated inlet line with an auxiliary flow for a rapid measurement of NH$_3$. The use of the heated line helps...
reducing the adsorption of the NH$_3$ on the walls of the line, by increasing the adsorption and desorption rates, whereas the auxiliary flow decreases the residence time of the gas in the line. Moreover, the laboratory characterization of the system response time under different conditions was used to deconvolve the ambient NH$_3$ data in order to remove the remaining time delay and broadening of the peaks observed in the measured NH$_3$ signal.

Chapter 2 provides an overview of the methodologies applied in this study. It includes the description of the mobile laboratory set-up (Sect. 2.1), the instrumentation (Sect. 2.2), and the source apportionment techniques (Sect. 2.3).

Chapter 3 is dedicated to the characterization of the pollution sources in Xi’an and Beijing during extreme haze events (peak concentration above 1000 µg m$^{-3}$). An entire section in this chapter is dedicated to the interpretation and optimization of the source apportionment for an improved identification and quantification of OA sources. For each city, the results are discussed comparing the characteristics of the airborne particles during severe haze events (visibility below 2 km) and the reference periods (visibility above 2 km). Differences between the different periods and locations in terms of chemical composition, diurnal patterns, size distributions and sources of OA are discussed in detail. The effect of RH on the aqueous phase production of sulfate during the extreme haze events and the major sources of polycyclic aromatic hydrocarbons (PAHs, measured with the AMS) are also reported.

Chapter 4 is focused on the mobile measurements in Tartu and Tallinn (Estonia). This work presents the first detailed in-situ measurements of major air pollutants (including NR-PM$_{2.5}$, eBC, and trace gases) in the two biggest cities in Estonia. The sources of organic aerosols were investigated by means of positive matrix factorization. Furthermore, the highly time-resolved mobile measurements allowed for the identification of different source areas within the urban ranges and the determination of regional background concentrations as well as urban increments of the individual components from different sources.

Chapter 5 focuses on the study of NH$_3$. An entire section is dedicated to the optimization of the NH$_3$ sampling system, the characterization of the measurement set-up and the algorithm used for the deconvolution of the measured NH$_3$ signals. The mobile measurements in Tartu, Tallinn and Zurich are then combined to identify and quantify the major sources of ammonia in the urban areas. The mobile measurements in areas strongly affected by traffic emissions (including tunnel drives in Zurich) were used to estimate and compare the traffic emission factors in the three different locations.

Chapter 6 summarizes the major conclusions obtained from this study and the future perspectives in terms of methodology, future ambient measurements and application of the results presented in this thesis into air quality models.
2 Methodology

2.1 Instrumentation

Table 2.1 contains all deployed instruments, measured parameters and their time resolution for the three measurement campaigns presented in this work. A detailed description of the instrumentation follows below.

**Table 2.1**: Instruments list, measured compound and time resolution for the measurements in (1) China, (2) Estonia, and (3) Switzerland.

<table>
<thead>
<tr>
<th>(1) Stationary measurements in China: Xi’an (13.12.13-06.01.14) and Beijing (09.01.14-26.01.14)</th>
<th>Instruments</th>
<th>Measured components</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosols</td>
<td>HR-ToF-AMS</td>
<td>Size resolved chemical composition of NR-PM$_{2.5}$</td>
<td>1 min (25 sec V-mode, 25 sec W-mode, 10 sec switch)</td>
</tr>
<tr>
<td></td>
<td>Aethalometer</td>
<td>eBC</td>
<td>1 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(2) Mobile measurements in Estonia: Tartu (10.03.14-17.03.14) and Tallinn (25.03.14-01.04.14)</th>
<th>Instruments</th>
<th>Measured components</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosols</td>
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<tr>
<td></td>
<td>Aethalometer</td>
<td>eBC</td>
<td>1 sec</td>
</tr>
<tr>
<td>Gas</td>
<td>NH$_3$ (Picarro)</td>
<td>NH$_3$</td>
<td>3 sec</td>
</tr>
<tr>
<td></td>
<td>CO$_2$ (Licor)</td>
<td>CO$_2$, H$_2$O</td>
<td>1 sec</td>
</tr>
</tbody>
</table>
**2.1.1 Aerosol mass spectrometer**

**2.1.1.1 Measurement principle**

The high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) measures online size-resolved mass spectra of the NR aerosol species (DeCarlo et al., 2006). Briefly, aerosol particles are sampled through an aerodynamic lens and are focused into a narrow beam. The NR components (defined as those that flash vaporize at 600°C and ~10^7 Torr) are vaporized after impaction on a heated tungsten surface (600°C) and the resulting gas is ionized via electron impact (EI) and analyzed by a mass spectrometer. A schematic of the instrument is shown in Fig. 2.1a, where three main sections of the instrument can be distinguished:

- **Sampling chamber (PM$_{2.5}$ inlet):** Newly developed aerodynamic lens and inlet were used in this work in order to extend the measured fraction by the AMS to PM$_{2.5}$. The transmission efficiencies for the traditional PM$_1$ lens (Liu et al., 2007) and the new PM$_{2.5}$ lens (Williams et al., 2013) are shown in Fig. 2.1b. The standard aerodynamic lens of the AMS efficiently transmits particles between 90 nm and 700 nm in vacuum aerodynamic diameter ($d_{va}$). The transmission efficiency decreases to 30% at 1000 nm. In contrast, the PM$_{2.5}$ lens used here efficiently transmits particles between 80 nm and up to at least 3 µm. The new lens system comprises a critical orifice that sets the mass flow rate to about 1.4 cm$^3$ s$^{-1}$, a relaxation chamber to improve the transmission of large particles, and the aerodynamic lens which work with higher operating pressure than the traditional lens to improve the focusing of large particles. Additional details about the design and characterization of this system can be found in Williams et al. (2013).

- **Sizing chamber (ToF region):** When the particles exit the aerodynamic lens they reach the vacuum of the ToF region (maintained at ~ 10$^{-5}$ Torr). The size-dependence of the particle velocity in the sizing chamber allows for the determination of the particle $d_{va}$ by measuring the particle time-of-flight. Polystyrene latex size standards are used for the
velocity calibration (Jayne et al., 2000). The chopper wheel can alternately block and unblock the particle beam yielding the bulk particle mass spectra (MS mode) or modulate the beam (~150 Hz) yielding size-resolved spectra (PToF mode) (Drewnick et al., 2005).

- **Detection chamber (TOF mass spectrometer):** In the particle detection chamber (~10⁻⁷ Torr), the NR components are flash vaporized after impaction on a heated tungsten surface (600°C). Coupled to the vaporizer, a heated tungsten filament emits electrons at 70 eV that ionize the gas molecules. The ionized molecules are injected in the mass spectrometer region where they are selected in terms of their mass-to-charge ratio (m/z). Two operational modes can be set in the mass spectrometer, which are differentiated according to the ion flight path into V- and W-modes (De Carlo et al., 2006). The longer path that the ions follow in the W-mode compared to the V-mode results in a higher mass resolution but decreased measurement sensitivity. Thus, high concentrations are required to obtain good signal to noise ratios in the W-mode, which was therefore only used during the measurements in China.

![Figure 2.1: (a) Schematic of a high-resolution time-of-flight AMS (HR-ToF-AMS); (b) Lens transmission efficiencies for the PM₁ lens (Liu et al., 2007) and the PM₂.₅ lens (Williams et al., 2013).](image)

### 2.1.1.2 Mass quantification

AMS data were analyzed in Igor Pro 6.3 (WaveMetrics) using the SQUIRREL and PIKA analysis software. Ambient particles comprise thousands of individual chemical species that are measured simultaneously in the AMS. A major drawback of the AMS is the use of a high energy ionization method, which causes substantial fragmentation of the parent ions. Therefore, at each m/z the total signal is usually the sum of several particle-phase species. The contribution
of each chemical species at a given $m/z$ is calculated based on a fragmentation table (Allan et al., 2004; Canagaratna et al., 2007). This table is derived from empiric fragmentation patterns of pure test substances and the knowledge of isotopic ratios of the various atoms. The fragmentation table is adjusted manually in a way to rule out interferences from the air beam signal (i.e. from N$_2$, O$_2$, CO$_2$ and H$_2$O).

The mass concentration of aerosol chemical species ($C_s$) is quantified from the detected ion rate ($I_s$) as follows:

$$C_s = \frac{10^{12}MW_{NO_3}}{RIE_s I_{NO_3} Q N_A} \sum_{i=1}^{n} I_{s,i}$$

where $I_{s,i}$ is the detected ion rate for each $m/z$, $MW_{NO_3}$ the molecular weight of nitrate, $N_A$ Avogadro’s number, $Q$ the volumetric sample flow rate, $IE$ the ionization efficiency (number of ions detected per molecule of parent species, in the order of around $10^{-6}$) and $RIE_s$ the relative ionization efficiency of the species relative to nitrate.

Ammonium nitrate is used as calibration species because its IE, density and shape are well defined, it is well focused in the aerodynamic lens, it doesn’t bounce in the vaporizer and it vaporizes very efficiently. Assuming a linear relationship between the ionization efficiencies, the IE of all other species can be related to the one of nitrate using:

$$\frac{IE_s}{MW_s} = \frac{RIE_s}{MW_{NO_3}} I_{NO_3}$$

Calibrations with NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ were performed several times during each campaign and allowed for the determination of $I_{NO_3}$, $RIE_{NH_4}$ and $RIE_{SO_4}$, while standard values derived from laboratory studies were used for the $RIE_{OA}$ and $RIE_{Cl}$.

To account for the particle losses due to transmission efficiency through the lens ($CE_L$) and bouncing at the vaporizer ($CE_b$) a composition-dependent collection efficiency (CDCE) correction was applied (Middlebrook et al., 2012). In order to reduce uncertainties in the $CE_b$ and possible transmission losses of large particles at high (RH), the ambient particles were dried using a nafion drier (Perma Pure MD-110) before entering the AMS. By operating at a higher pressure and therefore higher particle velocity, the PM$_{2.5}$ aerodynamic lens could in principle enhance the particle bounce. However, the comparison between the measured PM$_{2.5}$ mass (NR species and eBC) with gravimetric measurements on filters collected during the measurements in China indicate that there is no important loss of mass in the AMS due to enhanced particle bounce.
2.1.2 Aethalometer

The Aethalometer (Magee Scientific) measures the concentration of the light absorbing carbonaceous aerosols (mainly black carbon) by measuring the attenuation (ATN) of a beam of light transmitted through a quartz fiber filter tape where the aerosols are continuously deposited. In the latest versions of Aethalometer the ATN is measured simultaneously at seven different wavelengths covering the ultra-violet to the near-infrared wavelength range (370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm and 950 nm), useful for studies of aerosol light absorption, atmospheric optics, radiative transfer, emissions testing and source apportionment.

The attenuation of the light through the filter can be described using Beer-Lambert’s law:

\[ I = I_0 e^{-b_{\text{abs}}x} \]  

(2.3)

where \( I_0 \) is the intensity of the incoming light, \( I \) the remaining intensity after passing the filter, \( b_{\text{abs}} \) is the absorption coefficient, and \( x \) the thickness of the filter. The ATN is calculated as the ratio of the signal intensity transmitted through a clean portion of the filter tape acting as a blank \( (I_0) \) and the aerosol-containing filter spot \( (I) \):

\[ \text{ATN} = \ln \frac{I_0}{I} \]  

(2.4)

The attenuation coefficient \( (b_{\text{ATN}}) \) is proportional to the change in ATN over the time (Hansen et al., 1984):

\[ b_{\text{ATN}} = \frac{A}{Q} \frac{\Delta \text{ATN}}{\Delta t} \]  

(2.5)

where \( A \) is the filter spot area, and \( Q \) the volumetric flow rate.

Like all filter based techniques that measure attenuation, the Aethalometer suffers from the absorption enhancement due to multiple scattering of the light by the filter substrate and by scattering from non-absorbing particles embedded in the filter. On the other hand, an increased presence of absorbing particles on the filter surface at higher filter loadings (shadowing effect) can result in apparent reduced optical path lengths through the filter, yielding an apparent reduction of the absorption. Therefore, the calibration factors \( C \) and \( R(\text{ATN}) \) are introduced to convert the aethalometer attenuation measurements \( (b_{\text{ATN}}) \) to real absorption coefficients \( (b_{\text{abs}}) \) (Weingartner et al., 2003):

\[ b_{\text{abs}} = \frac{b_{\text{ATN}}}{C \times R(\text{ATN})} \]  

(2.6)
In this work two Aethalometer models were deployed, the AE-31 and the AE-33, respectively. The AE-33 combines the measurements at two different spots of the tape filter where aerosols are collected in parallel at different loading rates for an online correction of the aforementioned artifacts (Drinovec et al., 2015), while the data of the AE-31 were manually corrected using the corrections described in Weingartner et al. (2003) and Sandradewi et al. (2008b). The eBC mass concentration can then be determined using specific mass absorption cross sections (MAC):

\[ BC = \frac{b_{abs}(\lambda)}{MAC(\lambda)} \]

MAC values provided by the manufacturer were used in this work (Drinovec et al., 2015).

### 2.1.3 NH₃ analyzer

The NH₃ analyzer deployed in this work (G1103-t; Picarro Inc.) is a real time, trace gas monitor that measures ammonia (NH₃) based on cavity ring-down spectroscopy (CRDS). The CRDS method measures the absorption of a pulse of light of a specific wavelength trapped in an optical cavity (i.e. two mirrors facing each other), to infer the concentration of the absorbing substance in the gas mixture in the cavity.

The intensity of the light within the cavity can be described as an exponential function of time:

\[ I = I_0 e^{-t/\tau} \]

The intensity of the trapped light will decrease by a fixed percentage at each round trip within the cell due to (1) reflectivity losses and (2) absorption and scattering by the medium within the cell. The decay constant, \( \tau \), represents the time needed for the light to drop to 1/e of the total initial intensity ("ring-down" time) and depends on the loss mechanisms within the cavity. The decay constant for an empty cavity, \( \tau_0 \), depends on mirror loss and various optical phenomena (e.g. scattering and refraction):

\[ \tau_0 = \frac{n}{c} \times \frac{l}{1 - R + X} \]

where \( n \) is the index of refraction within the cavity, \( c \) the speed of light in vacuum, \( l \) the cavity length, \( R \) the mirror reflectivity and \( X \) takes into account all other optical losses. The presence of absorbing species in the cavity will increase the losses according to the Beer-Lambert’s law (Eq. 2.3):

\[ \tau = \frac{n}{c} \times \frac{l}{1 - R + X + b_{abs} \times l} \]
The molar absorptivity, $\epsilon$, and analyte concentration, $C$, can be determined from the ratio of the two ring-down times. If $X$ can be neglected:

$$\frac{\tau_0}{\tau} = 1 + \frac{b_{abs} \times l}{1 - R} = 1 + \frac{2.303 \times \epsilon \times l \times C}{1 - R}$$  \hspace{1cm} (2.10)

The optical cavities of the Picarro instrument incorporate precise temperature and pressure control systems to ensure stable measurements over long time periods. Moreover a high-precision wavelength monitor maintains the spectral position ensuring accurate peak quantification and reducing the sensitivity to interfering species.

Instrument calibrations performed as a part of this work showed a linear and precise measurement of NH$_3$ levels in the range 0-300 ppb. The measurement time resolution is approximately 3 seconds, but the response and recovery times of the instrument depend on the range of operation. Moreover, since ammonia is a very sticky compound, the use of an inlet line further increases the response and recovery times. In order to reduce this effect, we deployed a heated inlet line (PTFE, $d_{out}$: 6mm, L: 1m, T: 110°C) with an auxiliary flow (~5 l min$^{-1}$). The use of such inlet system significantly reduced the measurement delay and allowed for the measure of point sources with the mobile laboratory. Moreover, a post-measurement correction of the data was performed in order to deconvolve the NH$_3$ signal and to correct for the remaining delay and peak broadening. All details about the measurement set-up and the NH$_3$ deconvolution are described in Sect. 5.3.

### 2.1.4 CO$_2$, CO and CH$_4$ analyzers

Two CO$_2$ analyzers were deployed in this work: a CO$_2$/H$_2$O differential analyzer (LI-7000, Li-cor Inc.) and a CRDS analyzer for CO$_2$/CO/CH$_4$/H$_2$O (G2401, Picarro Inc.).

In the LI-7000, a gas of known concentration (which can be zero, i.e. after passing a dedicated scrubber) is measured in a reference cell, and the unknown gas is measured in the sample cell. An infrared source provides radiation through both optical paths and its absorption is measured by CO$_2$ and H$_2$O detectors simultaneously. As the infrared absorption per mole CO$_2$ changes with total pressure and diluent gas composition, a water correction is performed to obtain accurate CO$_2$ concentrations. The instrument provides continuous concentrations in the sample cell as well as the differential concentration.

The Picarro G2401 Analyzers uses CRDS measurements to simultaneously measure CO$_2$, CO, CH$_4$ and H$_2$O and ambient levels. More details about this method can be found in Sect. 2.2.3. Also in this case the concentrations of all measured species are corrected by the presence of water to avoid interferences.
2.2 Mobile laboratory

The mobile measurements in Switzerland and Estonia were performed using the Paul Scherrer Institute (PSI) mobile platform, an IVECO 35S14V Daily van (length 6 m; width 2 m; height 3 m), equipped with a diesel particulate filter to reduce the danger of black carbon self-contamination during measurements (Mohr et al., 2011).

Figure 2.2 shows a schematic of the instrumental set-up in the mobile laboratory. The air is drawn through the main inlet, which is located at the front of the van at 3.2 m above the ground. The main inlet consists of a 4 cm inner diameter stainless steel tube, where the flow is kept at a constant velocity of about 11 m s\(^{-1}\) (around 5200 l min\(^{-1}\)) for near-isokinetic sampling during driving conditions (assuming an average velocity of 40 km h\(^{-1}\)). Two stainless steel tubes with inner diameter of 8 mm distribute the sample air to the two instrument racks located in the front and the back of the van. The CO\(_2\) analyzers were mounted in the front rack and were connected to the main inlet through a Teflon (PTFE) line with inner diameter of 6 mm. The particle phase-instruments were mounted in the back rack and were connected with a 6 mm inner diameter copper line to the main inlet. For the NH\(_3\) analyzer a heated PTFE line (110 °C) was used to decrease the time delay of the NH\(_3\) detection due to its adsorption on the inlet walls. To further minimize this delay, the NH\(_3\) inlet line was kept as short as possible (total length of 1 m) by sampling the air out of the side window of the van instead of through the main inlet. An auxiliary flow of 5 l min\(^{-1}\) was maintained in the NH\(_3\) inlet in order to decrease the residence time of the gas in the line. Also in the AMS inlet an auxiliary flow was required, in this case to prevent the higher flow to the Aethalometer (~5 l min\(^{-1}\)) causing problems in the much lower flow of the AMS (~0.1 l min\(^{-1}\)). Some important parameters for the mobile measurements, including GPS, temperature, relative humidity and radiation were also recorded.

![Figure 2.2: Schematic of the PSI mobile laboratory instrumental set-up. The CO\(_2\)-Picarro analyzer was only available for the measurements in Estonia.](image-url)
2.3 Source apportionment techniques

Figure 2.3: Particle loss in the sampling line of the mobile laboratory calculated using the Particle Loss Calculator by Von der Weiden-Reinmüller et al. (2009). The considered particle loss mechanisms include diffusion, sedimentation, turbulent inertial deposition, and inertial deposition in a bend.

Although no device for the preselection of the aerosol sizes (such as impactors, cyclones...) was mounted in the inlet of the mobile platform, the largest particles are assumed to be lost in the inlet lines. Thus, the size range of the measured particles depends on the inlet losses and the instrumental cut-off. The particle losses in the inlet line were estimated using the Particle Loss Calculator from Von der Weiden et al. (2009). Losses from diffusion, sedimentation, turbulent inertial deposition, and inertial deposition in a bend were considered in this calculation. The results reported in Fig. 2.3 show that 50 % of the particles with diameter of 5.1 µm are lost in the inlet lines. Furthermore, the losses are regarded as negligible (< 10 %) in the size range where the AMS PM$_{2.5}$ lens efficiently transmits particles (see Sect. 2.2.1.1 for more details on AMS transmission efficiency).

2.3 Source apportionment techniques

Source apportionment is a methodological approach to describe and quantify the major source categories contributing to the observed concentrations of particulate matter in the atmosphere.

Two main source apportionment strategies can be distinguished:

- Bottom-up: Using emission factors of known sources (measured in ambient and laboratory studies) and their temporal evolution (determined from aging experiments) to create emission maps or to model the source contributions in a local, regional or global scale.
- **Top-down**: Performing statistical analysis on ambient measurements to quantitatively attribute the measured concentrations to specific sources, processes or locations. Statistical methods used to quantify the sources of aerosols at a particular site (or “receptor site”) are also called receptor models.

### 2.3.1 Receptor models

A fundamental assumption of the receptor models is the conservation of the mass and the number of measured species between the emission source and the receptor site. As shown in Fig. 2.4 (Viana et al., 2008), a wide range of receptor models are currently available in the literature. The main difference between them is the degree of knowledge about the pollution sources required prior to the application of receptor models. At the higher end of this scale, the chemical mass balance (CMB) model requires a complete knowledge of the composition of the emissions for all relevant sources. In the lower extreme, the principal component/factor analysis models (including principal component analysis or PCA, positive matrix factorization or PMF and UNMIX) apportion the sources based exclusively on internal correlations in the observations at the receptor site. However, it is a common problem in such analyses that the resulting components or factors may represent mixtures of emission sources instead of independent source profiles. Between the two extremes, the hybrid models (e.g. multilinear engine (ME) or Constrained Physical Receptor Model (COPREM)) are able to combine the advantages and disadvantages of CMB and factor analysis, by allowing the setting of specific parameters according to the existing knowledge of the researchers regarding e.g. some regional source profiles.

![Figure 2.4: Different approaches to quantify source contributions using receptor models as a function of a priori knowledge required about the pollution sources. Specific models are shown in italics and with dotted arrows. (Adapted from Viana et al., 2008).](image-url)
2.3 Source apportionment techniques

2.3.1.1 Positive matrix factorization

PMF (Paatero and Tapper, 1994) is a bilinear unmixing receptor model widely used for the source apportionment of atmospheric aerosols. The algorithm approximates the measurements (here the input matrix of AMS organic mass spectra as a function of time, \( X \)) by a linear combination of several static factors (here factor profiles, \( G \)) and their contributions over time (\( F \)):

\[
X = G \times F + E
\]

(2.11)

where \( E \) is the residual matrix that reflects the imperfections in the model description. All entries in the solution matrices \( F \) and \( G \) are required to contain non-negative values by default.

In addition to \( X \), the corresponding matrix of uncertainties is required as a model input. To guide the solution based on the more accurate entries in the data matrix, the algorithm solves Eq. (2.11) minimizing the object function \( Q \) which is given by the squared residuals \( (e_{ij}) \) weighted by their corresponding uncertainty \( (\sigma_{ij}) \):

\[
Q = \sum \sum \left( \frac{e_{ij}}{\sigma_{ij}} \right)^2
\]

(2.12)

The PMF algorithm minimizes \( Q \) using the conjugate-gradient method towards a local/global minimum. The minimum of the obtained solution can be explored using mathematically equally valid solutions with pseudo-rotations (see below).

Some of the major challenges of PMF are related to the user subjectivity introduced in the selection of the number of factors and the identification of the factors. Therefore, it is extremely important that the user investigates the consistency of the PMF solution internally (e.g. profile structures, chemical fingerprints...) and externally (e.g. correlation with tracers, diurnal, weekly and seasonal patterns, synoptic trends...).

Additionally, PMF solutions possess rotational ambiguity (Paatero et al., 2002), i.e. mathematically equally valid solutions \( (G' \) and \( F' \)) can be obtained if the matrixes \( G \) and \( F \) are multiplied by any arbitrary matrix \( (T) \) and its inverse \( (T^{-1}) \), respectively:

\[
X = (G \times T) \times (T^{-1} \times F) + E = G' \times F' + E
\]

(2.13)

Bootstrap is an effective approach to partially explore the rotational ambiguity (i.e. the presence of local minima) of the solution and provides an upper limit for the rotational uncertainty (Paatero et al., 2014). This statistical method is based on the creation of replicate input matrixes \( (X_{bs} \) and \( S_{bs} \)) perturbing the original data \( (X \) and \( S \)) by resampling. This is done by randomly reorganizing the rows of the original matrixes, so that some rows of the original matrix are present several times, while other rows are removed. Thus, bootstrap analyses are
also helpful to study the effects of outliers on the PMF solution. Running PMF with a high number of replicates provides an estimate of the uncertainty of the PMF solution.

In PMF the factor profiles are considered to be static, i.e. the evolution of the aerosol chemical composition between the emission source and the measurement site is not taken into account. For this reason, it is often difficult to cleanly separate factors that have similar chemical fingerprints (e.g. cooking and traffic) by means of PMF.

### 2.3.1.2 Multilinear engine

When PMF fails to separate sources with similar chemical composition, or when a minor source that is known to be present wants to be separated, advanced factor analysis models can be used. Among them, in the ME approach some a priori information about one or more sources can be used as an additional input in the model. The α value is the most commonly used technique available within the ME model.

In the α value approach, one or more factor profiles (rows of $\mathbf{F}$) or factor time series (columns of $\mathbf{G}$) can be constrained by the user. The strength of the constrains is regulated by the scalar $\alpha$, which determines the extent to which the final $\mathbf{G}$ or $\mathbf{F}$ are allowed to vary from the input, according to:

$$f_{j,\text{solution}} = f_j \pm \alpha \cdot f_j \quad (2.14)$$

$$g_{i,\text{solution}} = g_i \pm \alpha \cdot g_i \quad (2.15)$$

The constraint can be applied to the entire profile ($f_j$) or time series ($g_i$) or to individual elements of the profile or time series only. Sensitivity tests on the tightness of the constrain are essential for the interpretation of environmentally reasonable solutions.

### 2.3.2 Aethalometer model

The Aethalometer-based source apportionment is a two-component model developed by Sandradewi et al. (2008a) to apportion $b_{abs}$ (measured at seven wavelengths) into its traffic ($b_{abs, tr}$) and wood burning ($b_{abs, wb}$) contributions. Assuming that only these two sources have an influence on $b_{abs}$:

$$b_{abs,\text{total}}(\lambda) = b_{abs, tr}(\lambda) + b_{abs, wb}(\lambda) \quad (2.16)$$

This separation is accomplished by taking advantage of the enhanced absorption of eBC from wood burning (eBC$_{wb}$) in the ultraviolet wavelength range, which is related to the presence of significant light-absorbing organic and humic-like substances (HULIS) in the wood smoke. As shown in Fig. 2.5 (Sandradewi et al., 2008b), wood burning aerosols have a strong spectral dependence, whereas traffic emissions (eBC$_{tr}$, the dominant source in the summer...
measurements) dominate the absorption in the near-infrared range and have only a very weak wavelength dependence. This wavelength dependence of $b_{abs}$ can be described by the power law $b_{abs}(\lambda) \sim \lambda^\alpha$ where $\alpha$ is the Ångström exponent (Ångström, 1929).

![Figure 2.5: Wavelength dependence of $b_{abs}$ from a small wood fire in the laboratory, and from ambient measurements in Roveredo (Switzerland) during winter (traffic and wood burning emissions) and summer (mostly traffic emissions). The solid lines represent the exponential fits to $b_{abs}$ over all seven wavelengths and the dashed lines represent the power law fits of $b_{abs}$ in the wavelength ranges 370–520 nm and 660–950 nm (Sandradewi et al., 2008b).](image)

The eBC$\text{tr}$ and eBC$\text{wb}$ contributions can therefore be derived using the measurements at two different wavelengths (e.g. 470 and 950 nm) as follows (Sandradewi et al., 2008a):

$$\frac{b_{abs,\text{tr}}(470 \text{ nm})}{b_{abs,\text{tr}}(950 \text{ nm})} = \left(\frac{470}{950}\right)^{-\alpha_{\text{tr}}}$$  \hspace{1cm} (2.17)

$$\frac{b_{abs,\text{wb}}(470 \text{ nm})}{b_{abs,\text{wb}}(950 \text{ nm})} = \left(\frac{470}{950}\right)^{-\alpha_{\text{wb}}}$$  \hspace{1cm} (2.18)

$$BC_{\text{tr}} = BC_{880} \times \frac{b_{abs,\text{tr}}(950 \text{ nm})}{b_{abs,\text{total}}(950 \text{ nm})}$$  \hspace{1cm} (2.19)
Previously, also other combinations of wavelengths have been used in this model (e.g. 370 and 880 nm or 470 and 880 nm, see Perron et al. (2010), Herich et al. (2011) and Fuller et al. (2014)). The choice of the wavelengths and of the Ångström exponents used in this work is based on the findings in Zotter et al. (2016), where radiocarbon (¹⁴C) measurements of elemental carbon (EC) were combined with Aethalometer data to determine the best $\alpha$ pair. This was evaluated by fitting the source apportionment results of the Aethalometer (in particular $eBC_{tr}/eBC$) against the fossil fraction of EC ($EC_f/EC$) derived from $¹⁴C$ measurements. This analysis resulted in $\alpha_{tr} = 0.9$ and $\alpha_{wb} = 1.68$ fitting best the data when using the attenuations measured at 470 and 950 nm. Other wavelength combinations were also tested but in all cases, especially when 370 nm was used, the residuals of the fit increased.

This method for the separation of traffic and wood burning contributions to eBC has been successfully applied in many locations in Europe where coal burning is negligible (e.g. Favez et al., 2010; Herich et al., 2011; Sciare et al., 2011; Crilley et al., 2015). However, in certain environments coal burning used for industrial purposes or residential heating can also be an important source of eBC (e.g. China, Poland...). As the optical properties of eBC from coal combustion are still very uncertain, the use of the Aethalometer model is not recommended in such environments. Additional laboratory and ambient measurements are needed in order to characterize the emissions from coal combustion and to study the effect of such emissions on the different wavelengths of the Aethalometer.
New insights into PM$_{2.5}$
chemical composition and sources
in two major cities in China during extreme haze events using aerosol mass spectrometry

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Abstract

During winter 2013–2014 aerosol mass spectrometer (AMS) measurements were conducted for the first time with a novel PM$_{2.5}$ (particulate matter with aerodynamic diameter ≤ 2.5 µm) lens in two major cities of China: Xi’an and Beijing. We denote the periods with visibility below 2 km as extreme haze and refer to the rest as reference periods. During the measurements in Xi’an an extreme haze covered the city for about a week and the total non-refractory (NR)-PM$_{2.5}$ mass fraction reached peak concentrations of over 1000 µg m$^{-3}$. During the measurements in Beijing two extreme haze events occurred, but the temporal extent and the total concentrations reached during these events were lower than in Xi’an. Average PM$_{2.5}$ concentrations of 537 ± 146 and 243 ± 47 µg m$^{-3}$ (including NR species and equivalent black carbon, eBC) were recorded during the extreme haze events in Xi’an and Beijing, respectively. During the reference periods the measured average concentrations were 140 ± 99 µg m$^{-3}$ in Xi’an and 75 ± 61µg m$^{-3}$ in Beijing. The relative composition of the NR-PM$_{2.5}$ evolved substantially during the extreme haze periods, with increased contributions of the inorganic components (mostly sulfate and nitrate). Our results suggest that the high relative humidity present during the extreme haze events had a strong effect on the increase of sulfate mass (via aqueous phase oxidation of sulfur dioxide). Another relevant characteristic of the extreme haze is the size of the measured particles. During the extreme haze events, the AMS showed much larger particles, with a volume weighted mode at about 800 to 1000 nm, in contrast to about 400 nm during reference periods. These large particle sizes made the use of the PM$_{2.5}$ inlet crucial, especially during the severe haze events, where 39 ± 5 % of the mass would have been lost in the conventional PM$_{1}$ (particulate matter with aerodynamic diameter ≤ 1 µm) inlet. A novel positive matrix factorization procedure was developed to apportion the sources of organic aerosols (OA) based on their mass spectra using the multilinear engine (ME-2) controlled via the source finder (SoFi). The procedure allows for an effective exploration of the solution space, a more objective selection of the best solution and an estimation of the rotational uncertainties. Our results clearly show an increase of the oxygenated organic aerosol (OOA) mass during extreme haze events. The contribution of OOA to the total OA increased from the reference to the extreme haze periods from 16.2 ± 1.1 to 31.3 ± 1.5 % in Xi’an and from 15.7 ± 0.7 to 25.0 ± 1.2 % in Beijing. By contrast, during the reference periods the total OA mass was dominated by domestic emissions of primary aerosols from biomass burning in Xi’an (42.2 ± 1.5 % of OA) and coal combustion in Beijing (55.2 ± 1.6 % of OA). These two sources are also mostly responsible for extremely high polycyclic aromatic hydrocarbon (PAH) concentrations measured with the AMS (campaign average of 2.1 ± 2.0 µg m$^{-3}$ and frequent peak concentrations above 10 µg m$^{-3}$). To the best of our knowledge, this is the first data set where the simultaneous extraction of these two primary sources could be achieved in China by conducting on-line AMS measurements at two areas with contrasted emission patterns.
3.1 Introduction

China, the fastest developing country in the history of the world, has been facing severe pollution problems in the last decades in response to rapid industrialization and economic growth. These problems include soil, water and air contamination. In terms of air pollution, large parts of the country are frequently affected by heavy smog events, causing widespread environmental and health issues. A recent study that investigated the link between premature mortality and several emission sources in urban and suburban environments, estimated 1.3 million premature deaths in China in 2010 due to outdoor air pollution (Lelieveld et al., 2015).

Atmospheric PM$_{2.5}$ (particulate matter with aerodynamic diameter ≤ 2.5 µm) affects climate, visibility and human health. The PM$_{2.5}$ fraction is widely used as an air quality metric, as long-term exposure to this fraction has been linked to increased lung cancer rates (Hu and Jiang, 2014), acute bronchitis and asthma (J. J. Gao et al., 2015). Moreover, some of the known PM$_{2.5}$ combustion sources in China have been shown to dominate emissions of carcinogenic species, including polycyclic aromatic hydrocarbons (PAH) (Xu et al., 2006; Zhang and Tao, 2009; Huang et al., 2014; Wei et al., 2015).

In China, severe pollution events often occur during wintertime, when stagnant meteorological conditions confine the gas- and particle-phase pollutants at the ground level. The particles can either be directly emitted as primary aerosols (e.g., particles emitted from combustion sources) or formed in the atmosphere by condensation of oxidation products of sulfur dioxide, nitrogen oxides and volatile organic compounds (secondary aerosol).

The first step for developing air pollution control strategies requires the identification of the major sources and processes producing airborne particles. Most previous aerosol studies in the areas of Xi’an and Beijing, two major Chinese cities, are based on filter measurements (Cao et al., 2012; Wang et al., 2013; Huang et al., 2014; Ho et al., 2015; M. Gao et al., 2015; P. Wang et al., 2015; Xu et al., 2015; Yang et al., 2015). Carbonaceous materials, water-soluble ions (e.g., sulfate, SO$_4^{2-}$, nitrate, NO$_3^-$, and ammonium, NH$_4^+$) and mineral dust have been found to be major constituents of fine particles in both cities during wintertime. During haze days, elevated concentrations of secondary ion species contribute considerably to the decrease in visibility (J. J. Gao et al., 2015; Zhang et al., 2015a). High relative humidity resulting in enhanced water uptake by the hygroscopic aerosol particles and formation of secondary aerosol have been suggested as an important factor during haze events in China (Sun et al., 2013b; Y. H. Wang et al., 2015). Using aerosol mass spectrometry measurements of filters collected during a haze event in four different cities in China including Beijing and Xi’an, Huang et al. (2014) showed that the haze can be driven to a large extent by secondary aerosol formation. Furthermore, dust-related particles and biomass burning were identified as major contributors to the primary aerosol in Xi’an, while coal combustion particles dominated the primary aerosol in Beijing. However, filter measurements have a limited time resolution, and are often insufficient to characterize the rapid evolution of atmospheric aerosols or distinguish
emission sources. Furthermore, filter measurements may suffer from sampling and measurement artifacts (e.g., loss of semi-volatile species due to evaporative processes during the sampling or absorption of gases into the filter material). Real-time measurements of aerosol particle composition with high time resolution have been conducted in wintertime in Beijing using various online mass spectrometers (e.g., Sun et al., 2013a, 2014; Zhang et al., 2014). These studies identified several primary sources, including traffic, coal combustion and cooking emissions. Sun et al. (2013a) found coal combustion particles to dominate the organic aerosol (OA) in Beijing in wintertime (on average 33 % of the OA) and enhanced contribution of this factor during polluted periods. Lower contributions of coal combustion aerosol were found in measurements performed in January 2013 (Zhang et al., 2014; Sun et al., 2014), with coal combustion explaining 15 and 19 % of the total OA, respectively. Among all three studies, the average contribution of traffic to the OA varied between 11 and 18 %, while cooking emissions explained between 12 and 20 % of the OA. However, all these studies failed to resolve a factor related to biomass burning, which is known to be a major particle source in winter. In addition, each study reported two to three oxygenated OA (OOA) components resulting from secondary processes. Secondary organic aerosol (SOA) was found to dominate the OA mass concentrations in January 2013 (54 % of OA in Zhang et al., 2014, and 55 % in Sun et al., 2014), with increased relative contribution during more polluted days. Similar real-time measurements in other Chinese cities, including Xi’an, are scarce, preventing an accurate assessment of the spatial variation of the aerosol composition and sources in China during haze events.

Despite the widespread use of PM$_{2.5}$ as an air quality standard, previous online aerosol mass spectrometry measurements have only been able to measure the submicron fraction. In this work we present the first online high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) measurements of the non-refractory (NR)-PM$_{2.5}$ fraction in two large Chinese cities during extreme and moderate pollution periods. The application of novel source apportionment techniques using the multi-linear engine tool (ME-2) provides an improved identification and quantification of OA sources compared to conventional positive matrix factorization (PMF) analysis. PAHs were quantified from AMS data and the contributions from their corresponding sources were determined.

### 3.2 Methodologies

#### 3.2.1 Measurement campaign

Measurements were performed from 13 December 2013 to 6 January 2014 in Xi’an (34.23° N, 108.88° E, 10 m above ground level) and from 9 to 26 January 2014 in Beijing (40.00° N, 116.38° E, 20 m a.g.l.).
Xi’an, with over 8 million inhabitants in 2013, is the largest city in western China. Besides the local anthropogenic emissions, the region is often affected by the transport of dust particles from the Gobi desert and by the accumulation of pollutants when stagnant air masses are confined in the Guanzhong basin. The sampling site was located within the high-tech area south-west from the urban core, surrounded by many office buildings, some factories and construction sites. Nearby streets were sporadically watered during high pollution periods to minimize road dust resuspension.

Beijing, the capital of China, with over 20 million inhabitants in 2013 is one of the largest and most populated cities in the world. The city is located in a plain which extends to the east and to the south and is surrounded by mountains from the southwest to the northeast. The sampling site in Beijing was located in a residential area north of the urban core, near the Olympic Park. A large canteen was located about 20 m from the sampling site. Moreover, two main roads were situated at about 800 m in south and west directions. In Beijing, equivalent black carbon (eBC) concentration was measured in a separate location with similar characteristics, situated 2.8 km south from the sampling site described above.

3.2.2 Instrumentation

3.2.2.1 Aerosol Mass Spectrometer

An HR-ToF-AMS (Aerodyne Research Inc.) was deployed for online measurements of size segregated mass spectra of NR-PM$_{2.5}$. A detailed description of the instrument can be found elsewhere (Jayne et al., 2000; DeCarlo et al., 2006; Canagaratna et al., 2007). Briefly, a particle beam sampled through an aerodynamic lens is either alternately blocked and unblocked, yielding the bulk particle mass spectra (MS mode), or modulated by a spinning chopper wheel (~125Hz), yielding size-resolved spectra (PToF mode) (Drewnick et al., 2005). In both operational modes, NR particles are flash vaporized by impact on a heated tungsten surface (heated to about 600°C) at ~10$^{-7}$ Torr. The resulting gases are ionized by electron ionization (EI, ~70 eV) and the mass-to-charge ratios (m/z) of the resulting fragments are determined by the ToF mass spectrometer. The AMS was alternated between lower and higher mass resolution modes (V and W modes, respectively) each minute. For each of these modes, the AMS measured 25 s in MS mode, 25 s in PToF mode and the remaining 10 s were used to change configuration between V and W modes.

While commonly only the PM$_1$ fraction (particulate matter with aerodynamic diameter ≤ 1 µm) is accessible by the AMS, for this work we have equipped the AMS with a recently developed aerodynamic lens which extends the measured particle size to PM$_{2.5}$. This lens efficiently transmits particles between 80 nm and up to at least 3 µm and was well characterized by Williams et al. (2013). A ~2 m length copper tube (12 mm outer diameter) was used to connect a total suspended particles (TSP) inlet to the AMS. As the flow into the
AMS is relatively low (\( \sim 0.8 \text{ L min}^{-1} \)), an auxiliary flow of \( \sim 4 \text{ L min}^{-1} \) was maintained in this line in order to decrease particles losses. After the split with the auxiliary flow and before entering the AMS, the sampling air was drawn through a naifion drier in order to reduce uncertainties in the bounce-related collection efficiency (CE\(_b\)) and RH-dependent differences in aerodynamic sizing.

AMS data were analyzed in Igor Pro 6.3 (WaveMetrics) using the SQUIRREL (version 1.52L) and PIKA (1.11L) analysis software. Standard relative ionization efficiencies (RIE) were assumed for organics, nitrate and chloride (RIE = 1.4, 1.1 and 1.3, respectively) and experimentally determined for sulfate and ammonium (RIE = 1.48 and 3.37, respectively). The CE\(_b\) was corrected for by using a composition-dependent collection efficiency (CDCE) algorithm by Middlebrook et al. (2012). Detailed studies of particle bounce in the AMS were not conducted for the larger particles sampled here; additionally, in principle the PM\(_{2.5}\) lens could enhance particle bounce by operating at a higher pressure and thus yielding increased particle velocity for a given size. However, the comparison between total measured PM\(_{2.5}\) mass (NR species and eBC, 24 h average) with gravimetric measurements on filters (collected also in the PM\(_{2.5}\) range at room temperature) suggests that these losses are not significant in the current study (see Fig. A.1 in the Appendix). Specifically, during the period for which filter measurements are available, the total measured PM\(_{2.5}\) from AMS and aethalometer is similar or greater than the gravimetric measurements. The comparison between these two techniques is biased by the higher cut-off of the PM\(_{2.5}\) lens of the AMS combined with the presence of large particles during the extreme haze events, the increased loss of ammonium nitrate on the filters during extreme haze events, and the deposition of dust, other refractory compounds and water on the filters. However, the comparison provides evidence that in our case there is no important loss of mass in the AMS due to enhanced particle bounce.

### 3.2.2.2 Aethalometer

Two aethalometers (Magee Scientific) were deployed for the determination of the aerosol attenuation at seven different wavelengths with a time resolution of 1min. From the change in the light attenuation, optical properties of the aerosol and eBC concentrations were retrieved. An aethalometer model AE-33 was deployed in Xi’an, whereas a model AE-31 was deployed in Beijing. The newly developed model AE-33 uses a double spot technique for real-time loading compensation (Drinovec et al., 2015), while the data of the AE-31 were manually corrected for this effect after acquisition using the procedure of Weingartner et al. (2003). A PM\(_{2.5}\) cyclone was located in front of the main inlet of the aethalometers. The particles were transmitted from the cyclone to the aethalometer through a \( \sim 3 \text{ m of copper tube (12 mm outer diameter)} \) at a flowrate of \( \sim 4 \text{ L min}^{-1} \).
3.2 Methodologies

3.2.3 Source apportionment techniques

3.2.3.1 OA source apportionment

Source apportionment was performed on the organic AMS data using PMF as implemented by the multilinear engine (ME-2; Paatero, 1997) and controlled via the interface SoFi coded in Igor Wavemetrics (Source Finder; Canonaco et al., 2013).

PMF is a bilinear unmixing receptor model which enables the description of the variability of a multivariate database as the linear combination of static factor profiles and their corresponding time series. This is achieved by solving Eq. (3.1), where $X$ is the measurement matrix (consisting of $i$ rows and $j$ columns), $G$ contains the factor time series, $F$ the factor profiles and $E$ the model residuals. The model uses a least squares approach to iteratively minimize the object function $Q$ (Eq. (3.2)), defined as the sum of the squared residuals ($e_{ij}$) weighted by their respective uncertainties ($\sigma_{ij}$).

$$X = G \times F + E$$  \hspace{1cm} (3.1)

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{e_{ij}}{\sigma_{ij}}\right)^2$$  \hspace{1cm} (3.2)

In our case, the model input consists of a data matrix and an error matrix of OA mass spectra, where the rows represent the time series and the columns contain the ions fitted in high resolution (HR) for the V mode data. Considering only the mass from the HR fits (up to $m/z$ 115), 10 ± 8 % of the OA mass was excluded. The initial error values were calculated by the HR-AMS data analysis software previously described (PIKA) and a minimum error corresponding to the measurement of a single ion was enforced (Ulbrich et al., 2009). Further, as suggested by Paatero and Hopke (2003), variables with signal-to-noise ratio (SNR) lower than 0.2 were removed and variables with SNR between 0.2 and 2 were down-weighted by increasing their error by a factor of 3. Finally, all variables directly related to $m/z$ 44 in the organic fragmentation table (i.e., $m/z$’s 16, 17, 18 and 28) (Allan et al., 2004) were excluded for the PMF analysis to appropriately weight the variability of $m/z$ 44 in the algorithm and were reinserted post-analysis. After the aforementioned corrections were applied, the final input matrix contained 270 ions and 50909 points in time (with steps of 60 s). PMF was solved using the multi-linear engine (ME-2; Paatero, 1999), which in contrast to unconstrained PMF analyses enables complete exploration of the rotational ambiguity (i.e., different combinations of the matrices $G$ and $F$ can give solutions with the same mathematical quality) of the solution space. For computational efficiency, in this study this was achieved by directing the solution towards environmentally meaningful rotations using the $a$ value approach. This method constrains one or more output factor profiles to fall within a predetermined range governed by the combination of an input profile and a range-defining scalar ($a$ value). For example, in the
Chapter 3 OA chemical composition and sources during haze events in China

3.2.3.2 eBC source apportionment

As mentioned in Sect. 3.2.2.2, light attenuation was measured at seven wavelengths ranging from the ultraviolet to near-infrared, namely 370, 470, 520, 590, 660, 880 and 950 nm. The eBC from wood burning (eBC\textsubscript{wb}) can be distinguished from eBC emitted by traffic (eBC\textsubscript{tr}) by exploiting the enhanced absorption of eBC\textsubscript{wb} in the ultraviolet range (Sandradewi et al., 2008a). This method for the separation of wood burning and traffic contributions to eBC was developed and successfully applied in environments where no other major combustion sources were present. However, in China coal is widely used in some industrial sectors and for heating purposes, too. The optical properties of eBC from coal combustion remain very uncertain and the effect of coal emissions on the different wavelengths of the aethalometer is still unknown. Yang et al. (2009) estimated an Angstrom exponent for coal burning aerosol of 1.46 from ambient measurements. This value falls between the more established Angstrom exponents for traffic (α\textsubscript{tr} = 0.9 to 1.1) and wood burning (α\textsubscript{wb} = 1.6 to 1.8) (Zotter et al., 2016). Thus, the presence of coal emissions makes the use of the method for eBC source apportionment rather uncertain.

The OA source apportionment results (see Sect. 3.2.4.2) show rather high mass loadings of coal combustion OA (CCOA) in Beijing (23.4 ± 0.6 µg m\textsuperscript{-3} on average and 53.8 ± 1.3 % relative contribution to OA mass), but a very low mass fraction from this source in Xi’an (10.5 ± 0.4 µg m\textsuperscript{-3} on average and only 9.2 ± 0.3 % relative contribution to OA mass). Using these results, we estimated the ratio of eBC/CCOA to be 0.037 ± 0.006 in Beijing. This was accomplished by fitting eBC as a linear combination of the three identified combustion sources: traffic (hydrocarbon-like OA, HOA), biomass burning (biomass burning OA, BBOA) and coal combustion (CCOA). Although the eBC measurements in Beijing were conducted at 2.8 km south of our sampling site, the reconstruction of the eBC concentration based on OA primary fractions from ME-2 shows a very good agreement with the measured eBC (see Fig. A.2) and the obtained eBC/CCOA ratio is in good agreement with previous values reported in literature (Zhang et al., 2008). Using the ratio eBC/CCOA obtained for Beijing, we estimate that coal combustion contributed on average only 2.2 ± 1.4 % to the measured eBC in Xi’an. Moreover, also for Xi’an the reconstruction of eBC by means of the combustion OA sources is very
successful (as shown in Fig. A.2). Therefore, we conclude that the method described in Sandradewi et al. (2008a) to separate eBC\textsubscript{wb} and eBC\textsubscript{tr} can be reasonably applied to our data from Xi’an, but not in the case of Beijing.

For the eBC source apportionment in Xi’an, Angstrom exponents of 0.9 and 1.7 were considered for traffic and wood burning, respectively, following the suggestions in Zotter et al. (2016) presenting a re-evaluation of the method developed in Sandradewi et al. (2008a). The eBC\textsubscript{wb} to BBOA ratio was found to be 0.14, which is in good agreement with previous reported values (Gilardoni et al., 2011; Zotter et al., 2014). The ratio eBC\textsubscript{tr} to HOA was 0.79, which is lower than the ratios reported in previous European studies (El Haddad et al., 2013 and references therein), but is in good agreement with results derived from measurements in China (Huang et al., 2012; Zhou et al., 2014). This difference in the eBC\textsubscript{tr} to HOA ratio at the two locations is most probably related to the higher percentage of gasoline vehicles in China compared to Europe. Specifically, according to DeWitt et al. (2015), an eBC\textsubscript{tr} to HOA of around 0.8 corresponds to a diesel fuel share of about 40 to 50 \%. This estimation is in good agreement with results derived from measurements in China, dominated by heavy- and medium-duty vehicles.

3.2.4 AMS-PAH quantification

PAH concentrations were quantitatively determined from the high-resolution AMS data. All details about the method used can be found in Bruns et al. (2015) and references therein. The following PAH molecular ions [M]\textsuperscript{+} were fitted in the HR spectra: [C\textsubscript{10}H\textsubscript{8}]\textsuperscript{+} (128), [C\textsubscript{12}H\textsubscript{8}]\textsuperscript{+} (152), [C\textsubscript{14}H\textsubscript{8}]\textsuperscript{+} (176), [C\textsubscript{14}H\textsubscript{10}]\textsuperscript{+} (178), [C\textsubscript{16}H\textsubscript{10}]\textsuperscript{+} (202), [C\textsubscript{18}H\textsubscript{10}]\textsuperscript{+} (226), [C\textsubscript{18}H\textsubscript{12}]\textsuperscript{+} (228), [C\textsubscript{20}H\textsubscript{12}]\textsuperscript{+} (252), [C\textsubscript{22}H\textsubscript{12}]\textsuperscript{+} (276), [C\textsubscript{22}H\textsubscript{14}]\textsuperscript{+} (278), [C\textsubscript{24}H\textsubscript{12}]\textsuperscript{+} (300) and [C\textsubscript{24}H\textsubscript{14}]\textsuperscript{+} (302), with the nominal mass in parentheses. In addition to the aforementioned molecular ions, other associated fragments were also considered, including [M-H]\textsuperscript{+}, [M-2H]\textsuperscript{+}, [M]\textsuperscript{2+} and [M-H]\textsuperscript{2+} and the \textsuperscript{13}C-isotopes of singly charged ions. To reduce uncertainty in the quantification of the associated ions, the ratios between molecular ions and their corresponding fragments were determined during periods with high PAH concentrations and then applied to the entire data set. Due to possible interference with ions from non-PAH compounds, the fragments that presented low correlation with their corresponding molecular ions (i.e., \( R^2 \) below 0.6 for [C\textsubscript{13}H\textsubscript{6}]\textsuperscript{+} to [C\textsubscript{13}H\textsubscript{7}]\textsuperscript{+} and [C\textsubscript{15}H\textsubscript{6}]\textsuperscript{+} to [C\textsubscript{15}H\textsubscript{7}]\textsuperscript{+} ratios) were not taken into account in the analysis. In cases of overlap between a molecular ion and associated fragments (e.g., [M-2H]\textsuperscript{+} from [C\textsubscript{14}H\textsubscript{10}]\textsuperscript{+} overlaps with the molecular ion [C\textsubscript{14}H\textsubscript{8}]\textsuperscript{+}) the fragments were not included. As for the non-PAH organics, the RIE for PAHs was assumed to be 1.4 and the dependency of the collection efficiency (CE\textsubscript{b}) on the chemical composition of the aerosol was estimated using a composition-dependent collection efficiency (CDCE) algorithm (Middlebrook et al., 2012). Previous works found that PAH quantified from AMS measurements were systematically higher than PAH determined from filter measurements (Bruns et al., 2015). These differences were mostly attributed to
filter artifacts (predominantly negative artifacts, i.e., volatilization of PAH on the filter surface). However, also the AMS-PAH analysis is subject to uncertainties. The PAH RIE considered in this work (1.4) is at the lower end of the values found in literature (e.g., Dzepina et al., 2007, measured RIEs between 1.35 and 2.1 for four PAH standards), and the reported PAH values would decrease by 33.3% if a higher RIE (2.1) were considered. Moreover, our results might be affected by interferences with fragments from other PAH classes at the quantified m/z’s. To assess the contribution of these interferences we analyzed the electron impact ionization mass spectrum (Linstrom and Mallard, 2016) of major PAHs derivatives including alkylated, oxygenated and nitro-PAHs (43 compounds). The fragmentation patterns of alkylated- and oxygenated-PAHs suggests that their response at the m/z’s of interest is highly unlikely. On the other hand, nitro-PAHs exhibit a small response at some fragments of interest, but yield mainly fragments at odd m/z. In addition to the molecular ions mentioned above, we have considered as PAHs the ions \([C_{11}H_{7}]^+\) (139), \([C_{13}H_{7}]^+\) (163), \([C_{13}H_{9}]^+\) (165), \([C_{15}H_{9}]^+\) (189) and \([C_{16}H_{7}]^+\) (199) and their related associated fragments. These fragments at odd masses were observed to derive from the fragmentation of PAHs using laser desorption (Bente et al., 2009); they contribute to 32% of the total PAH mass quantified here. Due to all the limitations mentioned above, PAH concentrations presented here have to be considered as the absolute highest estimates and we will refer to this chemical family as AMS-PAHs.

### 3.3 Interpretation and optimization of OA source apportionment

A key consideration for PMF analysis is the number of factors selected by the user. As currently no methodical and completely objective approach exists for choosing the right number of factors, this selection is generally evaluated through comparisons of the time series of the factor and external tracers as well as the analyses of factor mass spectra and diurnal patterns. In this work we present a detailed source apportionment that has been optimized to minimize the user subjectivity on the solution and better estimate the uncertainties of the final solution.

In a first step, we examined a range of solutions with two to eight factors from unconstrained runs (see Fig. A.3). The solution that best represented the data set is the five-factor solution, which yields factors interpreted as hydrocarbon-like OA (HOA), biomass burning OA (BBOA), coal combustion OA (CCOA), cooking OA (COA) and oxygenated OA (OOA). The HOA profile is distinguished by the presence of alkyl fragment signatures (Ng et al., 2011), with prominent contributions of non-oxygenated species at m/z 43 (C\(_3\)H\(_7\)\(^+\)), m/z 55 (C\(_4\)H\(_7\)\(^+\)) and m/z 57 (C\(_4\)H\(_9\)\(^+\)). BBOA is characterized by the presence of signals at m/z 60 (C\(_2\)H\(_4\)O\(_2\)\(^+\)) and m/z 73 (C\(_3\)H\(_5\)O\(_2\)\(^+\)), which are known fragments from anhydrous sugars present in biomass smoke (Alfarra et al., 2007). The CCOA profile, which has been previously identified in other locations (Dall’Osto et al., 2013), is characterized by the presence of unsaturated hydrocarbons, with higher explained variability of these unsaturated fragments at higher m/z. The COA profile is very similar to the HOA spectra but has higher contributions of the oxygenated ions at m/z 55
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(C₃H₅O⁺) and m/z 57 (C₃H₅O⁺). Finally, the OOA profile is characterized by a very high m/z 44 (CO₂¹⁺). COA is not resolved in solutions with a lower number of factors. Meanwhile, when a six-factor solution is considered, OOA splits into two factors with very similar profiles and whose time series reflect the change in the instrument tuning (Fig. A.3). Further increasing the number of factors does not improve the interpretation of the data, as the new factor time series and spectral profiles are highly correlated with those extracted from lower order solutions and cannot be explicitly associated to distinct sources or processes.

Although the unconstrained five-factor solution appears to be a reasonable representation of the data, the mass spectral profiles indicate mixing between the sources. This is specifically the case between HOA and BBOA, where the HOA profile contains a higher than expected contribution of C₂H₄O₂⁺ (m/z 60), and between COA and OOA, with a rather high contribution of CO₂⁺ (m/z 44) in the COA profile. Precisely, in the unconstrained solution the m/z 60 in HOA is 0.009 ± 0.001 % (standard deviation from average over 10 seed runs), compared to 0.002 ± 0.002 % obtained from the average of multiple ambient data sets (Ng et al., 2011). Likewise, the m/z 44 in the unconstrained COA profile is 0.069 ± 0.001 %, compared to 0.013 ± 0.004 % obtained as an average of previously reported COA spectra (He et al., 2010; Crippa et al., 2013a; Wolf, 2014).

To decrease the influence of BBOA on the apportionment of HOA, we constrained HOA using the profile from Crippa et al. (2013a), which is characterized by a minor contribution of m/z 60. Note that while other approaches were explored throughout the entire analysis, including the use of other HOA profiles or increase of the factor number, the BBOA-HOA separation could not be significantly improved. As the vehicular fleet in China and Europe are significantly different, e.g., higher diesel contribution in Europe, the use of a European profile to apportion traffic emissions in China could introduce significant errors. However, the comparison between HOA spectra from Europe (fleet dominated by diesel) and from the United States (fleet dominated by gasoline), shows that the variability among two European spectra (Mohr et al., 2012; Crippa et al., 2013a) is comparable to the variability among HOA spectra from the United States and Europe (Docherty et al., 2011; Crippa et al., 2013a). This was evaluated by means of cosine similarity analysis, which resulted in Θ_{HOA(Europe-Europe)} = 0.93 and Θ_{HOA(Europe-US)} = 0.92. Thus, we show that HOA emissions from different types of cars have similar profiles. Although constraining the HOA improves the HOA-BBOA separation, it compromises the apportionment of cooking emissions, with a higher background mass and an unexpectedly high concentration overnight in the diurnal trend. To avoid the mixing of COA with other sources, the COA profile of Crippa et al. (2013a) was constrained. While some differences are expected between the Chinese and European cooking activities, cosines similarity analysis indicate very good correlations (Θ_{COA(Europe-China)} = 0.97 on average) between the COA profile from Paris (Crippa et al., 2013) and four spectra from different types of Chinese cooking (CC1 to CC4 in He et al., 2010). Moreover, the use of α values allows for a certain re-adjustment of the input profiles (for both HOA and COA), minimizing the effect of using non-
local input profiles. In the following we discuss the sensitivity of the results to the $\alpha$ values used to constrain the HOA and COA factor profiles.

Considering $\alpha$ values between 0 and 1 with a step of 0.1 for both HOA and COA yields 121 possible combinations of $\alpha$ values. A set of three criteria was established to assess the solutions that represent environmentally better the OA fractions.

1. Minimization of m/z 60 in HOA. A threshold for the maximal fractional contribution of m/z 60 in HOA was set to 0.006 based on profiles derived from multiple ambient data sets (mean $\pm 2\sigma$ from Ng et al., 2011). The fractional contribution of m/z 60 to the normalized HOA profiles varied between 0.0016 and 0.0092 % over the full $\alpha$ value space. This criterion eliminated all solutions with an $\alpha$ value for HOA of 1, as shown in Fig. A.4.

2. Optimization of COA diurnals. Unambiguous chemical markers for cooking emissions are not yet clearly established, hindering their use for the optimization of the apportionment of this source. A valuable characteristic for the identification of COA is the analysis of its diurnal trends: near the emissions source (e.g., in an urban area) COA typically has a distinctive diurnal with maxima at lunch and dinner times. In order to categorize the solutions, a novel approach using cluster analysis was utilized. The normalized COA diurnals of all studied $\alpha$ value combinations were grouped using k means cluster analysis. This technique aims at grouping the observations into $k$ clusters, by minimizing the first term ($T_1$) from the cost function (CF) shown in Eq. (3.4). This term represents the sum of the Euclidian distances between each observation ($x_i$) and its respective cluster center ($\mu_i$). The results from the cluster analysis are shown in Fig. 3.1, for two-, three-, and four-cluster solutions. For each solution, the first panel shows all diurnals pertaining to the different clusters, the second plot shows the diurnal pattern of the cluster center and the third plot shows the clusters’ attribution in the $\alpha$ value space. An issue encountered in cluster analysis is the determination of the number of clusters ($k$) that best describes the data. Increasing $k$ decreases $T_1$, while adding complexity to the solution. A common approach to select the optimal number of clusters is to explicitly penalize the higher order solutions for complexity by using the Bayesian information criterion (BIC). This penalty is introduced with the second term ($T_2$) in Eq. (3.4), given by the product of the number of clusters ($k$) and the logarithm of the dimensionality of the cluster ($D = 24$ h in our case):

$$CF = T_1 + T_2 = ||x_i - \mu_i||^2 + k \times \log(D) \quad (3.4)$$

Figure 3.2a shows a minimum in the cost function at three clusters, which are therefore selected to represent the different types of COA diurnals. From the three-cluster solution in Fig. 3.1, the diurnals of the purple cluster exhibit a higher background concentration over the full day, which are difficult to reconcile with the expected COA emission trends. The red and blue clusters have both lower background values; however the blue cluster has some peaks over the night hours that are not expected from COA emissions. Moreover, the solutions in the red cluster are more similar to previously reported COA spectra (He et al., 2010; Crippa et al., 2011).
3.3 Interpretation and optimization of OA source apportionment

2013a; Wolf, 2014), as they have a lower contribution of m/z 44 compared to the solutions in the other two clusters (see Fig. A.5). Specifically, the average relative contribution of m/z 44 in the COA spectra from literature previously mentioned is 0.013 ± 0.004 %, which is in good agreement with the relative contribution of 0.013 ± 0.002 % found for the red cluster. As the spectrum for the blue and purple clusters have higher contributions of m/z 44 (0.026 ± 0.008 and 0.025 ± 0.019 %, respectively), only the solutions belonging to the red cluster are considered as good solutions. A disadvantage of the k means algorithm is that the solution space might have several local minima and therefore the result could strongly depend on the initialization. Hence, 100 random initializations of the algorithm were performed and only the a value combinations that fell into the red cluster more than 95 % of the time were retained as good solutions. Combining these results with the criterion previously applied on the HOA profile, we obtained the range of accepted a values combinations shown in Fig. 3.2b.

Figure 3.1: Cluster analysis on the normalized COA diurnal trends from the evaluated a value space. Results from two-, three- and four-cluster solutions are presented (from top to bottom), using different colors to represent the clusters. For each solution the left plot represents all COA diurnals colored with the color of the corresponding cluster, the center plot represents the normalized diurnals of the cluster centers and the right plot represents the cluster assignment for all considered a value combinations.
3. Factor-tracer correlation. The following correlations between the identified primary sources and the external tracers were considered:

\[
PAH_{\text{calculated}}(t) = a \times \text{BBOA}(t) + b \times \text{CCOA}(t) + c \times \text{HOA}(t)
\] (3.5)

\[
e\text{BC}_{\text{tr,calculated}}(t) = \left( \frac{e\text{BC}_{\text{tr}}}{\text{HOA}} \right)_{\text{median}} \times \text{HOA}(t)
\] (3.6)

\[
e\text{BC}_{\text{wb,calculated}}(t) = \left( \frac{e\text{BC}_{\text{wb}}}{\text{BBOA}} \right)_{\text{median}} \times \text{BBOA}(t)
\] (3.7)

In all cases, low concentration points (below the 5th percentile, \(P_{0.05}\)) were discarded. Note that the separation between \(e\text{BC}_{\text{tr}}\) and \(e\text{BC}_{\text{wb}}\) was only possible with the data collected in Xi’an (see Sect. 3.2.3.2). Moreover, as the \(e\text{BC}_{\text{wb}}\) does not follow the BBOA time series during the haze event (see discussion in Sect. 3.4.2), only data from the reference period was considered for this analysis. The linear relation between AMS-PAH and BBOA, CCOA and HOA will be discussed in detail in the source apportionment result section (Sect. 3.4.3).

For each of these parameters, the normalized difference, \(S\), between the measured and calculated marker concentrations was retrieved for all accepted \(a\) value combinations using Eq. (3.8). The standard deviations of \(S\), which are considered as an estimate of the variability between the factor and its corresponding marker, were combined in quadrature as shown in Eq. (3.9):
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\[ S = \frac{F_{\text{measured}} - F_{\text{calculated}}}{F_{\text{measured}}} , \quad \text{with } F=\text{AMS-PAH, eBC}_{tr} \text{ and eBC}_{wb} \quad (3.8) \]

\[ \sigma_{\text{ALL}} = \sqrt{(\sigma_{\text{AMS-PAH}})^2 + (\sigma_{\text{eBC}_{tr}})^2 + (\sigma_{\text{eBC}_{wb}})^2} \quad (3.9) \]

where \( \sigma_{\text{ALL}} \) is the object function that needs to be minimized for the optimization of the selected solutions and is represented with a color scale in Fig. 3.2c. The standard deviation of the individual parameters (\( \sigma_{\text{AMS-PAH}}, \sigma_{\text{eBC}_{tr}} \) and \( \sigma_{\text{eBC}_{wb}} \)) within the accepted \( a \) value space are shown in the Supplement (Fig. A.6). As seen from Fig. 3.2c, the solution obtained using an \( a \) value of 0.9 for the HOA profile and 0.6 for the COA profile, has the minimum \( \sigma_{\text{ALL}} (\sigma_{\text{min}} = 0.94) \).

In order to establish the stability of the solution at a certain \( a \) value combination with respect to the measurement uncertainty, we examined the variability of \( \sigma_{\text{min}} \) for the best solution, by reinitializing 50 times the ME-2 algorithm with different input matrices. For each repetition, the elements of the OA input matrix were varied within twice their uncertainties (OA ± 2OA\text{error}). All of the 50 solutions satisfied the two criteria previously described (i.e., minimization of \( m/z \) 60 in HOA and optimization of COA diurnal) and \( \sigma_{\text{ALL}} \) presented 7.5 \% variability among the 50 iterations. Considering all solutions inside the 95 \% confidence interval (i.e., twice its variability, \( \sigma_{\text{ALL}} < \sigma_{\text{min}} + 15.0 \% \)) to represent the data equally well compared to the best solution, all \( a \) value combinations within the red region in Fig. 3.2c were retained. All results presented hereon are averaged over all this possible \( a \) value combinations, and their standard deviation is considered as our best estimation of ME-2 errors. Note that these errors are very likely lower estimates of the model uncertainties, as the solution space could not be fully explored. The error bars in Fig. 3.3 represent the variability of each \( m/z \) fraction (standard deviation) across all good solutions in the \( a \) value space. As this retained range of solution is a direct consequence of our input error estimate, we assessed the sensitivity of our results to the input errors by running the algorithm by varying the OA input matrix within smaller limits (OA ± 1OA\text{error}). This lead to similar results as the method described above, with the only difference that two additional \( a \) value combinations (marked with the dashed line in the left corner of Fig. 3.2c) would not have been considered as good solutions in this case.

Compared to the unconstrained PMF (average over 10 seeds), the optimized solution (average over all good \( a \) value combinations) has more genuine factor profiles (Fig. 3.3), with decreased contributions of \( m/z \) 60 in the HOA spectra (from 0.009 ± 0.001 to 0.003 ± 0.001 \%) and of \( m/z \) 44 in the COA spectra (from 0.069 ± 0.001 to 0.013 ± 0.002 \%). In terms of the relative contributions of the different sources to the total OA (Fig. A.7), the optimized solution yielded significantly lower COA (7.0 ± 1.1 vs. 19.9 ± 0.1 \% in the unconstrained PMF) and HOA (15.1 ± 1.6 vs. 25.1 ± 0.1 \% in the unconstrained PMF). Moreover, \( \sigma_{\text{ALL}} \), the object function that we seek to minimize, decreases considerably from 3.3 ± 0.1 in the unconstrained solution to 1.0 ± 0.1 in the optimized solution. In terms of the model mathematical performance, there is only a moderate increase in the residuals in the optimized solution compared to the
unconstrained run. Specifically, $Q$ normalized by its expected value ($Q/Q_{\text{exp}}$) (Paatero and Hopke, 2009) increases from $7.5 \pm 0.1$ in the unconstrained solution to $8.5 \pm 0.4$ in the optimized solution. The correlations between the OA factors from the optimized solution and its corresponding tracers are presented in Fig. A.8. The correlation parameters ($R^2$ and slope) are reported in Table A.1 for the unconstrained and optimized solutions. Compared to the unconstrained solution, the correlations between COA and its marker ($C_6H_{10}O$) are higher in the optimized solution, while the correlations between OOA and NH$_4$ are slightly lower in this case, especially during the haze events.

Figure 3.3: Mass spectra of the five identified OA factors color coded with the chemical families; Spectra are averaged over all good $a$ value combinations and error bars represent the standard deviation of each $m/z$ over all the accepted solutions.

3.4 Results and discussion

3.4.1 Bulk PM$_{2.5}$ chemical composition

Figure 3.4a shows the temporal variations of the non-refractory (NR) chemical components measured by the AMS (OA, SO$_4$, NO$_3$, NH$_4$ and Cl) and eBC concentrations during the measurement periods in Xi’an and Beijing. The periods highlighted with a blue background relate to extreme haze events, which are defined by a visibility (reported in the top panel)
3.4 Results and discussion

below 2km (Zhang et al., 2015b). We recognize that the reduction of the visibility is partially
due to the increase of the aerosol water content as a result of the increase in the RH. However,
during the extreme haze periods a significant increase in the total aerosol burden is observed,
with total PM$_{2.5}$ mass reaching peak concentrations above 1000 µg m$^{-3}$ in Xi’an. Regarding the
chemical composition, Fig. 3.4a shows an increase in the inorganic aerosol species during the
extreme haze periods, while organic aerosols dominate the particle mass in the reference
periods (i.e., visibility above 2 km). In the medium panel of Fig. 3.4a, the ratio PM$_1$ to PM$_{2.5}$
mass is reported. This ratio was obtained from the integration of the collected PToF data. The
size distributions of each species were integrated over the full measured size range (up to 6000
nm) to determine the total mass measured with the PM$_{2.5}$ lens and until 800 nm as an
estimation of the mass that the commonly used PM$_1$ lens would have detected (the 50 % cut-
off diameter of the PM$_1$ inlet is at about 800 nm vacuum aerodynamic diameter, Liu et al.,
2007). As mentioned in Sect. 3.2.2.1, the actual upper cut-off of the PM$_{2.5}$ inlet has been
determined to be above 2.5 µm (Williams et al., 2013). This comparison between PM fractions
might suffer from the slow evaporation of some particles in PToF mode, which would lead to a
higher apparent $d_{va}$ and a calculated higher than true mass loss in the PM$_1$ lens. On the other
hand, it is possible that super-micron particles are more prone to particle bounce (Liu et al.,
2013). Despite the uncertainties related to this calculation, the importance of measuring the
PM$_{2.5}$ fraction in China is clear, especially during extreme haze events, where 39 ± 5 % of the
mass would have been lost in the PM$_1$ lens.

Figure 3.4: Bottom panel: time series of the AMS species and eBC mass concentrations for the full
measurement period; medium panel: ratio between the NR mass that would have been
measured using a PM$_1$ lens and the total mass measured with the PM$_{2.5}$ lens; top panel:
measured visibility.
As different emission sources can be present in the two measurement locations and some characteristics of the aerosols are expected to be distinct during the extreme haze periods, results are presented below for four different time frames: (1) Xi’an extreme haze (17–26 December 2013), (2) Xi’an reference (13 December 2013 to 6 January 2014, excluding extreme haze), (3) Beijing extreme haze (15–17 January 2014, with a small gap of some hours) and (4) Beijing reference (9–26 January 2014, excluding extreme haze). Table A.2 contains a summary of the mean concentrations of all measured compounds and OA sources during the four time periods.

The median diurnal trends of the AMS species and eBC are shown in the top panel of Fig. 3.5 (see the 25th and 75th percentiles in Fig. A.9). The extreme haze events in Beijing occurred twice over night and therefore the diurnals are incomplete and hard to interpret. The diurnal trends are rather flat during the extreme haze in Xi’an, and exhibit more variation (with maximum concentrations at night) for the reference periods in Xi’an and Beijing. This variation is strongly influenced by the evolution of the planetary boundary layer height (which governs the vertical dilution of pollutants) and by the diurnal cycle of the emissions. During the reference periods, the increased solar radiation induces the development of the mixing layer during daytime, and therefore the dilution of the pollutants. At night, the pollutant concentrations increase as a result of additional emissions in an increasingly shallower planetary boundary layer. During extreme haze periods, less solar radiation reaches the Earth’s surface (see Fig. A.10) and therefore dilution is reduced and particle concentrations remain elevated throughout the day.

Another important characteristic of the extreme haze events is the size of the measured particles. On average larger particles were detected during the extreme haze periods (size distribution modes at about 800 nm in Xi’an and between 800 and 1000 nm in Beijing) than during the reference periods (distribution modes at about 400 nm for both cities, Fig. 3.5).

As mentioned above, the mass of all aerosol components increased considerably during the extreme haze periods. The measured mean concentrations (and standard deviations) were 537 ± 146 and 243 ± 47 µg m⁻³ during the extreme haze periods in Xi’an and Beijing, and 140 ± 99 and 75 ± 61 µg m⁻³ for the reference periods in Xi’an and Beijing, respectively. As shown by the relative contributions in the bottom panel of Fig. 3.5, the increase in mass during the extreme haze events is particularly high for the inorganic species (NO₃, SO₄, NH₄ and Cl) and therefore, the resulting ratio of inorganic (inorg) to organic (org) species is much higher during the extreme haze periods. Specifically, inorg-org ratios of 1.3 and 1.4 were obtained for the extreme haze conditions in Xi’an and Beijing, while the ratio dropped to 0.6 and 0.8 for the reference periods in Xi’an and Beijing, respectively. The mass concentration and relative contribution of eBC is higher in Xi’an than in Beijing, probably due to a higher contribution of older cars in Xi’an.
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3.4.2 OA sources

In this section the final results of the OA source apportionment are presented. All results are averages of all $\alpha$ value combinations that were accepted using the methodology described in Sect. 3.3. The absolute concentrations and relative contributions of the OA sources over time are shown in Fig. 3.6a together with the time series of external tracers. The absolute concentrations of the sources have rather small variability across all good solutions (see Fig. A.11). The mean OA concentrations and relative contributions of the identified OA factors are shown in Fig. 3.6b for the four periods of interest. Lastly, the daily patterns of the absolute concentrations of the identified OA factors and the external tracers are reported in Fig. 3.7. Similar to the inorganic species and total OA, the diurnals of the OA factors are partially driven by the PBL dynamics, with increased dilution during daytime and accumulation of the particulate mass overnight. Nevertheless, some factor-dependent differences are evident. The 25th and 75th percentiles of these diurnals and the standard deviation among all considered $\alpha$ value combinations are reported in Fig. A.12. A potential source contribution function (PSCF)
analysis was performed to explore the geographical origin of the air masses during the measurements and to identify source regions and other transport-related pollution events (see Fig. A.13).

**OOA.** A pronounced increase in the OOA mass concentration is observed during the extreme haze periods (blue background in Fig. 3.6a), reflecting the importance of secondary organic aerosol formation under these conditions. This increase in mass is also reflected in an enhanced relative contribution of OOA to total OA during the extreme haze periods (from 16.2 ± 1.1 to 31.3 ± 1.5 % in Xi’an and from 15.7 ± 0.7 to 25.0 ± 1.2 % in Beijing). In terms of the diurnal trends, for all examined periods OOA concentrations remain rather constant during the day with only a slight increase in the late morning and afternoon. These increases are most probably related to regional production of OOA due to enhanced photochemical activity. These results are in agreement with the PSCF results, where shorter backward air mass trajectories during the extreme haze period in Xi’an indicate that regional emissions (within around 1000 km) might play a dominant role during the extreme haze. OOA concentrations are higher with northeast winds during the haze period in Xi’an (which might indicate a source region as there is not a characteristic diurnal variation for the wind direction), while for the reference periods in Xi’an and Beijing the OOA shows rather homogeneous spatial distributions.

**COA.** The COA average relative contribution to total OA is generally low for the extreme haze periods (3.6 ± 0.5 % in Xi’an, 5.8 ± 1.0 % in Beijing) and around 10 % (9.3 ± 1.6 % in Xi’an, 11.5 ± 1.9 % in Beijing) for the reference periods. For all four periods, COA shows a very distinct diurnal trend with strong peaks at lunch (between noon and 13:00 local time, LT) and dinner (19:00 to 20:00 LT) times. A small increase in the COA concentrations is also observed in the morning (06:00 to 07:00 LT), coinciding with breakfast time. The fragment ion C₆H₁₀O⁺ at m/z 98 has been suggested among others as a marker ion for the COA factor (Sun et al., 2011; Crippa et al., 2013a). Nevertheless, the correlation between these two components is very poor, especially during the extreme haze period in Xi’an (R² = 0.21, see Table A.1). This low correlation is mostly due to increased concentrations of C₆H₁₀O⁺ over the night hours, when COA decreases to background concentrations. Those night peaks coincide with the enhancement of BBOA, which in our case explains on average about 40 % of the mass of the C₆H₁₀O⁺ fragment. For all periods considered in the PSCF analyses, COA appears to come from a local source.

**CCOA.** Coal emissions are high in Beijing, dominating the OA burden with contributions greater than 45 % of the OA mass (46.8 ± 1.2 and 55.2 ± 1.6 % for extreme haze and reference periods, respectively). In comparison, in Xi’an CCOA is of lower importance (5.7 ± 0.1 and 14.0 ± 0.6 % for extreme haze and reference periods, respectively). The CCOA mass slightly increases during the haze periods (more clearly seen in the case of Xi’an), probably due to the accumulation of primary emissions during the stagnant conditions. CCOA concentrations decrease substantially during daytime, due to dilution of the emissions in a deeper PBL. CCOA
concentrations peak in the morning (at around 09:00 LT) and at night (starting to rise at 18:00 LT), probably due to domestic heating activities. Moreover, the CCOA is characterized by a strong peak in concentrations at around 03:00 to 04:00 LT, especially during the extreme haze period in Beijing. This peak, which is also present in the corresponding BBOA diurnal, might result from the late-night burning emissions in a shallower boundary layer or from the advection of evening emissions from the surrounding areas. The PSCF results indicate that the high concentrations of CCOA (and BBOA) measured at the sampling site in Beijing might be related to air masses coming from the southwest of the sampling site (from the Hebei region).

**BBOA.** Unlike CCOA, BBOA is much more important in Xi’an, comprising about 40 % of the OA mass in the two considered periods (43.4 ± 1.1 and 42.2 ± 1.5 % for extreme haze and reference periods, respectively). In Beijing instead, BBOA represents less than 15 % of the total OA (13.8 ± 0.8 and 8.9 ± 0.3 % for extreme haze and reference periods, respectively). Accordingly, while combustion emissions from domestic heating and cooking predominate the organic aerosol mass at both locations, our results highlight the clear difference in the type of fuel used for burning, with a higher fraction of coal burned in Beijing vs. a higher fraction of biomass burned in Xi’an. BBOA primary emissions appear to accumulate under the stagnant conditions during severe haze events. In particular, in the last days of extreme haze in Xi’an, very high concentrations of BBOA are perceived without a significant increase in eBCwb. Nonetheless, the temporal evolution of BBOA correlates with the ion C2H2O2+ at m/z 60 (overall $R^2 = 0.97$), confirming the assignment to BBOA. This specific episode might be related to special conditions with lower amounts of eBCwb (e.g., from smoldering conditions) or absorbing wood burning organic carbon (e.g., from smoldering conditions or aged emissions, which would result in an overestimation of eBCtr). The characteristics in the diurnal trends of BBOA are similar to those found in CCOA. The dilution of the particles in a deeper PBL during daytime results in a decrease in the BBOA concentration at around 16:00 LT, while peaks related to residential heating appear in the morning (between 09:00 to 10:00 LT) and at night (starting to rise at 18:00 LT). As already mentioned, there is a strong peak at around 03:00 to 04:00 LT in the BBOA signal, which is probably related to the late night biomass burning emissions in a shallower PBL. In Xi’an, the PSCF results show that high concentrations of BBOA (and also HOA and CCOA) are observed when the air parcels are transported to the sampling site from the northwest, indicating a possible major local pollution area northwest of the sampling site. In Beijing BBOA seems to be transported together with CCOA from the southwestern province of Hebei.

**HOA.** Despite the larger vehicle fleet in Beijing, higher concentrations of HOA are noticeable in Xi’an, possibly owing to a higher contribution of older cars. Accordingly, HOA is the third contributing source in Xi’an, explaining about 15 % of the OA mass (16.0 ± 1.6 and 18.3 ± 1.9 % for extreme haze and reference periods, respectively). By contrast, in Beijing, HOA is the least important component together with COA, explaining only around 9 % of the OA mass (8.6 ± 1.3 and 8.7 ± 1.2 % for extreme haze and reference periods, respectively). An
increase in HOA levels can be noticed during the haze periods, related to the accumulation of primary emissions under stagnant conditions. The HOA diurnals show peaks during morning and evening rush-hours (07:00 to 08:00 and 08:00 LT, respectively), as is typically the case for traffic-related pollutants. Additional peaks are observed in the HOA during the night hours (between 23:00 and 06:00 LT). These peaks might be related to truck activity, which is strongly enhanced during the night hours as in both cities truck activity is banned during the day. While during the extreme haze event in Xi’an the PSCF results indicate an HOA source region northwest from the sampling site, homogeneous distributions of the HOA factor are found for the reference periods in both Xi’an and Beijing, indicating a homogeneous distribution of this source.

Figure 3.6: (a) Time series of the OA sources and the external tracers and relative contribution of the different sources over time; (b) mean relative contributions of the OA sources for the four periods of interest. Errors represent the standard deviation among all good a value combinations.
3.4 Results and discussion

3.4.3 Effect of relative humidity on aerosol composition

As previously mentioned, periods identified as extreme haze in this study are characterized by high RH (see Fig. 3.4). We examine in Fig. 3.8 the impact of RH on aerosol concentration and composition following the approach proposed by Sun et al. (2013b). As we have identified different emission patterns in the two cities and the RH was only few times above 60 % in Beijing, the analysis is only performed for the case of Xi’an. In Fig. 3.8a, we display the mass concentrations of the NR aerosol species (top) and of the identified OA sources (bottom) as a function of RH, with RH bins of 10 % increments. The absolute mass concentrations of all aerosol species increase during extreme haze events, i.e. with RH. OA and sulfate show the largest increases compared to nitrate, ammonium and chloride. Among the OA sources, BBOA is strongly enhanced at higher RH, followed by OOA and HOA. In contrast, haze conditions seem to have a marginal impact on CCOA and COA concentrations. To exclude accumulation and dilution effects, we normalize in Fig. 3.8b aerosol species and OA fractions by the sum of the primary OA fractions (i.e., HOA, BBOA, CCOA and COA), as a surrogate for secondary aerosol precursors. For a better illustration, all the ratios were further normalized by their value at the first RH bin (10 – 20 %). At RH below 50 %, none of the normalized aerosol species show a clear trend with increasing RH, while at higher RH only sulfate shows a sizeable increase. A change in the emissions of the different primary sources is also observed, with an increase in the BBOA and HOA contributions during extreme haze events, as described in the previous section. Specifically, during the extreme haze period the contributions of BBOA and
HOA to the total primary OA increase from 47 to 64 % and from 17 to 21 %, respectively, while the contributions of CCOA and COA decrease from 14 to 6 % and from 22 to 8 %, respectively. Therefore, the normalization of the OA fractions produces an apparent increase in HOA and BBOA and a decrease in CCOA and COA with higher RH. These effects cannot therefore be unequivocally attributed to the change in RH. More importantly, although the OOA mass concentration increases from about 10 to 60 µg m$^{-3}$ when RH varies from 50 to 90 %, when normalized to its potential precursors, OOA does not show significant variability with RH. This suggests that unlike sulfate, whose production is highly enhanced in the aqueous phase at high RH, OOA production rates seem to be independent of RH.

Figure 3.8: (a) Average mass concentration of the organic and inorganic species (top) and of the different OA sources (bottom) as a function of RH. (b) Average mass concentration of the OA and inorganic species (top) and of the OA sources (bottom) normalized to the sum of all primary sources (HOA, BBOA, CCOA and COA) and represented as a function of RH. For better representation of the trends, all components were further normalized to their corresponding value in the first RH bin. Note: RH bins of 10 % in all cases.

The strong increase of the normalized sulfate at high RH suggests that aqueous phase oxidation of SO$_2$ could be an important process during extreme haze events. To investigate the oxidation degree of sulfur at different RH, the sulfur oxidation ratio ($F_{SO_4}$, Sun et al., 2006) was
calculated according to Eq. (3.10) (where \( n \) is the molar concentration) and is reported in Fig. 3.9 as a function of RH (note that this plot contains the full campaign data).

\[
F_{SO_4} = \frac{n[SO_4]}{n[SO_4] + n[SO_2]}
\]

(3.10)

As seen in Fig. 3.9, \( F_{SO_4} \) has a clear exponential trend with RH. At RH below 50 \%, \( F_{SO_4} \) is rather constant and low (about 0.045 on average), while for higher RH the oxidation ratio rapidly increases reaching 0.62 on average for the last RH bin (90 – 100 \%). This extremely high oxidation degree of sulfur under high RH is an indication that aqueous phase production of sulfate might play a very important role during extreme haze events in China, in good agreement with the results reported by Sun et al. (2013b) for wintertime in Beijing.

\[\text{Figure 3.9: Sulfur oxidation ratio (} F_{SO_4} \text{) as a function of RH, color-coded by date. Mean (square), median (middle horizontal line), 25th and 75th percentiles (} P_{25} – P_{75} \text{, box) and 10th and 90th percentiles (} P_{10} – P_{90} \text{, whiskers) are reported for each RH bin (10\% step).}\]

### 3.4.4 AMS-PAH sources

To identify all sources emitting PAHs, PMF was performed using the OA matrix as an input, with an additional column containing the total AMS-PAH mass concentration calculated from the AMS. AMS-PAH errors were calculated assuming a Poisson distribution and the goodness of the combination of the two data sets (OA and AMS-PAH) was evaluated examining the model residuals. The AMS-PAH weighted residuals, which are reported in Fig. A.14a, are distributed around zero. However a small increase in their weighted residuals (Fig. A.14b) is observed over night. The average AMS-PAH attribution was 28.9 ± 0.4 \% to BBOA, 57.0 ± 0.7 \% to CCOA and 14.1 ± 0.4 \% to HOA (errors denote the standard deviation from 10 seed runs). The same combined input matrix was afterwards tested in the ME-2 approach, with the HOA profile constrained with an \( a \) value of 0.9, the COA profile constrained with an \( a \) value of 0.6, and the AMS-PAHs unconstrained in all factors. Also in this case the AMS-PAHs were attributed...
to these three combustion sources with similar results (28.6 ± 0.4 % to BBOA, 62.0 ± 0.1 % to CCOA and 9.4 ± 0.3 % to HOA, with errors being the standard deviation among 10 seed runs).

Hence the measured AMS-PAHs in our data set can be fully attributed to biomass burning, coal burning and traffic emissions. Using a linear regression of BBOA, CCOA and HOA to fit the measured AMS-PAHs (see Eq. 3.5 in Sect. 3.3), very similar attributions of the mass are found (27.6 ± 0.7 % attributed to BBOA, 66.4 ± 0.4 % to CCOA and 6.0 ± 0.5 % to HOA). The result of this fit (averaged over all good a value combinations) is shown in Fig. 3.10a together with the total mass of the measured AMS-PAHs. As it can be seen from this time series, the linear regression can reconstruct the measured AMS-PAHs very precisely ($R^2 = 0.94$) and peaks of over 10 µg m$^{-3}$ of AMS-PAHs can be attributed to the combined biomass burning, coal combustion and traffic emissions. The high AMS-PAH concentrations lead to high AMSPAH to OA ratios (1.9 ± 0.7 % in Xi’an and 4.4 ± 2.2 % in Beijing) compared to previously reported values for Europe. This can be related to the different methodologies used to measure PAHs (e.g., volatilization of semi-volatile PAHs and oxidation of PAHs on filters). Moreover, in our case combustion sources, especially coal burning, explain a very large fraction of OA, which would enhance the AMS-PAH to OA ratio compared to Europe. In this regard, Chen et al. (2005) reported mean PAH to OC ratios of 28 % (i.e., PAH/OA of 17.5 % assuming OA/OC of 1.6) for bituminous coal and 0.8 % (i.e., PAH/OA of 0.5 %) for anthracite. Considering that a mixture of these two types of coal is used in the cities considered in this work and that the relative contribution of coal to the total OA is higher in Beijing than in Xi’an, the obtained AMS-PAH to OA ratios seem reasonable.

Figure 3.10b presents the average AMS-PAHs concentrations and relative contributions of the three combustion sources to the measured AMS-PAHs for the different measurement periods. During the extreme haze event in Xi’an, 63.8 ± 1.1 % of AMS-PAHs are attributed to biomass burning, 25.3 ± 0.4 % to coal combustion, and the rest (10.9 ± 0.9 %) to traffic emissions. For the reference period the contribution of coal increases to about 55.9 ± 0.9 %, the biomass burning influence decreases to around 36.4 ± 1.4 % and the traffic remains a minor contributor, explaining about 7.7 ± 0.8 % of the AMS-PAHs mass. In Beijing, coal emissions completely dominate over biomass burning and traffic emissions, and on average 88.1 ± 1.1 and 94.1 ± 0.3% of the measured AMS-PAHs can be attributed to coal during the extreme haze and reference periods, respectively. These results are in agreement with Huang et al. (2014), showing that coal burning emission is an asymmetric source of PAHs, compared to other combustion emissions.
3.5 Discussion and conclusions

This work presents a thorough analysis of extreme haze events (visibility below 2 km) which occurred in Xi’an and Beijing during winter 2013–2014. Online aerosol mass spectrometer analyses provided a detailed characterization of the chemical composition and size distribution of the aerosol components during the different measurement periods.

The extreme haze events were caused by a combination of primary emissions of particulate matter, generation of secondary aerosol, and stagnant meteorological conditions which confined the pollutants in the basin. Under such conditions, the mass concentrations of all aerosol components strongly increased, with resulting average PM$_{2.5}$ mass concentrations of 537 ± 146 µg m$^{-3}$ in Xi’an and 243 ± 47 µg m$^{-3}$ in Beijing (in contrast to 140 ± 99 and 75 ± 61 µg m$^{-3}$ average NR-PM$_{2.5}$ mass measured during the reference periods in Xi’an and Beijing, respectively). Among all aerosol components, sulfate and nitrate show the strongest enhancements during the extreme haze periods. Moreover, source apportionment of the organic aerosol (OA) fraction shows that also the formation of oxygenated organic aerosols (OOA) is strongly enhanced during the haze events. The high relative humidity characteristic of the periods with extreme haze was shown to favor the heterogeneous oxidation of SO$_2$ in deliquesced aerosols and can therefore drive the drastic increase in sulfate concentrations. In contrast, aqueous phase processing appears not to significantly affect the formation of OOA and the other inorganic species.
Another distinct feature of the aerosols during extreme haze events is their larger size compared to particles during lower pollution periods (the distribution mode of all NR aerosol compounds shifts from around 400 nm during the reference periods to about 800 to 1000 nm during extreme haze events in both cities). The growth of the particles is associated with high secondary aerosol fractions and condensation of semi-volatile compounds on preexisting particles. Given the large mean aerosol diameters found during the extreme haze periods, the use of a PM$_{2.5}$ inlet for the AMS was a crucial point for the meaningfulness of our results, as 39 ± 5 % of the mass would have been neglected if a standard PM$_{1}$ inlet had been deployed.

The use of a novel source apportionment technique (ME2), together with a systematic analysis focused on minimizing the effect of user subjectivity on the solution, allowed for the separation of the several primary sources of OA in the two cities under study. Compared to previous studies at a single site where the simultaneous extraction of coal and biomass burning factors is exceedingly challenging, this separation was possible here by including measurements at two contrasted sites with different exposure patterns. Our source apportionment results suggest that biomass burning (from domestic heating and agricultural activities) is a major source of OA in Xi’an during wintertime (representing 42 to 43 % of the OA mass), while coal emissions (from domestic heating, cooking and industrial processes) dominate the OA mass in Beijing (47 to 55 %). Coal combustion and biomass burning were also the major cause for very high concentrations of AMS-PAHs (on average 2.1 µg m$^{-3}$), known to be highly carcinogenic. Moreover, PSCF analyses indicate that these coal-related particles are at least partially transported from the industrial province of Hebei to the highly populated capital. Oxygenated organic aerosol (related to secondary processes) is also found to be an important contributor to the measured OA mass, mostly during the extreme haze events. The relative contribution of OOA increases from 16 to 31 % and from 16 to 25 % of OA mass during the extreme haze events in Xi’an and Beijing, respectively. Traffic emissions have a slightly larger impact in Xi’an (representing 15 to 20 % of the OA) than in Beijing (about 9 % of the OA), while cooking is a rather minor source in both cities (explaining 5 to 10 % of the OA mass). Considering these results, major efforts should be put into regulating more thoroughly the biomass and coal burning activities widely spread in urban areas in China and regulating the gaseous precursor emissions of organic and inorganic aerosols.

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Urban increments of gaseous and aerosol pollutants and their sources using mobile aerosol mass spectrometry measurements

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Chapter 4 Urban increments of gaseous and aerosol pollutants

Abstract

Air pollution is one of the main environmental concerns in urban areas, where anthropogenic emissions strongly affect air quality. This work presents the first spatially resolved detailed characterization of PM$_{2.5}$ (particulate matter with aerodynamic equivalent diameter $d_{\text{aero}} \leq 2.5$ μm) in two major Estonian cities, Tallinn and Tartu. The measurements were performed in March 2014 using a mobile platform. In both cities, the non-refractory (NR)-PM$_{2.5}$ was characterized by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) using a recently developed lens which increases the transmission of super-micron particles. Equivalent black carbon (eBC) and several trace gases including carbon monoxide (CO), carbon dioxide (CO$_2$), and methane (CH$_4$) were also measured. The chemical composition of PM$_{2.5}$ was found to be very similar in the two cities. Organic aerosol (OA) constituted the largest fraction, explaining on average about 52 to 60 % of the PM$_{2.5}$ mass. Four sources of OA were identified using positive matrix factorization (PMF): hydrocarbon-like OA (HOA, from traffic emissions), biomass burning OA (BBOA, from biomass combustion), residential influenced OA (RIOA, probably mostly from cooking processes with possible contributions from waste and coal burning), and oxygenated OA (OOA, related to secondary aerosol formation). OOA was the major OA source during nighttime, explaining on average half of the OA mass, while during daytime mobile measurements the OA was affected by point sources and dominated by the primary fraction. A strong increase in the secondary organic and inorganic components was observed during periods with transport of air masses from northern Germany, while the primary local emissions accumulated during periods with temperature inversions. Mobile measurements offered the identification of different source regions within the urban areas and the assessment of the extent to which pollutants concentrations exceeded regional background levels (urban increments). HOA, eBC, CO$_2$, and CO showed stronger enhancements on busy roads during the morning and evening traffic rush hours; BBOA had its maximum enhancement in the residential areas during the evening hours and RIOA was enhanced in both the city center (emissions from restaurants) and in the residential areas (emissions from residential cooking). In contrast, secondary components (OOA, sulfate (SO$_4$), nitrate (NO$_3$), ammonium (NH$_4$), and chloride (Cl)) had very homogeneous distributions in time and space. We were able to determine a total PM$_{2.5}$ urban increment in Tartu of 6.0 μg m$^{-3}$ over a regional background concentration of 4.0 μg m$^{-3}$ (i.e., a factor of 2.5 increase). Traffic exhaust emissions were identified as the most important source of this increase, with eBC and HOA explaining on average 53.3 and 20.5 % of the total increment, respectively.

4.1 Introduction

Atmospheric particulate matter (PM) plays a central role in many environmental processes through its influence on climate (radiative forcing; Myhre et al., 2013), the hydrological cycle (Ramanathan et al., 2001), and its adverse effects on health (Pope and Dockery, 2006). Major attention has been devoted to the study of the PM$_{2.5}$ fraction (particulate matter with an aerodynamic equivalent diameter $d_{\text{aero}} \leq 2.5$ μm), which has been linked to increased lung cancer rates (Hu and Jiang, 2014), acute bronchitis and asthma (M. Gao et al., 2015), and
4.1 Introduction

mortality (Dockery et al., 1993; Laden et al., 2006). Atmospheric particles can be classified as primary or secondary aerosols according to their formation processes. Primary particles are directly emitted, while secondary aerosols are formed from gas-phase precursors following chemical transformation in the atmosphere. Aerosols can be further classified in terms of their emission sources as natural sources (e.g., volcanic eruptions, wildfires, sea salt, dust, or biogenic emissions from plants) or anthropogenic sources (mostly from combustion processes, e.g., traffic and residential wood combustion).

Due to enhanced contributions of anthropogenic sources, air quality is commonly lower in urban areas compared to rural or suburban locations (Putaud et al., 2004). In Europe, annual average PM$_{2.5}$ mass concentrations in urban areas commonly vary between a few µg m$^{-3}$ up to 35 µg m$^{-3}$ (Putaud et al., 2010). The predominance of specific aerosol sources (e.g., residential, traffic, industry) or the implementation of new technologies (e.g., car fleet, heating systems) may strongly influence the levels and physicochemical characteristics of the pollutants in these locations. Moreover, certain orographic features and stagnant meteorological conditions may induce the accumulation of local pollutants (Putaud et al., 2004; Carbone et al., 2010; Squizzato et al., 2012). Likewise, long-range transport of continental air masses has been shown to influence PM in different urban areas in Europe (Niemi et al., 2009; Baker, 2010; Salvador et al., 2013; Beekmann et al., 2015; Di Gilioa et al., 2015; Ulevicius et al., 2016). While the PM levels and physicochemical properties of the particles are well characterized in Western Europe, data are scarce in Eastern European cities, especially in the Baltic region, hindering air quality assessment and quantification of the main aerosol sources.

In contrast to conventional stationary measurements, mobile measurements (including zeppelin, aircraft, and ground measurements) are suited for pollutant mapping, chasing of mobile sources or measurements in emission plumes, etc. Ground-based measurements by mobile platforms have been successfully performed in the last years to measure particles and trace gases from real-world traffic emissions (Bukowiecki et al., 2002, 2003; Pirjola et al., 2004, 2006, 2012; Kwak et al., 2014; Kyung Hwan et al., 2015) and from wood burning emissions (Pirjola et al., 2015). More recently, aerosol mass spectrometers (AMSs) have been deployed in mobile laboratories in order to determine the physical and chemical properties of submicron aerosols (PM$_{1}$, particulate matter with aerodynamic equivalent diameter $d_{aero}$ ≤ 1 µm) in urban environments like Zurich (Mohr et al., 2011), Paris (Von der Weiden-Reimmüller et al., 2014a, b), or Barcelona (Mohr et al., 2015). Moreover, a newly developed inlet for the AMS has been used to measure the chemical composition of the non-refractory (NR)-PM$_{2.5}$ fraction in the Po Valley (Wolf et al., 2015).

In this work we present the first detailed in situ mass spectrometric measurements of air pollutants in the two biggest cities in Estonia (Tallinn and Tartu). The measurements were performed using the Paul Scherrer Institute (PSI) mobile laboratory (Bukowiecki et al., 2002; Mohr et al., 2011; Wolf et al., 2015). The use of a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) with a novel PM$_{2.5}$ lens offered a detailed characterization of the NR-PM$_{2.5}$ fraction in the measurement areas. The spatial distributions of the sources of organic aerosols (OA), inorganic aerosols (nitrate (NO$_3$), sulfate (SO$_4$), ammonium (NH$_4$), and
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chloride (Cl)), equivalent black carbon (eBC), and some of the major gas-phase components (carbon monoxide (CO), carbon dioxide (CO₂), and methane (CH₄)) were determined in the urban areas. Such analyses allowed for the calculation of regional background and urban concentrations of the different gas- and particle-phase components and provided direct insights into the spatial resolution of local emissions and their impact on the air quality in different city areas. Long-range transport of pollutants and accumulation events as well as their effect on the particle- and gas-phase mass concentrations will also be discussed.

4.2 Methodologies

4.2.1 Measurement campaign

The measurements were performed in the two biggest cities in Estonia. Tallinn, the capital and the largest city of Estonia, has a population of 413 000 inhabitants (Statistical Database, 2015) and occupies an area of 158.3 km². Located on the northern coast of the country, Tallinn has some of the biggest ports in the Baltic Sea. Among them, the old city harbor is one of the busiest passenger harbors in the region. Tartu, with an area of 38.8 km² and more than 97 000 inhabitants in 2015 (Statistical Database, 2015), is the second largest city in Estonia. The city is situated in the center of southern Estonia, in the post glacial valley of the Emajõgi River, which influences the local meteorological conditions and favors the accumulation of local pollutants under frequent temperature inversions. Previous studies identified traffic emissions and residential heating as the major sources of air pollution in these two cities (Urb et al., 2005; Orru et al., 2011). An older vehicle fleet, the limited network capacity of the city streets (which generates congestions during rush hours), and the extensive use of studded tires have been reported to strongly enhance the signal of traffic emissions in the city center and major roads (Urb et al., 2005; Orru et al., 2011). Residential heating includes extensive use of inefficient wood and coal stoves with low stacks in both cities. In this regard, a detailed modeling study performed in Tallinn and Tartu (Orru et al., 2011) revealed that the city centers and the neighborhoods with local heating are exposed to much higher average PM₂.₅ concentrations compared to other areas of the cities.

The measurements took place from 10 to 17 March 2014 in Tartu and from 25 March to 1 April 2014 in Tallinn. Emission maps including residential wood combustion and industrial sources and the traffic emission rates in the major streets of the two cities are reported in Fig. B.1 in the Appendix. The driving routes were chosen in order to cover heavily trafficked roads, residential areas, and background sites with little local emissions. In Tallinn, streets close to the old town harbor were also included in the route. To obtain statistically significant spatial distributions of the major pollutants, 25 loops were performed at each location throughout the measurement periods at different times of the day. The average loop duration was about 72 min in Tartu and 112 min in Tallinn. Stationary measurements were typically performed overnight at a gasoline station in Tartu (influenced by city center and residential emissions) and at the Estonian Environmental Research Centre (EERC) in Tallinn (a background site). Meteorological data were recorded on a meteorological tower in Külitsa (around 10 km southeast from Tartu) and in the Tartu and Tallinn Zoo meteorological stations.
The most relevant parameters (including wind direction and speed, temperature, and precipitation) are reported in Fig. B.2 in the Appendix.

### 4.2.2 Mobile laboratory setup

A schematic of the instrumental setup in the PSI mobile platform is shown in Fig. B.3. The main inlet of the mobile platform was kept at a constant velocity of $\sim 11$ m s$^{-1}$ for isokinetic sampling during driving conditions, assuming an average velocity in the city of $\sim 40$ km h$^{-1}$. Two different inlet lines connected the main inlet to the aerosol and gas-phase instrumentation. The size cutoff of the inlet system was estimated to be around 5 $\mu$m. The deployed instruments, measured parameters and their time resolution are listed in Table 4.1. All parameters were determined with high time resolution (between 1 and 25 s), critical for the identification of source regions using a mobile platform.

An HR-ToF-AMS (Aerodyne Research Inc.) was deployed to measure the chemical composition of the NR-PM$_{2.5}$ aerosol, including NO$_3$, SO$_4$, NH$_4$, Cl, and OA. For this work, the AMS was equipped with a recently developed aerodynamic lens which extends the measured particle size to the PM$_{2.5}$ fraction (in contrast to the conventional PM$_1$ lens). The PM$_{2.5}$ lens efficiently transmits particles between 80 nm and up to at least 3 $\mu$m and has been well characterized by Williams et al. (2013) and tested in previous chamber and ambient studies (Wolf et al., 2015; Elser et al., 2016). The operating principle of the instrument can be found elsewhere (DeCarlo et al., 2006). A fumigation drier (Perma Pure MD-110) was set before the AMS inlet in order to dry the ambient particles and reduce uncertainties in the bounce-related collection efficiency (CEb) and possible transmission losses of large particles at high relative humidity.

A seven-wavelength Aethalometer (Magee Scientific, model AE33) was used to measure the aerosol light absorption and to determine the eBC concentrations. The measurement at seven different wavelengths (370, 470, 520, 590, 660, 880, and 950 nm) covers the range between ultraviolet and infrared and allows for the source apportionment of different eBC fractions (Sandradewi et al., 2008a; Zotter et al., 2015). Moreover, the dual spot measurement method automatically corrects for the loading effect and provides a real-time calculation of the loading compensation parameter (Drinovec et al., 2015).

The gas concentrations were measured by a Picarro-G2301 CO/CO$_2$/ CH$_4$ analyzer and a Licor-6262 CO$_2$ monitor. In addition, some important parameters for mobile measurements (GPS, temperature, relative humidity, and solar radiation) were also measured continuously.

<table>
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<th>Time resolution</th>
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<td>Size resolved chemical composition of NR-PM$_{2.5}$ eBC (absorption coefficient at 7(\lambda))</td>
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<td>Others</td>
<td>GPS, temperature, relative humidity, and solar radiation</td>
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4.2.3 AMS data analysis

AMS data were analyzed in Igor Pro 6.3 (WaveMetrics) using the standard ToF-AMS Data Analysis toolkit (SQUIRREL version 1.53G and PIKA version 1.12G). Based on standard NH₄NO₃ calibrations, the ionization efficiency (defined as ions detected per molecules vaporized) was determined to be 5.08 x 10⁻⁸ (average of five calibrations during the full measurement period). Standard relative ionization efficiencies (RIEs) were used for nitrate, chloride, and organics (RIE = 1.1, 1.3, and 1.4, respectively) and experimentally determined for sulfate and ammonium (RIE = 1.11 and 4.29, respectively). A composition-dependent CE algorithm by Middlebrook et al. (2012) was used in the calculation of ambient mass concentrations (Middlebrook et al., 2012).

4.2.4 Source apportionment techniques

4.2.4.1 OA source apportionment

To identify and quantify the major sources of OA in the different measurement areas, positive matrix factorization (PMF; Paatero and Tapper, 1994) was applied to the time resolved AMS data (see Table 4.1). The analysis was performed using the multilinear engine tool (ME-2; Paatero, 1997) implemented in the Source Finder interface (SoFi; Canonaco et al., 2013) coded in Igor Wavesmetrics.

PMF is a bilinear unmixing algorithm which, as defined in Eq. (4.1), allows the representation of a two-dimensional matrix of measured data (X) as a linear combination of a given number of static factors profiles (F) and their corresponding time series (G). The matrix E in Eq. (4.1) contains the model residuals. The model uses a least squares approach to iteratively minimize the object function Q described in Eq. (4.2):

\[ X = G \times F + E \]  \hspace{1cm} (4.1)

\[ Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left( \frac{e_{ij}}{\sigma_{ij}} \right)^2 \]  \hspace{1cm} (4.2)

where \( e_{ij} \) are the elements of the error matrix (E) and \( \sigma_{ij} \) are the respective uncertainties of X.

In our case, the model input are the data and error matrices of OA mass spectra, where the rows represent the time series (62,665 points, with steps of 25 s) and the columns contain the fits to the high-resolution data (292 ions). The organic mass obtained from the high-resolution fits (up to m/z 115) agrees with the mass calculated from the unit mass resolution integration (up to m/z 737) within ± 5%. The initial error values were calculated with the HR-AMS data analysis software PIKA. A minimum error corresponding to the measurement of a single ion was applied (Ulbrich et al., 2009). All variables with signal-to-noise ratio (SNR) lower than 0.2 were removed and the variables with SNR between 0.2 and 2 were down-weighted by
increasing their error by a factor of 3 (Paatero and Hopke, 2003). Moreover, all variables directly calculated from the CO$_2^-$ fragment using the organic fragmentation table (i.e., O$^-$, HO$^-$, H$_2$O$^-$, and CO$^-$) (Allan et al., 2004) were excluded from the PMF analysis to appropriately weight the variability of the CO$_2^-$; these ions were reinserted post-analysis.

The possibility of local minima in the solution space and the uncertainty of the PMF solution were investigated by means of bootstrap analysis. This statistical method is based on the creation of replicate datasets resulting from the perturbation of the original data by resampling. In each replicate, some randomly chosen rows of the original matrix are present several times, while other rows are removed (Paatero et al., 2014), such that the dimension of the data matrix is kept constant. This resulted in about 64% of the original points being used in each replicate. PMF was applied to 100 different replicates and the variations among these results were used to estimate the uncertainty of the initial PMF solution. Note that each bootstrap run is started from a different initialization point; thus, this methodology inherently includes the investigation of the classic seed variability. All convergent solutions were found to be consistent, suggesting that the solution is robust.

The results presented in this section were obtained by merging the measurements from the two measurement locations, as no major changes were observed if the source apportionment was performed for the individual cities.

4.2.4.2 eBC source apportionment

The Aethalometer measurements can be used to separate eBC from wood burning (eBC$_{wb}$) and from traffic (eBC$_{tr}$), by taking advantage of the spectral dependence of absorption, as described by the Ångström exponent (Ångström, 1929). Specifically, the enhanced absorption of wood burning particles in the ultraviolet and visible wavelengths region (370–520 nm) relative to that of traffic particles is used to separate the contributions of the two fractions. This method is described in detail in Sandradewi et al. (2008a) and has been successfully applied at many locations across Europe (Favez et al., 2010; Herich et al., 2011; Sciare et al., 2011; Crilley et al., 2015). For a proper separation of the eBC fractions, the Aethalometer data were averaged to 30 min in order to increase the SNR. Thus, the obtained fractions eBC$_{wb}$ and eBC$_{tr}$ could only be used for the correlations with the external tracers, but their spatial distributions could not be explored. The absorption Ångström exponent was calculated using the absorption measured at 470 and 950 nm and Ångström exponents of 0.9 and 1.7 were used for traffic and wood burning, respectively. More details on the choice of the wavelengths and Ångström exponents are presented in the Supplement.

4.3 Results and discussion

4.3.1 Pollutant concentrations and temporal variability

The temporal variation of all measured gas- and particle-phase components is shown in Fig. 4.1a. The type of measurement is indicated by different background colors (transparent for stationary measurements and orange for mobile measurements). The measurement period
included three distinct meteorological periods of transport of polluted air masses and accumulation of local emissions. These periods are referred to as special events (indicated by a red frame) and will be treated separately and discussed in detail in Sect. 4.3.4. While the AMS and Aethalometer were running almost continuously during the entire measurement period, there is a small gap in the CO₂, CO, and CH₄ data due to an instrument malfunction. Over the full measurement period, the average mass concentration of PM₂.₅ (NR-PM₂.₅ plus eBC) was 12.3 µg m⁻³. In the gas-phase, average concentrations of 414.1 ppm of CO₂, 0.24 ppm of CO, and 1.92 ppm of CH₄ were measured. In contrast to these relatively low average values, extremely high concentrations were often recorded during the mobile measurements due to local emissions from point sources (around 50 spikes with PM₂.₅ mass concentration exceeding 100 µg m⁻³). Such intermittent pollution plumes (expected in some areas in a city) cannot be detected from stationary measurements at an urban background site but may be associated with negative health impacts. As shown in Fig. 4.1b, neglecting the periods defined as special events, the PM₂.₅ average concentrations and relative contributions of the particle-phase species were very similar at the two locations. If we compare daytime (07:00 to 19:00, local time (LT)) and nighttime (19:00 to 07:00 LT) measurements, in both cities the average PM₂.₅ was higher during the day (11.0 µg m⁻³ in Tartu and 11.6 µg m⁻³ in Tallinn) than during the night (6.5 µg m⁻³ in Tartu and 7.1 µg m⁻³ in Tallinn) despite the development of the boundary layer and increased dilution during daytime. OA constituted in all cases the largest mass fraction, explaining on average 52.2 and 54.3 % of the PM₂.₅ mass in Tartu (during night- and daytime, respectively) and 55.2 and 60.1 % in Tallinn (during day- and nighttime, respectively). Primary emissions of eBC contributed on average 20.4 and 33.7 % in Tartu (during day- and nighttime respectively) and 13.4 and 26.9 % in Tallinn (during day- and nighttime, respectively), constituting a substantially higher fraction than at other European locations (Putaud et al., 2010). The remaining mass, 12 to 28 %, was related to secondary inorganic species, mostly ammonium sulfate and nitrate. These species were found to be neutralized within the uncertainties (ratio of NH₄ expected from an ion balance to NH₄ measured of 1.05, with R² = 0.95). During nighttime a decrease in the relative contribution of eBC was observed in favor of an enhanced contribution of the inorganic species.
4.3.2 Sources of OA

To properly represent the temporal variations of the OA, four factors were required: hydrocarbon-like OA (HOA), biomass burning OA (BBOA), residential influenced OA (RIOA), and oxygenated OA (OOA). The mass spectra of these factors are reported in Fig. 4.2. HOA is a primary source related to traffic emissions and its mass spectrum is characterized by the presence of alkyl fragment signatures (Ng et al., 2011), with prominent contributions of non-oxygenated species at m/z 43 (C\textsubscript{3}H\textsubscript{7}+), m/z 55 (C\textsubscript{4}H\textsubscript{7}+), and m/z 57 (C\textsubscript{4}H\textsubscript{9}+). As shown in Fig. B.4, a fairly good correlation is found between HOA and eBC\textsubscript{tr} (R\textsuperscript{2} = 0.4). Moreover, the ratio of HOA to eBC\textsubscript{tr} was 0.5, which is in good agreement with previous European studies (El Haddad et al., 2013, and references therein). BBOA is associated with domestic heating and/or agricultural biomass burning activities and shows characteristic high contributions of the oxygenated hydrocarbons at m/z 60 (C\textsubscript{6}H\textsubscript{10}O\textsuperscript{+}) and m/z 73 (C\textsubscript{7}H\textsubscript{12}O\textsuperscript{+}), which are known fragments from anhydrous sugars (Alfarra et al., 2007). BBOA correlates fairly well with eBC\textsubscript{wb} (R\textsuperscript{2} = 0.4), and the ratio of BBOA to eBC\textsubscript{wb} was 4.0 (Fig. B.4), which within the method uncertainties is consistent with previously reported values (Crippa et al., 2013b). The ratio BBOA to eBC\textsubscript{wb} was found to be very sensitive to the chosen Ångström exponent for traffic, and it increased to 4.8 when a slightly higher Ångström exponent (i.e., 1.0 instead of 0.9) was considered for traffic. RIOA is a hydrocarbon-rich factor that was required for a reasonable explanation of the variability in the data. Due to its increase in the residential areas, this factor was associated with residential emissions. Given its strong correlation (R\textsuperscript{2} = 0.9) with cooking markers such as the fragment ion C\textsubscript{6}H\textsubscript{10}O\textsuperscript{+} at m/z 98 (Sun et al., 2011; Crippa et al., 2013a), we expect that a great part of this factor is related to cooking emissions (see Fig. B.4).
Moreover, as in previously reported cooking spectra (Mohr et al., 2012), the RIOA mass spectrum shows a higher m/z 55 to m/z 57 ratio than HOA. However, in the absence of diurnal trends due to the driving conditions, the separation of cooking emissions from other residential emissions (such as domestic coal and waste burning) was not possible. OOA is associated with aged emissions and secondary organic aerosol formation, and its profile is characterized by a very high m/z 44 (CO$_2$). In general, OOA increases simultaneously with the secondary species (especially NO$_3$), but the ratio among these components changes during special events (Fig. B.4).

Figure 4.2: Mass spectra of the four OA sources identified with PMF. From top to bottom: hydrocarbon-like OA (HOA), biomass burning OA (BBOA), residential influenced OA (RIOA), and oxygenated OA (OOA). Error bars indicate the standard deviation among 100 bootstrap runs.

Table 4.2: Correlation coefficients ($R^2$) between the OA profiles from the four-factor solution and literature profiles. The different nomenclatures used in the literature for the OOA factors have been homogenized to a semi-volatile OOA (SVOOA) and a low-volatility OOA (LVOOA).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HOA-HOA</td>
<td>0.82</td>
<td>0.96</td>
<td>0.72</td>
<td>0.78</td>
</tr>
<tr>
<td>BBOA-BBOA</td>
<td>0.86</td>
<td>0.68</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RIOA-COA</td>
<td>–</td>
<td>0.83</td>
<td>–</td>
<td>0.81</td>
</tr>
<tr>
<td>OOA-SVOOA</td>
<td>0.96</td>
<td>0.72</td>
<td>0.90</td>
<td>0.71</td>
</tr>
<tr>
<td>OOA-LVOOA</td>
<td>0.91</td>
<td>0.93</td>
<td>0.94</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Some important diagnostic parameters of the source apportionment (including $Q/Q_{exp}$, factor–marker correlation, and time series and profile residuals for solutions with different number of factors) are reported in Fig. B.5. The correlation coefficients ($R^2$) between factors and markers significantly increase when a fourth factor is included but are not improved when a fifth factor is added. The addition of the fourth factor, which enabled the extraction of RIOA, allows explaining additional structures in the residuals’ time series and unsaturated fragments in the residuals mass spectrum. Including a fifth factor also improves the model mathematical quality by additionally explaining $C_{xH_yN_w}$ and biomass burning (at $m/z$ 60 and 73) related fragments. The additionally extracted factor in the five-factor solution, referred to as “unknown”, has elevated contributions from oxygenated fragments often related to secondary organic aerosols ($m/z$ 44) and BBOA ($m/z$ 60 and 73) but also a time series that unambiguously relates this factor to a spatially variable primary emission source. In effect, the majority (62 %) of this factor contribution arises from a split in the BBOA factor from the four-factor solution (the rest comes from the residuals and the OOA). Moreover, the sum of the contributions of the “unknown” factor and the BBOA from the five-factor solution matches the BBOA contributions from the four-factor solution ($R^2 = 0.97$ and slope = 1.15 as shown in Fig. B.6). This split in the BBOA is very likely a direct consequence of the variable nature of this combustion source, but the two BBOA-like factors extracted in the five-factor solution could not be related to different emission processes. Furthermore, the addition of this factor did not affect the spectral profiles and time series of the other factors and their correlations with their respective markers and did not aid the interpretation of the data. Therefore, we considered the four-factor solution as an optimal representation of our data. Table 4.2 contains the correlation coefficients ($R^2$) between the OA profiles from the four-factor solution and available literature profiles (Aiken et al., 2009; Mohr et al., 2012; Setyan et al., 2012; Crippa et al., 2013a). The high correlations obtained in all cases support the use of a four-factor solution and strengthen the link between the RIOA and cooking emissions ($R^2$ of about 0.8 between RIOA and cooking tracer).

Figure 4.3a represents the time series of the absolute mass (top panel) and relative contributions (bottom panel) of the retrieved OA sources for the two measurement locations. The variability of these time series over 100 bootstrap runs was relatively low, as shown in Fig. B.9. In both cities, the three primary sources (HOA, BBOA, and RIOA) exhibit a very spiky temporal behavior, while the secondary source (OOA) is characterized by a relatively smooth time series. Figure 4.3b reports the averaged total OA mass and relative contributions of the OA sources during the measurements in Tartu (top panel) and Tallinn (bottom panel). The reported errors (which correspond to the standard deviation among 100 bootstrap runs) are an indication of the high stability of the solution. Overall, the relative errors vary between 3 and 7 %, except for the RIOA, which shows slightly higher variability during nighttime (relative error of 11 % in Tartu and 13 % in Tallinn). Similarly to the total PM$_{2.5}$ mass and as reported in Fig. 4.3b, neglecting the special events, a strong daily cycle can be observed in the total OA mass, with higher concentrations during daytime (6.0 and 6.3 $\mu$g m$^{-3}$ in Tartu and Tallinn, respectively) than during nighttime (3.4 and 4.2 $\mu$g m$^{-3}$ in Tartu and Tallinn, respectively). This difference is mostly driven by the increase of primary aerosol emissions (HOA, BBOA, and RIOA) during the day. This structure is observed independently of the nature
of the measurements (stationary or mobile), indicating that except for the periods where emissions from point sources are sampled, the OA concentrations and sources are rather homogeneous across the sampling area. In terms of relative contribution, OOA is dominant during nighttime, explaining on average between 42 and 44 % of the OA mass in Tartu and Tallinn, respectively. The relative contribution of HOA to total OA mass is higher during daytime (32 % in Tartu and 27 % in Tallinn) than during nighttime (20 % in Tartu and 11 % in Tallinn). RIOA is also enhanced during daytime in Tartu (27 % compared to 20 % during nighttime) and has similar relative contributions for day- and nighttime in Tallinn (20 and 22 %, respectively). In contrast, BBOA shows similar relative contributions for day- and nighttime in Tartu (representing about 17 % of the OA mass) and slightly lower contributions during daytime in Tallinn (20 % during daytime and 25 % at nighttime).

Figure 4.3: (a) Temporal evolution of the absolute mass (top panel) and relative contributions (bottom panel) of the four OA sources over the full measurement period; (b) average OA mass concentrations and relative contributions of the OA sources for the measurements in Tartu (top panel) and Tallinn (bottom panel), with day- and nighttime distinction. Errors indicate the standard deviation among 100 bootstrap runs. Note: special events were excluded.

4.3.3 Spatial distributions, regional background, and urban increments

The average spatial distributions of the four OA sources, SO₄, NO₃, eBC, CO₂, and CO are represented in Figs. 4.4 and 4.5 for Tartu and Tallinn, respectively. The spatial distributions of the additionally measured gas and particle components are reported in Figs. B.10 and B.11. All loops for which all the instruments were running (except CO₂, CO, and CH₄ in Tallinn) were averaged on a grid with grid cells of 250 m². In order to get comparable distributions from different days of measurements, the fifth percentile ($P_{05}$) was subtracted from each single loop for all components. The subtraction of $P_{05}$ was found to be optimal to decrease the variability among different loops enough to make them comparable. However, as it will be discussed in the following, $P_{05}$ was not always sufficient to capture the regional background concentrations. The color scales in Figs. 4.4 and 4.5 represent the averaged enhancement
over the background concentrations of each source/species. For a better visualization, the maximum of the color scale was set at the 75th percentile ($P_{75}$) for $\text{SO}_4$, $\text{NO}_3$, $\text{eBC}$, $\text{CO}_2$, and $\text{CO}$. Moreover, the highest 75th percentile among all OA sources (i.e., 1.2 $\mu$g m$^{-3}$ in Tartu and 2.4 $\mu$g m$^{-3}$ in Tallinn) was used as a maximum for the four OA sources in order to facilitate the comparison among them. Lastly, the sizes of the points represent the number of measurement points that were averaged in each case. The correlation coefficients ($R^2$) between the spatial distributions of all sources and components are reported in Table B.1 in the Appendix.

Figure 4.4: (a) Driving route in Tartu: the red trace represents the GPS data, the yellow star the stationary measurements location, and the blue dots the monitoring stations of the Estonian Environmental Research Institute (EERC); (b) wind conditions during the mobile measurements in Tartu: red traces represent the wind direction and speed for the single loops and the average of all loops is represented in blue; (c to k) average spatial distributions of all identified OA sources (panels c to f) and other measured components (panels g to k) in Tartu. The color scales represent enhancement over the background concentrations; the maximum of the color scales is fixed to the 75th percentile of the average enhancement of each component in panels (g) to (k) and to the highest 75th percentile among all OA sources in panels (c) to (f). The sizes of the points represent the number of points that were averaged in each case.
Figure 4.5: (a) Driving route in Tallinn: the red trace represents the GPS data, the yellow star the stationary measurements location, and the blue dots the monitoring stations of the Estonian Environmental Research Institute (EERC); (b) wind conditions during the mobile measurements in Tallinn: red traces represent the wind direction and speed for the single loops and the average of all loops is represented in blue; (c to k) average spatial distributions of all identified OA sources (panels c to f) and other measured components (panels g to k) in Tallinn. The color scales represent enhancement over the background concentrations; the maxima of the color scales have been fixed to the 75th percentile of the average enhancement of each component in panels (g) to (k) and to the highest 75th percentile among all OA sources in panels (c) to (f). The sizes of the points represent the number of points that have been averaged in each case (note: less data available for CO).
4.3 Results and discussion

Longitude profiles of the enhancements of all considered components were obtained for Tartu by averaging the calculated enhancements in longitude bins (using the same grid of 250 m² as above). These results are shown in Fig. 4.6 (averages and standard deviation among all loops), Fig. B.12 (median and first and third quartiles), and Fig. B.13 (separation of all loops into time bins of 2 h). The longitude profiles in Figs. 4.6 and B.12 allowed for the calculation of regional background concentrations and urban increments, as defined by Lenschow et al. (2001) and reported in Table 4.3. The urban concentrations, which are given by the sum of the regional background and the urban increment, represent a mix of urban background and curbside locations. While the averaged profiles take into account the effects of the measured point sources in the urban area (mostly traffic and residential emissions), the use of the median profiles is expected to represent more selectively the urban background concentrations. We note that the influence of curbside increments may not be completely removed when using median increments (e.g., accumulation of traffic emissions due to street canyon effects), and therefore these increments might be biased high and should be regarded as our highest estimates of urban background concentrations. In the following we will present the results related to the average profiles, followed by the results from the median profiles reported in parenthesis. In all cases, the longitude profiles were fitted using sigmoid functions (black curves). In order to have a constant averaging city area, the fitting limits (indicated with blue and pink arrows) and the x value of the sigmoid’s midpoint (Xₘ) were determined from the fit of the total PM₂.₅ mass (NR-PM₂.₅ plus eBC) and imposed to all other components. In most cases the base of the sigmoid function is slightly above zero. This indicates that the subtracted Pᵢ₅ did not represent the full regional background, which is therefore given by the sum of the average Pᵢ₅ and the base of the sigmoid function. Note that the initial subtraction of Pᵢ₅ would not be necessary if the longitudinal profile of each single loop could be fitted. However, this is not possible due to the high concentration variability within each single loop. A sensitivity analysis was performed by using Pᵢ₅ instead of Pᵢ₅ and no major changes were observed in the final results. As shown by the wind rose in Fig. 4.4b, during the drives in Tartu the wind was predominantly from the west. However, the background concentrations measured at the eastern side of the loop do not seem to be affected by the transport of pollutants from the urban area, as the base values obtained for the eastern side are equal or lower than those from the western side (see Table 4.3). As the differences between the west and east fits are in most cases rather low, we use the west–east averages of the base values to calculate the urban increments concentrations in Table 4.3.

In Tartu, the three primary OA sources (HOA, BBOA, and RIOA) show a clear enhancement in the city center compared to the suburban areas (Figs. 4.6 and B.12). Moreover, different source regions (see Fig. 4.4c–f) and emission times (see Fig. B.13) can be distinguished inside the urban area. For example, maximum HOA concentrations are observed on highly congested roads, especially at sites under stop-and-go conditions and show a maximum enhancement in the morning and evening traffic rush hours (07:00 to 09:00 and 15:00 to 17:00 LT). The spatial distributions of the eBC, CO₂, and CO (Fig. 4.4i–k) are consistent with that of HOA (R² of 0.61, 0.59, and 0.58, respectively), which indicates that these species originate mostly from traffic. BBOA is strongly enhanced in the residential areas, consistent with the distribution of residential wood combustion sources shown in Fig.
B.1. The maximum BBOA enhancement is seen in the evening hours (15:00 to 21:00 LT) when domestic heating is more active. RIOA shows enhanced contributions in both, the residential areas (probably related to domestic cooking emissions) and the major roads in the city center (probably related to cooking emissions from restaurants). The maximum enhancement of RIOA is also seen in the evening hours (15:00 to 19:00 LT), during and after the evening maximum of HOA. In contrast, OOA (Fig. 4.4f) and the other secondary species (SO₄, NO₃, NH₄, and Cl; see Figs. 4.4g–h and B.10) show very homogeneous spatial distribution over the whole measurement area (as expected from their secondary nature), and no clear dependence on the time of the day can be seen for the OOA (Fig. B.13). Although slight enhancements are observed in these components close to residential areas (OOA enhancement of 0.8 µg m⁻³), these increases are negligible within the measurement and source apportionment uncertainties.

Figure 4.6: Average longitude profiles of the enhancements of all measured components and sources in Tartu. Colored curves represent the average enhancement of each source/components over 26 loops and the grey shaded area is the standard deviation among them. The average enhancements were fitted with sigmoid functions (black curves). The fitting limits (pink and blue arrows in top panel) and the sigmoid’s midpoint (Xₒ) were determined from the fit of the total PM₂.₅ mass (NR-PM₂.₅ plus eBC) and then imposed to the other components/sources. Dashed black lines indicate a non-standard or bad fit (described in each case in the plot) and the results of these fits are represented in parentheses in Table 4.2. Notes: the spike found in the east for RIOA, OOA, and SO₄ is not representative, as it is related to one single measurement point. The spike in CH₄ in the west side is related to consistent increases of this component nearby a cowshed and will be further investigated in a future publication.
4.3 Results and discussion

As reported in Table 4.3, the PM$_{2.5}$ mass concentration in Tartu shows an urban increment of 6.0 (4.6) µg m$^{-3}$ over a regional background concentration of 4.0 (3.5) µg m$^{-3}$. This leads to urban PM$_{2.5}$ mass concentrations of up to 10 (8.1) µg m$^{-3}$, which represents an increase of a factor 2.5 (2.3) in the particle mass concentration in the urban area compared to the regional background. About half of this enhancement is related to the emissions of eBC, which shows an increase of 3.2 (2.3) µg m$^{-3}$ over a regional background of 1.1 (0.58) µg m$^{-3}$. Thus, the urban concentration of eBC is 4.2 (2.9) µg m$^{-3}$, which represents an enhancement of a factor 3.9 (5.0) of eBC in the urban area. The primary OA sources explain a great part of the remaining increase in the PM$_{2.5}$ mass: HOA is increased by a factor 3.6 (3.0) in the urban area and has a contribution of 1.7 (1.0) µg m$^{-3}$ to the urban concentration; RIOA is enhanced by a factor 2.0 (2.3), contributing 1.7 (1.0) µg m$^{-3}$ to the urban concentration; and BBOA is enhanced by a factor 3.1 (2.4) and contributes with 1.0 (0.52) µg m$^{-3}$ to the urban concentrations. In contrast, OOA and the inorganic species (SO$_4$, NO$_3$, NH$_4$, and Cl) show very low increases in the urban area, resulting in a total urban increment below 0.21 µg m$^{-3}$ (average and median). In the gas phase, CO$_2$ shows an increase of 8.3 (5.3) ppm over a regional background of 403.5 ppm (both average and median); CO is increased by 0.15 (0.11) ppm over a regional background of 0.16 (0.14) ppm, which represents an increase of a factor 1.9 (1.7); while CH$_4$ shows very similar concentrations inside and outside the city, with average (and median) regional background of 1.90 ppm and urban concentrations of 1.91 ppm.

Similar results were obtained for Tallinn (see Figs. 4.5 and B.11). However, given the larger extension of this city, it was not possible to include a real regional background site in the route. Therefore, the longitude profiles and urban increments could not be properly explored for Tallinn. However, different source regions can still be distinguished within the examined area. Thus, the spatial distribution of HOA (Fig. 4.5c) is in agreement with those of eBC, CO$_2$, and CO (Fig. 4.5i–k) and shows substantial increases in areas with high traffic and on major streets in the city center with significant stop-and-go conditions. BBOA (Fig. 4.5d) has higher contributions in the residential areas, especially in region 2 of the driving route, where there is a very high density of residential wood combustion sources (see Fig. B.1). Compared to Tartu, in Tallinn the spatial distribution of RIOA (Fig. 4.5e) is more homogeneous, with only slight enhancements in the residential area and in the city center. Finally, OOA (Fig. 4.5f) exhibits a small enhancement in the city center area, which again coincides with small increases in the secondary inorganic species concentrations (see Figs. 4.5g–h and B.11) that are insignificant within the measurement and source apportionment uncertainties. Enhanced SO$_4$ levels are also found in the northern part of the route, likely from local ship emissions (Lack et al., 2009). Winds from the west and east were observed during the mobile measurements in Tallinn (Fig. 4.5b). In order to identify possible processes influencing the spatial distributions of the measured pollutants for the two different wind patterns, the average spatial distributions were calculated for all loops with western wind (7 loops) and loops with eastern wind (16 loops, excluding drives during accumulation events). The results of these analyses are reported in the supplementary information (Figs. B.14 and B.15) and show that, in general, the wind direction did not have an effect on the identified source areas and similar enhancements were found for both types of winds. A detailed analysis of these spatial distributions shows that BBOA, SO$_4$, and NO$_3$ are more strongly enhanced during western winds, while HOA is more enhanced for eastern wind conditions. This difference is most
probably related to the presence of western winds during the weekend (enhanced residential emissions) and eastern winds during the weekday measurements (enhanced traffic emissions).

**Table 4.3**: Results obtained from the average (a) and median (b) longitude profiles for each measured component/source. \( P_{0.5} \) represents the averaged fifth percentile subtracted for the calculation of the enhancements; base and increment values were obtained from the sigmoid fits; the regional background is given as the sum of \( P_{0.5} \) and the average base value; urban concentrations are the sum of the regional background and the average urban increment; the factor increase represents the ratio between the urban and the regional backgrounds. Values in parentheses represent non-standard or bad fits and were not used in the calculations.

### (a) Average longitude profiles

<table>
<thead>
<tr>
<th>Component</th>
<th>( P_{0.5} ) (( \mu g \cdot m^{-3} ))</th>
<th>Base (west)</th>
<th>Base (east)</th>
<th>Base (average)</th>
<th>Increment (west)</th>
<th>Increment (east)</th>
<th>Increment (average)</th>
<th>Regional background</th>
<th>Urban concentration</th>
<th>Factor increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM(_{2.5})</td>
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<td>2.6</td>
<td>1.8</td>
<td>2.2</td>
<td>5.6</td>
<td>6.3</td>
<td>6.0</td>
<td>4.0</td>
<td>10.0</td>
<td>2.5</td>
</tr>
<tr>
<td>HOA (( \mu g \cdot m^{-3} ))</td>
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<td>0.24</td>
<td>0.29</td>
<td>1.2</td>
<td>1.3</td>
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<td>0.47</td>
<td>1.7</td>
<td>3.6</td>
</tr>
<tr>
<td>BBOA (( \mu g \cdot m^{-3} ))</td>
<td>0.11</td>
<td>0.24</td>
<td>0.19</td>
<td>0.21</td>
<td>0.60</td>
<td>0.75</td>
<td>0.67</td>
<td>0.32</td>
<td>1.0</td>
<td>3.1</td>
</tr>
<tr>
<td>RIOA (( \mu g \cdot m^{-3} ))</td>
<td>0.27</td>
<td>0.44</td>
<td>(0.30)</td>
<td>0.44</td>
<td>0.72</td>
<td>(1.9)</td>
<td>0.72</td>
<td>0.71</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>OOA (( \mu g \cdot m^{-3} ))</td>
<td>0.44</td>
<td>0.42</td>
<td>0.32</td>
<td>0.37</td>
<td>0.024</td>
<td>0.11</td>
<td>0.069</td>
<td>0.81</td>
<td>0.87</td>
<td>1.1</td>
</tr>
<tr>
<td>SO(_4) (( \mu g \cdot m^{-3} ))</td>
<td>0.29</td>
<td>0.075</td>
<td>0.055</td>
<td>0.065</td>
<td>0.032</td>
<td>0.051</td>
<td>0.042</td>
<td>0.035</td>
<td>0.39</td>
<td>1.1</td>
</tr>
<tr>
<td>NO(_3) (( \mu g \cdot m^{-3} ))</td>
<td>0.095</td>
<td>0.075</td>
<td>0.076</td>
<td>0.075</td>
<td>0.042</td>
<td>0.038</td>
<td>0.040</td>
<td>0.017</td>
<td>0.21</td>
<td>1.2</td>
</tr>
<tr>
<td>NH(_4) (( \mu g \cdot m^{-3} ))</td>
<td>0.079</td>
<td>0.032</td>
<td>0.028</td>
<td>0.030</td>
<td>0.012</td>
<td>0.016</td>
<td>0.014</td>
<td>0.11</td>
<td>0.12</td>
<td>1.1</td>
</tr>
<tr>
<td>Cl (( \mu g \cdot m^{-3} ))</td>
<td>0.012</td>
<td>0.036</td>
<td>0.035</td>
<td>0.035</td>
<td>0.022</td>
<td>0.022</td>
<td>0.022</td>
<td>0.047</td>
<td>0.069</td>
<td>1.5</td>
</tr>
<tr>
<td>eBC (( \mu g \cdot m^{-3} ))</td>
<td>0.34</td>
<td>0.06</td>
<td>0.54</td>
<td>0.75</td>
<td>3.0</td>
<td>3.3</td>
<td>3.2</td>
<td>1.1</td>
<td>4.2</td>
<td>3.9</td>
</tr>
<tr>
<td>CO(_2) (ppm)</td>
<td>403.0</td>
<td>0.99</td>
<td>0.04</td>
<td>0.52</td>
<td>7.8</td>
<td>8.9</td>
<td>8.3</td>
<td>405.5</td>
<td>41.19</td>
<td>1.0</td>
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<tr>
<td>CO (ppm)</td>
<td>0.14</td>
<td>0.028</td>
<td>0.012</td>
<td>0.020</td>
<td>0.14</td>
<td>0.15</td>
<td>0.15</td>
<td>0.16</td>
<td>0.31</td>
<td>1.9</td>
</tr>
<tr>
<td>CH(_4) (ppm)</td>
<td>1.90</td>
<td>0.0060</td>
<td>0.0014</td>
<td>0.0012</td>
<td>0.0047</td>
<td>0.012</td>
<td>0.0083</td>
<td>1.90</td>
<td>1.91</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### (b) Median longitude profiles

<table>
<thead>
<tr>
<th>Component</th>
<th>( P_{0.5} ) (( \mu g \cdot m^{-3} ))</th>
<th>Base (west)</th>
<th>Base (east)</th>
<th>Base (average)</th>
<th>Increment (west)</th>
<th>Increment (east)</th>
<th>Increment (average)</th>
<th>Regional background</th>
<th>Urban concentration</th>
<th>Factor increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM(_{2.5})</td>
<td>1.8</td>
<td>1.8</td>
<td>1.6</td>
<td>1.7</td>
<td>4.6</td>
<td>4.6</td>
<td>4.6</td>
<td>3.5</td>
<td>8.1</td>
<td>2.3</td>
</tr>
<tr>
<td>HOA (( \mu g \cdot m^{-3} ))</td>
<td>0.18</td>
<td>0.16</td>
<td>0.13</td>
<td>0.14</td>
<td>0.66</td>
<td>0.66</td>
<td>0.66</td>
<td>0.33</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>BBOA (( \mu g \cdot m^{-3} ))</td>
<td>0.11</td>
<td>0.088</td>
<td>0.12</td>
<td>0.11</td>
<td>0.35</td>
<td>0.27</td>
<td>0.31</td>
<td>0.22</td>
<td>0.52</td>
<td>2.4</td>
</tr>
<tr>
<td>RIOA (( \mu g \cdot m^{-3} ))</td>
<td>0.27</td>
<td>0.29</td>
<td>0.15</td>
<td>0.17</td>
<td>0.58</td>
<td>0.60</td>
<td>0.59</td>
<td>0.45</td>
<td>1.0</td>
<td>2.3</td>
</tr>
<tr>
<td>OOA (( \mu g \cdot m^{-3} ))</td>
<td>0.44</td>
<td>0.28</td>
<td>0.26</td>
<td>0.27</td>
<td>0.084</td>
<td>0.096</td>
<td>0.090</td>
<td>0.71</td>
<td>0.80</td>
<td>1.1</td>
</tr>
<tr>
<td>SO(_4) (( \mu g \cdot m^{-3} ))</td>
<td>0.29</td>
<td>0.064</td>
<td>0.053</td>
<td>0.059</td>
<td>0.029</td>
<td>0.039</td>
<td>0.034</td>
<td>0.35</td>
<td>0.38</td>
<td>1.1</td>
</tr>
<tr>
<td>NO(_3) (( \mu g \cdot m^{-3} ))</td>
<td>0.095</td>
<td>0.043</td>
<td>0.053</td>
<td>0.048</td>
<td>0.056</td>
<td>0.039</td>
<td>0.047</td>
<td>0.14</td>
<td>0.19</td>
<td>1.3</td>
</tr>
<tr>
<td>NH(_4) (( \mu g \cdot m^{-3} ))</td>
<td>0.079</td>
<td>0.028</td>
<td>0.026</td>
<td>0.027</td>
<td>0.0094</td>
<td>0.011</td>
<td>0.010</td>
<td>0.11</td>
<td>0.12</td>
<td>1.1</td>
</tr>
<tr>
<td>Cl (( \mu g \cdot m^{-3} ))</td>
<td>0.012</td>
<td>0.022</td>
<td>0.025</td>
<td>0.024</td>
<td>0.024</td>
<td>0.019</td>
<td>0.021</td>
<td>0.035</td>
<td>0.06</td>
<td>1.6</td>
</tr>
<tr>
<td>eBC (( \mu g \cdot m^{-3} ))</td>
<td>0.34</td>
<td>0.45</td>
<td>0.027</td>
<td>0.24</td>
<td>2.0</td>
<td>2.5</td>
<td>2.3</td>
<td>0.58</td>
<td>2.9</td>
<td>5.0</td>
</tr>
<tr>
<td>CO(_2) (ppm)</td>
<td>403.0</td>
<td>0.95</td>
<td>0.051</td>
<td>0.50</td>
<td>5.0</td>
<td>5.6</td>
<td>5.3</td>
<td>403.5</td>
<td>408.8</td>
<td>1.0</td>
</tr>
<tr>
<td>CO (ppm)</td>
<td>0.14</td>
<td>0.011</td>
<td>&lt; 0.001</td>
<td>0.0052</td>
<td>0.096</td>
<td>0.12</td>
<td>0.11</td>
<td>0.14</td>
<td>0.25</td>
<td>1.7</td>
</tr>
<tr>
<td>CH(_4) (ppm)</td>
<td>1.90</td>
<td>0.0032</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.0051</td>
<td>0.011</td>
<td>0.0079</td>
<td>1.90</td>
<td>1.91</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\( ^a \) Excluding special events; \( ^b \) (X\(_2\) test failed); \( ^c \) Excluding spike.

### 4.3.4 Special events: transport and accumulation of pollutants

Enhanced concentrations of secondary species including OOA, \( SO_4 \), \( NO_3 \), and \( NH_4 \) were measured during the first measurement day in Tartu (see Figs. 4.1a and 4.3a). The analysis of the 24 h back trajectories reported in Fig. 4.7a indicates that these mostly secondary components were probably transported from continental Europe, in particular from northern Germany. The later decrease in the concentrations of these species coincides with clean air masses originating from the Northern Atlantic at higher altitudes above ground level. As reported in Fig. 4.7b, during this transport event the average \( PM_{2.5} \) mass concentration
increased to 28.3 µg m\(^{-3}\) (compared to average concentrations of 11.0 µg m\(^{-3}\) measured during daytime and 6.5 µg m\(^{-3}\) during nighttime). This increase in mass is mostly related to the increased concentrations of the secondary components, especially of NO\(_3\) and OOA. Accordingly, the relative contributions of the inorganic species to the total NR-PM\(_{2.5}\) increased to over 44% during the transport event (compared to 12% for daytime and around 28% for nighttime averages) and the relative contribution of the OOA to total OA increased to 56% (compared to 25% for daytime and 42% for nighttime averages). It is worthwhile to note that the source separation is more uncertain during the transport event due to lower statistics and increased mixing (if the transported air contains multiple sources). This is especially the case for RIOA, which has a relative error of 41% (estimated by the bootstrapping procedure) during the transport event.

During the nights of 28 and 29 March, very high concentrations of organics (exceeding 200 µg m\(^{-3}\)), eBC (above 15 µg m\(^{-3}\)) and CO\(_2\) (up to 500 ppm) were measured in Tallinn, as shown in Fig. 4.8a. Relatively short back trajectories originating from the Baltic Sea (northwest and west of the sampling site) and at high altitudes were obtained for these periods (not reported). Moreover, as shown in Fig. 4.8a, during such accumulation events wind speed was close to zero and a strong near-ground temperature inversion (i.e., a positive temperature difference between the ground and 22 m a.g.l.) was observed. Under such conditions, the vertical mixing is suppressed and the local pollutants are trapped at the surface. As reported in Fig. 4.8b, during the accumulation periods the average PM\(_{2.5}\) mass increased up to 41.7 µg m\(^{-3}\), with OA explaining 73% of the total mass. This increase was mostly related to the increase of the primary aerosols, mainly HOA and BBOA, which explained 33 and 37% of the OA mass, respectively.

Figure 4.7: (a) 24 h back trajectories (NOAA HYSPLIT MODEL) of the air masses ending at the sampling location (Tartu) during the transport event (10 March between 10:00 and 22:00 LT, left panel) and the successive hours (from 10 March at 23:00 LT until 11 March at 08:00 LT, right panel). (b) PM\(_{2.5}\) mass concentration and chemical composition (top panel) and OA mass concentration and relative contributions of the OA sources (bottom panel) during the measurements in Tartu during daytime, nighttime, and transport event. Errors indicate the standard deviation among 100 bootstrap runs.
Figure 4.8: (a) Temporal evolution of the OA sources, eBC and CO₂, wind speed, and 170–22 m (temperature difference between ground level and at 22 m above ground level) during the accumulation events in Tallinn. (b) PM₂.₅ mass concentration and chemical composition (top panel) and OA mass concentration and relative contributions of the OA sources (bottom panel) during the measurements in Tallinn during daytime, nighttime, and accumulation events. Errors indicate the standard deviation among 100 bootstrap runs.

4.4 Conclusions

Mobile measurements allowed for the study of the spatial distributions of major gas- and particle-phase pollutants in two urban areas in Estonia, permitting the identification of particular source areas and the determination of regional background concentrations and urban increments for the individual components/sources. A comprehensive set of instruments including a HR-ToF-AMS (with a newly developed inlet to measure the NR-PM₂.₅ fraction), a seven-wavelength Aethalometer and several gas-phase monitors were deployed in the mobile laboratory to retrieve a detailed chemical characterization of the PM₂.₅ fraction and the concentrations of several trace gases with high time resolution.

The measurements were performed in March 2014 in the two major cities of Estonia (Tallinn and Tartu) and no major differences were found in the chemical composition at the two sites. Higher mass concentrations were always measured during daytime, when point sources were sampled during mobile measurements. Under regular meteorological conditions, OA represented the largest mass fraction (on average 52.2 to 60.1 % of PM₂.₅), while the relative contribution of the inorganic species (mostly SO₄, NO₃, and NH₄) strongly increased during the transport of polluted air masses from northern Germany. Four sources of OA were identified by means of PMF: three primary sources (HOA, BBOA, and RIOA) and a secondary OA (OOA). Although the RIOA is thought to be dominated by cooking emissions, contributions from other residential emissions to this factor cannot be excluded. For example, waste burning is known to be a common process in some cities in Estonia (Maasikmets et al., 2015). However, to properly separate the contribution of waste burning
from other co-emitting sources, laboratory studies of direct emissions need to be performed in the future. While OOA dominated the OA mass during nighttime (on average 42.3% in Tartu and 43.8% in Tallinn), the primary sources explained the major fraction of OA during daytime (75.2% in Tartu and 68.3% in Tallinn, with similar contributions from the three sources). During the period with transport of polluted air masses aforementioned, the OOA relative contribution was enhanced. In contrast, HOA, RIOA, and BBOA were strongly enhanced during periods characterized by temperature inversions, which induced the accumulation of locally emitted primary pollutants (primary OA and eBC). Different source regions were identified inside the two urban areas. All traffic related pollutants (including HOA, eBC, CO₂, and CO) were strongly enhanced on the major city roads, especially in areas with stop-and-go conditions during the morning and evening rush hours. BBOA showed a clear increase in the residential areas during the evening hours (due to domestic heating), while RIOA (believed to be strongly influenced by cooking emissions) was enhanced in both the city center (from restaurant cooking emissions) and in the residential areas (from domestic cooking). In contrast, the secondary components (including OOA, SO₄, NO₃, NH₄, and Cl) had very homogeneous spatial distributions, with no clear enhancement in the urban areas (within the measurement uncertainties) or at certain times of the day. For Tartu, regional background concentrations and urban increments of all measured components/sources were also determined. On average, the PM₂.₅ mass had an enhancement inside the city of 6.0 µg m⁻³ over the regional background concentration of 4.0 µg m⁻³. This urban increment was strongly related to the enhancement of eBC (3.2 µg m⁻³) and the primary OA sources (on average 1.2 µg m⁻³ from HOA, 0.67 µg m⁻³ from BBOA and 0.72 µg m⁻³ from RIOA), while the secondary components (OOA, SO₄, NO₃, NH₄, and Cl) did not contribute to a substantial enhancement. Moreover, the good correlation found between eBC with HOA indicates that up to 74% of the enhancement in the PM₂.₅ is related to traffic emissions in the urban area. CO₂ and CO, which were also found to be strongly correlated with HOA, had an average urban increment of 8.3 and 0.15 ppm over regional background concentrations of 403.5 and 0.15 ppm, respectively.

Our results show that mobile measurements are a very powerful technique for spatial characterization of the major pollutants in urban areas. The methodology presented in this work can be generalized to other cities in order to determine the influence of human activity on the particle sources and levels in different areas of a city and the related health effects.

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High contributions of vehicular emissions of ammonia in three European cities derived from mobile measurements

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Chapter 5 Sources of ammonia in three European cities

Abstract

Ambient ammonia (NH$_3$) measurements were performed with a mobile platform in three European cities: Zurich (Switzerland), Tartu (Estonia) and Tallinn (Estonia) deploying an NH$_3$ analyzer based on cavity ring-down spectroscopy. A heated inlet line along with an auxiliary flow was used to minimize NH$_3$ adsorption onto the inlet walls. In addition, a detailed characterization of the response and recovery times of the measurement system was used to deconvolve the true NH$_3$ signal from the remaining adsorption-induced hysteresis. Parallel measurements with an aerosol mass spectrometer were used to correct the observed NH$_3$ for the contribution of ammonium nitrate, which completely evaporated in the heated line at the chosen temperature, in contrast to ammonium sulfate. In this way a quantitative measurement of ambient gaseous NH$_3$ was achieved with sufficient time resolution to enable measurement of NH$_3$ point sources with a mobile sampling platform.

The NH$_3$ analyzer and the aerosol mass spectrometer were complemented by an aethalometer and various gas-phase analyzers to enable a complete characterization of the sources of air pollution, including the spatial distributions and the regional background concentrations and urban increments of all measured components. Although at all three locations similar increment levels of organic aerosols were attributed to biomass burning and traffic, traffic emissions clearly dominated the city enhancements of NH$_3$, equivalent black carbon (eBC) and carbon dioxide (CO$_2$). Urban increments of 3.4, 1.8 and 3.0 ppb of NH$_3$ were measured in the traffic areas in Zurich, Tartu and Tallinn respectively, representing an enhancement of 36.6, 38.3 and 93.8 % over the average background concentrations. Measurements in areas strongly influenced by traffic emissions (including tunnel drives) were used to estimate emission factors (EF) for the traffic-related pollutants. The obtained median EFs range between 136.8 to 415.1 mg kg$^{-1}$ fuel for NH$_3$, 157.1 to 734.8 mg kg$^{-1}$ fuel for eBC and 39.9 to 324.3 mg kg$^{-1}$ fuel for HOA. Significant differences were found between the EFs of certain components in the three cities, which were partially linked to an older vehicle fleet in Estonia compared to Switzerland. Using the determined EFs we show that traffic can fully explain the NH$_3$ enhancements in the three cities and also presents a non-negligible fraction of the background concentrations, which are mostly related to agricultural activities. Moreover, the estimated total contribution of traffic to NH$_3$ at all three locations is in good agreement with the available emission inventories.

5.1 Introduction

Ammonia (NH$_3$) is a major component of the total reactive nitrogen and the predominant gaseous base in the atmosphere. Therefore, NH$_3$ has major environmental implications, including the eutrophication and acidification of natural ecosystems, which can lead to changes in the species composition (Fangmeir et al., 1994; Krupa, 2003; Bobbink et al., 2010). In the atmosphere, gaseous NH$_3$ will neutralize sulfuric and nitric acid leading to the formation of ammonium sulfate ((NH$_4$)$_2$SO$_4$), ammonium hydrogen sulfate (NH$_4$HSO$_4$) and ammonium nitrate (NH$_4$NO$_3$). These species are the most abundant secondary inorganic compounds in the atmospheric aerosols or PM$_{2.5}$ (particulate matter with aerodynamic diameter below 2.5 µm)
and thus have significant implications for regional air quality, health effects, visibility, cloud formation and radiative balance. \( \text{NH}_3 \) can enhance particle nucleation by several orders of magnitude, which affects climate by increasing the number of potential cloud condensation nuclei (Kirkby et al., 2011). The accurate knowledge of \( \text{NH}_3 \) current atmospheric levels, emission sources and spatial distribution (compared to the pre-industrial era) is fundamental for the assessment of its influence on climate and other ecosystem aspects.

Current estimates of global \( \text{NH}_3 \) emissions vary between 35 and 65 Tg N year\(^{-1}\) (Bouwman et al., 1997; Sutton et al., 2013). Combining emission inventories with global models, Sutton et al. (2013) modeled the spatial distributions of \( \text{NH}_3 \) emissions and reported the dominant sources in each region. \( \text{NH}_3 \) emissions vary strongly by region, with emission hotspots in China, India, central Africa and northern Europe. In most regions, the dominant \( \text{NH}_3 \) sources are livestock and crops, while biomass burning is the main \( \text{NH}_3 \) source across central Africa. However, in urban areas additional anthropogenic sources can be significant. These sources include road traffic, residential coal and biomass burning, industrial \( \text{NH}_3 \) and fertilizer production, waste management, and human and pets emissions (Sutton et al., 2000; Reche et al., 2012).

\( \text{NH}_3 \) emissions from gasoline vehicles equipped with a three-way catalyst (TWC) have been shown to be an important source of \( \text{NH}_3 \) in areas with heavy traffic (e.g. Perrino et al., 2002; Reche et al., 2015). In the TWC, \( \text{NH}_3 \) is generated as a side product in the NO\(_x\) reduction process (Huai et al., 2003). Remote sensing in London showed a strong increase in traffic-derived \( \text{NH}_3 \) emission factors (from 520 to 970 mg\( \text{NH}_3 \) kg\(_{\text{fuel}}\)^{-1}) when catalyst-equipped vehicles were introduced in the UK fleet in 1992, while since the introduction of Euro 3 vehicles in the year 2000, \( \text{NH}_3 \) emissions have monotonically decreased, reaching in 2012 similar values to the pre-catalyst times (Carslaw and Rhys-Tyler, 2013). Laboratory dynamometer studies have shown large variability in the emission factors of ammonia for various types of TWC equipped-vehicles, temperatures and driving cycles (e.g. Durbin et al., 2002; Heeb et al., 2006; Huai et al., 2005; Suarez-Bertoa et al., 2014). Furthermore, the recent introduction of the selective catalytic reduction system (SCR) with its addition of urea or \( \text{NH}_3 \) in heavy-duty vehicles (HDV) and more recently in diesel light-duty vehicles (LDVs) resulted in increased \( \text{NH}_3 \) emissions from traffic, which needs further investigation.

Real-time measurements of \( \text{NH}_3 \) are hindered by the adsorption of \( \text{NH}_3 \) on the sampling lines, which severely degrades the measurement time resolution. In this work, we use specially designed inlets and correction algorithms for a quantitative characterization of \( \text{NH}_3 \) point sources with a mobile sampling platform in three European cities: Zurich (Switzerland), Tartu (Estonia) and Tallinn (Estonia). Such mobile measurements enabled the characterization of the spatial distribution of \( \text{NH}_3 \) in the three cities, the determination of \( \text{NH}_3 \) regional background concentrations and urban increments and the calculation of emission factors (EFs) from specific sources under real world conditions. Traffic EFs were estimated for \( \text{NH}_3 \), equivalent black carbon (eBC) and hydrocarbon-like (HOA) and were used to assess the contribution of traffic to the measured \( \text{NH}_3 \) levels inside the cities.
Chapter 5 Sources of ammonia in three European cities

5.2 Methodologies

5.2.1 Measurement campaigns and mobile laboratory set-up

Mobile measurements were performed for approximately one week in Zurich (9 to 19 October 2013), Tartu (10 to 17 March 2014) and Tallinn (25 March to 1 April 2014). The mobile measurements were mostly performed during daytime, while stationary measurements where additionally performed overnight in Tartu and Tallinn. Driving routes were designed to include different areas of the cities and were covered repeatedly during the measurement campaign (20 to 30 times) in order to obtain statistically significant spatial distributions of the measured compounds. Meteorological parameters recorded at the Nabel station (Swiss National Air Pollution Monitoring Network) Zurich-Kaserne are reported in Fig. C.1.

All details about the mobile laboratory set-up have been reported by Elser et al. (2016b) and only a brief description follows. The Paul Scherrer Institute mobile platform (IVECO Turbo Daily Transporter, detailed description in Bukowiecki et al., 2002) was used as rolling platform for the on-road measurements. An NH3-Picarro analyzer (G1103-t) was used to measure real-time NH3 concentrations. The measurement principle is based on cavity ring-down spectroscopy (CRDS), i.e. the measurement of the absorption of a pulse of light of a specific wavelength trapped in an optical cavity is used to determine the concentration of the absorbing substance in the gas mixture in the cavity. Although the instrument measures with fast time resolution (3 seconds), the observed response may be significantly delayed by adsorption of NH3 onto the inlet walls, often resulting in overall equilibration time scales on the order of minutes to hours. As high time resolution is required to study local sources with the mobile measurements, a new inlet system was tested and used (see Sect. 5.3). Moreover, post measurement corrections were applied to minimize the remaining measurement delays and deconvolve the original NH3 signal. Additionally, a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) was deployed to investigate the size resolved chemical composition of the non-refractory (NR)-PM2.5 aerosol (including nitrate (NO3), sulfate (SO4), ammonium (NH4), chloride (Cl), and organic aerosols (OA)). A seven-wavelength Aethalometer (Magee Scientific, model AE33) was used to measure the light absorption from carbonaceous aerosols and determine the concentrations of equivalent black carbon (eBC) (Drinovec et al., 2015) and diverse gas-phase analyzers were deployed to monitor CO2, CO and CH4 (Licor-7000 CO2/H2O used in all three measurement campaigns and Picarro-G2401 CO/CO2/CH4/H2O used in Tartu and Tallinn).

5.2.2 Source apportionment

Positive matrix factorization (PMF, Paatero and Tapper, 1994) was used to identify and quantify the major sources of OA at the three measurement sites. PMF is a bilinear unmixing model which represents the measurements (matrix X containing the time series of organic fragments at each m/z) as the linear combination of a given number of static factor profiles (in matrix F) and the related time series (in matrix G):
5.3 Optimization of the NH$_3$ sampling system and deconvolution of the NH$_3$ signal

\[ \mathbf{X} = \mathbf{G} \times \mathbf{F} + \mathbf{E} \]  

(5.1)

where $\mathbf{E}$ represents the model residuals. The model aims to minimize the object function $Q$, defined as the sum of squared model errors ($e_{ij}$) weighted by their respective measurement uncertainties ($\sigma_{ij}$):

\[ Q = \sum_i \sum_j \left( \frac{e_{ij}}{\sigma_{ij}} \right)^2 \]  

(5.2)

All details about the OA source apportionment strategy using Source Finder (SoFi; Canonaco et al., 2013) are reported in the Supplementary Information for Zurich (Figs. C.5 to C.7) and in a previous publication (Elser et al., 2016b) for Tartu and Tallinn. In all cases, the four-factor solution was found to represent best the data and the obtained factors were identified as hydrocarbon-like OA (HOA), biomass burning OA (BBOA), cooking OA (COA) or residential-influenced OA (RIOA) and oxygenated OA (OOA). While in Zurich the identification of the COA was supported by the diurnal profiles of such factor, in Estonia the diurnals were more distorted by the mobile nature of the measurements and therefore the influence of other residential emissions (e.g. coal or waste burning) couldn’t be excluded.

The Aethalometer model described in Sandradewi et al. (2008a) was used for the source apportionment of eBC. This method exploits the enhanced absorption of wood burning particles in the ultraviolet and visible wavelengths region relative to that of traffic particles to separate the contributions of these sources (denoted eBC$_{wb}$ and eBC$_{tr}$, respectively). The absorption measured at 470 and 950 nm was used to calculate the Ångström exponent and, following the suggestions in Zotter et al. (2016), Ångström exponents of 0.9 and 1.7 were used for traffic and wood burning, respectively. For a correct separation of the two fractions, the Aethalometer data was averaged to 30 min in order to increase the signal to noise ratio. Therefore, the resulting eBC fractions could only be used for the study of the correlations with the sources of OA, but not for the study of point sources or spatial distributions.

5.3 Optimization of the NH$_3$ sampling system and deconvolution of the NH$_3$ signal

The high water solubility and polarity of NH$_3$ causes significant adsorption onto sampling line surfaces, severely degrading measurement time resolution. Without specially designed inlets and/or correction algorithms, these time delays are often large enough to prevent quantitative measurements from mobile platforms, let alone source resolution. To minimize this effect, NH$_3$ was sampled through a 4 mm I.D., 1 m long PTFE inlet line heated to 110 °C (to decrease the net adsorption) along with an auxiliary flow of 5 l min$^{-1}$ (to decrease the residence time in the line).

Fig. 5.1 illustrates laboratory calibrations of the system response time using different inlet systems: standard line (PTFE, I.D: 4 mm, L: 1 m), heated line (standard inlet at $T$: 110 °C), auxiliary flow (standard inlet with $F_{aux}$: 5 l min$^{-1}$), and heated line with auxiliary flow (standard inlet at $T$: 110 °C and with $F_{aux}$: 5 l min$^{-1}$). Different concentrations of NH$_3$ (NH$_3$ set) were
generated with a calibrated permeation tube and injected stepwise in the sampling system until equilibrium was reached (Fig. 5.1a). The measurement of NH₃ is very precise and accurate (NH₃ meas / NH₃ set = 0.95, with R² = 0.99) over a wide range of concentrations (Fig. 5.1b). However, a substantial adsorption-induced delay is still observed in the NH₃ response time, especially at low concentrations. Heating the inlet line and adding an auxiliary flow significantly reduce the time required to reach equilibrium.

The equilibration of NH₃ on the tube walls can be described by a Langmuir-type process, where the quantity of the adsorbed NH₃ depends on the surface/NH₃ thermodynamics (e.g. number of available sites), which is driven by the concentration of gaseous NH₃ and the tube temperature. The equilibration profile of the measured NH₃ (NH₃ meas), i.e. the transition from the perturbed state to the new equilibrium state, follows second order kinetics with respect to the NH₃ surface concentration. The dynamic response of NH₃ meas under these conditions has the form of a double exponential function:

\[
\frac{\text{NH₃ meas}}{\text{NH₃ set}} = 1 + A_1 \times e^{-\frac{t}{\tau_1}} + (1 - A_1) \times e^{-\frac{t}{\tau_2}}
\]

(5.3)

Here, t is the time elapsed after perturbation (change in NH₃ set concentration), and \(\tau_1\) and \(\tau_2\) represent the equilibration times weighted by the exponential pre-factors \(A_1\) and \((1-A_1)\), respectively.

During mobile sampling, changes in NH₃ concentrations are very rapid and typically constrained to a limited range. Consequently, these changes are not expected to induce a large perturbation in the adsorbed NH₃ surface concentration. As such, the dynamic response of gaseous NH₃ concentrations in the tube does not significantly depend on the amount of NH₃ adsorbed, and can therefore be approximated by a pseudo-first order process. Such a process can be represented based on the balance of NH₃ molecular flows in the tube, assuming that any difference between the measured and set NH₃ concentrations beyond the gas residence time in the inlet line (negligible) is related to the adsorption of NH₃ onto the inlet surface:

\[
\frac{d\text{NH₃}}{dt} = k_{\text{eq}} \times \text{NH₃ set} - k_{\text{eq}} \times \text{NH₃ meas}
\]

(5.4)

In this expression, \(k_{\text{eq}}\) is the first-order equilibration rate of NH₃ in the inlet line. Equilibration rates and time scales (\(\tau_{\text{eq}} = k_{\text{eq}}^{-1}\)) were calculated at different temperatures, inlet flows and NH₃ concentrations (Fig. 5.1c and 5.1d), from the weighted average of \(\tau_1\) and \(\tau_2\) determined from our calibration data (Fig. 5.1a) using Eq. (3). \(k_{\text{eq}}\) shows the expected linear increase against the NH₃ concentrations. In the range of ambient concentrations a minor change in these rates, below a factor two, can be anticipated. The NH₃ equilibration time was significantly minimized by heating the inlet to 110 °C (decrease in \(\tau_{\text{eq}}\) by a factor of 1.5) and by adding an auxiliary flow of 5 l min⁻¹ (decrease in \(\tau_{\text{eq}}\) by a factor of 4.1). These improved settings are then used for the measurements of NH₃ in ambient air.

Despite these improvements, delays in ambient NH₃ signals were still observed. This is illustrated in Fig. C.2 for the case of traffic-related emissions during tunnel drives in Zurich, where the measured NH₃ signal exhibited delayed and broader peaks compared to the other
5.3 Optimization of the NH$_3$ sampling system and deconvolution of the NH$_3$ signal

Traffic tracers. By rearranging Eq. (4) and using the concentration dependent equilibration rates determined experimentally, the measured NH$_3$ signals (NH$_3$ \text{meas}) was deconvolved to estimate the real NH$_3$ concentration in the atmosphere (NH$_3$ \text{set} or NH$_3$ \text{deconvolved}):\
\[
NH_3 \text{ set} = \frac{dNH_3}{dt} + \frac{k_{eq}(NH_3 \text{ meas}) \times NH_3 \text{ meas}}{k_{eq}(NH_3 \text{ meas})}
\] (5.5)

The dependence of $k_{eq}$ on the NH$_3$ concentration was derived from calibrations conducted without an auxiliary flow. The example shown in Fig. C.2 illustrates that this correction significantly improves the agreement between NH$_3$ \text{deconvolved} and other pollutants concomitantly emitted in the tunnels. In all cases the correlation coefficients are significantly higher after the correction is applied, i.e. $R^2$ for NH$_3$ vs. eBC increased from 0.32 to 0.41, for NH$_3$ vs. CO$_2$ from 0.55 to 0.78 and for NH$_3$ vs. HOA from 0.35 to 0.60 (Table C.1). Note that if the standard inlet set-up (without heating and auxiliary flow) had been deployed, many peaks of NH$_3$ at ambient relevant concentrations would not have been detected and the deconvolution of the signal would not have been possible. Moreover, although the deconvolution algorithm amplifies the measurement noise, the mean error introduced in this way is only important at very low concentrations and decreases to a few percent at concentrations above 30 ppb (Fig. C.3).

Another potentially important issue encountered during the measurement of gaseous NH$_3$ is the interference from particulate ammonium. At 110°C, ammonium salts present in the atmosphere (mainly NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$), can volatilize in the inlet line creating a positive artifact in the NH$_3$ measurement. Here, we take advantage of the AMS to estimate the concentration of NH$_3$ derived from the particle phase. Laboratory tests showed that under the above conditions NH$_4$NO$_3$ fully evaporates in the heated line, whereas all the (NH$_4$)$_2$SO$_4$ remains in the particle-phase (see Fig. C.4). Accordingly, the measured NH$_3$ concentrations represent the aggregate of gas phase NH$_3$ and particle phase NH$_4$NO$_3$. Ambient NH$_3$ concentrations were corrected by subtracting the NH$_3$ corresponding to the NH$_4$NO$_3$ measured with the AMS. At all three locations the gas phase NH$_3$ dominated over the particulate fraction, i.e. NH$_3$ \text{gas}/NH$_3$ \text{gas+particle} of 0.98 (0.92; 0.99) (median ($Q_1$; $Q_3$)), 0.97 (0.80; 0.99) and 0.94 (0.79; 0.99) where obtained for Zurich, Tartu and Tallinn, respectively.
5.4 Results and discussion

5.4.1 Temporal variability of NH$_3$

The temporal evolution of NH$_3$ and other primary pollutants including CO$_2$, CO (available only for the measurements conducted in Estonia), eBC, HOA, BBOA and COA or RIOA are shown in Fig. 5.2 for Zurich and in Fig. C.8 for Estonia. The time series of the additional measured components and sources are reported in Figs. C.7 and C.9 for Zurich and in a previous publication for Tartu and Tallinn (Elser et al., 2016b). The NH$_3$ background concentrations show a considerable day-to-day variability, consistent with that of regional pollutants such as secondary aerosols (SO$_4$, NO$_3$, NH$_4$, and OOA) and of CO$_2$. During the city measurements, NH$_3$ background concentrations (defined here as the 5$^{th}$ percentile ($P_{0.05}$) of the concentrations for each round of measurements) ranged between 5 to 19 ppb in Zurich, 2 to 10 ppb in Tartu and 2 to 5 ppb in Tallinn. The higher NH$_3$ background concentrations detected in Zurich compared to Tartu and Tallinn might be related to the more intense agricultural activity in Switzerland,

\[ \text{Figure 5.1: Laboratory calibrations of the NH}_3\text{ analyzer using different inlet systems. (a) System (inlet plus analyzer) response time at different concentration ranges. (b) Concentration calibration curve, fitted with linear function. (c) Equilibration time (t}_{eq}) of the system for the concentration ranges shown in (a), fitted with exponential functions. (d) $k$ equilibration ($k_{eq} = \tau_{eq}^{-1}$) for the concentration ranges shown in (a), fitted with linear functions. The average slope determined for the calibrations without an auxiliary flow was used to fit the calibrations with the auxiliary flow (for which only one point is available).} \]
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although effects from different meteorological conditions or differences in the specific agricultural activities ongoing in the different measurement periods also need to be considered. Discrete events with NH$_3$ concentrations reaching approximately 50 ppb were observed in all three cities, while peaks up to 200 ppb were measured during tunnel drives in Zurich.

![Figure 5.2: Time series of ammonia (NH$_3$), carbon dioxide (CO$_2$), carbon monoxide (CO), equivalent black carbon (eBC), hydrocarbon-like organic aerosol (HOA), biomass burning organic aerosol (BBOA) and cooking organic aerosol (COA) for the measurements in Zurich.](image)

5.4.2 Spatial distributions and urban increments

The spatial distributions of the measured compounds were calculated for the three measurement locations as described in Elser et al. (2016b), and only a brief description is given here. The enhancement of each species of interest over its background concentrations was determined by subtracting the 5th percentile ($P_{05}$) of its concentration during the single loops. The enhancement time series of each compound was then averaged over a spatial grid with grid cells of 100 m$^2$ in Zurich and 250 m$^2$ in Tartu and Tallinn. Figure 5.3 shows the average spatial distribution of the combustion related compounds, including NH$_3$, CO$_2$, eBC, HOA and BBOA, at the three measurement locations. The color scale indicates the average enhancement (with the maximum of the scale set to the 75th percentile for better visualization), and the point size represents the number of measurement points that were averaged. The spatial distributions of all other measured components can be found in Fig. C.10 (Zurich) and in Elser et al. (2016b) (Tartu and Tallinn).

At all three locations, the spatial distributions of NH$_3$, CO$_2$ and eBC are consistent with the distribution of HOA, showing higher enhancements in the city center and areas with elevated traffic. Relatively high correlations are observed between these traffic-related components, with $R^2$ ranging between 0.25 and 0.82 for the individual cities (Fig. C.11).
contrast, the spatial distribution of BBOA is significantly different (especially in Tartu and Tallinn), with higher enhancements observed in residential areas. In the traffic areas of Zurich, \(NH_3\) shows enhancements \((P_{75} - P_{05})\) of 3.4 ppb over an average background concentration \((P_{05})\) of 9.3 ppb, which represents an increase of about 36.6 % (Fig. C.12). A similar relative increase in \(NH_3\) was observed in the areas influenced by traffic in Tartu, with enhancements \((P_{75} - P_{05})\) of 1.8 ppb over the average background concentration of 4.7 ppb (i.e. an increase of 38.3 %), while in Tallinn \(NH_3\) was up to 93.8 % higher in the traffic areas of the city due to both high enhancements \((P_{75} - P_{05}\) of 3.0 ppb) and lower background concentrations (3.2 ppb, on average).

An alternative way to determine the regional background concentrations and the urban increments is to use the longitude profiles as defined by Lenschow et al. (2001) and described in Elser et al. (2016b). Such analysis could only be performed for Tartu, as no proper regional background areas were included in the routes in Tallinn and Zurich. The longitude profile of the \(NH_3\) enhancement in Tartu was obtained by averaging the enhancements in longitude bins (see Fig. C.13) and was fitted with a sigmoid function to determine regional background concentrations of 5.1 ppb (average) and 5.4 ppb (median), and urban increments of 0.6 ppb (average) and 0.3 ppb (median), i.e. an increase of 12 % (average) and 6 % (median) in \(NH_3\) within the full city area of Tartu (see Table C.2).

Note that although at all three locations the measured levels of HOA and BBOA were comparable (enhancement \((P_{75} - P_{05})\) of 0.84 µg m\(^{-3}\) HOA and 0.68 µg m\(^{-3}\) BBOA in Zurich, 1.17 µg m\(^{-3}\) HOA and 0.82 µg m\(^{-3}\) BBOA in Tartu, and 2.17 µg m\(^{-3}\) HOA and 2.37 µg m\(^{-3}\) BBOA in Tallinn), the spatial distributions and their correlations (Figs. 5.3 and C.10) suggest that traffic dominates the emissions of \(NH_3\), \(CO_2\) and eBC. This is also supported by Fig. C.14, which shows that biomass burning emissions didn’t significantly influence the levels of \(NH_3\), \(CO_2\) and eBC.

### 5.4.3 Traffic emission factors

Mobile measurements are uniquely suited for the estimation of pollutant emission factors from specific point or line sources, e.g. traffic, under real world conditions. Although many test bench studies report detailed vehicular emissions, the number of tested vehicles is often limited and laboratory/driving conditions strongly influence the results.

The tunnel drives in Zurich allowed for the calculation of traffic emission profiles for \(NH_3\), eBC and HOA, under the reasonable assumption that the enhancements inside the tunnel are due to traffic emissions. The EFs were calculated by integrating the area below the peaks observed in the traffic-related pollutants when driving through the tunnels (see Fig. C.2) as follows:

\[
EF = \frac{\int (C_i - C_{i,0}) \cdot \frac{MW_{CO_2}}{MW_C} \cdot w_c}{\int (C_{CO_2} - C_{CO_2,0})} , \text{ with } i = NH_3, \text{ eBC and HOA} \tag{5.6}
\]

where the subscript 0 indicates the background concentrations measured at the entrance of the tunnel, \(MW_{CO_2}\) and \(MW_C\) are the molecular weights of \(CO_2\) and carbon, and \(w_c = 0.85\) is the...
mass fraction of carbon in gasoline (or diesel) fuel. The integration area extends from the rising edge of the peak (where the background concentrations are assigned) until the peak tail reaches again the background levels. Five different tunnels were included in the calculation of the tunnel-based EFs in Zurich. While these comprise highway and city tunnels of variable lengths (400 to 3300 m) and variable average speeds from 30 to 90 km h\(^{-1}\), no trend was observed in the estimated EFs with the different measurement conditions.

![Figure 5.3](image)

**Figure 5.3:** Spatial distributions of the enhancements (over the background concentrations) of NH\(_3\), CO\(_2\), eBC, HOA and BBOA at the three measurement locations.
Similarly, event-based traffic EFs were estimated for all three locations by integrating traffic-related peaks during the city drives. Periods with high concentrations of NH$_3$, CO$_2$, eBC and HOA (above P$_{25}$) and low concentrations of BBOA (below P$_{50}$) were considered for the selection of the events used for the calculation of the EFs (see Fig. C.15). As for the tunnel measurements, the background concentrations were subtracted prior to the integration of the peaks in order to exclude the influence of sources other than traffic. A total of twenty traffic events were separated for Tartu and Tallinn, while only ten clear traffic peaks were distinguished in Zurich.

**Figure 5.4:** NH$_3$, eBC, HOA and CO traffic emission factors calculated from tunnel drives in Zurich (tunnel-based) and from city measurements in Zurich, Tartu and Tallinn (event-based).

The mean values and the variability of the tunnel-based and event-based traffic EFs are represented as box-and-whiskers in Fig. 5.4 and reported in Table C.3 in the Supplementary. The estimated EFs reflect the high variability in real world traffic emission factors, as already observed in previous ambient and test bench studies (e.g. Carslaw and Rhys-Tyler, 2013; Suarez-Bertoa et al., 2014). Table 5.1 presents the results of unpaired t-tests on the distributions of the EFs reported in Fig. 5.4. No significant differences (i.e. $p$-value > 0.025) are observed between the EFs estimated in Zurich using the tunnel-based and event-based methods, which indicates that the uncertainties in both methods are lower than the variability of the EFs. In contrast, clear differences can be seen between the event-based EFs in the three cities, especially for eBC and HOA. The median NH$_3$ EFs estimated for Zurich and Tallinn are fairly similar (212 and 199 mg kg$^{-1}$ fuel, respectively), and no significant difference was found between their distributions. In comparison, the NH$_3$ EF was estimated to be a factor two higher in Tartu (415 mg kg$^{-1}$ fuel), which represents a clear difference relative to Zurich and Tallinn ($t$-test on NH$_3$ distributions; $p_{\text{Zurich-Tartu}} = 0.006$ and $p_{\text{Tartu-Tallinn}} = 0.0003$, respectively).
estimated for eBC are always similar or higher to those of NH$_3$. The lowest eBC EF was estimated for Zurich (230 mg kg$^{-1}$ fuel), followed by Tallinn (476 mg kg$^{-1}$ fuel) and Tartu (735 mg kg$^{-1}$ fuel). The lowest eBC EF was estimated for Zurich (230 mg kg$^{-1}$ fuel), followed by Tallinn (476 mg kg$^{-1}$ fuel) and Tartu (735 mg kg$^{-1}$ fuel). The t-test results confirm the significance of these differences (t-test on eBC distributions; $p_{\text{Zurich-Tartu}} = 8.8 \times 10^{-7}$, $p_{\text{Zurich-Tallinn}} = 1.1 \times 10^{-5}$, $p_{\text{Tartu-Tallinn}} = 9.8 \times 10^{-4}$). For HOA, a much lower EF was estimated in Zurich (40 mg kg$^{-1}$ fuel) compared to Tallinn (137 mg kg$^{-1}$ fuel) and Tartu (324 mg kg$^{-1}$ fuel). While the significance of the differences between the HOA EFs observed in Tartu and Tallinn is not clear, the differences between Zurich and the two Estonian cities is significant (t-test on HOA distributions; $p_{\text{Zurich-Tartu}} = 0.0071$, $p_{\text{Zurich-Tallinn}} = 3.0 \times 10^{-5}$, $p_{\text{Tartu-Tallinn}} = 0.034$). These observed differences will be explained in detail below.

Table 5.1: p-values from unpaired (two sample) t-tests between the distributions of the EFs obtained from the tunnel measurements in Zurich and the city measurements in Zurich, Tartu and Tallinn. The numbers in grey indicate no significant difference (i.e. $p$-value > 0.025).

<table>
<thead>
<tr>
<th>p-value</th>
<th>Tunnels vs. Zurich vs.</th>
<th>Zurich vs.</th>
<th>Zurich vs.</th>
<th>Tartu vs. Tallinn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tunnels vs. Zurich</td>
<td>Tartu</td>
<td>Tallinn</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.19</td>
<td>0.0061</td>
<td>0.86</td>
<td>2.9 $\times$ 10^{-4}</td>
</tr>
<tr>
<td>eBC</td>
<td>0.94</td>
<td>8.8 $\times$ 10^{-7}</td>
<td>1.1 $\times$ 10^{-5}</td>
<td>9.8 $\times$ 10^{-4}</td>
</tr>
<tr>
<td>HOA</td>
<td>0.81</td>
<td>0.0071</td>
<td>3.0 $\times$ 10^{-5}</td>
<td>0.034</td>
</tr>
</tbody>
</table>

To investigate differences in the vehicular fleets at the three measurement locations, Fig. 5.5 displays the event-based EFs of NH$_3$ against those of eBC. The reported NH$_3$-eBC isopleths for the different Euro classes and gasoline:diesel shares were determined using literature average EFs for gasoline and diesel vehicles for each Euro-class. Despite the large scatter in the EFs, clear trends can be observed in the median EFs for Zurich, Tartu and Tallinn. The estimated gasoline:diesel share shows a certain variability among the three cities, gasoline vehicles representing around 44 % of the total fleet in Zurich, 49 % in Tartu and 33 % in Tallinn. However, a wider spread is observed in the NH$_3$ EFs calculated for each city, suggesting a large variability in the diesel:gasoline shares. This is somehow expected given the different spatial distributions of light and heavy duty vehicles within the same city. Meanwhile clear differences in the BC EFs between the different cities suggest a significant difference between the average fleet age in Zurich (between EURO 4 and EURO 5), Tallinn (slightly higher than EURO 4) and Tartu (EURO 3). This difference is consistent with fuel consumption data by the different vehicle shares in Switzerland and in Estonia, indicating a higher contribution of Euro3 vehicles in Estonia (Fig. C.16).

While NH$_3$ is mostly emitted from the gasoline vehicles equipped with a TWC, eBC and HOA are dominated by the emissions of old diesel vehicles not equipped with a diesel particulate filter (DPF). As shown by Carslaw and Rhys-Tyler (2013), since the introduction of the Euro 3 the NH$_3$ emissions from the TWC gasoline vehicles have decreased linearly with the manufacturing year of the car. In contrast to this gradual decrease in the NH$_3$ emissions, the emissions of eBC and HOA from diesel vehicles got sharply reduced with the introduction of the DPF (Euro 5). Thus, the higher share of emissions from Euro 3 vehicles in Estonia compared to Switzerland can explain the large difference in the HOA and eBC EFs for the two countries, as well as the much lower difference in the NH$_3$ EFs. The differences in the EFs estimated for
the two Estonian cities can also partially be related to differences in the car fleet age in these two cities. In fact, as shown in Fig. C.17, the fleet in Harju county (which includes Tallinn) is characterized by newer vehicles compared to Tartu county. Considering this county level data (which includes only cars), we estimated an average EURO 2.3 for Tartu county and EURO 2.9 for Harju county. However, our results for Tartu and Tallinn show larger differences, which are probably related to the measurement of a higher fraction of diesel vehicles in Tallinn, where the driving route included an outbound road with high density of diesel trucks. Indeed, the EFs estimated for Tallinn show a lower gasoline:diesel share (33 %:67 %) compared to Tartu (49 %:51 %), an indication that our average EFs obtained for Tallinn seem to be slightly biased by higher diesel emissions.

Figure 5.5: EFs of NH$_3$ versus eBC (points in light colours from event-based analyses; median and interquartile range highlighted) for the three measurement locations. The NH$_3$-eBC isopleths for the different Euro classes were determined fitting a linear function between the literature average EFs for gasoline and diesel vehicles for each Euro-class (Andre et al., 2006; Alves et al., 2013, 2015; Carslaw and Rhys-Tyler, 2013; Huang et al., 2013; Lopes et al., 2013; May et al., 2014). The same literature EFs were used to determine the isopleths for the fleet composition, which were also fitted with a linear function.

5.4.4 Traffic contribution to measured NH$_3$ and comparison with emission inventories

As previously stated, the analyses of the spatial distributions and their correlations indicate that traffic may dominate NH$_3$ emissions within the three cities. We estimated the contribution of traffic related NH$_3$ ($N_{NH_3}^{traffic}$), by considering HOA as our best available traffic tracer and the average emission ratio of NH$_3$ to HOA ($E_{R(NH_3,HOA)}$) from the event-based analyses. We compare the estimated traffic related NH$_3$ ($N_{NH_3}^{traffic}$) to the total measured NH$_3$ ($N_{NH_3}^{meas}$) by means of the residual to uncertainty ratio ($R/U$):
5.4 Results and discussion

\[ \frac{R}{U} = \frac{NH_3 \text{ fit} - NH_3 \text{ meas}}{\sigma_{NH_3 \text{ fit}}} = \frac{ER(NH_3, HOA) \times HOA - NH_3 \text{ meas}}{\sigma_{ER(NH_3, HOA)} \times HOA} \]  \hspace{1cm} (5.7)

where \( \sigma_{NH_3 \text{ fit}} \) is the standard deviation of the fitted \( NH_3 \) traffic contribution and is given by the product of the standard deviation of the event-based \( ER(\sigma_{ER(NH_3, HOA)}) \) and HOA. The frequency and spatial distributions of \( R/U \) are reported in Fig. 5.6 for the three measurement locations. In all cases, the frequency distributions of \( R/U \) are all tightly clustered between -1 and +1 (variance (\( \sigma^2 \)) between 0.23 and 0.28) with a slightly positive bias, indicating that within our measurement variability the \( NH_3 \) enhancements for all single points could be explained by traffic emissions, in the three urban areas. As shown by the spatial distributions of \( R/U \), there are only few points in each city with \( R/U \leq -2 \) (i.e. \( NH_3 \) not fully explained by traffic) and none with \( R/U \geq 2 \) (i.e. \( NH_3 \) from traffic overestimated). Moreover, the positive \( R/U \) values are mostly found in areas with low \( NH_3 \) concentrations (indicated with the marker size in Fig. 5.6). The points with negative \( R/U \) might be related to the presence of additional sources of \( NH_3 \), e.g. industrial plants, waste containers, and emissions from agriculture. Although such point sources are in general very hard to assess, we found evidence that the unexplained \( NH_3 \) in the city suburban area south-west of Tartu was related with cowsheds emissions, which was supported by enhancements in \( CH_4 \) concentrations (see Fig. C.18).

**Figure 5.6:** Frequency and spatial distributions of the residuals to uncertainty ratios (\( R/U \)) from the fit of \( NH_3 \) with HOA and the traffic EFs for the three measurement locations.
Although we demonstrate that in the three cities traffic dominates the emissions of NH$_3$, the maximum enhancements of NH$_3$ in the traffic areas are of the same order or lower than the background concentrations (i.e. $(P_{75}-P_{05})$ of 3.4, 1.8 and 3.0 ppb compared to $P_{05}$ of 9.3, 4.7 and 3.2 ppb in Zurich, Tartu and Tallinn, respectively). Thus, the background concentrations remain the dominant source of NH$_3$ in all cases (especially in Zurich and Tartu) and need to be further investigated. By fitting the NH$_3$ background concentrations using the HOA and the traffic EFs, we find that traffic can explain 9.8 % of the NH$_3$ background in Zurich, 7.7 % in Tartu, and up to 23.8 % in Tallinn, as shown in Fig. C.19. Note that this approach considers the deposition processes of NH$_3$ to be negligible compared to the dilution of both HOA and NH$_3$. The unexplained NH$_3$ background concentrations are most probably related to the regional background of NH$_3$, which is expected to be dominated by agricultural emissions.

Considering both the enhancements $(P_{75}-P_{05})$ in the cities and its contribution to the background concentrations, traffic explains 33.9 %, 33.3 % and 60.7 % of the total NH$_3$ measured in Zurich, Tartu, and Tallinn, respectively. Significant spatial differences in the traffic contributions to NH$_3$ emissions are also observed in the inventories compiled for the EURODELT-III modelling inter-comparison exercise (Bessagnet et al., 2016; Ciarelli et al., 2016), as shown in Fig. C.19. Specifically, the traffic contribution to NH$_3$ emissions is on average 11.5 % for the cells that include Zurich (6.5 % in the cell south of Zurich and 16.5 % in the cell north of Zurich), 5.5 % for the cells that include Tartu (6.8 % in the cell south of Tartu and 4.2 % in the cell north of Tartu), and 43.3 % for the cell that includes Tallinn. Considering the city-coverage in the cells of interest and our evaluation of the traffic contributions to the background concentrations and urban increments of NH$_3$ for the three measurement locations, we can roughly estimate from our measurements a contribution of traffic to NH$_3$ emissions of 13.0 %, 8.9 % and 32.7 % for the cells that include Zurich, Tartu, and Tallinn, respectively. As shown in Fig. C.20 these estimates compare fairly well with the cell averages of the emission inventory.

5.5 Conclusions

In this work we combine measurements of NH$_3$, CO$_2$, eBC and the chemical composition of the NR-PM$_{2.5}$ (measured by AMS) to identify and characterize the major sources of NH$_3$ and their distributions in three European cities: Zurich (Switzerland), Tartu (Estonia) and Tallinn (Estonia). The use of a heated line with auxiliary flow reduced the adsorption of NH$_3$ on the inlet walls, significantly reducing the response and recovery times of the NH$_3$ measurement. In addition, a detailed characterization of the system response and recovery times was used to deconvolve the NH$_3$ signal from the remaining adsorption-induced hysteresis, enabling a quantitative characterization of NH$_3$ point sources with a mobile sampling platform.

The background concentrations (defined as 5$^{th}$ percentile, $P_{05}$) of NH$_3$ ranged between 2 and 19 ppb, with higher levels observed in Zurich (on average 9.3 ppb, compared to 4.7 ppb in Tartu and 3.2 ppb in Tallinn) probably due to more intense agricultural activity. In all three locations, NH$_3$ was strongly enhanced in the traffic areas of the city, and its spatial distribution was consistent with those of HOA, eBC and CO$_2$. Average enhancements $(P_{75} - P_{05})$ of 3.4, 1.8
and 3.0 ppb of NH$_3$ were measured in the traffic areas in Zurich, Tartu and Tallinn respectively, representing an enhancement of 36.6, 38.3 and 93.8 % over the average background concentrations.

Although the levels of organic aerosols from biomass burning and traffic were comparable in all three locations, traffic clearly dominates the increments of NH$_3$, equivalent black carbon (eBC) and carbon monoxide (CO). Traffic EFs of NH$_3$, eBC, HOA and CO were estimated using measurements in urban areas highly influenced by traffic, as well as tunnels near Zurich, and were used to characterize the composition of the traffic fleet in the three cities. A similar gasoline:diesel share was estimated for the three locations (gasoline vehicles representing around 44 % of the total fleet in Zurich, 50 % in Tartu and 33 % in Tallinn), but a newer vehicle fleet yields lower EFs in Zurich than Tartu or Tallinn. Based on the retrieved EFs, traffic fully explained the NH$_3$ enhancements in the three cities, and up to 8 to 24 % of the background concentrations, which are hypothesized to result from agricultural activities. Considering the traffic contributions to the background and the city enhancement of NH$_3$, we estimate that 33 to 61 % of the NH$_3$ measured in the three cities is related to traffic emissions. These results compare fairly well with the available emission inventories for the three cities.

Acknowledgments. This work was carried out in the framework of the public procurement “Determination of Chemical Composition of Atmospheric Gases and Aerosols in Estonia” of the Estonian Environmental Research Centre (Reference number: 146623), funded by the Estonian–Swiss cooperation program “Enforcement of the surveillance network of the Estonian air quality: Determination of origin of fine particles in Estonia”. We also acknowledge the support of the Swiss National Science Foundation (IZERZ0 142146) and the funding for the measurements in Zurich by the Federal Office for the Environment (FOEN) in Switzerland. Jay G. Slowik acknowledges the support of the Swiss National Science Foundation (starting grant no. BSSGI0 155846).
Conclusions and outlook

Air pollution is a problem of high concern in densely populated urban areas due to the intensive anthropogenic emissions present in the urban agglomerations and their effect on public health. According to a recent study of the WHO, more than 80% of the people living in urban areas that monitor air pollution are exposed to air quality levels that exceed the recommended limits for PM$_{2.5}$ and PM$_{10}$. Although air pollution is a worldwide problem, it impacts more severely developing countries. In 2010, China (with 1.36 million deaths a year) and India (with 0.65 million deaths a year) lead the list of the highest premature mortality due to outdoor air pollution.

This thesis aimed for a better characterization and quantification of the major gaseous and particulate pollutants in urban areas. Mass spectrometer measurements were performed in wintertime for 1-3 weeks in Xi’an (China), Beijing (China), Tartu (Estonia), Tallinn (Estonia), and Zurich (Switzerland). The use of a HR-ToF-AMS allowed for the online size-resolved chemical characterization of the NR aerosols (OA, SO$_4$, NO$_3$, NH$_4$ and Cl). Positive matrix factorization was then applied to identify and quantify the major sources of OA in the different measurement locations. While previous AMS studies have been limited to the measurement of the PM$_1$ fraction, a newly developed PM$_{2.5}$ lens was used here to extend the measured fraction to PM$_{2.5}$. Combining the AMS measurements with the measurement of eBC, we accessed the bulk PM$_{2.5}$ fraction (neglecting small contributions of dust and other refractory compounds). In Estonia and Switzerland the measurements were performed on a mobile platform, which enabled the investigation of the spatial distributions of the measured compounds and the identification of characteristic source areas within the cities. Such measurements also allowed the determination of regional background concentrations and urban increments, based on which the direct influence of anthropogenic emissions of different pollutants can be unequivocally assessed. The mobile platform was also equipped with several gas-phase monitors to measure the concentrations of the major gas-phase pollutants, including CO, CO$_2$, CH$_4$ and NH$_3$. A heated inlet set-up was deployed for the NH$_3$ measurements in order to
The measurements in China represent the first online characterization of the chemical composition and size distribution of the PM$_{2.5}$ during extreme haze events (visibility below 2 km) using a HR-ToF-AMS. During the extreme haze events (caused by stagnant meteorological conditions that confine the aerosols in the basin) average PM$_{2.5}$ concentrations of 537 and 243 µg m$^{-3}$ were recorded in Xi’an and Beijing, respectively. Among all aerosol components, SO$_4$, NO$_3$ and OOA showed the strongest enhancements. The high RH characteristic of the extreme haze events was shown to favor the heterogeneous oxidation of SO$_2$ in deliquesced aerosols, but didn’t seem to significantly affect the formation of NO$_3$ and OOA. The size of the particles also increased drastically during the extreme haze events (distribution modes shifted from around 400 nm to 800-1000 nm), due to the condensation of semi-volatile compounds on preexisting particles and the formation of secondary aerosol. The use of the PM$_{2.5}$ inlet was crucial in the presence of such large particles, and we estimated that almost 40 % of the mass would have been lost in the conventional PM$_{1}$ inlet during the extreme haze events. Systematic source apportionment analyses, focused on minimizing the user subjectivity on the solution selection, allowed for the separation of the several primary sources of OA in the two cities. Biomass burning (from domestic heating and agricultural activities) was the dominant source of OA in Xi’an (42 to 43 % of the total OA mass), while coal emissions (from domestic heating, cooking and industrial processes) dominated the mass in Beijing (47 to 55 % of OA mass). These two combustion sources were also identified as the major cause for very high PAH concentrations measured with the AMS (campaign average of 2.1 µg m$^{-3}$). In contrast, traffic and cooking emissions represented only small fractions of the OA mass in both locations (5 to 20 % of the mass).

Much lower concentrations were measured in the three European cities, with average PM$_{2.5}$ mass concentrations of 9.1 µg m$^{-3}$ in Tartu, 15.6 µg m$^{-3}$ in Tallinn, and 17.8 µg m$^{-3}$ in Zurich. Four sources of OA were identified in all three cases, including traffic, biomass burning, residential/cooking emissions and OOA. The primary sources dominated the OA mass during day-time and were strongly enhanced in specific areas of the cities, while the oxygenated component dominated the OA mass during night-time and was homogeneously distributed over the areas covered with our routes. The measured concentrations were occasionally strongly enhanced due to the transport of air masses from northern Germany to Estonia (which induced a strong increase in the secondary species (SO$_4$, NO$_3$, NH$_4$ and OOA)) or due to temperature inversions which induced the accumulation of local primary emissions (eBC and primary OA sources). Excluding such exceptional cases, for Tartu we were able to estimate an average PM$_{2.5}$ urban increment of 6.0 µg m$^{-3}$ over a regional background concentration of 4.0 µg m$^{-3}$. This strong increment was related to the enhancement of eBC and the primary OA sources inside the city, of which 74 % could be attributed to traffic emissions.

The use of a heated inlet with an auxiliary flow significantly decreased the response time of NH$_3$ measurements, which in turn enabled the identification of point sources with the mobile platform. The subsequent deconvolution of the NH$_3$ signal using the calibration parameters successfully minimized the remaining measurement delay. The comparison of the
spatial distributions of NH$_3$ and the other measured components during the mobile measurements in Tartu, Tallinn, and Zurich, elucidated significant correlations between NH$_3$ and traffic related pollutants (HOA, CO$_2$, CO and eBC). Traffic EFs of NH$_3$, eBC and HOA were determined for the three measurement locations. The estimated EFs show a high variability, characteristic of real world emissions, but significant differences can be observed between the three cities. The lowest EFs were determined for Zurich, followed by Tallinn and Tartu. These differences were attributed to the older vehicle fleet in Estonia compared to Switzerland. Average enhancements ($P_{75} - P_{05}$) of 3.4, 1.8 and 3.0 ppb of NH$_3$ were measured in the traffic areas of Zurich, Tartu and Tallinn respectively, which represent an enhancement of 36.6, 38.3 and 93.8 % over the average NH$_3$ background concentrations. Using the estimated EFs we demonstrate that within our uncertainties traffic emissions can fully explain the enhancements of NH$_3$ in the three cities, and up to 8 to 24 % of its urban background. Considering the traffic contributions to the background and the city enhancement of NH$_3$, we estimate that 33 to 61 % of the NH$_3$ measured in the three cities is related to traffic emissions, which compares fairly well with the available emission inventories for the three cities.

In this thesis we have provided innovative methods to investigate the sources of air pollution in urban areas. Novel source apportionment approaches have been developed to properly separate the several primary sources of OA present in Xi’an and Beijing. Similar methods can be applied in the future in other extremely polluted areas (e.g. India). Moreover, we demonstrate that combining several gas and particle phase measurements together with the use of a mobile platform may provide better insights into the pollution sources and their spatial distributions in urban areas. Results presented in this work are therefore ideally suited to improve street level modelling of air pollution, providing fundamental information for epidemiological studies. Furthermore, the use of a mobile platform together with a careful selection of the measurement roots and instrumentation deployed have proven very effective in separating the influence of different anthropogenic sources on the concentration of trace gases and particles and the determination of their emission factors. While here we were able to provide emission factors from car exhausts under real world driving conditions, similar measurements in areas highly impacted by residential heating emissions (e.g. Alpine valleys) will be required for the determination of characteristic emission factors of gas and particle phase components from biomass burning. While we could relate the urban increments of NH$_3$ to traffic emissions, the sources influencing the background concentrations of NH$_3$ were not fully identified. Additional measurements of emission factors of other important anthropogenic sources of NH$_3$ (e.g. various agricultural emissions) should be achieved in the future.

While the AMS has become a routine instrument in aerosol research, recent instrumental developments like a newly developed mechanical chopper system will allow a higher transmission of aerosol particles and improved signal-to-noise ratios. Furthermore, a novel filter inlet for gases and aerosols (Figero) (Lopez-Hilfiker et al., 2014) coupled with the AMS will allow online analysis of both gas and particle molecular composition. Future measurements may also include an Extractive Electro Spray Ionization-Time of Flight-Mass Spectrometer (EESI-Tof-MS) (Gallimore et al., 2013) to measure detailed chemical composition of soluble organic aerosols compounds that are extracted and ionized by a solvent
electrospray, producing molecular ions with minimal fragmentation and improving therefore the measurement of highly functionalized, high-molecular weight compounds. Moreover, a Proton Transfer Reaction – Mass Spectrometer (PTR-MS) might be used in future measurements to determine the composition of the gas-phase volatile organic components, as combined AMS and PTR-MS source apportionment has been shown to be a successful approach to separate OOA from different sources (Crippa et al., 2013c).
Supplement of:
New insights into PM$_{2.5}$ chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry

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Table A.1: Squared Pearson coefficient (top) and ratios (bottom) derived from the correlations between the OA sources and its external time series for the four periods of interest as represented in Fig. A.8. The values reported in parenthesis are related to the unconstrained source apportionment solution (average of 10 runs).

<table>
<thead>
<tr>
<th>Source</th>
<th>Xi'an</th>
<th>Beijing</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Extreme haze</td>
<td>Reference</td>
<td>Extreme haze</td>
</tr>
<tr>
<td>OOA vs. NH$_4$</td>
<td>0.22 (0.50)</td>
<td>0.71 (0.83)</td>
<td>0.38 (0.63)</td>
</tr>
<tr>
<td>COA vs. C$<em>6$H$</em>{10}$O</td>
<td>0.21 (0.008)</td>
<td>0.58 (0.29)</td>
<td>0.44 (0.2)</td>
</tr>
<tr>
<td>CCOA vs. AMS-PAH</td>
<td>0.57 (0.61)</td>
<td>0.59 (0.60)</td>
<td>0.96 (0.97)</td>
</tr>
<tr>
<td>BBOA vs. C$_2$H$_4$O$_2$</td>
<td>0.98 (0.96)</td>
<td>0.96 (0.88)</td>
<td>0.79 (0.80)</td>
</tr>
<tr>
<td>BBOA vs. eBC$_{wb}$</td>
<td>0.33 (0.34)</td>
<td>0.53 (0.53)</td>
<td>N.A.</td>
</tr>
<tr>
<td>HOA vs. eBC$_{tr}$</td>
<td>0.61 (0.67)</td>
<td>0.61 (0.62)</td>
<td>0.56 (0.64)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ratio (source/marker)</th>
<th>Xi'an</th>
<th>Beijing</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Extreme haze</td>
<td>Reference</td>
<td>Extreme haze</td>
</tr>
<tr>
<td>OOA/NH$_4$</td>
<td>0.99 (0.74)</td>
<td>1.08 (0.64)</td>
<td>0.67 (0.42)</td>
</tr>
<tr>
<td>COA/C$<em>6$H$</em>{10}$O</td>
<td>60 (219)</td>
<td>144 (267)</td>
<td>126 (372)</td>
</tr>
<tr>
<td>CCOA/AMS-PAH</td>
<td>3.4 (2.4)</td>
<td>5.5 (3.3)</td>
<td>10.8 (8.4)</td>
</tr>
<tr>
<td>BBOA/C$_2$H$_4$O$_2$</td>
<td>51 (39)</td>
<td>54 (39)</td>
<td>29 (34)</td>
</tr>
<tr>
<td>BBOA/eBC$_{wb}$</td>
<td>10.8 (8.3)</td>
<td>4.9 (3.6)</td>
<td>N.A.</td>
</tr>
<tr>
<td>HOA/eBC$_{tr}$</td>
<td>1.18 (0.62)</td>
<td>1.6 (2.6)</td>
<td>N.A.</td>
</tr>
</tbody>
</table>
Table A.2: Mean concentration and standard deviation for all measured compounds and sources for the four periods of interest.

<table>
<thead>
<tr>
<th>Mean conc. (µg m⁻³)</th>
<th>Xi’an</th>
<th>Beijing</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Extreme haze</td>
<td>Reference</td>
<td>Extreme haze</td>
<td>Reference</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>537 ± 146</td>
<td>140 ± 99</td>
<td>243 ± 47</td>
<td>75 ± 61</td>
</tr>
<tr>
<td>OA</td>
<td>216 ± 85</td>
<td>76 ± 56</td>
<td>103 ± 33</td>
<td>42 ± 37</td>
</tr>
<tr>
<td>SO₄</td>
<td>119 ± 30</td>
<td>12 ± 12</td>
<td>47 ± 15</td>
<td>12 ± 11</td>
</tr>
<tr>
<td>NO₃</td>
<td>71 ± 12</td>
<td>14 ± 11</td>
<td>43 ± 11</td>
<td>7.4 ± 5.6</td>
</tr>
<tr>
<td>NH₄</td>
<td>31 ± 15</td>
<td>11.4 ± 10.6</td>
<td>14.9 ± 5.1</td>
<td>5.3 ± 5.4</td>
</tr>
<tr>
<td>Cl</td>
<td>62 ± 12</td>
<td>11.3 ± 9.0</td>
<td>35.4 ± 7.9</td>
<td>8.4 ± 6.6</td>
</tr>
<tr>
<td>eBC</td>
<td>39 ± 16</td>
<td>15.0 ± 9.5</td>
<td>3.4 ± 1.1</td>
<td>1.5 ± 1.3</td>
</tr>
<tr>
<td>OOA</td>
<td>47 ± 12</td>
<td>5.4 ± 8.9</td>
<td>14.7 ± 5.5</td>
<td>2.4 ± 3.1</td>
</tr>
<tr>
<td>HOA</td>
<td>49 ± 41</td>
<td>23 ± 27</td>
<td>12.9 ± 9.0</td>
<td>6.9 ± 9.9</td>
</tr>
<tr>
<td>BBOA</td>
<td>67 ± 40</td>
<td>22 ± 20</td>
<td>15.1 ± 9.6</td>
<td>4.6 ± 6.9</td>
</tr>
<tr>
<td>CCOA</td>
<td>7.7 ± 8.0</td>
<td>5.7 ± 4.1</td>
<td>33 ± 23</td>
<td>16 ± 18</td>
</tr>
<tr>
<td>COA</td>
<td>33 ± 16</td>
<td>15.8 ± 8.7</td>
<td>19 ± 10</td>
<td>10.0 ± 9.6</td>
</tr>
<tr>
<td>PAH</td>
<td>3.5 ± 2.2</td>
<td>1.6 ± 1.1</td>
<td>4.0 ± 2.7</td>
<td>1.9 ± 2.2</td>
</tr>
</tbody>
</table>
Figure A.1: Comparison between mass concentrations obtained from gravimetric measurements of PM$_{2.5}$ filters (black) and total mass measured with AMS and Aethalometer (blue); Gravimetric analysis only available for the first part of measurements in Xi’an.

Figure A.2: (a) Time series of the measured eBC (black) and the eBC calculated (blue) as a linear combination of HOA, BBOA and CCOA for the full measurements period. (b) Correlation between measured and calculated eBC in Xi’an (top) and Beijing (bottom).
Figure A.3: (a) PMF profiles for four, five and six factor solution (from left to right); (b) Time series of the identified profiles for four, five and six factors (from left to right).
Figure A.4: Relative contribution of m/z 60 in HOA profile over the investigated $a$ value space; Acceptable contributions according to Ng et al. (2011) inside red area (mean ± 2σ).

Figure A.5: Averaged COA mass spectra for red cluster (top), blue cluster (center) and purple cluster (bottom) of the three clusters solution shown in Fig. 3.1. The error bars represent the standard deviation among all solutions in the final $a$ value range.
Figure A.6: Investigated a value space with color code showing the standard deviation of the normalized difference between the measured external time series and their fits calculated using the source apportionment results for: (a) AMS-PAH and BBOA, CCOA and HOA; (b) eBC$_{tr}$ and HOA; (c) eBC$_{wb}$ and BBOA.

Figure A.7: Comparison of the unconstrained and optimized solutions in terms of the relative contributions of the OA sources for the four periods of interest.
Figure A.8: Scatter plots between OA sources from the optimized solution and their external tracers; Colors are used to indicate the different periods of interest.

Figure A.9: Median diurnal trends for AMS species and eBC during the four periods of interest. Shaded area represents the 25th and 75th percentiles ($P_{25}$ and $P_{75}$) of the diurnals.
Figure A.10: Meteorological parameters during the measurement periods including visibility, wind speed, total radiation, net radiation, dew point, pressure, relative humidity and temperature (from top to bottom); Blue time series were retrieved in situ in the measurement locations and green time series were recorded in nearby local meteorological stations.
Figure A.11: Time series of the OA sources with black shadow representing the standard deviation among all good $a$ value combinations.
Figure A.12: Median diurnal trends for OA sources during the four periods of interest. Light shaded area represents the 25th and 75th percentiles ($P_{25}$ and $P_{75}$) and strong shaded area represents the standard deviation among all good $\sigma$ value combinations.
Figure A.13: Source regions of the OA sources identified with PSCF analysis for 3 periods of interest (the period with extreme haze in Beijing has too few points for statistically significant PSCF analysis). The color code indicates the normalized cell probability averaged for the 3 possible back-trajectory heights (i.e. the probability that a certain pollutant was originated from a certain cell). The marker size is given by a weighting factor that takes into account the standard deviation from results at different heights and the back-trajectory counting statistic error. A detailed description of the PSCF methodology can be found in Polissar et al. (1999). The analyses were performed on 72-h wind back-trajectories calculated at 3 different altitudes above the receptor site (i.e. 100, 500, and 1000 m). The backward air mass trajectories were calculated using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4; Draxler and Hess, 1998) with a time resolution of 1 hour. Precipitation was taken into account by considering that rain above 0.1 mm h\(^{-1}\) (Bressi et al., 2014) will result in the wet deposition of the pollutant. An altitude threshold was set to 500 m (sensitivity analyses performed by setting this threshold to 500 m, 1000 m and 1500 m above ground, indicate that the results are not significantly affected by this parameter) and a lower mass threshold corresponding to the 75th percentile (P\(_{75}\)) was used for the mass concentrations (this threshold was tested at P\(_{50}\), P\(_{75}\) and P\(_{90}\); results were found to be similar at P\(_{50}\) and P\(_{75}\) while using P\(_{50}\) did not provide statistically robust results).
Figure A.14: (a) Weighted AMS-PAH residuals histogram (blue distribution) and Gaussian fit (black curve); (b) Diurnal variation of weighted AMS-PAH residuals.
Supplement of:
Urban increments of gaseous and aerosol pollutants and their sources using mobile aerosol mass spectrometry measurements

Miriam Elser¹, Carlo Bozzetti¹, Imad El-Haddad¹, Marek Maasikmets², Erik Teinemaa², Rene Richter¹, Robert Wolf¹, Jay G. Slowik¹, Urs Baltensperger¹, and André S. H. Prévôt¹

¹Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232, Villigen PSI, Switzerland
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Table B.1: Correlation coefficient ($R^2$) between the spatial distributions of all sources and components.

<table>
<thead>
<tr>
<th></th>
<th>HOA</th>
<th>BBOA</th>
<th>RIOA</th>
<th>OOA</th>
<th>SO$_4$</th>
<th>NO$_3$</th>
<th>NH$_4$</th>
<th>eBC</th>
<th>CO$_2$</th>
<th>CO</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOA</td>
<td>0.02</td>
<td>0.32</td>
<td>0.02</td>
<td>0.04</td>
<td>0.09</td>
<td>0.16</td>
<td>0.10</td>
<td><strong>0.61</strong></td>
<td><strong>0.59</strong></td>
<td><strong>0.58</strong></td>
<td>0.06</td>
</tr>
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<td>BBOA</td>
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Figure B.1: Emission maps for (a) Tartu and (b) Tallinn. Green dots indicate residential wood combustion sources, blue markers indicate industrial sources (mainly local boiler houses) and the color of the main streets represents the traffic emission rates.
Figure B.2: Meteorological conditions during measurements periods in Tartu (data from the Tartu monitoring station) and Tallinn (data from the Zoo monitoring station).

Figure B.3: Schematic of the mobile laboratory instrumental set-up.
eBC source apportionment:

The choice of the wavelengths and of the angstrom exponents used in this work are based on the findings in Zotter (2015), where radiocarbon ($^{14}$C) measurements of elemental carbon (EC) are combined with Aethalometer data to determine the Ångström exponents characteristic for wood burning ($\alpha_{wb}$) and traffic ($\alpha_{tr}$) emissions. The best $\alpha$ values were evaluated by fitting the source apportionment results of the Aethalometer (in particular $\text{BC}_{tr}/\text{BC}$) against the fossil fraction of EC ($\text{EC}_{f}/\text{EC}$) derived from $^{14}$C measurements. The best fitting $\alpha_{tr} = 0.9$ and $\alpha_{wb} = 1.68$ were obtained, when using the attenuation measured at 470 and 950 nm.

Other wavelength combinations were also tested but in all cases, especially when 370 nm was used, the residuals of the fit were worse. Moreover it is known that the 370 nm channel of the Aethalometer is more sensitive to artefacts, including response to light absorbing SOA and the adsorption of VOCs on the filter.
Figure B.4: (a) Temporal evolution of the OA sources (left axis) and the external tracers (right axis) over the full measurements period. (b) Correlations of the OA sources with their external tracers. Grey points are relative to periods considered as special events and were not considered for the linear fits. Note: All data was averaged to 30 minutes resolution, for which the separation eeBC_{tr} and eeBC_{wb} was possible.
Figure B.5: Source apportionment diagnostics for increasing number of factors: (a) Q/Q_{exp}; (b) Correlation coefficient (R^2) between OA sources and external factors; (c) Decrease in Q/Q_{exp} time series; (d) Decrease in Q/Q_{exp} profiles.
Figure B.6: Correlation between the BBOA time series from the four-factor solution and the sum of the BBOA and the ‘unknown’ time series in the five-factor solution.

Figure B.7: PMF factor mass spectra for three-, four- and five-factor solutions (from left to right).
Figure B.8: PMF factor temporal evolution for three-, four- and five-factor solutions.

Figure B.9: Temporal evolution of mass concentration of the four identified OA sources over the full measurement period. Black shaded area represents the standard deviation among 100 bootstrap runs.
Figure B.10: Average spatial distributions of (c) NH$_4$, (d) Cl and (e) CH$_4$ in Tartu. The color scales represent enhancement over the background concentrations; the maximum have been fixed to the 75$^{th}$ percentile of the average enhancement of each component. The sizes of the points represent the number of points that have been averaged in each case.

Figure B.11: Average spatial distributions of (c) NH$_4$, (d) Cl and (e) CH$_4$ in Tallinn. The color scales represent enhancement over the background concentrations; the maximum have been fixed to the 75$^{th}$ percentile of the average enhancement of each component. The sizes of the points represent the number of points that have been averaged in each case (Note: less data available for CH$_4$).
Figure B.12: Median longitude profiles of the enhancements of all measured components and sources in Tartu. Colored curves represent the median enhancement of each component/source over 26 loops and the grey shaded area represents the first and third quantiles (Q1 and Q3). The median enhancements were fitted with sigmoid functions (black curves). The fitting limits (pink and blue arrows in top panel) and the sigmoid’s midpoint ($X_0$) were determined from the fit of the total PM$_{2.5}$ mass (NR-PM$_{2.5}$ plus eBC) and then imposed to the other components/sources. The dashed black lines indicate a non-standard fit (described in each case in the plot) and the results of these fits are represented in parenthesis and grey color in Table 4.2.b. Notes: The spike found in the east for RIOA, OOA and SO$_4$ is not representative, as it is related to one single measurement point. The spike in CH$_4$ in the west side is related to consistent increases of this component nearby a cowshed and will be further investigated in a future publication.
Figure B.13: Average longitude profiles of the enhancements of the OA sources in Tartu separated into time-bins of two hours of local time (LT).
Figure B.14: Left: Average spatial distributions of the OA sources in Tallinn for west and east winds. The color scale represents the enhancement over the background concentrations and the sizes of the points represent the number of points that have been averaged in each case. The data related to special events is not considered. Right: Distribution of the normalized differences between the east- and west-related spatial distributions for each compound. $x_0$ indicates the center of the gauss function used to fit each distribution.
Figure B.15: Left: Average spatial distributions of the inorganic components (SO$_4$, NO$_3$, NH$_4$, and Cl), eBC and CO$_2$ in Tallinn for west and east winds. The color scales represent the enhancement over the background concentrations and the size the number of points that have been averaged in each case. The data related to special was excluded for these analyses. Right: Distribution of the normalized differences between the east- and west-related spatial distributions for each compound. $X_0$ indicates the center of the gauss function used to fit each distribution.
Supplement of:
High contributions of vehicular emissions of ammonia in three European cities derived from mobile measurements

Miriam Elser¹, Imad El-Haddad², Marek Maasikmet³, Carlo Bozzetti⁴, Robert Wolf⁵, Giancarlo Ciarelli⁵, Jay G. Slowik⁶, Rene Richter⁶, Erik Teinemaa⁷, Christoph Hüglin⁷, Urs Baltensperger⁸, and André S.H. Prévôt⁹

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²Estonian Environmental Research Centre, 10617, Tallinn, Estonia
³Swiss Federal Laboratories for Materials Science and Technology, EMPA, 8600, Dübendorf, Switzerland

Submitted to Atmos. Environ.
Figure C.1: Meteorological parameters during the measurements in Zurich. Data from NABEL (National Air Pollution Monitoring Network) Zurich-Kaserne monitoring station. Meteorological parameters for Tartu and Tallinn can be found in our previous publication (Elser et al., 2016b).
Figure C.2: Traffic tracers during tunnel measurements in Zurich (T1 to T12). Due to adsorption of NH$_3$ in the system lines, the measured NH$_3$ signal (green trace) shows broader peaks and a time delay in comparison to all other tracers. The mathematical deconvolution of the measured NH$_3$ as described in the main text allowed removing such adsorption effects and the determination of real NH$_3$ concentrations (pink trace). Using the $k_{eq}$ determined from the calibrations with the standard inlet we have estimated how the measured NH$_3$ signal would look like if no heating and auxiliary flow would have been used (blue dashed lines). In such case, several peaks of NH$_3$ ambient relevant concentrations would not have been detected and the deconvolution algorithm could not be successfully applied.
Table C.1: Correlation coefficient ($R^2$) between all traffic related pollutants measured during tunnel drives in Zurich: NH$_3$ measured (NH$_3$ meas) and deconvolved (NH$_3$ dec), eBC, CO$_2$ and HOA.

<table>
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<tr>
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<th>CO$_2$</th>
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Figure C.3: Average mean bias and mean error introduced by the deconvolution algorithm at different concentration steps of the calibration curves for the heated line and the heated line with auxiliary flow (final measurement set-up).
Figure C.4: Tests of volatilization of ammonium salts in the heated line. Different concentrations of (NH$_4$)$_2$SO$_4$ (top) and NH$_4$NO$_3$ (bottom) were injected in the inlet system, the particle-phase compounds were monitored with the AMS (NH$_4$, SO$_4$ and NO$_3$) and the gas phase with the NH$_3$ analyzer. The measurement position was switched between the beginning and the end of the heated line. MilliQ water was used to flash-clean the system between the different concentration steps. For increasing (NH$_4$)$_2$SO$_4$, no major changes were observed in the NH$_3$ signal, an indication that (NH$_4$)$_2$SO$_4$ doesn’t evaporate in the heated inlet. However, 10.9 ± 3.7 % of the particle-phase mass was lost on average in the line (difference between measurements before and after the heated line). This mass loss fraction was found to be constant for decreasing temperatures up to ambient values, which indicates that it is most probably explained by the loss of particles to the walls of the inlet and excludes the evaporation of (NH$_4$)$_2$SO$_4$ in the inlet line. In the case of NH$_4$NO$_3$, at each concentration step there was an increase in the NH$_3$ signal which is consistent with the complete volatilization of the injected NH$_4$NO$_3$ in the inlet line. This is also consistent with the AMS measuring background values of NH$_4$ and NO$_3$ after the heated line.
Appendix C Supplement of Chapter 5

Figure C.5: (a) $Q/Q_{\exp}$ for increasing number of factors; (b) Correlation coefficient ($R^2$) between OA sources and external factors for three-, four-, and five-factors solution; (c) Average relative contributions of the OA sources for three-, four-, and five-factors solution; (d) Decrease in $Q/Q_{\exp}$ time series for increasing number of factors; (e) Decrease in $Q/Q_{\exp}$ profile for increasing number of factors.

(*) Additional factor in 5-factors solution added to BBOA
As a first step, positive matrix factorization (PMF) was performed on the matrix of organic aerosols (OA) varying the number of factors between 1 and 7. The four-factor solution was found to represent best this dataset and the obtained factors were identified as hydrocarbon-like OA (HOA), biomass burning OA (BBOA), cooking OA (COA) and oxygenated OA (OOA). Typical characteristics and markers for these profiles have been described in detail in previous publications (Alfarra et al., 2007; Ng et al., 2011; Sun et al., 2011). Figure C.5 contains important source apportionment diagnostics including $Q/Q_{\text{exp}}$, factor–marker correlation, and time series and profile residuals for solutions with increasing number of factors. As shown in panel (b), the correlation coefficient ($R^2$) between the identified OA sources and their external markers improves considerably when increasing from three to four factors, but stays rather constant when a fifth factor is added. Moreover, the addition of the fourth-factor allows the separation of the BBOA, explaining additional structures in the residuals time series (panel (d)).
and biomass burning related fragments in the residuals profile (at m/z 60 and 73). The addition of a fifth factor induces a split of the BBOA time series that allowed the explanation in the residuals of N-containing fragments. Such split is expected given the variable nature of biomass smoke, but we couldn’t relate these two different BBOA time series to different emission processes. However, considering the sum of the BBOA and the additional factor in the five-factor solution, we do not observe any significant change in correlations or relative contribution (panel (c)) compared to the four-factor solution. Therefore, we considered the four-factor solution as the optimal representation of the data.

Bootstrap analyses (Paatero et al., 2014) were performed to simultaneously investigate the possibility of local minima in the solution space and the rotational ambiguity of the PMF four-factor solution. The same approach was applied for the dataset from Estonia and more details about this method can be found in Elser et al. (2016). From a total of hundred bootstrap runs, 81 solutions were considered to be optimal solutions and were averaged to obtain the final PMF solution reported in Fig. C.6. The remaining 19 solutions didn’t separate the BBOA and were therefore rejected. Such solutions showed instead a split in the OOA factor time series which we couldn’t attribute to a distinct processes (e.g. semi-volatile and low-volatility OOA). The profiles of the two obtained OOAs were very similar ($R^2=0.88$) and the additional OOA explained background variability.
Figure C.7: Time series of the identified OA sources: hydrocarbon-like OA (HOA), biomass burning OA (BBOA), cooking OA (COA) and oxygenated OA (OOA). The grey shaded areas behind the time series indicate the standard deviation among 81 bootstrap runs.
Figure C.8: Time series of ammonia (NH₃), carbon dioxide (CO₂), carbon monoxide (CO), equivalent black carbon (eBC), hydrocarbon-like organic aerosol (HOA), biomass burning organic aerosol (BBOA) and residential influenced organic aerosol (RIOA) for the measurements in Tartu and Tallinn.
Figure C.9: Time series of the AMS species (OA, SO$_4$, NO$_3$, NH$_4$ and Cl) during measurements in Zurich.
Figure C.10: Average spatial distribution of the enhancements (over the background concentrations) of COA, OOA, SO$_4$, NO$_3$, Cl and NH$_4$ in Zurich.
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Figure C.13: Average (left) and median (right) longitude profiles of the enhancements of NH$_3$ in Tartu. Grey shaded area represents the standard deviation of the averaged enhancement or the interquartile range for the median enhancement. The longitude profiles were fitted with sigmoid functions (black curves). The fitting limits and the sigmoid’s midpoint were determined from the fit of the total PM$_{2.5}$ mass (Elser et al., 2016b) and then imposed to the NH$_3$. Dashed black lines indicate a bad fit.
Table C.2: Regional background and urban increments of NH$_3$ and other traffic-related pollutants in Tartu. Results obtained from the fitting of the average and median longitude profiles (NH$_3$ in Fig. C.13 and CO$_2$, eBC and HOA in Elser et al. (2016b)). $P_{05}$ represents the averaged fifth percentile subtracted for the calculation of the enhancements; base and increment values were obtained from the sigmoid fits; the regional background is given by the sum of $P_{05}$ and the average base value; urban concentrations are the sum of the regional background and the average urban increment; the factor increase represents the ratio between the urban and the regional backgrounds.

(a) Excluding special events.

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<th></th>
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Figure C.14: Time series of the enhancements of eBC, HOA, NH$_3$, CO$_2$ and BBOA during a selected period of measurements in Tallinn. It is clearly seen that during periods with high BBOA there is no significant signal in the rest of compounds, which are mostly related to traffic emissions.
Figure C.15: Selection of the peaks for the determination of city event-based EFs. Time series represent background subtracted city drive measurements. Pink background indicates periods influenced by traffic emissions (i.e. with high concentrations of NH$_3$, CO$_2$, eBC and HOA and low concentrations of BBOA). The higher peaks within the selected periods were chosen for the calculation of the event-based EFs.

Table C.3: Median and interquartile range of the EFs of NH$_3$, eBC, HOA and CO reported in Fig. 5.4 for each measurement location.

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<th>Median [P$<em>{25}$-P$</em>{75}$] NH$_3$ (mg kg$^{-1}$ fuel)</th>
<th>eBC (mg kg$^{-1}$ fuel)</th>
<th>HOA (mg kg$^{-1}$ fuel)</th>
<th>CO (mg kg$^{-1}$ fuel)</th>
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<td>39.9 [33.8-51.1]</td>
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<td>137.1 [93.6-187.8]</td>
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Curriculum Vitae

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Education

04/2013-09/2016  PhD, Department of Environmental Systems Science (D-USYS) at ETH Zurich (ETHZ) and Laboratory of Atmospheric Chemistry (LAC) at Paul Scherrer Institute (PSI). Dissertation advisor: Prof. Dr. Urs Baltensperger

01/2011-11/2012  Master studies in Physics with specialization in Geophysics, Physics of the Environment and Cultural Heritage at the University of Milan (UNIMI), Italy.
Thesis: “Ultrafine particles in the atmosphere: sampling and characterization methods”. Supervised by Prof. Dr. Roberta Vecchi
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09/2009-12/2010  Bachelor studies in Physics with specialization in Applied Physics at the University of Milan (UNIMI), Italy.
Thesis: “Validation of climate simulation models for the Italian territory (rainfall simulations)”. Supervised by Prof. Dr. Maurizio Maugeri
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09/2006-07/2009  Physics studies at the University of Mallorca (UIB), Spain.

International conferences and meetings

American Association for Aerosol Research 34th Annual Conference, Minneapolis, USA, 2015 (two oral presentations)

European Aerosol Conference, Milan, Italy, 2015 (oral presentation)

16th Annual AMS Users Meeting, Milan, Italy, 2015 (oral presentation)

European Geosciences Union General Assembly 2014, Wien, Austria, 2014 (poster)

European Aerosol Conference, Prag, Czech Republic, 2013

14th Annual AMS Users Meeting, Prag, Czech Republic, 2013
Publications


