Organic aerosol source apportionment in Zurich using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) – Part 1: Biogenic influences and day–night chemistry in summer

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Abstract. Improving the understanding of the health and climate impacts of aerosols remains challenging and is restricted by the limitations of current measurement techniques. Detailed investigation of secondary organic aerosol (SOA), which is typically the dominating fraction of the organic aerosol (OA), requires instrumentation capable of real-time, in situ measurements of molecular composition. In this study, we present the first ambient measurements by a novel extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS). The EESI-TOF-MS was deployed along with a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) during summer 2016 at an urban location (Zurich, Switzerland). Positive matrix factorization (PMF), implemented within the Multilinear Engine (ME-2), was applied to the data from both instruments to quantify the primary and secondary contributions to OA. From the EESI-TOF-MS analysis, a six-factor solution was selected as the most representative and interpretable solution for the investigated dataset, including two primary and four secondary factors. The primary factors are dominated by cooking and cigarette smoke signatures while the secondary factors are discriminated according to their daytime (two factors) and night-time (two factors) chemistry. All four factors showed strong influence by biogenic emissions but exhibited significant day–night differences. Factors dominating during daytime showed predominantly ions characteristic of monoterpene and sesquiterpene oxidation while the night-time factors included less oxygenated terpene oxidation products, as well as organonitrates which were likely derived from NO₃ radical oxidation of monoterpenes. Overall, the signal measured by the EESI-TOF-MS and AMS showed a good correlation. Further, the two instruments were in excellent agreement in terms of both the mass contribution apportioned to the sum of POA and SOA factors and the total SOA signal. However, while the oxygenated organic aerosol (OOA) factors separated by AMS analysis exhibited a flat diurnal pattern, the EESI-TOF-MS factors illustrated significant chemical variation throughout the day. The captured variability, inaccessible from AMS PMF analysis, was shown to be consistent with the variations in the physiochemical processes influencing chemical composition and SOA formation. The improved source separation and interpretability of EESI-TOF-MS results suggest it to be a promising approach to source apportionment and atmospheric composition research.

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1 Introduction

Atmospheric aerosols impact visibility, human health, and climate on global scale; therefore a detailed knowledge of chemical composition, sources, and processes is a fundamental prerequisite to develop appropriate mitigation policies. Organic aerosols are an important fraction of the chemical composition and are classified as primary (POA) when directly emitted to the atmosphere and secondary (SOA) when formed in the atmosphere through the oxidation of gas-phase precursors, yielding less volatile products which condense to the particle phase (Hallquist et al., 2009). Overall, organic aerosols account for 20 %–60 % of the total fine particulate mass in the continental mid-latitude atmosphere and up to 90 % in tropical forested areas (Kanakidou et al., 2005; Carlton et al., 2009). POA emissions typically include combustion of fossil fuels, direct injection of unburnt fuel and lubricants, industrial emissions, plant matter debris, biomass burning, cooking emissions, and biogenic emissions (De Gouw and Jimenez, 2009; Hayes et al., 2013). Current models estimate that SOA accounts for a dominant fraction of the total organic particulate mass in the lower troposphere, typically between 50 % (in polluted urban areas) and 90 % (Jimenez et al., 2009; Hallquist et al., 2009; Pye and Seinfeld, 2010; Spracklen et al., 2011). However our capability to characterize SOA is limited (Heald et al., 2008; Shiravas-tava et al., 2017). SOA precursors can have either biogenic or anthropogenic origins, and although key precursor gases for SOA formation are known, the absolute and relative contributions of different sources to SOA remain challenging to determine. Globally, SOA is dominated by oxidation products of biogenic volatile organic compounds, (including the monoterpenes α-pinene, one of the largest sources of secondary biogenic particulate matter worldwide) resulting in an estimated 90 % of SOA from biogenic emissions compared to only 10 % from anthropogenic sources (Hallquist et al., 2009). However, it has been shown that interaction between biogenic and anthropogenic volatile organic compounds can significantly enhance SOA production and affect its properties (Weber et al., 2007; De Gouw and Jimenez, 2009; Kautzman et al., 2010; Glasius et al., 2011; Hoyle et al., 2011; Emanuelsson et al., 2013; Setyan et al., 2014; Moise et al., 2015). Further, anthropogenic SOA disproportionally affects regions with a higher population and thereby exerts a larger impact on global health than suggested by its global average concentration. Elucidating the sources and physico-chemical processes governing SOA concentrations requires measurement techniques with high temporal and chemical resolution, which have proven challenging to achieve. The molecular composition of aerosol particles has so far mostly been investigated offline, using filter or cascade impactor samples, which are based on a time-integrating sampling step (typically 1 to 24 h) followed by post-analysis. This method provides detailed information on individual chemical species and/or functional groups in SOA but can be affected by compositional changes due to adsorption, evaporation, and chemical reactions during sample collection, storage, and/or transfer (Turpin et al., 2000; Hallquist et al., 2009). Further, many sources and processes affecting SOA have characteristic timescales that are too short for this measurement approach. Several online techniques have been developed, which couple thermal desorption and/or hard ionization with online mass spectrometry. A major advantage of the online techniques over offline techniques is their time resolution (Nozière et al., 2015). For instance, the Aerodyne aerosol mass spectrometer (AMS) and the CHARON PTR-ToF-MS are both able to describe bulk compositional properties of OA. However, the AMS subjects OA molecules to significant thermal decomposition and ionization-induced fragmentation. While thermal decomposition does not significantly influence the CHARON, the proton transfer reaction is of sufficiently high energy that molecules of the type found in SOA undergo significant fragmentation, with the signal from the parent ion comprising a very small fraction of the total (Müller et al., 2017). In order to retrieve information at the molecular level while avoiding ionization-induced fragmentation, a few online semi-continuous measurement techniques using soft ionization or thermal desorption have been developed (e.g. FIGAERO-CIMS; Lopez-Hilfiker et al., 2014 and TAG, Williams et al., 2006). These instruments have better chemical resolution and reduced thermal decomposition but still low time resolution. Another important drawback is the segregation of collection and analysis stages, which similarly to offline techniques open the possibility of reaction on the collection substrate and/or transfer artefacts. Alternatively, a soft ionization called aerosol flowing atmospheric-pressure afterglow (AeroFAPA) is also available. This technique allows mass spectrometric analysis of organic aerosols in real time and it consists of an ion source based on a helium glow discharge at atmospheric pressure. Ionization of the analytes occurs in the afterglow region after thermal desorption and produces mainly intact quasi-molecular ions (Brüggemann et al., 2015). The method is best suited for polar analytes with high volatilities and low molecular weights though, while for compounds with low vapour pressures, containing long carbon chains and/or high molecular weights, desorption and ionization is in direct competition with oxidation of the analytes, leading to the formation of adducts and oxidation products, which impede a clear signal assignment in the acquired mass spectra. In addition, the ionization pathways are not well-constrained, which makes non-linear behaviour likely. All these limitations (decomposition, fragmentation, reaction–transfer artefacts) are particularly problematic for SOA species, which is the fraction of sources and reactions that are least understood. Therefore, instrumentation is urgently needed that can assess original molecular information of organic aerosol, online, with high time resolution and with a linear response to mass.
Here we present the first field deployment of a recently developed extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) (Lopez-Hilfiker et al., 2019), which to our knowledge is the first instrument capable of online OA measurements at atmospheric concentrations using a controlled ionization scheme without thermal decomposition, ionization-induced fragmentation, or separated collection–analysis stages. The field campaign took place during summer 2016 at an urban background site in Zurich, the largest city in Switzerland; the companion paper presents results from a subsequent winter campaign (Qi et al., 2019). This study compares EESI-TOF-MS and AMS results in terms of both bulk composition and source apportionment to characterize the EESI-TOF-MS field performance and gain new insight into the sources and physicochemical processes governing OA composition.

2 Method

2.1 Field campaign

Continuous online measurements were performed between June and July 2016 at the Swiss National Air Pollution Monitoring Network (NABEL) station located in Zürich Kaserne, Switzerland (47°22′42″N, 8°31′52″E, 410 m a.s.l. – above sea level) (Herich et al., 2011). Zürich has a population of 1.3 million, and the site is located in the central metropolitan area, in a courtyard approximately 500 m south of the main train station. This location is not affected by major emissions from industries, but surrounded by roads with rather low traffic, apartment buildings, small businesses, and restaurants. The NABEL measurement station includes a number of long-term measurements, including trace gas monitors for nitrogen oxides (NOx) and ozone (O3), Thermo Environmental Instruments 49C, Thermo Electro Crop., Waltham, MA) and meteorological data including temperature, relative humidity, solar radiation, and wind speed and direction. For the intensive campaign, a separate trailer was deployed to house an additional suite of gas and particle instrumentation, including the EESI-TOF-MS and several other mass spectrometers, as described below.

The measurement site has been characterized in previous studies as “urban background” for PM10, PM2.5, and PM1 and additional air quality parameters (Hueglin et al., 2005; Lanz et al., 2007a, b; Daellenbach et al., 2016). The city of Zurich is a hub for railways, roads, and air traffic and is thus useful to assess different sources of SOA depending on location and seasonality. Lanz et al. (2007a, b) reported the first PMF study on an AMS dataset acquired at this site in summer 2005 and identified six factors, including traffic, wood burning, cooking, and a charbroiling-related source along with two secondary sources discriminated according to their volatility and degree of oxygenation. Additional studies on summer OA measurements provided further discrimination of sources including primary vs. secondary and fossil vs. non-fossil. Also, studies at other sites in Europe demonstrated that during summer carbonaceous aerosols are mainly of biogenic origin, emitted through either primary emissions or gas-phase oxidation products from biogenic volatile organic compounds (BVOCs) (Genberg et al., 2011; Yttri et al., 2011). Biogenic SOA (BSOA) has been shown to dominate over combustion-derived aerosols during summer (Gelencsér et al., 2007; Genberg et al., 2011; Yttri et al., 2011).

2.2 Instrumentation

Particle composition was measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and an extractive electrospray time-of-flight mass spectrometer (EESI-TOF-MS). A scanning mobility particle sizer (SMPS) measured particle size distributions. Here we focus on particle-phase composition and organic aerosol source apportionment via positive matrix factorization (PMF).

2.2.1 High-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS)

The non-refractory particle composition was monitored by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) equipped with a PM1 aerodynamic lens (DeCarlo et al., 2006; Canagaratna et al., 2007). The HR-ToF-AMS was operated with a temporal resolution of 1 min. Briefly, aerosol particles are continuously sampled through an aerodynamic lens, which focuses the particles into a narrow beam and accelerates them to a velocity inversely related to their vacuum aerodynamic diameter. The beam impacts a heated element (600°C, 10−7 torr), where the non-refractory components flash-vaporize. The resulting gas is ionized by electron impact (EI, 70 eV), and ion mass-to-charge ratios (m/z) are analysed by a time-of-flight mass spectrometer. The instrument was calibrated for ionization efficiency (IE) at the beginning and at the end of the campaign using 400 nm NH4NO3 particles following a mass-based method. A composition-dependent collection efficiency (CDCE) was used to correct the measured aerosol mass according to the algorithm of Middlebrook et al. (2012). Data analysis was performed in Igor Pro 6.3 (Wave Metrics) using SQUIRREL 1.57 and PIKA 1.16.

The PMF source apportionment technique (Sect. 2.3) requires as input the time series of ions from high-resolution mass spectral fitting along with their corresponding uncertainties. In the case of the AMS, the measurement uncertainties considered in the error matrix account for electronic noise, ion-to-ion variability at the detector, and ion counting statistics (Allan et al., 2003). Following the recommendation of Paatero and Hopke (2003), variables (m/z) with low signal-to-noise ratio (SNR < 0.2) were removed, whereas “weak” variables (0.2 < SNR < 2) were down-weighted by a
factor of 2. Further, all variables calculated during the AMS data analysis as a constant fraction of $m/z$ 44 (CO$_2^+$), i.e. the OA contributions to O$_2^+$, OH$^+$, H$_2$O$_2$ and CO$_2^+$, were excluded from PMF analysis to avoid overweighting CO$_2^+$. The contributions of these ions were recalculated after obtaining a solution and reinserted in the factor profiles presented here; the total factor mass was likewise corrected. Isotopic species were likewise excluded from the PMF solver and rescaled afterwards to their parent ions. The final input matrix contained 281 ions (excluding isotopes and CO$_2$-dependent ions and 285 ions including the CO$_2$-dependent ions) between $m/z$ 12 and 120 at a resolution of 3000–4000 $m/\Delta m$ and 22 182 points in time (with steps of 60 s).

2.2.2 Extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS)

The EESI-TOF-MS provides online, near-molecular-level measurements of organic aerosol composition with high time resolution. The system, which is described in detail elsewhere (Lopez-Hilfiker et al., 2019), consists of a recently developed EESI source integrated with a commercial time-of-flight mass spectrometer capable of mass resolution up to $\sim$ 4000 Th Th$^{-1}$ (Tofwerk AG, Thun, Switzerland). Briefly, particles and gases are continuously sampled through a multi-channel extruded carbon denuder which removes most gas-phase species with high efficiency. After the denuder, particles intersect a spray of charged droplets generated by a conventional electrospray probe and soluble components are extracted. The droplets enter the mass spectrometer through a heated stainless steel capillary, wherein the electrospray solvent evaporates and ions are ejected. Although the capillary is heated to 250°C, the effective temperature experienced by the anlyte molecules is much lower due to the short residence time, and no thermal decomposition is observed. The resulting ions are analysed by a portable high-resolution time-of-flight mass spectrometer with an atmospheric pressure interface (API-TOF-MS) (Junninen et al., 2010). The electrospray solution was a 50:50 water / methanol mixture doped with 100 ppm NaI, with spectra detected in positive mode. The NaI dopant almost entirely suppresses ionization pathways other than formation of Na$^+$ adducts, yielding a linear response to mass (without significant matrix effects) and simplifying spectral interpretation. The EESI-TOF-MS alternated between direct sampling (8 min) and sampling through a particle filter (3 min) to provide a measurement of instrument background (including spray); the difference between these two spectra yields the ambient aerosol composition. Data analysis, including high-resolution peak fitting, was performed using Tofware version 2.5.7 (Tofwerk AG, Thun, Switzerland).

Overall the EESI-TOF-MS measured for 3 consecutive weeks during summer in Zurich, achieving > 85 % data coverage. The remaining ~15 % loss of data acquisition was due to instrumental issues, e.g. clogged electrospray capillary resulting in loss of the signal or “dirty solution” to substitute (contamination from ambient air decreasing the purity of the solution). Concentrations of inorganic species were very low (see Fig. S1 in the Supplement) and a Nafion diffusion dryer was used to prevent major changes in relative humidity. No ion-dependent relative response factors were applied. The (NaI)Na$^+$ signal, an approximate surrogate for ion source stability, varied by ±7.3 % (relative standard deviation) across the entire campaign and exhibited no systematic drift (Fig. S2), and no corrections relating to sensitivity drift were applied.

Source apportionment analysis on the EESI data included 507 ions between $m/z$ 139 and 401, all of which were detected as adducts with Na$^+$ except for nicotine, which was observed with an extra hydrogen (C$_{10}$H$_{14}$N$_2$H$^+$, $m/z$ 163,123), likely due to hydrogen abstraction from water. Because of this unique ionization pathway, its relative sensitivity is less certain and its response to a changing particle matrix is poorly constrained, e.g. non-linear response to mass is a possibility. However, the good agreement between the PMF factors for the AMS and the EESI, discussed in Sect. 3.3, suggests that any such non-linearities are not significant. One unidentified ion was also included in the analysis. The final input matrix contained 4436 points in time (with steps of 300 s, re-averaged from original 2 s). The input matrix of data and error was calculated as follows. (1) Raw data with time resolution of 2 s were processed with Tofware, including high-resolution peak fitting, to generate an initial data matrix including mass spectra from both direct ambient sampling and the filter blank. (2) Filter periods were interpolated to yield an estimated background spectrum during ambient measurements. (3) The estimated background was subtracted from the ambient spectrum and the resulting difference matrix re-averaged to 300 s time resolution for PMF analysis. (4) Ions whose signal was dominated by spray and/or instrument/gas background as defined by a signal-to-noise ratio (SNR) below 2 were excluded from further analysis. (5) The error matrix was calculated according to Eq. (1) following the model of Allan et al. (2003), which accounts for uncertainties related to the measurements ($\delta_{ij}$) and to the background ($\beta_{ij}$).

$$\sigma_{ij} = \sqrt{\delta_{ij}^2 + \beta_{ij}^2}$$

(1)

The raw measured signal from the EESI-TOF-MS is acquired in ions per seconds (cps) but throughout the text and figures we report the signal measured by the EESI-TOF-MS in terms of the mass flux of ions to the microchannel plate detector (ag s$^{-1}$), to facilitate interpretation of PMF results and comparison with other instruments, both of which are typically described in terms of mass rather than moles. The mass flux of ions is calculated as follows:

$$M_x = I_x \times (MW_x - MW_{cc})$$

(2)
where $M_x$ is the mass flux of ions in attogrammes per second and $x$ represents the measured molecular composition. $I_x$ is the recorded signal (cps) measured by the EESI-TOF-MS. $M_W$ and $M_W^{cc}$ represent the molecular weight of the ion and the charge carrier (e.g. $H^+$, $Na^+$), respectively. Note that this measured mass flux can be related to ambient concentration by the instrument flow rate, EESI extraction–ionization efficiency, declustering probability, and ion transmission, where several of these parameters are ion-dependent (Lopez-Hilfiker et al., 2019).

### 2.3 Source apportionment

Source apportionment was performed separately on the organic HR-ToF-AMS and EESI-TOF-MS mass spectral time series using positive matrix factorization (PMF) as implemented by the Multilinear Engine (ME-2) (Paatero, 1997) and controlled via the interface SoFi (Source Finder, version 6.39; Canonaco et al., 2013) programmed in Igor Pro (WaveMetrics, Inc.). PMF is a bilinear receptor model used to describe measurements (in this case the matrix of organic mass spectra as a function of time) as a linear combination of static factor profiles (i.e. characteristic mass spectra), corresponding to specific emission sources and/or atmospheric processes, and their time-dependent source contributions as shown in the following equation (Paatero and Tapper, 1994):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} \times f_{kj} + e_{ij}. \quad (3)$$

Here $x_{ij}$, $g_{ik}$, $f_{kj}$, and $e_{ij}$ are matrix elements of the measurement, factor time series, factor profiles, and residual matrices, respectively. The subscript $i$ corresponds to time, $j$ corresponds to $m/z$, and $k$ corresponds to a discrete factor. The number of factors in the PMF solution, $p$, is determined by the user. The factor profiles are static, but their concentrations vary with time. Equation (3) is solved for $G$ and $F$ using a least-squares algorithm that iteratively minimizes the quantity $Q$, defined as the sum of the square of the uncertainty-weighted residuals ($e_{ij}/\sigma_{ij}$):

$$Q = \sum_{i} \sum_{j} \left( \frac{e_{ij}}{\sigma_{ij}} \right)^2. \quad (4)$$

Whereas PMF does not require any a priori assumption regarding sources, ME-2 (Paatero, 1999) enables the inclusion of external data and/or constraints in the PMF model to improve factor resolution and uncertainty analysis. This allows for intelligent rotational control of the retrieved solution. That is, because different combinations of $G$ and $F$ can yield solutions with similar mathematical quality, constraining one or more factor profiles can direct the model towards environmentally reasonable, optimally unmixed solutions. The first application of constrained profiles to AMS data was performed by Lanz et al. (2007b) and demonstrated improved model performance by resolving spectrally or temporally similar sources not well-separated by conventional PMF. Here constraints are applied by requiring one or more factor profiles to fall within a predetermined range defined by a combination of a reference profile and a scalar ($\alpha$) determining the tightness of constraint. The $\alpha$ value ($0 \leq \alpha \leq 1$) determines the extent to which the resolved factors ($f_{ij,\text{solution}}$) and ($g_{i,\text{solution}}$) may deviate from input values ($f_{ij}$, $g_i$). The following conditions need to be fulfilled:

$$f_{ij,\text{solution}} = f_{ij} \pm \alpha \times f_{ij}. \quad (5)$$

Because of post-PMF renormalization, the actual profile may contain elements that exceed the boundaries defined by Eq. (5). 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 must be evaluated subjectively to provide the most interpretable solution. Factor identification and interpretation likewise require user judgement. Criteria utilized here include investigation of the retrieved factor profiles for distinctive chemical signatures, diurnal cycle characteristics, and correlations between the time series of factors and external measurements. In addition, the evolution of the residual time series as a function of the number of resolved factors is also evaluated (Ulbrich et al., 2009; Canonaco et al., 2013; Crippa et al., 2014).

### 3 Results

#### 3.1 AMS PMF

Figure S1 shows time series of the species concentrations measured by the AMS over the full period of measurements. The organic mass dominates NR-PM1 with a contribution of 74 % compared to only a 26 % contribution from inorganic mass. The total measured organic mass reached a maximum concentration of $\sim 30 \mu g m^{-3}$ during the measurement period, with an average concentration of $\sim 3 \mu g m^{-3}$. We note evidence of both long-term events and short-term spikes. We selected a five-factor unconstrained PMF solution containing three primary and two secondary factors. The primary factors consisted of hydrocarbon-like organic (HOA) related to traffic, cooking-related organic aerosol (COA), and cigarette-smoke-related factor (CS-OA). The secondary factors were separated by their oxygen content, which has been empirically related to volatility (Jimenez et al., 2009), and are classified here as less-oxidized oxygenated organic aerosol (LO-OOA) and more-oxidized oxygenated organic aerosol (MO-OOA) (Zhang et al., 2011). The five-factor solution was preferred because the four-factor solution was not able to separate the HOA and COA factors, while the six-factor solution added an additional OOA factor with a noisy time series for which no physical interpretation could be found. Higher-order solutions with up to 10 factors likewise yielded
no additional interpretable factors. Figure 1 shows the mass spectra of the five-factor solution with ions colour-coded according to their chemical family \((C_{x}H_{y}O_{z}, C_{x}H_{y}N_{p}, C_{x}H_{y}O_{z}N_{p}, H_{2}O_{z})\) and “other”, which includes \(C_{x}O_{y}, C_{x}O_{z}, \) and sulfur-containing ions). The factor time series and diurnal patterns are shown in the Supplement (Fig. S3). The dominant source in mass is LO-OOA, especially during the period with higher temperature, followed by MO-OOA. Specific local events are instead dominated by the primary sources.

The HOA factor is related to fossil fuel combustion, mainly from traffic emissions. These emissions are typically dominated by engine-lubricating oil and consist mainly of \(n\)-alkanes, branched alkanes, cycloalkanes, and aromatics, leading to high signal of the ions \(C_{x}H_{2n+1}^{+}\) and \(C_{x}H_{2n-1}^{+}\) (Ng et al., 2011). Prominent contributions of non-oxygenated species at \(m/z\) 43 \((C_{3}H_{7}^{+})\), \(m/z\) 55 \((C_{4}H_{9}^{+})\) and \(m/z\) 57 \((C_{4}H_{11}^{+})\) can be observed. Similar to the results of other studies (e.g. Lanz et al., 2007a, b; Ulbrich et al., 2009; Zhang et al., 2011) HOA exhibits temporal correlations with primary vehicular emissions tracers, such as elemental carbon from traffic (EC) and NO\(_{x}\) (Zhang et al., 2005).

The COA factor is similar to HOA in that a large fraction of the signal is contributed by \(C_{x}H_{y}^{+}\) ions. However, COA has distinctive mass spectral features, typical of the fragmentation of fatty acids. Characteristic peaks include \(C_{3}H_{2}O^{+}\) at \(m/z\) 55, \(C_{3}H_{5}O^{+}\) at \(m/z\) 57, and higher-molecular-weight oxygenated fragments: \(C_{3}H_{6}O^{+}\) \((m/z\) 84\), \(C_{6}H_{10}O^{+}\) \((m/z\) 98\), and \(C_{7}H_{12}O^{+}\) \((m/z\) 112\). In addition, the COA and HOA factors could be differentiated on the basis of the signal ratio of \(C_{3}H_{2}O^{+}\) to \(C_{3}H_{5}O^{+}\) as the COA spectrum tends to show a substantially higher \(m/z\) 55 to \(m/z\) 57 ratio (Mohr et al., 2009; Sun et al., 2011). Reliable molecular tracers of cooking emissions are not typically available, but Fig. S3b shows a diurnal pattern with significant peaks during mealtimes, consistent with previous studies.

The CS-OA factor is related to a cigarette smoke signature and the profile is similar to previously reported smoking-related factors measured at Jungfraujoch (Fröhlich et al., 2015) and a German soccer stadium (Faber et al., 2013). Similar to HOA and COA, the profile includes a strong contribution from \(C_{x}H_{y}^{+}\), but for CS-OA is shifted towards less saturated ions (branched and \(n\)-alkanes, cycloalkanes, and alcohols). Relevant signal can be observed at \(m/z\) 41 \((C_{3}H_{7}^{+})\) and \(m/z\) 43 \((C_{3}H_{9}^{+}\) and \(C_{2}H_{5}O^{+}\) and also fragments from aromatic compounds at \(m/z\) 77 \((C_{6}H_{5}^{+})\), 91 \((C_{7}H_{9}^{+}\), 105 \((C_{8}H_{11}^{+}\) and 119 \((C_{9}H_{11}^{+}\). In addition, this factor is unique in having a significant contribution from \(C_{5}NH_{10}N^{+}\) \((m/z\) 84\), which has been attributed to \(n\)-methylpyrrolidine, a tracer for cigarette smoke (Struckmeier et al., 2016). Furthermore, the CS-OA factor exhibits a significantly higher \(N:C\) ratio \((0.02)\) compared to the other factors \((\text{range from 0.003 to 0.01})\) and explains most of the organic nitrogen signal.

Finally, the OOA factors are characterized by a very high contribution of the signal at \(m/z\) 44 \((CO_{2}^{+})\), typical of AMS SOA profiles. The LO-OOA spectrum is characterized by prominent peaks at \(m/z\) 43 \((C_{2}H_{3}O^{+}\) and \(m/z\) 28 \((CO^{+}\). It resembles LO-OOA factors determined in previous studies at urban sites, as well as newly formed aerosol from forest emissions.
emissions and biogenic SOA from chamber studies (Zhang et al., 2007; Lanz et al., 2007a, b; Ulbrich et al., 2009; Hao et al., 2009, 2014; Kiendler-Scharr et al., 2009; Ng et al., 2010; Sun et al., 2010). LO-OOA has an atomic O : C ratio of 0.40 (consistent with the global average of LO-OOA of 0.35 ± 0.14; Ng et al., 2010) while the second OOA factor, MO-OOA, is more oxidized with an O : C ratio of 0.50. The mass spectrum of the latter is dominated by m/z 44 (CO$_2^+$) and m/z 28 (CO$^+$). The profile is similar to MO-OOA factors reported at various locations, including urban areas and the boreal forest (Allan et al., 2006; Ulbrich et al., 2009; Sun et al., 2010; Raatikainen et al., 2010; Hao et al., 2014). Overall, LO-OOA includes less oxygenated and possibly freshly oxidized species while MO-OOA includes highly oxygenated species. Furthermore, the LO-OOA / MO-OOA ratio is higher, particularly on days with higher OOA concentration, which in turn correspond to sunny weather and warmer temperatures. The strong correlation of this factor with local ambient temperature indicates that LO-OOA is locally formed and possibly linked with SOA formed from the oxidation of biogenic emissions (Fig. S5). Similar findings have been reported by Canonaco et al. (2015) at the same site for summer OA measured by an aerosol chemical speciation monitor (ACSM). During summer afternoons, when photochemical processes are most vigorous, the formation of semi-volatile oxygenated organic aerosol (SVOOA) is enhanced compared to low-volatility oxygenated organic aerosol (LVOOA) formation, which typically occurs on a timescale of hours. This is likely due to the formation of semi-volatile oxygenated aerosol produced from biogenic precursor gases, especially monoterpenes, whose emissions increase with ambient temperature.

The diurnal patterns of these two factors are flatter than the POA factors, however the LO-OOA concentrations started increasing from early morning, most likely due to condensation of semi-volatile species and fresh formation of OOA due to photochemistry. Afterwards this factor continuously decreased, possibly due to boundary layer expansion and photochemical conversion to MO-OOA (Fig. 4). However, the LO-OOA concentration remained significantly higher than other primary emissions which suggests that LO-OOA probably forms from the oxidation of primary emissions and/or continued conversion of less oxidized gas-phase products into the particle phase. Furthermore, a correlation between the concentrations of LO-OOA and nitrate (NO$_3^-$) was observed (R = 0.47). Particulate nitrate also represents semi-volatile secondary species, which share similarity with LO-OOA in terms of volatility and its partitioning behaviour with temperature while the MO-OOA time series are is correlated with sulfate (SO$_4^{2-}$) (R = 0.6), representing a less volatile fraction and suggesting that MO-OOA is related to longer-lived aged regional SOA (Lanz et al., 2007a, b). Overall, the LO-OOA and MO-OOA components account for 46 % and 25 % of the total organic aerosol mass observed, respectively, dominating the total OA concentration. Due to the extent of fragmentation occurring in the AMS system, it was not possible to gain any more information about SOA sources apart from their oxygenation–volatility pattern. The inclusion in the analysis of more highly detailed chemical composition, provided by the new EESI-TOF-MS system, allowed us to distinguish, with more detail, the SOA processes of formation and oxidation pathways, as outlined in the following.

### 3.2 EESI-TOF PMF

#### 3.2.1 Selection and overview of the solution

We present in the following a PMF analysis on the first-ever ambient EESI-TOF-MS data. As discussed in the previous section, PMF analysis of AMS data indicates SOA to be the dominant component but does not provide any direct chemical information indicating the SOA sources. In contrast, PMF analysis of EESI-TOF-MS data yielded several organic aerosol factors related to secondary OA formation. Factors were separated according to different mass spectral fingerprints and ageing processes for a total of six factors including both POA and SOA. The six-factor solution presented throughout the text is the averaged solution among 795 accepted bootstrap runs (out of 1000 total). The bootstrap analysis is discussed in detail in Sect. 3.2.5 and is based around random selection of the $a$ value constraints on the profile of a cooking-related factor (COA$_{EESI}$) (with $a$ values selected in the range 0 to 0.1, with a step size of 0.1), with the COA$_{EESI}$ anchor profile constrained using the cleaner cooking-related factor profile retrieved in the seven-factor solution. Critically, we consider all solutions classified as being reasonable and unmixed (according to the evaluation in Sect. 3.2.5) to be of equal merit. Therefore the base case solution represents only a single, quasi-randomly selected solution out of this large set (rather than an optimized solution), and we consider the average of all acceptable solutions to be the best representation of the source apportionment analysis.

An overview of the factor profiles, time series, and diurnal patterns is presented in Figs. 2–4, respectively. Note that the diurnal pattern presented in Fig. 4 refers to the entire measurement period while Fig. S4 shows the diurnal patterns for the same factors calculated for only the overlapping measurement period between EESI-TOF-MS and AMS. We observed two primary factors: cooking-related OA (COA$_{EESI}$) and cigarette-smoke-related OA (CS-OA$_{EESI}$). Four SOA factors were resolved: two daytime SOA factors (DaySOA1$_{EESI}$ and DaySOA2$_{EESI}$) and two nighttime factors (NightSOA1$_{EESI}$ and NightSOA2$_{EESI}$). Each factor is described in further detail in the following sections.

A common criterion used to assess the selection of the number of factors is the examination of $Q/Q_{\text{exp}}$ for an increasing number of solution factors to evaluate the fraction of explained variation in the data. For unconstrained solutions, the $Q/Q_{\text{exp}}$ value decreased smoothly from 5.4 to 4.0 as the number of factors increased from 2 to 10, providing little in-
sight into the optimal number of factors. The six-factor solution was chosen after constraining the cleaner cooking profile retrieved from the seven-factor solution within the bootstrap analysis (Sect. 3.2.5). The solution with one factor fewer provided a mixed primary emissions factor, while the seven-factor solution resulted in an additional non-interpretable splitting of the daytime SOA (as did higher-order solutions).

Figure 4 shows the diurnal patterns of all individual factors as well as of the sum of all four SOA factors from the EESI-TOF-MS analysis and sum of the two OOA factors from the AMS analysis. The pattern of the sum of all SOA factors is basically flat. However, each individual SOA factor exhibits strong and distinctive variation. The diurnal pattern of DaySOA1\textsubscript{EESI} exhibits a factor of 2 enhancement in signal between 15:00 and 21:00 LT while the DaySOA2\textsubscript{EESI} exhibits the same magnitude of enhancement in signal around 12:00 LT without a consistent decrease before 01:00 LT. This shift in time between the two factors could reflect gradients in composition according to lifetime of the compounds, production time, partitioning, and reactive environment. Con-
fatty acids and alcohols, which are typical of cooking emissions. The COA EESI also being available. 

Further, the EESI-TOF-MS is probably more sensitive than other techniques, as it is derived from the pyrolysis of cellulose and hemicellulose. The study from Bertrand et al. (2018) shows C\(_{\text{6}}\)H\(_{10}\)O\(_{5}\) (m/z 185), which is attributed to levoglucosan and commonly used as an indicator for primary aerosols originating from biomass combustion (Hennigan et al., 2010; Giannini et al., 2012) as it is derived from the pyrolysis of cellulose and hemicellulose. The study from Bertrand et al. (2018) shows C\(_{\text{6}}\)H\(_{10}\)O\(_{5}\) (m/z 185) to be a very prominent peak in the EESI-TOF-MS mass spectrum of fresh wood burning emissions. Further, the EESI-TOF-MS is probably more sensitive to levoglucosan than to bulk SOA (Lopez-Hilfiker et al., 2019). During this study, levoglucosan is likely emitted from open cooking activities in the vicinity of the measurement site.

The COA\(_{\text{EESI}}\) and COA\(_{\text{AMS}}\) factor time series are well correlated (R = 0.65) during the overlapping measurement period (20 to 27 June) (Fig. 3), with both showing clear peaks at lunchtime and dinner time (Figs. 4 and S4).

The CS-OA\(_{\text{EESI}}\) mass spectrum is dominated by C\(_{10}\)H\(_{14}\)N\(_2\) (nicotine, m/z 163.12) and C\(_{6}\)H\(_{10}\)O\(_{5}\) (levoglucosan), which contribute 15% and 10%, respectively, to the profile signal. Levoglucosan is also a known product of pyrolysis of simple sugars present in tobacco (Talhout et al., 2006). Other prominent signals occur at m/z 197.04 (C\(_{7}\)H\(_{10}\)O\(_{5}\)), 199.09 (C\(_{7}\)H\(_{12}\)O\(_{5}\)), 203.1 (C\(_{6}\)H\(_{12}\)O\(_{6}\)), 215.05 (C\(_{7}\)H\(_{12}\)O\(_{6}\)), 227.05 (C\(_{8}\)H\(_{12}\)O\(_{6}\)), and 313.05 (C\(_{9}\)H\(_{14}\)O\(_{12}\)). The CS-OA\(_{\text{EESI}}\) shows strong correlation with the AMS factors traffic (HOA\(_{\text{AMS}}\), R = 0.6) and cigarette smoke (CS-OA\(_{\text{AMS}}\), R = 0.73). The correlation further improves when considering the two sources together (R = 0.77) suggesting a certain extent of mixing of the two sources within the same factor. The discrimination of a separate factor related solely to traffic was not possible, even investigating solutions with a higher number of factors, where only additional non-interpretable secondary sources were discriminated. The inability of the EESI-TOF-MS to resolve a clear traffic-related factor is likely due to the insensitivity of the instrument to the hydrocarbons dominating these emissions (Sect. 3.3). The diurnal pattern of CS-OA\(_{\text{EESI}}\) shows a peak during the evening between 21:00 and 23:00 LT, during which the courtyard in which the measurement site is located is typically more crowded. Overall, as expected, the primary factors show low O : C ratios of 0.38 and 0.43 and high H : C ratios of 1.75 and 1.7 for COA\(_{\text{EESI}}\) and CS-OA\(_{\text{EESI}}\), respectively.

### 3.2.3 Secondary daytime factors

Two daytime SOA factors (DaySOA\(_{\text{1EESI}}\) and DaySOA\(_{\text{2EESI}}\)) were resolved from the EESI-TOF-MS PMF analysis (Fig. 2), both of which contain strong signatures of terpene oxidation products. Prominent monoterpenes-derived ions in the DaySOA\(_{\text{2EESI}}\) factor profile include m/z 239.09 (C\(_{10}\)H\(_{16}\)O\(_{5}\)), 255.08 (C\(_{10}\)H\(_{16}\)O\(_{6}\)), and 271.079 (C\(_{10}\)H\(_{16}\)O\(_{7}\)) while other peaks are tentatively identified as sesquiterpene oxidation products, i.e. m/z 275.16 (C\(_{15}\)H\(_{24}\)O\(_{3}\)), 307.15 (C\(_{15}\)H\(_{24}\)O\(_{5}\)), and 325.162 (C\(_{15}\)H\(_{25}\)O\(_{6}\)). The latter species could also be dimers from monoterpenes/isoprene oxidation products. However, the absence of signal from C\(_{19}\) and C\(_{20}\) compounds suggests that dimer concentrations are low in Zurich. This may be due to suppression of dimerization by NO\(_x\) (Yan et al., 2016; Kürt et al., 2016) and is consistent with the dimer fraction here being low compared to that observed in the Finnish boreal forest and with both ambient 

![Image](58x488 to 293x727)

Figure 4. Diurnal variations in the EESI-TOF-MS PMF factors on the left axis (µg s\(^{-1}\)) and counterpart diurnal variations from the AMS PMF analysis on the right axis (µg s\(^{-1}\)). The diurnal variations are presented here for the entire measurement period (see Fig. S4 for the overlapping period only). SOA\(_{\text{EESI}}\) and OOA\(_{\text{AMS}}\) denote the sums of all the secondary factors.
measurements being lower than that of α-pinene ozonolysis in a NOx-free simulation chamber (Pospisilova et al., 2019). Thus, we believe that the above-mentioned species are likely related to sesquiterpene oxidation products. Overall, the C10H16Oz series accounts for 6.2% of the total profile signal for DaySOA1EESI and 5.3% for DaySOA2EESI (2.5%, 2%, 4.4%, and 5.1% for COA1EESI, CS-OA1EESI, NightSOA1EESI, and NightSOA2EESI) while the C15H24−28Oz series accounts for 1% of the total profile signal for DaySOA1EESI and 2.3% for DaySOA2EESI. Furthermore, other significant series of compounds are present including (C9H14Oz) accounting for 5.8% and 5.2%, (C7H10Oz) accounting for 4.7% and 3.5%, and (C8H12Oz) accounting for 6.4% and 5.6% of the total profile signal for DaySOA1EESI and for DaySOA2EESI.

The two DaySOA factor spectra are compared in more detail in Fig. 5a, with the carbon number distribution shown in Fig. 5b. DaySOA1EESI is more shifted towards ions with lower m/z and carbon number. These species with fewer than 10 carbon atoms can represent fragmentation products from terpene oxidation either in the gas phase (Molteni et al., 2019) followed by condensation or during ageing in the condensed phase (Pospisilova et al., 2019). However, fragmentation results in products progressively more difficult to distinguish from ring-opening products from the oxidation of aromatic precursors, and therefore we cannot rule out a contribution to these ions from aromatic oxidation products. DaySOA2EESI is instead shifted towards higher masses with a carbon atom number typical of sesquiterpene oxidation products and/or dimerization. Overall the two secondary daytime factors show a high apparent O : C ratio of 0.63 and 0.58 and similar apparent H : C ratios of 1.64 and 1.66 for DaySOA1EESI and DaySOA2EESI, respectively, consistent with the expected values for biogenic precursors of SOA, which exhibit an H : C ratio from 1.2 to 1.7 (Daellenbach et al., 2019) and specifically monoterpenes and sesquiterpenes with a H : C ratio of 1.6.

The two daytime SOA factors exhibit not only different chemistry but also a different dependency on ambient temperature. Figure 6 shows the correlation of the two daytime SOA factors with the hourly ambient temperature. While DaySOA1EESI does not show a clear dependency on temperature DaySOA2EESI increases exponentially with temperature, consistent with known relationships for terpene emissions and biogenic aerosol in terpene-dominated regions (Leaitch et al., 2011; Vlachou et al., 2018). This supports the interpretation of DaySOA2EESI as a factor related to local oxidation of biogenic VOCs and DaySOA1EESI as a factor related to more aged or regional air masses. Figure S5 shows the equivalent relation with temperature for the AMS secondary factors; we note that LO-OOAAMSm exhibits an exponential increase with temperature similar to
In the spectrum can be observed for the C\(\text{SOA}\) (Xu et al., 2015; Zhang et al., 2018). Dominant peaks monoterpenes to contribute a large fraction of the night-time products (e.g. C\(\text{H}_\text{10}\text{O}_\text{4}\text{N}\), which can be observed at m/z 268.08 (C\(\text{H}_{15}\text{O}_5\text{N}\), 284.07 (C\(\text{H}_{15}\text{O}_7\text{N}\), 300.07 (C\(\text{H}_{15}\text{O}_8\text{N}\), and 316.06 (C\(\text{H}_{15}\text{O}_9\text{N}\) and contribute 1.6 %, 1.5 %, 1.8 %, and 1.5 %, respectively, to the profile signal, resulting in the highest contributions compared to all the other factors except for C\(\text{H}_{15}\text{O}_7\text{N}\) and C\(\text{H}_{15}\text{O}_8\text{N}\), which contribute \(\sim 1.3 \%\) and \(\sim 1.7 \%\) to the Night\(\text{SOA}_\text{EESI}\) profile signal (ag \(\text{s}^{-1}\)). These species are consistent with NO\(_3\) oxidation products of atmospherically relevant monoterpenes such as limonene (Faxon et al., 2018).

The Night\(\text{SOA}_\text{EESI}\) likewise exhibits a strong and consistent diurnal cycle, with a daily maximum at approximately 09:00 LT, minimum at 21:00 LT, and smooth transitions in between. Like Night\(\text{SOA}_\text{EESI}\), Night\(\text{SOA}_\text{EESI}\) exhibits strong signatures from organonitrates. However, contributions from non-nitrogen-containing species consistent with limonene and \(\alpha\)-pinene ozonolysis and photo-oxidation are also evident, e.g. C\(\text{H}_\text{16}\text{O}_5\text{S}_\text{6}\) and C\(\text{H}_\text{16}\text{O}_4\text{S}_\text{6}\) (Bate- man et al., 2009; Kahnt et al., 2014; Park et al., 2017), as well as species probably consistent with multi-generation terpene chemistry or aromatic oxidation products suggesting a certain extent of influence from photochemistry, consistent with the diurnal morning peak of this factor. Dominant compounds in the spectrum can be observed at m/z 286.09 (C\(\text{H}_{15}\text{O}_7\text{N}\)), 211.058 (C\(\text{H}_\text{12}\text{O}_2\text{N}\)), 225.07 (C\(\text{H}_\text{12}\text{O}_3\)), 239.09 (C\(\text{H}_{16}\text{O}_5\text{S}\)), and 197.042 (C\(\text{H}_{10}\text{O}_3\)) contributing 1.9 %, 1.3 %, 1.3 %, 1.2 %, and 0.9 %, respectively, to the total profile signal resulting in the highest contributions among all the other factor signals except for the two Day\(\text{SOA}_\text{EESI}\) factors, where they contribute with higher percentages between 1.3 % and 3 % to the profile signal. Overall the two secondary night-time factors show similar O : C ratios (~ 0.6) and H : C ratios (~ 1.65) while the N : C ratio is higher for Night\(\text{SOA}_\text{EESI}\) (0.46) than for Night\(\text{SOA}_\text{EESI}\) (0.3).

Figure S5 shows the correlations of the two night-time SOA factors with ambient temperature. We note that the
NightSOA1_{EESI} increases to some extent with temperature, consistent with biogenic aerosol and with the behaviour of DaySOA2. The effect is clear for the night points while not visible for the day points, which is expected from the diurnal pattern of the factor going almost to zero during the day. On the other hand, the NightSOA2_{EESI} does not show any clear dependency on the temperature, suggesting a combined effect of partitioning, additional chemistry, and possibly additional sources. Overall, during the day there will generally be higher terpene emissions due to higher temperature, but also higher dilution due to an enhanced boundary layer height compared to the night, suggesting that, by compensation, terpene-related SOA formation in the lowest layers of the atmosphere might be similar. As a consequence DaySOA2_{EESI} and NightSOA1_{EESI} might represent first-generation chemistry with different oxidants reflecting the availability during the time of the day while DaySOA1_{EESI} and NightSOA2_{EESI} might represent second-generation chemistry oxidation products. As an example, some highly functionalized oxidation products from α-pinene photooxidation like C_{10}H_{16}O_{5} are thought to be second-generation oxidation products (McVay et al., 2016). As a consequence of the extensive decomposition and fragmentation occurring in the AMS system, which particularly affects organonitrates (Farmer et al., 2010), we were not able to resolve any factor related to night chemistry or specific factor dominated by a nitrate signature to compare with the night-time SOA factors from the EESI-TOF-MS analysis. However, the organonitrate-derived signal in the AMS and that of the EESI-TOF-MS are well correlated. Figure 8 shows the time series of the sum of all C_{x}H_{y}O_{z}N^{+} ions from the AMS and [C_{x}H_{y}O_{z}N_{p}]Na^{+} ions from the EESI-TOF-MS, with R = 0.7. For the AMS analysis the MO-OOA_{AMS} is the factor that contributes the most to these nitrogen-containing fragments mentioned above (∼ 50 %) followed by the CS-OA_{AMS} (∼ 20 %), while for the EESI-TOF-MS analysis the NightSOA1_{EESI} is the major contributor to the nitrogen-containing species (∼ 35 %) followed by NightSOA2_{EESI} (∼ 20 %).

### 3.2.5 Bootstrap analysis

Bootstrap analysis (Davison and Hinkley, 1997) was conducted to determine the statistical stability and uncertainties of the EESI-TOF-MS PMF solution and evaluate some trends in specific ions and the extent to which factors are discrete versus basis vectors describing compositional gradients. Bootstrap analyses generate a set of new input data and error matrices for analysis from random resampling of the original input data. This resampling perturbs the input data by randomly choosing rows (time points) of the original matrix which are present several times, while other rows...
are removed (Paatero et al., 2014); the overall dimensions of
the data matrix are kept constant for each resampling. The re-
sampled data made up on average \( \sim 64 \% \) of the total original
data per bootstrap run. We performed 1000 bootstrap runs for
a six-factor solution with all factors unconstrained except for
\text{COA}_{\text{EESI}}, which as discussed above was constrained using
the cooking-related spectrum obtained from the seven-factor
unconstrained solution. The cleaner spectra and higher cor-
relation with \text{AMS} cooking factor (\text{COA}_{\text{AMS}}) compared to
the cooking profile discriminated in the unconstrained six-
factor solution, where a clear mixing with other profiles was
still present and an additional not meaningful SOA profile
was present, resulted from a splitting of the SOA factor in
the solution with one factor fewer. The \( \alpha \) value of the con-
strained \text{COA}_{\text{EESI}} was randomly selected for each bootstrap
iteration within the range of 0 to 1 with a 0.1 step size. Note
that each bootstrap run is started from a different initializa-
tion point; thus, this methodology also includes the investi-
gation of seed-based variability, accounting for the possibility
of local minima in the solution space.

A particular point of interest in the bootstrap analysis was
the extent to which (day and/or night) SOA factors mix with
each other. Thus, it is important to characterize solutions
where factors are distinct or mixed and, in the case of mixing,
to characterize the type of mixing (i.e. which factors are
mixed). For this purpose, we adapted the method of Vla-
chou et al. (2018). The key steps in this method are as fol-
lows: (1) creation of a six-factor base case: this was synthe-
sized from the unconstrained seven-factor solution described
above to optimize \text{COA}_{\text{EESI}}, with the split SOA mathemati-
cally combined into a single factor (see Fig. S6 for the seven-
factor solution); (2) Spearman correlation between the time
series and the profiles of each factor from the base case and
a bootstrap solution are used to sort the bootstrap factors,
yielding a correlation matrix with the highest correlation val-
ues on the diagonal; (3) each correlation coefficient on the
matrix diagonal is compared to those on the intersecting row
and column to evaluate whether it is the highest by a statisti-
cally significant margin (based on a preselected significance
level \( p \) from a \( t \) test). Vlachou et al. (2018) rejected any so-
lution failing to meet this criterion; here we retain the solu-
tion but classify it as “mixed”. For mixed solutions, we then
determined which factor(s) was mixed (i.e. which factor(s)
had time series that could not be unambiguously linked to a
unique base case factor based on the statistical significance
test described above) and classified solutions according to
combinations of mixed factors. This allowed a systematic ex-
ploration of bootstrapped solutions most likely to have per-
turbed the boundaries between selected SOA factors.

The analysis of Vlachou et al. (2018) utilized a
\( p \) value \( = 0.05 \); here we conducted a sensitivity test cover-
ning \( p \) values ranging from 0.05 to 0.6. For \( p \) values lower
than 0.3, the only mixing observed was among \text{POA} fac-
tors (e.g. \( p \) value \( = 0.2 \) yielded mixing between \text{COA}_{\text{EESI}}
and \text{POA}_{\text{EESI}} for \( \sim 100 \) runs based on time series analysis
and \( \sim 80 \) runs based on profile analysis). A \( p \) value of 0.4
showed mixing \text{NightSOA}1_{\text{EESI}} with \text{NightSOA}2_{\text{EESI}} and/or
\text{DaySOA}2_{\text{EESI}} for \( \sim 50 \) runs based on time series analysis,
while \( \sim 10 \) bootstrap runs showed profile mixing between
\text{DaySOA}1_{\text{EESI}} and \text{DaySOA}2_{\text{EESI}}. However, visual analysis
of these mixed-SOA solutions at \( p = 0.4 \) showed solutions
where both the factor profiles and time series were not dis-
tinguishable from the base case. We therefore concluded that
the SOA factor separation is robust, supporting our treatment
of these factors as discrete entities rather than highly interre-
lated descriptors of composition gradients.

We applied, at this point, a significance threshold of 0.3
(\( p \) value from \( t \) test analysis) and extracted all the solutions
classified as unmixed. This resulted in 795 accepted solutions
out of 1000 runs, with an average \( a \) value of the constrained
\text{COA}_{\text{EESI}} profile of 0.399. Figure 9 characterizes the averaged
extracted solution from the bootstrap analysis, showing the
means and standard deviations of these 795 accepted solu-
tions for the diurnal patterns (Fig. 9a) and factor mass spec-
tra standard deviations against relative intensities (Fig. 9b).

The uncertainties of the model (which correspond to the stan-
dard deviations among retained solutions) are also presented
in Fig. 9 and indicate the high stability of the solution. First
we calculated the diurnals, then the standard deviation of the
mean diurnals across all bootstrap runs. Thus, the error bars
describe variability across solutions (i.e. model uncertainty)
and deliberately exclude day-to-day variability in the actual
data.
The median percentage uncertainties for the profiles varied between 5.3% and 12% where the highest uncertainties were related to the night-time SOA factors. The highest diurnal variability was related to CS-OA\textsubscript{EESI} and DaySOA\textsubscript{2EESI}. Overall, the uncertainties were not of sufficient magnitude to disrupt the diurnal gradients discussed above or to significantly affect the apportionment of key ions discussed above. This highlights the relatively discrete nature of the factors.

3.3 EESI-TOF-MS and AMS comparison

Figure 10a shows the bulk comparison between the EESI-TOF-MS and the AMS total signal for the overlapping measurement period. The AMS total signal represents the time series of measured organic mass concentration while the EESI-TOF-MS total signal is the sum of the mass fluxes of every detected ion (neglecting Na\textsuperscript{+} mass and excluding ions that are high intensity but spray-dominated). Further, no relative sensitivity corrections were applied for the EESI-TOF-MS even though it is known that there is some sensitivity variability (Lopez-Hilfiker et al., 2019).

The results of the two instruments are correlated ($R = 0.81$) despite the assumption that all EESI-TOF-MS ions have the same response factor and even though the AMS-measured mass includes a primary source related to traffic (HOA\textsubscript{AMS}) that consists mainly of compounds that are insoluble in the electrospray droplets and therefore not visible in the EESI-TOF-MS.

The cooking factors (COA) and the cigarette smoke factors (CS-OA) retrieved from each instrument are in good agreement with each other as well, although with lower correlation compared to the secondary factors ($R = 0.64$ and $R = 0.73$, respectively). The AMS–EESI-TOF-MS correlation for CS-OA further suggests that even though nicotine does not ionize by adduct formation with Na\textsuperscript{+}, this alternate pathway does not introduce significant nonlinearities in its detection, at least under the conditions encountered in Zurich during summer. Similar performance was obtained for nicotine detection during winter measurements in Zurich (Qi et al., 2019). Note that the slopes retrieved from the linear correlation in Fig. 10a are proportional to the EESI-TOF-MS mean sensitivity of the compounds comprising each factor.
Figure 10. (a) Total aerosol signal measured by the EESI-TOF-MS versus OA measured by the AMS, with the points coloured by time. An overall bulk sensitivity to OA can also be estimated from (1.9 × 10⁻⁸). (b) Correlations of the CS-OA and COA factors and of SOA (total SOA estimated by EESI-TOF-MS and AMS) from the two instruments, where SOA is colour-coded by the N : C ratio (yellow dots represent N : C ≥ 0.032). We estimate bulk sensitivities of 3.2 × 10⁻⁸ ions per molecule to SOA, 2.8 × 10⁻⁸ ions per molecule to CS-OA, and 9.0 × 10⁻⁹ ions per molecule to COA. (c, d) Atomic ratios, i.e. H : C and O : C ratios for SOA and the CS-OA and COA factors.

The slope is nearly a factor of 2 higher for SOA than for COA, which may be due to a combination of two factors. First, it is expected that the EESI-TOF-MS may be more sensitive to the highly oxygenated and highly water-soluble components in SOA than to the fatty acids in COA. Second, the AMS relative ionization efficiency for COA has recently been suggested to be approximately 2 times higher for COA than for bulk organics, due to the higher molecular weight and thermal decomposition characteristics of the molecules comprising COA (Reyes-Villegas et al., 2018). Nevertheless, these correlations indicate that the EESI-TOF-MS signal linearly relates to mass concentration even for complex ambient aerosol and also suggest that the overall EESI-TOF-MS sensitivity to OA is not subject to significant variation during the study even if the composition-dependent relative sensitivities are actually unknown. Therefore, we assume that factor-specific sensitivities are not needed for the interpretation of the EESI PMF solution where the factors describe the variability in composition.

Figure 10c and d show the atomic H : C and O : C ratios, respectively, for the total SOA as well as the COA and CS-OA factors determined from the EESI-TOF-MS and AMS data. In terms of O : C ratio, the SOA factors show fair consistency with values around 0.6 and 0.5 for the EESI-TOF-MS and AMS analysis, respectively. For the COA and CS-OA factors, the O : C ratio is much lower for the AMS (≈ 0.1) than for the EESI-TOF COA (≈ 0.4). This is again consistent with a reduced sensitivity of the EESI-TOF-MS to hydrocarbon-like molecules due to a lower extraction and/or ionization efficiency. On the other hand the H : C ratios are slightly higher for the EESI-TOF-MS measurements with values of ≈ 1.6, ≈ 1.7, and ≈ 1.8 for SOA, CS-OA, and COA, respectively, compared to ≈ 1.3, ≈ 1.4, and ≈ 1.6, respectively, for the AMS analysis. Similar results were also observed for winter aerosol in Zurich (Qi et al., 2019) and for ageing experiments of wood burning emissions in an environmental chamber (Bertrand et al., 2018). This could suggest a reduced sensitivity of the EESI-TOF-MS to low H : C compounds (e.g. aromatic oxidation products) relative to terpene SOA. Alternatively, given that the EESI-TOF-MS sensitivity to laboratory-generated SOA from single-component precursors roughly decreases with decreasing molecular weight (Lopez-Hilfiker et al., 2019), it may be that compounds with a lower H : C ratio occur predominantly in ions with lower carbon number.

Because the first step in EESI-TOF-MS detection is a rapid extraction into the methanol / water droplets generated by the electrospray, one possibility for the observed discrepancies in the O : C ratios is the possibility for the observed discrepancies in the O : C ratios between the AMS and the EESI-TOF-MS could be incomplete extraction of less soluble components in the EESI-TOF-MS. To investigate this, we compare the O : C ratios from the AMS factors retrieved in the current
study (COA_{AMS} 0.1, HOA_{AMS} 0.057, and OOA_{AMS} 0.42–0.5) with those from offline AMS source apportionment of aqueous filter extracts, where water-insoluble components are not detected. The offline-AMS method yields O: C ratios consistent with the online AMS (COA_{offline} 0.10, HOA_{offline} 0.06, and OOA_{offline} 0.51) (Bozzetti et al., 2017). In contrast, the EESI-TOF-MS ratios are significantly higher (COA_{EESI} 0.38 and SOA_{EESI} 0.56–0.62) despite extraction into a water / methanol mixture rather than water only. This suggests that the EESI extraction process (i.e. solubility) alone cannot explain the discrepancies between the two instruments. Note that this assumes no kinetic limitations on solubility and extraction, as the offline method applies a water extraction for 20 min, while the EESI-TOF-MS uses a very fast extraction in water / methanol; however, this assumption is likely valid as laboratory tests suggest complete extraction of particles by the EESI-TOF-MS in the measured size range (Lopez-Hilfiker et al., 2019).

The bulk variabilities of the H : C and O : C ratios for the total EESI-TOF-MS signal vs. that of the AMS are presented in Fig. S7. The trends shown there are consistent with and explained by those of the individual factors as discussed above.

The contribution of each factor from the EESI-TOF-MS PMF analysis over the entire campaign is reported in Fig. 11 along with the total signal measured from the EESI-TOF-MS (ag s^{-1}) and the total measured mass from the AMS (µg m^{-3}) (panel a). We note that periods with higher signal correspond to periods with higher ambient temperature, above 25 °C (23–24 June and 1–2 and 6–7 July). These days are characterized by high contributions from the SOA factors, and when temperature exceeded 30 °C (23–24 June) the contribution of the DaySOA2_{EESI} was higher compared to DaySOA1_{EESI}. It has been shown previously that oxidized biogenic VOCs can considerably enhance particulate mass during heat waves (Guenther et al., 1993; Churkina et al., 2017), suggesting a probable relation of the SOA sources discriminated in these analyses with biogenic emissions and especially suggesting a relation between DaySOA2_{EESI} and oxidation of freshly emitted terpenes from vegetation as previously presented in Fig. 6.

The night-time composition is significantly different, with NightSOA2_{EESI} in particular often being at or above 50% of the total SOA as measured by the EESI-TOF-MS while the AMS analysis does not allow identification of this factor. We note that according to Fig. 4 (bottom panel) the total AMS OOA is well-correlated with the sum of all four EESI-TOF-MS SOA factors, indicating that the high contribution of NightSOA2_{EESI} reflects a large contribution to the total SOA mass rather than an anomalously high relative sensitivity in the EESI-TOF-MS. This demonstrates the extent to which important chemical variabilities is missed by the AMS PMF analysis. Figure 12 shows pie charts of the mean EESI-TOF-MS factor contributions over the entire measurement period (Fig. 12a), for only the measurement period overlapping with the AMS (Fig. 12b) and the mean AMS factor contributions (Fig. 12c). We note that the relative contributions of the factors retrieved from the EESI-TOF-MS analysis are consistent for the two measurement periods, with only small variability. This supports the applied approach of comparing the AMS and EESI-TOF-MS PMF solutions for the entire available periods, despite the limited temporal overlap. Overall the primary factors contribute up to ~20% for the EESI-TOF-MS analysis while they reach up to ~30% of the total measured mass for the AMS. The secondary factors on the other hand contribute up to ~80% of the total apportioned signal for the EESI-TOF-MS analysis and ~70% of the total apportioned mass for the AMS.

Between the two instruments, the COA factors exhibit the strongest difference in contribution, with COA_{AMS} accounting for 11.6% of the total measured organic mass, while COA_{EESI} for the overlapping period reaches only 5.7%. This could be a consequence of the underestimation of the rela-
Figure 12. (a) Pie charts of the EESI-TOF-MS factor mean contributions (%) to the total measured signal for (a) the entire measurement period and (b) the period overlapping with the AMS measurements; (c) the AMS factor mean contributions (%) to the total measured organic mass.

Figure 13. Explained and unexplained variability for a subset of compounds from the EESI-TOF-MS PMF analysis weighted on the explained variability of each factor. The subset of molecules has been selected according to the interesting species among all the variables in the analysis. Species are ordered according to their chemical composition. On average the C\textsubscript{5} species contribute 1.7 \% to the total signal measured, the C\textsubscript{9}H\textsubscript{14}O\textsubscript{x} \sim 4 \%, C\textsubscript{10}H\textsubscript{16}O\textsubscript{x} \sim 4.6 \%, C\textsubscript{16}−\textsubscript{18} \sim 0.7 \%, C\textsubscript{10}H\textsubscript{17}O\textsubscript{x} \sim 1.7 \%, C\textsubscript{9}H\textsubscript{15}O\textsubscript{x} \sim 1.1 \%, C\textsubscript{10}H\textsubscript{15}N\textsubscript{2} \sim 2.5 \%, C\textsubscript{6}H\textsubscript{10}O\textsubscript{5} \sim 3.5 \%, and the remaining C\textsubscript{6}H\textsubscript{10}O\textsubscript{x} \sim 0.5 \%.

tive ionization efficiency (RIE) of COA\textsubscript{AMS}, discussed earlier, which would result in an overestimation of its measured mass (Reyes-Villegas et al., 2018). Accounting for this effect, e.g. considering a COA RIE of 2 instead of the default 1.4 value, the COA\textsubscript{AMS} contribution would decrease to 7.2 \% and as a consequence the HOA\textsubscript{AMS}, CS-OA\textsubscript{AMS}, LOOOA\textsubscript{AMS}, and MO-OOA\textsubscript{AMS} contributions would be 7.1 \%, 11.2 \%, 48.2 \%, and 26 \%, respectively, improving in this way the agreement with the COA factor extracted from the EESI-TOF-MS analysis. The RIE is although only one of the possible explanations; another possible reason is that the AMS collection efficiency is likely closer to 1 if cooking aerosols are externally mixed (Middlebrook et al., 2012).

Figure 13 shows the explained variation (EV) of each factor for selected ions in the EESI-TOF-MS dataset, as well as the variation that cannot be explained by the solution. This is a dimensionless quantity that indicates how much each computed factor explained a row (\textit{G}) or a column (\textit{F}) of the input data matrix, \textit{X}. EV values can be interpreted as the scaled version of the elements of the input matrix, where the loading of each chemical species in each factor is normalized to 1 (Eq. 12, Canonaco et al., 2013).

The compounds explained most by a single factor are nicotine (C\textsubscript{10}H\textsubscript{15}N\textsubscript{2}), of which \sim 80 \% of EV is explained by the cigarette factor alone (CS-OA\textsubscript{EESI}), and the fatty acids (C\textsubscript{16}−\textsubscript{18} in Fig. 13), of which up to 78 \% of EV is explained by the cooking factor alone (COA\textsubscript{EESI}). The variability of the nitrogen-containing compounds is mostly explained by the secondary night-time factors, and with increasing oxygenation, the contributions from the primary factors are drastically reduced. Further, we include in the analysis two series of compounds likely deriving from biogenic emissions (C\textsubscript{9}H\textsubscript{14}O\textsubscript{x} and C\textsubscript{10}H\textsubscript{16}O\textsubscript{x}), where EV by the DaySOA\textsubscript{EESI} factors is higher for the more oxygenated species, while EV of less oxygenated species is increased for the NightSOA\textsubscript{EESI} and primary factors. This is consistent with temperature-driven partitioning, causing the less oxygenated (and thus more volatile) compounds to be depleted in the particle phase during the day. We also included in the analysis two series of compounds that are com-
monly related to fossil sources (C₅ species), and we note the same effect consistent with partitioning described above. Finally, the C₆H₁₀O₃ contribution to the total profile signal is 54 % and 45 % for the primary and secondary factors, respectively, while its variability is almost equally explained by the primary and secondary factors with similar contributions of 46 % and 54 %, respectively. This suggests that most likely this chemical formula does not exclusively represent levoglucosan (or other sugars emitted from cellulose pyrolysis), which is enhanced in primary biomass combustion emissions and under summer conditions can be quickly oxidized (Bertrand et al., 2018b). Instead, significant contributions from non-sugar isomers generated by gas-phase oxidation (similar to the rest of the C₆H₁₀O₃ series) are likely. For the last series of compounds the primary factors contribute ∼ 30 % and the secondary factors ∼ 70 % to the total signal while in terms of explained mass weighted variability the series is explained by up to 18 % and 81 % by primary and secondary factors, respectively. Overall, we were able, with the EESI-TOF-MS PMF analysis, to separate more SOA factors compared to the AMS analysis where all variability related to secondary components is included in MO-OOAAMS and LO-OOAAMS. Further, the DaySOA₂EESI and NightOOA₁EESI appear related to specific processes (local daytime terpene oxidation and local night-time terpene oxidation, respectively). On the other hand, the DaySOA₁EESI and NightOOA₂EESI factors could not be unambiguously related to a single source of gaseous precursors. These last factors are also more closely related to each other and likely a convolution of VOC emissions sources and the atmospheric reactions/timescales for conversion to PM.

This result is conceptually similar to PMF analysis of NO₃ CIMS measurements of gas-phase highly oxygenated molecules (HOMs) by Yan et al. (2016) in the Finnish boreal forest during spring 2012. Several factors were separated and related to different oxidation mechanisms. Overall the most significant separation was observed between daytime and night-time; the daytime profiles appeared to be dominated by light HOMs and organonitrates derived from monoterpenes chemistry initiated by OH reaction in the presence of NO while the night-time profiles appeared to be dominated by HOM dimers deriving from the oxidation of monoterpenes with O₃ and NO₂. Despite compositional differences between the gas and particle phases, several ions having common molecular formulae are identified in both studies and also have similar temporal behaviour. We use these correlations together with the better-understood gas-phase chemistry, giving rise to the chosen ions to infer the major processes affecting the particle phase. For example, C₁₀H₁₄O₁₄N was found to be the major organonitrile representative of daytime HOMs (Yan et al., 2016) and in the current study shows the highest contributions from the DaySOA₁EESI and NightSOA₂EESI factors. Another example is C₁₀H₁₂O₄N, which was considered a tracer molecule of daytime processes initiated by O₃ reaction there, while in the current study its variability is mostly explained by the less source-specific DaySOA₂EESI and NightSOA₁EESI factors. On the other hand, fingerprint molecules related to night-time chemistry in Finland, e.g. C₁₀H₁₄O₇ and C₁₀H₁₄O₉, are mostly explained by NightSOA₂EESI and even more so by DaySOA₁EESI in the current study. This suggests that the variability is strongly driven by local source characteristics and environmental conditions, including daylight hours and oxidant concentrations, of oxidant and terpene sink variability. Similarly, Zhang et al. (2018) investigated the nature of monoterpenes SOA (MTSOA) from FIGAERO-CIMS analysis in a forested area in the southeastern United States influenced by anthropogenic pollution. They found that different chemical processes involving nitrogen oxides (NOₓ), during day and night, play a central role in the monoterpenes SOA produced, suggesting a strong anthropogenic–biogenic interaction affecting the ambient aerosol. The diurnal pattern of MTSOA was flat, but specifically they found that the majority of daytime MTSOA was due to fragmentation products of RO₂ + NO while during night-time monoterpenes were most likely oxidized by NO₃, which is primarily formed by NO₂+O₃. Overall a large fraction of the identified species in the MTSOA are also present in the current study and contribute with different abundance to all four SOA factors discriminated, suggesting once more the strong biogenic influence of secondary aerosol in summer at the measurement site.

4 Conclusions

We present the first field deployment of a novel extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS), the first instrument capable of near-molecular measurements of organic aerosol (OA) at ambient concentrations using a controlled ionization scheme without thermal decomposition, ionization-induced fragmentation, or separated collection–analysis stages. The EESI-TOF-MS measured for 3 weeks during summer in Zurich, Switzerland, achieving > 85 % data coverage without any systematic drift and signal stability within ±7.3 % (relative standard deviation). Overall, the campaign demonstrated the EESI-TOF-MS to be a sufficiently robust instrument for field operation. Positive matrix factorization (PMF) analysis of EESI-TOF-MS mass spectra yielded two primary organic aerosol factors: cooking-related OA (COAₑESI) characterized by long-chain fatty acids and levoglucosan (likely influenced by nearby open-cooking activities) and cigarette smoke OA (CS-OAₑESI), with a strong nicotine signature, as well as four secondary factors. The SOA factors were subdivided into two factors enhanced during the day (DaySOA₁EESI and DaySOA₂EESI) and two during night and/or early morning (NightSOA₁EESI and NightSOA₂EESI). All four factors showed strong contribution from ions characteristic of monoterpenes oxidation. Signatures consistent with sesquiter-
pene oxidation products were also observed in the daytime
factors. DaySOA2 exhibited a strong exponential relation-
ship with temperature, and the DaySOA1EESI factor mass
spectrum was slightly shifted towards ions with fewer car-
don atoms. These differences suggest that DaySOA2EESI
is more influenced by local oxidation of biogenic emis-
sions, whereas DaySOA1EESI represents more aged aerosol
with possible anthropogenic influences from the oxidation
of light aromatics. Two secondary night-time factors were
also observed, with one peaking between midnight and
04:00 LT (NightSOA1EESI) and the other (NightSOA2EESI)
gradually increasing after sunset to reach a maximum be-
tween 07:00 and 09:00 LT. NightSOA1EESI included less
oxygcnated terpene oxidation products, as well as organoni-
trates, likely derived from NO3 radical oxidation of monoter-
penes. NightSOA2EESI contained the same signatures with
somewhat reduced organonitrate content, as well as a
stronger contributions from aromatic oxidation products con-
sistent with the onset of photochemistry.

The EESI-TOF-MS analysis was supported and corrobo-
rated by the AMS PMF analysis. We observed a good cor-
relation between the total EESI-TOF-MS and AMS organic
signals. The apportionment to the sum of POA and SOA fac-
tors was very similar in terms of mass contribution, and the
agreement between the total SOA signals measured by the
two instruments was remarkable. However, the diurnal pat-
terns of the SOA factors disclosed a different picture. While
the total sum of the SOA factors exhibited a rather flat diur-
nal pattern for both instruments, the two AMS OOA fac-
tors illustrated significant chemical variation throughout the
day. The variation in chemical composition described by the
EESI-TOF-MS factors was consistent with various physico-
chemical processes influencing SOA formation, which was
described by the AMS PMF solution. Further, the O : C
ratio between the two instruments was correlated but offset,
and similar differences were found for the H : C ratio. These
differences may be due to higher sensitivity of the EESI sys-
tem for terpene-derived SOA than aromatic-derived SOA or
higher sensitivity to higher molecular weight species (Lopez-
Hilfiker et al., 2019). Overall this work highlights the impor-
tance of real-time, highly chemically resolved data, such as
that provided by the EESI-TOF-MS, for identification of the
key sources and physicochemical processes governing SOA
composition, such as the biogenic emission influences and
day–night chemistry identified here.

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