Variations in the chemical composition of the submicron aerosol and in the sources of the organic fraction at a regional background site of the Po Valley (Italy)

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Abstract

Fine particulate matter (PM) levels and resulting impacts on human health are in the Po Valley (Italy) among the highest in Europe. To build effective PM abatement strategies, it is necessary to characterize fine PM chemical composition, sources and atmospheric processes on long time scales (>months), with short time resolution (<day), and with particular emphasis on the predominant organic fraction. Although previous studies have been conducted in this region, none of them addressed all these aspects together. For the first time in the Po Valley, we investigate the chemical composition of non-refractory submicron PM (NR-PM_1) with a time-resolution of 30 minutes at the regional background site of Ispra during one full year, using an Aerosol Chemical Speciation Monitor (ACSM) under the most up-to-date and stringent quality assurance protocol. The identification of the main components of the organic fraction is made using the Multilinear-Engine 2 algorithm implemented within the latest version of the SoFi toolkit. In addition, with a view of a potential implementation of ACSM measurements in European air quality networks as a replacement of traditional filter-based techniques, parallel multiple off-line analyses were carried out to assess the performance of the ACSM in the determination of PM chemical

species regulated by Air Quality Directives. The annual NR-PM_1 level monitored at the study site (14.2 µg/m^3) is among the highest in Europe, and is even comparable to levels reported in urban areas like New York City and Tokyo. On the annual basis, submicron particles are primarily composed of organic aerosol (OA, 58% of NR-PM_1). This fraction was apportioned into oxygenated OA (OOA, 66%), hydrocarbon-like OA (HOA, 11% of OA), and biomass burning OA (BBOA, 23%). Among the primary sources of OA, biomass burning (23%) is thus bigger than fossil fuel combustion (11%). Significant contributions of aged secondary organic aerosol (OOA) are observed throughout the year. The unexpectedly high degree of oxygenation estimated during wintertime is probably due to the contribution of secondary BBOA and the enhancement of aqueous phase production of OOA during cold months. BBOA and nitrate are the only components of which contributions increase with the NR-PM_1 levels. Therefore, biomass burning and NO_x emission reductions would be particularly efficient in limiting submicron aerosol pollution events. Abatement strategies conducted during cold seasons appear to be more efficient than annual-based policies. In a broader context, further studies using high-time resolution analytical techniques on a long-term basis for the characterization of fine aerosol should help better shape our future air quality policies, which constantly need refinement.

1. Introduction

The Po Valley region - located in northern Italy - is amongst the most polluted areas in Europe (van Donkelaar et al., 2010; EEA, 2013). Annual $PM_{2.5}$ (particulate matter with an aerodynamic diameter below 2.5 µm) mean concentrations can significantly exceed the European $PM_{2.5}$ annual limit value (25 µg/m^3 in 2015, European Directive 2008/50/EC) and the recommendations of the World Health Organization ($PM_{2.5}$ annual average of 10 µg/m^3; WHO, 2006) at urban (e.g. Bologna, 35.8 µg/m^3) and regional background sites (e.g. Ispra, 32.2 µg/m^3; Putaud et al., 2010). Consequently, $PM_{2.5}$ impacts on human health are among the most severe in Europe (EC, 2005), while impacts on the local radiative forcing are substantial (Clerici and Mélin, 2008; Ferrero et al., 2014; Putaud et al., 2014b). Effective PM abatement strategies are thus needed in the Po Valley and require an in-depth knowledge of the chemical composition of fine PM, to quantify its sources and the atmospheric processes leading to its secondary formation.

In this region, high levels of fine aerosol are mostly due to the conjunction of i) high pollutant emissions related to industrial, transport, biomass burning and agricultural activities - the Po river basin hosting 37% of the Italian industries, 55% of the livestock and contributing 35% of the Italian agricultural production (WMO et al., 2012) - and ii) the specific geography and topography of this area - a flat basin

surrounded by the Alps and Apennine Mountains dominated by weak winds that favour the accumulation of pollutants (Decesari et al., 2014; Kukkonen et al., 2005; Pernigotti et al., 2012). As a consequence, PM levels are not only high in urban areas but also at regional and rural background sites, which are key locations for investigating air pollution due to their distance from local sources and local phenomena. Measurements of fine PM mass and chemical composition at rural background sites are in addition specifically required in the current European Directive on air quality (EU, 2008).

Previous studies have investigated the properties of fine aerosols at regional and rural background sites of the Po valley region, including their chemical characteristics (e.g. Carbone et al., 2014; Putaud et al., 2002, 2010; Saarikoski et al., 2012), and their main sources (Belis et al., 2013; Gilardoni et al., 2011; Larsen et al., 2012; Perrone et al., 2012). Fine aerosols are primarily made of organics (30-80% of fine PM mass, depending on the site and season studied), followed by ammonium nitrate and ammonium sulfate. Their main sources are fossil fuel, biomass burning and biogenic emissions to name a few. In addition, studies based on aerosol mass spectrometer measurements have been conducted in the Po valley, with the aim of characterizing specific phenomena (e.g. fog events, cooking aerosols) or seasons (Dall'Osto et al., 2015; Decesari et al., 2014; Gilardoni et al., 2014; Saarikoski et al., 2012). In studies dealing with long time-series (entire season or year), the chemical composition of fine aerosol is generally measured with a relatively low time resolution (typically 24 hours), thus preventing from studying its diurnal variation and short-lived chemical-physical processes. When documented with higher time-resolutions (1 hour or less), aerosol chemical composition and its sources are usually characterized for intensive campaigns of a few weeks only, hence not suitable to depict the seasonal or yearly air quality situation. In addition, the complexity of the fine organic fraction (e.g. Jimenez et al., 2009) requires state-of-the-art analytical and source apportionment (SA) techniques to identify organic aerosol chemical properties and sources.

The recently developed Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc., Ng et al., 2011a) is suitable to fill these gaps by providing the chemical composition of non-refractory submicron aerosols (NR-PM_1) with a time resolution of 30 min, while operating on long time scales. Even though promising results have been recently reported (e.g. Budisulistiorini et al., 2014; Canonaco et al., 2013, 2015; Minguillón et al., 2015; Ng et al., 2011a; Petit et al., 2015; Ripoll et al., 2015; Sun et al., 2012), this technique is still novel and requires additional field deployment to test its consistency with independent methods for the monitoring of fine PM chemistry (e.g. filter measurements). In addition, information on the accuracy of this technique is of paramount importance given the growing number of ACSMs in Europe and the necessity to build a network of quality assured and harmonized instruments

for comparability of results – at present about 20 ACSMs are in operation in Europe (http://www.psi.ch/acsm-stations/overview-full-period) within the frame of the EU ACTRIS network (Aerosols, Clouds, and Traces gases Research InfraStructure, http://www.actris.eu/). Moreover, by using receptor models, the apportionment of organic aerosol (OA) into its major components - hydrocarbon-like (HOA), biomass burning (BBOA) and oxygenated OA (OOA) - can be performed (Lanz et al., 2007; Zhang et al., 2011 and references therein).

In this study, we used an ACSM during one year with a 30-min time-resolution at a regional background site of the Po Valley and performed subsequent SA analyses with the aim of: i) describing the high time resolved chemical composition of NR-PM_1 on a long time-scale, to better understand the physicochemical processes driving its temporal variations, ii) apportioning the organic fraction into its main sources, iii) identifying PM abatement strategies to efficiently reduce NR-PM_1 pollution events at regional background areas of the Po valley, and iv) assessing the atmospheric consistency of ACSM measurements when compared to independent analytical methods, to evaluate its possible implementation in future European Air Quality networks.

2. Material and methods

2.1. Sampling site

Measurements were conducted at the European Commission – Joint Research Centre (EC-JRC) Ispra site (45°48'N, 8°38'E, 217 m a.s.l.; Fig. S1), which is part of the European Monitoring and Evaluation Programme (EMEP) measurement network (http://www.nilu.no/projects/ccc/sitedescriptions/it/index.html) and the Global Atmosphere Watch (GAW) regional stations (http://www.wmo.int/pages/prog/arep/gaw/measurements.html). It is located on the northwest edge of the Po Valley region, 60 km northwest of the Milan urban area. It can be regarded as a "regional/rural background" site following the criteria recommended by the European Environment Agency (Larssen et al., 1999). For simplicity, the term "regional background site" will be used in the following although comparisons with rural background sites from other studies will also be reported. Further information on the study site can be found in Putaud et al. (2014b).

2.2. Aerosol Chemical Speciation Monitor (ACSM)

The recently developed ACSM (Aerodyne Research Inc., ARI) was used to measure the non-refractory (NR) chemical composition (organics, nitrate, sulfate, ammonium, chloride) of submicron particles (PM_1) with a 30-min time resolution. The operating principle of the ACSM is similar to the widespread

Aerodyne aerosol mass spectrometer (Canagaratna et al., 2007; Jayne et al., 2000), with the difference that the former does not inform on the size distribution of the chemical composition of NR-PM_1. A full description of the ACSM can be found in Ng et al. (2011a). Briefly, an aerodynamic lens is used to focus submicron particles (50% transmission range of 75-650 nm; Liu et al., 2007), which are then vaporized in high vacuum, ionized by electron ionization (at 70 eV) and detected by a quadrupole mass spectrometer (Pfeiffer Vacuum Prisma Plus RGA). Two different quadrupole-ACSMs (Q-ACSMs) were used in this study (from March 2013 to February 2014): Q-ACSM#1 from 01 March to 18 August 2013 and Q-ACSM#2 from 20 June 2013 to 28 February 2014. Note that Q-ACSM#2 was not running from 3 November to 18 December due to its participation in the first inter-ACSM comparison exercise (Crenn et al., 2015). The reproducibility and consistency with independent measurements are discussed in Sect. 3.1. In the following, orthogonal regressions are reported unless otherwise stated.

Both ACSMs were operated with the latest Data Acquisition (DAQ 1.4.3.8 to 1.4.4.5) and Data Analysis (DAS 1.5.3.0 to 1.5.3.2) software (ARI, https://sites.google.com/site/ariacsm/mytemplate-sw) available at the time of use, which are developed within Igor Pro 6.32A (Wavemetrics). Recommendations provided by Aerodyne (2010a, 2010b) and Ng et al. (2011a) were followed for the operation, calibration and data analysis of the ACSMs. Ammonium nitrate calibrations were performed seasonally and used for the determination of experimental nitrate response factors (RF) and ammonium relative ionization efficiencies (RIE, see Sect. S1 for further details). Annual average and season-dependent experimental RF and RIE values were alternatively applied to assess whether the ACSM is stable over multi-seasonal periods (see Sect. 3.1 for results). Seasons are defined as spring (MAM), summer (JJA), autumn (SON) and winter (DJF). RIEs for organics, nitrate and chloride (1.4, 1.1 and 1.3, respectively) were taken from the literature (Canagaratna et al., 2007; Takegawa et al., 2005). RIE for sulfate was experimentally determined based on ammonium sulfate calibrations for ACSM#2, and was taken from the literature for ACSM#1 (see Sect. S1). Collection efficiencies (CE) set as i) a fixed 0.5 value (e.g. Budisulistiorini et al., 2013) or ii) following the composition-dependent CE algorithm introduced by Middlebrook et al. (2012) were compared in order to determine the most appropriate CEs (see Sect. 3.1 for results).

2.3. Additional analytical techniques

Additional measurements routinely performed at the JRC-Ispra site are used in this study (see Putaud et al., 2014a for a full description). $PM_{2.5}$ was sampled on quartz fibre filters (Pall, 2500 QAT-UP) with a Partisol PLUS 2025 sampler equipped with a carbon honeycomb denuder operating at 16.7 L/min from

01 March 2013 to 28 February 2014 with daily filter changes at 08:00 UTC. Major ions (NH_4^+, K^+, NO_3^-, SO_4^{2-}, etc.) are analysed by ion chromatography (Dionex DX 120 with electrochemical eluent suppression) after extraction in Milli-Q water (Millipore). Organic and elemental carbon (OC and EC, respectively) are quantified by a thermal-optical method (Sunset Dual-optical Lab Thermal-Optical Carbon Aerosol Analyzer) using the EUSAAR-2 protocol (Cavalli et al., 2010). Equivalent black carbon (BC) is measured by a Multi Angle Absorption Photometer (MAAP, Thermo Scientific, model 5012) applying an absorption cross section of 6.6 m^2/g of equivalent black carbon at the operation wavelength of 670 nm. Particle volume concentrations are determined with a home-made Differential Mobility Particle Sizer (DMPS) combining a Vienna-type Differential Mobility Analyser (DMA) and a Condensation Particle Counter (CPC, TSI 3010), following the European Supersites for Atmospheric Aerosol Research (EUSAAR) specifications for DMPS systems (Wiedensohler et al., 2012). Meteorological variables (temperature, pressure, relative humidity, precipitation, wind speed and direction) are determined from a weather transmitter WXT510 (Vaisala, Finland). Solar radiation is measured by a CM11 pyranometer (Kipp and Zonen, The Netherlands).

2.4. Apportionment of the organic fraction

The organic fraction was apportioned using the Positive Matrix Factorization approach (PMF, Lanz et al., 2007; Paatero and Tapper, 1994; Ulbrich et al., 2009; Zhang et al., 2011) by applying the Multilinear Engine 2 algorithm (ME-2, Paatero, 2000) implemented in the SoFi tool (v4.8, Canonaco et al., 2013; Crippa et al., 2014). Details on the theory and application of PMF and ME-2 can be found in the aforementioned studies. Briefly, PMF aims at factorizing an initial X matrix (representing the temporal variation of *m/z* signals here) into two F and G matrices (representing factor profiles and contributions, respectively) putting a constraint of non-negativity on F and G matrices. Contrary to the classical program used to resolve PMF (e.g. PMF2, PMF3), ME-2 allows any element of the F and G matrices to be constrained with a certain degree of freedom. This ME-2 approach has been typically used to constrain full factor profiles (e.g. Amato et al., 2009; Crippa et al., 2014), specific elemental ratios (e.g. Sturtz et al., 2014) or specific species contribution (e.g. Crawford et al., 2005) in a given factor profile.

In our study, ME-2 is applied with and without constraining factor profiles (FPs), using the so-called *a*-value approach (Canonaco et al., 2013) in the former case, which can be described as follows:

$$(f_{k,j})_{solution}=(f_{k,j})_{reference} \pm a.(f_{k,j})_{reference} \quad (1)$$

where k and j are the indexes for the factors and the species, respectively, $f_{k,j}$ is the element (k, j) of the F matrix, the index "solution" stands for the PMF user solution, "reference" for the reference profile and

"*a*" is a scalar defined between 0 and 1 (e.g. applying an *a*-value of 0.10 lets ±10% variability to our FP solution with respect to the reference FP). Following Crippa et al. (2014), we perform a sequence of runs with i) unconstrained PMF, ii) fixed HOA, iii) fixed HOA and BBOA, iv) fixed HOA, BBOA and cooking OA (COA) factors before selecting the most appropriate solution. Uncertainties are calculated using the DAS 1.5.3.0 version following the methodologies of Allan et al., 2003a and Ulbrich et al. (2009). *m/z* 12 and 13 are removed for SA analysis since negative signals are observed most of the time. Reference factor profiles (RFPs) are taken from ambient deconvolved spectra from the Aerosol Mass Spectrometry (AMS) spectral database (Ulbrich et al., 2015). HOA and BBOA profiles are taken from Ng et al. (2011c) (average of profiles from multiple studies) and COA from Crippa et al. (2013). Different *a*-values are tested (see Sect. 3.2) applying i) relative standard deviations of averaged RFPs defined for every *m/z* (i.e. assuming that the chosen averaged RFPs are representative of our data set), ii) recommendations of Crippa et al. (2014) based on the SA of 25 European AMS data sets and iii) comparison with independent measurements (e.g. NOx, CO, BC, etc.). Solutions from 2 to 8 factors are investigated in order to choose the appropriate number of factors (see Sect. S2 and 3.2).

3. Quality assurance / quality control

3.1. Quality assurance / quality control of ACSM measurements

Ammonium nitrate calibrations performed on each ACSM are shown in Fig. S2. RF_{NO3} and RIE_{NH4} do not present significant seasonal variability - e.g. for ACSM#2 RF_{NO3}=4.7E-11±0.2E-11 $A.\mu g^{-1}.m^3$ - , suggesting constant calibration factors may be used throughout the campaign. On the other hand, calibration factors exhibit substantial discrepancies between both ACSMs (e.g. RF_{NO3} of 2.5E-11 and 4.7E-11 $A.\mu g^{-1}.m^3$ for ACSM#1 and #2, respectively), suggesting that instrument-specific factors are necessary. Applying constant and composition-dependent CEs does not lead to noticeable differences (e.g. for NR-PM_1: r^2=0.97, slope=1.00±0.00, y-intercept=0.10±0.03 $\mu g/m^3$, n=14842) due to i) low sampling line RH (e.g. typically below 30% for ACSM#2), and ii) few high-nitrate-content events (only 5% of data exhibits ammonium nitrate mass fractions >40%, defined as high by Middlebrook et al., 2012). The Middlebrook et al. (2012) algorithm is however preferred since slightly acidic aerosols are observed at the study site (on average sulfate plus nitrate against ammonium in $\mu eq/m^3$: r^2=0.96, slope=1.21±0.00, intercept=0.01±0.00 $\mu eq/m^3$, n=14842).

A comparison performed between the two ACSMs used in this study during a 2-month summer period is shown in Fig. S3. Very good correlations are observed for every chemical component ($0.91<r^2<0.98$, n=1402, hourly average) - chloride excluded - with slopes relatively close to one

(0.87<slopes<1.42), indicating a fairly good comparability between both instruments. One of the two ACSMs also participated in the first-ever inter-ACSM comparison exercise performed between 13 different European Q-ACSMs during 3 weeks in Paris, France (Crenn et al., 2015). Satisfactory performances - defined by |z-scores|<2 - are reported for our instrument regarding every chemical component and NR-PM_1 mass, attesting the consistency of our measurements with other European sites.

Measurements performed by the ACSM and independent off-line and on-line analytical techniques are compared in Figure 1 and Table 1. An overall good agreement is found for every major components throughout the year (typically r^2>0.8), although discrepancies are observable for specific species and seasons. On the annual scale, a good agreement (r^2=0.77, n=317) is found between organics from ACSM and OC from filter measurements in spite of expected filter sampling artefacts (Maimone et al., 2011; Turpin et al., 2000; Watson et al., 2009). Even better agreements are observed on a seasonal basis (r^2~0.9), with steeper slopes in summer compared with winter, which likely reflects the different degrees of oxygenation of organics among seasons (leading to different OM-to-OC ratios). However, these slopes cannot be directly regarded as the OM-to-OC ratios due to i) differences in size fractions between both methods (PM_1 for ACSM and $PM_{2.5}$ for filter measurements) and ii) uncertainties related to RIE_{Org} for ACSM measurements (Budisulistiorini et al., 2014; Ripoll et al., 2015). An estimation of the OM-to-OC ratio for submicron organics applying the methodology described by Canagaratna et al. (2015) is discussed in Sect. 4.2. Good correlations are observed for nitrate during all seasons (r^2>0.9) but summer (r^2=0.5), which is most likely related to enhanced evaporative losses of ammonium nitrate from filter during the latter season (Chow et al., 2005; Schaap et al., 2004). Slopes range from 0.9 to 1.4 - summer excluded - which is comparable to what is reported elsewhere (Budisulistiorini et al., 2014; Crenn et al., 2015; Ripoll et al., 2015). Very good correlations are observed for sulfate in every season (r^2=0.9-1.0) with slopes close to 1 (0.9-1.1, winter excluded), consistent with its presence in the submicronic size fraction and its low volatility leading to the minimization of sampling artefacts. Note that discrepancies have been reported when comparing sulfate measured by the ACSM (Petit et al., 2015) or the AMS (Zhang, 2005) with independent measurements. Our results suggest that ammonium sulfate calibrations should be performed to experimentally determine sulfate RIEs, which appear to be instrument-specific but stable over several months. Although aerosols are slightly acidic on average at the study site, ammonium mostly neutralizes nitrate and sulfate throughout the campaign and thus exhibits behaviour in between the two latter compounds. Higher uncertainties are associated with chloride from filter quantification, resulting in no agreement with ACSM measurements in summer

when the concentrations are the lowest (r^2=0.00), and fairly good agreement during the other seasons (r^2=0.64-0.77). The high slope observed for the ACSM#1 (e.g. 2.1 during spring) compared to the fairly good slopes observed for ACSM#2 (0.7-1.1) suggests that chloride RIE might be instrument-specific and require appropriate calibrations for its accurate quantification (see also Riffault et al., 2013 on this topic).

The sum of NR-PM_1 components and BC has been compared to the volume concentration of PM_1. Good agreement is found between both variables (r^2>0.8) giving further confidence on the consistency of our ACSM measurements. The annual average particle density estimated from this comparison (i.e. slope) is 1.6, which is typical of ambient aerosol particles densities (1.5-1.9 in Hand and Kreidenweis, 2002; Hu et al., 2012; McMurry et al., 2002; Pitz et al., 2003, 2008). The higher densities observed during spring and summer (1.9-2.0) than autumn and winter (1.3-1.5) are likely due to the enhanced contribution of secondary aerosol and aged particles during the former period (Pitz et al., 2008).

3.2. Quality assurance / quality control of organic source apportionment

First, during the aforementioned inter-ACSM comparison study (Crenn et al., 2015), source apportionment of organics was performed based on data from 13 Q-ACSMs (Fröhlich et al., 2015), including one ACSM used in the present study. Satisfactory performances (|z-scores|<2) are reported for our ACSM using a similar approach as adopted in this study. This result demonstrates that our instrument and the associated data treatment, including the source apportionment modelling, are capable of accurately identifying and quantifying OA sources.

3.2.1. Model configurations

Regarding our specific study, the configuration applied to reach the optimal SA of organics is thoroughly discussed in Sect. S2 (constrained factor profiles, number of factors, *a*-values and integration-period durations). Briefly, constraining both HOA and BBOA factors result in satisfactory solutions with relevant factor profiles, time series and daily cycles. Other configurations (e.g. unconstrained factors) lead to unsatisfactory results with high seed variability, mixing of factors or absence of key fragments in identified profiles (e.g. absence of *m/z* 43 and 44 in BBOA contrary to what is reported in Heringa et al., 2011, Fig. S4). Solutions applying different number of factors are investigated. Three-factors (HOA, BBOA and OOA) are retained during spring, autumn and winter whereas two factors (HOA and OOA) are most suitable during summer. A lower number of factors

results in a mixing of them, whereas a higher number generates additional factors - e.g. semi-volatile OOA (SV-OOA) during summer, OOA-BBOA during autumn - which are not satisfactory - e.g. missing fragments or poor correlations with external data, see Table S1. BBOA cannot be clearly identified during summer i.e. in this season agricultural waste burning contributions are estimated to be minor (maximum 3-4% of OA, Sect. S2). Note that COA could not be evidenced, likely due to the type of site studied (regional background) and the lower sensitivity, time- and mass-to-charge-resolution of the ACSM compared to classical AMS instruments (further discussed in Sect. S2; see also Dall'Osto et al., 2015 on this subject). Uncertainties associated with factor contributions are estimated by performing sensitivity tests on *a*-values, which are regarded as the most subjective input parameters. Five scenarios putting very low to very high constraints on the reference factor profiles have been defined (see Table S2). Comparable solutions in terms of relative contributions (Fig. S5) and agreement with independent measurements (Table S2) are found when applying low to high constraints following the empiric recommendations of Crippa et al. (2014). Unsatisfactory solutions are generally reached under the extreme scenarios (fully fixed factor profiles and *m/z* specific standard deviations of reference factor profiles). We decided to apply low constraints (i.e. *a*-values of 0.1 and 0.5 for HOA and BBOA, respectively) to let as much freedom as possible to our factor profiles while remaining in the range of plausible solutions. SA was performed on 3-months, 6-months and 1-year datasets. Although comparable solutions are found for each configuration (number of factors, factor profiles, diurnal cycles, comparisons with external data), applying SA on seasonal datasets was preferred since i) the seasonal variability of factor profiles is captured and ii) questionable results are observed in summer for 6-months and 1-year configurations (see Sect. S2). When comparing the sum of OA factor concentrations and measured OA on the annual scale, OA is very well modelled (r^2=0.97, slope=0.98±0.00, intercept=0.1±0.0 μg/m^3, n=14842).

3.2.2. Model optimal solution

Factor profiles, contributions and daily cycles of the optimal SA solution are presented in Figure 2. Independent factor profiles and time series are found for each season, which is a prerequisite for having reliable SA solutions. HOA is identified during every season and exhibits a profile dominated by alkyl fragments such as *m/z* 55 (from the $C_nH_{2n-1}^+$ ion series) and *m/z* 57 (from $C_nH_{2n+1}^+$ ion series; Ng et al., 2011c). Its relative contribution is characteristic of traffic emissions, exhibiting a peak in the morning, and higher contributions during weekdays than weekends (e.g. averages of 14 and 9%, respectively, in autumn, Fig. S6). BBOA is found during every season except summer and has a profile similar to that of

HOA, except for the high contribution of *m/z* 60 ($C_2H_4O_2^+$) and 73 ($C_3H_5O_2^+$), which have been suggested as biomass burning markers (Lee et al., 2010 and references therein). A distinct daily cycle with higher contributions during night-time than daytime is observed, in addition to higher contributions during weekends than weekdays (e.g. averages of 24 and 21%, respectively, in spring, Fig. S6), consistent with residential heating emissions. The low BBOA concentrations modelled during late spring and early autumn, as well as the small increased contribution observed during the morning also suggest residential heating emissions. OOA is identified thanks to the predominant contribution of *m/z* 44 (CO_2^+) and 43 ($C_2H_3O^+$). The higher contribution of f_{44} (defined as *m/z* 44 to total organic signal; 0.17-0.23 depending on seasons) with respect to f_{43} (defined similarly; 0.05-0.09) suggests that this OOA factor is highly oxidized and presents low volatility (LV-) rather than semi-volatility (SV-) OOA characteristics (see Jimenez et al., 2009 and Zhang et al., 2011 for definitions of these components). This statement is supported by very good correlations (r^2=0.96-0.99) found between our unconstrained OOA profiles and the average low-volatility OOA (LV-OOA) profile reported by Ng et al. (2011c) from 6 AMS studies. Interestingly, our OOA profiles present slight seasonal differences that likely reflect changes in source contributions and/or physical-chemical processes in this factor. For instance, f_{60} in OOA profiles is enhanced in winter (0.014) compared with other seasons (0.001-0.004), which suggests that biomass burning contributes to this factor during the aforementioned season, consistent with different studies reporting f_{60} in secondary OA from biomass burning (e.g. Cubison et al., 2011; Heringa et al., 2011; see Sect. S2). Note that the mass spectral resemblance of primary humic-like substances to LV-OOA might also partly explain this observation (e.g. Young et al., 2015), i.e. that a small fraction of primary OA is found in this factor. Daily cycles are comparable for all seasons with a bimodal pattern characterized by a small peak during night-time and a prominent peak during daytime. The latter peak suggests that a fraction of (LV-) OOA could be locally rather than regionally produced on the time scale of few hours only, likely due to enhanced photochemical activities during daytime. The former peak could be due to i) the condensation of highly oxygenated semi-volatile material favoured by night-time thermodynamic conditions or ii) a contribution of SV-OOA in our OOA factor, which is generally dominated by LV-OOA. The absence of an f_{44} night-time peak (Sect. 4.2) suggests that the second assumption is more probable implying that both SV-OOA and LV-OOA influence our OOA factor.

3.2.3. Time series comparisons

Comparisons between our OA factors, *m/z* tracer and independent species time series are shown in Table 2. OOA time series show very good agreement with Org_43 (organic signal at *m/z* 43)

and Org_44 (r^2>0.8 and 0.9, respectively) and relatively good agreement with secondary inorganic species (e.g. r^2≥0.5 for ammonium), indicating that this factor can be regarded as a surrogate for secondary organic aerosols. Comparisons with sulfate (a low-volatility species) and nitrate (a semi-volatile species) confirm that our OOA factor might be a mix of SV- and LV-OOA, since better agreement is found with one or the other compound depending on the season studied. BBOA exhibits very good coefficients of determination when compared with its presumable fragment tracers Org_60 and Org_73 (r^2>0.97), giving further confidence on its appropriate quantification. Good correlations are generally found between BBOA and BC (r^2≥0.5, except for summer) indicating that a large proportion of BC stems from biomass burning, consistent with previous findings at the study site (Gilardoni et al., 2011, from EC measurements). A good agreement is also observed with CO (r^2≥0.7), as already reported in the Alpine valleys (e.g. Gaeggeler et al., 2008). HOA is not as well correlated with external data or specific *m/z*, which could be related to i) the absence of clear *m/z* tracers for this factor due to similarities with BBOA profile, ii) the absence of clear external tracers due to co-emissions by fossil fuel and biomass burning activities of BC, CO and NOx and iii) possible uncertainties associated with the apportionment between HOA and BBOA. The first two assumptions are supported by the better agreement observed between HOA and *m/z* fragments or independent data during summer (e.g. r^2=0.52, n=2208 between HOA and BC) and specific months (e.g. May, September), when biomass burning contributions are negligible. Although uncertainties associated with the accurate apportionment of HOA and BBOA cannot be excluded (e.g. due to rotational ambiguity), several factors evidence the robustness of the results and indicate that a mixing of both factors is unlikely, since HOA and BBOA present i) independent factor time series during all seasons (r^2=0.1-0.2), ii) distinct and relevant daily cycles and iii) no significant *α*-value variability.

4. Results and discussion

The meteorological representativeness of this one-year measurement is assessed by comparing the solar irradiation, precipitation, and temperature monthly averages to the ones measured during 1990-2010 at the study site (Fig. S7). Comparable seasonal averages are generally found in our study and during the bidecadal reference period. Nevertheless compared to 1990-2010, Spring 2013 was rainier, Summer 2013 slightly warmer and sunnier, and Winter 2013-2014 rainier. Further information regarding the representativeness of measurements performed at the study site during the year 2013 can be found in Putaud et al. (2014a).

4.1. Chemical composition of NR-PM_1

An overview of the chemical composition of NR-PM_1 retrieved during this campaign is shown in Figure 3. The annual averaged NR-PM_1 mass reported here (14.2 μg/m^3) ranges amongst the highest NR-PM_1 levels (7th out of 41 sites) reported at rural and urban downwind sites in Europe (Crippa et al., 2014) and worldwide (Jimenez et al., 2009; Zhang et al., 2007, 2011). Please note that these previous studies are based on typically one month of measurements in different seasons. It is comparable to NR-PM_1 levels reported during specific campaigns in the urban areas of New York City (USA, 12 μg/m^3, Weimer et al., 2006), Tokyo (Japan, 12-15 μg/m^3, Takegawa et al., 2006) or Manchester (UK, 14 μg/m^3, Allan et al., 2003a, 2003b). Our annual average NR-PM_1 mass is higher than the 10 μg/m^3 guideline given by the World Health Organization for the annual average $PM_{2.5}$ mass (including refractory and non-refractory compounds; WHO, 2006). After similar conclusions have been drawn for $PM_{2.5}$ and PM_{10} size fractions (Putaud et al., 2010), the Po Valley appears to be one of the most polluted regions in Europe with regard to NR-PM_1 levels this time. Submicron aerosol particles are mostly made of organics (58%), nitrate (21%), sulfate (12%) and ammonium (8%; Figure 3). The predominance of organics is typical of urban downwind sites (e.g. average of 52% reported in Zhang et al., 2011). On the other hand, the noticeable proportion of nitrate is characteristic of urban sites (18% in Zhang et al., 2011), which likely reflects the substantial influence of anthropogenic activities emissions at our regional site. As a result, sulfate exhibits particularly low contributions at the study site compared with other locations (generally >20% in Zhang et al., 2011).

NR-PM_1 levels present a clear seasonality with higher levels during spring (~18 μg/m^3) and winter (~15 μg/m^3) compared with summer and autumn (~12 μg/m^3). Higher levels were expected during cold months due to enhanced biomass burning emissions and lower boundary layer heights (BLH), as previously observed at the study site (Putaud et al., 2013). Expected seasonal variations of the chemical composition of NR-PM_1 are observed, with i) higher nitrate contributions during the cold season which favours its partitioning in the condensed phase (Clegg et al., 1998), ii) higher sulfate contributions during summer, which can e.g. be associated with enhanced photochemical production (Seinfeld and Pandis, 2006) and lower amount of rainout (Fig. S7), and iii) relatively stable contributions for ammonium (mainly neutralizing the two previous species) and organics (discussed later on).

A focus will now be made on daily cycles of the chemical composition of NR-PM_1 (Figure 4), displayed for the first time during the 4 seasons in the Po Valley, thanks to the high time resolution and stability of the ACSM. On the annual scale, daily cycles of NR-PM_1 levels are characterized by significantly higher concentrations during night-time than daytime, likely due to lower BLH, higher wood

burning emissions (during cold seasons) and lower temperatures favouring the partitioning of semi-volatile inorganic (mainly ammonium nitrate) and organic material in the condensed phase, to name a few. A distinct peak is however observed around noon, probably caused by enhanced photochemical production of secondary organic compounds, and increased BLH favouring downward mixing of advected pollution, especially during summer (Figure 4; Decesari et al., 2014). Note that this annual daily pattern is the combination of distinct daily cycles varying with the season studied (Figure 4). In terms of relative chemical composition, organics are dominating NR-PM_1 mass independently of the time of the day, with median contributions ranging from ~60 to 70%. Nitrate exhibits higher contribution during night-time due to its abovementioned semi-volatile nature. Sulfate shows unexpected daily cycles with significantly different (99.99% confidence level) relative contributions - and absolute concentrations - during daytime (~15% of NR-PM_1 mass around noon) compared to night-time (~10% around midnight, Figure 4), although its formation was expected to occur mainly over longer time scales (i.e. days) in cloud droplets (Ervens et al., 2011). This observation could be due to i) local production of sulfate with increased photochemical production around noon at the study site and/or ii) diurnal changes of the atmospheric stratification in the Po Valley as described by Saarikoski et al. (2012) and Decesari et al. (2014), enhancing aged particle contribution during the middle of the day and the afternoon. Non-refractory chloride (mostly NH_4Cl, Huang et al., 2010) exhibits very low contributions independently of the hour of the day (medians below 0.5% of NR-PM_1 mass) with however a slight increase at night, which is likely due to its presumable semi-volatile nature here.

4.2. Focus on organic aerosols

An overview of the contribution of HOA, BBOA and OOA to OA is shown in Figure 5. On the annual average, the organic fraction is dominated by the secondary component (OOA, 66%). Although this OOA contribution is substantial, higher proportions are generally reported at rural and urban downwind sites worldwide (90 and 82% of OA on average, respectively, Zhang et al., 2011). This lower relative contribution of OOA is related to the higher contribution of (primary) BBOA in our study (23% of OA on the annual average) compared to the previous ones. Considerable contributions of BBOA are explained by the specific location of the study site in the vicinity of the Alps, where biomass burning is a major contributor to OA (Belis et al., 2011; Herich et al., 2014; Lanz et al., 2010). Biomass burning emissions hence substantially affect OA levels on the annual scale here. The contribution of HOA is comparatively smaller (11%), indicating that despite the expected large contributions of fossil fuel emissions (i.e. traffic and industrial emissions), those are not the major sources of primary OA at the study site. On the other

hand, it is likely that fossil fuel emissions of volatile organic compounds (VOCs) - which are OOA precursors - contribute to our OOA levels as reported elsewhere (Gentner et al., 2012; Volkamer et al., 2006). At the study site, Gilardoni et al. (2011) previously estimated on the basis of ^{14}C analyses that secondary organic carbon stemming from fossil emissions might represent 12% of OC on the annual average. In other words, fossil fuel emissions could represent approximately a quarter (12+11=23%) of total OA mass when both primary and secondary OA fractions are accounted for. The analysis of the components' seasonal variations shows relatively stable HOA contributions (9-14%), higher contributions of BBOA during cold seasons due to residential heating (up to 36% of OA on average during winter) and higher OOA contributions during summer related to enhanced photochemical production (86% of OA on average).

OA can be further characterized investigating specific organic fragments. *m/z* 44 (mainly CO_2^+) and 43 (mainly $C_2H_3O^+$) signals give insights on the nature of OA, as the former is primarily related to acids or acid-derived species whereas the latter is mostly associated with non-acid oxygenates (Duplissy et al., 2011; Ng et al., 2011b). Daily variations of both f_{44} and f_{43} are shown in Figure 6, along with other major organic fragments. On average, f_{44} is predominant with respect to f_{43} (15 and 7%, respectively), which indicates that acid species dominate the OA composition with respect to non-acid oxygenates. Both fragments present different daily patterns underlying distinct mechanisms of formation. Acids' contributions are enhanced during daytime, which could be explained by photochemical processes and/or daily BLH variations as already discussed for sulfate. Non-acid oxygenates exhibit higher contributions during night-time than daytime. This pattern could be due to i) the formation of semi-volatile non-acids during night-time by e.g. condensation (Lanz et al., 2007), ii) their degradation during daytime by e.g. fragmentation reactions (Daumit et al., 2013) and/or iii) their conversion into acid-related species during daytime by e.g. functionalization or oligomerization reactions (Daumit et al., 2013). It should be specified that the enhancement of f_{44} during daytime and the increasing of f_{43} during night-time only represent a small fraction of their total contributions to OA (Figure 6), suggesting that most acid and non-acid oxygenates have been formed before reaching our sampling site, i.e. have been imported from other regions. The other major OA fragments (*m/z* 29, 55, 57 and 60) present i) constant contributions for f_{29} due its various emission sources (HOA, BBOA, OOA; Ng et al., 2011c), ii) the absence of lunch peak for f_{55} (and also for the absolute contributions of *m/z* 55) consistent with the presumable low influence of cooking emissions, iii) morning and evening peaks for f_{57} characteristic of fossil fuel emissions and iv) higher contributions during night-time for f_{60} in agreement with its biomass burning origin.

Using f_{43} and f_{44}, the oxygen-to-carbon (O/C), OM-to-OC (OM/OC), hydrogen-to-carbon (H/C) ratios and the carbon oxidation state (OSc) have been estimated for total OA based on the methodologies described by Aiken et al. (2008), Kroll et al. (2011) and Ng et al. (2011b), and applying the parameterization defined in Canagaratna et al. (2015), which can be summarized as follows:

$$O/C = 4.31\, f_{44} + 0.079 \quad (1)$$

$$OM/OC = 1.28\, O/C + 1.17 \quad (2)$$

$$H/C = 1.12 + 6.74\, f_{43} - 17.77\, f_{43}^{2} \quad (3)$$

$$OSc = 2*O/C - H/C \quad (4)$$

with H/C (and therefore OSc) being estimated only if f_{44}>0.05 and f_{43}>0.04 (Canagaratna et al., 2015). Uncertainties associated with these estimates - in particular based on ACSM measurements - are discussed in Sect. S3 (see also Fig. S8). Comparisons with studies using (HR-ToF-) AMS instruments will not be reported and only variations within this dataset will be discussed (see Sect. S3). Seasonal and annual O/C, OM/OC, H/C and OSc are shown in Figure 7. High O/C, OM/OC and OSc are found on the annual scale (medians of 0.7, 2.1 and -0.2, respectively), reflecting once more the aged, oxidized properties of organic matter at the study site, consistent with the predominance of the OOA component. Little seasonal variations are observed for the aforementioned variables hence highlighting the high degree of oxidation of OA throughout the year (Figure 7). The unexpectedly high degree of oxygenation of OA observed during cold seasons despite the increased contribution of primary BBOA (with OM/OC ratios of 1.4-1.6) could be explained by the contribution of secondary BBOA in our OOA factor during these cold seasons, which could be associated with the enhancement of e.g. dicarboxylic and ketocarboxylic acid contents (Kundu et al., 2010) that have extremely high OM/OC ratios (up to 3.8 and 3.1, respectively, Turpin and Lim, 2001). This assumption is supported by the higher proportion of f_{60} in our OOA factor (discussed in Sect. 3.2 and S2), as well as the surprisingly high OM/OC ratio observed for OOA during winter (2.5 compared to 2.2-2.4 during the other seasons). Note that Canonaco et al. (2015) also report a higher f_{44} in (LV-) OOA in winter compared to summer in Zurich (Switzerland). According to these authors, this could be due to enhanced aqueous-phase production of (LV-) OOA in clouds or hygroscopic aerosols in winter, which would lead to higher levels of oxygenation compared to gas-phase oxidation mechanisms typically occurring during summer.

4.3. Possible implications for PM abatement strategies

In order to investigate the characteristics of fine aerosol pollution events, the variations of NR-PM_1 chemical composition and OA factors' contributions as a function of total NR-PM_1 mass are examined.

This investigation is made on the annual (Figure 8, discussion below) and seasonal scales (Fig. S9, discussion in Sect. S4). Distinct trends are observed depending on the chemical species and OA components studied. The proportion of nitrate is clearly enhanced with increasing NR-PM_1 levels (from ~10 to >30% when [NR-PM_1]>30 μg/m^3) indicating that nitrate - or NO_x - abatement policies should be highly effective when attempting to limit PM_1 pollution events in the Upper Po Valley. Sulfate shows an opposite trend with decreasing relative contribution when NR-PM_1 mass increases (e.g. <5% when [NR-PM_1]> 50 μg/m^3), likely due to the lower concentrations of sulfate during cold seasons, when the highest number of pollution events is observed. The proportion of organics is substantial (48-66%) independently of NR-PM_1 mass, justifying once again the importance of determining its sources to design adequate abatement policies. When focusing on the organic fraction, BBOA is the only OA factor exhibiting increased contributions (from ~10 to >40%) with increased NR-PM_1 mass (from <10 to >60 μg/m^3), which points out the PM abatement potential of effective biomass burning emission reductions. HOA levels are rather constant throughout the year and therefore their proportions steadily decrease when NR-PM_1 levels increase, implying that local fossil fuel related emissions of primary OC are not the main responsible for submicron pollution events observed at the study site on the annual scale. Although OOA always represents a major fraction of OA (41-75% depending on the mass bin studied), its contribution steadily decreases with increasing NR-PM_1 mass. This unexpected result signifies that even though aged, secondary, oxidised organics are the main contributor to OA on the annual average (66%), they do not play a prominent role in fine PM acute pollution events.

Current European legislations set daily and/or annual PM limit values depending on the size fraction addressed (Directive 2008/50/EC). Volume size distributions suggest that approximately 90% of the $PM_{2.5}$ mass concentration is borne by particles below an aerodynamic diameter of 1 μm at the study site (Putaud et al., 2014a). Therefore, measures tackling the main constituents of the submicron aerosol fraction would be efficient for complying with $PM_{2.5}$ legislations. Based on the chemical characterization of NR-PM_1 and SA of its organic fraction with a time-resolution of 30 min over 1-year, this study provides new evidence which could orient PM abatement strategies also at similar regional background sites of the Po Valley. On the annual scale, OA and especially OOA should be of main concern given their predominance in NR-PM_1 chemical composition (Figure 3). On the seasonal scale, efforts should be directed towards the cold seasons (winter and early spring), for which the highest NR-PM_1 levels are observed, due to specific meteorological conditions (e.g. low BLH, low temperatures) and emission sources (e.g. biomass burning, Figure 3 and Figure 5). In particular, measures addressing emissions of

543 NO_x and BBOA would be the most efficient for reducing the magnitude and frequency of PM pollution
544 events (Figure 8).

545 Recommendations for PM abatement strategies are formulated here from a legislative perspective,
546 which aims at decreasing PM levels. Although diminishing PM levels should help reducing PM impacts,
547 the existence of a direct causal relationship can be debatable since each chemical component has a
548 specific effect on human health (WHO, 2013), the radiative forcing (Boucher et al., 2013) or ecosystems
549 (e.g. Carslaw et al., 2010). For instance, implementing policies aiming at mitigating nitrate
550 concentrations - as suggested previously in this section - would likely have limited health benefits
551 according to toxicological studies (Reiss et al., 2007; Schlesinger and Cassee, 2003), and should lead to
552 an increased global warming (Boucher et al., 2013). On the other hand, measures reducing BBOA levels
553 should be beneficial, since the cardio-vascular effects of biomass burning particles have been widely
554 reported in the literature (Bølling et al., 2009; Miljevic et al., 2010; Naeher et al., 2007) and could be
555 similar to those of traffic-emitted particles (WHO, 2013 and references therein), whereas their impacts
556 on the radiative forcing could be null (Boucher et al., 2013). Strategies aiming at reducing solely PM
557 mass are therefore limited, and an assessment of their impacts - e.g. using integrated assessment
558 models (Carnevale et al., 2012; Janssen et al., 2009) with appropriate parameterizations of fundamental
559 processes - would be beneficial.

560

561 ## 5. Conclusion and perspectives

562 The NR-PM_1 chemical composition and the apportionment of the organic fraction have been
563 investigated for the first time with this completeness at a regional background site of the Po valley
564 (Italy), using high time-resolution (30 min) and long term (1 year) measurements with a state-of-the-art
565 quality assured ACSM and the most advanced factor analysis methods. Comparisons between two
566 ACSMs show very good time series correlations for the major compounds ($0.91<r^2<0.98$, n=1402) with
567 however discrepancies in their absolute concentrations (0.9<slopes<1.4). These results are promising
568 with regard to the consistency of ACSM measurements at different locations, but also underlines the
569 importance of conducting inter-ACSM comparisons to define common protocols and assure data
570 comparability among the European ACSM network (see Crenn et al., 2015). Comparisons between ACSM
571 and independent analytical technique measurements show an overall good agreement for major
572 components throughout the year (typically $r^2>0.8$). Discrepancies observed in time series correlations
573 and quantifications (i.e. slopes) for specific species and seasons (e.g. nitrate in summer) are attributed
574 to filter sampling artefacts. These results are encouraging regarding the potential implementation of

ACSMs in air quality networks as a replacement of traditional filter-based techniques, to measure the artefact-free chemical composition of fine aerosols with high time-resolution. Additional comparison studies are nevertheless needed to support our results, and further technical development allowing the refractory carbon fraction to be accounted for is required.

NR-PM_1 and PM_1 levels measured in the upper Po Valley (14.2 and 15.3 $\mu g/m^3$ on the annual average, respectively) are among the highest reported in Europe, stressing the need for implementing effective PM abatement strategies in this region. On average, the chemical composition of non-refractory submicron aerosol is dominated by organic aerosol (58% of NR-PM_1), which is composed of HOA (11% of OA), BBOA (23%) and OOA (66%). Fossil fuel combustion is thus not a major source of primary OA in this area of the Po Valley. Primary BBOA significantly contributes to OA on the annual average and especially during winter (36%). Our OOA component is highly oxidised and aged with an LV-OOA spectral signature, a large proportion of acid-related species and high OM/OC ratios. Highly oxidised OA properties are observed during all seasons, surprisingly including winter, which could reflect secondary BBOA influence and OOA aqueous-phase formation processes during cold seasons. Further research aiming at identifying the sources of OOA - including secondary BBOA using e.g. high resolution mass spectrometric techniques (Crippa et al., 2013) or proton nuclear magnetic resonance (Paglione et al., 2014) - and better estimating O/C, OM/OC and OSc parameters would be beneficial.

Specific recommendations for PM abatement strategies at a regional level can be suggested. The higher frequency of particulate pollution peaks observed during cold seasons suggests an orientation of future policies towards these periods. BBOA and nitrate present increasing relative contributions with increasing fine aerosol levels, which suggests that wood burning and NO_x emission reductions should notably decrease NR-PM_1 pollution events. Note that these recommendations are only formulated in the perspective of reducing PM levels, assuming a subsequent reduction of PM impacts. Additional dimensions - e.g. specific impacts of each chemical component, short versus long-term exposure, co-benefit of sanitary and climatic impacts - should also be considered when defining PM abatement strategies. In a broader context, the use of high time resolution analytical techniques for the measurement of PM pollution properties can help better shape our future air quality policies.

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Tables and Figures

Table 1. Consistency of ACSM measurements: comparison between ACSM and independent analytical techniques using orthogonal regression analyses. Slopes and intercepts are indicated ± uncertainties.

	r^2					slope					intercept				
	Sp	Su	Au	Wi	An	Sp	Su	Au	Wi	An	Sp	Su	Au	Wi	An
Org vs OC	0.91	0.90	0.86	0.92	0.77	2.18 ± 0.07	2.92 ± 0.10	1.87 ± 0.09	1.26 ± 0.04	1.72 ± 0.04	-0.29 ± 0.37	-1.07 ± 0.32	-0.28 ± 0.36	0.74 ± 0.37	0.61 ± 0.25
Nitrate	0.95	0.53	0.96	0.92	0.91	1.37 ± 0.03	4.27 ± 0.25	1.28 ± 0.03	0.86 ± 0.03	1.28 ± 0.02	0.42 ± 0.18	0.64 ± 0.11	0.48 ± 0.10	0.62 ± 0.11	0.48 ± 0.09
Sulfate	0.96	0.97	0.92	0.86	0.95	1.05 ± 0.02	0.98 ± 0.02	0.96 ± 0.04	1.38 ± 0.06	1.00 ± 0.01	-0.01 ± 0.04	0.02 ± 0.06	0.04 ± 0.07	-0.25 ± 0.06	0.00 ± 0.03
Ammonium	0.92	0.70	0.91	0.95	0.90	1.03 ± 0.03	1.00 ± 0.06	0.93 ± 0.04	0.81 ± 0.02	0.99 ± 0.02	-0.04 ± 0.07	-0.04 ± 0.07	-0.12 ± 0.05	0.03 ± 0.03	-0.08 ± 0.03
Chloride	0.75	0.00	0.59	0.78	0.52	2.68 ± 0.13	-0.13 ± 0.09	0.68 ± 0.06	1.13 ± 0.07	1.75 ± 0.06	0.04 ± 0.01	0.03 ± 0.00	0.04 ± 0.00	-0.02 ± 0.01	0.02 ± 0.01
Mass vs volume	0.87	0.82	0.88	0.85	0.81	1.91 ± 0.01	1.95 ± 0.02	1.45 ± 0.01	1.34 ± 0.01	1.63 ± 0.01	-1.16 ± 0.19	-1.36 ± 0.18	-2.45 ± 0.19	-0.11 ± 0.20	-1.09 ± 0.11

Legend: Sp: spring (March-April-May), Su: summer (June-July-August), Au: autumn (September-October-November), Wi: winter (December-January-February), An: annual. Independent analytical techniques refer to i) EC-OC Sunset Analyzer for OC from $PM_{2.5}$ sampling, ii) Ion Chromatography for ions from $PM_{2.5}$ sampling and iii) DMPS for volume concentrations (see Sect. 2.3 for more details). Mass refers to NR-PM_1+BC. Intercepts are in $\mu g/m^3$. Slopes are in g/cm^3 for mass vs volume and dimensionless otherwise.

1071 Table 2. Comparison (coefficient of determination, r^2) between SA factors, organic *m/z* tracers and independent species time series. BC stands

1072 for Black Carbon; Org_i stands for organic signal at *m/z* i (i=43, 44, 60, 67, 73, 81).

1073

	HOA					BBOA					OOA				
	Org_67	Org_81	NOx	CO	BC	Org_60	Org_73	NOx	CO	BC	Org_43	Org_44	NH4	SO4	NO3
SPRING	0.60	0.55	0.03	0.08	0.28	0.99	0.97	0.32	0.81	0.70	0.88	0.94	0.76	0.43	0.77
SUMMER	0.90	0.91	0.07	0.40	0.52			-			0.97	0.94	0.54	0.60	0.19
AUTUMN	0.63	0.61	0.07	0.10	0.24	0.99	0.97	0.06	0.68	0.47	0.82	0.92	0.47	0.53	0.38
WINTER	0.58	0.57	0.34	0.33	0.39	0.98	0.97	0.20	0.66	0.63	0.80	0.99	0.50	0.39	0.66

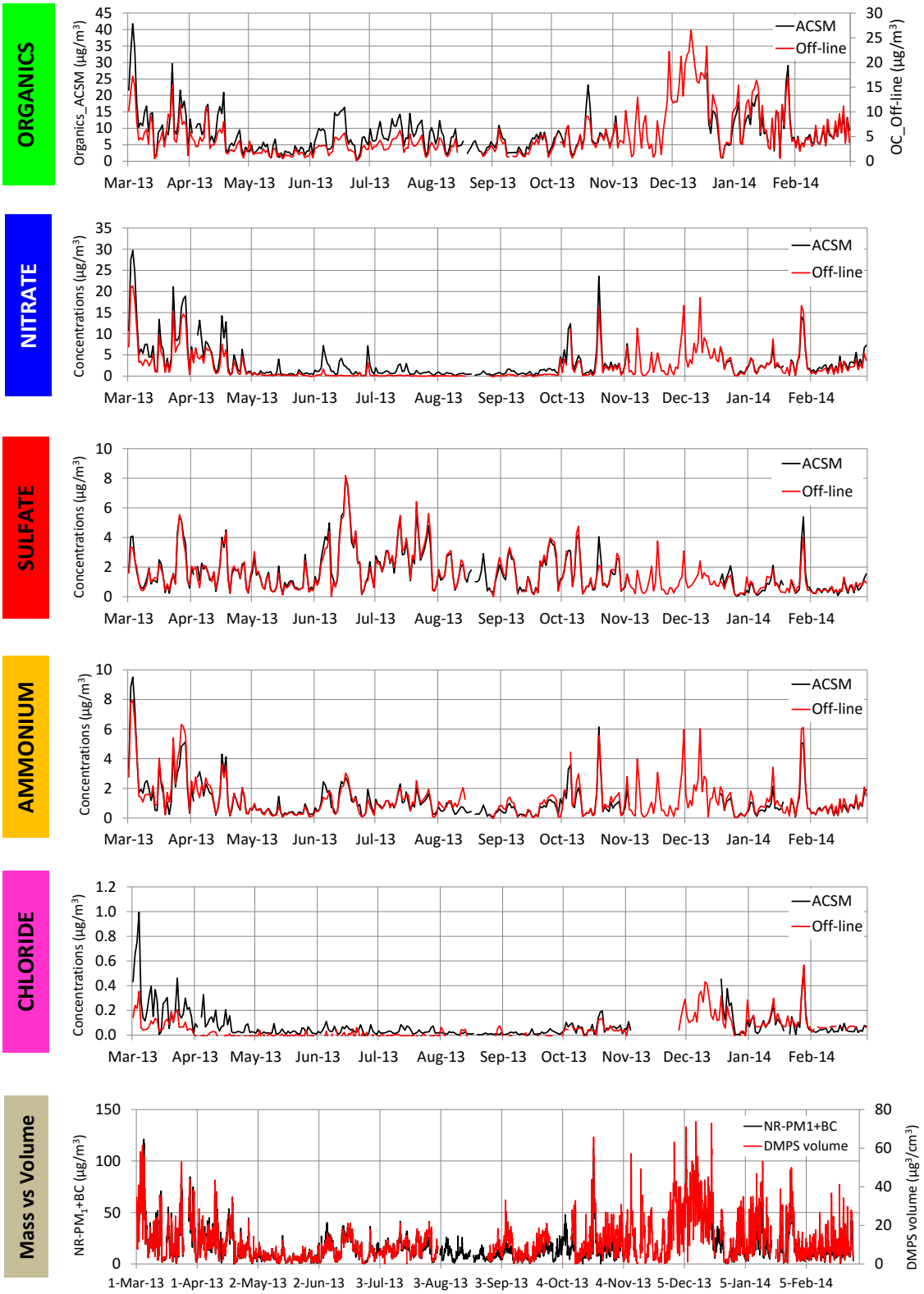


Figure 1. Comparison between measurements performed with the ACSM and other co-located analytical techniques. See Table 1 and Sect. 2.3 for more details.

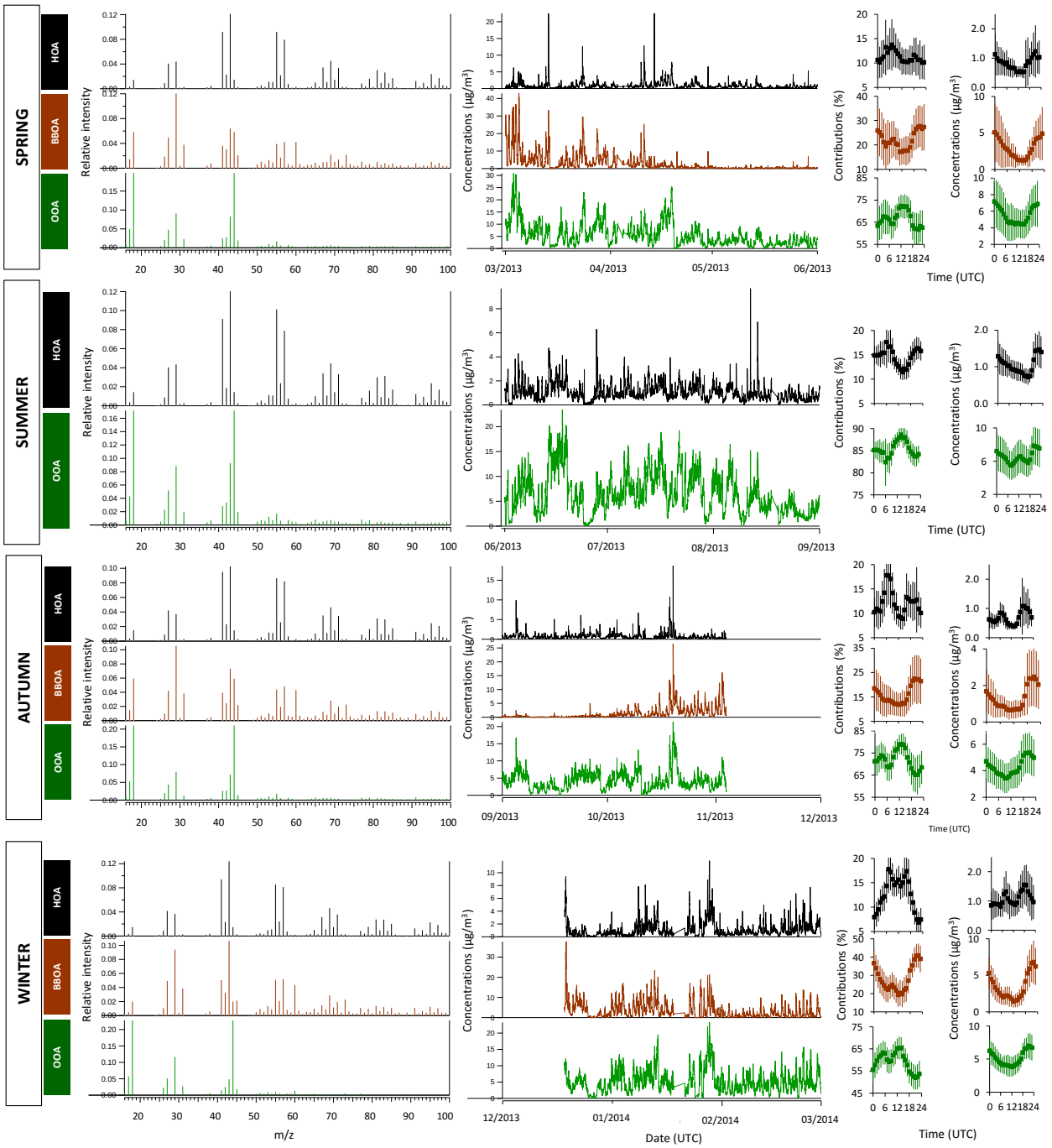


Figure 2. Organic source apportionment presented by season: factor profiles (left), time series (middle) and daily cycles (right, error bars represent 1 standard deviation). Seasons are defined as Spring: MAM, Summer: JJA, Autumn: SON and Winter: DJF.

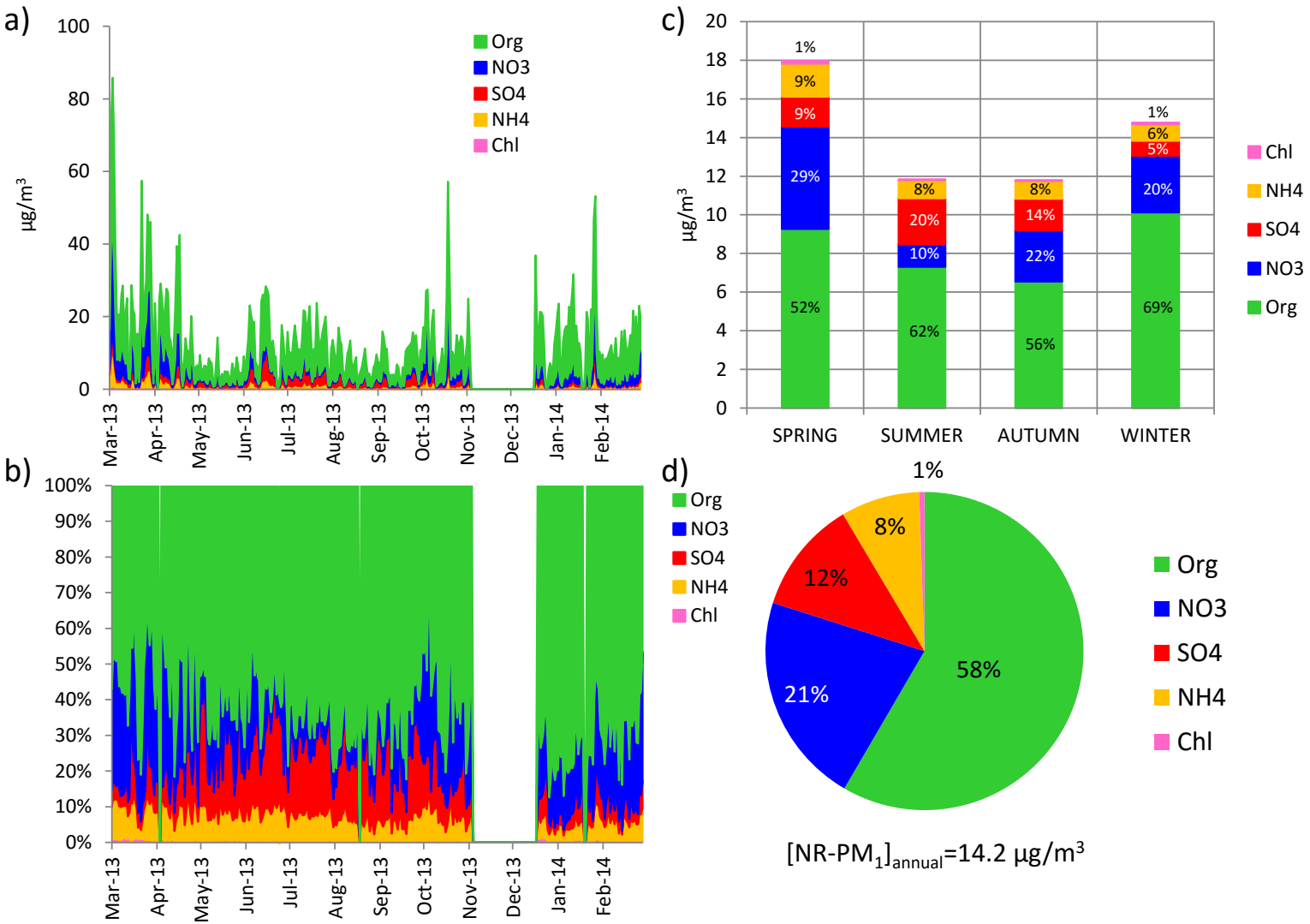


Figure 3. Overview of the chemical composition of NR-PM_1 at Ispra (Po Valley, Italy): daily absolute (a) and relative (b) chemical composition; seasonal (c) and annual (d) averages.

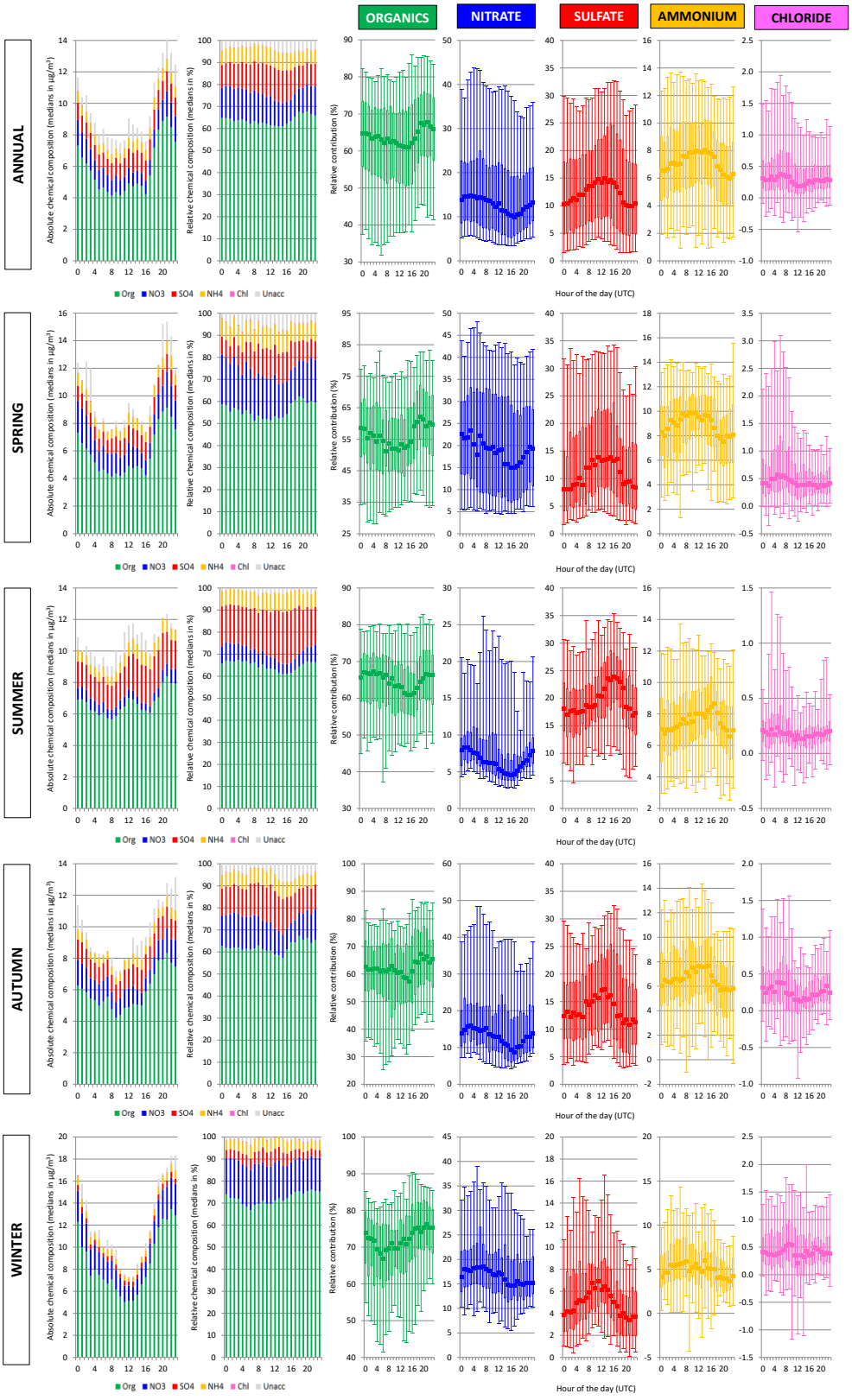
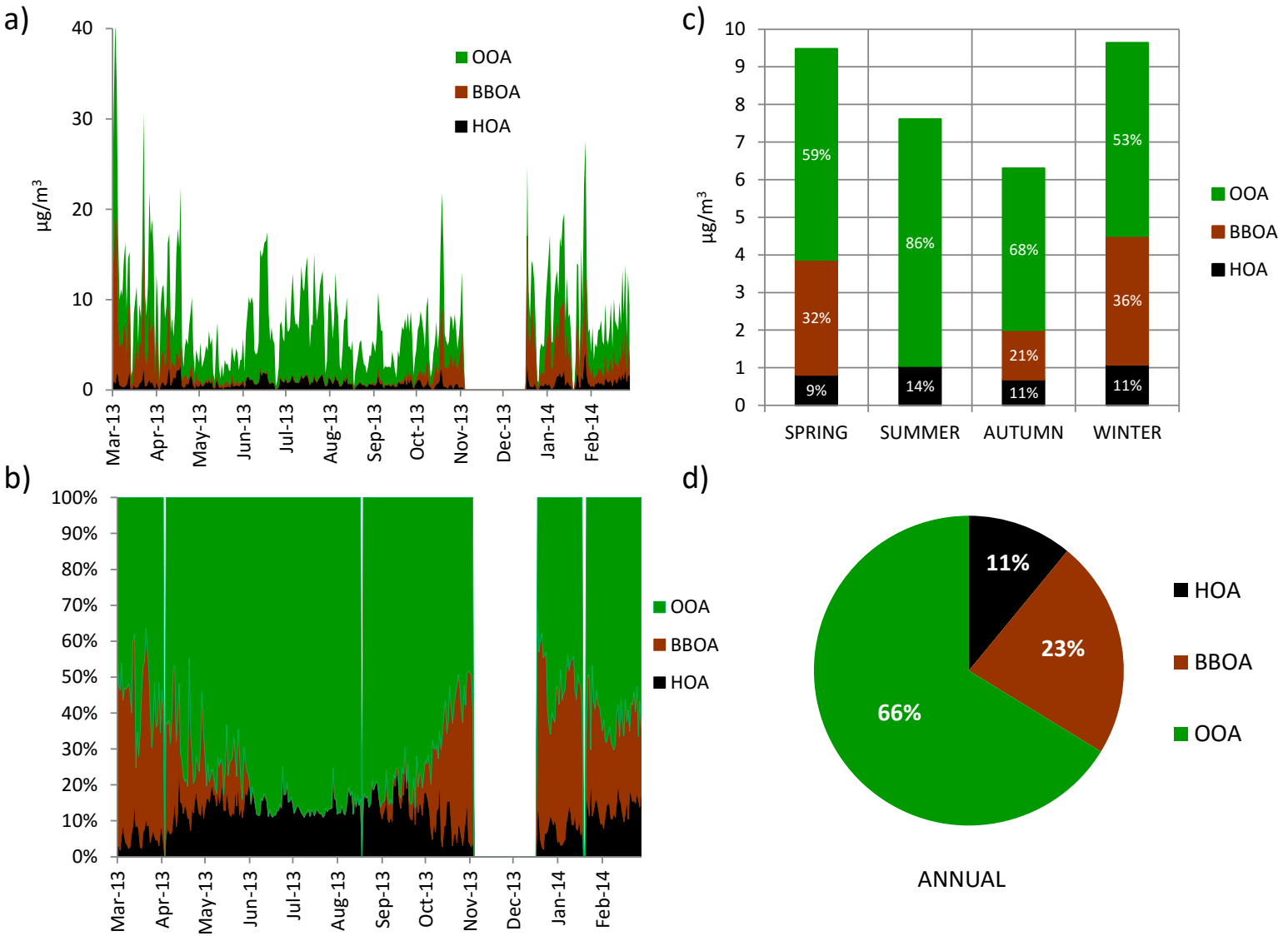
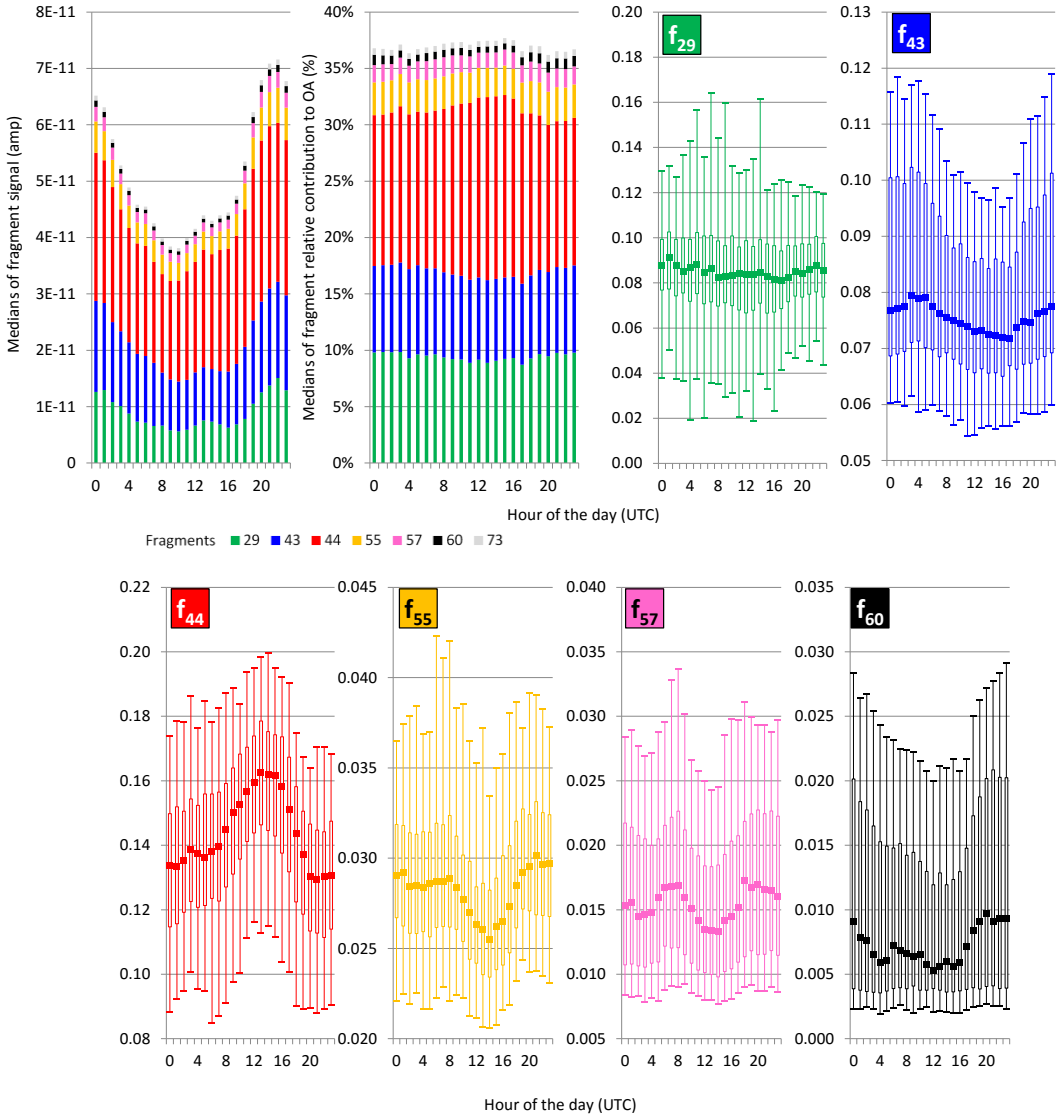


Figure 4. Daily cycles of NR-PM_1 chemical composition on the annual and seasonal scales. Unacc: unaccounted mass, whisker plots are constructed from the 5th, 25th, 50th, 75th and 95th percentiles.



1087

1088 Figure 5. Overview of HOA, BBOA and OOA contributions to organic aerosols; see legend Figure 3.



1089

1090 Figure 6. Annual statistics describing the daily cycles of the major organic fragments. Box plots are constructed from the 5th, 25th, 50th, 75th and

1091 95th percentiles.

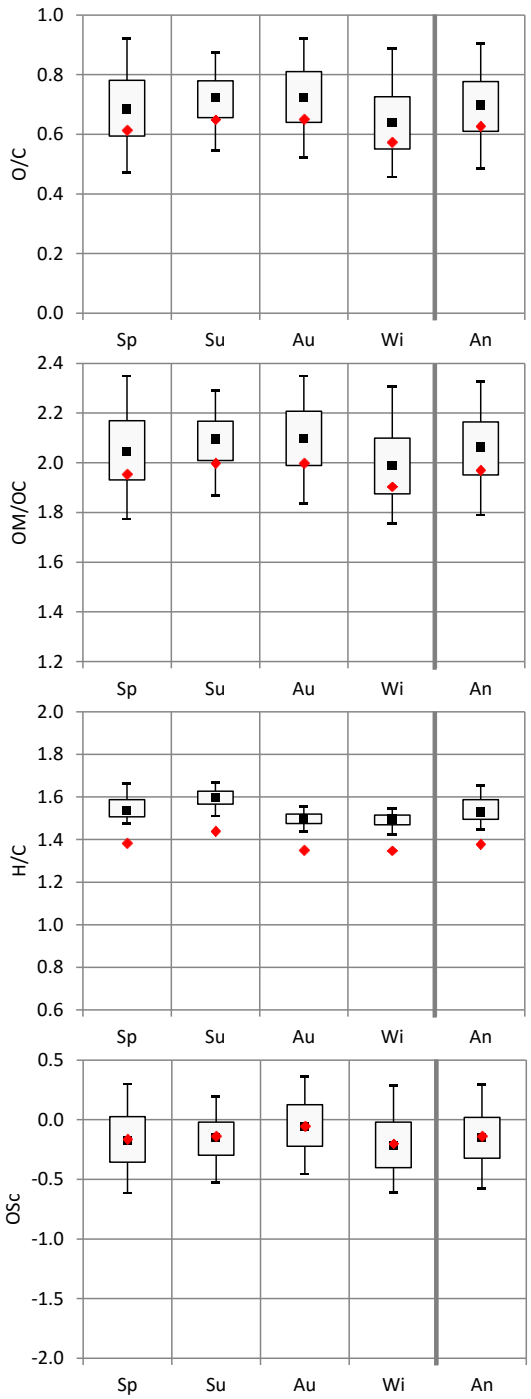
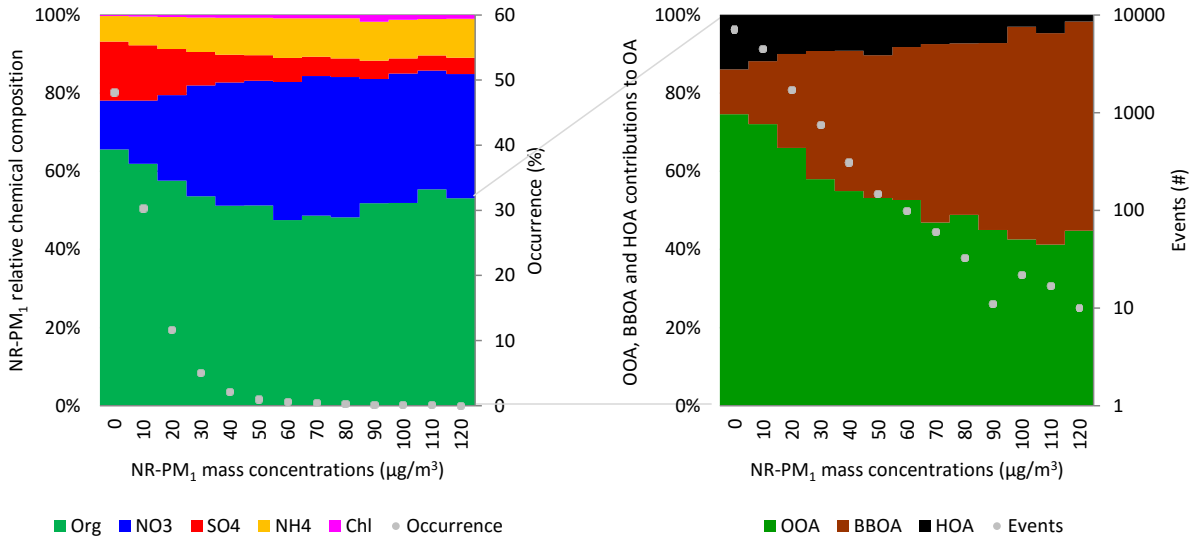


Figure 7. Seasonal and annual O/C, OM/OC, H/C and OSc of ambient OA. Sp: spring (MAM), Su: summer (JJA), Au: autumn (SON), Wi: winter (DJF), An: annual. Black: 5th, 25th, 50th, 75th and 95th percentiles estimates following Canagaratna et al. (2015); red: median estimates following Aiken et al. (2008) for O/C and OM/C, Ng et al. (2011b) for H/C and Aiken et al. (2008), Kroll et al. (2011) and Ng et al. (2011b) for OSc. Note that the authors do not recommend comparing absolute O/C, OM/OC and OSc values reported here with other AMS studies, given the uncertainties associated with f_{44} quantifications from ACSM measurements (please see text).



1100

1101 Figure 8. NR-PM_1 relative chemical composition (left) and OA factor contributions (right) averages as a
1102 function of NR-PM_1 mass concentrations (bins of 10 µg/m^3). Occurrence (%, left) and number of
1103 pollution events (#, right) are indicated (solid dots) for each NR-PM_1 bin. Note that one event
1104 corresponds to one 30 minute average.