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## Seasonal characterization of submicron aerosol chemical composition and organic aerosol sources in the southeastern United States: Atlanta, Georgia and Look Rock, Tennessee

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## Abstract

A yearlong near-real-time characterization of non-refractory submicron aerosol (NR- $PM_1$ ) was conducted at an urban (Atlanta, Georgia) and rural (Look Rock, Tennessee) site in the southeastern US using the Aerodyne aerosol chemical speciation monitor

- <sup>5</sup> (ACSM) collocated with established air-monitoring network measurements. Seasonal variations in organic aerosol (OA) and inorganic aerosol species are attributed to meteorological conditions as well as anthropogenic and biogenic emissions in this region. The highest concentrations of NR-PM<sub>1</sub> were observed during winter and fall seasons at the urban site and during spring and summer at the rural site. Across all seasons and at
- <sup>10</sup> both sites, NR-PM<sub>1</sub> was composed largely of OA (50–76%) and inorganic sulfate (12– 31%). Six distinct OA sources were resolved by positive matrix factorization applied to the ACSM organic mass spectral data collected from the two sites over the one year of near-continuous measurements at each site: hydrocarbon-like OA (HOA), biomass burning OA (BBOA), semi-volatile oxygenated OA (SV-OOA), low-volatility oxygenated
- OA (OOA), isoprene-derived epoxydiol (IEPOX) OA (IEPOX-OA), and 91Fac OA (a factor dominated by a distinct ion at *m/z* 91 fragment ion previously observed in biogenic influenced areas). LV-OOA was observed throughout the year at both sites and contributed 30–66 % of total OA mass. HOA was also observed during the entire year only at the urban site (15–24 % of OA mass). BBOA (15–33 % of OA mass) was observed
- <sup>20</sup> during winter and fall, likely dominated by local residential wood burning emission. Although SV-OOA contributes quite significantly (~ 27%), it was observed only at the urban site during colder seasons. IEPOX-OA was a major component (27–41%) of OA at both sites, particularly in spring and summer. An ion fragment at m/z 75 is proposed as an additional marker for IEPOX-OA, as it is shown to correlate well with the
- m/z 82 ion shown to be associated with the aerosol mass spectrum of IEPOX-derived secondary organic aerosol (SOA). The contribution of 91Fac to the total OA mass was quite low at the urban site (~ 9%), but was significant (21–23%) at the rural site during warmer months. Comparison of 91Fac OA time series with SOA tracers measured from



filter samples collected at Look Rock suggests that isoprene oxidation through a pathway other than IEPOX SOA chemistry may contribute to its formation. Other biogenic sources could also contribute to 91Fac, but there remains a need to resolve the exact source of this factor based on its significant contribution to rural OA mass.

#### 5 1 Introduction

Characterization of the chemical composition of atmospheric fine aerosol is important, because of its adverse human health effects (Pope III and Dockery, 2006) and possible impacts on the Earth's climate system (Forster et al., 2007). Aerosol with aerodynamic diameters ≤ 1 µm (PM<sub>1</sub>) play a significant role in scattering and/or absorbing solar radiation as well as cloud formation (IPCC, 2013). Long-term regional characterizations of ambient PM<sub>1</sub> is required to understand their sources, formation, and aging mechanisms, as well as their atmospheric lifetimes. This information will lead to more accurately constrained air quality models for making regulatory decisions to mitigate the potential adverse impacts of PM<sub>1</sub>.

Over the past decade, online aerosol mass spectrometry (AMS) has been used to extensively characterize ambient non-refractory (NR)-PM<sub>1</sub> (Zhang et al., 2007; Jimenez et al., 2009; Ng et al., 2010; Crippa et al., 2014); however, prior studies were limited by short measurement periods (weeks to a several months) because the need for intensive instrument maintenance required the continuous on-site presence of skilled

- <sup>20</sup> personnel in order to generate high quality data. The Aerodyne aerosol chemical speciation monitor (ACSM) based on the AMS technology has been modified to allow for long-term operation with less maintenance (Ng et al., 2011b). The ACSM has been recently used for long-term NR-PM<sub>1</sub> measurements (Petit et al., 2015; Ripoll et al., 2015; Parworth et al., 2015; Zhang et al., 2015) and shown to be durable and comparable to data collected from existing fine personal monitoring networks (Pudiculisticrini et al.)
- to data collected from existing fine aerosol monitoring networks (Budisulistiorini et al., 2014).



Worldwide studies have shown that tropospheric PM<sub>1</sub> mass is dominated by organic aerosol (OA) (Zhang et al., 2007; Jimenez et al., 2009). While inorganic aerosol constituents, such as sulfate and nitrate, are largely anthropogenic in origin, both anthropogenic and biogenic sources can contribute to OA. OA consists of aerosol di-<sup>5</sup> rectly emitted into the atmosphere, primary organic aerosol (POA), and aerosol formed from atmospheric oxidation of volatile organic compounds (VOCs), secondary organic aerosol (SOA). POA sources include fossil fuel combustion from vehicles, power generation, and residential burning (cooking and heating) as well as forest fires (Kanakidou et al., 2005). Although POA contributions to urban OA mass may be significant during morning traffic, SOA exceeds POA, especially at midday or in the afternoon. SOA has

<sup>10</sup> morning traffic, SOA exceeds POA, especially at midday or in the afternoon. SOA has been observed to contribute upwards of 90 % to the total OA mass (Docherty et al., 2008), indicating the critical role of photochemical processes in SOA formation.

Anthropogenic emissions are the predominant sources of ambient aerosol in urban areas, whereas a regional component that is comprised of a combination of anthro-

- pogenic and biogenic contributions can also be significant, especially urban areas surrounded by dense forests, such as Atlanta, Georgia (GA). Studies in Atlanta characterizing the chemical components of ambient aerosol collected during different seasons (Lee et al., 2002; Kim et al., 2003; Butler et al., 2003); however, they were limited by low-time or -mass resolution. A recent study reported that non-fossil carbon derived
- from modern sources (e.g., biogenic) accounts for 50 % of carbon at two urban sites and 70–100 % of carbon at 10 near-urban or remote sites in the US (Schichtel et al., 2008). Additionally, isoprene-derived SOA has been recently observed to contribute substantially to SOA in downtown Atlanta during summer (Budisulistiorini et al., 2013; Xu et al., 2015). The isoprene-derived SOA was attributed to the heterogeneous chem-
- istry of isomeric isoprene epoxydiols (IEPOX), known oxidation products of isoprene under both low- (Paulot et al., 2009) and high-NO (Jacobs et al., 2014) conditions, in the presence of acidic sulfate aerosol (Budisulistiorini et al., 2013).

Biogenic hydrocarbons and their oxidation products are major contributors to ambient fine aerosol in rural areas where anthropogenic sources are absent (Budisulistiorini



et al., 2015). In summer 2001, the fraction of non-fossil carbon was reported to vary from 66–80% of total carbon at Look Rock (LRK), Great Smoky Mountains National Park (GSMNP), TN, indicating the likely importance of photochemical oxidation of biogenic VOCs (BVOCs) (Tanner et al., 2004a). Sulfate did not show significant diurnal variability at LRK, TN, suggesting that local meteorological conditions are minimally influential in determining concentrations of long-lived species (Tanner et al., 2005). Moreover, OC at this location is the primary component of SOA in summer, while POA

from wood burning can contribute significantly during fall (Ke et al., 2007).
 Because previous studies on detailed OA composition in the southeastern US are
 limited by low-time resolution, we undertook a two-year study comparing near-real-time chemical characterizations of NR-PM<sub>1</sub> collected for one-year at the urban Jefferson Street (JST) site in downtown Atlanta, GA and a subsequent year at the rural LRK site located in the GSMNP, TN. NR-PM<sub>1</sub> was sampled, chemically characterized and quantified over a two-year period spanning 2012–2013 using the ACSM. OA sources
 were seasonally analyzed by positive matrix factorization (PMF). OA factors resolved by PMF were compared with collocated data collected from both air-monitoring sites in order to associate them with specific types of OA sources.

#### 2 Methods

## 2.1 Fine aerosol sampling and data analysis

- Real-time continuous chemical measurements were conducted during 2012–2013 at a downtown urban site (JST) in Atlanta, GA, and at a rural/forested site (LRK) in GSMNP, TN, respectively. Detailed descriptions of both sites have been published (Budisulistiorini et al., 2013, 2015). Briefly, the JST site is one of several research sites of the Southeastern Aerosol Research and Characterization (SEARCH) network.
- The JST site is located in a mixed industrial-residential area about 4.2 km northwest of downtown Atlanta and within approximately 200 m of a bus maintenance yard and



several warehouse facilities to the south and southwest (Hansen et al., 2003; Solomon et al., 2003). Decreases of sulfate and non-methane organic carbon (NMOC) have been observed from 1999–2013 at SEARCH network sites (including JST) (Hidy et al., 2014). The LRK site is located on a ridge-top on the northwestern edge of the GSMNP downwind of urban areas, such as Knoxville and Maryville, TN, and small farms with animal grazing areas. In summer, up-slope flow carries pollutants emitted in the valley during early morning to the LRK site by mid-morning, and in the evening down-slope flow accompanies a shift of wind direction to the south and east that could isolate the site from fresh primary emissions from the valley and allows aged secondary species to accumulate (Tanner et al., 2005). Decreases of PM<sub>2.5</sub> mass from 1999–2013 at LRK

to accumulate (Tanner et al., 2005). Decreases of PM<sub>2.5</sub> mass from 1999–2013 at LR was attributed to decline in sulfate and OC concentrations (Tanner et al., 2015).

Ambient NR-PM<sub>1</sub> was analyzed using the Aerodyne ACSM in a similar manner at both sites. Details of NR-PM<sub>1</sub> sampling at the JST and LRK sites have been described in Budisulistiorini et al. (2013, 2015). Briefly, the ACSM was operated with a sampling flow rate of 21 min<sup>-1</sup> resulting in a regidence time of (200 for PM) in the compliance time of (200 for PM).

- <sup>15</sup> flow rate of  $3 \text{Lmin}^{-1}$ , resulting in a residence time of < 2 s for  $\text{PM}_{2.5}$  in the sampling line. The aerodynamic lens mounted on the ACSM inlet continuously samples  $\text{PM}_1$ from the bypass  $\text{PM}_{2.5}$  sampling line (Ng et al., 2011b). Particle-laden air was dried using a 50-tube Nafion dryer (Perma Pure PD-50T-24SS) in which a dry air delivered a  $7 \text{Lmin}^{-1}$  of sheath of dry air to keep the sample air relative humidity (RH) well be-
- <sup>20</sup> low 10 %, preventing condensation within the sampling line that could adversely affect the collection efficiency (CE) of PM<sub>1</sub> and clog the ACSM sampling inlet. The ACSM was tuned for ionizer and electronic offset and calibrated for ionization efficiency on site periodically every season throughout each year of sampling. Mass calculation of aerosol constituents is described in detail elsewhere (Ng et al., 2011b). At both sites,
- a CE value of 0.5 for all species was used based on evaluation of composition dependent CE as described in Budisulistiorini et al. (2013, 2015). Correlations of combined aerosol mass concentrations of ACSM NR-PM<sub>1</sub> and collocated elemental carbon (EC; Sunset Labs) at JST and black carbon (BC; Magee Sci. Model AE 21 Aethalometer) at LRK, with aerosol volume concentrations of PM<sub>1</sub> measured by the Scanning Elec-



trical Mobility System-Mixing Condensation Particle Counter (SEMS-MCPC, Brechtel Manufacturing Inc.) were strong ( $r^2 > 0.8$ ), suggesting an aerosol density of 1.75 at JST (Budisulistiorini et al., 2014) and 1.52 g cm<sup>-3</sup> at LRK (Budisulistiorini et al., 2015) during summer, and a density of 1.46 g cm<sup>-3</sup> (Fig. S1 in the Supplement) during winter at LRK. Operational issues, prevented measurements by the SEMS-MCPC during other seasons at both the JST and LRK sites. Therefore, we estimated dry density of ambient PM<sub>1</sub> based on average particle composition for each season, and the assumption of organic, inorganic, and EC densities are 1.2, 1.77 (Turpin and Lim, 2001), and 1.77 g cm<sup>-3</sup> (Park et al., 2004), respectively. The estimated dry aerosol densities at both the JST and LRK sites are provided in Table S3. Estimated values for winter and summer at the LRK site and summer at the JST site were close to measured values (within 10–20%). Therefore, we applied a CE value of 0.5 on all seasonal datasets. If a CE of 1 is used, the estimated aerosol density is < 1 g cm<sup>-3</sup>, which is much lower than the suggested bulk organic and inorganic aerosol densities of 1.27 and 1.77 g cm<sup>-3</sup>, re-

<sup>15</sup> spectively (Cross et al., 2007).

#### 2.2 Organic aerosol characterization by PMF

Details of PMF analysis of the organic mass fraction have been described previously (Lanz et al., 2007; Ulbrich et al., 2009; Zhang, 2011). The PMF2 algorithm (Paatero and Tapper, 1994) was used in robust mode via PMF Evaluation Tool panel (PET v2.04) using the methods outlined in Ulbrich et al. (2009) and Zhang et al. (2011). Only the

- using the methods outlined in Ulbrich et al. (2009) and Zhang et al. (2011). Only the mass range m/z 12–120 was utilized for PMF because no organic fragment ions are possible at m/z < 12 and low transmission efficiency for ions with m/z > 120 (Ng et al., 2011b), which results in low signal-to-noise ratios as well as possible interferences from naphthalene at m/z 128 signal.
- PMF analysis was performed separately for winter, spring, summer and fall seasons at both the JST and LRK sites. Solutions were chosen based on the quality of PMF fits as well as interpretability when compared to reference mass spectra (Ng et al., 2011a; Robinson et al., 2011) and independent gas- and particle-phase measurements



(Budisulistiorini et al., 2013, 2015). For each analysis, uncertainty of selected factor solutions was investigated with different seeds (SEED parameter varied from 0 to 100, in steps of 5), FPEAK parameters, and 100 bootstrapping runs. Correlations of PMF factors with external tracers and reference mass spectra are provided in Tables S1 and
 S2, and PMF factors diagnostics are provided in Figs. S2–S9.

## 2.3 Estimation of aerosol acidity by ISORROPIA

The thermodynamic model, ISORROPIA-II (Fountoukis and Nenes, 2007; Nenes et al., 1999), was used to estimate aerosol pH. Inputs for the model include aerosol-phase sulfate, nitrate, and ammonium as µmolm<sup>-3</sup>, measured by the ACSM under ambient
 conditions. In addition, RH and temperature obtained from the SEARCH network and the National Park Service (NPS) for JST and LRK sites, respectively, were used as inputs. Inputs of ammonia for the JST site were obtained from SEARCH and for LRK site, from the Ammonia Monitoring Network (AMoN; TN01/Great Smoky Mountains National Park – Look Rock). ISORROPIA-II predicted particle hydronium ion concentration per volume of air (H<sup>+</sup>, µgm<sup>-3</sup>) and aerosol liquid water content (LWC, mol L<sup>-1</sup>). Calculation of aerosol pH follows that of Eq. (4) in Budisulistiorini et al. (2015).

#### 3 Results and discussion

## 3.1 Seasonal submicron aerosol chemical composition, pH, and LWC

Seasonally averaged NR-PM<sub>1</sub> was typically higher at JST compared to LRK, espe cially during colder seasons (fall and winter) when anthropogenic primary emissions are higher; however, during warmer seasons (spring and summer) the average NR-PM<sub>1</sub> concentrations were similar at both sites (Fig. 1; Table 1). The highest average seasonal concentration of urban NR-PM<sub>1</sub> was observed during the fall, whereas the summer season yielded the highest average NR-PM<sub>1</sub> concentration at the rural site.
 Interestingly, these patterns correspond to OA and sulfate seasonal trends, suggesting



the important roles of these species to total  $NR-PM_1$  mass at urban and rural sites across the southeastern US.

At the LRK site, average OA loadings increased from spring (~ 3.2 μgm<sup>-3</sup>) to summer (~ 5.3 μgm<sup>-3</sup>), and then decreased in fall (~ 2.8 μgm<sup>-3</sup>), which is likely related
to BVOC emissions that depend on leaf surface area, solar radiation, and ambient temperature (Guenther et al., 2006). A different pattern was observed at the urban site, where average OA loadings were highest during the fall (8.2 μgm<sup>-3</sup>) and winter (7.2 μgm<sup>-3</sup>) seasons, suggesting contributions from biomass burning-related OA and non-biogenic sources. Generally, average % OA contributions to NR-PM<sub>1</sub> were higher in spring and summer at both urban and rural sites, implying the role of biogenic SOA formation increased during these periods. Contributions of POA and SOA are further discussed in Sect. 3.2 below.

Average sulfate concentrations were highest in summer for LRK and fall for JST, respectively, which may contribute to enhanced SOA formation (Y.-H. Lin et al., 2013; Xu

- et al., 2015; Budisulistiorini et al., 2015). Changes of sulfate concentrations at LRK are suggested to mainly affected by changes in SO<sub>2</sub> emission that occur nearby and/or further upwind (Tanner et al., 2015). At JST, SO<sub>2</sub> emissions from nearby coal-fired power plants could contribute to sulfate seed aerosol to provide a surface for heterogeneous acid-catalyzed reactions leading to enhancement of SOA. The average ammonium and
- nitrate contribution to seasonal average NR-PM<sub>1</sub> loadings is small compared to those of OA and sulfate. Both species showed similar trends at the urban site, where they were highest during colder seasons (i.e., winter and fall), while showing no significant fluctuations during the duration of the study at LRK. This observation is consistent with previous studies (Tanner et al., 2004b; Olszyna et al., 2005) reporting that average con-
- <sup>25</sup> tributions of ammonium and nitrate are not significant for rural PM<sub>1</sub>. Average chloride loadings were low (<  $0.1 \,\mu g m^{-3}$ ), indicating that chloride is not a significant contributor to inorganic aerosol mass in this region. The increasing average contributions from the sum of sulfate, ammonium, and nitrate in winter and fall at JST suggests the important



role of inorganics in NR-PM<sub>1</sub>, in accord with observation in other major urban areas (Y. Sun et al., 2011; Petit et al., 2015).

The lowest seasonal average pH were observed in summer (1.45) for JST and in fall (1.53) for LRK, as illustrated in Fig. 1. On the other hand, the highest seasonal <sup>5</sup> average pH were 2.01 for JST and 1.81 for LRK which were observed during winter. Overall, seasonal aerosol pH is 1.5-2.0 at both sites indicates that NR-PM<sub>1</sub> in the southeastern US is acidic year round, which is consistent with a recent study by Guo et al. (2015). Figure 1 shows that no direct correlation exists between aerosol pH and OA. However, this does not necessarily rule out the potential role of aerosol acidity in enhancing SOA formation in light of laboratory studies demonstrating a significant pH effect (Gao et al., 2004; Surratt et al., 2007; Y. Lin et al., 2013). Uncertainty of aerosol acidity estimation by ISORROPIA-II by omission of organic sulfate as input (Lin et al., 2014) could lead to under-prediction of aerosol acidity and the observed lack of correlation with OA. Seasonal averages of LWC were highest during summer at both JST (33.97 mol L<sup>-1</sup> of aerosol) and LRK (38.17 mol L<sup>-1</sup>) sites. It should be noted that 15 the possible LWC contributions from OA are not included because a technique, such as that recently used by Guo et al. (2015) to measure this quantity is lacking at our sites.

Studies have suggested that reactive uptake decreases with enhanced RH (Nguyen et al., 2014; Gaston et al., 2014); however, some isoprene-derived SOA tracers were elevated by high RH (Zhang et al., 2011). Although organic water fraction in total LWC was found to be significant by Guo et al. (2015); pH prediction using ISORROPIA-II based on inorganic ions alone was found to give a reasonable estimate. Hence, the lack of correlation in this study between OA and LWC based only on inorganic water



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#### 3.2 Seasonal OA characterizations

#### 3.2.1 Winter

Seasonal mass spectra and time series of OA factors resolved from PMF analysis at both JST and LRK sites are depicted in Figs. 2a and 3a, respectively. PMF analysis of winter OA yielded a four-factor solution at JST and a two-factor solution at LRK. Hydrocarbon-like OA (HOA), biomass-burning OA (BBOA), semi-volatile oxygenated OA (SV-OOA), and low-volatility oxygenated OA (LV-OOA) factors (Ng et al., 2011a) were resolved from the JST dataset, whereas only the BBOA and LV-OOA factors were resolved from the LRK dataset. The temporal variation of the HOA factor correlates well ( $r^2 > 0.7$ ) with black carbon (BC), carbon monoxide (CO), and reactive nitrogen species (NO<sub>y</sub>) (Tables S1). Moreover, its diurnal variation (Fig. 4b) showed a morning peak, consistent with an expected contribution from vehicular emissions (Zhang et al., 2007).

The BBOA factor concentration increased during the night and decreased during the day (Fig. 4a), which could be related to residential and non-residential wood burning as well as planetary boundary layer (PBL) dynamics. BBOA at the LRK site also showed a large nighttime peak with a gradual decrease during the day. The large peak appears to result from a short period of intense biomass burning that occurred in 15– 18 March 2013. Since a source for this event could not be identified, we do not report it specifically in this study. The time series of BBOA showed moderate correlation ( $r^2 = 0.2-0.5$ ; Tables S1 and S2) with BC, suggesting that it is likely influenced by some local sources (e.g., fires). BBOA mass spectra from JST and LRK were highly correlated ( $r^2 \sim 0.7$ ), indicating similarity of the sources. Comparisons of the BBOA mass spectra with reference mass spectra showed correlation with other OOA factors (Ta-

<sup>25</sup> bles S1 and S2), a known caveat in resolution of BBOA based on unit mass resolution (UMR) data such as that from ACSM measurements (Wood et al., 2010). The similarity of BBOA and OOA factors mass spectra could indicate aged BBOA factor, which was observed to have enhanced signals at m/z 18, 29 and 44 ions and low signals at m/z



60 and 73 ions (Bougiatioti et al., 2014). However, the BBOA factor observed at JST and LRK displayed enhanced signal at m/z 44 ion but retained signals at m/z 60 and 73 ions, suggesting that it was not as oxidized as the aged BBOA factor.

- LV-OOA is characterized by high fraction of total ion intensity at m/z 44 ( $f_{44}$ ) resulting from high oxygen content (Ng et al., 2011a) and is the most abundant OA type at both JST and LRK (Table 1). Maxima around midnight at JST and in the mid-afternoon at LRK (Fig. 4b) were not significant, indicating that LV-OOA concentration is relatively constant throughout the day in this region. LV-OOA has been shown to correlate with non-volatile secondary species (Jimenez et al., 2009). Lack of temporal correlation between LV-OOA and sulfate has been observed to depend on oxidation degree of
- urban ambient aerosol (Y. L. Sun et al., 2011). We observed weak correlations ( $r^2 < 0.2$ ) between LV-OOA and sulfate at both sites. Ratio of organic-to-sulfate ratio was used to track photochemical aging of biogenic SOA (Henry and Donahue, 2012). Large variability of LV-OOA : sulfate ratio (Fig. S10) at LRK and JST could indicate gradual
- <sup>15</sup> photochemical aging process in winter. This might cause lack of correlation with sulfate, as previously seen in New York City (Y. L. Sun et al., 2011). On the other hand, the mass spectral comparison of LV-OOA from both sites were strongly correlated ( $r^2 \sim 1$ ; Fig. S11), possibly suggesting similar sources of LV-OOA at these sites.

SV-OOA, which was observed only in urban OA, is the most abundant OA. An  $f_{44}$  smaller than that of LV-OOA indicates the factor is less oxidized and thus semivolatile (Ng et al., 2011a). The temporal variation of SV-OOA was moderately correlated ( $r^2 \sim 0.4$ ) with nitrate (Fig. 3; Table S1) while the mass spectrum was well correlated with previously resolved 82Fac and IEPOX-OA factors (82Fac and IEPOX-OA are equivalent and are characterized by a distinct ion at m/z 82) (Robinson et al., 2011;

<sup>25</sup> Budisulistiorini et al., 2013, 2015). However, low isoprene emissions during winter do not support the association of the SV-OOA factor is associated with IEPOX-derived SOA. The diurnal profile of SV-OOA showed an increase in the evening and decrease in the morning, similar to the BBOA profile and HOA factors. This variability suggests an influence of nitrate-radical chemistry on nighttime SOA formation (Xu et al., 2015).



It is noted here that we acknowledge the potential role of diurnal PBL dynamics or loss processes (e.g. deposition) in contributing to diurnal patterns observed here for the PMF factors.

## 3.2.2 Spring

- <sup>5</sup> PMF analysis of spring OA resulted in a four-factor solution (i.e., HOA, LV-OOA, 91Fac, and IEPOX-OA) for the JST site and a three-factor solution (i.e., LV-OOA, 91Fac, and IEPOX-OA) for the LRK site (Fig. 2b). The average concentration of HOA in Atlanta was significantly lower in spring (0.55 μg m<sup>-3</sup>) than in winter (1.69 μg m<sup>-3</sup>), but the diurnal pattern was similar (Figs. 3a and 4b) and temporal correlation with primary species
   (r<sup>2</sup> ~ 0.6) was strong (Table S1). Average LV-OOA concentration at JST also was the lowest in spring (1.42 μg m<sup>-3</sup>), which might be attributed to warming temperatures that elevate the PBL and enhance atmospheric mixing. Diurnal variation of rural LV-OOA showed a small diurnal maximum in the afternoon, whereas no variation was observed for JST LV-OOA (Fig. 4b). LRK LV-OOA showed moderate correlation with sulfate (r<sup>2</sup> >
- <sup>15</sup> 0.4; Table S2), while no correlation was found for JST LV-OOA. Comparison of mass spectra revealed the same strong correlation ( $r^2 \sim 1$ ; Fig. S11) between JST and LRK LV-OOA factors observed in winter, suggesting possible similar sources over regional scale.

A third factor resolved from Atlanta OA was assigned as 91Fac rather than SV-OOA based on a higher oxidation level ( $f_{43}/f_{44} = 0.12$ ), and better correlation ( $r^2 = 0.44$ ) with the 91Fac reference mass spectrum (Robinson et al., 2011) than with SV-OOA ( $r^2 < 0.4$ ). Average mass contributions of 91Fac to total OA are lower at JST (< 10%) than LRK (21%), and do not vary substantially throughout the day (Fig. 4b). The JST and LRK 91Fac were highly correlated ( $r^2 ~ 1$ ), indicating nearly identical composition. During spring and summer, the average 91Fac concentration at the LRK site ( $0.7-1.2 \,\mu g m^{-3}$ ) is slightly higher than at JST ( $0.3-0.6 \,\mu g m^{-3}$ ) (Fig. 3a), suggesting a higher emission sources at the rural site. 91Fac has been attributed to various sources: monoterpene-derived SOA (Budisulistiorini et al., 2015) and biogenic SOA



(Chen et al., 2014). 91Fac had also been attributed to aged BBOA (Robinson et al., 2011), however, recent field study identified ions at at m/z 18, 29, and 44 as markers for aged BBOA but not m/z 91 ion (Bougiatioti et al., 2014). Since BBOA was not resolved from OA measurements at either location in spring, aging of BBOA seems unlikely fit to be the source of 91Fac in this study, although it cannot be definitely ruled out, 91Fac will be further discussed in Sect. 3.5.

The IEPOX-OA factor, attributed to IEPOX heterogeneous chemistry (Budisulistiorini et al., 2013; Lin et al., 2012), was resolved from datasets at both JST and LRK. It was the second most abundant OA type after LV-OOA at JST, but the most abundant at LRK

- (Table 1). The average IEPOX-OA concentration was slightly higher at LRK than at JST, consistent with increasing isoprene emission during spring, with higher concentrations near densely forested areas like at GSMNSP, TN. Diurnal patterns of IEPOX-OA are different at JST and LRK. At LRK, IEPOX-OA increased in the afternoon and remained high until evening, suggesting that this factor is driven by photooxidation of isoprene.
- <sup>15</sup> At JST, the diurnal pattern of IEPOX-OA followed that of total OA, where it slightly decreased during the day before it increased again in the evening, which is different from previous observations at JST during summer 2011 (Budisulistiorini et al., 2013). Nevertheless, the mass spectra of IEPOX-OA at JST and LRK are tightly correlated  $(r^2 \sim 1)$ , indicative of similar composition.

#### 20 3.2.3 Summer

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PMF analysis of summer OA resolved the same factors as spring at both sites: HOA, LV-OOA, 91Fac, and IEPOX-OA factors at JST, and LV-OOA, 91Fac, and IEPOX-OA factors at LRK (Fig. 2c). Average HOA mass concentration at JST increased in summer, but its contribution to total OA was lower than from spring (Fig. 3, Table 1). Temporal variation of HOA was well correlated ( $r^2 \sim 0.6$ ) with BC, CO, and NO<sub>x</sub> (Table S1) and the diurnal pattern was similar to that of spring (Fig. 4b).

Average LV-OOA concentrations at both sites also increased in summer; however, the proportional contribution decreased as a result of a larger contribution of IEPOX-



OA at JST and 91Fac at LRK (Fig. 3, Table 1). The time series of LV-OOA correlated weakly with sulfate ( $r^2 \sim 0.2$ ) at JST, but more strongly correlated with sulfate at LRK ( $r^2 = 0.6-0.7$ ) (Table S2). The diurnal profile of rural LV-OOA showed a local maximum in mid-afternoon tracking with the sulfate diurnal profile (Fig. 4). At JST, LV-OOA and

- <sup>5</sup> sulfate increased slightly during mid-morning, and while LV-OOA remained high, sulfate decreased in the evening. Comparison of JST and LRK LV-OOA mass spectra revealed a strong correlation ( $r^2 = 0.95$ ). Ratios of LV-OOA : sulfate at both sites were on average > 1, suggesting the LV-OOA was aged. The large variability of LV-OOA : sulfate ratio at LRK could indicate that LV-OOA was aging gradually.
- <sup>10</sup> Average concentrations of the 91Fac OA at both sites were higher in summer than spring. The relative contribution to total OA remained constant at JST, but increased at LRK (Table 1, Fig. 3). The diurnal profile of 91Fac at LRK showed a local maximum around noon, whereas no diurnal variation was observed at JST. No correlation was observed for time series of 91Fac with inorganics in Atlanta, but a moderate correlation  $(r^2 \sim 0.5)$  with nitrate was observed at LRK (Tables S2). Correlation of the mass spectra
- at the two sites was slightly less ( $r^2 \sim 0.9$ ) than in spring. 91Fac at both sites were less aged compared to LV-OOA based on average ratios of 91Fac:sulfate were < 1. Variability of LRK 91Fac, however, was large suggesting that it was gradually aged during spring.
- Both average IEPOX-OA concentration and relative contribution to total OA mass increased at JST. At LRK, the average concentration of IEPOX-OA reached a maximum in summer, but the relative contribution was lower due to the increasing contribution from 91Fac. Concentrations of IEPOX-OA at both sites are comparable (Fig. 3c), suggesting that in summer this factor may become spatially homogeneous in the south-
- eastern US. Since measurements at JST and LRK were conducted at different years, meteorological changes might play role in site-to-site comparison. At LRK, IEPOX-OA showed a small increase around noon, while at JST there was a local maximum in the mid-afternoon, suggesting an influx of IEPOX-OA likely transported from surrounding forested areas. The time series of IEPOX-OA was moderately correlated with nitrate



 $(r^2 \sim 0.4)$  at JST, whereas at LRK, stronger correlations  $(r^2 > 0.5)$  with inorganics (i.e., sulfate, nitrate and ammonium) were observed.

## 3.2.4 Fall

At JST, PMF analysis of fall OA resulted in similar a four-factor solution similar to that of winter OA (i.e., HOA, BBOA, SV-OOA, and LV-OOA), while at LRK a three-factor solution was resolved (i.e., LV-OOA, 91Fac, and IEPOX-OA) (Fig. 2d). The concentration of HOA increased to a level comparable to that in winter (Fig. 3). The correlations of the time series of HOA with BC, CO, and NO<sub>x</sub> ( $r^2 > 0.7$ ) were similar to spring and summer and slightly stronger than in winter (Table S1). The diurnal profile of HOA appears similar to that in winter (Fig. 4).

At JST, the BBOA factor was resolved again from OA in fall with average concentration and fractional contribution to total OA less than from winter. BBOA was not resolved from OA at LRK. The diurnal profile of BBOA during fall at JST appeared similar to that in winter, suggesting similar emission sources as well as possible PBL effect during these two colder seasons. SV-OOA was also resolved from JST OA in fall with slightly higher average concentration and fractional contribution than in winter. The diurnal profile of fall SV-OOA was similar to that in winter, suggesting similar sources and role of PBL.

LV-OOA was resolved from OA at both JST and LRK. Average concentrations of LV-OOA remained relatively constant from summer to fall at both the urban and rural sites (Fig. 3). However, the contribution of LV-OOA to total OA at LRK increased due to decreasing concentrations of other OA factors (i.e., IEPOX-OA and 91Fac) (Table 1). JST LV-OOA did not show diurnal variation, whereas LRK LV-OOA increased in midmorning and reached a maximum around mid-afternoon. Temporal variation of LV-OOA was weakly correlated ( $r^2 \sim 0.2$ ) with inorganics at JST, but moderately correlated ( $r^2 =$ 0.4–0.5) at LRK. Strong correlation of LV-OOA mass spectra ( $r^2 \sim 1$ , slope = 0.8–1.1; Fig. S1) at JST and LRK indicates a similar or identical source.



The concentration and fractional contribution of 91Fac resolved from OA at LRK were much lower in fall than summer (Fig. 3, Table 1). No significant diurnal variation or correlations with inorganics was observed. IEPOX-OA concentration decreased in fall as expected from reduced isoprene emissions. Time series of IEPOX-OA were not correlated with any secondary species. The diurnal profile of IEPOX-OA showed a small peak around noon, suggesting that SOA formation was still occurring.

## 3.3 Seasonal changes and contribution of OA sources

Figure 3a and b illustrates annual temporal variations of PMF factors resolved from the JST and LRK. HOA was observed throughout the year at JST and contributes significantly to total OA, on average 20–24 % (Table 1). Seasonal average mass concentration of HOA varies from 0.5–2 µg m<sup>-3</sup> (Fig. 3c). Wider standard deviations in winter and fall suggest more variability in HOA mass in Atlanta during these seasons. LV-OOA, which was also observed throughout the year, contributes on average 30–43 % of the total OA. Seasonal average concentration of LV-OOA is relatively constant between 1–

<sup>15</sup> 3 μg m<sup>-3</sup> with less mass variability in summer and more variability in winter. PBL might have a role in the higher variability of HOA and LV-OOA at JST during winter. At LRK, LV-OOA was also observed throughout the year, accounting for a large proportion of total OA in winter, up to 66 % (Table 1). Similar to JST, seasonal average concentration at LRK was 1–3 μg m<sup>-3</sup>, with slightly more mass variability in winter and fall than in spring and summer.

BBOA and SV-OOA were both observed during winter and fall at JST. BBOA seasonal average concentration is about  $1-2\,\mu\text{gm}^{-3}$ , accounting on average 15–19% of total OA. Standard deviations of mass concentrations indicate large variability of BBOA in winter, which narrows in fall (Fig. 3c). BBOA was observed only during winter at LRK.

<sup>25</sup> The average concentration of BBOA at LRK was consistently ~  $1 \mu g m^{-3}$  (Fig. 3b), but several episodes of high levels resulted in a large standard deviation (Fig. 3b and c). SV-OOA was resolved only at JST and only in the fall and winter (Fig. 3a), implying that it might be formed from local aging process or transported from nearby areas. Seasonal



average concentration of SV-OOA was  $1-2 \mu g m^{-3}$ , contributing approximately 26 and 28 % of the total OA in winter and fall, respectively. During spring and summer, SV-OOA concentrations were probably at or below the ACSM limits of detection.

- IEPOX-OA concentrations at both sites were elevated throughout spring and summer in accord with expected enhanced emission and photochemistry of isoprene (Fig. 3a and b). In Atlanta (JST), average concentration of IEPOX-OA was ~ 1  $\mu$ gm<sup>-3</sup> (32 % of total OA) in spring and ~ 2  $\mu$ gm<sup>-3</sup> (37 %) in summer (Table 2, Fig. 4c). Mass variability of IEPOX-OA in summer was large, primarily as a result of a sharp peak in early July, when levels were as high as ~ 4  $\mu$ gm<sup>-3</sup>. In contrast to JST, IEPOX-OA was observed in
- <sup>10</sup> spring, summer, and fall at LRK. Average IEPOX-OA concentrations was  $1.35 \,\mu g m^{-3}$ in spring and  $2.13 \,\mu g m^{-3}$  in summer, contributing 41 and 40 % of total OA mass, respectively. In fall, the average IEPOX-OA concentration decreased to  $0.78 \,\mu g m^{-3}$ , accounting for 27 % of OA mass, consistent with loss of foliage as a major source of isoprene emission and in accord with this explanation, IEPOX-OA was not observed
- <sup>15</sup> during winter. Standard deviations at LRK were large in both spring and summer and concentrations were similar to those observed at JST during summer.

91Fac OA was observed during spring and summer at JST and LRK, and through the fall season only at LRK. Seasonal average concentration of 91Fac was <  $1 \mu g m^{-3}$  (9% of total OA) at JST. However, at LRK, the seasonal average concentrations were

20 0.68 μg m<sup>-3</sup> (21 %) in spring, 1.25 μg m<sup>-3</sup> (23 %) in summer, and 0.25 μg m<sup>-3</sup> (9 %) in fall. Further discussion about the possible source(s) of 91Fac is presented in Sect. 3.5.

## 3.4 IEPOX-OA factor: fragment ion contributions

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The IEPOX-OA factor has been observed in chamber experiments, field and sources datasets (Hu et al., 2015). Temporal variation of the m/z 82 fragment ion associated with LV-OOA, IEPOX-OA, and 91Fac (Fig. 5a and b) shows that the IEPOX-OA factor

is the predominant contributor to m/z 82 at both LRK and JST in spring and sum-



mer. However, during fall the LV-OOA factor becomes a significant contributor at LRK (Fig. 5b).

In addition to the ion at m/z 82 fragment, the IEPOX-OA mass spectra show distinct fragment ions at m/z 53 and m/z 75. Figure 5c presents scatter plots of the fractional contributions of ions at m/z 53 ( $f_{53}$ ) and 75 ( $f_{75}$ ) vs. the contribution of the ion at m/z 82 ( $f_{82}$ ) to IEPOX-OA mass spectra.  $f_{75}$  and  $f_{82}$  show a strong linear relationship ( $r^2 = 0.90$ ; slope = 0.499±0.081) over different locations and seasons, while  $f_{53}$  and  $f_{82}$ are more weakly correlated ( $r^2 = 0.35$ ). Mass spectra generated by thermal decomposition of isomeric authentic 3-MeTHF and IEPOX standards directly atomized into the

- <sup>10</sup> Aerodyne HR-ToF-AMS show major fragments at m/z82 (mostly  $C_5H_6O^+$ ), m/z 53 (mostly  $C_4H_5^+$ ), 75 (mostly  $C_3H_7O_2^+$ ), and 100 (mostly  $C_5H_8O_2^+$ ) (Lin et al., 2012). While ions at m/z 53 and 75 were prominent in ACSM mass spectra acquired from the atomization of filter extracts of laboratory-generated IEPOX-derived SOA (Budisulistiorini et al., 2013) and in the IEPOX-OA factor resolved from field studies using the ACSM
- <sup>15</sup> (Budisulistiorini et al., 2015), both sources gave a prominent ion at m/z 101 (C<sub>5</sub>H<sub>9</sub>O<sub>2</sub><sup>+</sup>) rather than m/z 100. The scatterplot of  $f_{101}$  against  $f_{82}$  does not show a linear relationship ( $r^2 = 0.05$ ), perhaps as a consequence of the low intensity of m/z 101 compared to the other ion fragments. Although parameterizations of IEPOX-OA factor based on its markers (Hu et al., 2015) was not done in this study, we offer insights for the role of the m/z 82 fragment ion over different seasons in southeastern US. Figure 5 suggests that the m/z 75 fragment ion could serve as an additional marker ion for IEPOX-OA
- identification. Here we have estimated from our field data, the intensity of the ion at m/z 75 is about half that of the ion at m/z 82 in IEPOX-OA mass spectra.

#### 3.5 Insights into 91Fac OA formation

<sup>25</sup> Studies have reported significant time variation of an m/z 91 fragment ion (C<sub>3</sub>H<sub>7</sub>O<sub>3</sub><sup>+</sup>) measured by the Aerodyne AMS, which correlated strongly with OA mass during isoprene photooxidation under low-NO<sub>x</sub> and low-RH conditions in a chamber pre-seeded



with ammonium sulfate (Surratt et al., 2006). Relation of this AMS fragment ion to peroxide formation isoprene photooxidation (Surratt et al., 2006) and terpene ozonolysis (Chen et al., 2014) has also been suggested. Recently, a 91Fac factor was resolved from PMF analysis of atmospheric measurements over densely forested areas where isoprene emissions were dominant (Robinson et al., 2011; Budisulistiorini et al., 2015).

- High-volume PM<sub>2.5</sub> filter samples at the LRK during 1 June–17 July 2013 were analyzed offline for biogenic SOA tracers by ultra performance liquid chromatography/diode array detection-electrospray ionization-high-resolution quadrupole time-of-flight mass spectrometry (UPLC/DAD-ESI-HR-QTOFMS) (Budisulistiorini et al., 2015). SOA tracers from isoproper array detection are from isoproper and provide time of the second se
- <sup>10</sup> ers from isoprene ozonolysis chemistry (Riva et al., 2015) and monoterpene oxidation chemistry were detected (Table 2) in addition to tracers of isoprene photooxidation. SOA tracers of isoprene ozonolysis were moderately correlated ( $r^2 = 0.2-0.5$ ) with both IEPOX-OA and 91Fac, and several SOA tracers of isoprene ozonolysis correlated more strongly with 91Fac than monoterpene-derived SOA tracers ( $r^2 = 0.1-0.4$ ).
- Figure 6 shows the correlation of m/z 91 of 91Fac at JST and LRK during spring and summer with NO<sub>x</sub> and the ion at m/z 82 of the IEPOX-OA factor. NO<sub>x</sub> and biogenic source(s) represented by m/z 82 ion of IEPOX-OA factor did not appear to influence formation of 91Fac during summer at JST. At LRK, 91Fac was not correlated with NO<sub>x</sub>. However, a weak correlation with the m/z 82 ion of IEPOX-OA factor might indicate that biogenic source(s) contributed to 91Fac formation at LRK.

At the LRK site, isoprene mixing ratios were up to 12 ppb during the 2013 SOAS campaign as measured by online high-resolution proton transfer reaction time-of-flight mass spectrometry (HR-PTR-TOFMS) (Budisulistiorini et al., 2015). The moderate correlations with isoprene ozonolysis and photooxidation tracers suggest that 91Fac could

<sup>25</sup> be related to isoprene chemistry but not specifically related to the IEPOX pathway. The abundance of 91fac warrants additional study to determine the source, since multiple sources might contribute to this factor. While there appears to be correlation with isoprene-derived SOA in this study, 91Fac has been resolved from SOA produced in monoterpene-influenced sites (Slowik et al., 2011).



#### 4 Conclusions

Seasonal characterization of NR-PM<sub>1</sub> collected in the southeastern US revealed that OA is the most abundant species, accounting for 50–65% at LRK and 65–75% at JST. Sulfate is the most abundant inorganic species throughout the year, accounting

- for 20–30 and 10–20 % at the rural and urban site, respectively. Nitrate and ammonium followed as the third and fourth most abundant inorganic species, respectively, and were dependent on the season and location. The highest average concentrations of OA, sulfate and ammonium were observed during summer season at LRK and during fall at JST.
- <sup>10</sup> Characterization of OA using PMF resolved a combined six factors at JST and LRK sites, with different factors being resolved depending on location and season. HOA and SV-OOA were resolved only at JST that represent urban OA. BBOA, LV-OOA, IEPOX-OA, and 91Fac were resolved from both sites during different seasons. HOA contributions to total OA mass were fairly consistent (15–25%) over four seasons; its
- <sup>15</sup> contribution peaked during winter. SV-OOA was observed only during colder seasons, having a consistent seasonal contribution of 27%. BBOA was only observed during winter and fall seasons, and on average contributed ~ 17% to the total OA mass, with the higher contribution of BBOA at LRK that represent rural site was likely due to a single, significant burning event.
- Average IEPOX-OA contributions during warmer seasons were 40 and 35% at the rural and urban sites, respectively. While the IEPOX-OA resolved from PMF is characterized by the fragment ion at m/z 82, strong correlation of the fractional contributions of the ions m/z 82 and 75 fragment ions to IEPOX-OA mass spectra ( $f_{75}/f_{82} \sim 0.5$ ) suggests that both ions can serve as markers for IEPOX-OA. Average 91Fac OA con-
- tributions were ~ 9 and 22 % at the urban and rural sites, respectively. Based on correlations with SOA tracer analysis performed offline, 91Fac showed an overall higher correlation with SOA markers of isoprene ozonolysis and photooxidation than with



monoterpene oxidation. This might indicate that 91Fac at LRK could be influenced by isoprene chemistry.

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#### References

- Bougiatioti, A., Stavroulas, I., Kostenidou, E., Zarmpas, P., Theodosi, C., Kouvarakis, G.,
   <sup>15</sup> Canonaco, F., Prévôt, A. S. H., Nenes, A., Pandis, S. N., and Mihalopoulos, N.: Processing of biomass-burning aerosol in the eastern Mediterranean during summertime, Atmos. Chem. Phys., 14, 4793–4807, doi:10.5194/acp-14-4793-2014, 2014.
- Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Marth, W. J., Baumann, K., Edgerton, E. S., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T., Gold, A., and Surratt, J. D.: Real-time continuous characterization of secondary organic aerosol derived from isoprene epoxydiols in downtown Atlanta, Georgia, using the aerodyne aerosol chemical
  - speciation monitor, Environ. Sci. Technol., 47, 5686–5694, doi:10.1021/es400023n, 2013. Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Baumann, K., Edgerton, E. S., Kollman, M. S., Ng, N. L., Verma, V., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T.,
- Weber, R.J., and Surratt, J. D.: Intercomparison of an Aerosol Chemical Speciation Monitor (ACSM) with ambient fine aerosol measurements in downtown Atlanta, Georgia, Atmos. Meas. Tech., 7, 1929–1941, doi:10.5194/amt-7-1929-2014, 2014.



- Budisulistiorini, S. H., Li, X., Bairai, S. T., Renfro, J., Liu, Y., Liu, Y. J., McKinney, K. A., Martin, S. T., McNeill, V. F., Pye, H. O. T., Nenes, A., Neff, M. E., Stone, E. A., Mueller, S., Knote, C., Shaw, S. L., Zhang, Z., Gold, A., and Surratt, J. D.: Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the
- <sup>5</sup> 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee, ground site, Atmos. Chem. Phys. Discuss., 15, 7365–7417, doi:10.5194/acpd-15-7365-2015, 2015. Butler, A. J., Andrew, M. S., and Russell, A. G.: Daily sampling of PM<sub>2.5</sub> in Atlanta: results of the first year of the assessment of spatial aerosol composition in Atlanta study, J.Geophys.Res., 108, SOS 3-1–SOS 3-11, doi:10.1029/2002JD002234, 2003.
- <sup>10</sup> Chen, Q., Farmer, D. K., Rizzo, L. V., Pauliquevis, T., Kuwata, M., Karl, T. G., Guenther, A., Allan, J. D., Coe, H., Andreae, M. O., Pöschl, U., Jimenez, J. L., Artaxo, P., and Martin, S. T.: Submicron particle mass concentrations and sources in the Amazonian wet season (AMAZE-08), Atmos. Chem. Phys., 15, 3687–3701, doi:10.5194/acp-15-3687-2015, 2015.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D., Dall'Osto, M., Dav, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Frenev, E., Hilde-

- <sup>15</sup> burnis, D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A.-M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Organic aerosol componeated drawad from 25 AMS, deta aerosol componeated drawad from 25 AMS, deta aerosol compo-
- nents derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach, Atmos. Chem. Phys., 14, 6159–6176, doi:10.5194/acp-14-6159-2014, 2014.

Cross, E. S., Slowik, J. G., Davidovits, P., Allan, J. D., Worsnop, D. R., Jayne, J. T., Lewis, D. K., Canagaratna, M., and Onasch, T. B.: Laboratory and ambient particle density determinations

- using light scattering in conjunction with aerosol mass spectrometry, Aerosol Sci. Tech., 41, 343–359, doi:10.1080/02786820701199736, 2007.
  - Docherty, K. S., Stone, E. A., Ulbrich, I. M., DeCarlo, P. F., Snyder, D. C., Schauer, J. J., Peltier, R. E., Weber, R. J., Murphy, S. M., Seinfeld, J. H., Grover, B. D., Eatough, D. J., and Jimenez, J. L.: Apportionment of primary and secondary organic aerosols in southern
- <sup>30</sup> California during the 2005 Study of Organic Aerosols in Riverside (SOAR-1), Environ. Sci. Technol., 42, 7655–7662, doi:10.1021/es8008166, 2008.
  - Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dor-



land, R.: Changes in atmospheric constituents and in radiative forcing, in: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK, and New York, NY, USA, 153–179, 2007.

<sup>5</sup> Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K<sup>+</sup>-Ca<sup>2+</sup>-Mg<sup>2+</sup>-NH<sub>4</sub><sup>+</sup>-Na<sup>+</sup>-SO<sub>4</sub><sup>2-</sup>-NO<sub>3</sub><sup>-</sup>-Cl<sup>-</sup>-H<sub>2</sub>O aerosols, Atmos. Chem. Phys., 7, 4639–4659, doi:10.5194/acp-7-4639-2007, 2007.

Gao, S., Ng, N. L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J., Yoo, K. Y., Beauchamp, J. L., Hodyss, R. P., Flagan, R. C., and Seinfeld, J. H.: Particle phase acidity

- and oligomer formation in secondary organic aerosol, Environ. Sci. Technol., 38, 6582–6589, doi:10.1021/es049125k, 2004.
  - Gaston, C. J., Riedel, T. P., Zhang, Z., Gold, A., Surratt, J. D., and Thornton, J. A.: Reactive uptake of an isoprene-derived epoxydiol to submicron aerosol particles, Environ. Sci. Technol., 48, 11178–11186, doi:10.1021/es5034266, 2014.
- <sup>15</sup> Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr., J. R., Carlton, A. G., Lee, S.-H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211–5228, doi:10.5194/acp-15-5211-2015, 2015.

Hansen, D. A., Edgerton, E. S., Hartsell, B. E., Jansen, J. J., Kandasamy, N., Hidy, G. M.,

- and Blanchard, C. L.: The southeastern aerosol research and characterization study: Part 1

   Overview, J. Air Waste Manage., 53, 1460–1471, doi:10.1080/10473289.2003.10466318, 2003.
  - Henry, K. M. and Donahue, N. M.: Photochemical aging of α-pinene secondary organic aerosol: effects of OH radical sources and photolysis, J. Phys. Chem. A, 116, 5932–5940, doi:10.1021/jp210288s, 2012.

- Hidy, G. M., Blanchard, C. L., Baumann, K., Edgerton, E., Tanenbaum, S., Shaw, S., Knipping, E., Tombach, I., Jansen, J., and Walters, J.: Chemical climatology of the southeastern United States, 1999–2013, Atmos. Chem. Phys., 14, 11893–11914, doi:10.5194/acp-14-11893-2014, 2014.
- <sup>30</sup> Hu, W. W., Campuzano-Jost, P., Palm, B. B., Day, D. A., Ortega, A. M., Hayes, P. L., Krechmer, J. E., Chen, Q., Kuwata, M., Liu, Y. J., de Sá, S. S., Martin, S. T., Hu, M., Budisulistiorini, S. H., Riva, M., Surratt, J. D., St. Clair, J. M., Isaacman-Van Wertz, G., Yee, L. D., Goldstein, A. H., Carbone, S., Artaxo, P., de Gouw, J. A., Koss, A., Wisthaler, A., Mikoviny, T.,



Karl, T., Kaser, L., Jud, W., Hansel, A., Docherty, K. S., Robinson, N. H., Coe, H., Allan, J. D., Canagaratna, M. R., Paulot, F., and Jimenez, J. L.: Characterization of a realtime tracer for Isoprene Epoxydiols-derived Secondary Organic Aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements, Atmos. Chem. Phys. Discuss., 15, 11223– 11276. doi:10.5194/acpd-15-11223-2015, 2015.

IPCC: Climate Change 2013: The Physical Science Basis, Contribution of Working Group I to the Fifth Assessment Report to the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK and New York, NY, USA, 33–118, 2013.

- Jacobs, M. I., Burke, W. J., and Elrod, M. J.: Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, Atmos. Chem. Phys., 14, 8933–8946, doi:10.5194/acp-14-8933-2014, 2014.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E., Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn A. M. Williams, I. B. Wood, F. C. Middlebrook, A. M. Kolb, C. F., Baltensperger, I.
- born, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525–1529, doi:10.1126/science.1180353, 2009.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C.,
  Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K.,
  Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053–1123, doi:10.5194/acp-5-1053-2005, 2005.
- Ke, L., Ding, X., Tanner, R. L., Schauer, J. J., and Zheng, M.: Source contributions to carbonaceous aerosols in the Tennessee Valley Region, Atmos. Environ., 41, 8898–8923, doi:10.1016/j.atmosenv.2007.08.024, 2007.



- Kim, E., Hopke, P. K., and Edgerton, E. S.: Source identification of Atlanta aerosol by positive matrix factorization, J. Air Waste Manage., 53, 731–739, doi:10.1080/10473289.2003.10466209, 2003.
- Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical
- Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, Atmos. Chem. Phys., 7, 1503–1522, doi:10.5194/acp-7-1503-2007, 2007.
  - Lee, S., Murphy, D. M., Thomson, D. S., and Middlebrook, A. M.: Chemical components of single particles measured with Particle Analysis by Laser Mass Spectrometry (PALMS) during
- the Atlanta SuperSite Project: focus on organic/sulfate, lead, soot, and mineral particles, J. Geophys. Res., 107, 4003, doi:10.1029/2000JD000011, 2002.

Lin, Y., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S. L., Knipping, E. M., Edgerton, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.: Isoprene epoxydiols as precursors to secondary organic aerosol formation: acid-catalyzed

- reactive uptake studies with authentic compounds, Environ. Sci. Technol., 46, 250–258, doi:10.1021/es202554c, 2012.
  - Lin, Y., Zhang, H., Pye, H. O. T., Zhang, Z., Marth, W. J., Park, S., Arashiro, M., Cui, T., Budisulistiorini, S. H., Sexton, K. G., Vizuete, W., Xie, Y., Luecken, D. J., Piletic, I. R., Edney, E. O., Bartolotti, L. J., Gold, A., and Surratt, J. D.: Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides, P. Natl.
- aerosol formation from isoprene photooxidation in the presence of nitrogen oxides, P. N Acad. Sci. USA, 110, 6718–6723, doi:10.1073/pnas.1221150110, 2013.

- Lin, Y., Budisulistiorini, S. H., Chu, K., Siejack, R. A., Zhang, H., Riva, M., Zhang, Z., Gold, A., Kautzman, K. E., and Surratt, J. D.: Light-absorbing oligomer formation in secondary organic aerosol from reactive uptake of isoprene epoxydiols, Environ. Sci. Technol., 48, 12012– 12021, doi:10.1021/es503142b, 2014.
- Lin, Y.-H., Knipping, E. M., Edgerton, E. S., Shaw, S. L., and Surratt, J. D.: Investigating the influences of SO<sub>2</sub> and NH<sub>3</sub> levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches, Atmos. Chem. Phys., 13, 8457–8470, doi:10.5194/acp-13-8457-2013, 2013.
- Nenes, A., Pandis, S. N., and Pilinis, C.: Continued development and testing of a new thermodynamic aerosol module for urban and regional air quality models, Atmos. Environ., 33, 1553–1560, doi:10.1016/S1352-2310(98)00352-5, 1999.



- Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets
- <sup>5</sup> from Aerosol Mass Spectrometry, Atmos. Chem. Phys., 10, 4625–4641, doi:10.5194/acp-10-4625-2010, 2010.

10

15

25

- Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M., and Worsnop, D. R.: Real-time methods for estimating organic component mass concentrations from aerosol mass spectrometer data, Environ. Sci. Technol., 45, 910–916, doi:10.1021/es102951k, 2011a.
- Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol, Aerosol Sci. Tech., 45, 780–794, doi:10.1080/02786826.2011.560211, 2011b.
- Nguyen, T. B., Coggon, M. M., Bates, K. H., Zhang, X., Schwantes, R. H., Schilling, K. A., Loza, C. L., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Organic aerosol formation from the reactive uptake of isoprene epoxydiols (IEPOX) onto non-acidified inorganic seeds, Atmos. Chem. Phys., 14, 3497–3510, doi:10.5194/acp-14-3497-2014, 2014.
- Olszyna, K. J., Bairai, S. T., and Tanner, R. L.: Effect of ambient NH<sub>3</sub> levels on PM<sub>2.5</sub> composition in the Great Smoky Mountains National Park, Atmos. Environ., 39, 4593–4606, doi:10.1016/j.atmosenv.2005.04.011, 2005.
  - Paatero, P. and Tapper, U.: Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111–126, doi:10.1002/env.3170050203, 1994.
  - Park, K., Kittelson, D., Zachariah, M., and McMurry, P.: Measurement of inherent material density of nanoparticle agglomerates, J. Nanopart. Res., 6, 267–272, doi:10.1023/B:NANO.0000034657.71309.e6, 2004.

Parworth, C., Fast, J., Mei, F., Shippert, T., Sivaraman, C., Tilp, A., Watson, T., and Zhang, Q.:
 Long-term measurements of submicrometer aerosol chemistry at the Southern Great Plains

(SGP) using an Aerosol Chemical Speciation Monitor (ACSM), Atmos. Environ., 106, 43–55, doi:10.1016/j.atmosenv.2015.01.060, 2015.



- Petit, J.-E., Favez, O., Sciare, J., Crenn, V., Sarda-Estève, R., Bonnaire, N., Močnik, G., Dupont, J.-C., Haeffelin, M., and Leoz-Garziandia, E.: Two years of near real-time chemical composition of submicron aerosols in the region of Paris using an Aerosol Chemical Speciation Monitor (ACSM) and a multi-wavelength Aethalometer, Atmos. Chem. Phys., 15, 2985–3005, doi:10.5194/acp-15-2985-2015, 2015.
- Pope III, C. A. and Dockery, D. W.: Health effects of fine particulate air pollution: lines that connect, J. Air Waste Manag., 56, 709–742, 2006.

5

20

- Ripoll, A., Minguillón, M. C., Pey, J., Jimenez, J. L., Day, D. A., Sosedova, Y., Canonaco, F., Prévôt, A. S. H., Querol, X., and Alastuey, A.: Long-term real-time chemical characterization
- of submicron aerosols at Montsec (southern Pyrenees, 1570 m a.s.l.), Atmos. Chem. Phys., 15, 2935–2951, doi:10.5194/acp-15-2935-2015, 2015.
  - Robinson, N. H., Hamilton, J. F., Allan, J. D., Langford, B., Oram, D. E., Chen, Q., Docherty, K., Farmer, D. K., Jimenez, J. L., Ward, M. W., Hewitt, C. N., Barley, M. H., Jenkin, M. E., Rickard, A. R., Martin, S. T., McFiggans, G., and Coe, H.: Evidence for a significant propor-
- tion of Secondary Organic Aerosol from isoprene above a maritime tropical forest, Atmos. Chem. Phys., 11, 1039–1050, doi:10.5194/acp-11-1039-2011, 2011.
  - Schichtel, B. A., Malm, W. C., Bench, G., Fallon, S., McDade, C. E., Chow, J. C., and Watson, J. G.: Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States, J. Geophys. Res., 113, D02311, doi:10.1029/2007JD008605, 2008.
  - Slowik, J. G., Brook, J., Chang, R. Y.-W., Evans, G. J., Hayden, K., Jeong, C.-H., Li, S.-M., Liggio, J., Liu, P. S. K., McGuire, M., Mihele, C., Sjostedt, S., Vlasenko, A., and Abbatt, J. P. D.: Photochemical processing of organic aerosol at nearby continental sites: contrast between urban plumes and regional aerosol, Atmos. Chem. Phys., 11, 2991–3006, doi:10.5194/acp-11-2991-2011, 2011.
  - Solomon, P. A., Chameides, W., Weber, R., Middlebrook, A., Kiang, C. S., Russell, A. G., Butler, A., Turpin, B., Mikel, D., Scheffe, R., Cowling, E., Edgerton, E., St. John, J., Jansen, J., McMurry, P., Hering, S., and Bahadori, T.: Overview of the 1999 Atlanta Supersite Project, J. Geophys. Res., 108, 8413, doi:10.1029/2001JD001458, 2003.
- <sup>30</sup> Sun, Y., Zhang, Q., Zheng, M., Ding, X., Edgerton, E. S., and Wang, X.: Characterization and source apportionment of water-soluble organic matter in atmospheric fine particles (PM<sub>2.5</sub>) with high-resolution aerosol mass spectrometry and GC-MS, Environ. Sci. Technol., 45, 4854–4861, doi:10.1021/es200162h, 2011.



Sun, Y. L., Zhang, Q., Schwab, J. J., Chen, W. N., Bae, M. S., Lin, Y. C., Hung, H. M., and Demerjian, K. L.: A case study of aerosol processing and evolution in summer in New York City, Atmos. Chem. Phys., 11, 12737–12750, doi:10.5194/acp-11-12737-2011, 2011.

Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigiel-

- ski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, J. Phys. Chem. A, 110, 9665–9690, doi:10.1021/jp061734m, 2006.
  - Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Effect of acidity on secondary organic aerosol formation from isoprene, Environ. Sci. Technol., 41, 5363–5369, doi:10.1021/es0704176, 2007.
- Tanner, R. L., Parkhurst, W. J., and McNichol, A. P.: Fossil sources of ambient aerosol carbon based on <sup>14</sup>C measurements special issue of aerosol science and technology on findings from the fine particulate matter supersites program, Aerosol Sci. Tech., 38, 133–139, doi:10.1080/02786820390229453, 2004a.

10

20

- <sup>15</sup> Tanner, R. L., Parkhurst, W. J., Valente, M. L., and David Phillips, W.: Regional composition of PM<sub>2.5</sub> aerosols measured at urban, rural and "background" sites in the Tennessee valley, Atmos. Environ., 38, 3143–3153, doi:10.1016/j.atmosenv.2004.03.023, 2004b.
  - Tanner, R. L., Bairai, S. T., Olszyna, K. J., Valente, M. L., and Valente, R. J.: Diurnal patterns in PM<sub>2.5</sub> mass and composition at a background, complex terrain site, Atmos.Environ., 39, 3865–3875, doi:10.1016/j.atmosenv.2005.03.014, 2005.
  - Tanner, R. L., Bairai, S. T., and Mueller, S. F.: Trends in concentrations of atmospheric gaseous and particulate species in rural eastern Tennessee as related to primary emissions reductions, Atmos. Chem. Phys. Discuss., 15, 13211–13262, doi:10.5194/acpd-15-13211-2015, 2015.
- <sup>25</sup> Turpin, B. J. and Lim, H. J.: Species contributions to PM<sub>2.5</sub> mass concentrations: revisiting common assumptions for estimating organic mass, Aerosol Sci. Tech., 35, 602–610, doi:10.1080/02786820119445, 2001.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric

- <sup>30</sup> data, Atmos. Chem. Phys., 9, 2891–2918, doi:10.5194/acp-9-2891-2009, 2009.
  - Wood, E. C., Canagaratna, M. R., Herndon, S. C., Onasch, T. B., Kolb, C. E., Worsnop, D. R., Kroll, J. H., Knighton, W. B., Seila, R., Zavala, M., Molina, L. T., DeCarlo, P. F., Jimenez, J. L., Weinheimer, A. J., Knapp, D. J., Jobson, B. T., Stutz, J., Kuster, W. C., and Williams, E. J.:



Investigation of the correlation between odd oxygen and secondary organic aerosol in Mexico City and Houston, Atmos. Chem. Phys., 10, 8947–8968, doi:10.5194/acp-10-8947-2010, 2010.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-

- VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, P. Natl. Acad. Sci. USA, 112, 37–42, doi:10.1073/pnas.1417609112, 2015.
- <sup>10</sup> Zhang, H., Surratt, J. D., Lin, Y. H., Bapat, J., and Kamens, R. M.: Effect of relative humidity on SOA formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding oligoesters under dry conditions, Atmos. Chem. Phys., 11, 6411–6424, doi:10.5194/acp-11-6411-2011, 2011.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R.,

- Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., De-Carlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species
- in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophys. Res. Lett., 34, L13801, doi:10.1029/2007GL029979, 2007.
  - Zhang, Q. Q.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, Anal. Bioanal. Chem., 401, 3045–3067, 2011.

Zhang, Y. J., Tang, L. L., Wang, Z., Yu, H. X., Sun, Y. L., Liu, D., Qin, W., Canonaco, F.,

Prévôt, A. S. H., Zhang, H. L., and Zhou, H. C.: Insights into characteristics, sources, and evolution of submicron aerosols during harvest seasons in the Yangtze River delta region, China, Atmos. Chem. Phys., 15, 1331–1349, doi:10.5194/acp-15-1331-2015, 2015.



**Table 1.** Seasonal averaged mass concentrations of non-refractory  $PM_1$  (NR-PM<sub>1</sub>) in  $\mu gm^{-3}$ , percent contributions of organic and inorganic species measured by the Aerodyne ACSM and PMF factors resolved from Atlanta, GA (JST site) and Look Rock, TN (LRK site) during 2012 and 2013.

	Winter		Spring		Summer		Fall	
	JST	LRK	JST	LRK	JST	LRK	JST	LRK
NR-PM <sub>1</sub>	$10.50 \pm 7.32$	$4.77 \pm 3.32$	$6.19 \pm 2.85$	$5.59 \pm 3.47$	$8.78 \pm 4.46$	$8.39 \pm 4.44$	$12.47 \pm 6.72$	$4.55 \pm 2.55$
OA	69.0%	50.2%	75.9%	57.8%	70.0%	63.4 %	65.9%	62.1 %
SO4-	13.4 %	30.6 %	12.0 %	26.9%	17.4%	24.5%	15.8%	21.6%
NO <sub>3</sub>	9.3%	9.2 %	5.6%	6.1%	4.5%	3.8%	9.3%	7.2%
$NH_4^{\downarrow}$	7.9%	9.9%	6.3%	9.0%	7.9%	8.2%	8.6%	9.1 %
CI	0.3%	0.1%	0.2%	0.1%	0.1%	0.1%	0.3%	0.0%
OA speciation	on							
HOA	24 %	NA	17%	NA	15 %	NA	20 %	NA
BBOA	19%	33 %	NA	NA	NA	NA	15%	NA
SV-OOA	26 %	NA	NA	NA	NA	NA	28 %	NA
LVOOA	30 %	66 %	43%	37 %	39 %	36 %	37 %	63 %
91Fac	NA	NA	9%	21 %	9%	23 %	NA	9%
IEPOX-OA	NA	NA	32 %	41 %	37 %	40 %	NA	27 %

NA is not available or resolved from PMF analysis. PMF analysis yielded some residuals of unresolved OA mass that make up the remaining percentage of OA factors.

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**Table 2.** Correlations of PMF factors resolved from OA measurements at LRK, TN against SOA tracers from monoterpene chemistry and isoprene ozonolysis quantified during 2013 SOAS.

	IEPOX-OA	LV-OOA	91Fac	Ref.
Monoterpene SOA tracers				
C <sub>10</sub> H <sub>18</sub> O <sub>5</sub> S	0.28	0.26	0.39	(1)
C <sub>10</sub> H <sub>16</sub> O <sub>7</sub> S <sup>a</sup>	0.42	0.26	0.37	(1)
C <sub>10</sub> H <sub>17</sub> NO <sub>7</sub> S	0.00	0.00	0.01	(1)
C <sub>9</sub> H <sub>15</sub> NO <sub>8</sub> S <sup>a</sup>	0.12	0.22	0.22	(1)
C <sub>10</sub> H <sub>17</sub> NO <sub>1</sub> 0S	0.11	0.15	0.26	(1)
C <sub>8</sub> H <sub>12</sub> O <sub>4</sub> (Terpenylic acid) <sup>a</sup>	0.32	0.36	0.41	(2)
C <sub>9</sub> H <sub>14</sub> O <sub>4</sub> (Pinic acid)	0.12	0.21	0.19	
C <sub>10</sub> H <sub>16</sub> O <sub>4</sub> (Hydroxy pinonic acid)	0.15	0.21	0.25	
C <sub>10</sub> H <sub>16</sub> O <sub>3</sub> (Pinonic acid)	0.10	0.17	0.20	(0)
C <sub>7</sub> H <sub>10</sub> O <sub>4</sub> (Terebic acid)	0.21	0.32	0.27	(3)
C <sub>8</sub> H <sub>12</sub> O <sub>6</sub> (MBTCA)	0.15	0.27	0.14	(4)
C <sub>10</sub> H <sub>16</sub> O <sub>6</sub> (DTAA)	0.35	0.42	0.42	(2)
Isoprene ozonolysis tracers <sup>b</sup>				
C₄H <sub>8</sub> O <sub>6</sub> S	0.46	0.40	0.51	(5,6)
C <sub>5</sub> H <sub>12</sub> O <sub>6</sub> S	0.39	0.19	0.35	(5,6)
$C_5H_{10}O_5S$	0.19	0.19	0.22	(6)
C <sub>5</sub> H <sub>10</sub> O <sub>6</sub> S	0.33	0.38	0.41	(6)
$C_8H_{10}O_4S$	0.00	0.07	0.03	(6)
C <sub>6</sub> H <sub>12</sub> O <sub>7</sub> S	0.24	0.33	0.48	(6)
C <sub>9</sub> H <sub>14</sub> O <sub>6</sub> S	0.21	0.30	0.38	(6)
C <sub>9</sub> H <sub>16</sub> O <sub>7</sub> S	0.38	0.50	0.46	(6)
$C_{10}H_{20}O_9S$	0.36	0.29	0.39	(6)

<sup>a</sup> Budisulistiorini et al. (2015).

<sup>b</sup> Only night time samples were used in PMF factor correlation with isoprene ozonolysis tracers. References: (1) Surratt et al. (2008); (2) Claeys et al. (2009); (3) Yasmeen et al. (2010); (4) Szmigielski et al. (2007); (5) Safi Shalamzari et al. (2013); (6) Riva et al. (2015).











**Figure 2.** Mass spectra of PMF factors resolved from (a) winter, (b) spring, (c) summer, and (d) fall datasets at JST and LRK sites. The PMF factors from JST site are color-coded, while the same factor from LRK site is in light blue.











**Figure 4.** Diurnal variations of **(a)** OA and inorganic species measured by ACSM and **(b)** OA factors resolved by PMF analysis from winter, spring, summer, and fall measurements at the JST site (solid lines) and LRK site (dash lines).





**Figure 5.** Temporal variations of the m/z 82 fragment ion ( $C_5H_6O^+$ ) contribution to IEPOX-OA, 91Fac, and LV-OOA factors (a) at the JST site during spring and summer seasons, and (b) at the LRK site during spring, summer, and fall seasons. (c) Scatterplots of the m/z 53 (possibly  $C_4H_5^+$ ), m/z 75 (possibly  $C_3H_7O_2^+$ ), and m/z 101 (possibly  $C_5H_9O_2^+$ ) fragment ions from the IEPOX-OA mass spectra vs. the m/z 82 fragment ion from the same mass spectra over different seasons at the JST and LRK sites. ACSM measures unit mass resolution (UMR), thus the proposed formulas are based on previous study using HR-ToF-AMS (Lin et al., 2012). The asterix marker is the respective ion fragments of IEPOX-OA mass spectra resolved from OA measurements during summer 2011 at the JST site (Budisulistiorini et al., 2013).





**Figure 6.** Scatter plots of m/z 91 of 91Fac factor vs. (a) NOx and (b) m/z 82 of IEPOX-OA factor at JST and LRK sites during spring and summer seasons.

