

Sources of organic aerosol investigated using organic compounds as tracers measured during CalNex in Bakersfield

Yunliang Zhao,¹ Nathan M. Kreisberg,² David R. Worton,^{1,2} Gabriel Isaacman,¹ Drew R. Gentner,³ Arthur W. H. Chan,¹ Robin J. Weber,¹ Shang Liu,⁴ Douglas A. Day,^{4,5} Lynn M. Russell,⁴ Susanne V. Hering,² and Allen H. Goldstein^{1,3}

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[1] To investigate the major sources of summertime organic aerosol (OA) and provide insights into secondary organic aerosol (SOA) formation, positive matrix factorization analysis was performed on a large set of organic species measured during the California at the Nexus of Air Quality and Climate Change (CalNex) campaign in Bakersfield, CA. Six OA source factors were identified, including one representing primary organic aerosol (POA); four different types of SOA representing local, regional, and nighttime production; and one representing a complex mixture of additional OA sources that were not further resolvable. POA accounted for an average of 15% of measured OA. The complex mixture of additional OA sources contributed an average of 13% of measured OA. The combined contribution of four types of SOA to measured OA averaged 72% and varied diurnally from 78% during the day to 66% at night. Both regional and local SOA were significant contributors to measured OA during the day, but regional SOA was the larger one, especially in the afternoon. Although contributions to SOA from oxidation of biogenic gas-phase compounds were less constrained, they were evident and dominantly occurred at night. The formation of SOA is indicated to be mainly through gas-to-particle condensation of gas-phase oxidation products during the day. Our results indicate that effective control measures to reduce summertime OA in Bakersfield should focus on reducing sources of gas-phase organics that serve as SOA precursors during the day, and it is more effective to reduce SOA precursors at the regional scale in the afternoon.

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1. Introduction

[2] Organic compounds constitute a major mass fraction (20%–90%) of atmospheric fine particulate matter in most environments [Kanakidou et al., 2005]. These organic compounds have been categorized into either primary organic aerosol (POA), directly emitted from various primary sources such as food cooking and vehicle exhausts [e.g., Schauer

et al., 1999a, 1999b, 2002a], or secondary organic aerosol (SOA), formed in the atmosphere through chemical reactions [Odum et al., 1997; Jang et al., 2002; Robinson et al., 2007; Kroll and Seinfeld, 2008]. The majority of organic aerosol (OA) in rural and urban areas is secondary [Zhang et al., 2007; Shrivastava et al., 2007; Williams et al., 2010; Jimenez et al., 2009]. Therefore, identifying major components of OA and quantifying their contributions to OA have important implications for air quality regulation.

[3] Source apportionment between POA and SOA has generally been done based on the chemical analyses through one of three ways: (i) bulk organic spectra measured by the Aerodyne Aerosol Mass Spectrometer [e.g., Jimenez et al., 2009; Zhang et al., 2011], (ii) thermal-optical elemental carbon (EC)/organic carbon analyzer [e.g., Turpin et al., 1991; Strader et al., 1999], and (iii) molecular speciation measured by gas chromatograph/mass spectrometer (GC/MS) [e.g., Shrivastava et al., 2007; Williams et al., 2010]. In comparison with the bulk organic analysis, the molecular speciation resolves a smaller fraction of OA, but the identified organic compounds can serve as tracers for specific source types [Schauer et al., 1996; Schauer and Cass, 2000] and provide information for understanding SOA formation in the atmosphere [e.g., Kleindienst et al., 2007; Williams et al., 2010].

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¹Department of Environmental Science, Policy, and Management, University of California, Berkeley, California, USA.

²Aerosol Dynamics Inc., Berkeley, California, USA.

³Department of Civil and Environmental Engineering, University of California, Berkeley, California, USA.

⁴Scripps Institution of Oceanography, University of California, San Diego, California, USA.

⁵Now at Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, Colorado, USA.

Corresponding author: A. H. Goldstein, Department of Civil and Environmental Engineering, University of California, 151 Hilgard Hall, Berkeley, California 94720-3110, USA. (ahg@berkeley.edu)

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Two common source apportionment methods using organic compounds are the chemical mass balance (CMB) and positive matrix factorization (PMF) models [e.g., *Schauer et al.*, 1996; *Shrivastava et al.*, 2007; *Williams et al.*, 2010].

[4] The CMB model uses organic compounds to estimate contributions to OA from a variety of sources, such as biomass burning, meat cooking, or diesel vehicle emissions, but requires a priori knowledge of their source profiles as inputs to solve the model [*Schauer et al.*, 1996; *Schauer and Cass*, 2000; *Zheng et al.*, 2002]. As a result, CMB analysis is sensitive to the provided source profiles [*Robinson et al.*, 2006; *Subramanian et al.*, 2007]. The products and SOA yields measured for a few known volatile organic compounds (VOCs) oxidized in chamber experiments have been considered as source profiles of SOA [*Kleindienst et al.*, 2007; *Stone et al.*, 2009]. However, the relevance of these source profiles is limited to these known compounds and the specific experimental conditions used in the chamber to derive these profiles. Source profiles for SOA are difficult to establish due to the complexity of oxidation processes and the wide range of precursors and atmospheric conditions, so the CMB model has typically been unable to provide adequate constraints on the SOA mass or composition. Although SOA mass can be estimated by the CMB model as the difference between apportioned OA and measured OA, the amount of SOA estimated by this approach is less constrained [*Schauer et al.*, 1996; *Zheng et al.*, 2002; *Subramanian et al.*, 2007].

[5] The PMF model uses covariance between organic compounds to categorize them into unique groups or factors that could represent emissions from contemporaneous source or formation processes [*Shrivastava et al.*, 2007; *Zhang et al.*, 2009; *Williams et al.*, 2010]. Since source profiles are not required as model inputs, factors likely representing poorly constrained or unknown sources, such as SOA, can be determined. Characterization of these factors based on their compositions and temporal variations therefore provides an effective tool for differentiating complex sources [*Shrivastava et al.*, 2007; *Zhang et al.*, 2009; *Williams et al.*, 2010]. Past work has demonstrated the ability of the PMF analysis to separate multiple types of SOA with distinct diurnal patterns in the absence of known source profiles [*Williams et al.*, 2010]. Despite its utility for source apportionment, PMF analysis is not widely performed on organic compounds in the particle phase because it typically requires a larger number of samples and subsequently poses significant challenges when speciated measurements of OA are made by filter sampling with 24 h collection periods in the field followed by solvent extraction in the laboratory for analysis [*Jaekels et al.*, 2007; *Shrivastava et al.*, 2007]. Recently, speciated measurements of OA have been facilitated by the development of an in situ thermal desorption aerosol gas chromatography instrument (TAG) which provides hourly time resolved speciation analysis of OA [*Williams et al.*, 2006]. As a result of the hourly time resolution, the TAG provides as many data points in a few weeks of measurements as solvent extracted filters do in a year, thus enabling PMF analysis on organic compounds in a short field campaign and improving the capability to capture the variability in concentrations of OA caused by source emissions and atmospheric processes. By performing PMF analysis on the TAG data, past work has shown that nine different types of OA in an urban environment were resolved, including various SOA and POA sources [*Williams et al.*, 2010].

[6] Bakersfield, CA, was one of two supersites of the California at the Nexus of Air Quality and Climate Change (CalNex) campaign in June 2010. Prior to the CalNex campaign, studies of source apportionment of OA in the Bakersfield region were made with the EC-tracer method and CMB model and focused on OA in winter [*Magliano et al.*, 1999; *Strader et al.*, 1999; *Schauer and Cass*, 2000]. Neither the EC-tracer method nor the CMB model was able to provide insights into different SOA types. Moreover, the primary sources of OA and volatile organic compounds and the concentrations of oxidants in the atmosphere would vary significantly in different seasons. These differences can lead to the different chemical compositions of OA which requires different control strategies. Recently, results of studies of major OA components and SOA formation in the Bakersfield area during the CalNex campaign have been reported [*Liu et al.*, 2012; *Rollins et al.*, 2012]. *Liu et al.* [2012] showed that OA accounted for the majority of the mass of summertime particulate matters and SOA was the dominant component of OA in the Bakersfield site. Additionally, *Liu et al.* [2012] suggested that the majority of SOA was likely formed through gas-to-particle condensation of oxidation products of VOCs. *Rollins et al.* [2012] reported that organic nitrate aerosol accounted for one third of nighttime increase of OA and suggested that reductions in NO_x emissions can reduce OA concentrations. In this study, we take a different approach to investigate source contributions to OA and atmospheric processes to form SOA using a wide range of organic tracers. Compared with bulk organic mass spectra [*Liu et al.*, 2012] and organic nitrates [*Rollins et al.*, 2012], these organic tracers provide unique information for both OA sources and SOA formation pathways. For example, *Zhao et al.* [2013] has shown that multiple gas-to-particle partitioning pathways contributed to SOA formation in the Bakersfield area by examining the measured gas/particle partitioning of known SOA tracers. By performing PMF analysis on organic compounds measured by the TAG during the CalNex field campaign, distinct factors have been extracted, which are associated with specific source types and atmospheric processes based on measured organic compounds, including both primary and secondary organic tracers, in the context of an urban area and the agricultural, natural, and industrial sources present in the region. Based on these identified source types, the effective strategies to reduce OA concentrations are suggested.

2. Methods

2.1. Sampling and Chemical Analysis

[7] Speciated measurements of OA were made with a TAG during the CalNex campaign from 31 May to 27 June 2010 at the Bakersfield supersite, CA. A detailed description of the TAG was provided elsewhere [*Williams et al.*, 2006], and details on updates and operation of the TAG used in this work were provided by *Zhao et al.* [2013]. Briefly, the TAG was updated by adding an activated charcoal denuder into the sampling inlet, as a parallel sampling line to a bypass line made of stainless tubing, so that the gas-phase organics can be efficiently removed by this denuder in the upstream of the collection cell while the ambient air is sampled through the denuder [*Zhao et al.*, 2013]. As a result, the particle-phase organics can be measured with minimal sampling artifacts

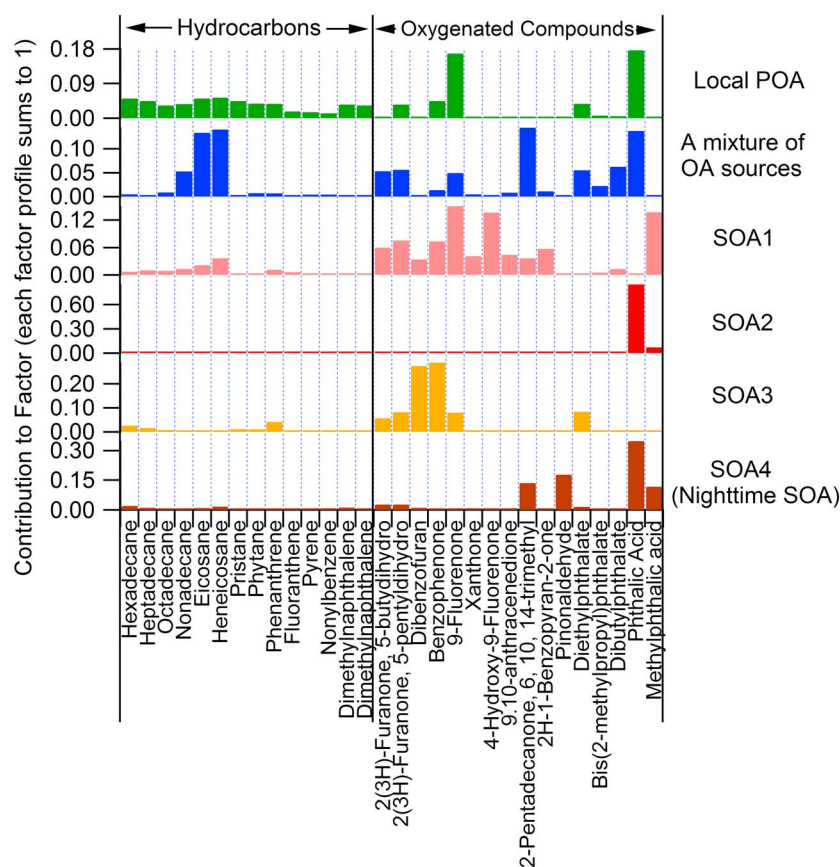


Figure 1. PMF factor profiles. Compounds are generally grouped into hydrocarbons and oxygenated organic compounds.

due to the adsorption of gas-phase organics on the surface of the collection cell.

[8] During sampling, ambient air was pulled at 10 L/min through a PM_{2.5} cyclone from the center of a larger transport flow of 200 L/min drawn from ~5 m above the ground through a 6 in. inner diameter rigid duct, through either the denuder line or a bypass line, and then delivered into an impactor-based collection cell for collection of organics. Only particle-phase organics were expected to be collected while the ambient air was sampled through the denuder (“denuded sample”) and total organics (the sum of collected gas-phase and particle-phase organics) were collected while the ambient air was sampled through the bypass line (“undenuded sample”). The sampling flow was alternated between the denuder line and the bypass line. Following sampling, collected organics were thermally desorbed and injected into a GC/MS for analysis. Identification and quantification of individual compounds were achieved using a quadrupole mass spectrometer (Agilent, 5973) calibrated based on responses to authentic standards that were manually injected into the collection cell at regular intervals throughout the campaign [Kreishberg *et al.*, 2009]. During this campaign, TAG measurements were made in two periods wherein the sampling durations were different. The sampling duration of each sample was 90 min from 31 May to 9 June (Sampling Period I) and 30 min from 10 to 27 June (Sampling Period II). Longer sampling time in Sampling Period I was used to collect a large amount of

organics to facilitate looking for organic molecular tracers for major OA sources. As concentrations of organic molecular tracers measured in Sampling Period I, especially tracers for SOA, were higher than their detection limits, the sampling time was reduced in order to better capture variability in concentrations of organic species. Over the 27 days of measurements, 244 samples of speciated OA were acquired by sampling through denuder line, and over 100 particle-phase organic compounds were identified and quantified.

[9] Supporting measurements conducted concurrently that were relevant to data analysis and discussions in this study included detailed characterization of meteorological conditions, OA, and VOCs. Wind speed and direction were monitored by a propeller wind monitor (R.M. Young, 5130). Details on measurements of submicron OA made with an aerodyne high-resolution time-of-flight aerosol mass spectrometer (AMS) were provided by Liu *et al.* [2012]. VOCs were measured by an automated in situ GC-flame ionization detector/MS system [Gentner *et al.*, 2012]. In addition, ozone was measured using a UV photometric ozone analyzer (Dasibi Inc., model 1008 RS).

2.2. PMF Procedures

[10] The positive matrix factorization (PMF) model describes observed concentrations of organic species as the linear combination of the contributions from a number of

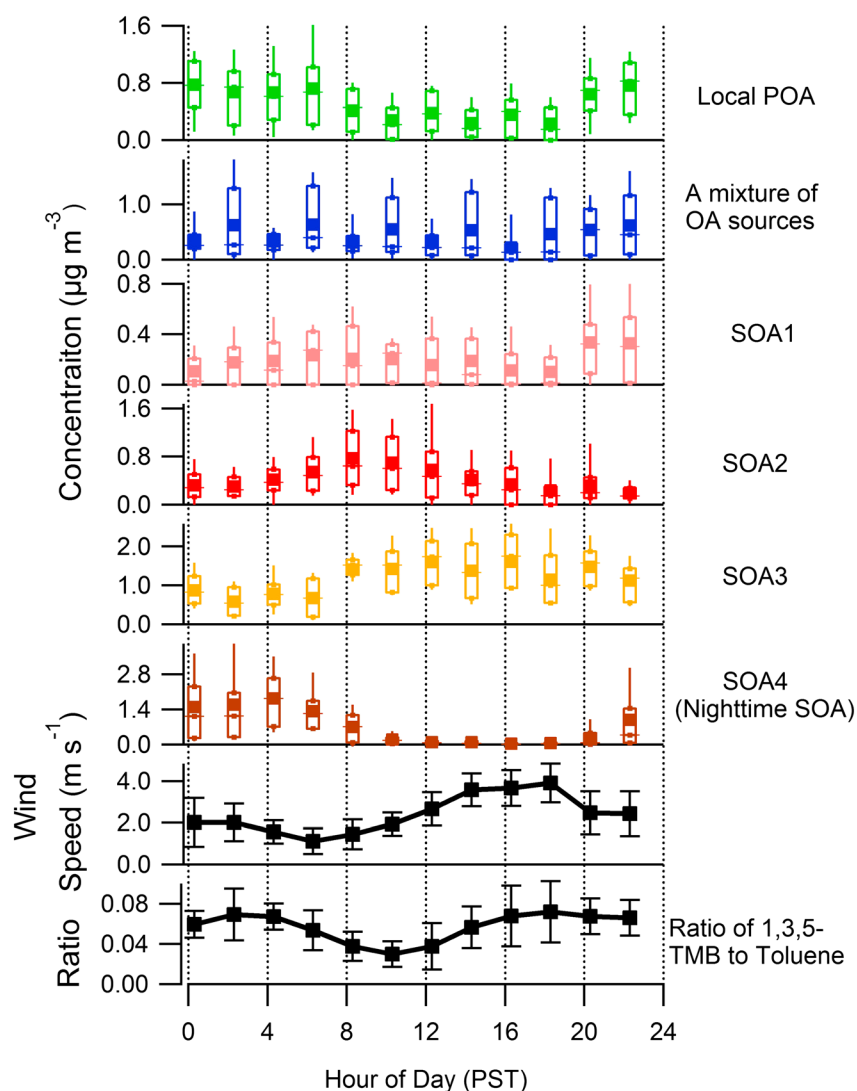


Figure 2. Average diurnal profiles of the mass concentration of each factor, wind speed, and the ratio of 1,3,5-TMB to toluene. In the box plots, the centerline of each box is the median mass concentration, the top and bottom of the box are the 75th and 25th percentiles, the top and bottom whiskers are the 90th and 10th percentiles, and the solid square maker is the mean concentration. In diurnal profiles of wind direction and the ratio of 1,3,5-TMB to toluene, the mean value is plotted with ± 1 standard deviation.

sources with constant profiles [Paatero and Tapper, 1993; Hopke, 2003; Reff *et al.*, 2007; Ulbrich *et al.*, 2009]:

$$x_{ij} = \sum_p g_{ip} f_{pj} + e_{ij} \quad (1)$$

where x_{ij} is the concentration of species j measured in sample i , g_{ip} is the contribution of factor p to sample i , f_{pj} is the concentration of species j in factor p and e_{ij} is the residual not fit by the model. PMF solves the equations for g_{ip} and f_{pj} to best reproduce x_{ij} without a priori knowledge of them based on the selected number of factors (p). The solution to PMF minimizes the object function Q defined as

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{s_{ij}} \right)^2 \quad (2)$$

where s_{ij} is the estimated uncertainty of species j measured in sample i .

[11] As the PMF model allows data points to be individually weighted, the uncertainties associated with organic compounds at different concentration levels can be estimated separately. By estimating the uncertainty using this approach, missing data points can be weighted by assigning a larger uncertainty to them, so compounds or days with many missing points do not need to be removed. This approach provides an advantage over many other methods by achieving longer timelines of observations [Polissar *et al.*, 1998]. In our study, compounds in some samples were not detected because of their low ambient concentrations and short sampling duration. For these data points, one third of the detection limit for each compound was assigned as the concentration, and the uncertainty associated with each of these data points was four times of its concentration, similar to the estimation made by Polissar *et al.* [1998]. The uncertainties for the data points with measured concentrations were estimated using the same equations described by Williams *et al.* [2010]. However, the detection limit of each

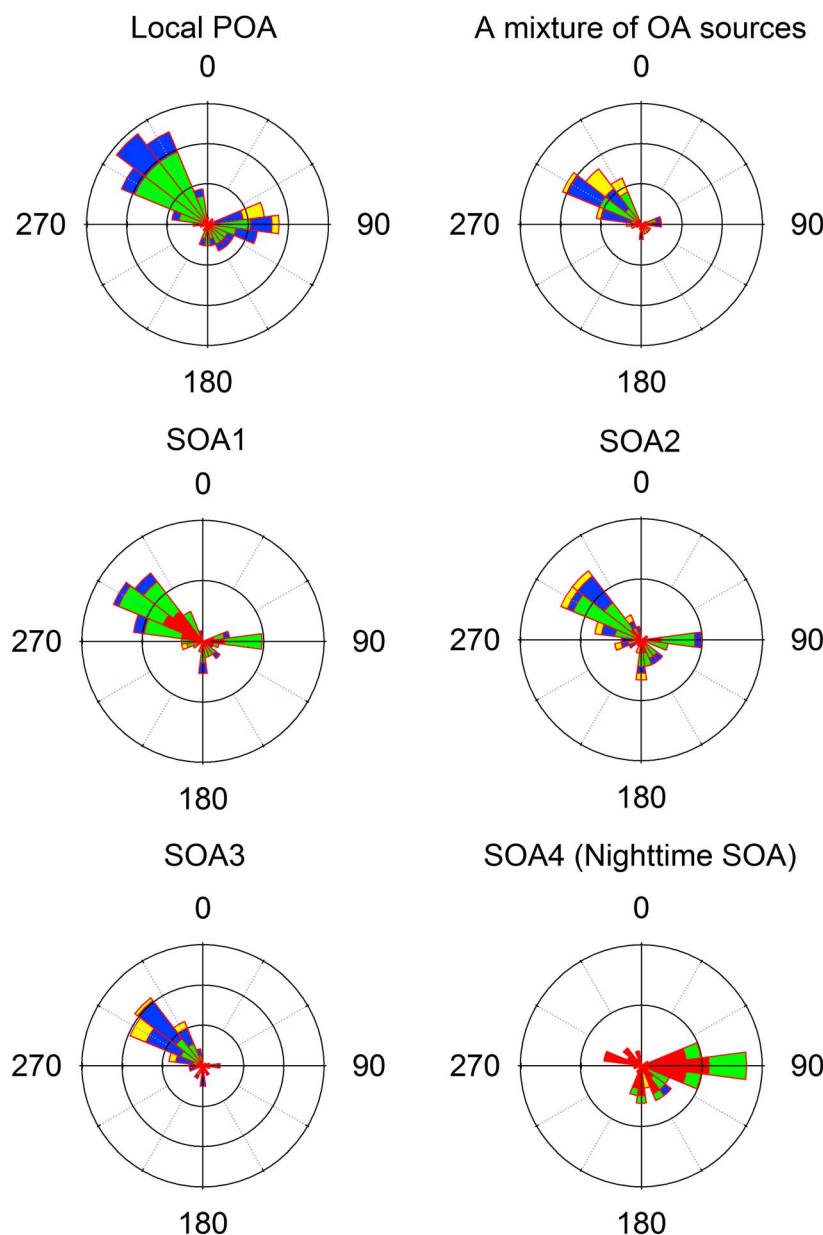


Figure 3. Wind rose plots for six PMF factors using only concentrations larger than the mean concentration in each factor to emphasize the major contributing source directions. The direction from which wind blows is shown in degrees, with 0° (360°) as north, 90° as east, 180° as south, and 270° as west. The relative concentration level is indicated by different colors: yellow > blue > green > red. The frequency of observations is represented by the length of each wedge.

compound was used in our study to better account for the instrument noise, instead of instrument precision derived from the standard deviation of the difference between consecutive data points used by Williams *et al.* [2010].

[12] The criteria we used for inclusion of compounds in PMF analysis were that the timeline of observations covered the entire period of TAG measurements, the compounds were measured in the particle phase (denuded samples), and the percentage of above detection limit data points was greater than 50% over the full timeline of observations. As a result, 30 compounds (listed in Figure 1) in 244 samples were included in the PMF analysis. PMF analysis was applied using the Igor based PMF Evaluation Panel v2.04 [Ulbrich *et al.*, 2009].

[13] Detailed discussions of determination of the optimum number of PMF factors can be found in the literature of Reff *et al.* [2007], Ulbrich *et al.* [2009], and Williams *et al.* [2010], and interpretability of these factors is an important criterion. In our study, the linkage between factors and specific OA source types or atmospheric processes was initially made based on the existing knowledge of specific sources of individual compounds in each factor and was further corroborated by their diurnal profiles and supporting measurements, such as VOCs and meteorological conditions.

[14] Although the sum of concentrations of all compounds included in PMF analysis accounted for only a small fraction of AMS measured OA, the mass contribution of each factor

to measured OA can be calculated by a multivariate fit of the temporal contributions of PMF factors onto total AMS measured submicron OA mass concentrations [Reff *et al.*, 2007; Williams *et al.*, 2010]. Submicron OA accounted for 75% of the organic mass in PM_{2.5} during this field campaign [Liu *et al.*, 2012]. The sum of these calculated mass contributions of factors to OA were defined as reconstructed OA. The regression coefficients for factors provide an additional constraint on the number of factors to be included, since negative regression coefficients are a good indication that the number of factors exceeds the optimum [Reff *et al.*, 2007].

2.3. PMF Results

[15] The variability of the TAG data was best explained by six factors with a value of Q/Q_{expected} equal to 2.5 with F_{peak} (the rotation force parameter, a tool used to explore rotations of the solutions of a given number of factors) set to zero (see Figure S1 in the supporting information). Since the interpretability was an important criterion in determining the optimal number of factors, five-factor and seven-factor solutions were also explored. In comparison with the six-factor solution, the five-factor solution resulted in a convolution of factors 1 and 5 (Figure S2 in the supporting information). The seven-factor solution split factor 6, which was a mixture of anthropogenic and biogenic SOA factors, without providing additional meaningful information (Figure S3 in the supporting information). Because sampling time intervals were different in the two sampling periods, the effect of time intervals on PMF results was examined by averaging the data points in Sampling Period II to have the same time interval as those in Sampling Period I. Six factors were extracted by PMF analysis from the data set with the same time interval in both sampling periods. The correlation coefficient (r) between the similar factors from these two PMF analyses was ~ 1.0 for all four SOA factors, 0.84 for factor 1, and 0.75 for factor 2. The diurnal variations for factors extracted from the same time interval data set displayed the trends as the PMF using different sampling time intervals in the two sampling periods but were less distinct than those due to the lower time resolution. We therefore chose to examine the six-factor solution from PMF analysis using the actual measurement time intervals in both sampling periods in detail to characterize the major components of OA. To facilitate the following discussion, we defined 8:00–20:00 PST as the day and 20:00–8:00 PST as the night.

2.3.1. Factor 1: Local POA

[16] We defined factor 1 as local POA. This factor had the highest contribution from hydrocarbons among the six factors (Figure 1) and had a diurnal profile with higher concentrations at night, consistent with buildup of local emissions into a shallow nighttime boundary layer (Figure 2). Higher concentrations of this factor occurred during the night, at low wind speeds, and with wind coming from all directions (Figures 2 and 3), indicating that it originated mainly from local sources because the Bakersfield site was located near the southern end of the San Joaquin Valley. One of the two main oxygenated compounds present in this factor was 9-fluorenone, which has been identified in primary emissions from motor vehicles [Schauer *et al.*, 1999b]. The other prominent oxygenated compound present in this factor was phthalic acid. Phthalic acid has been used as a tracer for anthropogenic SOA [Schauer *et al.*, 2002b; Fine *et al.*, 2004; Shrivastava *et al.*, 2007], but its average concentration in this factor

accounted for less than 1% of its total measured concentration. We therefore consider this a very minor contribution of SOA adding to this POA dominated factor.

[17] The major known POA sources in Bakersfield were wood burning, meat cooking, and motor vehicles [Schauer *et al.*, 2000], and the average contribution of unknown POA sources to OA was small ($\sim 10\%$) [Schauer *et al.*, 2000; Strader *et al.*, 1999]. Detected tracers for primary emissions in our study were hopanes for motor vehicles and retene for biomass burning [Schauer *et al.*, 1996; Schauer and Cass, 2000]. These tracers were not included in PMF analysis because over 50% of their data points were undetected in denuded samples. Concentrations of POA did not correlate well with those of hopanes. Retene was only observed in a few samples. The major sources of POA are not indicated by their tracers. The reason could be that the contribution of POA to total OA is much smaller than SOA. More information is provided in section 4.

2.3.2. Factor 2: A Mixture of OA Sources

[18] We defined factor 2 as a mixture of OA sources, consisting of both POA and SOA that were unable to be further resolved. While hydrocarbons accounted for a significant fraction of this factor, there was a smaller fraction of each polycyclic aromatic hydrocarbon and a larger fraction of each phthalate relative to the POA factor (Figure 1). Additionally, an SOA tracer, 6,10,14-methyl-2-pentadecanone [Shrivastava *et al.*, 2007], apparently contributed to this factor, relative to the POA factor wherein this tracer was not discernible. The composition of this factor suggests that it was composed of a variety of sources and atmospheric chemical processes. The large differences in the concentration range in alternating intervals of its 2 h diurnal profile were attributed to very different concentrations of this factor observed during the two sampling periods (Figure S4 in the supporting information). The concentrations in Sampling Period I were higher than those in Sampling Period II and were plotted in every other sampling interval. As shown in Figure S4 (supporting information), the concentrations of factor 1 (POA) also displayed differences between the two sampling periods and were smaller in Sampling Period I than those in Sampling Period II. Therefore, the higher concentrations of factor 2 in Sampling Period I could be ascribed to inclusion of more inseparable POA components. The effect of different time intervals in the two sampling periods on PMF results has been shown to be minor. Additionally, strong agreement was found between factors extracted from TAG and AMS data (see section 5). The less amount of POA resolved from factor 2 in Sampling Period I therefore would represent the real atmospheric conditions. The diurnal profiles of the concentration of this factor in two sampling periods were also examined separately, but neither of them had a clear diurnal profile, suggesting again that this factor was most likely a mixture of OA sources.

2.3.3. Factor 3: SOA1

[19] We defined factor 3 as SOA1. The contribution of organic species to this factor was dominated by oxygenated compounds (Figure 1). Methyl phthalic acid has been used as a tracer for anthropogenic SOA [Fine *et al.*, 2004; Williams *et al.*, 2010] and 9,10-anthraquinone has been observed as an oxidation product of PAHs [Helmig *et al.*, 1992; Helmig and Harger, 1994]. The elevated concentration of this factor during 20:00–24:00 PST (Figure 2) was attributed to the low wind

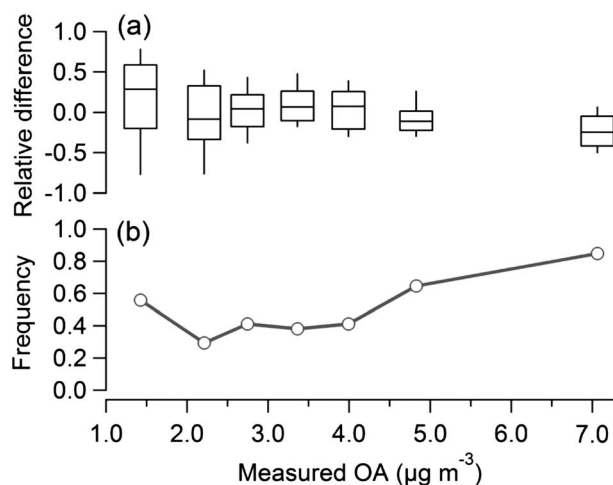


Figure 4. (a) The box plot of the relative difference between reconstructed and measured OA. The centerline of each box is the median of the data, the top and bottom of the box are 75th and 25th percentiles, and the top and bottom whiskers are the 90th and 10th percentiles. The total number of data points is evenly distributed to each concentration interval. (b) The frequency of OA concentrations in each interval observed at night throughout TAG measurements.

speed and low temperature, which would cause the accumulation of gas-phase oxygenated compounds and subsequently favor condensation of them onto particles to contribute to SOA. These condensable oxygenated compounds can be formed locally, and probably include some organic nitrates [Rollins *et al.*, 2012], and can also be produced upwind and transported to the site during the afternoon along with SOA3 (discussed below).

2.3.4. Factor 4: SOA2

[20] We defined factor 4 as SOA2. The contribution of organic species to this factor was dominant from two SOA tracers, phthalic acid and methyl phthalic acid, though other compounds, both hydrocarbons and oxygenated compounds, were present but with much smaller contributions. Evidence that this factor was associated with photochemically produced SOA is apparent when comparing the diurnal profile of this factor with that of the ratio of 1,3,5-trimethylbenzene (TMB) to toluene. Because both 1,3,5-TMB and toluene have similar source types in Bakersfield [Gentner *et al.*, 2012] and 1,3,5-TMB reacts faster with the hydroxyl (OH) radical than toluene does [Atkinson and Arey, 2003], a smaller ratio of 1,3,5-TMB to toluene indicates that the air mass is more oxidized. An opposite trend between the average diurnal profile of this factor and that of the ratio of 1,3,5-TMB to toluene clearly shows that higher concentrations of this factor occurred when gas-phase organics were more oxidized (Figure 2). The highest concentration of this factor occurred in the morning (8:00–9:00 PST) when the wind speed was low (Figure 2), indicating that this SOA was formed locally.

2.3.5. Factor 5: SOA3

[21] We defined factor 5 as SOA3. The concentration of this factor peaked in the afternoon (Figure 2) and correlated with ozone ($r=0.62$). The contribution of organic species to this factor was dominated by oxygenated compounds (Figure 1).

However, the diurnal profile of the ratio of 1,3,5-TMB to toluene did not correlate well with this factor, especially in the afternoon (Figure 2). The afternoon ratio of 1,3,5-TMB to toluene was close to the nighttime ratio, indicating that observed VOCs were fresh and emitted locally without having undergone significant oxidation. Therefore, we infer that SOA in this factor was not dominantly formed through local VOC oxidation by the OH radical but instead was composed primarily of regionally formed, transported SOA. This inference is further supported by relatively high wind speeds (from the northeast) during the observations of high concentrations of this factor (Figures 2 and 3). The high wind speed would carry regional source contributions to the observation site and would dilute local source contributions.

2.3.6. Factor 6: Nighttime SOA (SOA4)

[22] We defined factor 6 as nighttime SOA (SOA4). This factor had its higher concentrations at night with the dominant contribution from SOA tracers of phthalic acid, methyl phthalic acid, 6,10,14-methyl-2-pentadecanone and pinonaldehyde. Pinonaldehyde is a volatile oxidation product of a biogenic VOC, α -pinene, and can contribute to SOA by forming low volatility products, such as dimers [Tolocka *et al.*, 2004; Liggio and Li, 2006]. The factors influencing gas/particle partitioning of pinonaldehyde at this site have been examined in a separate paper [Zhao *et al.*, 2013]. Deconvolution of biogenic and anthropogenic contributions is difficult due to the covariation of chemical transformations leading to SOA, but it is evident that biogenic VOC oxidation products contributed to SOA4 as the higher concentrations of this factor were more frequently observed when the wind blew from the vegetated areas located to the east of the field site (Figure 3).

3. Reconstructed OA

[23] Reconstructed OA based on PMF factors was compared with measured OA to evaluate the capability of the PMF factors derived using organic compounds to capture the variability in concentrations of atmospheric OA. The average concentration of submicron OA measured by AMS was $3.7 \pm 1.8 \mu\text{g m}^{-3}$ throughout the period of TAG measurements, and the average concentration of reconstructed OA was $3.5 \pm 1.6 \mu\text{g m}^{-3}$. Furthermore, good agreement between the reconstructed and measured OA was demonstrated by the relative difference between them that was less than 20% for over 70% of observations (Figure 4a). The relative difference was calculated using the difference between reconstructed OA and measured OA divided by measured OA. The larger relative differences between reconstructed and measured OA mostly occurred at the lower OA concentrations and the negative differences were consistently present at higher OA concentrations. The distribution of the relative difference as a function of the OA concentration could be attributed to larger uncertainties assigned to organic species included in PMF analysis when the atmospheric OA concentrations were low and lack of inclusion of additional organic tracers in the current data set when the atmospheric OA concentrations were high. As shown by Figure 4b, high OA concentrations were mostly observed at night. Organic nitrates have been shown to significantly contribute to nighttime OA in this region [Rollins *et al.*, 2012]. However, no tracers for organic nitrates were identified through TAG measurements in this study.

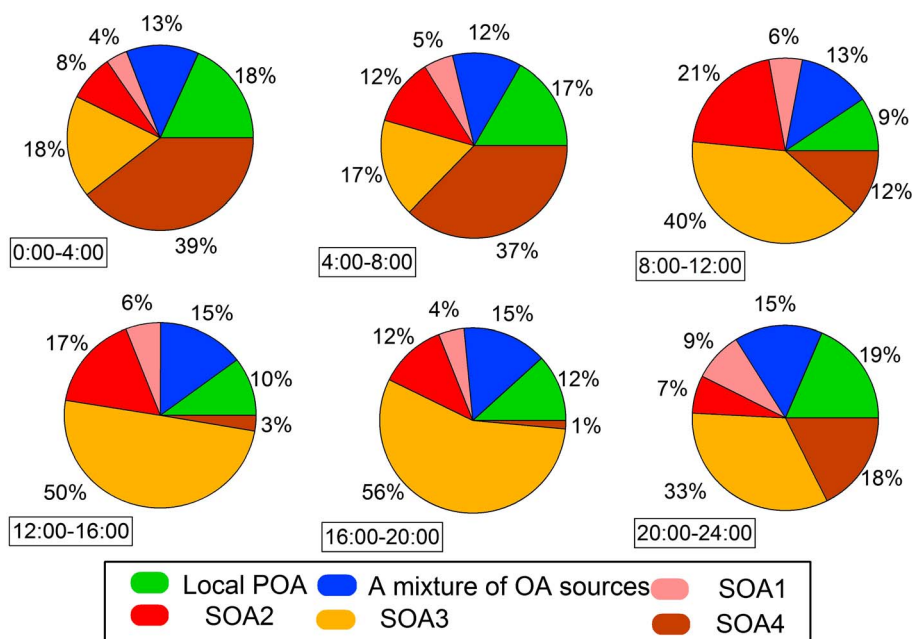


Figure 5. Mean diurnal mass fraction contribution of each factor to total OA displayed in six different periods. The mass concentration of each factor in corresponding time interval is shown in Figure S5 in the supporting information.

4. Source Contributions to OA Mass

[24] The local POA source accounted for an average of 15% of measured OA. The average contribution of POA to measured OA could be up to 28% if all of the mass of the mixture of OA sources was assumed to be POA, but this is surely an overestimate. The emissions in the Bakersfield region are highly complex with cars, trucks, oil and gas extraction and refining operations, agricultural activities, and other sources all potentially contributing some to this POA factor. However, the contributions from specific primary sources cannot be examined in this study because they are small, shown by both lower concentrations of tracers for them and the low POA contribution to total OA, and PMF analysis cannot reliably separate very small factors among the noise and variation of the larger factors.

[25] The contribution of the sum of four types of SOA (SOA1–SOA4) averaged 72% of measured OA and could be up to 85% if the mass in the mixture of OA sources was only considered as SOA. The dominance of SOA in measured OA derived from organic species in this study is consistent with the results reported by Liu et al. (2012) based on PMF analysis of AMS observations in the same site which showed that 80% to 90% of total OA was made up of SOA. We conclude that efforts to control atmospheric OA in this region must focus on understanding and then controlling the sources of SOA precursors or factors leading their transformation into SOA.

[26] The diurnal cycle of the relative contribution of each identified factor to OA (Figure 5 and Figure S5 in the supporting information) was calculated to highlight the dominant component of OA in different periods of the day and night. The largest daytime contributor to measured OA was regional SOA (SOA3), accounting for ~50% of measured OA throughout the day. Nighttime SOA (SOA4) was the

largest contributor to measured OA at night and accounted for 39% of measured OA, but its contribution to measured OA was much smaller during the day, down to ~1% in the afternoon (16:00–20:00 PST). Local SOA (SOA2) also contributed substantially to measured OA during the day and accounted for 21% of measured OA when it reached its highest concentration in the morning (8:00–12:00 PST). The smaller local SOA (SOA1) accounted for less than 10% of measured OA over all periods of the day. The majority of measured OA was composed of local (SOA2, 12%–21%) and regional (SOA3, 40%–56%) during the day. We therefore conclude that control of SOA precursor emissions on both local and regional scales are needed to effectively reduce the daytime OA concentrations, and it is more effective to reduce SOA precursors at the regional scale in the afternoon.

5. Formation Pathways of SOA

[27] Controlling emissions of pollutants involved in the formation of SOA have the potential to reduce OA concentrations [e.g., Liggio and Li, 2006; Na et al., 2007]. In areas where biogenic emissions are oxidized in the presence of anthropogenic pollutants such as SO₂, NO_x, and black carbon, it has become increasingly apparent that SOA formation from biogenic VOCs is substantially enhanced [Goldstein et al., 2009; Surratt et al., 2010; Carlton et al., 2010; Spracklen et al., 2011]. Rollins et al. [2012] has shown that reductions in NO_x can reduce the OA concentration in the Bakersfield region because of the involvement of NO_x in formation of organic nitrates. Here we suggest that the dominant formation pathway for each identified SOA type can be implied by the pathways of SOA tracers contributing to SOA. The pathways of these oxygenated compounds contributing to SOA in each factor were used to

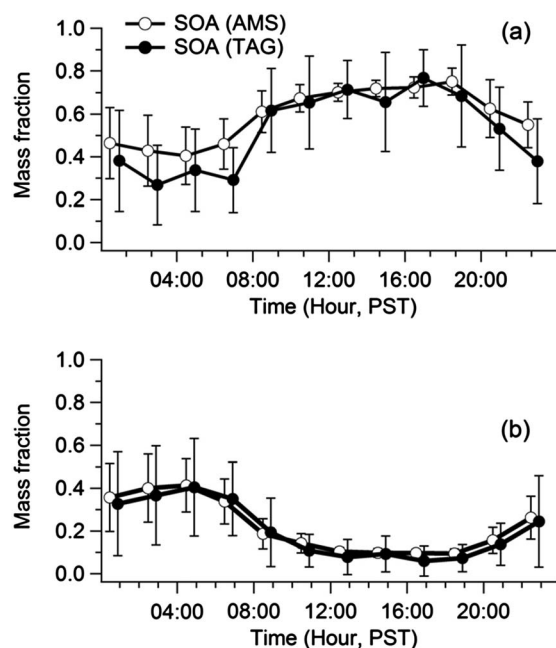


Figure 6. (a) Average diurnal profiles of the mass fraction of daytime SOA in measured OA. TAG daytime SOA is the sum of SOA2 and SOA3 (this study), and AMS daytime SOA is the sum of high O/C aromatic SOA, high O/C alkane SOA, and petroleum SOA [Liu *et al.*, 2012]. (b) Average diurnal profiles of the mass fraction of nighttime SOA in measured OA. TAG nighttime SOA is the sum of SOA1 and SOA4, and AMS nighttime SOA is the sum of low O/C alkane SOA and nighttime OA. The TAG data are shifted slightly to the right for clarity. The vertical bar is 1 standard deviation of the mean.

draw a distinction between direct gas-to-particle condensation wherein oxidation reactions produce low volatility products that condense, secondary gas-to-particle condensation wherein nonoxidation reactions produce lower volatility products that condense, such as reactions between carboxylic acids and ammonia, and reactive uptake wherein compounds expected to be in the gas-phase enter the particle phase through acid-catalyzed reactions. Evidence for these formation pathways occurring in the Bakersfield area during CalNex based on individual compounds—specifically phthalic acid, pinonaldehyde, and 6,10,14-trimethyl-2-pentadecanone has been explored and reported by Zhao *et al.* [2013]. Ketones entered the particle phase primarily through direct gas-to-particle condensation, while phthalic acid was shown to enter the particle phase mainly through reaction with ammonia in the gas phase [Zhao *et al.*, 2013]. It is likely that SOA1 and SOA3 were formed at least partially by direct gas-to-particle condensation because the dominant contribution to the factor profiles of these two factors was from compounds with the ketone functional group. The factor profile of SOA2 was dominated by particle-phase phthalic acid formed through reactions with gas-phase ammonia, indicating the reactions between carboxylic acids and ammonia played a significant role in the formation of SOA2. This formation pathway could be site-specific because it needs excess ammonia to allow these reactions with carboxylic acids to occur. For SOA4 (i.e., the nighttime SOA), the factor profile contained pinonaldehyde,

as well as phthalic acid and 6,10,14-trimethyl-2-pentadecanone. The presence of pinonaldehyde in the factor profile indicates the occurrence of particle-phase reactions in the particles [Zhao *et al.*, 2013]. However, the relative contribution to nighttime OA from these particle-phase reactions cannot be distinguished from the gas-to-particle condensation. Zhao *et al.* [2013] has shown that secondary gas-to-particle partitioning and reactive uptake can substantially increase contributions of phthalic acid and pinonaldehyde to SOA, relative to direct gas-to-particle partitioning. Therefore, control of pollutants involved in these pathways of gas-to-particle partitioning such as ammonia would also lead to reductions in OA concentrations, in addition to control of organic precursors. However, the effectiveness of the reduction in SOA concentrations by controlling ammonia needs further investigation. For example, the reduction in ammonia emissions would lead to the increase of the aerosol acidity which subsequently could improve the SOA formation from particle-phase reactions [Jang *et al.*, 2002; Liggió and Li, 2006].

[28] To substantiate that the formation pathways of SOA can be indicated by individual compounds, SOA factors derived from PMF analysis of organic species measured by TAG (“TAG factors”) were compared to those from PMF analysis of bulk organic mass spectra measured by AMS (“AMS factors”) (Figures 6a and 6b). The AMS factors related to SOA were low O/C alkane SOA, high O/C alkane SOA, low O/C aromatic SOA, high O/C aromatic SOA, petroleum SOA, and nighttime OA [Liu *et al.*, 2012]. These AMS factors were averaged according to the sampling time of TAG measurements. Different types of SOA factors were generally grouped into daytime SOA and nighttime SOA to facilitate the comparison. The SOA factor was categorized into daytime SOA if there was an enhancement in the diurnal profile of its mass fraction in total OA occurring during the day, and was categorized into nighttime SOA if there was an enhancement in the diurnal profile of its mass fraction in total OA occurring during the night. The diurnal profile of the mass fraction of each SOA factor was used for selection of daytime and nighttime SOA because the enhancement in the mass fraction of each SOA factor in total OA indicates a more significant role of this factor playing in the increase of OA concentrations. As a result, daytime SOA factors were SOA2 and SOA3 in TAG factors and high O/C alkane, high O/C aromatic, and petroleum SOA in AMS factors in Liu *et al.* [2012]. The diurnal profile of the mass fraction of TAG daytime SOA (the sum of SOA2 and SOA3) was consistent with that of AMS daytime SOA (the sum of high O/C alkane, high O/C aromatic, and petroleum SOA) (Figure 6a). Consistency in the diurnal profile of the mass fraction of nighttime SOA between TAG nighttime SOA (the sum of SOA1 and SOA4) and AMS nighttime SOA factors (the sum of low O/C alkane SOA and nighttime OA) was also found (Figure 6b). Liu *et al.* [2012] suggested that nighttime OA in AMS factors included both SOA and POA signature, but nighttime OA was considered as SOA for comparison. The remaining factors related to SOA were a mixture of OA sources in TAG factors and low O/C aromatic SOA in AMS factors. The average mass fraction of a mixture of OA sources was approximately the same as that of low O/C aromatic SOA. The consistency of SOA factors between these two studies supports the claim that oxygenated organic compounds measured by the TAG are able to capture the trend of SOA formation.

6. Conclusions and Atmospheric Implications

[29] PMF analysis was performed on 244 particle-phase speciated organic samples, acquired over the span of 1 month, to investigate OA sources. The variability of this data set was best explained by six types of OA sources using PMF analysis. The concentrations of reconstructed OA based on these six factors were in good agreement with the concentrations of measured OA. Local POA accounted for 15% of measured OA. SOA was the dominant component of measured OA throughout the day and night. SOA (the sum of SOA1–SOA4) accounted for an average of 72% of measured OA with the average diurnal variation in the range from 66% at night to 78% during the day. Regional SOA (SOA3, 56%) was dominant during the afternoon and nighttime SOA (SOA4, 39%) was dominant during the night. Local SOA (SOA2) contributed substantially in the morning, accounting for 21% of measured OA.

[30] Our results suggest that the formation of summertime SOA in this Bakersfield region occurred through multiple pathways, some of which may be regionally specific due to the unique mixture of emissions in this air shed. SOA in SOA1 and SOA3 is suggested to be formed dominantly through direct gas-to-particle condensation. Secondary gas-to-particle partitioning is suggested to be one of major pathways for the formations of local SOA (SOA2). Particle-phase reactions contribute to a discernible amount to formation of nighttime SOA, but their contributions are not well constrained in this study. We conclude that direct gas-to-particle partitioning is the dominant pathway to form SOA in the Bakersfield region.

[31] Since SOA is the dominant component of summertime OA, control of SOA is the most effective strategy to reduce OA. However, the best control measure for each type of SOA (SOA1–SOA4) to enable effective reductions in OA concentrations is likely different. During the day, reducing SOA requires control of SOA precursor emissions on both local and regional scales, and control of regional SOA precursor emissions is likely more effective to reduce SOA in the afternoon. Control of ammonia emissions would reduce the formation of local SOA (SOA2). However, the reductions in ammonia emissions could increase the formation of nighttime SOA. Further studies are required to investigate the effects of control of ammonia on reductions in the overall OA. At night, SOA formed from oxidation of biogenic and anthropogenic SOA precursors is evident, yet their contributions are unable to be estimated separately and consequently a clear strategy to control nighttime SOA is not suggested in this study, in addition to control of NO_x suggested by Rollins *et al.* [2012].

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