## Organic aerosol composition and sources in Pasadena, California, during the 2010 CalNex campaign

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[1] Organic aerosols (OA) in Pasadena are characterized using multiple measurements from the California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign. Five OA components are identified using positive matrix factorization including hydrocarbon-like OA (HOA) and two types of oxygenated OA (OOA). The Pasadena OA elemental composition when plotted as H: C versus O: C follows a line less steep than that observed for Riverside, CA. The OOA components from both locations follow a common line, however, indicating similar secondary organic aerosol (SOA) oxidation chemistry at the two sites such as fragmentation reactions leading to acid formation. In addition to the similar evolution of elemental composition, the dependence of SOA concentration on photochemical age displays quantitatively the same trends across several North American urban sites. First, the OA/ $\Delta$ CO values for Pasadena increase with photochemical age exhibiting a slope identical to or slightly higher than those for Mexico City and the northeastern United States. Second, the ratios of OOA to odd-oxygen (a photochemical oxidation marker) for Pasadena, Mexico City, and Riverside are similar, suggesting a proportional relationship between SOA and odd-oxygen formation rates. Weekly cycles of the OA components are examined as well. HOA exhibits lower concentrations on Sundays versus weekdays, and the decrease in HOA matches that predicted for primary vehicle emissions using fuel sales data, traffic counts, and vehicle emission ratios. OOA does not display a weekly cycle-after accounting for differences in photochemical aging —which suggests the dominance of gasoline emissions in SOA formation under the assumption that most urban SOA precursors are from motor vehicles.

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## 1. Introduction

[2] Atmospheric aerosols have been the subject of intensive ongoing research due to their important impacts on the radiative forcing of climate, which occur through several mechanisms that include the scattering and absorption of solar radiation as well as the alteration of the formation and properties of clouds [International Panel on Climate Change, 2007]. In addition, atmospheric aerosols reduce visibility [Watson, 2002] and increase cardiac and respiratory disease in humans [Dockery and Pope, 1994; Dockery et al., 1993]. The impact of aerosols on climate, the environment, and human health is determined, in part, by particle size and chemical composition. In many environments, a large fraction  $(\sim 50\%)$  of the submicron aerosol mass in the troposphere is organic aerosol (OA), but the sources, composition, and chemical processing of OA are not well understood [Jimenez et al., 2009]. Generally, OA is comprised of thousands of individual compounds that are either directly emitted into the atmosphere (i.e., "primary" OA or "POA") or formed though chemical reactions involving gas phase precursors (i.e., "secondary" OA or "SOA"). The multiple sources and complexity of molecular composition represent major challenges for understanding and prediction of OA properties.

[3] Elevated aerosol concentrations are often associated with megacities such as Los Angeles (LA). Particulate matter concentrations in LA are among the highest in the United States (American Lung Association, State of the air, 2011, http://www.stateoftheair.org/), and multiple previous measurement campaigns have aimed to characterize aerosols in this region. These campaigns include the 1987 Southern California Air Quality Study [Lawson, 1990], the 1997 Southern California Ozone Study (SCOS97-NARSTO) [Croes and Fujita, 2003], the Study of Organic Aerosol at Riverside, which took place in the summer (SOAR-1) and fall (SOAR-2) of 2005 [Docherty et al., 2011], and the 2009 Pasadena Aerosol Characterization Observatory (PACO) [Hersey et al., 2011]. In addition, several research flights were performed over California and LA during the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites Campaign (ARCTAS-CARB) [Jacob et al., 2010]. Using data from these campaigns, it has been shown that SOA represents a majority of the total OA mass in both Riverside [Docherty et al., 2008] and Pasadena, CA [Hersey et al., 2011], which is similar to findings in other urban regions [Jimenez et al., 2009]. The gas phase precursors for SOA potentially have many sources including vehicle emissions, the biosphere, biomass burning, and food cooking [Bahreini et al., 2012; Hodzic et al., 2010; Schauer et al., 1999, 2002b]. Also, vehicle emissions, food cooking, biomass burning, and primary biogenics have all been identified as sources of POA in the South Coast Air Basin [Williams et al., 2010; Wonaschutz et al., 2011].

[4] The California Research at the Nexus of Air Quality and Climate Change (CalNex) field campaign was conducted in 2010 and was a multi-institution effort to address outstanding questions regarding atmospheric chemistry processes over the state of California and the adjacent Pacific coastal region [*Ryerson et al.*, 2013]. The CalNex campaign featured several research aircraft, the research vessel Atlantis off the California coast, and two ground sites in Pasadena and Bakersfield. A major scientific goal for

CalNex was to improve scientific understanding of atmospheric aerosols in California and, specifically, to characterize important SOA precursors and formation pathways, as well as the impacts of aerosols on radiative forcing and cloud formation [National Oceanic and Atmospheric Administration, 2008]. For CalNex, the Pasadena ground site was uniquely equipped to characterize aerosols and, especially, organic aerosols. In total, approximately 70 gas and particle phase measurements were taken at the site representing, to our knowledge, one of the largest studies of aerosols and their precursors. A full list of the instrumentation is available in the CalNex overview [Ryerson et al., 2013] and also at http://tinyurl.com/CalNex. Additionally, the ground site featured many state-of-the-art aerosol instruments including several that had never been fielddeployed previously.

[5] Here we present a detailed analysis of aerosol measurements from multiple instruments, including online and offline bulk and single particle methods, deployed to the Pasadena ground site during CalNex. The goals of this work are to quantitatively evaluate SOA formation for the South Coast Air Basin and compare it against other major urban regions, as well as to determine the contributions of various sources to organic aerosol mass loadings. In particular, the relative importance of diesel versus gasoline emissions in secondary organic aerosol formation has been a source of scientific controversy [Bahreini et al., 2012; Gentner et al., 2012] and will be examined here. To achieve these goals, the following approach is utilized: (1) using positive matrix factorization (PMF), the components of OA are identified and characterized (section 3.2); (2) the POA emission ratios with elemental carbon (EC) and CO are determined and rationalized (section 3.3); (3) the dependence of SOA concentration on photochemical age is quantified and compared against previous measurements conducted in Riverside, Mexico City, and the northeastern United States (section 3.4); and (4) the weekly cycles (or lack thereof) in POA and SOA concentrations are analyzed in the context of understanding the relative contributions to each from diesel and gasoline motor vehicles (section 3.5). The unique findings of this work include the observation of a similar SOA formation rate for Pasadena versus other urban locations, the first reported weekly cycle for POA concentrations, and an improved analysis of the contribution of diesel emissions to SOA formation based on the lack of a weekly cycle in SOA concentrations.

### 2. Experimental

## 2.1. CalNex Ground Site in Pasadena, CA

[6] The CalNex Pasadena ground site was located on the California Institute of Technology (Caltech) campus in Pasadena, CA (34.1406 N, 118.1225 W, 236 m above mean sea level). The measurement period was 15 May 2010 00:00 to 16 June 2010 00:00 (local time). The Pasadena ground site was located 18 km northeast of downtown Los Angeles. Pasadena lies within the South Coast Air Basin, which is bordered on the north and east by the San Gabriel, San Bernardino, and San Jacinto mountains as well as on the southwest by the Pacific Ocean. Pasadena is part of the dense, urban Los Angeles metropolitan area. The prevailing wind direction during daytime in Pasadena was from

the southwest due to the sea breeze, which brought air masses from the Santa Monica and San Pedro Bays through central Los Angeles to Pasadena (FLEXPART back trajectories are available in section A of the supporting information). At nighttime, winds were weaker and were most frequently from the southwest or southeast. Sunrise and sunset were approximately 05:30 and 20:00 (local time) during the sampling period. Boundary layer height, temperature, and relative humidity (RH) data are presented in section A of the supporting information.

## 2.2. AMS Sampling and Analysis

[7] The concentrations of submicron nonrefractory  $(nrPM_1)$ organic and inorganic (nitrate, sulfate, ammonium, chloride) aerosol particles were measured using an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (hereinafter referred to as "AMS") [DeCarlo et al., 2006]. The AMS sampled from an inlet equipped with a PM<sub>2.5</sub> cyclone located 2 m above the roof of the container housing the instrument. The sampled air passed through a 6.8 m insulated copper inlet line and a dryer prior to analysis by the AMS. The resulting data were averaged over 2.5 min intervals. The ion paths through the time-of-flight chamber were alternated between "V" and "W" modes every 150 s, and the reported concentrations correspond to V-mode acquisition periods only. Size distributions were acquired during every V-mode acquisition by operating the AMS in particle time-of-flight mode [Jimenez et al., 2003]. All data were analyzed using standard AMS software (SOUIRREL v1.51 and PIKA v1.10) within Igor Pro 6.2.1 (WaveMetrics, Lake Oswego, OR) (D. Sueper, ToF-AMS Analysis Software, 2011, http://cires.colorado.edu/ jimenez-group/wiki/index.php/ToF-AMS Analysis Software).

[8] It is well known that for most ambient sampling conditions, a collection efficiency (CE) correction must be applied to the AMS data to account for particle bounce from the AMS vaporizer [Middlebrook et al., 2012]. Mass concentrations are typically calculated with a default CE of 0.5. The degree to which particles bounce, and hence collection efficiency, is a function of particle phase, which is influenced by the relative humidity of the sampling line, the acidity/neutralization of the sulfate content, the ammonium nitrate content, and the organic liquid content [Middlebrook et al., 2012]. The sample flow was dried as described above, and the sulfate content was largely neutralized (see Appendix). Thus, these experimental parameters are not expected to impact CE. Ammonium nitrate concentrations varied widely during the measurement period though, and accordingly, a nitrate-dependent CE is applied following Nemitz [2010]. Quantifying the organic liquid content is challenging for ambient samples; however, the ratio of AMS mass to Scanning Mobility Particle Sizer (SMPS) mass exhibits no dependence on the amount of OA oxidation as measured by O: C indicating that phase changes associated with organic material are either not occurring or are not influencing the particle bounce and CE. In total, the aerosol mass concentrations measured by the AMS after applying the CE correction, which ranged from 0.5 to 0.7, are consistent with most other measurements from the Pasadena ground site. The relevant intercomparisons are discussed in section B of the supporting information for this paper, including details regarding how mass concentrations are calculated from SMPS number distributions.

[9] High-resolution (HR) analysis of the mass spectra, including application of the HR AMS fragmentation table, was carried out following previously published procedures [*Aiken et al.*, 2007, 2008]. The reported AMS mass concentrations were determined from the HR AMS spectra and are very similar to unit mass resolution (UMR) concentrations, within 5%, that are determined using the UMR fragmentation table of *Allan et al.* [2004]. The HR fragmentation table was also used to obtain the OA mass spectral matrix for the PMF analysis described in the next paragraph.

[10] The OA mass spectral matrix was deconvolved into components using PMF, a receptor-based factorization model [Paatero and Tapper, 1994]. The application of PMF to AMS spectra has been discussed in detail previously [Ulbrich et al., 2009; Zhang et al., 2011]. The same method is used here including the PMF2 algorithm, which is run in robust mode via the PMF Evaluation Tool panel (v2.03). The high-resolution organic aerosol mass spectra for the entire CalNex campaign were analyzed, and the full range of the high-resolution spectra was utilized  $(m/z \ 12-204)$ . Error matrices were calculated using the methods of Allan et al. [2003] and Ulbrich et al. [2009]. Weak variables (i.e., m/z's) with lower signal-to-noise ratios (0.2 < S/N < 2) were down-weighted by a factor of 3, and bad variables  $(S/N \le 0.2)$  were down-weighted by a factor of 10 following the recommendations of Paatero and Hopke [2003]. For the results presented here, the model error was set to zero.

# 2.3. Colocated CalNex Measurements Utilized in This Study

[11] A SMPS (Model 3936, TSI Inc.) measured ambient number distributions between 7 and 690 nm mobility diameter. The SMPS was operated at a sampling frequency of 5 min and used the same inlet as the AMS (including drier) except that the aerosol flow passed through an additional 2.1 m of copper inlet line (0.3 lpm flow). For the SMPS, the aerosol flow rate was 0.3 lpm and the sheath flow rate was 3 lpm. Ambient particle number distributions were also measured from 60 to 1000 nm using an Ultra-High Sensitivity Aerosol Spectrometer (Droplet Measurement Technologies), which also used the same inlet as the AMS (including drier), but the sample flow passed through an additional 2 m of inlet line (0.3 lpm flow). A White-Light Optical Particle Counter (WLOPC; Climet model 208 fitted with a multichannel analyzer) measured size distributions from 500 to 4000 nm. Hourly PM<sub>2.5</sub> organic carbon (OC) and elemental carbon (EC) concentrations were measured using a Sunset Labs field OC/EC analyzer [Peltier et al., 2007]. Blank-corrected optical OC and EC data from the Sunset field analyzer are reported here. Measurements of refractory black carbon (rBC) were performed with a Single Particle Soot Photometer (Droplet Measurement Technologies) [Schwarz et al., 2006], as well as with a Soot Particle Aerosol Mass Spectrometer (SP-AMS; Aerodyne Research and Droplet Measurement Technology) [Onasch et al., 2012]. The concentrations of semivolatile and particulate organic molecular tracers were measured by 2-D Thermal Desorption Aerosol Gas Chromatography Mass Spectrometry (2DTAG; UC-Berkeley and Aerosol Dynamics) [Worton et al., 2012]. PM<sub>2.5</sub> nitrate and sulfate concentrations were measured with a Particle-Into-Liquid Sampling and Ion Chromatography (PILS-IC) system [Orsini et al., 2003]. The Particle Analysis by Laser

Mass Spectrometry (PALMS) instrument provided number fractions for individual particle composition classes from 190 to 4000 nm [*Froyd et al.*, 2009; *Thomson et al.*, 2000]. The PALMS instrument also measures scattered light from single particles allowing for calculation of particle size in addition to particle classification. Volume concentrations of the different PALMS particle classes were calculated by multiplying the volume concentration size distribution determined from the SMPS or WLOPC measurements by the fractions of the different PALMS particle types in each size bin. Particle optical extinction for PM<sub>1</sub> was measured at 532 nm and 630 nm by a Cavity Attenuated Phase Shift instrument [*Kebabian et al.*, 2007; *Massoli et al.*, 2010]. All of the online measurements described in this paragraph were located at the CalNex ground site described above.

[12] Data from offline particulate matter measurements are included in this paper as well. In particular, size-resolved elemental concentrations were determined by X-ray fluorescence (XRF) analysis of Mylar substrates from a rotating drum impactor. The XRF analysis was performed at the Advanced Light Source at Lawrence Berkeley National Lab. Using the XRF results, the mineral dust concentration corresponding to oxides of Al, Si, Ca, K, Fe, and Ti is estimated from the elemental concentrations following the method of Simon et al. [2011] and Malm et al. [1994]. The particulate metal concentration is calculated as the sum of the mass concentrations of Mg, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, and Pb. The Cl concentrations from XRF measurements are reported as refractory chloride (rCl), since the placement of samples under vacuum for analysis is expected to cause evaporation of nonrefractory species such ammonium chloride. The time resolution of the XRF data was 1.5 h. Offline OC measurements of high-volume PM<sub>2.5</sub> samples collected with quartz fiber filters were performed using three separate sets of filters and two laboratory-based Sunset Labs OC/EC analyzers (NIOSH TOT protocol). For clarity, the three sets of filters are named according to the institution that collected them: Georgia Institute of Technology (GIT), U.S. Environmental Protection Agency (EPA), and University of North Carolina (UNC). Following the technique of Russell et al. [2009], Fourier transform infrared (FTIR) spectroscopy analysis of Teflon filter samples provided PM2.5 OA and organic functional group mass concentrations. All samples for offline analyses were collected at about 12 m above ground level on the roof of the Keck Building located on the Caltech campus approximately 0.3 km southwest of the ground site.

[13] The concentration of  $O_3$  was measured by UV differential absorption (49c Ozone Analyzer, Thermo Scientific), and CO concentrations were measured by two vacuum-UV resonance fluorescence instruments (AL5001 and AL5002, Aerolaser) [*Gerbig et al.*, 1999]. An in situ Gas Chromatography Mass Spectrometry (GC-MS) instrument provided the mixing ratios for a variety of VOCs [*Gilman et al.*, 2009]. A fluorescence assay by gas expansion instrument was utilized to determine the OH concentrations were measured using chemiluminescence (42i-TL with Mo converter, Thermo Scientific), and NO<sub>2</sub> was measured with Cavity-Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS) [*Thalman and Volkamer*, 2010]. The CE-DOAS instrument was located on the Caltech Millikan Library roof,

which is approximately 45 m tall and 0.5 km southwest of the Pasadena ground site.

[14] Meteorological data were acquired by a station that included a temperature/RH sensor (Campbell Scientific Inc., HMP35C) and a wind monitor (R.M. Young, 05103). The boundary layer height was determined using a ceilometer (Vaisala, CL31) following the method described by Haman et al. [2012], and the ceilometer results have been shown to be consistent with boundary layer heights from Weather Research Forecasting (WRF) modeling [Washenfelder et al., 2011]. To track the origins of the air masses sampled at the ground site, a modified version of the FLEXPART Lagrangian particle dispersion model [Stohl et al., 2005] was used to calculate back trajectories of air masses based on advection and turbulent mixing processes. The main modification consists of using time-averaged winds from the WRF (version 3.3) meteorology model instead of instantaneous winds to improve uncertainties within the FLEXPART model [Brioude et al., 2012]. The WRF output has a spatial grid of  $4 \text{ km} \times 4 \text{ km}$ , with a temporal resolution of 30 min and 60 vertical levels. Lastly, all linear regressions in this paper are performed as orthogonal distance regressions (ODR) using Igor Pro 6.2.1 software.

## 3. Results and Discussion

# 3.1. Total Submicron Aerosol Composition at the Pasadena Ground Site During CalNex

[15] While the focus of this paper is OA, a survey of the total aerosol composition can provide valuable context for the OA analysis, and providing such a context is the goal of this section (3.1). (Note: Comparisons with previous campaigns as well as additional figures regarding the total submicron aerosol composition are shown in section C of the supporting information.) The time series for the nrPM<sub>1</sub> species and EC are shown in Figure 1b. In addition, the diurnal cycles of the nrPM<sub>1</sub> species and EC are shown in Figure 2a. The time series for metals, mineral dust, and refractory chloride (rCl) are shown in Figure 1c, and for comparison, the PALMS particle type time series are included in Figure 1 as well (Figures 1d and 1e). The fractional composition of the total submicron mass is determined by combining the AMS, Sunset Analyzer, XRF, and PALMS measurements, and is summarized in Figure 2c. (Note: See Figure 2 caption for details regarding which instrument measured each species as well as how the PALMS data are converted to mass concentration.) In the interpretation of the data in Figures 1 and 2, it is important to consider some differences in size cuts of the measurements. First, the XRF measurements used in Figures 1 and 2 correspond to a size cut of 1150 nm aerodynamic diameter. By linearly interpolating the size-resolved XRF measurements, the average overestimate relative to the actual PM<sub>1</sub> concentrations was found to be approximately 30%. Second, the online Sunset OC/EC analyzer was equipped with a PM<sub>2.5</sub> cyclone for most of the campaign. From 12 to 16 June, the EC measurement was performed while switching between  $PM_{2.5}$  and  $PM_1$  cyclones, and the ratio of the  $PM_1$ EC to the linearly interpolated PM<sub>2.5</sub> EC was 0.93 (±0.19 standard deviation). Thus, while the EC data in Figures 1 and 2 may overestimate the true  $PM_1$  EC concentrations, it is expected that this error will be reasonably small (~7%). Despite these overestimates of refractory mass, the total

HAYES ET AL.: AEROSOL COMPOSITION IN PASADENA



**Figure 1.** (a) CO concentration. (b) The nonrefractory aerosol concentrations sampled by the AMS. The measured species are organics (OA), nitrate (NO<sub>3</sub>), sulfate (SO<sub>4</sub>), ammonium (NH<sub>4</sub>), and nonrefractory chloride (nrCl). The elemental carbon (EC) concentration was measured in situ by a Sunset analyzer. For completeness, the EC data include occasional periods when a PM<sub>1</sub> cyclone was used instead of a PM<sub>2.5</sub> cyclone (12–16 June). (c) Refractory aerosol mass concentrations as measured by XRF (rCl: refractory chloride). Particle type volume concentrations measured by the PALMS for (d) PM<sub>1</sub> and (e) for particles between 1 and 2.5 µm diameters. All size cuts are aerodynamic diameters, and the PALMS data have been converted from geometric diameters (1 µm aerodynamic diameter = 0.784 µm geometric diameter).

 $PM_1$  concentration is still dominated by nonrefractory species (OA + sulfate + nitrate + ammonium + nrCl) that account for 93% of the measured mass. Similarly, particle types measured by the PALMS instrument that are predominately composed of nonrefractory material comprised 90% of submicron aerosol volume (Figure 3).

[16] A clear diurnal cycle is observed for most nrPM<sub>1</sub> species. As shown in Figure 2, the maxima in the EC and CO (commonly used combustion emission tracers) diurnal cycles are both observed between 12:00 and 13:00 PDT (local time). These maxima do not coincide with the Los Angeles County morning rush hour, which occurs between about 06:00 and 08:00 PDT [*Caltrans*, 2010]. Instead, they appear to result from polluted air masses initially emitted in the source-rich regions west and south of Pasadena. The wind speed and wind direction measured at the ground site are consistent with the transport of this plume to Pasadena over several hours. In addition, FLEXPART back trajectories show that the air masses over the Pasadena ground site when EC and CO concentrations are highest have significant

footprint residence times over downtown LA as well as the Ports of LA and Long Beach, which are regions with significant combustion emissions.

[17] Compared to EC and CO, the OA concentrations peak later in the day, about 3 pm, which corresponds to the same time of day when air masses over the Pasadena ground site were the most photochemically processed (Figure 2b). The photochemical age for the air mass over the Pasadena site was calculated with two different methods: first, by using the ratio of 1,2,4-trimethylbenzene to benzene, as described in Parrish et al. [2007], and second, by defining the photochemical age as  $-\log_{10}(NO_x/NO_y)$  similar to *Kleinman* et al. [2008]. All photochemical ages were calculated using a standard OH radical concentration of  $1.5 \times 10^6$  mol cm<sup>-</sup> For reference, the daily OH radical concentrations averaged for the whole campaign at the Pasadena site was  $1.3 \times 10^6$ mol cm<sup>-3</sup>. Interestingly, when using the NO<sub>y</sub>/NO<sub>y</sub> method, the photochemical age slowly increases from 00:00 to 06:00 local time, likely due to N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> formation, which are  $NO_x$  sinks [*Chang et al.*, 2011]. Outside of this



**Figure 2.** (a) Diurnal profiles for the nonrefractory  $PM_1$  mass concentrations (from AMS) and for EC (from Sunset Analyzer). (b) Diurnal cycles of CO and photochemical age. The photochemical age is determined using the method of *Parrish et al.* [2007] and the ratio of 1,2,4-trimethylbenzene to benzene (solid line), or following *Kleinman et al.* [2008] and defining the photochemical age as  $-\log_{10}(NO_x/NO_y)$  (dashed line). (c) Average PM<sub>1</sub> mass concentration (in  $\mu g/m^3$ ) for the ground site (15 May 00:00 to 16 June 00:00) including both refractory and nonrefractory components. Concentrations of mineral dust, metals, and refractory chloride (rCl) were determined from XRF. The sodium concentration is estimated from PALMS sea-salt volume concentrations using a NaNO<sub>3</sub> density of 2.1 g cm<sup>-3</sup> [*Zelenyuk et al.*, 2005] and a sodium to sea-salt mass ratio of 0.308 [*Hall and Wolff*, 1998]. All error bars indicate standard errors of the means.

time range, however, the diurnal cycles of the two photochemical age estimates show good agreement. [18] The diurnal cycle for OA is relatively flat and low dur-

ing the early morning hours, 00:00 to 06:00, suggesting a

small role for nighttime chemistry driven by either nitrate radicals or aqueous chemistry (RH peaked during this time of day). The lack of aqueous chemistry may be driven by the low oxidant concentrations at night. In parallel work,



**Figure 3.** Average volume concentration (in  $\mu$ m<sup>3</sup> cm<sup>-3</sup>) of the different PALMS particle types for (a) PM<sub>1</sub> and (b) particles between 1 and 2.5  $\mu$ m diameters at the Pasadena ground site during CalNex. Size ranges correspond to aerodynamic diameters.

*Zhang et al.* [2012] showed that for Pasadena, the aerosol water was not an important absorbing phase and instead the partitioning coefficient for organics was correlated with OA mass. This result suggests that semivolatile organic compounds are primarily partitioning to the organic phase.

[19] The submicron nitrate diurnal cycle is different from OA with a peak in the morning. The afternoon decrease in nitrate can be attributed to both vertical dilution due to the increase in boundary layer height as well as the higher temperatures and lower RH values that favor evaporation of ammonium nitrate [Neuman et al., 2003]. In Pasadena, both nitric acid and ammonia exhibit peaks around noon and elevated concentrations in the afternoon, which is consistent with volatilization of ammonium nitrate [Veres et al., 2011; Ellis et al., manuscript in preparation, 2012]. The diurnal cycle of sulfate is not influenced by temperature because ammonium sulfate is nonvolatile at atmospheric temperatures, and the sulfate maximum is observed in the afternoon, which may be due to advection to the ground site from sources west and south of Pasadena and/or photochemical production of sulfate.

[20] In addition to the diurnal cycles, substantial multiday variability is evident in Figure 1. In particular, from 2 to 6 June, there appears to be a high pollution episode where a steady increase in organic aerosol concentrations occurs that is most evident during the nighttime and morning hours. A similar, second high pollution episode is observed at the end of the campaign (13-16 June). These episodes were likely the result of synoptic conditions that trapped pollution in the LA Basin overnight in the boundary layer and in residual layers aloft that tend to contain more aged air [Lu and Turco, 1995]. Recirculation of pollution in the LA Basin has been recognized for several decades [e.g., Blumenthal et al., 1978; Moore et al., 1991; Ulrickson and Mass, 1990]. Additionally, a distinct period of greater marine influence is observed between 20 and 25 May. The highest concentrations of rCl are observed during this period, as well as a prominent rCl diurnal cycle (Figure 1c). Dimethyl sulfoxide concentrations, a well-known indicator of marine influence, are also elevated during this period and exhibit a similar diurnal pattern (data not shown).

[21] The PALMS single-particle instrument provides important complementary information regarding aerosol composition at the Pasadena ground site. In particular, the PALMS is capable of characterizing refractory and supermicron aerosols that cannot be measured using the AMS. As stated in the first sentence of this section, the focus of this paper is OA, but a survey of the total aerosol composition can provide valuable context for the OA analysis, hence the inclusion of the PALMS results here. The volume concentration time series for particle composition types identified by the PALMS single-particle instrument are shown in Figures 1d and 1e. In addition, the campaign average volume concentrations are summarized in the pie charts shown in Figures 3a and 3b. The particle composition types were identified from PALMS mass spectra following the method described in Froyd et al. [2009]. For instance, biomass burning spectra are identified by a prominent K<sup>+</sup> peak along with organic peaks and a lack of other metals. Vanadium with organic species was used as a tracer to identify aerosol from heavy oil combustion (e.g., from ship engines), which allows for the definition of a particle class termed "Oil Combustion" similar

to previous work with other single-particle instruments that studied emissions from commercial ports [Ault et al., 2009; Healy et al., 2009]. Since the PALMS is a single-particle instrument, it is capable of determining aerosol mixing state. One consideration when comparing the PALMS results against the AMS and other measurements is that the classification of particles typically follows the most abundant components in a particle, but the PALMS volume concentration for each particle type also includes secondary material on the particle that may even dominate the particle volume at the time of detection. For the Pasadena ground site, it was observed that all the particle types contained substantial amounts of nitrate, sulfate, and organics, which indicates that condensation of secondary material is occurring on primary aerosols (e.g., sea salt and mineral dust) and/or particle mixing is occurring through coagulation. The nitrate observed on sea-salt particles is also at least partially due to the heterogeneous reaction between sea salt and nitric acid as discussed in the Appendix. An important conclusion that can be made from the data in Figure 3 is that the PM<sub>1</sub> aerosol volume concentration is dominated by sulfate/OA/nitrate type particles and the supermicron aerosol is dominated by sea-salt particles. These findings are generally consistent with the mass concentration data from XRF and AMS measurements. The PALMS biomass burning results are discussed further in section 3.2.3.

# **3.2.** Source Apportionment of Organic Aerosol Mass by Positive Matrix Factorization

# 3.2.1. Mass Spectra, Time Series, and Diurnal Cycles of the Organic Aerosol Components

[22] The OA components from the PMF analysis were identified by their mass spectra, diurnal cycles, and elemental composition, as well as by the concentration ratios and correlations of their time series with tracers. Figure 4 shows the mass spectra and time series for the five identified components. Additionally, Figure 5 shows the diurnal profiles of the OA components and the campaign-average fractional contribution of each component to the total OA concentration, as well as a stacked plot illustrating the fractional contributions to OA mass by time of day. A summary of correlations between the OA components and various tracers is provided in section D of the supporting information. The five PMF components identified are (1) hydrocarbon-like organic aerosol (HOA), (2) cooking-influenced organic aerosol (CIOA), (3) local organic aerosol (LOA), (4) semivolatile oxygenated organic aerosol (SV-OOA), and (5) low-volatility oxygenated organic aerosol (LV-OOA). The naming based on volatility is adopted according to several studies showing a relationship between high oxygenation and lower volatility for the OOA components [e.g., Cappa and Jimenez, 2010; Huffman et al., 2009; Jimenez et al., 2009; Lanz et al., 2007; Ulbrich et al., 2009]. The HOA component has been previously described as a surrogate for primary combustion OA, and the SV-OOA and LV-OOA components as surrogates for "fresher" and "aged" SOA, respectively. [Aiken et al., 2008; Jimenez et al., 2009; Ulbrich et al., 2009; Zhang et al., 2007b]. The identification of CIOA is consistent with previous research that has shown food cooking, which includes activities such as seed oil frying and meat charbroiling, is an important source of fine organic aerosol in urban environments [e.g., Mohr et al., 2011; Schauer et al., 2002b]. The precise source (or sources)



**Figure 4.** (a) Mass spectra for the five components identified in the PMF analysis. The mass spectra are colored by the ion type to indicate the contribution of each ion type to the mass spectra. For clarity, spectra are shown only to m/z 150, although spectra were measured up to m/z 204. (b) Time series of the PMF components.

of the LOA component is not known; however, similar, highly variable, nitrogen-rich components have been identified in Mexico City [*Aiken et al.*, 2009]; Riverside, CA [*Docherty et al.*, 2011]; Crete [*Hildebrandt et al.*, 2011]; and New York City [*Sun et al.*, 2011]. This component is termed "local organic aerosol" because the LOA time series exhibits high-frequency fluctuations that indicate a relatively local source for this component. (Autocorrelation plots of the component time series are shown in Figure D-7 of the supporting information.) The LOA mass represents only a small portion of the total OA mass (5%). Still, the reoccurrence of LOA in different urban areas is an interesting finding. Additional details regarding how the PMF solution was selected are provided in section D of the supporting information.

[23] The mass spectra and elemental ratios of the five components displayed in Figure 4a are similar to those reported in previous studies [e.g., *Aiken et al.*, 2009; *Hersey et al.*, 2011; *Mohr et al.*, 2011]. For HOA, O:C is relatively high (0.14) but not out of the range of previously reported values. For instance, O:C values as low as 0.02 (Riverside, CA) and 0.03 (Barcelona) [*Docherty et al.*, 2011; *Mohr et al.*, 2011] and as high as 0.16 (Mexico City) and 0.17 (Beijing) have been reported for HOA components [*Aiken et al.*, 2009; Huang et al., 2010]. The diurnal cycle of HOA is similar to that of EC (and rBC) with a peak between 13:00 and 14:00 PDT (local time), and HOA and EC (and rBC) show high correlation (see Table D-1 in the supporting information and section 3.3 below). Therefore, as discussed in section 3.1, for other primary emissions, it appears that a large portion of the HOA is transported to Pasadena over a period of several hours from the west and south, which is consistent with the relatively high HOA oxidation. Evidence that HOA is dominated by primary sources is given in section 3.4.1. In addition, the Van Krevelen diagram analysis described in the next section indicates that the types of oxygen-containing functional groups in HOA are different from OOA (on average), which suggests a different oxidation pathway(s). A possible cause for the oxygen content in HOA is therefore heterogeneous oxidation, although other causes including primary emission of oxygenates cannot be conclusively ruled out using the results reported here. The CIOA component is more oxygenated than HOA, which is consistent with previous reports and the known presence of oxygenated compounds such as fatty acids and cholesterol in food cooking aerosol [Mohr et al., 2011; Robinson et al., 2006; Sun et al., 2011]. The HOA and CIOA spectra are compared in detail in section D of the supporting



**Figure 5.** (a) Diurnal profiles for the PMF components. Shaded regions indicate uncertainties calculated using bootstrapping [*Ulbrich et al.*, 2009]. (b) Diurnal profiles of the PMF components by percent mass. (c) Diurnal profiles of the oxygen-to-carbon and hydrogen-to-carbon elemental ratios for the total OA mass. Error bars indicate the standard error of the mean. (d) The campaign average contribution of each PMF component to the PM<sub>1</sub> organic aerosol mass concentration.

information. The diurnal cycle of CIOA exhibits peaks near mealtimes with a smaller peak between 14:00 and 15:00 PDT and a larger peak between 21:00 and 22:00 PDT similar to the cooking organic aerosol diurnal cycles observed for other field measurements [*Allan et al.*, 2010; *Crippa et al.*, 2013; *Mohr et al.*, 2011; *Sun et al.*, 2011]. The lunchtime and dinnertime peaks are both slightly delayed from traditional American mealtimes. The delays could be due to transport time from areas south and west of Pasadena. The delay in the dinnertime peak may also be the result of the convolution of the emission rates with the lower boundary layer in the evenings and thus reduced vertical dilution of CIOA.

[24] Both SV-OOA and LV-OOA display higher O:C compared to the other OA components for Pasadena, and LV-OOA is the most oxygenated as expected for more aged SOA. The SV-OOA and LV-OOA O:C values (0.38 and 0.8, respectively) are similar to those measured at Barcelona (0.32 and 0.75), New York City (0.38 and 0.68), and Riverside (0.29 and 0.72) [Docherty et al., 2011; Mohr et al., 2011; Sun et al., 2011], and are consistent with the range of O:C values for OOA reported by Ng et al. [2011]. The diurnal cycle of SV-OOA is very strong and peaks in the afternoon. This pattern is likely due to photochemical age peaking at a similar time compared to when SOA precursors emitted during the morning rush hour arrive in Pasadena (along with EC and CO). The temporal variability

of SV-OOA therefore indicates this component is closely linked to in-basin photochemical production of SOA, as has been seen in other studies [*Aiken et al.*, 2009]. In contrast, LV-OOA does not show a strong diurnal variation on average, but the LV-OOA time series does vary substantially during the campaign measurement period. In particular, there is an increasing trend in LV-OOA concentrations during the 2–6 June period when there is evidence for recirculation of polluted air within the South Coast Air Basin impacting aerosol concentrations. A buildup of LV-OOA concentrations during this period is consistent with describing this component as "aged," since the OA is expected to be increasingly oxidized during periods of recirculation.

[25] The mass spectrum of LOA is distinct from the other OA components and contains prominent ions that are characteristic of amines:  $CH_4N^+$  (m/z 30),  $C_2H_4N^+$  (m/z 42),  $C_3H_6N^+$  (m/z 56),  $C_3H_8N^+$  (m/z 58),  $C_5H_{10}N^+$  (m/z 84), and  $C_5H_{12}N^+$  (m/z 86) [*McLafferty and Turecek*, 1993]. The large contribution of nitrogen to this factor (N : C = 0.05) is explained by the substantial presence of these ions. The contribution of LOA to the total mass for each listed amine fragment ranges from 4% for  $CH_4N^+$  to 89% for  $C_5H_{12}N^+$ . In total, the LOA component accounts for 34% of the measured amine mass, and the contributions from the other PMF components are 31% (LV-OOA), 15% (HOA), 13% (SV-OOA), and 8% (CIOA). As discussed in section D of



**Figure 6.** Van Krevelen diagram for Pasadena during the CalNex campaign (red crosses) and for Riverside, CA during the SOAR-1 campaign (blue crosses). The PMF factors identified for Pasadena (hexagons) and Riverside (squares) are shown as well. The linear regression analyses correspond to the total OA data.

the supporting information, the correlations of LOA with other measured species (e.g., VOCs and metals) suggest that LOA sources are related to industrial processes, especially paint application, but the results are not conclusive.

[26] Shown in Figure 5c are the diurnal profiles for the total OA elemental ratios (O:C and H:C). The diurnal trend in the elemental ratios is mostly consistent with the trends in the OA components determined from the PMF analysis. In the early morning hours, the O:C ratio is the highest, which suggests the presence of highly aged, likely secondary, aerosol. Indeed, during this period, LV-OOA is the dominant OA component. In the afternoon (~14:00), there is a strong decrease in O: C, which can be attributed to the arrival of POA at the Pasadena ground site and/or the formation of fresh secondary organic aerosol. In the evening (~21:30), there is second minimum in the O:C, but this occurs during a period of low photochemical age (Figure 2), which implies that the ground site is impacted at this time by POA. As seen in Figure 5, this evening O: C minimum matches the peak in CIOA, a primary OA component with relatively low oxygen content. An interesting difference between the PMF and elemental ratio diurnal trends is the peak in H:C that is observed in the morning (~08:00) and is likely due to primary emissions from the local morning rush hour. This peak is 3 to 4 times smaller than the H:C peaks for the afternoon and evening events also associated with POA, however, indicating a very weak influence from the local rush hour. The PMF analysis is not expected to resolve components that are less than approximately 5% of the OA mass [Ulbrich et al., 2009], and therefore, the absence of this weak local contribution in the PMF results is not surprising.

[27] From Figure 5d, if total OOA is taken as a surrogate for SOA, and the sum of HOA, CIOA, and LOA is taken as a surrogate for POA, then it can be concluded that SOA is dominant at the Pasadena ground site, which is consistent with earlier findings in Riverside, CA [Docherty et al., 2008].

On average, the total OA mass for the measurement period is composed of 66% OOA (SV-OOA+LV-OOA), and this percentage lies between that observed for a selection of "urban" and "urban downwind" sites [*Zhang et al.*, 2007b]. This percentage is also similar to previous results from measurements based in Pasadena. In particular, *Hersey et al.* [2011] reported that during the PACO campaign in May/ June 2009, 77% of OA was classified as OOA, and *Turpin et al.* [1991] reported that during the summer of 1984, SOA contributed roughly half of the OA mass. In contrast, there is a wide range of SOA to OA ratios reported for areas east of Pasadena over the past several decades (~20–70%) [*Docherty et al.*, 2008, and references therein].

# **3.2.2.** The Atmospheric Evolution of H:C Versus O:C and the Elemental Ratios of the Organic Aerosol Components

[28] To relate the elemental composition of the OA components to each other as well as to the bulk OA, the H: C and O: C values from the combined AMS/PMF analysis are plotted in a Van Krevelen diagram (Figure 6). Within a Van Krevelen diagram, more oxidized organic compounds lie at the lower right, and different oxidation reactions fall along individual straight lines. For instance, oxidation of a methylene group (-CH2-) to a carbonyl group (-C(=O)-) corresponds to a slope of -2, and oxidation of a methylene group to an alcohol group (-C(-OH)) corresponds to a slope of 0. Other reactions or combinations of reactions relevant to OA may lead to a variety of slopes in the Van Krevelen diagram as well, which makes attributing a particular slope to a specific chemical reaction difficult in the case of ambient field measurements. Despite this complexity, the Van Krevelen diagram is still useful for constraining the reactions that are responsible for the aging of OA, including for SOA models and their comparison to measurements [e.g., Murphy et al., 2011].

[29] Elemental ratios have been reported previously for the SOAR-1 campaign in Riverside, CA [*Heald et al.*, 2010], and these data are included in Figure 6 as well. The slope of the Van Krevelen diagram for bulk OA is different when comparing the data from Pasadena and Riverside. The regression analysis for Pasadena results in a best-fit slope of -0.64, whereas a slope of -1.1 is obtained for Riverside. However, when the OOA factors are analyzed alone, they correspond to a line with a slope of -0.55 similar to other field measurements [*Ng et al.*, 2011], which is consistent with methylene fragmentation reactions leading to carboxylic acids.

[30] Given that the composition and chemical evolution of OOA in Pasadena and Riverside are similar within this analysis, the differences in the slopes for bulk OA in the Van Krevelen diagram cannot be explained by changes in SOA oxidation chemistry. The composition of the HOA measured at the two locations is dissimilar, however. The HOA in Riverside exhibits a very low O:C ratio (0.02), while in Pasadena, HOA is more oxidized (O:C=0.14). Thus, it is proposed that the different slope for Riverside is due to the atmospheric mixing of fresh HOA-rich particles into the air mass above the site. In Riverside, the addition of less oxidized HOA to the air mass results in the steep slope observed in that location. Contrastingly, in Pasadena the more oxidized HOA does not influence the slope strongly when mixing occurs because the Pasadena HOA falls near the line defined by the OOA components in the Van Krevelen diagram.

[31] Based on the diurnal cycles of HOA for the two sites, it seems that that the Pasadena HOA is more oxidized because it has undergone more photochemical aging relative to the Riverside HOA. In Riverside, the HOA concentration peaks in the morning as expected for fresh emissions from the local morning rush hour traffic [*Docherty et al.*, 2011], consistent with the location of the Riverside site downwind and nearby large highways. In Pasadena, the HOA concentration peaks around 13:30, however, due to advection over several hours from the west and south. We note that the major combustion tracers follow similar diurnal trends for the two sites.

[32] It was also observed by Ng et al. [2011] that HOA components occupy a different space of the Van Krevelen diagram relative to OOA and display variability that can be approximated by a line with a -2 slope. The HOA components for Riverside and Pasadena shown in the Van Krevelen diagram presented here follow a similar line, which is indicative of HOA aging. As described already, a slope of -2 is consistent with functionalization of a methylene chain with carbonyls. For Pasadena, the HOA component also correlated with several ketones (see 2DTAG data discussed in section D of the supporting information), which provides further evidence that carbonyl groups may be an important oxygen-containing functional group for HOA.

# **3.2.3.** Constraints on the Biomass Burning Contribution to the Organic Aerosol Mass

[33] An apparent discrepancy between the combined AMS/PMF analysis and the PALMS measurements is that the latter classified 12% of the PM<sub>1</sub> aerosol volume as biomass burning but the AMS does not show a significant amount of biomass burning influence as indicated by the ratio of the organic mass at m/z 60 to total organic mass ( $f_{60}$ ) [Cubison et al., 2011]. (Note: The possible contribution of organic acids to  $f_{60}$  is accounted for by simultaneously analyzing  $f_{44}$  in an  $f_{44}$  versus  $f_{60}$  plot as described previously by Cubison et al.) Also, a biomass burning organic aerosol component is not identified in the PMF analysis, in which OA components accounting for about 5% or more of the OA mass are expected to be resolved [Ulbrich et al., 2009]. Acetonitrile, a tracer for biomass burning, is generally near background concentrations (100-150 parts per trillion by volume, pptv) except for several high concentration events that are short in duration, do not correlate with the PALMS biomass burning particles, and could be related to nearby solvent use (e.g., in the Caltech campus). It is possible that potassium-containing particles from sources other than biomass burning such as meat cooking [Hildemann et al., 1991; Schauer et al., 1999], which can represent a substantial fraction of the potassium in some urban regions [Aiken et al., 2010; Zhang et al., 2010], may be classified as biomass burning by the PALMS algorithm due to the presence of potassium and abundant organic species. If cooking activities were the dominant source of the PALMS biomass burning particles, however, then the PALMS biomass burning volume concentration would be expected to correlate with the CIOA mass concentration, which is not the case (R = -0.03). An alternative explanation is that the primary biomass burning mass is small, and there is a large amount of secondary mass that has condensed on the biomass burning particles. (Similarly, the primary biomass burning particles may have coagulated with secondary aerosol particles.)

The particles would then be classified as biomass burning by the PALMS algorithm, but their measured volume would be significantly increased by secondary material (e.g., SOA, nitrate, sulfate, and ammonium). Finally, it is also possible that the biomass burning particles are very aged as the result of long-range transport and that due to aging, they are difficult to identify with the AMS biomass burning tracers or PMF [Cubison et al., 2011]. When the observations described in this paragraph are evaluated together, then the best explanation for the discrepancy is that while 12% of submicron particles (by volume) contained some biomass burning material, the overall mass of these particles at the Pasadena ground site was dominated by condensation or particle coagulation of nonbiomass burning material. Based on the limit of AMS/PMF analysis to resolve small fractions of OA, we estimate that primary biomass burning material contributed <5% to submicron aerosol mass during the study.

## **3.3.** Evaluation of Primary Organic Aerosol Emission Ratios With EC and CO

[34] The HOA concentration correlates strongly with EC determined from the online Sunset analyzer (R = 0.71), and the ratio of HOA to EC can provide valuable insight regarding the source of this OA component. To explore this correlation further, a scatter plot of HOA versus EC mass concentration data is plotted in Figure 7a. The data points in the plot are colored with the corresponding NO<sub>v</sub> to  $\Delta CO$ ratios. Periods with higher diesel influence are expected to exhibit higher (NO<sub>v</sub>/ $\Delta$ CO) [Ban-Weiss et al., 2008a; Parrish et al., 2007]. The ratio is not corrected for dry deposition losses of nitric acid though, and thus, it cannot be treated as a quantitative metric. In addition, the gray-shaded areas in Figure 7a indicate the range of POA to EC emission ratios for gasoline and diesel vehicles that were measured during summer 2006 at the Caldecott Tunnel in California [Ban-Weiss et al., 2008b]. The HOA to EC ratios at the Pasadena ground site overlap the range of POA to EC ratios from the Caldecott Tunnel. A linear regression analysis of the Pasadena data yields a line with a slope of 1.82, which is close to the upper limit of the POA to EC ratios reported in the tunnel study. The Pasadena ratio is at times higher, but this difference could be due to changes in the emission ratios of vehicles between 2006 and 2010, or the larger influence of cold starts for our data set versus warm-running vehicles for the Caldecott Tunnel. In Pasadena, for periods more influenced by diesel emissions, as indicated by high (NO<sub> $\nu$ </sub>/ $\Delta$ CO), generally lower HOA to EC ratios are observed. Specifically, the best-fit slope is 1.51 for  $(NO_v/\Delta CO) > 0.124$ , which corresponds to the highest 10th percentile of  $(NO_{\nu}/\Delta CO)$ values. This finding is consistent with the emission ratios reported by Ban-Weiss et al. [2008b] and suggests that both diesel and gasoline vehicle emissions are contributing to the HOA mass.

[35] A correlation between HOA and CO is also observed (R=0.59). A stronger correlation is observed between CO and the sum of HOA and CIOA (R=0.71), however. Shown in Figure 7b is a scatter plot of the CO and the HOA+CIOA data. The improved correlation when the CIOA mass concentration is added to the HOA mass concentration is surprising because cooking is not considered a major source of carbon monoxide, although it is a significant source of organic aerosol [*Allan et al.*, 2010; California Air Resources Board, California



**Figure 7.** (a) HOA versus EC concentration measured in situ by the Sunset analyzer. Fits are shown for the entire plot (solid line) and for only data points corresponding to high  $NO_y/\Delta CO$  ratios (dashed line). The gray-shaded regions indicate the range of expected slopes for gasoline and diesel vehicles based on the reported emission ratios of *Ban-Weiss et al.* [2008b] and a 1.34 OM : OC. (b) The sum of HOA and CIOA versus CO concentration. Linear fits are shown for data points corresponding to high HOA (solid line) and high CIOA concentrations (dashed line).

emission inventory data, 2008, http://www.arb.ca.gov/ei/ emsmain/emsmain.htm; Harley et al., 1997]. Emissions of CO have been measured from certain cooking activities [Lee et al., 2001], but it is still a possibility that the CIOA component contains particulate mass from noncooking sources that also emit CO (e.g., gasoline vehicles). Therefore, it is most reasonable to characterize this component as "cookinginfluenced" but not purely from cooking sources. It should be noted that different PMF solution rotations were explored using the FPeak parameter as discussed in the supporting information. There are rotations that exhibit lower correlations between CIOA and CO, but HOA + CIOA always displays a higher correlation than HOA with CO (within the constraint of not substantially diminishing the correlation between HOA and rBC). In addition, these alternative solutions exhibit lower correlations between HOA and rBC, as well as between HOA + CIOA and CO.

[36] The data in Figure 7b are also colored by the relative amount of CIOA, so that the ratios of HOA to CO and CIOA to CO can be at least partially resolved. For periods when HOA concentrations are high (i.e., greater than 90% of the sum of HOA and CIOA), the correlation with CO is very strong (R=0.9) and the linear slope is  $6.4 \,\mu g \,\mathrm{m}^{-3} \,\mathrm{ppmv}^{-1}$  when using a CO background (x intercept) of 105 ppbv, which is comparable to slopes found in previous studies [Aiken et al., 2009]. In contrast, for periods when CIOA concentrations are high, the linear slope is  $13 \,\mu g \,m^{-3} \,ppmv^{-1}$ , more than twice that for HOA. The steeper slope for CIOA is indicative of significant cooking sources for CIOA that, as stated earlier, produce a larger amount of organic aerosol relative to CO [McDonald et al., 2003]. A lower limit on the relative amount of CIOA mass from cooking sources can be estimated using the observation that the linear regression slope of CIOA is about twice that of HOA when the mass concentrations are plotted versus CO. Assuming that CO is overwhelmingly from vehicle emissions and no CO is emitted from cooking sources, then CIOA would be 50% from cooking sources on average with the remainder from vehicle emissions (i.e., the additional cooking organic aerosol mass would double the mass concentration versus CO slope relative to HOA). This percentage is a lower limit because some CO could be coemitted with cooking organic aerosol, for instance, from burning of charcoal [Bhattacharya et al., 2002], and that would raise the percentage of CIOA from cooking above 50%. This approach is a simplistic approximation, but the lower limit appears to be reasonable given that the diurnal cycles and spectral characteristics of CIOA are consistent with previous studies. In addition, comparison of the CIOA concentration against that predicted from the amount of organic mass measured by the AMS at m/z 55 following Mohr et al. [2011] indicates that approximately 75% of CIOA is from cooking sources (see section D of the supporting information for the details of this comparison). A higher percentage up to almost 100% is also possible given the uncertainties in the comparison.

[37] An alternative approach for analyzing the correlation with CO is to use a multilinear regression instead of filtering the data for periods of high HOA or CIOA influence. For completeness, a multilinear regression was performed where HOA and CIOA were the independent variables and CO was the dependent variable. Emission ratios of 8.0 and  $16 \,\mu g \, m^{-3} \, p m v^{-1}$  were obtained for HOA and CIOA, respectively (using 105 ppbv background CO as above). This result is similar to that described in the preceding paragraph, which indicates both approaches for treating the data are robust.

# **3.4.** The Quantitative Dependence of Secondary Organic Aerosol Concentration on Photochemical Oxidation

## 3.4.1. Increases in the Organic Aerosol to $\Delta CO$ Ratio With Photochemical Age

[38] To evaluate if the timescales and efficiency of SOA formation observed in Pasadena are similar to other urban regions the evolution of (OA/ $\Delta$ CO) as a function of photochemical age is plotted in Figure 8, where  $\Delta$ CO is the CO concentration enhancement over its background concentration. The background CO is estimated to be between 85 and 125 ppbv using CO measurements taken aboard the NOAA WP-3D aircraft off the LA coastline at altitudes less



Figure 8. The evolution of  $OA/\Delta CO$  versus photochemical age for Pasadena during CalNex. The measured ratios are averaged into 25 bins according to photochemical age. The enhanced CO ( $\Delta$ CO) is the ambient CO minus the estimated background CO (105 ppb). The standard error of OA/ $\Delta$ CO is smaller than the size of the data point and therefore is not plotted. Instead, error bars representing the uncertainty in the ratio due to an uncertainty of ±20 ppbv in background CO are shown. Photochemical age is determined by two methods: (1) following *Parrish et al.* [2007] and using the ratio of 1,2,4-trimethylbenzene to benzene (green), and (2) following Kleinman et al. [2008] and defining the photochemical age as  $-\log_{10}(NO_x/NO_v)$  (red). All photochemical ages have been standardized to an OH radical concentration of  $1.5 \times 10^6$  mol cm<sup>-3</sup>, and the corresponding OH exposure for a given photochemical age is shown on the top axis. The gray region is adapted from DeCarlo et al. [2010] and represents the evolution of OA/ $\Delta$ CO observed in the northeastern United States and the Mexico City area. The black horizontal line is the ratio of (HOA + CIOA + "background LVOOA") to  $\Delta$ CO. (Inset) Evolution of the PMF component concentrations normalized to  $\Delta CO$  versus photochemical age. Data are binned according to photochemical age.

than 200 m (Latitude range: 32 to 35, Longitude range: -117to -120). A concentration of 102 ppbv was the minimum observed and concentrations below 110 ppbv were regularly observed. Accordingly, the background CO was taken to be 105 ppb when calculating (OA/ $\Delta$ CO), and the error bars in Figure 8 represent the variability in the data if the background CO is taken to be either 85 or 125 ppb. Given the observed CO values off the LA coastline this range represents a conservative estimate of the uncertainty in background CO. The CO enhancement is assumed to be a conservative tracer of urban combustion emissions that are also a source of aerosols and aerosol precursors, and thus, normalizing the OA concentration to CO will remove the effect of dilution. Photochemical formation of CO from VOCs or destruction of CO by OH reactions were estimated to perturb CO concentrations minimally over these time and spatial scales [Griffin et al., 2007].

[39] The gray region in Figure 8 represents  $OA/\Delta CO$ versus photochemical age observations from previous campaigns in Mexico City and the northeastern United States as summarized by DeCarlo et al. [2010]. All the data sets display an increase in the OA/ $\Delta$ CO ratios with photochemical age due to secondary organic aerosol formation. The Pasadena OA/ACO versus photochemical age plot follows the upper limit of the range of previously reported values, although the differences should not be over interpreted given the uncertainties associated with the background CO determination (indicated by the error bars) and the photochemical age calculations. The photochemical age uncertainty has been discussed extensively in previous papers and is due to, in part, the presence of mixed sources with different emission profiles and spatial distributions [e.g., Kleinman et al., 2007; Parrish et al., 2007]. We evaluate this potential source of error in section E of the supporting information, and use sensitivity studies to determine that photochemical age may be underestimated by approximately 10% in our analysis. This error is in the accuracy rather than the precision, and thus, it does not impact relative comparisons for Pasadena such as the weekday versus Sunday comparison described below. The underestimation may impact comparisons with other campaigns though, and thus it is concluded that SOA production per unit CO in the South Coast Air Basin is not different from other locations given our estimated errors. (In section E of the supporting information, we also demonstrate that OH radical chemistry dominates over Cl radical chemistry in the oxidation of the VOCs used to calculate photochemical age.) The data in Figure 8 suggest that similar precursors are responsible for SOA production in Pasadena, Mexico City, and the northeastern United States, and that the precursors are emitted proportionally to CO. These conditions then imply a relatively constant mix of the important SOA precursor and CO sources across the locations discussed.

[40] To understand the similarity in OA/ $\Delta$ CO, it is important to consider the emission ratios for SOA precursors (e.g.,  $\Delta VOC/\Delta CO$ ), especially given the long-term decrease of CO concentrations in the United States [Parrish et al., 2002] that could potentially influence OA/ $\Delta$ CO values. The emission ratios of aromatic, alkyne, and alkene VOCs with CO have remained constant between 2002 and 2010, as has the ratio for acetaldehyde [Warneke et al., 2012], a species that correlates strongly with OOA (R = 0.81 in Pasadena) and is dominated by secondary sources after sufficient photochemical processing of emissions. Furthermore, it has been shown that urban VOC emissions at different locations in the U.S. have similar composition and emission ratios with CO (within a factor of 2) [de Gouw et al., 2012; Warneke et al., 2007]. The similarity of OA/ $\Delta$ CO values described here for different campaigns spanning several years is consistent with the lack of change in  $\Delta VOC/\Delta CO$  over spatial and temporal scales for the U.S. However, in Mexico City, the  $\Delta VOC/\Delta CO$  ratios are on average about a factor of 2 higher than that in the U.S. [Bon et al., 2011], but the OA/ $\Delta$ CO values for Mexico City are not substantially higher than that for Pasadena or the northeastern U.S. This observation highlights the possibility that there may be unmeasured organic compounds that are SOA precursors and do not follow the  $\Delta VOC/\Delta CO$  emission trends discussed above. Lastly, we note that while plotting  $OA/\Delta CO$  versus photochemical age should account for differences in the amount of aging, the average daily OH radical concentrations at the sites were fairly similar where measurements were available:  $1.3 \times 10^6 \text{ mol cm}^{-3}$  for Pasadena and  $1.5 \times 10^6 \text{ mol cm}^{-3}$  for Mexico City [*Hodzic and Jimenez*, 2011].

[41] Marked in Figure 8 is the sum of HOA, CIOA, and background LV-OOA (LVOOA<sub>PCA=0</sub>) divided by CO. The ratio of HOA+CIOA to CO is determined from the linear regression analysis of the data in Figure 7b, and the background LV-OOA to CO ratio is the average of LV-OOA divided by CO at photochemical ages less than 0.05 days (Figure 8 inset). Several explanations are possible for the source of background LV-OOA. First, some very aged SOA may be present due to recirculation in the LA basin, for which the photochemical tracers have mostly decayed away. However, the similarity in calculated photochemical ages using either (trimethylbenzene/benzene) or  $(NO_v/NO_v)$ suggests that this scenario is not the case, since the high deposition velocity of nitric acid would lead to an observed discrepancy between the two methods at high photochemical ages. A second plausible explanation is "dark" SOA production from ozone or nitrate radicals that will react with alkenes and PAHs. An important piece of evidence to support this possibility would be an increase in  $OA/\Delta CO$ at low photochemical ages as the time of day approached sunrise, since the increase in morning traffic would lead to fresh emissions that decrease photochemical age and react with ozone or nitrate radical to form SOA. This phenomenon is not observed, however, which indicates that "dark" SOA is not an important source of the background LV-OOA, consistent with the expected minor contribution of alkenes to SOA in urban areas [Dzepina et al., 2009; Wood et al., 2010].

[42] A third explanation is that marine OA may be contributing to the background LV-OOA. However, the very low OA concentrations, less than  $0.2 \,\mu g \, m^{-3}$ , over the open ocean west of California for periods with low pollution influence (P. K. Quinn, NOAA, personal communication, 2012) indicate that this source is less important. In addition, low marine OA concentrations,  $0.5 \,\mu g \, m^{-3}$ , have been measured by an AMS in La Jolla, CA (located on the California coast 170 km southeast of Pasadena) [*Liu et al.*, 2011], which is an amount similar to other marine studies [*Russell et al.*, 2010], and would only account for a third of the background LV-OOA.

[43] The last and most likely explanation for the background LV-OOA is the influence of biogenic sources that emit SOA precursors but relatively small amounts of 1,2,4trimethylbenzene, benzene, NO<sub>x</sub>, and CO [Slowik et al., 2010]. If the air mass above Pasadena was influenced by a biogenic source, an increase in OA/ $\Delta$ CO would be observed, but the photochemical age as measured by the ratio of (1,2,4trimethylbenzne/benzene) or  $(NO_y/NO_y)$  would not be significantly altered. Back trajectories for air reaching Pasadena during CalNex often travel over the coastal California mountain ranges where biogenic VOC emissions are large (see section A of the supporting information). Interestingly, at low photochemical ages (less than 0.05 days), there is a general increase in  $OA/\Delta CO$  with the sum of the concentrations of the two isoprene oxidation products measured by the GC-MS. In particular, when averaging the data into the three bins corresponding to low, medium, and high concentrations of MVK plus methacrolein, the binned OA/ $\Delta$ CO

increases from 21 to  $26 \,\mu g \, \text{sm}^{-3} \, \text{ppmv}^{-1}$  (standard errors are less than 0.5) from the lowest third to the highest third. This observation indicates that biogenic sources are influencing OA/ $\Delta$ CO. Furthermore, <sup>14</sup>C measurements for selected days during CalNex show that in the early morning hours when LV-OOA is dominant (compared to other OA components and EC), about 50% of total carbon is nonfossil (e.g., from modern sources) [*Bahreini et al.*, 2012]. These results are consistent with biogenic sources influencing the OA/ $\Delta$ CO ratio and substantially contributing to background LV-OOA (P. Zotter et al., manuscript in preparation, 2012).

[44] In the Figure 8 inset, the organic mass to  $\Delta$ CO ratio is plotted for each PMF component. The ratio increases for SV-OOA and LV-OOA with photochemical age consistent with both components being dominated by secondary sources. In contrast, the ratios for HOA, CIOA, and LOA do not vary substantially with photochemical age, which strongly supports that these three components are dominated by primary sources. The data in Figure 8 also allow for estimating the amount of background OA (i.e., OA from long range transport). As described above, the concentration of LV-OOA at the lowest photochemical ages should approximately correspond to background OA. Taking LV-OOA/ $\Delta$ CO for the lowest age bin in Figure 8 and multiplying it by the  $\Delta$ CO for this bin yields a background OA concentration of 1.5 µg m<sup>-3</sup>.

[45] For HOA, heterogeneous oxidation could potentially increase or decrease the magnitude of HOA/ $\Delta$ CO through either functionalization or fragmentation reactions, respectively. Given the Van Krevelen diagram analysis described above in section 3.2.2, fragmentations reactions appear not to be the dominant oxidation pathway. This conclusion is consistent with the recent work of Lambe et al. [2012] that showed that for larger alkanes, the onset of fragmentation occurs at an O:C of about 0.3, which is much higher than the O: C of HOA reported here (0.14). For functionalization reactions, based on the OM : OC ratio of 1.3 for HOA and an estimated OM: OC of 1.2 for an un-oxidized alkane chain, it is calculated that the increase in HOA mass due to oxidation is only 8%, which is smaller than the standard deviation (21%) of the data shown in Figure 8. Condensation of primary semivolatile organic compounds could also potentially increase HOA/ACO since the averaged OA mass concentration increases with photochemical age from 5 to  $15 \,\mu g \,m^{-3}$ for the binned data shown in Figure 8. However, an increase in HOA/ $\Delta$ CO with photochemical age is not observed in Figure 8. This result is consistent with the calculated change in HOA concentrations due to partitioning. Specifically, using the volatility distribution for POA and primary semivolatile organic compounds reported by Robinson et al. [2007], it is calculated that the increase in HOA concentrations (and HOA/ $\Delta$ CO) would be only 28% for an increase of OA from 5 to  $15 \,\mu g \,m^{-3}$ . This calculated increase is similar in magnitude to the standard deviation of HOA/ $\Delta$ CO and, hence, would be hard to discern. In addition, it is substantially smaller than the increase observed for SV-OOA/ $\Delta$ CO (540%) and LV-OOA/ $\Delta$ CO (300%). The considerations described in this paragraph also apply to CIOA and LOA but are more difficult to quantify for these components given the lack of literature data (e.g., fragmentation reaction studies and volatility distributions).



**Figure 9.** Time series for OOA (the sum of SV-OOA and LV-OOA) and  $O_x$  (the sum of  $O_3$  and  $NO_2$ ). (Inset) Scatter plot of OOA versus  $O_x$  with linear fit and colored by time of day. The best-fit slope is 0.146 ( $R^2 = 0.53$ ). A fixed *x* intercept of 15 ppmv  $O_x$  is used in the fitting procedure identical to previously published work.

# 3.4.2. Correlation of Oxygenated Organic Aerosols With the Photochemical Oxidation Marker Odd-Oxygen $(O_3 + NO_2)$

[46] Odd-oxygen,  $O_x$ , concentrations are closely linked to the extent of photochemical oxidation in an air mass because O<sub>3</sub> production results from OH reactions with VOCs and CO. Therefore, the ratios of OOA to odd-oxygen provide another metric for quantifying the dependence of SOA concentration on photochemical oxidation. Following the work of Herndon et al. [2008] and Wood et al. [2010], we examine the correlations of  $O_x$  instead of  $O_3$  to account for the titration of  $O_3$  by fresh NO emissions which produces NO<sub>2</sub>. When comparing the time series of total OOA (SV-OOA+LV-OOA) versus  $O_x$  in Figure 9, similar temporal changes are observed  $(R^2=0.53)$ , but the correlation is stronger during the more polluted periods of high OOA concentrations that occurred in June ( $R^2 = 0.72$  for the 2–6 June high pollution period). It has also been observed that for long-range transported air, the correlation vanishes due to differing losses and ongoing chemistry of SOA and O<sub>x</sub> [Dunlea et al., 2009]. In Pasadena, the regression slope for OOA versus  $O_x$  is  $0.146(\pm 0.001) \ \mu g \ sm^{-3} \ ppbv^{-1}$  (Figure 9 inset). The data in the scatter plot are colored by time of day, and interestingly, the slope observed for the morning (06:00-12:00 PDT) is steeper than the slope in the afternoon (12:00–18:00 PDT):  $0.183(\pm 0.004)$  versus  $0.163(\pm 0.002)$  µg sm<sup>-3</sup> ppbv<sup>-1</sup>. This trend has also been observed in other field measurements [Herndon et al., 2008; Wood et al., 2010] and has been attributed to several factors including increased evaporation of SV-OOA, mixing with air aloft that contains residual OOA and  $O_x$  during boundary layer growth, and OOA production occurring on shorter timescales than O<sub>x</sub>. The slopes of identical analyses for Riverside, CA and Mexico City are 0.142  $(\pm 0.004)$  and  $0.156(\pm 0.001) \ \mu g \ sm^{-3} \ ppbv^{-1}$  [Aiken et al., 2009; Docherty et al., 2011], which are similar to the Pasadena ground site. This agreement indicates that the ratios of the SOA to  $O_x$  production rates are remarkably constant for the different sites suggesting similar SOA and  $O_x$  formation chemistries on average. As discussed by Wood et al. [2010],

changes in the  $OOA/O_r$  ratio would be expected at locations where the relative concentrations of SOA and  $O_x$  precursors are different. In Houston, for instance, ratios as low as  $0.030 \,\mu g \, sm^{-3} \, ppbv^{-1}$  were found in correlation analyses during periods impacted by large petrochemical plant emissions. This observation was explained by very high concentrations of light alkenes that cause high ozone concentrations but are not expected to contribute greatly to SOA formation. Contrastingly, in Riverside, the relative concentrations of SOA and  $O_x$  precursors are expected to be similar to Pasadena given that urban VOC emissions have similar composition and emission ratios throughout the U.S. [Warneke et al., 2007] and have not changed over the past several years [Warneke et al., 2012]. In Mexico City, the emission ratios for VOCs (i.e., VOC/CO) are generally higher by a factor of approximately 2 [Bon et al., 2011], which would impact both SOA and  $O_x$  production rates proportionally. An important exception is the emission ratios for propane and butane, which were disproportionality high in Mexico City due to liquid petroleum use [Apel et al., 2010]. The contribution of these light VOC compounds was found to be small for O<sub>x</sub> production and zero for SOA production, however [Wood et al., 2010]. Similar to the OA/ $\Delta$ CO discussion in the preceding section, the consistency in OOA/O<sub>x</sub> for multiple field campaigns suggests a relatively constant mix of different O<sub>3</sub> and SOA precursor sources, leading to similar production ratios across multiple urban locations in North America. As also discussed above, the insensitivity of OA/ $\Delta$ CO to differences in VOC/CO suggests unmeasured precursors, but if these unidentified species were emitted in proportion to other VOCs, then consistent OOA/  $O_r$  values would be expected for the different locations.

[47] Chlorine radicals are expected to play a larger role in ozone formation for Pasadena and Riverside in comparison to Mexico City, since the first two locations are near the Pacific Ocean. The contribution of chlorine radical chemistry to the total ozone concentration is a topic of current research [*Young et al.*, 2012]. Still, published work [*Knipping and Dabdub*, 2003] indicates that in Pasadena and Riverside, it is relatively small and, as a percentage, less than the 30%



**Figure 10.** Diurnal profiles, calculated using means, of HOA, EC, rBC, CIOA, CO, and Benzene for weekdays and Sundays during CalNex.

uncertainty for AMS measurements [*Middlebrook et al.*, 2012], which is expected to dominate in the OOA/O<sub>x</sub> comparison. Thus, the similarity of OOA/O<sub>x</sub> between the three locations is consistent with previous work on chloride radical chemistry in the South Coast Air Basin.

[48] Meteorological parameters could also influence  $OOA/O_x$  in a number of ways through changes in OOA partitioning with temperature or increases in the importance of aqueous chemistry at high RH. These parameters do not appear to be important for the OOA/ $O_x$  analysis presented here, however. The average temperatures and RHs for the different sites with similar OOA/Ox were as follows: 18 °C and 83% (Pasadena), 27 °C and 53% (Riverside), and 16 °C and 50% (Mexico City). While higher temperatures in Riverside will favor partitioning of OOA to the vapor phase, the measured volatility of OA for Riverside [Huffman et al., 2009] indicates the amount of evaporation will be small (less than 10%) and, thus, will have little effect on  $OOA/O_x$ . Additionally, the higher RH in Pasadena relative to Riverside and Mexico City may not influence OOA concentrations given that aerosol water was not an important absorbing phase [Zhang et al., 2012] as discussed in section 3.1.

# 3.5. Weekly Cycles for Organic Aerosol Components 3.5.1. Weekly Cycles: Primary Organic Aerosols

[49] It is well known that in California and the South Coast Air Basin, a large decrease in on-road diesel vehicle activity occurs on weekends, which leads to significant reductions in atmospheric species associated with diesel vehicles such as  $NO_x$ , EC, specific VOCs, and particulate nitrate [*Marr and Harley*, 2002; *Millstein et al.*, 2008; *Pollack et al.*, 2012]. To explore if primary organic aerosols show an analogous weekend effect in Pasadena during CalNex, the diurnal cycles for HOA, EC, rBC, CIOA, CO, and benzene are plotted for weekdays and Sundays separately in Figure 10. Included in the Sunday diurnal cycle is data from the Memorial Day holiday, which occurred on a Monday and exhibited traffic patterns typical of Sundays [*Caltrans*, 2010]. Thus, the "Sunday" diurnal cycle combines data from 6 days. Saturday data are not included in Figure 10 to avoid carryover effects from the preceding Friday. Carryover effects on Mondays appear to have little impact on the weekday diurnal cycle with less than 3% change in the average daily concentrations when Mondays are omitted from averaging and no qualitative change in the diurnal cycles. Thus, Monday data are included with the other weekday data in Figure 10.

[50] The EC (and rBC) concentration decreases on Sundays to  $71(\pm 6)\%$  of its weekday average and has a very different diurnal cycle. A similar change is observed for HOA, which decreases to  $82(\pm 4)\%$  of its weekday average. (Note: Uncertainties are the standard errors of the mean.) The decrease in concentrations is consistent with the weekend effect and the importance of diesel vehicle emissions as a source for HOA and EC (and rBC). In contrast, CO concentrations when integrated over the entire day are not substantially different on Sundays versus weekdays, and the average concentration on Sundays is  $99.4(\pm 0.3)\%$  of the weekday average. The CO diurnal cycles are dissimilar probably due to changes in traffic patterns. Benzene displays a similar lack of change on Sundays increasing to  $105(\pm 3)\%$ of the weekday average. Since gasoline vehicles are an important source of CO and benzene [Fruin et al., 2001; Schauer et al., 2002a], the lack of a weekend effect for these compounds is consistent with previous studies that demonstrated similar overall activity for gasoline vehicles on weekends compared to weekdays [Marr and Harley, 2002; Pollack et al., 2012]. The CIOA concentrations are elevated on Sundays by 161(±4)% displaying a weekly cycle distinctly different from the other species in Figure 10. An increase in barbecuing on weekends has been reported previously for the South Coast Air Basin [Chinkin et al., 2003], which is consistent with elevated CIOA concentrations on weekends. However, given the limited corroborating evidence and lack of previous long-term observations of cooking emissions (to our knowledge), further studies are needed to make a confident conclusion regarding the weekly variations in cooking organic aerosol.

[51] The observed decreases in HOA and EC concentrations on Sundays can be compared against the expected decreases in their emissions, estimated from a combination of data on fuel sales (California State Board of Equalization, Fuel Taxes Statistics and Reports, 2011, http://www.boe.ca.gov/ sptaxprog/spftrpts.htm, hereinafter referred to as California State Board of Equalization, online report, 2011), emission ratios [*Ban-Weiss et al.*, 2008b], and traffic volume [*Caltrans*, 2010]. The first step to obtain the estimates is calculating the percentage of weekday EC and HOA attributable to diesel emissions using equation (1) below.

$$\frac{EC_{\text{Diesel}}}{EC_{\text{Total}}} = \frac{ER_{\text{Diesel}} \times FS_{\text{Diesel}}}{(ER_{\text{Diesel}} \times FS_{\text{Diesel}}) + (ER_{\text{Gasoline}} \times FS_{\text{Gasoline}})} \quad (1)$$

[52] In equation (1), *ER* is the emission ratio for diesel and gasoline vehicles taken from *Ban-Weiss et al.* [2008b], and *FS* is the gasoline and diesel fuel sales reported for the state of California during May and June 2010 (California State Board of Equalization, online report, 2011). An analogous equation is used for HOA. The *ER* is defined as the amount



**Figure 11.** (a) The evolution of OA/ $\Delta$ CO versus photochemical age for Pasadena during CalNex separated by day of the week. The enhanced CO ( $\Delta$ CO) is the ambient CO minus the estimated background CO (105 ppb). Error bars indicate the standard errors. Photochemical age is determined using the method of *Parrish et al.* [2007]. (b) Also shown is the analogous plot for OOA with the linear ODR fits of the data.

of EC (or HOA) emitted per unit fuel burned, and the values used in this work are 0.022 (gasoline EC), 0.86 (diesel EC), 0.031 (gasoline HOA), and 0.41 g kg<sup>-1</sup> (diesel HOA). It is assumed that the monthly fuel sales are representative of weekday fuel use in the South Coast Air Basin. Following this method, it is estimated that diesel emissions account for 87 (±3)% of EC and 70(±10)% of HOA. The second step utilizes daily vehicle miles traveled (VMT) data for Los Angeles County to calculate that during the campaign truck traffic decreased 44% on Sundays relative to weekdays [*Caltrans*, 2010]. This figure lies within the range of other estimates for weekend reductions of heavy-duty vehicle traffic [*Chinkin et al.*, 2003]. Finally, an estimate of EC concentrations on Sunday relative to weekdays,  $\Delta EC_{sun}$  (%), can be calculated as follows (an analogous equation can be used for HOA).

$$\Delta EC_{\text{Sun}} = \frac{EC_{\text{Diesel}}}{EC_{\text{Total}}} \times \frac{(Truck \ VMT)_{\text{Sun}}}{(Truck \ VMT)_{\text{WD}}} + \frac{EC_{\text{Gas}}}{EC_{\text{Total}}} \times \frac{(Non - Truck \ VMT)_{\text{Sun}}}{(Non - Truck \ VMT)_{\text{WD}}} + \frac{EC_{\text{Background}}}{EC_{\text{Total}}}$$
(2)

[53] Using equation (2), the Sunday concentrations of EC and HOA are estimated to be  $64(\pm 3)\%$  and  $72(\pm 6)\%$  of their weekday concentrations, respectively. To estimate these values, the nontruck VMT on Sundays versus weekdays was taken to be equal because of the similarity in the average daily CO and benzene concentrations. In addition, the background EC is the average of the values from Langridge et al. [2012], 40( $\pm$ 20) ng m<sup>-3</sup>, and the background HOA,  $70(\pm 40)$  ng m<sup>-3</sup>, was calculated from EC using the slope of HOA to EC reported in Figure 7. (Note: The uncertainties for the calculated Sunday reductions in EC and HOA include the uncertainties in the background concentrations reported in Langridge et al.) For comparison, the observed average Sunday EC and HOA concentrations at the Pasadena ground site are  $71(\pm 6)\%$  and  $82(\pm 4)\%$  of the weekday averages, respectively. The agreement between the estimated and observed values is good, given the need for several approximations to obtain the estimate. The reduction in HOA is less than the reduction in EC for both the estimated and

observed values, due to the greater portion of HOA emitted from gasoline vehicles. It is noted that in contrast to HOA, the CIOA concentration is higher on Sundays as discussed above, and the combination of the two opposite trends leads to a net increase of POA on the weekends.

[54] An important assumption of this analysis is that the only sources of EC are on-road diesel and gasoline emissions, as well as the background from long-range transport. Transport is the single largest source of EC in the United States, and in the absence of biomass burning, it accounts for 81% of emitted EC. Within the transport sector, EC emissions are dominated by on-road and non-road diesel (U.S. Environmental Protection Agency, Black carbon: Basic information, 2012, http://www.epa.gov/blackcarbon/ basic.html). Another question is whether commercial marine emissions may have a substantial contribution to the EC budget. To address this consideration, we examined the correlation between EC and the oil combustion particles identified by the PALMS instrument, which are presumably from shipping activities. We observed a low correlation ( $R^2 = 0.24$ ), which is consistent with commercial marine EC emissions not substantially impacting the ground site. Ultimately, accounting for only three sources of EC (on-road diesel, on-road gasoline, and a background) is a simplifying assumption, but one that is consistent with emission inventories and other observations. The reasonableness of this assumption is further supported by the closure obtained between the calculated and measured weekly cycles.

# **3.5.2.** Weekly Cycles: Secondary Organic Aerosols and Constraining the Importance of Diesel Emissions

[55] To evaluate the weekly cycle for secondary organic aerosols, OA/ $\Delta$ CO versus photochemical age is plotted in Figure 11a for weekdays and Sundays. Also shown is the analogous plot for total OOA (Figure 11b). The OOA plot is similar for weekdays versus Sundays, and linear regression analyses of the data yield slopes of 108(±5) and 98(±8) µg sm<sup>-3</sup> ppmv<sup>-1</sup> for weekdays and Sundays, respectively. (Note: The data fitted are averages resulting from binning the raw data according to photochemical age, and the averages are weighted by the standard errors of the *x* and *y* data.) After propagation of error, these slopes correspond to a ratio of 1.1(±0.1) for weekdays to weekends. Following the estimation method described by

Bahreini et al. [2012], and using a 44% decrease in diesel traffic on Sundays as determined above, this ratio corresponds to diesel emissions accounting for 19(+17/-21)% of the OOA mass. Also, a consistently higher photochemical age is observed on Sunday versus weekdays due to the higher oxidant concentrations resulting from reduced NO<sub>x</sub> emissions. These results are in good agreement with other CalNex papers that address weekday/weekend effects [Bahreini et al., 2012; Pollack et al., 2012]. In particular, they are consistent with the conclusion reported by Bahreini et al. [2012] that gasoline emissions are substantially more important than diesel emissions in the formation of secondary organic aerosol mass within the LA Basin, since a large decrease in the OOA/ $\Delta$ CO ratio is not observed on weekends when there is less diesel traffic. It should be noted as well that the results present here are better constrained than the Bahreini et al. analvsis because the PMF results are used to obtain OOA/ $\Delta$ CO rather than relying on estimated values of POA/ACO to calculate OOA/ $\Delta$ CO and because of the more precise binning by photochemical age.

[56] We note that for the diesel versus gasoline analysis presented in the preceding paragraph, three important assumptions are made. First, it is assumed that SOA precursors in the South Coast Air Basin are dominated by motor vehicle emissions. While this is consistent with measured VOC/CO ratios [*Warneke et al.*, 2012], the possibility of important and unidentified SOA precursors from nonvehicular sources cannot be completely ruled out. Therefore, further research is needed to constrain the contribution of nonvehicular sources to SOA.

[57] The second important assumption is that some of the SOA measured may be due to long-range transport, which is not accounted for in the preceding analysis. To at least partially account for this possible source of error, we repeat the analysis above but only for photochemical ages above 0.1 days. Photochemical ages above 0.1 days generally occur during daytime when the higher amount of SV-OOA versus LV-OOA indicates that SOA production is more local and recent. The resulting slopes of the regression analyses are 121( $\pm$ 7) and 115( $\pm$ 10)  $\mu g$  sm<sup>-3</sup> ppmv<sup>-1</sup> for weekdays and Sunday, respectively, and then the ratio of the slopes is  $1.0(\pm 0.1)$ . This ratio corresponds to diesel emissions accounting for -2(+21/-26)% of the OOA mass. The upper limit of this range is less than that for the original analysis (36%) for all photochemical ages. Thus, we report the 19(+17/-21)% result, since it is more conservative and represents the entirety of the campaign.

[58] The third assumption made in this analysis is that SOA yields do not change on weekends when NO<sub>x</sub> concentrations are lower. To test the impact of this assumption, the branching ratios for the high-NO<sub>x</sub> and low-NO<sub>x</sub> VOC oxidation channels were calculated following the same method as described in *Dzepina et al.* [2011]. It is found that the high-NO<sub>x</sub> channel dominates on both weekdays and Sundays with mean branching ratios of 99% and 91%, respectively (see section F of the supporting information for box-and-whiskers plots). Using the NO<sub>x</sub>-dependent yields of *Tsimpidi et al.* [2010], this difference in branching ratio would correspond to an increase in weekend SOA yields of 1% (assuming a 7  $\mu$ g/m<sup>3</sup> OA concentration) for the aromatic precursors that dominate SOA formation from VOCs [*Dzepina et al.*, 2011; *Dzepina et al.*, 2009]. This difference in yields would

only change the determined diesel contribution by about 2%, which is much smaller than our reported uncertainty. Thus, the assumption that SOA yields do not change on weekends is robust. However, it should be noted that primary semivolatile and intermediate volatility compounds may have an important contribution to SOA formation in the South Coast Air Basin [*Robinson et al.*, 2007], but their NO<sub>x</sub>-dependent SOA yields are not well constrained.

## 4. Conclusions

[59] Ambient aerosol measurements were made using a suite of aerosol composition instruments, including online and off-line bulk and single particle methods at the Pasadena ground site during May and June 2010 as part of the CalNex campaign. Organic aerosols account for 41% of the total submicron aerosol mass. An in-depth analysis of OA in Pasadena was carried out including a comparison to measurements from previous field campaigns. Positive matrix factorization analysis of the high-resolution mass spectra resolved five components from the total organic mass. The identified components are hydrocarbon-like organic aerosol (HOA, primary combustion), cooking-influenced organic aerosol (CIOA), semivolatile oxygenated organic aerosol (SV-OOA, fresh secondary), low volatility oxygenated organic aerosol (LV-OOA, aged secondary), and amine-rich local organic aerosol (LOA) that accounts for a small amount of the OA mass. A large majority of the OA mass is classified as oxygenated/secondary (66%), but there are important contributions from the primary components with HOA and CIOA accounting for 12% and 17% of the total OA mass, respectively. To compare the OA oxidation reactions occurring in different regions of the South Coast Air Basin, the Van Krevelen diagrams for Pasadena and Riverside are analyzed and it is observed that OOA components follow a similar line with a slope of -0.55.

[60] The HOA component correlates well with EC, and the emission ratio of HOA to EC varies with the relative importance of diesel versus gasoline vehicle emissions at the Pasadena ground site. The dependence of secondary organic aerosol concentration on photochemical oxidation is quantitatively similar to other urban field sites suggesting similar SOA chemistry and sources. First, the OA to  $\Delta$ CO ratios for Pasadena increase with photochemical age and closely resemble the upper limit of analogous data from Mexico City and the northeastern United States. Thus, within experimental error, the OA production per unit CO is the same in Pasadena compared to other locations. Second, the OOA to odd-oxygen ratios for Pasadena are similar to those observed in Riverside and Mexico City, which indicates that SOA and odd-oxygen production rates are proportional across the different sites. Both HOA and EC exhibit weekly cycles with substantially lower concentrations on Sundays versus weekdays consistent with the well-known weekday/weekend effect in the South Coast Air Basin. The decreases in HOA and EC concentrations are quantitatively similar to those predicted for their emissions using fuel sales, traffic counts, and literature vehicle emission ratios. In contrast, OOA does not display a strong weekly cycle-after controlling for differences in photochemical ages-which is consistent with the dominance of gasoline emissions in SOA formation, insofar as nonvehicular emissions of SOA precursors are minor. In total, the findings reported here highlight several quantitative similarities in SOA properties observed in Pasadena, Riverside, Mexico City, and the northeastern United States including the ratios of SOA to odd-oxygen, the increases in OA/ $\Delta$ CO with photochemical age, and the evolution of elemental composition. These observations are consistent with a relatively constant mix of sources of CO, O<sub>3</sub> precursors, and SOA precursors across urban locations in North America.

# Appendix A: Size Distributions, Chemical Aging of Sea Salt, and Particulate Charge Balance

[61] Displayed in Figure A1 are the AMS size distributions (Figure A1a), XRF size distributions (Figure A1c), and the contribution of all species to the total aerosol mass as a function of particle size (Figure A1d). The rBC size distribution was measured by the SP-AMS and is normalized to the total EC concentration measured by the online Sunset analyzer. As seen in Figure A1d, the smaller particles, especially those below 200 nm, are predominately composed of OA. In contrast, the larger particles have an increasing inorganic contribution due to nitrate, sulfate, ammonium, and the non-EC refractory components. The AMS size distributions have a gradual cut of approximately PM1 and can have a tail due to slow evaporating particles [Canagaratna et al., 2004] and should be interpreted accordingly. Also shown in Figure A1e are the PALMS size distributions, which feature a broad submicron mode that is dominated by the sulfate/ organic/nitrate particle type as well as a supermicron mode composed primarily of sea salt. The PALMS distributions above 2.5 µm and below 200 nm underestimate concentrations due to instrument limitations associated with both the PALMS and WLOPC.

[62] Further information about the OA, nitrate, and sulfate size distributions can be inferred from comparisons of various PM1 and PM2.5 measurements. For sulfate and OA, the comparisons indicate that on average, an overwhelming majority of the mass for these species is below 1 µm, but for nitrate, there appears to be a substantial amount mass above 1 µm. Specifically, a regression analysis of OC concentrations from the AMS, a PM1 instrument, and several PM2.5 OC time series taken from the GIT, EPA, and UNC filter samples results in slopes greater than 0.81, when the AMS data are plotted on the y axis (supporting information section B contains further details about the OA, sulfate, and nitrate comparisons). This observation indicates that less than about 20% of the OC mass is above 1 µm. Similarly, a regression analysis of sulfate concentrations from the AMS and a PM<sub>2.5</sub> PILS-IC instrument results in slope of 1.01 leading to the conclusion that the sulfate mass above 1 µm is insignificant on average. The regression analysis of AMS and PILS-IC concentration data for nitrate results in a much different finding and exhibits slope of 0.64 that is also dependent on sea-salt concentrations measured by the PALMS instrument. These observations indicate that a substantial amount of nitrate mass is present above 1 µm, about 35%, and that the supermicron nitrate is at least partially comprised of sodium nitrate from chemical aging of sea salt by nitric acid although some supermicron ammonium nitrate may be present as well. The PILS-IC inlet was alternated between PM<sub>1</sub> and PM<sub>2.5</sub> cyclones for a portion of the

measurement period (12-16 June), which provides data that can also be used to assess the amount of sulfate and nitrate between 1 and 2.5  $\mu$ m. The linear regressions of the PM<sub>1</sub> and linearly interpolated PM2 5 data indicate that 34% and 80% of the nitrate and sulfate mass were present below  $1 \,\mu\text{m}$ . (Note: Interpolation of the PM<sub>2.5</sub> data is necessary since only a single inlet and cyclone were used for the PILS-IC measurement preventing simultaneous measurements with different size cuts.) Similar to the AMS versus PILS comparison, these percentages indicate that the supermicron mass represents a greater fraction of the PM<sub>2.5</sub> mass for nitrate relative to sulfate. When using the PILS data with alternating cyclones, a larger percentage of supermicron mass is found than in the AMS versus PILS comparison. This difference may be due to the stronger influence of sea salt during the portion of the campaign when the cyclones were alternated, as clearly seen in the PALMS time series (Figure 1e), which is consistent with substantial amounts of sodium nitrate, and to a lesser extent sodium sulfate, above 1 µm. The aging of sea salt upon exposure to pollution is described further in the next paragraph.

[63] Both the CalNex XRF and PALMS measurements provide quantitative information about non-EC refractory materials including sea salt. An important detail regarding the measurement of particulate chloride is that XRF is assumed to measure refractory chloride (rCl) since the XRF samples are placed under vacuum before measurements [Johnson et al., 2008]. The nonrefractory and refractory chloride fractions are thought to be predominately ammonium chloride [Salcedo et al., 2006] and sodium chloride (from sea salt), respectively [Malm et al., 1994; Simon et al., 2011]. Sodium data are not available from XRF due to measurement limitations, but the sodium mass concentration can be estimated from PALMS sea-salt volume concentrations as described in the Figure 2 caption. For fresh sea salt, the expected ratio of chloride to sodium mass concentrations is 1.8 [Finlayson-Pitts and Pitts, 2000]. However, a ratio of 0.12 is observed for rCl to sodium at the Pasadena ground site indicating that the sodium chloride in sea-salt aerosol has undergone a substantial amount of chemical processing by nitric and sulfuric acid, which depletes the amount of chloride ions in the sea-salt aerosol by converting sodium chloride to sodium nitrate and sodium sulfate [Gard et al., 1998]. For Pasadena, a fractional chloride depletion of 94% is calculated using the following equation described by Zhuang et al. [1999]. (In equation (A1), all concentrations are in units of  $mol m^{-3}$ .)

$$Depletion = \frac{[Cl]_{\text{original}} - [Cl]}{[Cl]_{\text{original}}} \times 100\% = \frac{1.174[Na] - [Cl]}{1.174[Na]} \times 100\%$$
(A1)

[64] This agrees with qualitative results from the PALMS mass spectra, which show significant displacement of chloride and accumulation of nitrate on individual sea-salt particles that correlated with nitric acid concentrations.

[65] The acidity of the submicron aerosols in Pasadena can be evaluated by comparing the measured ammonium mass concentration against the amount needed to fully neutralize the measured sulfate, nitrate, and chloride, which is termed here



**Figure A1.** (a) Size distributions measured by the AMS. Also shown is rBC measured by the SP-AMS. Note: The AMS size distributions have a gradual cut of approximately  $PM_1$  and can have a tail due to slow evaporating particles and should be interpreted accordingly. (b) The ratio of rCl to Mg plotted versus particle size. Ratio is calculated using mass concentrations from XRF for 20 May 00:00 to 25 May 00:00. (c) Distribution for refractory components measured by XRF. (d)  $PM_1$  size distributions by percent mass. The XRF data are calculated by interpolating the original data to provide sufficient data points to create the stacked plot. Note: rBC concentrations below 100 nm may be underestimated due to instrument limitations. Sodium is estimated from the PALMS data as described in the Figure 2 caption. (e) Distributions of particle types measured by the PALMS. Volume distributions determined from the SMPS and WLOPC are shown as well. For the size range overlap of the SMPS and WLOPC, each particle type has two data points in each size bin, which is due to mapping the PALMS particle fractions onto the two sizing instruments.

"NH4<sup>+</sup> predicted." The AMS measurements of nonrefractory aerosol composition were used for this charge balance calculation. Particles are considered acidic if the measured ammonium concentration is substantially lower than the predicted values [Zhang et al., 2007a]. As seen in Figure A2a, overall, the particles appear to be bulk neutralized by ammonium with a majority of the data near the one-to-one line. It should be noted that the measured amines are not accounted for in the predicted ammonium, but even if it is assumed that the amines are all present as salts, the impact on the fit is minimal with the slope changing from 1.02 to 0.99 or 0.96 when AMS or FTIR measurements of amines are used, respectively. There are selected periods when the measured ammonium concentrations are not sufficient to neutralize the anions, especially at lower concentrations. These periods are more easily observed in the histogram shown in Figure A2b. The low ammonium measured-to-predicted ratios may be due to more acidic particles, but based on PALMS spectra only, about 0.1% of particles contained sulfate that was highly acidic  $(NH_4^+: SO_4^{2-} < 1)$  [*Froyd et al.*, 2009]. An alternative explanation then is the presence of sodium cations that are not

accounted for in Figures A2a and A2b. Typically when using AMS data to evaluate particle acidity, it must be assumed that ammonium is the only significant cation, and cations from sources such as sea salt are ignored [*Aiken et al.*, 2009; *Docherty et al.*, 2011; *Zhang et al.*, 2007a]. For Pasadena, however, sodium concentration data can be estimated from PALMS measurements providing an opportunity to evaluate the role of sea salt in particle neutralization. (Note: The PALMS data were restricted to the submicron size range to match the AMS measurements.) In Figure A2c, there is a clear dependence of the ammonium measured-to-predicted ratios on the fraction of cations that are sodium (ratios are taken from molar units), which indicates that sodium plays a role in the charge balance.

[66] An important consideration when evaluating particle neutralization is whether the sodium cations are present as sodium nitrate or sodium chloride, and if those species can be vaporized by the AMS heater for detection. From the charge balance calculations above, it appears that anions associated with sodium are detected by the AMS indicating that at least a fraction of the sodium nitrate evaporates



**Figure A2.** (a) Scatter plot of the measured ammonium versus " $NH_4^+$  predicted," which is calculated using the concentrations of nitrate, sulfate, and chloride, as well as assuming full neutralization by ammonium (all data from AMS). (b) Histogram for the ratios of the measured ammonium to the  $NH_4^+$  predicted. A Gaussian distribution is shown in the histogram for reference and is generated using the standard deviation of the data. (c) Scatter plot of the measured-to-predicted ratios versus the ratios of sodium to the total cations (ammonium plus sodium). Sodium is estimated from the PALMS sea-salt concentrations as described in the Figure 2 caption.

rapidly (~1 s) in the AMS. The chloride depletion results indicate that a large majority of the sodium is present as sodium nitrate, which is more volatile than sodium chloride and, thus, more readily detected by the AMS, in which the vaporizer temperature was operated at approximately 600 °C. Therefore, it appears that counter ions associated with sodium from sea salt do impact the AMS measurements of charge balance.

[67] Previously, Docherty et al. [2011] demonstrated that for Riverside during the SOAR-1 campaign, organonitrates and organosulfates impacted the charge balance calculation. These species add to the nitrate and sulfate mass measured by the AMS [Farmer et al., 2010] due to fragmentation of the molecular parent, but do not contribute the expected amount of ionic charge, which leads to apparent particle acidity. An important contrast between Pasadena and Riverside is that the deviation between measured ammonium and NH<sub>4</sub><sup>+</sup> predicted occurs at low concentrations for Pasadena but at high concentrations for Riverside. In addition, the measured versus predicted scatter plot for Pasadena has slope close to one, 1.02, whereas the analogous plot for Riverside has a lower slope of 0.86. (Note: Sodium from sea salt is not accounted for in either slope.) For Riverside, the deviation in the slope from one was attributed to organosulfates and organonitrates. For Pasadena, the charge balance calculation does not appear to be significantly impacted by

organosulfates or organonitrates, which implies that the concentrations for these species are relatively low. This conclusion is supported by measurements from other instruments. The PALMS instrument observed that the isoprene-derived organosulfate, IEPOX sulfate ester, comprised <0.01% of submicron aerosol mass in Pasadena, which supports the negligible role of organosulfates in this location. (Note: The mass abundance for the IEPOX sulfate ester was determined using detailed laboratory calibrations that were performed for a previous study [*Froyd et al.*, 2010].) Furthermore, FTIR measurements of organonitrates [*Day et al.*, 2010] found that concentrations were less than 2% of the measured nitrate (by AMS) on average, which is much lower than the percentage estimated in Riverside (10%).

[68] Combining the discussions of size distributions and sea salt aging from above, in Figure A1b the rCl to Mg ratio is shown as function of particle size for the period of high marine influence identified in section 3.1 (20–25 May 2010). During this period, rCl and Mg are correlated in the larger XRF size bins (R > 0.62), and the ratio of the Mg PM<sub>1</sub> mass concentration to the PALMS sea-salt PM<sub>1</sub> mass concentration is very close to the expected ratio for sea salt: 0.044 versus 0.039, respectively (R=0.6) [*Finlayson-Pitts and Pitts*, 2000]. Thus, Mg is taken to be predominately from sea salt, which allows for calculating the amount of chloride depletion following an approach analogous to that described for sodium. (Data are not shown for smaller particle diameters since a strong correlation between rCl and Mg is not observed.) The rCl to Mg ratio is fairly constant with particle size from 660 to 3010 nm d<sub>va</sub> indicating similar amounts of chloride depletion. Additionally, the average rCl to Mg ratio (2.0) corresponds to 86% chloride depletion, which is similar to 94% chloride depletion calculated using the estimated sodium data from the PALMS instrument. In general, the sea salt measured in Pasadena appears to be very aged mostly from chemical reactions with nitric acid. The extensive chloride depletion observed in Pasadena is consistent with previous work including modeling studies that predicted ~80% chloride depletion in Riverside, CA [Knipping and Dabdub, 2003], and single particle mass spectra of aged sea salt, also from Riverside, which showed extensive chloride depletion [Hughes et al., 2000]. In addition, chloride depletions of 71 and 74% were reported for coarse mode aerosol in Upland and Rubidoux, CA, respectively [Eldering et al., 1991]. These values are lower than that observed for Pasadena in this study, which may be due to the Eldering et al. percentages corresponding to particles greater than 2.2 µm in diameter.

[69] The extensive depletion of chloride from sea salt suggests that appreciable amounts of chlorine radicals may be present due to the photolysis of photolabile chlorinated gases such as HCl, ClNO<sub>2</sub>, and Cl<sub>2</sub>. Oxidation reactions of organics by chlorine radicals that produce organochlorines in the particle phase would then be possible. To investigate this possibility, the concentrations of several organochlorine fragments were determined from the AMS measurements  $(CCl^+, C_2HCl^+, CCl_2^+, C_2Cl_2^+, C_2HCl_2^+, CHOCl_2^+)$ . The relative concentration of these species compared to the total OA is very small, on average less than 0.1% and always less than 0.4%. In addition, the 2DTAG identified only one chlorine-containing OA compound, chlorophthalic acid, which represents less than 1% of the total phthalic acid concentration. These results are also consistent with FTIR spectra of filter samples collected during the CalNex campaign, which do not display vibrational resonances for acid chlorides  $(730-550 \text{ cm}^{-1})$  or alkyl chlorides  $(785-540 \text{ cm}^{-1})$ . It is noted though that quantification of organochlorines by FTIR is difficult due to Teflon filter interferences in the same spectral region. In total, these measurements provide no evidence for organochlorines representing a substantial portion of the OA mass, but the methods utilized here are not optimal for the detection of organochlorines.

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$\frac{1}{2}$	Supporting Material for:
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41	Supporting Material Sections:
42	Section A: CalNex Pasadena Ground Site Meteorology & Back-Trajectories
43	
44	Section B: Instrument Comparisons & Selected Diagnostics
45	
46	Section C: Comparisons to Previous Campaigns in Los Angeles Area and Additional
47	Aerosol Composition Figures
48	
49	Section D: Selection of PMF Solution & Additional PMF Figures
50	
51	Section E: Evaluation of Photochemical Age Error
52	
53	Section F: NO <sub>x</sub> Branching Ratios: Box-and-Whiskers Plot



**Figure A-1:** Time series and diurnal profiles for planetary boundary layer height (PBL), temperature, and relative humidity at the Pasadena ground site during CalNex.



**Figure A-2:** Wind roses for the Pasadena ground site during CalNex organized by time of day (PDT). Zero on the polar coordinate is north and radial distance indicates relative frequency.



**Figure A-3:** Average 48 h FLEXPART back-trajectories for air masses arriving at the Pasadena ground site. Colors represent the footprint residence times. Each panel corresponds to a different time-of-day and is the average for June  $2^{nd}$  through June  $6^{th}$ . The grey triangle indicates the location of the Pasadena ground site.



**Figure A-4:** Average 48 h FLEXPART back-trajectories for air masses arriving at the Pasadena ground site. Colors represent the footprint residence times. Each panel corresponds to a different time-of-day and is the average for June 9<sup>th</sup> through June 11<sup>th</sup>. The grey triangle indicates the location of the Pasadena ground site.



**Figure A-5:** Average 48 h FLEXPART back-trajectories for air masses arriving at the Pasadena ground site. Colors represent the footprint residence times. Each panel corresponds to a different time-of-day and is the average for June 12<sup>th</sup> through June 14<sup>th</sup>. The grey triangle indicates the location of the Pasadena ground site.

59

## Section B: Instrument Comparisons & Selected Diagnostics

This section provides information that supports the validity of the AMS measurements. In 60 Figure B-1 the time series of submicron aerosol mass concentration measured by the AMS and 61 calculated from the SMPS and UHSAS number distributions are shown along with correlation 62 plots for the various instruments. (Note: the UHSAS number distribution was determined using a 63 refractive index of 1.515, which corresponds to dry ammonium sulfate at 1050 nm. A very brief 64 discussion of refractive index and optical properties is contained in the next paragraph.) The 65 AMS only measures non-refractory aerosol, and to partially compensate for this limitation the 66 rBC concentration from the SP2 is added to the AMS time series. The AMS also does not 67 measure mass from other refractory sources such as sea salt or mineral dust. These species are 68 not expected to significantly impact the instrument comparison though, because the relative 69 70 amount of the non-EC refractory mass is less than 5% of the total  $PM_1$  aerosol mass (Figure 2B, main text). Similarly, the PALMS instrument quantified the sum of mineral/road dust and sea 71 salt to be 9% of total submicron volume (Figure 3A, main text). The AMS and SMPS 72 instruments show good agreement, and a linear regression analysis of the two data results in a 73 slope of 1.03 ( $R^2 = 0.85$ ) as shown in Panel C. The agreement between the AMS and UHSAS is 74 not as good (slope = 1.28,  $R^2 = 0.84$ ) when the UHSAS data is truncated at 740 nm geometric 75 diameter to approximate the 1 µm aerodynamic diameter size cut of the AMS (Panel D). Given 76 the reasonable agreement between the AMS and SMPS as well as other instruments (see below), 77 78 it appears that the UHSAS, including the uncertainties in the conversion to volume and the 79 estimation of refractive index, may be responsible for this discrepancy. It is noted that from 6/480 through 6/6 there are extended periods when the AMS measurement is lower than both the SMPS and UHSAS. This period exhibits an unusually large amount of mass above 740 nm 81

(estimated geometric diameter, equivalent to an estimated vacuum aerodynamic diameter of 1080 nm using the average density of 1.46 g cm<sup>-3</sup> calculated from the AMS and SP2 aerosol composition measurements.) as measured by the UHSAS (Panel B). Similarly, PALMS measurements show a large volume concentration of sulfate/OA/nitrate particles above 784 nm geometric diameter during this period (Figure 1 in main paper). The discrepancy from 6/4 through 6/6 is therefore attributed to a period of unusually large particles, which are near and above the 1 µm aerodynamic diameter size cut for measurement by the AMS.

The SMPS measurements are also validated by calculating the Mie scattering from the 89 number size distribution data, and then comparing the result against extinction measurements 90 (Figure B-2). The extinction measurements are from the CAPS instrument and were taken at 532 91 92 and 630 nm. Good agreement between the calculated scattering and measured extinction is observed when using an index of refraction 1.54, which is the average for dry ammonium sulfate 93 and ammonium nitrate [Kleinman et al., 2007]. The refractive index of OA will vary depending 94 95 on composition, but an average value of 1.55 is often assumed when predicting optical properties 96 [Dick et al., 2007; Kleinman et al., 2007]. The particles were dried before measurements by the 97 SMPS and CAPS. It should be noted that the amount of black carbon at the site is relatively 98 small, and thus, scattering dominates the aerosol extinction [Thompson et al., 2012], which 99 allows for the direct comparison of calculated scattering and measured extinction performed 100 here.

101 To further examine the AMS data, the concentrations of nitrate and sulfate aerosols 102 measured by the AMS and the PILS-IC instrument were compared (Figure B-3). An important 103 consideration when carrying out this comparison is that the PILS-IC was equipped with a  $PM_{2.5}$ 104 inlet, which transmits larger particles that cannot be measured AMS. For sulfate the agreement is 105 generally good, and a linear ODR regression analysis of the two data sets results in a best-fit slope of 1.01 ( $R^2 = 0.84$ ). The same analysis for nitrate results in a slope of only 0.64 ( $R^2 =$ 106 0.85), however. A possible explanation for the discrepancy between the nitrate measurements is 107 the presence of super-micron sodium nitrate that is formed when sea salt reacts with nitric acid as 108 discussed in the Appendix of the main text. To test this hypothesis, the regression analysis for 109 110 nitrate was repeated using only periods with PALMS sea salt volume concentrations of less than  $0.35 \ \mu\text{m}^3 \text{ cm}^{-3}$ , which corresponds to the 5<sup>th</sup> percentile of the data. A substantial improvement in 111 agreement is observed with the slope increasing to 0.89 (from 0.64). For the sake of 112 113 completeness the same test was performed on the sulfate data, but there is only a small increase in the slope to 1.09 (from 1.01). Interestingly, the excellent agreement between the PILS-IC and 114 AMS sulfate, as well as the weak dependence on PALMS sea salt concentrations in the sulfate 115 scatter plot, suggests that little sodium sulfate has been formed from the reaction of sea salt and 116 sulfuric acid. Despite the technical differences between the AMS and PILS-IC, after accounting 117 for the presence of sodium nitrate in the supermicron mode there is reasonable agreement 118 between these two instruments with respect to sulfate and nitrate concentrations. 119

The comparisons of the AMS organic mass (OM) with multiple other measurements of 120 organic aerosols at the Pasadena ground site exhibits reasonable agreement. The different OM 121 and OC measurements are listed in Table B-1, and the results of the OM and OC comparisons 122 are summarized Table B-2 and Figure B-4. In Panel A of Figure B-4 the AMS OM<sub>1</sub> (the 123 subscript indicates the size cut in  $\mu$ m) and the online Sunset organic carbon mass (OC<sub>2.5</sub>) are 124 plotted together and a strong correlation between the two measurements is observed. The AMS 125  $OM_1$  and online Sunset  $OC_{2.5}$  data (Panel B) yield an R<sup>2</sup> value of 0.76, but the regression slope of 126 3.3 is significantly higher than the expected range of 1.4 - 2.3 [Aiken et al., 2008; Turpin et al., 127

2001]. Such a large discrepancy is outside the AMS uncertainty bounds of ±30% [*Middlebrook et al.*, 2012]. While the exact reason for this discrepancy is unclear it may be related, at least
partially, to the presence of a denuder upstream of the Sunset carbon analyzer. Specifically, the
denuder may cause volatilization of particulate OC from the collection filter that is induced by
re-equilibration of organic concentrations after removal of vapor-phase organics by the denuder
[*Grover et al.*, 2008].

A scatter plot of the AMS OM<sub>1</sub> versus the OC<sub>2.5</sub> measured from two sets of filter samples 134 collected by the Georgia Institute of Technology (GIT) and U.S. Environmental Protection 135 Agency (EPA) groups (Panel C) yields very reasonable slopes of 1.7 and 1.9 ( $R^2 = 0.82$  and  $R^2 =$ 136 0.80, respectively). These slopes are similar to the  $OM_1:OC_1$  of 1.7 that was determined from the 137 elemental analysis of the AMS mass spectra. The OC<sub>2.5</sub> concentration was also measured on a 138 third set of filter samples collected by the University of North Carolina (UNC) group. For the 139 140 UNC OC<sub>2.5</sub> measurement the slope obtained from the regression analysis (Panel D) is 1.4, which is lower than the other filter samples. This difference seems to be related to the collection times 141 for the filter samples. The UNC samples included several intensive sampling periods of 6 h or 142 less, whereas the GIT and EPA filters were switched daily. If only the daily UNC samples are 143 included in the regression analysis a slope of 1.8 is obtained, which is similar to the GIT and 144 EPA samples. The AMS OM<sub>1</sub> and the FTIR OM<sub>2.5</sub> obtained from filter samples are compared in 145 Panel E resulting in a regression slope of 1.3 ( $R^2 = 0.63$ ). Both the filters analyzed by FTIR as 146 well as the UNC filters exhibit higher amounts of organics relative to the 24 hr filters when the 147 148 collection times are shorter, which is likely due to evaporation losses of semi-volatiles from the 149 daily samples [Russell et al., 2009b]. Furthermore, high temperatures on the asphalt-coated roof where the filter samplers were located may have increased the influence of evaporation. It should 150
151 be noted that all the analyses are for  $PM_{2.5}$  particles except the AMS, which is a  $PM_1$  instrument. The impact of the different size cuts on the comparison can be evaluated by estimating that 15% 152 of the PM<sub>2.5</sub> organic mass is present between 1 and 2.5 µm on average. This percent is 153 determined from online Sunset OC measurements that were performed while switching between 154 155 a  $PM_{2.5}$  and  $PM_1$  cyclone from 6/12 through 6/16. Accounting for this additional mass that is not measured by the AMS would increase the slopes for the regression analyses, but the corrected 156 157 values for the GIT, EPA, and UNC filter samples would still fall within the expected range of 1.2 158 -2.2 for OM/OC (the expected 1.7 value with a  $\pm 30\%$  uncertainty range for the AMS, and 159 neglecting the uncertainty of the OC measurements).

For completeness, the slopes from linear ODR regression analyses for each possible 160 pairing of OM or OC measurements are summarized in Table B-2 along with R<sup>2</sup> values. The 161 AMS measurements of  $OM_1$  are converted to  $OC_1$  using the  $OM_1:OC_1$  ratios determined from 162 the elemental analysis of the AMS mass spectra. In general, the AMS and all three of the filter 163 OC<sub>2.5</sub> measurements (GIT, EPA, UNC) are in agreement within the uncertainties, exhibiting 164 slopes between 0.81 and 1.14 and  $R^2$  values higher than 0.60. The lowest correlations are for 165 comparisons with the UNC filter samples, which is likely due to different slopes observed in the 166 167 regression analyses for the 24 h versus intensive UNC sampling periods. If comparing only 24 h OC<sub>2.5</sub> data from the UNC group against the AMS as well as the EPA and GIT filter samples, then 168 all the  $R^2$  values are higher than 0.78. The online Sunset  $OC_{2.5}$  measurement shows good 169 correlation with the AMS and the filter OC measurements ( $R^2 \ge 0.75$ ), but it is systematically 170 lower by about a factor of two against all other measurements, which might be due to the 171 denuder utilized in the online Sunset OC<sub>2.5</sub> measurement as described in the preceding 172 paragraph. Alternatively, the un-denuded  $OC_{2.5}$  filter samples may be impacted by a positive 173

174 artifact due to adsorbing volatile organic gases, although the agreement between the online AMS  $OC_1$  and offline filter  $OC_{2.5}$  indicates that this positive artifact is not impacting other 175 comparisons. Lastly, when comparing the 24 h FTIR OM<sub>2.5</sub> against the 24 h GIT and EPA filter 176  $OC_{2.5}$  the slope is considerably lower than the expected OM:OC ratio, and the correlation 177 between the measurements is only moderate ( $R^2 \ge 0.52$ ). One possible reason for the low FTIR 178 OM<sub>2.5</sub> concentrations and the lack of a strong correlation is that the evaporation of organics from 179 the FTIR samples was more extensive. The UNC filter  $OC_{2.5}$  shows better agreement with the 180 FTIR OM<sub>2.5</sub> results (FTIR OM<sub>2.5</sub> : UNC OC<sub>2.5</sub> = 1.29,  $R^2 \ge 0.76$ ), which is expected since these 181 samplers were located closer to each other on the Keck Building rooftop, and both analyses 182 included intensive samples. Selecting only the intensive periods slightly improves the best-fit 183 slope in the regression analysis (1.33 vs. 1.29). As discussed above the AMS  $OM_1$  and FTIR 184  $OM_{2.5}$  agree reasonably well although the FTIR  $OM_{2.5}$  is somewhat lower (AMS  $OM_1$  : FTIR 185  $OM_{2.5} = 1.25$ ,  $R^2 \ge 0.63$ ). This observation is consistent with previous comparisons that have 186 shown FTIR measurements tend to be lower than and less correlated with AMS measurements 187 when carried out in urban areas [Russell et al., 2009a]. 188

**Table B-1:** Summary of the different OM and OC measurements taken on the Caltech campus
during the CalNex campaign (GIT = Georgia Institute of Technology, EPA = U.S.
Environmental Protection Agency, UNC = University of North Carolina). Note: the intensive
periods for the UNC Filter OC and FTIR OM coincided.

	Online/Offline?	Location	Dates for Sampling	Number of Samples	Time Resolution	Size Cut
AMS	Online	Ground Site	5/15-6/15	3681	2.5 min	$PM_1$
Sunset Online OC	Online	Ground Site	5/15-6/15	775	44 min	PM <sub>2.5</sub>
GIT Filter OC	Offline	Keck Roof	5/15-6/15	31	23 h	PM <sub>2.5</sub>
<b>EPA Filter OC</b>	Offline	Keck Roof	5/15-6/15	32	23 h	PM <sub>2.5</sub>
UNC Filter OC	Offline	Keck Roof	5/15-6/13	58	23 h, or 3-6 h	PM <sub>2.5</sub>
FTIR OM (Scripps)	Offline	Keck Roof	5/15-6/15	57	23 h, or 3-6 h	$PM_{2.5}$

**Table B-2:** Slopes and correlation coefficients for regression analyses of various OM and OC measurements located on the CalTech campus during CalNex (GIT = Georgia Institute of Technology, EPA = U.S. Environmental Protection Agency, UNC = University of North Carolina). *Note:* FTIR results correspond to FTIR OM data, while all other data sets are exclusively OC.

Slope	AMS OC <sub>1</sub>	FTIR OM <sub>2.5</sub> (Scripps)	Online Sunset OC <sub>2.5</sub>	GIT Filter OC <sub>2.5</sub>	EPA Filter OC <sub>2.5</sub>	UNC Filter OC <sub>2.5</sub>	(y data)
AMS OC <sub>1</sub>			-		-	_	
FTIR OM <sub>2.5</sub> (Scripps)	1.25 <sup>a</sup>						
Sunset Online OC <sub>2.5</sub>	1.95	3.13					
GIT Filter OC <sub>2.5</sub>	0.99	0.83	0.48				
EPA Filter OC <sub>2.5</sub>	1.13	0.99	0.56	1.14			
UNC Filter OC <sub>2.5</sub>	0.81	1.29	0.41	1.12	0.88		
(x data)							
		FTIR	Online			UNC	
$\mathbb{R}^2$	AMS OC <sub>1</sub>	OM <sub>2</sub> c	Sunset	GIT Filter	EPA Filter	Filter	
	1	(Scripps)	OC <sub>2.5</sub>	OC <sub>2.5</sub>	$OC_{2.5}$	OC <sub>2.5</sub>	
AMS OC <sub>1</sub>	1	(Scripps)	OC <sub>2.5</sub>	OC <sub>2.5</sub>	OC <sub>2.5</sub>	OC <sub>2.5</sub>	
AMS OC <sub>1</sub> FTIR OM <sub>2.5</sub> (Scripps)	0.63 <sup>a</sup>	(Scripps)	OC <sub>2.5</sub>	OC <sub>2.5</sub>	OC <sub>2.5</sub>	OC <sub>2.5</sub>	
AMS OC <sub>1</sub> FTIR OM <sub>2.5</sub> (Scripps) Sunset Online OC <sub>2.5</sub>	0.63 <sup>a</sup> 0.75	(Scripps)	OC <sub>2.5</sub>	OC <sub>2.5</sub>		OC <sub>2.5</sub>	
$\begin{array}{c} AMS \ OC_1 \\ FTIR \ OM_{2.5} \ (Scripps) \\ Sunset \ Online \ OC_{2.5} \\ GIT \ Filter \ OC_{2.5} \end{array}$	0.63 <sup>a</sup> 0.75 0.78	(Scripps) 0.49 0.52	0.86	OC <sub>2.5</sub>	OC <sub>2.5</sub>	OC <sub>2.5</sub>	
$\begin{array}{c} AMS \ OC_1 \\ FTIR \ OM_{2.5} \ (Scripps) \\ Sunset \ Online \ OC_{2.5} \\ GIT \ Filter \ OC_{2.5} \\ EPA \ Filter \ OC_{2.5} \end{array}$	0.63 <sup>a</sup> 0.75 0.78 0.78	(Scripps) 0.49 0.52 0.55	0.86 0.82	OC <sub>2.5</sub>	OC <sub>2.5</sub>	OC <sub>2.5</sub>	

<sup>a</sup>The AMS vs. FTIR comparison is for OM vs. OM.

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**Figure B-1:** (**A**) Time series of mass concentrations as measured by the AMS, SMPS, and UHSAS. rBC from the SP2 has been added to the AMS time series. The SMPS and UHSAS mass concentrations are calculated assuming spherical particles and using an estimated density obtained from the AMS and rBC measurements [*Zhang et al.*, 2005]. (**B**) The mass over 740 nm estimated geometric diameter, equivalent to ~1080 vacuum aerodynamic diameter, as measured by the UHSAS. (**C**) Scatter plot of the AMS plus rBC versus SMPS mass concentrations with linear fit. (**D**) Scatter plot of the AMS plus rBC versus UHSAS mass concentrations. The total UHSAS mass (red markers) and the UHSAS mass for particles less than 740 nm in geometric diameter (blue markers) are displayed. The linear fit corresponds to the UHSAS mass below 740 nm geometric diameter.



**Figure B-2:** (A) Time series of extinction measured by the CAPS instrument (green line) and Mie scattering calculated from SMPS data (black markers). Both traces correspond to a wavelength of 532 nm, and the Mie scattering was calculated using a refractive index of 1.54, which is the average for  $(NH_4)_2SO_4$  and  $NH_4NO_3$  [*Kleinman et al.*, 2007]. (B) Time series of CAPS extinction (red line) and calculated Mie scattering (black markers). Both traces correspond to a wavelength of 630 nm, and the Mie scattering was calculated using the same index of refraction (1.54). (C) Scatter plot of calculated Mie scattering and CAPS extinction for 532 nm with a linear fit of the data. (D) Scatter plot of calculated Mie scattering and CAPS extinction for 630nm with a linear fit of the data.



**Figure B-3:** (A) Time series of nitrate mass concentration measured by the AMS and the PILS-IC instrument. (B) Time series of sulfate mass concentration measured by the AMS and the PILS-IC instrument. (C) Scatter plot of the AMS and PILS-IC nitrate mass concentrations. Linear fits are shown for the entire data set (solid line), and also for selected periods with low PALMS sea salt concentrations (dashed line). (D) Scatter plot of the AMS and PILS-IC sulfate mass concentrations. Linear fits are shown for the entire data set (black solid line), and also for periods with low PALMS sea salt concentrations dashed line). The PALMS data corresponds to a PM<sub>2.5</sub> size cut.



**Figure B-4:** (A) Times series of the OM<sub>1</sub> measured by the AMS and the OC<sub>2.5</sub> measured online by the Sunset Labs OC/EC analyzer. (B) Scatter plot of the AMS OM<sub>1</sub> versus the online Sunset OC<sub>2.5</sub>. (C) Plot of the AMS OM<sub>1</sub> versus the OC<sub>2.5</sub> measured using two sets of filter samples collected by the Georgia Institute of Technology group (gold) and the EPA group (blue). (D) Plot of the AMS OM<sub>1</sub> versus the OC<sub>2.5</sub> measured from the UNC group filter samples. (E) Plot of the AMS OM<sub>1</sub> versus the OM<sub>2.5</sub> determined from FTIR measurements. The lines in Panels B – E represent linear fits of the data. Subscripts indicate measurement size cut in  $\mu$ m and for aerodynamic diameter.

## Section C: Comparisons to Previous Campaigns in Los Angeles Area and Additional Aerosol Composition Figures

In Table C-1 the campaign average mass concentrations reported for CalNex are 208 compared against those from three previous campaigns that took place in the LA basin: SOAR-1 209 210 [Docherty et al., 2011], PACO [Hersey et al., 2011], and SCAQS [Chow et al., 1994]. It should be noted that the PACO campaign consisted of three periods, and for the purpose of this 211 comparison the first and third periods were selected, since those portions of PACO took place at 212 the same time of year as CalNex and SOAR-1, respectively. The fractional composition is 213 similar between the sites despite the different locations and years for the campaigns, as well as 214 215 the utilization of different measurement techniques during the SCAQS campaign. The dominant fraction is OA, which accounts for about half of the total mass. Sulfate and nitrate are the next 216 largest fractions ranging between 16 - 30% and 14 - 22% of the total mass, respectively. The 217 218 relative amount of ammonium is surprisingly consistent between the campaigns accounting for 12 - 13% of the total mass, while the chloride is a small percentage for all the studies. In 219 Pasadena, Riverside, and Burbank EC accounted for 3 - 6% of the aerosol mass concentration, 220 respectively. 221

The fraction of organic signal at m/z 44, termed  $f_{44}$ , is often taken as an indicator of relative oxygen content in OA because in ambient measurements m/z 44 is typically dominated by the CO<sub>2</sub><sup>+</sup> ion. The scatter plot of O/C and  $f_{44}$  shown in Figure C-1 confirms and quantifies this relationship for Pasadena during CalNex. (Note: CO<sub>2</sub><sup>+</sup> was not separated using the highresolution data for this figure, but on average CO<sub>2</sub><sup>+</sup> accounted for 95% of the organic signal measured at m/z 44.) In addition, Figure C-1 includes the best-fit lines determined from regression analyses of the CalNex data as well as for Riverside and Mexico City. All three lines are similar, which supports the validity of the AMS measurements for Pasadena and provides a sample of the variability of the O/C to  $f_{44}$  relationship across different field sites and time periods.

Shown in Figure C-2 is the relative contribution of each species to the submicron mass as 232 233 a function of the total mass. A probability density distribution of the submicron mass is displayed as well (right axis). All data represent three hour averages. The relative composition does not 234 vary greatly between low and high concentration periods. Nitrate becomes more important with 235 increasing total concentrations (up to 29%). OA is important at all concentrations and is typically 236 237 40% of PM<sub>1</sub>. The data in Figure C-2 illustrate that OA and ammonium nitrate contribute substantially to the number of high PM<sub>1</sub> events. Shown in Figure C-3 is the relative contribution 238 239 of each PMF component to the OA mass as a function of the total OA mass (similar to Figure C-2). A probability density of the OA mass is displayed as well (right axis). The relative OA 240 241 composition is increasingly dominated by OOA, and in particular SV-OOA, during high concentration periods. As discussed previously, OA is an important contributor to the total 242 submicron mass at all concentrations. Combining the data shown in Figures C-2 and C-3, it can 243 then be concluded that freshly formed SOA, likely from photochemical production within the 244 basin, contributes substantially to the number of high PM<sub>1</sub> events along with nitrate. As 245 discussed in Section 3.1 many of the highest PM<sub>1</sub> concentrations occur during periods when 246 synoptic conditions (e.g., low boundary layer heights) trap pollution in the LA Basin. 247

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250 Table C-1: Summary of campaign average mass concentrations as a percent of the total nrPM<sub>1</sub> and EC during CalNex, SOAR-1, PACO, and SCAQS. (Note: Campaign average EC 251 concentrations were not reported for PACO. Given the low concentrations of EC observed for 252 253 selected days during PACO however, the impact on the calculated percentages is likely to be small.) 254

	CalNex <sup>a</sup>	SOAR-1 <sup>b</sup>	PACO (I) <sup>c</sup>	PACO (III) <sup>d</sup>	SCAQS <sup>e,f,g</sup>
Location	Pasadena	Riverside	Pasadena	Pasadena	Burbank
OA	43	45	42	55	43
Nitrate	22	22	15	15	14
Sulfate	18	17	30	16	24
Ammonium	13	12	13	13	12
Chloride	<1	<1	<1	<1	<1
EC	3	4	N/A	N/A	6

255

<sup>a</sup> May 15<sup>th</sup> to Jun 16<sup>th</sup>, 2010 (AMS and Sunset EC measurements) <sup>b</sup> Jul 15<sup>th</sup> to Aug 15<sup>th</sup>, 2005 (AMS and Sunset EC measurement) <sup>c</sup> May 22<sup>nd</sup> to Jun 12<sup>th</sup>, 2009 (AMS measurements) <sup>d</sup> Jul 10<sup>th</sup> to Aug 4<sup>th</sup>, 2009 (AMS measurements) <sup>e</sup> Jun 9<sup>th</sup> to Sept 3<sup>rd</sup>, 1987 (Selected Days)

<sup>f</sup>PM<sub>2.5</sub>, OC measurement converted to OM using OM:OC of 1.7, water-soluble inorganics only

<sup>g</sup> Chloride, nitrate, and sulfate measured by ion chromatography, ammonium measured by colorimetry, OC measured by thermal manganese oxidation.



**Figure C-1:** Scatter plot of  $f_{44}$  versus O/C calculated from HR-ToF-AMS high resolution data. A linear ODR fit of the CalNex data is shown along with the similar results from Riverside, CA [*Docherty et al.*, 2011] and Mexico City [*Aiken et al.*, 2008].



**Figure C-2:** The fraction of the total submicron aerosol mass contributed by different aerosol species as a function of the total mass. Also shown is a histogram of the total submicron aerosol mass for CalNex (right axis).



**Figure C-3:** The fraction of the OA mass contributed by different components as a function of the total OA mass. Also shown is a histogram of the total OA mass for CalNex (blue, right axis).

259

## Section D: Selection of PMF solution & Additional PMF Figures

260 This section describes the process for selecting the 5-component PMF solution that is described in the main text. An in-depth description of PMF and its application to AMS data is 261 262 not included here as it has already been provided in previous publications [*Paatero et al.*, 1994; 263 Ulbrich et al., 2009], and instead we focus on the specific analysis of the CalNex data set. The 264 selection of the solution was based on the mass spectral profiles, the time series, diurnal cycles, and the correlations of the components with time series for tracer species. Panel A of Figure D-1 265 summarizes the types and mass fractions of the different components identified as the number of 266 components is systematically increased from 3 to 10 (for FPeak=0). The 3-component solution is 267 268 similar to that found for PMF analyses of other data sets with HOA, SV-OOA, and LV-OOA 269 components identified. If the number of components is increased to four, then CIOA is also resolved. The mass fraction of HOA is substantially reduced in the 4-component solution 270 271 compared to the 3-component solution. Furthermore, HOA in the 3-component solution exhibits 272 a unique evening peak, and in the 4-component solution CIOA displays this peak instead of HOA. Together these observations suggest that a large portion of the CIOA mass is classified as 273 HOA in the 3-component solution. We conclude that the CIOA component is distinct from the 274 other components, and in particular HOA, based on it substantially different diurnal cycle 275 (Figure 5A, main text), and the dramatic improvement in the correlation of HOA with rBC (R 276 277 increases from 0.55 to 0.72) when increasing the number of components to four. This conclusion is further supported by the mass spectra as discussed in this section below. 278

Increasing the number of components to five leads to a third OOA component, but it is unclear if the additional component represents a different type of OOA given the lack of unique correlations with tracers. In contrast, at six components LOA is resolved, which is clearly 282 distinct from the previously identified components. The LOA component is nitrogen-rich, and 283 has a substantially different time series (Figure 4, main text). As described in the main text the LOA mass spectra is distinguished by prominent fragments that are characteristic of amines: 284  $CH_4N^+$  (*m*/*z* 30),  $C_2H_4N^+$  (*m*/*z* 42),  $C_3H_6N^+$  (*m*/*z* 56),  $C_3H_8N^+$  (*m*/*z* 58),  $C_5H_{10}N^+$  (*m*/*z* 84), 285  $C_5H_{12}N^+$  (m/z 86). The sum of the absolute residuals associated with these amines is plotted 286 287 versus number of components in Panel B of Figure D-1. This residual decreases with the number of components, but the decrease is largest between the five-component and six-component 288 solutions. In addition, there is only a slight decrease in the residuals when increasing the number 289 290 of components beyond six. Clearly, LOA in the 6-component solution is needed for PMF to properly account for amines in OA measured at the Pasadena ground site. 291

For PMF solutions with more than 6 components interpretation becomes increasingly 292 difficult. Numerous oxygen-rich components are identified, which could be classified as OOA. 293 294 Unique correlations to identify separate sources for these components are not found though. A 295 key limitation of PMF analysis is the assumption of a constant mass spectrum for each component. Thus, it is possible that the variable nature of the SOA spectrum with, for instance, 296 photochemical age leads to significant residuals in PMF, and when increasing the number of 297 components beyond six these residuals control the additional components in the PMF solution, 298 leading to more 'OOA' components [Ulbrich et al., 2009]. 299

Even in the 6-component solution it is unclear if the three OOA components represent distinct sources or chemical types. Specifically, for the 6-factor solution two of the three OOA components (OOA-2 and OOA-3) exhibit a high correlation in time (R=0.77) and very similar correlations with tracers (Figure D-2), which suggests these two components may not be distinct. Furthermore, OOA-3 is the most oxidized component, but does not show the strongest 305 correlation with sulfate, which is usually associated with more aged OOA [DeCarlo et al., 2010; 306 Sun et al., 2011; Ulbrich et al., 2009]. It is proposed therefore, that the OOA-3 factor results from artificial "splitting" and/or "mixing" of distinct components that is observed when too 307 many components are requested in a PMF solution [Ulbrich et al., 2009]. This artifact is likely 308 309 due to the fixed nature of the OOA spectra that do not fully capture the chemical variability of 310 SOA, which is a potentially larger source of residuals than omission of the LOA component. To address this problem while at the same time resolving the LOA component, the PMF analysis is 311 repeated after subtracting out the contribution of LOA to the mass spectral matrix. The LOA 312 313 contribution is determined from the 6-component solution of the original PMF analysis, and is included when summarizing the final PMF results. Thus, this method is equivalent to 314 constraining LOA to have a time series and mass spectrum that is invariant as the number of 315 component in increased similar to advanced factor analysis of Lanz et al. [2008]. It is also noted 316 that while selection of a PMF solution does require subjective 'user input', the exploration of 317 318 higher factor solutions and the recombination of factors that are indistinct has been previously reported in the literature [e.g., Docherty et al., 2011; Liu et al., 2011; Zhang et al., 2007]. 319

320 It should be noted that the LOA contribution to the total OA mass is small. Also, LOA exhibits a time series and mass spectra that contributes significantly to the PMF residual and is 321 quite different from the other components. Thus, it expected that subtracting the LOA 322 contribution only has a weak influence on the other PMF components. To verify this weak 323 influence, a correlation analysis was carried out that compared each component for the four 324 325 component solution without LOA subtracted against the five component solution in which the LOA was subtracted. In other words, the 4-component solution (HOA, CIOA, SVOOA, and 326 LVOOA) in the original PMF analysis is compared against the 5-component solution in the PMF 327

analysis with a fixed LOA contribution (HOA, CIOA, SVOOA, LVOOA, and LOA). As can be seen in Figure D-3 the time series and mass spectra of HOA, CIOA, SVOOA, and LVOOA for the two PMF methods are almost identical. The correlation plot for the HOA time series exhibits a slope of slightly lower than one (0.86) likely due to re-apportionment of HOA mass to LOA, but the correlation is still very high (R=0.97). In total, Figure D-3 indicates subtracting the LOA contribution does not substantially impact the other components in the PMF solution.

In Panel C of Figure D-1, the mass fraction and identities of the components are 334 summarized for the PMF analysis with the fixed LOA contribution. The 5-component solution is 335 the final solution described in the main text. Similar to the original PMF analysis, a dramatic 336 337 increase in the correlation of HOA and rBC is observed when the CIOA component is resolved in the 5-component solution (Panel D), and subsequent increases in the number of components 338 either marginally increase or decrease this correlation. This observation is consistent with 339 340 concluding that CIOA is distinct from the other components. In addition, the 6-component solutions for the two PMF analyses are similar, which is expected since the LOA contribution in 341 both analyses is identical. The similarity indicates that holding the LOA contribution fixed does 342 not create unforeseen changes in the PMF analysis. The Q/Qexp values for the various PMF 343 solutions are shown in Panels C and D. (Note: Q is the total sum of the squares of each residual 344 divided by its expected error, and  $Q_{exp}$  equals the degrees of freedom in the fitted data, which is 345 approximately the product of the number of rows and columns for the input mass spectral matrix. 346 In addition, Fpeak is a parameter that explores different "rotations" of the PMF solution where 347 the component time series are made more different or the component mass spectra are made 348 more different [Ulbrich et al., 2009].) For the final 5-component solution a reasonable Q/Q<sub>exp</sub> 349 value of 1.9 is obtained (Panel D). A Q/Qexp value near one indicates that the assumptions of the 350

bilinear PMF model are appropriate and that the estimation of the errors for the input data isaccurate.

Figure D-4 shows the value of  $Q/Q_{exp}$  as a function FPeak for the 5-component solution with the fixed LOA contribution. Minimum  $Q/Q_{exp}$  values are observed for FPeak equal to zero. In addition, the correlation of the HOA component time series with that of the external tracer rBC does not improve for non-zero FPeak values. Thus, the 5-component solution corresponding to FPeak = 0 is the final solution selected for further discussion in the main text. Additionally, Figure D-5 summarizes an analysis of the residuals for the final 5-component solution (with FPeak = 0).

It was recently shown by Mohr et al. [2011] that HOA and cooking organic aerosol can 360 361 be distinguished by their relative values of AMS  $f_{55}$  and  $f_{57}$ , which represent the fraction of the total OA at m/z 55 and m/z 57, respectively. The differences in  $f_{55}$  and  $f_{57}$  between the two 362 components are driven by the relative prominence of the oxygenated fragments  $C_3H_3O^+$  and 363  $C_{3}H_{5}O^{+}$  in the mass spectra of cooking organic aerosol. For the CalNex PMF solution, the mass 364 spectrum of the CIOA component (Figure 4A) shows the presence of these fragments, and they 365 represent a greater fraction of the signal at m/z 55 and m/z 57 for CIOA versus HOA. To further 366 explore if the mass spectra of HOA and CIOA for CalNex are consistent with previously 367 published studies,  $f_{55}$  versus  $f_{57}$  data for the two PMF components are plotted in Figure D-6A. 368 369 The lines in Figure D-6A are taken directly from Mohr et al. [2011] and represent linear fits of  $f_{55}$  versus  $f_{57}$  data from previously reported cooking organic aerosol and HOA PMF components 370 as well as from cooking and traffic source emission studies. Also plotted in Figure D-6A is  $f_{55}$ 371 versus  $f_{57}$  for the total time-resolved organic mass spectra after subtracting out the contribution of 372 SV-OOA and LV-OOA (the axes are labeled with 'OOA sub' to indicate this subtraction) so the 373

374 data reflects only contributions from primary components. The resulting data points are colored by the relative contribution of CIOA. The CIOA component lies along the line for cooking 375 source emissions, consistent with the description of CIOA as 'cooking-influenced' aerosol. The 376 HOA component at CalNex does not match the linear fits for HOA as well, but it does lie within 377 378 the range of the raw values used for the regression analysis in Mohr et al. [2011]. Since the differences between CIOA and HOA in  $f_{55}$  versus  $f_{57}$  space are related to oxygenated fragments, 379 it is possible that the higher HOA oxidation in our study may lead to changes in the HOA data 380 points in this space and explain the difference between the CalNex HOA component and the 381 382 linear fits from Mohr et al. [2011]. For the time-resolved data, when CIOA has a large contribution the data in  $f_{55}$  versus  $f_{57}$  space resembles cooking emission sources, whereas when 383 the CIOA contribution is low the data more closely resemble the expected HOA values. This 384 result supports the conclusion that the organic aerosol at the Pasadena ground site had substantial 385 contributions from both primary combustion and cooking sources. In addition, the CIOA and 386 387 HOA components contain spectral characteristics that are similar to analogous components and primary emissions from previous studies. 388

The robustness of the PMF CIOA component is verified by comparing the CIOA time 389 series against the concentration predicted for cooking organic aerosol using the estimation 390 method presented in Mohr et al. [2011], which is derived from several previous source emission 391 and PMF studies. Briefly, this method calculates the amount of cooking organic aerosol by 392 scaling up the measured organic concentration at m/z 55 after accounting for possible 393 394 interferences from other primary and secondary OA. A scatter plot of PMF CIOA versus the concentration calculated from m/z 55 is shown in Figure D-6B. For the entire CalNex data set 395 the slope is near one (0.98), but the correlation is not particularly strong (R=0.63). The data in 396

397 Figure D-6B are also colored by the amount of organic mass measured at m/z 44, which is an indicator for the relative influence of SOA [Aiken et al., 2009; Mohr et al., 2011; Ng et al., 398 2011]. It is observed that many periods with high m/z 44 exhibit a worse correlation, which is 399 expected given the known contribution of SOA compounds to m/z 55 as already mentioned. 400 Mohr et al. [2011] account for this interference by assuming the interference from SOA at m/z 55 401 402 is proportional to the amount of signal at m/z 44. This assumption may not hold in cases when multiple SOA sources with different amounts of aging are contributing to the organic mass at m/z403 44 and m/z 55 resulting in varying proportionalities. To minimize the impact of this interference 404 the data is fit a second time using only periods when m/z 44 is below its median value, which 405 results in a higher correlation (R=0.88) and lower slope (0.76). The difference of less than 25% 406 in average concentration represents reasonable agreement between the two methods, and can be 407 mostly explained by the 20% uncertainty in the scaling factor used in Mohr et al. [2011] to 408 calculate cooking organic aerosol from the organic mass measured at m/z 55. While the 409 possibility that PMF is apportioning non-cooking OA to the CIOA mass cannot be completely 410 ruled out, the comparison presented in this paragraph indicates a large majority of CIOA is from 411 cooking sources. 412

The time series of the PMF components can be further analyzed using an autocorrelation plot in which the correlation of each factor with itself is calculated for various time offsets. In this analysis species with high frequency fluctuations in concentrations (i.e., having many 'spikes' in their time series) will have a steep profile and vice versa. As seen in Figure D-7 the autocorrelation profiles of SV-OOA and LV-OOA are the flattest, which is consistent with the more regional nature of these components. Furthermore, the observation that the LV-OOA profile is less steep than SV-OOA supports the association of LV-OOA with aged secondary 420 organic aerosol that is expected to vary in concentration on longer time scales than fresh 421 secondary organic aerosol. In contrast, the HOA component has a steep profile at the shortest times and a flatter profile at longer times indicating that this component has both local and 422 423 regional sources. This finding is not surprising given that some HOA is generated by local traffic in the Pasadena area, but HOA is also advected to Pasadena from other areas in the LA Basin. 424 425 Interestingly, the CIOA component appears to be more dominated by local sources in comparison to HOA, which may be related to the lower wind speeds and reduced advection in 426 the evenings when CIOA is highest in concentration. Alternatively, if the atmospheric lifetime of 427 428 CIOA was shorter than HOA, then that would also result in a relatively steeper profile for CIOA. As described previously, the LOA component time series varies rapidly with time, and thus 429 430 displays the steepest profile in the auto-correlation plot, supporting the description of this factor as 'local' organic aerosol. 431

432 The correlations of the PMF component time series with various other species measured at the Pasadena ground site are summarized in Table D-1, and generally support the description 433 of the components discussed in the main text. For the readers convenience the correlations are 434 also summarized in a bar graph in Figure D-8. The most notable correlations are summarized in 435 this section. First, the primary combustion emissions tracers EC, rBC, NO<sub>x</sub>, CO, and primary 436 hydrocarbons correlate with HOA. A correlation is also observed between HOA and PM<sub>1.15</sub> Zn. 437 The correlation with Zn may be explained by abrasion of tire-tread by road surfaces, which is 438 thought to be a major source of Zn in urban atmospheres [Adachi et al., 2004; Councell et al., 439 440 2004; *Hjortenkrans et al.*, 2007; *Salma et al.*, 2006], although a comparably strong correlation is not observed for other metals that have been linked to brake wear or road dust.  $NO_x$  does not 441 exhibit as strong a correlation with HOA as the other primary combustion tracers, and this 442

observation is probably due to the short lifetime of  $NO_x$  and the multi-hour transport time for 443 advection of HOA from the more western portion of the LA basin to the Pasadena ground site. 444 Moreover, NO<sub>v</sub> correlates better with HOA than NO<sub>x</sub> (R of 0.63 versus 0.45) likely because 445 oxides of nitrogen emitted by vehicles have a longer atmospheric lifetime when measured as 446 NO<sub>v</sub>. Taken together, the correlations of the various species with HOA suggest that primary 447 448 vehicular emissions are the dominant source for this component. The primary combustion tracers do not correlate with CIOA with the exception of the moderate correlation with CO (R = 0.43). 449 The correlations of HOA and CIOA with CO, as well as the correlation of HOA with EC are 450 451 discussed in further detail in Section 3.2.3 of the main text. Previous work by Sun et al. [2011] reported that the AMS fragments  $C_5H_8O^+$  and  $C_6H_{10}O^+$  showed high correlations specific to 452 453 cooking organic aerosols, and this correlation is also observed for the PMF results presented here. However, these oxygenated fragments show an even stronger correlation with SV-OOA, 454 which suggests that these tracers are not highly specific to cooking OA. 455

The SV-OOA component correlates strongly with acetaldehyde and odd-oxygen. 456 Acetaldehyde is a well-known secondary photochemical product with direct emissions that are 457 quickly overwhelmed by secondary formation within hours of processing [Sommariva et al., 458 2011; Washenfelder et al., 2011], and odd-oxygen is a useful tracer for the oxidation of VOCs 459 [Herndon et al., 2008; Wood et al., 2010]. Thus, the strong correlation of these species with SV-460 OOA is consistent with treating this component as a surrogate for 'fresh' SOA. Previous 461 publications have reported a correlation between nitrate and SV-OOA at some locations [e.g. 462 463 DeCarlo et al., 2010; Ulbrich et al., 2009], but a similar correlation is not observed at the Pasadena ground site. The lack of correlation is likely due to the higher temperatures and 464 reduced RH in the afternoon at the ground site, which lead to the volatilization of ammonium 465

nitrate at the same time SV-OOA concentrations are typically increasing. For LV-OOA a strong
correlation with sulfate is observed that is consistent with other studies [*DeCarlo et al.*, 2010; *Sun et al.*, 2011; *Ulbrich et al.*, 2009] and has been previously attributed to the non-volatile
nature of both sulfate and LV-OOA as well as the formation of these species from secondary
sources. The correlation of OOA with odd-oxygen is discussed in detail in Section 3.2.4 of the
main text.

PM<sub>1.15</sub> Ti exhibits a correlation with LOA (R = 0.63). A strong peak in LOA concentrations occurred on the morning of June 5<sup>th</sup> (PDT), and a similar event is seen in the PM<sub>1.15</sub> Ti time series. Paint-pigment has been identified as a source of titanium particles in the atmosphere [*Alpert et al.*, 1981], and amines are often used in paint application and surface coatings [*Unnikrishnan et al.*, 2006]. Still, a lack of corroborating evidence prevents assigning LOA to any specific source with confidence.

Several other tracers are listed in Table 2. In particular, acetonitrile is a common tracer 478 479 for biomass burning emissions, and a lack of correlation with acetonitrile is initially observed (R < 0.1). In contrast, after filtering out the acetonitrile data with concentrations above 1.5 ppmv to 480 481 remove the possible influence of local solvent use, a moderately strong correlation is observed with CIOA (R = 0.67) despite the relatively low acetonitrile concentrations that are near 482 background levels. This correlation may be due to barbequing with biomass fuels such as 483 charcoal. Indicators for marine influenced air masses used in this study are dimethyl sulfide 484 (DMS) and PALMS sea salt volume concentrations [Malm et al., 1994; Zorn et al., 2008], as 485 well as methanesulfonic acid (MSA) [Gaston et al., 2010], which is measured by the PALMS as 486 487 a relative concentration [Froyd et al., 2010]. However, the low correlations observed between these indicators and all the PMF components provide little information about the role of marinesources.

The concentrations for a variety of organic species were quantified by 2DTAG 490 measurements. The correlations between a selection of these species and the PMF components 491 492 are summarized in Table D-2. For a variety of polycyclic aromatic hydrocarbons (PAHs), 493 phytane, dibenzofuran, and the lowest-volatility measured Hopane the correlation with HOA is strongest, which is not surprising given that these compounds are characteristic of primary 494 vehicle emissions [Schauer et al., 1999a; 2002a; Williams et al., 2010]. In addition, several 495 ketones and undecylbenzene exhibit a higher correlation with HOA than the other PMF 496 497 components, and it is known that ketones and aromatics are found in tailpipe emissions from gas 498 and diesel vehicles [Jakober et al., 2006; Jakober et al., 2008]. However, some species such as chrysene, a PAH, are clearly primary emissions, but show a similar level of correlation with both 499 500 HOA and SV-OOA. This observation may be due to the similar time-of-day that HOA and SV-501 OOA concentrations peak (13:00 - 14:00 versus 14:00 - 15:00), and the lower time resolution of the 2DTAG, which averaged samples over 85 minutes. Thus, periods of high HOA and SV-OOA 502 concentrations may appear to occur close to simultaneously on the time scale of the 2DTAG, 503 504 which unfortunately adds uncertainty to the comparison of the 2DTAG data against the PMF components. This concern may also explain the apparent correlation of HOA with some 505 oxygenates. Considering only the compounds that have the highest correlation with SV-OOA, 506 this component tracks the concentrations of several phthalic acids and other compounds 507 508 structurally similar to phthalates. This finding is consistent with the description of SV-OOA 509 presented here since phthalic acids are well-known tracers for SOA from anthropogenic VOCs [Williams et al., 2010]. In contrast, the LV-OOA component exhibits weaker correlations with 510

511 2DTAG compounds (R < 0.5), which is likely due to the poor transfer efficiency of highly 512 oxidized compounds that is typical in GC systems [*Williams et al.*, 2006].

For CIOA, a weak correlation is observed with pentadecane. It should be noted that n-513 alkanes have been identified in emissions from meat charbroiling [Schauer et al., 1999b], but 514 515 also from gasoline and diesel vehicle emissions [Schauer et al., 1999a; 2002a]. Thus, the 516 correlation with pentadecane does not distinguish between possible cooking or vehicle emission sources. Using one-dimensional TAG Williams et al. [2010] observed in Riverside that several 517 alkanoic acids and alkylnitriles were the highest contributors to food cooking aerosols, although 518 519 it is recognized that some of these compounds can have secondary sources. For CalNex, hexadecanoic acid correlates most strongly with SV-OOA rather than CIOA suggesting that 520 521 secondary sources of alkanoic acids are influencing the air mass above the ground site. However, if the correlation analysis is limited to only periods with low SV-OOA concentrations 522 523 (less than the median) then CIOA does exhibit the strongest correlation with hexadecanoic acid. The alkylnitriles correlate more strongly with other PMF components than CIOA, which 524 suggests that these compounds may not be good markers for cooking emissions in Pasadena 525 possibly because they are also associated with vehicle emissions [Williams et al., 2010]. 526 527 Cholesterol and oleic acid are known to be present in cooking emissions as well [Schauer et al., 1999b; 2002b]. For cholesterol its size and alcohol functionality limits the sensitivity of 2DTAG. 528 Oleic acid can be measured by the 2DTAG, but in the field its mass spectrum is difficult to 529 distinguish from the background unresolved complex mixture. 530

531 Many of correlations observed with the 2DTAG compounds are consistent with the 532 designations of the PMF components presented here, although there are two serious caveats. 533 First, a substantial number of compounds show correlations with HOA and SVOOA that are

- similar in strength (e.g., Chrysene), which is likely due to the similar diurnal cycles of HOA and
  SVOOA. Second, for CIOA a correlation with hexadecanoic acid is observed, but correlations
  with other cooking-related compounds are either weak (alkylnitriles) or cannot be determined
- 537 because of instrument limitations (cholesterol & oleic acid).

**Table D-1:** Correlations (R values) of PMF component time series with the time series of tracers measured at the Pasadena ground site during CalNex. Tracers have been grouped for clarity, and important correlations for each tracer are boldfaced and underlined. Campaign average mass concentrations for each PMF component are also shown in the second row.

						542
Tracer	HOA	CIOA	LOA	SVOOA	LVOOA	
Campaign						
Avg. Conc.	0.82	1.21	0.34	2.43	2.26	
$(\mu g m^{-3})$						
rBC	0.70	0.07	0.36	0.40	0.35	Primary
EC	0.71	0.03	0.43	0.46	0.33	Primary
NO <sub>x</sub>	0.45	0.26	0.28	0.01	-0.07	Primary
Benzene	0.71	0.37	0.44	0.37	0.42	Primary
СО	0.59	0.43	0.41	0.49	0.41	Primary
Zn (PM <sub>1.15</sub> )	0.52	-0.17	0.33	0.14	0.33	Primary
Acetonitrile <sup>a</sup>	0.47	<u>0.67</u>	0.47	0.03	0.48	Primary
Propane	0.65	0.17	0.49	0.44	0.42	Primary
n-Butane	0.58	0.13	0.48	0.36	0.38	Primary
Isobutane	0.59	0.21	0.51	0.37	0.42	Primary
<i>n</i> -Pentane	0.66	0.19	0.57	0.33	0.36	Primary
Isopentane	0.72	0.26	0.53	0.44	0.35	Primary
Ti (PM <sub>1.15</sub> )	0.33	-0.08	<u>0.63</u>	0.05	0.11	Primary
NOy	<u>0.63</u>	0.25	0.40	0.37	0.23	Primary + Secondary
O <sub>x</sub>	0.28	0.10	0.04	<u>0.73</u>	0.17	Secondary
Acetaldehyde	0.64	0.19	0.26	0.82	0.39	Secondary
DMS	0.06	0.11	0.03	-0.08	-0.04	Marine
PALMS Sea Salt	0.17	0.00	0.04	0.00	0.00	M '
Vol. Conc. (PM <sub>1</sub> )	0.17	0.08	0.04	-0.20	-0.06	Marine
MSA	-0.10	-0.03	-0.10	-0.18	-0.34	Marine
Chloride	0.16	0.01	0.13	0.01	0.31	AMS
Nitrate	0.38	-0.03	0.44	0.12	<u>0.70</u>	AMS
Ammonium	0.40	0.00	0.43	0.19	0.77	AMS
Sulfate	0.49	0.02	0.36	0.39	0.69	AMS
$C_5H_8O^+$	0.58	0.47	0.23	<u>0.86</u>	0.44	AMS
$C_{6}H_{10}O^{+}$	0.56	0.60	0.24	<u>0.71</u>	0.36	AMS

<sup>a</sup> Correlations correspond to only acetonitrile concentrations below 1.5 ppbv to eliminate potential contributions from nearby solvent use.

- **Table D-2:** Correlations (R) of PMF components with 2DTAG compounds. The highest
- correlation for each tracer is boldfaced and underlined. 2DTAG data are only available from 6/11
- 545 6/16. Only compounds with R > 0.5 are shown.

2DTAG Compound	HOA	CIOA	LOA	SVOOA	LVOOA	
Phenanthrene	<u>0.60</u>	0.47	0.29	0.39	-0.01	Н
1-Methylphenanthrene	0.54	0.48	0.22	0.46	0.03	Y
2-Methylphentanthrene	0.56	0.34	0.23	0.42	-0.10	D
1-Methylanthracene	0.58	0.41	0.26	0.46	-0.01	R
2-Methylanthracene	0.54	0.35	0.25	0.47	0.03	0
2-Phenylnaphthalene	0.58	0.28	0.36	0.48	0.14	С
Chrysene	0.58	0.27	0.24	<u>0.61</u>	0.21	А
Lowest-Volatility Hopane	<u>0.59</u>	0.38	0.41	0.49	0.15	R
Pentadecane	0.36	<u>0.52</u>	0.32	0.22	0.23	В
Octadecane	0.50	0.30	0.18	<u>0.51</u>	0.17	0
Phytane	<u>0.59</u>	0.29	0.31	0.45	0.15	Ν
Octacosane	0.46	0.05	0.08	<u>0.51</u>	0.10	S
Nonacosane	0.51	0.09	0.28	<u>0.71</u>	0.31	
Triacontane	0.52	0.05	0.22	<u>0.60</u>	0.25	
Hentriacontane	0.49	0.15	0.18	<u>0.61</u>	0.39	
Decylbenzene	0.54	0.34	0.27	<u>0.58</u>	0.20	
Undecylbenzene	<u>0.54</u>	0.36	0.25	0.48	0.11	
3-Methylphthalic Acid	0.51	0.03	0.12	<u>0.86</u>	0.20	0
4-Methylphthalic Acid	0.54	0.09	0.18	<u>0.81</u>	0.03	Х
Dimethylphthalic Acids	0.53	0.03	0.13	<u>0.82</u>	0.13	Y
Chlorophthalic Acid	0.49	0.14	0.23	<u>0.74</u>	0.16	G
1H-Indene-1,3(2H)-dione	0.42	-0.05	0.06	<u>0.80</u>	0.24	Е
delta-Decalactone	0.47	0.05	0.12	<u>0.72</u>	0.13	Ν
delta-Hexadecalactone	0.53	0.20	0.28	<u>0.76</u>	0.35	А
Pentadecanone	0.52	0.37	0.38	<u>0.54</u>	0.23	Т
Hexadecanone	0.58	0.31	0.26	<u>0.64</u>	0.31	Е
Heptadecanone	0.59	0.39	0.33	<u>0.64</u>	0.37	S
Octadecanone	<u>0.57</u>	0.21	0.31	0.54	0.07	
Nonadecanone	<u>0.50</u>	0.19	0.39	0.49	0.14	
Trimethylpentadecanone	<u>0.62</u>	0.22	0.39	0.59	0.36	
Fluorenone	0.47	0.21	0.10	<u>0.57</u>	0.24	
Hydroxyfluorenone	<u>0.54</u>	0.47	0.30	0.53	0.34	
Naphthalic Anhydride	0.49	0.11	0.17	<u>0.67</u>	0.17	
Benzophenone	0.66	0.37	0.36	<u>0.67</u>	0.43	
Benzyl Benzoate	0.68	0.35	0.38	<u>0.73</u>	0.30	
Isopropyl Myristate	<u>0.67</u>	0.00	0.62	0.45	0.15	
Dibenzofuran	<u>0.64</u>	0.39	0.32	0.47	0.05	
Hexadecanoic Acid (SV-OOA<2.4 µg/m3)	0.51	<u>0.66</u>	0.55	0.35	0.43	
Tetradecanenitrile	0.55	0.23	0.48	<u>0.59</u>	0.36	Nitrogen-
Hexadecanenitrile	0.46	0.34	0.28	<u>0.59</u>	0.47	Containing
Octadecanenitrile	0.44	0.35	0.28	<u>0.62</u>	0.48	
Phthalimide	0.56	0.23	0.22	<u>0.78</u>	0.36	
Homophthalimide	0.50	-0.01	0.13	<u>0.84</u>	0.22	



**Figure D-1:** (A) Stacked bar plot showing the relative contribution of each PMF component as a function of the number of components. (B)  $Q/Q_{exp}$  for the original PMF analysis (black line and markers) and the sum of the absolute values of the residuals for selected amine-containing ions (red line and markers). Both data traces are displayed as function of the number of components. (C) The relative contribution of each PMF component, similar to the figure on the top left, but for PMF solutions where the LOA contribution to the OA spectra is fixed. (D)  $Q/Q_{exp}$  for the PMF analysis with a fixed contribution from the LOA component versus number of components (black line with markers). The correlation of HOA with rBC is also displayed (green line and markers).



**Figure D-2:** Summary of correlations for the OOA components identified in the 6-component PMF solution (without a fixed LOA contribution to OA). The OM:OC ratio is indicated in the upper-right corner of each panel.



**Figure D-3:** Scatter plots of each component for the 4-component PMF solution and the 5component PMF solution with a fixed LOA contribution. The left column contains plots for the time series and the right column contains plots for the mass spectra.



**Figure D-4:** (Left Axis)  $Q/Q_{exp}$  for the selected 5-component solution with the fixed LOA contribution plotted as a function of FPeak. (**Right Axis**) Correlation between HOA and rBC from the SP2 as a function of FPeak for the selected 5-component solution.



**Figure D-5:** (A) Box-and-whisker plot of residuals for each organic ion scaled to the predicted error from the error matrix. The boxes represent that  $25^{th}$  and  $75^{th}$  percentiles, and the whiskers represent the 5<sup>th</sup> and 95<sup>th</sup> percentiles. (B) Time series of the residual organic mass (= measured mass – reconstructed mass from PMF). (C) Time series of Q/Q<sub>exp</sub> (i.e., the residual squared divided by the predicted error squared, which is then normalized to Q<sub>exp</sub>).



**Figure D-6:** (A) Scatter plot of  $f_{55, OOA sub}$  versus  $f_{57, OOA sub}$  colored by the relative amount of CIOA (markers). Also shown is  $f_{55}$  versus  $f_{57}$  for CIOA (black circle) and HOA (gray circle). The lines represent linear fits of  $f_{55}$  versus  $f_{57}$  data from previously reported cooking organic aerosol (COA) and HOA PMF factors (solid lines) as well as from cooking and traffic source emission studies (dashed lines). The linear fits are reproduced from Mohr et al. [2011]. (B) Scatter plot of CIOA concentration determined by PMF vs. COA concentration determined using the method of Mohr et al. Also shown are the linear regressions for the entire data set (solid line) and for periods when m/z 44 was below its median concentration of 0.47  $\mu$ g m<sup>-3</sup> (dashed line).



**Figure D-7:** Auto-correlations for the PMF component time series over +/-110 minutes.


**Figure D-8:** Bar graph summarizing the correlations of the PMF factors with key tracer species. The correlations are taken from Table D-1. The bars are colored by the tracer classification. Note: Acetonitrile correlations correspond to only acetonitrile concentrations below 1.5 ppbv to eliminate potential contributions from nearby solvent use.

## 556 Section E: Evaluation of Photochemical Age Error

Photochemical age is a quantity developed as a metric for parcels of air arriving at remote receptors sites, and it is derived by assuming that the parcel is decoupled from fresh emissions as it is transported [*Kleinman et al.*, 2007; *Parrish et al.*, 2007]. However, the Pasadena ground site is not a remote receptor site, and it is impacted by pollutants that have been emitted recently as well as transported from more distant locations. The goal of this section is to evaluate the potential errors that result from calculating the photochemical age for an air parcel that is receiving continued additions of pollutants as it is transported to the measurement location.

A simple model was built that calculates the observed photochemical age based on a 564 565 given distribution of ages within an air parcel. For the dense urban region of Los Angeles it has been assumed that emissions are constant as an air mass is advected from the coastline to the 566 Pasadena site [Washenfelder et al., 2011]. Under this assumption the weights of the ages in the 567 distribution will be equal, and the distribution will range from zero to two times the chosen 568 569 photochemical age. Thus, the model has only one input parameter: photochemical age. It is emphasized that in this analysis the flat distribution of ages assumed will not account for dilution 570 due to increasing boundary layer height, or diurnal cycles in emission rates and oxidant 571 572 concentrations. While different compounds could be used in the model, we specifically focus on the case of photochemical age calculated from the ratio of 1,2,4-trimethylbenzene (1,2,4-TMB) 573 to benzene and utilize the emission ratios and OH reaction rates from Parrish et al. [2007]. The 574 model calculation involves: (1) calculating the concentrations of benzene and 1.2,4-TMB for 575 576 each age, (2) calculating the total contribution to benzene and 1,2,4-TMB concentrations from all the age steps in the assumed age distribution, and (3) calculating the observed photochemical age 577 based on the VOC concentrations. 578

579 The results of the model are shown in Figure E-1 for a range of inputted photochemical 580 ages. For this analysis the error is defined as:

581 
$$Error = \frac{(Age)_{derived} - (Age)_{input}}{(Age)_{input}}$$

where  $(Age)_{derived}$  is the photochemical age that would be derived from the observed VOC ratios, 582 and  $(Age)_{input}$  is the age originally entered into the model. The error increases in magnitude with 583 photochemical age, and the age derived from the observed VOC ratios is systematically lower 584 than the actual average age. This trend can be explained by considering a hypothetical system 585 586 composed of a fresh and an aged air parcel of equal volumes. If each parcel started with the same concentrations of emissions including benzene and 1,2,4-TMB, then when the two parcels are 587 mixed together the age of the mixed air should be simply the average of the ages of each 588 589 individual parcel. However, since both benzene and 1,2,4-TMB are depleted in the aged air parcel due to chemical processing, in the photochemical age calculation the aged parcel has less 590 mathematical weight than the fresh parcel. This unequal weighting explains why observations, as 591 modeled here, will be systemically lower than the true average age of the mixed parcel. 592

593 The results reported here follow those previously published in Parrish et al. [2007], which concludes that VOC ratios are a useful metric for determining photochemical ages even if mixing 594 of different air masses occurs. Based on the analysis presented here we estimate an error of 595 approximately 10%, corresponding to the mean photochemical age, which biases the observed 596 ages towards lower values. While this is a significant source of uncertainty, it should only impact 597 the accuracy of the observed photochemical ages and not relative comparisons for Pasadena (e.g. 598 weekday vs. Sunday), insofar as the distribution of ages is consistent. This requirement is likely 599 satisfied given the day-to-day similarity in meteorology and diurnal cycles at the ground site. 600



**Figure E-1:** The error in the photochemical age derived from the observed VOC ratios as a function of the actual photochemical age. The observed VOC ratios are simulated using the model described in Section E. The actual photochemical age is the mean of the different ages in the age distribution.



**Figure E-2:** Branching ratio between OH and Cl oxidation for benzene and 1,2,4-trimethylbenzene. The ratio was calculated using the relative OH to Cl concentrations as well as the corresponding rate constants from Young et al. [2013]. For both VOCs the oxidation chemistry is dominated by OH radicals, which is consistent with the method used to estimate photochemical age.



**Figure F-1:** Box-and-whiskers plot for the  $NO_x$  branching ratio on Weekdays vs. Sundays. Ratio was calculating using the method described in [*Dzepina et al.*, 2009]. Crosses represent the mean value.

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