Organic Aerosol Composition and Sources in Pasadena, California during the 2010 CalNex Campaign

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Abstract

Organic aerosols (OA) in Pasadena are characterized using multiple measurements from the 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, California. 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/ΔCO 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 and emissions – which suggests the dominance of gasoline emissions in SOA formation under the assumption that most urban SOA precursors are from motor vehicles.

1. Introduction

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 [*IPCC*, 2007]. In addition, atmospheric aerosols reduce visibility [*Watson*, 2002] and increase cardiac and respiratory disease in humans [*Dockery et al.*, 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 (~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.

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, 2011], and multiple previous measurement campaigns have aimed to characterize aerosols in this region. These campaigns include the 1987 Southern California Air Quality Study (SCAQS) [*Lawson*, 1990], the 1997 Southern California Ozone Study (SCOS97-NARSTO) [*Croes et al.*, 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,

88   several research flights were performed over California and LA during the Arctic Research of the

89   Composition of the Troposphere from Aircraft and Satellites Campaign (ARCTAS-CARB)

90   [*Jacob et al.*, 2010]. Using data from these campaigns it has been shown that SOA represents a

91   majority of the total OA mass in both Riverside [*Docherty et al.*, 2008] and Pasadena, CA

92   [*Hersey et al.*, 2011], which is similar to findings in other urban regions [*Jimenez et al.*, 2009].

93   The gas phase precursors for SOA potentially have many sources including vehicle emissions,

94   the biosphere, biomass burning, and food cooking [*Bahreini et al.*, 2012; *Hodzic et al.*, 2010;

95   *Schauer et al.*, 1999; 2002b]. Also, vehicle emissions, food cooking, biomass burning, and

96   primary biogenics have all been identified as sources of POA in the South Coast Air Basin

97   [*Williams et al.*, 2010; *Wonaschutz et al.*, 2011].

98   The California Research at the Nexus of Air Quality and Climate Change (CalNex) field

99   campaign was conducted in Spring 2010, and was a multi-institution effort to address

100 outstanding questions regarding atmospheric chemistry processes over the state of California and

101 the adjacent Pacific coastal region [*Ryerson et al.*, manuscript submitted for J. Geophys. Res.-

102 Atmos., 2012]. The CalNex campaign featured several research aircraft, the research vessel

103 Atlantis off the California coast, and two ground sites in Pasadena and Bakersfield. A major

104 scientific goal for CalNex was to improve scientific understanding of atmospheric aerosols in

105 California, and specifically, characterize important SOA precursors and formation pathways, as

106 well as the impacts of aerosols on radiative forcing and cloud formation [NOAA, 2008]. For

107 CalNex the Pasadena ground site was uniquely equipped to characterize aerosols, and especially,

108 organic aerosols. In total approximately 70 gas and particle phase measurements were taken at

109 the site representing, to our knowledge, one of the largest studies of aerosols and their

110 precursors. A full list of the instrumentation is available in the CalNex overview [*Ryerson et al.*,

111   manuscript submitted for J. Geophys. Res.-Atmos., 2012] and also at: http://tinyurl.com/CalNex.

112   Additionally, the ground site featured many state-of-the-art aerosol instruments including several

113   that had never been field-deployed previously.

114   Here we present a detailed analysis of aerosol measurements from multiple instruments,

115   including on- and off-line bulk and single particle methods, deployed to the Pasadena ground site

116   during CalNex. The goals of this work are to quantitatively evaluate SOA formation for the

117   South Coast Air Basin and compare it against other major urban regions, as well as to determine

118   the contributions of various sources to organic aerosol mass loadings. In particular, the relative

119   importance of diesel versus gasoline emissions in secondary organic aerosol formation has been

120   a source of scientific controversy [*Bahreini et al.*, 2012; *Gentner et al.*, 2012] and will be

121   examined here. To achieve these goals the following approach is utilized: (1) using positive

122   matrix factorization (PMF) the components of OA are identified and characterized (Section 3.2),

123   (2) the POA emission ratios with elemental carbon (EC) and CO are determined and rationalized

124   (Section 3.3), (3) the dependence of SOA concentration on photochemical age is quantified and

125   compared against previous measurements conducted in Riverside, Mexico City, and the

126   northeastern United States (Section 3.4), and (4) the weekly cycles (or lack thereof) in POA and

127   SOA concentrations are analyzed in the context of understanding the relative contributions to

128   each from diesel and gasoline motor vehicles (Section 3.5). The unique findings of this work

129   include the observation of a similar SOA formation rate for Pasadena versus other urban

130   locations, the first reported weekly cycle for POA concentrations, and an improved analysis of

131   the contribution of diesel emissions to SOA formation based on the lack of a weekly cycle in

132   SOA concentrations.

133

2. Experimental

2.1. CalNex ground site in Pasadena, California

The CalNex Pasadena ground site was located on the California Institute of Technology (Caltech) campus in Pasadena, California (34.1406 N, 118.1225 W, 236 m above mean sea level). The measurement period was May 15 2010 00:00 – June 16 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 Material). At nighttime winds were weaker and were most frequently from the southwest or southeast. Sunrise and sunset were approximately 5:30 and 20:00 (local time) during the sampling period. Boundary layer height, temperature, and relative humidity (RH) data are presented in the Supporting Material (Figure A-1) along with wind roses (Figure A-2).

2.2. AMS sampling and analysis

The concentrations of submicron non-refractory ($nrPM_1$) 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 $PM_{2.5}$ cyclone located 2 m above the roof of the container housing the instrument. The sampled air passed through a 6.8

156 m insulated copper inlet line and a dryer prior to analysis by the AMS. The resulting data were

157 averaged over 2.5 minute intervals. The ion paths through the time-of-flight chamber were

158 alternated between "V" and "W" modes every 150 s, and the reported concentrations correspond

159 to V-mode acquisition periods only. Size distributions were acquired during every V-mode

160 acquisition by operating the AMS in particle time-of-flight (PToF) mode [*Jimenez et al.*, 2003].

161 All data were analyzed using standard AMS software (SQUIRREL v1.51 and PIKA v1.10)

162 within Igor Pro 6.2.1 (WaveMetrics, Lake Oswego, OR) [*Sueper*, 2011].

163   It is well-known that for most ambient sampling conditions a collection efficiency (CE)

164 correction must be applied to the AMS data to account for particle bounce from the AMS

165 vaporizer [*Middlebrook et al.*, 2012]. Mass concentrations are typically calculated with a default

166 CE of 0.5. The degree to which particles bounce, and hence collection efficiency, are a function

167 of particle phase, which is influenced by the relative humidity of the sampling line, the

168 acidity/neutralization of the sulfate content, the ammonium nitrate content, and the organic liquid

169 content [*Middlebrook et al.*, 2012]. The sample flow was dried as described above, and the

170 sulfate content was largely neutralized (see Appendix). Thus, these experimental parameters are

171 not expected to impact CE. Ammonium nitrate concentrations varied widely during the

172 measurement period though, and accordingly a nitrate-dependent CE is applied following Nemitz

173 et al. [2010]. Quantifying the organic liquid content is challenging for ambient samples, however

174 the ratio of AMS mass to Scanning Mobility Particle Sizer (SMPS) mass exhibits no dependence

175 on the amount of OA oxidation as measured by O:C indicating that phase changes associated

176 with organic material are either not occurring or are not influencing the particle bounce and CE.

177 In total, the aerosol mass concentrations measured by the AMS after applying the CE correction,

178 which ranged from 0.5 to 0.7, are consistent with most other measurements from the Pasadena

179   ground site. The relevant inter-comparisons are discussed in Section B of the Supporting

180   Material for this paper, including details regarding how mass concentrations are calculated from

181   SMPS number distributions.

182   High-resolution (HR) analysis of the mass spectra, including application of the HR AMS

183   fragmentation table, was carried out following previously published procedures [*Aiken et al.*,

184   2007, 2008]. The reported AMS mass concentrations were determined from the HR AMS spectra

185   and are very similar to unit mass resolution (UMR) concentrations, within 5%, that are

186   determined using the UMR fragmentation table of Allan et al [2004]. The HR fragmentation

187   table was also used to obtain the OA mass spectral matrix for the PMF analysis described in the

188   next paragraph.

189   The OA mass spectral matrix was deconvolved into components using PMF, a receptor-

190   based factorization model [*Paatero et al.*, 1994]. The application of PMF to AMS spectra has

191   been discussed in detail previously [*Ulbrich et al.*, 2009; *Q Zhang et al.*, 2011]. The same

192   method is used here including the PMF2 algorithm, which is run in robust mode via the PMF

193   Evaluation Tool panel (PET, v2.03). The high-resolution organic aerosol mass spectra for the

194   entire CalNex campaign were analyzed, and the full range of the high-resolution spectra was

195   utilized (m/z 12 – 204). Error matrices were calculated using the methods of Allan et al. [2003]

196   and Ulbrich et al. [2009]. Weak variables (i.e. m/z's) with lower signal-to-noise ratios ($0.2 < S/N$

197   < 2) were down-weighted by a factor of three, and bad variables ($S/N \leq 0.2$) were down-weighted

198   by a factor of 10 following the recommendations of Paatero and Hopke [2003]. For the results

199   presented here the model error was set to zero.

200

2.3. Co-located CalNex measurements utilized in this study

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 (UHSAS, 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 multi-channel analyzer) measured size distributions from 500 to 4000 nm. Hourly $PM_{2.5}$ 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 (SP2, Droplet Measurement Technologies) [*Schwarz et al.*, 2006], as well as with a Soot Particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research & Droplet Measurement Technology) [*Onasch et al.*, 2012]. The concentrations of semi-volatile and particulate organic molecular tracers were measured by 2-D Thermal Desorption Aerosol Gas Chromatography Mass Spectrometry (2DTAG, UC-Berkeley & Aerosol Dynamics) [*Worton et al.*, 2012]. $PM_{2.5}$ 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 – 4000 nm [*Froyd et al.*, 2009; *Thomson et al.*, 2000].

224 The PALMS instrument also measures scattered light from single particles allowing for

225 calculation of particle size in addition to particle classification. Volume concentrations of the

226 different PALMS particle classes were calculated by multiplying the volume concentration size

227 distribution determined from the SMPS or WLOPC measurements by the fractions of the

228 different PALMS particle types in each size bin. Particle optical extinction for PM_1 was

229 measured at 532 nm and 630 nm by a Cavity Attenuated Phase Shift (CAPS) instrument

230 [*Kebabian et al.*, 2007; *Massoli et al.*, 2010]. All of the online measurements described in this

231 paragraph were located at the CalNex ground site described above.

232 Data from offline particulate matter measurements are included in this paper as well. In

233 particular, size-resolved elemental concentrations were determined by X-ray Fluorescence (XRF)

234 analysis of Mylar substrates from a rotating drum impactor (RDI). The XRF analysis was

235 performed at the Advanced Light Source at Lawrence Berkeley National Lab. Using the XRF

236 results, the mineral dust concentration corresponding to oxides of Al, Si, Ca, K, Fe, and Ti is

237 estimated from the elemental concentrations following the method of Simon et al. [2011] and

238 Malm et al. [1994]. The particulate metal concentration is calculated as the sum of the mass

239 concentrations of Mg, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, and Pb. The Cl

240 concentrations from XRF measurements are reported as refractory chloride (rCl), since the

241 placement of samples under vacuum for analysis is expected to cause evaporation of non-

242 refractory species such ammonium chloride. The time resolution of the XRF data was 1.5 h.

243 Offline OC measurements of high volume $PM_{2.5}$ samples collected with quartz fiber filters were

244 performed using three separate sets of filters and two laboratory-based Sunset Labs OC/EC

245 analyzers (NIOSH TOT protocol). For clarity, the three sets of filters are named according to the

246 institution that collected them: Georgia Institute of Technology (GIT), U.S. Environmental

247   Protection Agency (EPA), and University of North Carolina (UNC). Following the technique of

248   Russell et al. [2009], Fourier Transform Infrared Spectroscopy (FTIR) analysis of Teflon filter

249   samples provided $PM_{2.5}$ OA and organic functional group mass concentrations. All samples for

250   offline analyses were collected at about 12 m above ground level on the roof of the Keck

251   Building located on the Caltech campus approximately 0.3 km southwest of the ground site.

252   The concentration of O_3 was measured by UV differential absorption (49c Ozone

253   Analyzer, Thermo Scientific), and CO concentrations were measured by two vacuum-UV

254   resonance fluorescence instruments (AL5001 & AL5002, Aerolaser) [*Gerbig et al.*, 1999]. An

255   in-situ Gas Chromatography Mass Spectrometry (GC-MS) instrument provided the mixing ratios

256   for a variety of VOCs [*Gilman et al.*, 2009]. A Fluorescence Assay by Gas Expansion (FAGE)

257   instrument was utilized to determine the OH concentration [*Dusanter et al.*, 2009]. The NO_x and

258   NO_y concentrations were measured using chemiluminescence (42i-TL with Mo converter,

259   Thermo Scientific), and NO_2 was measured with Cavity Enhanced Differential Optical

260   Absorption Spectroscopy (CE-DOAS) [*Thalman et al.*, 2010]. The CE-DOAS instrument was

261   located on the Caltech Millikan Library roof, which is approximately 45 m tall and 0.5 km

262   southwest of the Pasadena ground site.

263   Meteorological data were acquired by a station that included a temperature/RH sensor

264   (Campbell Scientific Inc., HMP35C) and a wind monitor (R.M. Young, 05103). The boundary

265   layer height was determined using a ceilometer (Vaisala, CL31) following the method described

266   by Haman et al. [2012], and the ceilometer results have been shown to be consistent with

267   boundary layer heights from Weather Research Forecasting (WRF) modeling [*Washenfelder et*

268   *al.*, 2011]. To track the origins of the air masses sampled at the ground site, a modified version of

269   the FLEXPART Lagrangian particle dispersion model [*Stohl et al.*, 2005] was used to calculate

270 back trajectories of air masses based on advection and turbulent mixing processes. The main

271 modification consists of using time-averaged winds from the WRF (version 3.3) meteorology

272 model instead of instantaneous winds to improve uncertainties within the FLEXPART model

273 [*Brioude et al.*, 2012]. The WRF output has a spatial grid of 4 km x 4 km, with a temporal

274 resolution of 30 min and 60 vertical levels. Lastly, all linear regressions in this paper are

275 performed as orthogonal distance regressions using Igor Pro 6.2.1 software.

3. Results and discussion

276

3.1. Total submicron aerosol composition at the Pasadena ground site during CalNex

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278 While the focus of this paper is OA, a survey of the total aerosol composition can provide

279 valuable context for the OA analysis, and providing such a context is the goal of this section

280 (3.1). (Note: Comparisons with previous campaigns as well as additional figures regarding the

281 total submicron aerosol composition are shown in Section B of the Supporting Material.) The

282 time series for the nrPM$_1$ species and EC are shown in Figure 1B. In addition, the diurnal cycles

283 of the nrPM$_1$ species and EC are shown in Figure 2A. The time series for metals, mineral dust,

284 and refractory chloride (rCl) are shown in Figure 1C, and for comparison the PALMS particle

285 type time series are included in Figure 1 as well (Panels D and E). The fractional composition of

286 the total submicron mass is determined by combining the AMS, Sunset Analyzer, XRF, and

287 PALMS measurements, and is summarized in Figure 2C. (Note: see the Figure 2 caption for

288 details regarding which instrument measured each species as well as how the PALMS data is

289 converted to mass concentration.) In the interpretation of the data in Figures 1 and 2 it is

290 important to consider some differences in size cuts of the measurements. First, the XRF

291 measurements used in Figures 1 and 2 correspond to a size cut of 1150 nm aerodynamic

292 diameter. By linearly interpolating the size-resolved XRF measurements the average

293 overestimate relative to the actual PM_1 concentrations was found to be approximately 30%.

294 Second, the online Sunset OC/EC analyzer was equipped with a $PM_{2.5}$ cyclone for most of the

295 campaign. From 6/12 through 6/16 the EC measurement was performed while switching between

296 a $PM_{2.5}$ and PM_1 cyclone, and the ratio of the PM_1 EC to the linearly interpolated $PM_{2.5}$ EC was

297 0.93 (±0.19 standard deviation). Thus, while the EC data in Figures 1 and 2 may overestimate the

298 true PM_1 EC concentrations, it is expected that this error will be reasonably small (~7%). Despite

299 these overestimates of refractory mass, the total PM_1 concentration is still dominated by non-

300 refractory species (OA + sulfate + nitrate + ammonium + nrCl) that account for 93% of the

301 measured mass. Similarly, particle types measured by the PALMS instrument that are

302 predominately composed of non-refractory material comprised 90% of submicron aerosol

303 volume (Figure 3).

304   A clear diurnal cycle is observed for most $nrPM_1$ species. As shown in Figure 2, the

305 maxima in the EC and CO (commonly used combustion emission tracers) diurnal cycles are both

306 observed between 12:00 and 13:00 PDT (local time). These maxima do not coincide with the Los

307 Angeles County morning rush hour, which occurs between about 06:00 and 08:00 PDT

308 [*Caltrans*, 2010]. Instead, they appear to result from polluted air masses initially emitted in the

309 source-rich regions west and south of Pasadena. The wind speed and wind direction measured at

310 the ground site are consistent with the transport of this plume to Pasadena over several hours. In

311 addition, FLEXPART back-trajectories show that the air masses over the Pasadena ground site

312 when EC and CO concentrations are highest have significant footprint residence times over

313 downtown LA as well as the Ports of LA and Long Beach, which are regions with significant

314 combustion emissions.

315   Compared to EC and CO, the OA concentrations peak later in the day, about 3 pm, which

316   corresponds to the same time-of-day when air masses over the Pasadena ground site were the

317   most photochemically processed (Figure 2B). The photochemical age for the air mass over the

318   Pasadena site was calculated with two different methods. First, using the ratio of 1,2,4-

319   trimethylbenzene to benzene, as described in Parrish et al. [2007]. Second, by defining the

320   photochemical age as $-\log_{10}(NO_x/NO_y)$ similar to Kleinman et al. [2008]. All photochemical

321   ages were calculated using a standard OH radical concentration of 1.5×10^6 molecules cm^{-3}. For

322   reference, the daily OH radical concentrations averaged for the whole campaign at the Pasadena

323   site was 1.3×10^6 molecules cm^{-3}. Interestingly, when using the NO_x/NO_y method, the

324   photochemical age slowly increases from 00:00 – 06:00 local time, likely due to N_2O_5 and

325   ClNO$_2$ formation, which are NO_x sinks [*Chang et al.*, 2011]. Outside of this time range however,

326   the diurnal cycles of the two photochemical age estimates show good agreement.

327   The diurnal cycle for OA is relatively flat and low during the early morning hours, 00:00

328   to 06:00, suggesting a small role for nighttime chemistry driven by either NO3 radicals or

329   aqueous chemistry (RH peaked during this time of day). The lack of aqueous chemistry may be

330   driven by the low oxidant concentrations at night. In parallel work, X Zhang et al. [2012] showed

331   that for Pasadena the aerosol water was not an important absorbing phase, and instead the

332   partitioning coefficient for organics was correlated with OA mass. This result suggests that semi-

333   volatile organic compounds are primarily partitioning to the organic phase.

334   The submicron nitrate diurnal cycle is different from OA with a peak in the morning. The

335   afternoon decrease in nitrate can be attributed to both vertical dilution due to the increase in

336   boundary layer height as well as the higher temperatures and lower RH values that favor

337   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 non-volatile 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.

In addition to the diurnal cycles, substantial multi-day variability is evident in Figure 1. In particular, from June 2nd through June 6th 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 (June 13th – June 16th). 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 et al.*, 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 et al.*, 1990]. Additionally, a distinct period of greater marine influence is observed between May 20th and 25th. 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).

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 super-micron 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

361 total aerosol composition can provide valuable context for the OA analysis, hence the inclusion

362 of the PALMS results here. The volume concentration time series for particle composition types

363 identified by the PALMS single-particle instrument are shown in Figures 1D and 1E. In addition,

364 the campaign average volume concentrations are summarized in the pie charts shown in Figures

365 3A and 3B. The particle composition types were identified from PALMS mass spectra following

366 the method described in Froyd et al. [2009]. For instance, biomass burning spectra are identified

367 by a prominent K^+ peak along with organic peaks and a lack of other metals. Vanadium with

368 organic species was used as a tracer to identify aerosol from heavy oil combustion (e.g. from

369 ship engines), which allows for the definition of a particle class termed 'Oil Combustion' similar

370 to previous work with other single-particle instruments that studied emissions from commercial

371 ports [*Ault et al.*, 2009; *Healy et al.*, 2009]. Since the PALMS is a single-particle instrument, it is

372 capable of determining aerosol mixing state. One consideration when comparing the PALMS

373 results against the AMS and other measurements is that the classification of particles typically

374 follows the most abundant components in a particle, but the PALMS volume concentration for

375 each particle type also includes secondary material on the particle that may even dominate the

376 particle volume at the time of detection. For the Pasadena ground site it was observed that all the

377 particle types contained substantial amounts of nitrate, sulfate, and organics, which indicates that

378 either condensation of secondary material is occurring on primary aerosols (e.g., sea salt and

379 mineral dust) and/or particle mixing is occurring through coagulation. The nitrate observed on

380 sea salt particles is also at least partially due to the heterogeneous reaction between sea salt and

381 nitric acid as discussed in the Appendix. An important conclusion that can be made from the data

382 in Figure 3 is that the PM_1 aerosol volume concentration is dominated by sulfate/OA/nitrate type

383 particles, and the super-micron aerosol is dominated by sea salt particles. These findings are

16

384 generally consistent with the mass concentration data from XRF and AMS measurements. The

385 PALMS biomass burning results are discussed further in section 3.2.3.

386 **3.2. Source apportionment of organic aerosol mass by positive matrix factorization**

387 **3.2.1. Mass spectra, time series, and diurnal cycles of the organic aerosol components**

388   The OA components from the PMF analysis were identified by their mass spectra, diurnal

389 cycles, and elemental composition, as well as by the concentration ratios and correlations of their

390 time series with tracers. Figure 4 shows the mass spectra and time series for the five identified

391 components. Additionally, Figure 5 shows the diurnal profiles of the OA components and the

392 campaign-average fractional contribution of each component to the total OA concentration, as

393 well as a stacked plot illustrating the fractional contributions to OA mass by time-of-day. A

394 summary of correlations between the OA components and various tracers is provided in Section

395 D of the Supporting Material. The five PMF components identified are: (1) Hydrocarbon-like

396 Organic Aerosol (HOA), (2) Cooking-Influenced Organic Aerosol (CIOA), (3) Local Organic

397 Aerosol (LOA), (4) Semi-Volatile Oxygenated Organic Aerosol (SV-OOA), and (5) Low-

398 Volatility Oxygenated Organic Aerosol (LV-OOA). The naming based on volatility is adopted

399 according to several studies showing a relationship between high oxygenation and lower

400 volatility for the OOA components [e.g. *Cappa et al.*, 2010; *Huffman et al.*, 2009; *Jimenez et al.*,

401 2009; *Lanz et al.*, 2007; *Ulbrich et al.*, 2009]. The HOA component has been previously

402 described as a surrogate for primary combustion OA, and the SV-OOA and LV-OOA

403 components as surrogates for 'fresher' and 'aged' SOA, respectively. [*Aiken et al.*, 2008;

404 *Jimenez et al.*, 2009; *Ulbrich et al.*, 2009; *Q Zhang et al.*, 2007b]. The identification of CIOA is

405 consistent with previous research that has shown food cooking, which includes activities such as

406   seed oil frying and meat charbroiling, is an important source of fine organic aerosol in urban

407   environments [e.g. *Mohr et al.*, 2011; *Schauer et al.*, 2002b]. The precise source (or sources) of

408   the LOA component is not known, however similar, highly variable, nitrogen-rich components

409   have been identified in Mexico City [*Aiken et al.*, 2009], Riverside, CA [*Docherty et al.*, 2011],

410   Crete [*Hildebrandt et al.*, 2011], and New York City [*Sun et al.*, 2011]. This component is

411   termed 'local organic aerosol' because the LOA time series exhibits high-frequency fluctuations

412   that indicate a relatively local source for this component. (Auto-correlation plots of the

413   component time series are shown in Figure D-7 of the Supporting Material.) The LOA mass

414   represents only a small portion of the total OA mass (5%). Still, the reoccurrence of LOA in

415   different urban areas is an interesting finding. Additional details regarding how the PMF solution

416   was selected are provided in Section D of the Supporting Material.

417   The mass spectra and elemental ratios of the five components displayed in Figure 4A are

418   similar to those reported in previous studies [e.g. *Aiken et al.*, 2009; *Hersey et al.*, 2011; *Mohr et*

419   *al.*, 2011]. For HOA, O:C is relatively high (0.14), but not out of the range of previously reported

420   values. For instance, O:C values as low as 0.02 (Riverside, CA) and 0.03 (Barcelona) [*Docherty*

421   *et al.*, 2011; *Mohr et al.*, 2011] and as high as 0.16 (Mexico City) and 0.17 (Beijing) have been

422   reported for HOA components [*Aiken et al.*, 2009; *Huang et al.*, 2010]. The diurnal cycle of

423   HOA is similar to that of EC (and rBC) with a peak between 13:00 and 14:00 PDT (local time),

424   and HOA and EC (and rBC) show high correlation (See Table D-1 in the Supporting Material,

425   and Section 3.3 below). Therefore, as discussed in Section 3.1 for other primary emissions, it

426   appears that a large portion of the HOA is transported to Pasadena over a period of several hours

427   from the west and south, which is consistent with the relatively high HOA oxidation. Evidence

428   that HOA is dominated by primary sources is given in Section 3.4.1. In addition, the Van

429 Krevelen diagram analysis described in the next section indicates that the types of oxygen-

430 containing functional groups in HOA are different from OOA (on average), which suggests a

431 different oxidation pathway(s). A possible cause for the oxygen content in HOA is therefore

432 heterogeneous oxidation, although other causes including primary emission of oxygenates cannot

433 be conclusively ruled out using the results reported here. The CIOA component is more

434 oxygenated than HOA, which is consistent with previous reports and the known presence of

435 oxygenated compounds such as fatty acids and cholesterol in food cooking aerosol [*Mohr et al.*,

436 2011; *Robinson et al.*, 2006; *Sun et al.*, 2011]. The HOA and CIOA spectra are compared in

437 detail in Section D of the Supporting Material. The diurnal cycle of CIOA exhibits peaks near

438 mealtimes with a smaller peak between 14:00 and 15:00 PDT and a larger peak between 21:00

439 and 22:00 PDT similar to the cooking organic aerosol diurnal cycles observed for other field

440 measurements [*Allan et al.*, 2010; *Crippa et al.*, 2013; *Mohr et al.*, 2011; *Sun et al.*, 2011]. The

441 lunchtime and the dinnertime peaks are both slightly delayed from traditional American

442 mealtimes. The delays could be due to transport time from areas south and west of Pasadena. The

443 delay in the dinner time peak may also be the result of the convolution of the emission rates with

444 the lower boundary layer in the evenings and thus reduced vertical dilution of CIOA.

445   Both SV-OOA and LV-OOA display higher O:C compared to the other OA components

446 for Pasadena, and LV-OOA is the most oxygenated as expected for more aged SOA. The SV-

447 OOA and LV-OOA O:C values (0.38 and 0.8, respectively) are similar to those measured at

448 Barcelona (0.32 & 0.75), New York City (0.38 & 0.68), and Riverside (0.29 & 0.72) [*Docherty*

449 *et al.*, 2011; *Mohr et al.*, 2011; *Sun et al.*, 2011], and are consistent with the range of O:C values

450 for OOA reported by Ng et al. [2011]. The diurnal cycle of SV-OOA is very strong and peaks in

451 the afternoon. This pattern is likely due to photochemical age peaking at a similar time compared

452 to when SOA precursors emitted during the morning rush hour arrive in Pasadena (along with

453 EC and CO). The temporal variability of SV-OOA therefore indicates this component is closely

454 linked to in-basin photochemical production of SOA, as has been seen in other studies [*Aiken et*

455 *al.*, 2009]. In contrast, LV-OOA does not show a strong diurnal variation on average, but the

456 LV-OOA time series does vary substantially during the campaign measurement period. In

457 particular, there is an increasing trend in LV-OOA concentrations during the June 2nd – June 6th

458 period when there is evidence for recirculation of polluted air within the South Coast Air Basin

459 impacting aerosol concentrations. A build-up of LV-OOA concentrations during this period is

460 consistent with describing this component as 'aged', since the OA is expected to be increasingly

461 oxidized during periods of recirculation.

462   The mass spectrum of LOA is distinct from the other OA components and contains

463 prominent ions that are characteristic of amines: CH_4N^+ (*m/z* 30), $C_2H_4N^+$ (*m/z* 42), $C_3H_6N^+$ (*m/z*

464 56), $C_3H_8N^+$ (*m/z* 58), $C_5H_{10}N^+$ (*m/z* 84), $C_5H_{12}N^+$ (*m/z* 86) [*McLafferty et al.*, 1993]. The large

465 contribution of nitrogen to this factor (N:C = 0.05) is explained by the substantial presence of

466 these ions. The contribution of LOA to the total mass for each listed amine fragment ranges from

467 4% for CH_4N^+ to 89% for $C_5H_{12}N^+$. In total, the LOA component accounts for 34% of the

468 measured amine mass, and the contributions from the other PMF components are 31% (LV-

469 OOA), 15% (HOA), 13% (SV-OOA), and 8% (CIOA). As discussed in Section D of the

470 Supporting Material, the correlations of LOA with other measured species (e.g. VOCs and

471 metals) suggest that LOA sources are related to industrial processes, especially paint application,

472 but the results are not conclusive.

473   Shown in Figure 5C are the diurnal profiles for the total OA elemental ratios (O:C and

474 H:C). The diurnal trend in the elemental ratios is mostly consistent with the trends in the OA

475   components determined from the PMF analysis. In the early morning hours, the O:C ratio is the

476   highest, which suggests the presence of highly aged, likely secondary, aerosol. Indeed, during

477   this period LV-OOA is the dominant OA component. In the afternoon (~14:00), there is a strong

478   decrease in O:C, which can be attributed to the arrival of POA at the Pasadena ground site and/or

479   the formation of fresh secondary organic aerosol. In the evening (~21:30) there is second

480   minimum in the O:C, but this occurs during a period of low photochemical age (Figure 2), which

481   implies that the ground site is impacted at this time by POA. As seen in Figure 5, this evening

482   O:C minimum matches the peak in CIOA, a primary OA component with relatively low oxygen

483   content. An interesting difference between the PMF and elemental ratio diurnal trends is the peak

484   in H:C that is observed in the morning (~08:00) and is likely due to primary emissions from the

485   local morning rush hour. This peak is three to four times smaller than the H:C peaks for the

486   afternoon and evening events also associated with POA however, indicating a very weak

487   influence from the local rush hour. The PMF analysis is not expected to resolve components that

488   are less than approximately 5% of the OA mass [*Ulbrich et al.*, 2009], and therefore, the absence

489   of this weak local contribution in the PMF results is not surprising.

490   From Figure 5D, if total OOA is taken as a surrogate for SOA, and the sum of HOA,

491   CIOA, and LOA is taken as a surrogate for POA, then it can be concluded that SOA is dominant

492   at the Pasadena ground site, which is consistent with earlier findings in Riverside, CA [*Docherty*

493   *et al.*, 2008]. On average the total OA mass for the measurement period is composed of 66%

494   OOA (SV-OOA + LV-OOA), and this percentage lies between that observed for a selection of

495   'urban' and 'urban downwind' sites [*Q Zhang et al.*, 2007b]. This percentage is also similar to

496   previous results from measurements based in Pasadena. In particular, Hersey et al. [2011]

497   reported that during the PACO campaign in May/June 2009 77% of OA was classified as OOA,

498 and Turpin et al. [1991] reported that during the summer of 1984 SOA contributed roughly half

499 of the OA mass. In contrast, there is a wide range of SOA to OA ratios reported for areas east of

500 Pasadena over the past several decades (~20 – 70%) [*Docherty et al.*, 2008 and references

501 therein].

3.2.2. The atmospheric evolution of H:C versus O:C and the elemental ratios of the organic

aerosol components

504   To relate the elemental composition of the OA components to each other as well as to the

505 bulk OA the H:C and O:C values from the combined AMS/PMF analysis are plotted in a Van

506 Krevelen diagram (Figure 6). Within a Van Krevelen diagram more oxidized organic compounds

507 lie at the lower right, and different oxidation reactions fall along individual straight lines. For

508 instance, oxidation of a methylene group ($-CH_2-$) to a carbonyl group ($-C(=O)-$) corresponds to

509 a slope of –2, and oxidation of a methylene group to an alcohol group ($-C(-OH)-$) corresponds

510 to a slope of zero. Other reactions or combinations of reactions relevant to OA may lead to a

511 variety of slopes in the Van Krevelen diagram as well, which makes attributing a particular slope

512 to a specific chemical reaction difficult in the case of ambient field measurements. Despite this

513 complexity the Van Krevelen diagram is still useful for constraining the reactions that are

514 responsible for the aging of OA, including for SOA models and their comparison to

515 measurements [e.g., *Murphy et al.*, 2011].

516   Elemental ratios have been reported previously for the SOAR-1 campaign in Riverside,

517 California [*Heald et al.*, 2010], and these data are included in Figure 6 as well. The slope of the

518 Van Krevelen diagram for bulk OA is different when comparing the data from Pasadena and

519 Riverside. The regression analysis for Pasadena results in a best-fit slope of –0.64 whereas a

520   slope of −1.1 is obtained for Riverside. However, when the OOA factors are analyzed alone they

521   correspond to a line with a slope of -0.55 similar to other field measurements [*Ng et al.*, 2011],

522   which is consistent with methylene fragmentation reactions leading to carboxylic acids.

523   Given that the composition and chemical evolution of OOA in Pasadena and Riverside

524   are similar within this analysis, the differences in the slopes for bulk OA in the Van Krevelen

525   diagram cannot be explained by changes in SOA oxidation chemistry. The composition of the

526   HOA measured at the two locations is dissimilar, however. The HOA in Riverside exhibits a

527   very low O:C ratio (0.02), while in Pasadena HOA is more oxidized (O:C = 0.14). Thus, it is

528   proposed that the different slope for Riverside is due to the atmospheric mixing of fresh HOA-

529   rich particles into the air mass above the site. In Riverside, the addition of less oxidized HOA to

530   the air mass results in the steep slope observed in that location. Contrastingly, in Pasadena the

531   more oxidized HOA does not influence the slope strongly when mixing occurs because the

532   Pasadena HOA falls near the line defined by the OOA components in the Van Krevelen diagram.

533   Based on the diurnal cycles of HOA for the two sites, it seems that that the Pasadena

534   HOA is more oxidized because it has undergone more photochemical aging relative to the

535   Riverside HOA. In Riverside, the HOA concentration peaks in the morning as expected for fresh

536   emissions from the local morning rush hour traffic [*Docherty et al.*, 2011], consistent with the

537   location of the Riverside site downwind and nearby large highways. In Pasadena the HOA

538   concentration peaks around 13:30, however, due to advection over several hours from the west

539   and south. We note that the major combustion tracers follow similar diurnal trends for the two

540   sites.

541   It was also observed by Ng et al. [2011] that HOA components occupy a different space

542   of the Van Krevelen diagram relative to OOA and display variability that can be approximated

543   by a line with a −2 slope. The HOA components for Riverside and Pasadena shown in the Van

544   Krevelen diagram presented here follow a similar line, which is indicative of HOA aging. As

545   described already, a slope of −2 is consistent with functionalization of a methylene chain with

546   carbonyls. For Pasadena, the HOA component also correlated with several ketones (see 2DTAG

547   data discussed in Section D of the Supporting Material), which provides further evidence that

548   carbonyl groups may be an important oxygen-containing functional group for HOA.

549   **3.2.3. Constraints on the biomass burning contribution to the organic aerosol mass**

550   An apparent discrepancy between the combined AMS/PMF analysis and the PALMS

551   measurements is that the latter classified 12% of the PM_1 aerosol volume as biomass burning, but

552   the AMS does not show a significant amount of biomass burning influence as indicated by the

553   ratio of the organic mass at *m/z* 60 to total organic mass (f_{60}) [*Cubison et al.*, 2011]. (Note: the

554   possible contribution of organic acids to f_{60} is accounted for by simultaneously analyzing f_{44} in an

555   f_{44} vs. f_{60} plot as described previously by Cubison et al.) Also, a Biomass Burning Organic

556   Aerosol (BBOA) component is not identified in the PMF analysis, in which OA components

557   accounting for about 5% or more of the OA mass are expected to be resolved [*Ulbrich et al.*,

558   2009]. Acetonitrile, a tracer for biomass burning, is generally near background concentrations

559   (100 − 150 pptv) except for several high concentration events that are short in duration that do

560   not correlate with the PALMS biomass burning particles, and could be related to nearby solvent

561   use (e.g. in the Caltech campus). It is possible that potassium-containing particles from sources

562   other than biomass burning such as meat cooking [*Hildemann et al.*, 1991; *Schauer et al.*, 1999],

563   which can represent a substantial fraction of the potassium in some urban regions [*Aiken et al.*,

564 2010; *X Zhang et al.*, 2010], may be classified as biomass burning by the PALMS algorithm due

565 to the presence of potassium and abundant organic species. If cooking activities were the

566 dominant source of the PALMS biomass burning particles however, then the PALMS biomass

567 burning volume concentration would be expected to correlate with the CIOA mass concentration,

568 which is not the case (R = -0.03). An alternative explanation is that the primary biomass burning

569 mass is small, and there is a large amount of secondary mass that has condensed on the biomass

570 burning particles. (Similarly, the primary biomass burning particles may have coagulated with

571 secondary aerosol particles.) The particles would then be classified as biomass burning by the

572 PALMS algorithm, but their measured volume would be significantly increased by secondary

573 material (e.g. SOA, nitrate, sulfate, and ammonium). Finally, it is also possible that the biomass

574 burning particles are very aged as the result of long-range transport, and due to aging they are

575 difficult to identify with the AMS biomass burning tracers or PMF [*Cubison et al.*, 2011]. When

576 the observations described in this paragraph are evaluated together, then the best explanation for

577 the discrepancy is that while 12% of submicron particles (by volume) contained some biomass

578 burning material, the overall mass of these particles at the Pasadena ground site was dominated

579 by condensation or particle coagulation of non-biomass burning material. Based on the limit of

580 AMS/PMF analysis to resolve small fractions of OA, we estimate that primary biomass burning

581 material contributed <5% to submicron aerosol mass during the study.

582 **3.3. Evaluation of primary organic aerosol emission ratios with EC and CO**

583   The HOA concentration correlates strongly with EC determined from the online Sunset

584 analyzer (R=0.71), and the ratio of HOA to EC can provide valuable insight regarding the source

585 of this OA component. To explore this correlation further a scatter plot of HOA versus EC mass

586 concentration data is plotted in Figure 7A. The data points in the plot are colored with the

587 corresponding NO_y to ΔCO ratios. Periods with higher diesel influence are expected to exhibit

588 higher $(NO_y/\Delta CO)$ [*Ban-Weiss et al.*, 2008a; *Parrish et al.*, 2007]. The ratio is not corrected for

589 dry deposition losses of nitric acid though, and thus it cannot be treated as a quantitative metric.

590 In addition, the grey shaded areas in Figure 7A indicate the range of POA to EC emission ratios

591 for gasoline and diesel vehicles that were measured during summer 2006 at the Caldecott Tunnel

592 in California [*Ban-Weiss et al.*, 2008b]. The HOA to EC ratios at the Pasadena ground site

593 overlap the range of POA to EC ratios from the Caldecott Tunnel. A linear regression analysis of

594 the Pasadena data yields a line with a slope of 1.82, which is close to the upper limit of the POA

595 to EC ratios reported in the tunnel study. The Pasadena ratio is at times higher, but this

596 difference could be due to changes in the emission ratios of vehicles between 2006 and 2010, or

597 the larger influence of cold starts for our dataset versus warm-running vehicles for the Caldecott

598 Tunnel. In Pasadena, for periods more influenced by diesel emissions, as indicated by high

599 $(NO_y/\Delta CO)$, generally lower HOA to EC ratios are observed. Specifically, the best-fit slope is

600 1.51 for $(NO_y/\Delta CO) > 0.124$, which corresponds to the highest 10th percentile of $(NO_y/\Delta CO)$

601 values. This finding is consistent with the emission ratios reported by Ban-Weiss et al. [2008b],

602 and suggests that both diesel and gasoline vehicle emissions are contributing to the HOA mass.

603   A correlation between HOA and CO is also observed (R = 0.59). A stronger correlation is

604 observed between CO and the sum of HOA and CIOA (R = 0.71) however. Shown in Figure 7B

605 is a scatter plot of the CO and the HOA+CIOA data. The improved correlation when the CIOA

606 mass concentration is added to the HOA mass concentration is surprising because cooking is not

607 considered a major source of carbon monoxide, although it is a significant source of organic

608 aerosol [*Allan et al.*, 2010; *CARB*, 2008; *Harley et al.*, 1997]. Emissions of CO have been

609 measured from certain cooking activities [*Lee et al.*, 2001], but it is still a possibility that the

610   CIOA component contains particulate mass from non-cooking sources that also emit CO (e.g.

611   gasoline vehicles). Therefore, it is most reasonable to characterize this component as 'cooking-

612   influenced', but not purely from cooking sources. It should be noted that different PMF solution

613   rotations were explored using the FPeak parameter as discussed in the Supporting Material.

614   There are rotations that exhibit lower correlations between CIOA and CO, but HOA+CIOA

615   always displays a higher correlation than HOA with CO (within the constraint of not

616   substantially diminishing the correlation between HOA and rBC). In addition, these alternative

617   solutions exhibit lower correlations between HOA and rBC, as well as between HOA+CIOA and

618   CO.

619   The data in Figure 7B are also colored by the relative amount of CIOA, so that the ratios

620   of HOA to CO and CIOA to CO can be at least partially resolved. For periods when HOA

621   concentrations are high (i.e. greater than 90% of the sum of HOA and CIOA) the correlation with

622   CO is very strong (R = 0.9) and the linear slope is 6.4 μg m^{-3} ppmv^{-1} when using a CO

623   background (x-intercept) of 105 ppbv, which is comparable to slopes found in previous studies

624   [*Aiken et al.*, 2009]. In contrast, for periods when CIOA concentrations are high the linear slope

625   is 13 μg m^{-3} ppmv^{-1}, more than twice that for HOA. The steeper slope for CIOA is indicative of

626   significant cooking sources for CIOA that, as stated earlier, produce a larger amount of organic

627   aerosol relative to CO [*McDonald et al.*, 2003]. A lower limit on the relative amount of CIOA

628   mass from cooking sources can be estimated using the observation that the linear regression

629   slope of CIOA is about twice that of HOA when the mass concentrations are plotted versus CO.

630   Assuming that CO is overwhelmingly from vehicle emissions and no CO is emitted from

631   cooking sources then CIOA would be 50% from cooking sources *on average* with the remainder

632   from vehicle emissions (i.e. the additional cooking organic aerosol mass would double the mass

633   concentration versus CO slope relative to HOA). This percentage is a lower limit because some

634   CO could be co-emitted with cooking organic aerosol, for instance from burning of charcoal

635   [*Bhattacharya et al.*, 2002], and that would raise the percentage of CIOA from cooking above

636   50%. This approach is a simplistic approximation, but the lower limit appears to be reasonable

637   given that the diurnal cycles and spectral characteristics of CIOA are consistent with previous

638   studies. In addition, comparison of the CIOA concentration against that predicted from the

639   amount of organic mass measured by the AMS at *m/z* 55 following Mohr et al. [2011] indicates

640   that approximately 75% of CIOA is from cooking sources (See Section D of the Supporting

641   Material for the details of this comparison). A higher percentage up to almost 100% is also

642   possible given the uncertainties in the comparison.

643   An alternative approach for analyzing the correlation with CO is to use a multi-linear

644   regression instead of filtering the data for periods of high HOA or CIOA influence. For

645   completeness, a multi-linear regression was performed where HOA and CIOA were the

646   independent variables and CO was the dependent variable. Emission ratios of 8.0 and 16 µg m^{-3}

647   ppmv^{-1} were obtained for HOA and CIOA, respectively (using 105 ppbv background CO as

648   above). This result is similar to that described in the preceding paragraph, which indicates both

649   approaches for treating the data are robust.

650   **3.4. The quantitative dependence of secondary organic aerosol concentration on**

651   **photochemical oxidation**

652   **3.4.1. Increases in the organic aerosol to ΔCO ratio with photochemical age**

653   To evaluate if the timescales and efficiency of SOA formation observed in Pasadena are

654   similar to other urban regions the evolution of (OA/ΔCO) as a function of photochemical age is

655 plotted in Figure 8, where ΔCO is the CO concentration enhancement over its background

656 concentration. The background CO is estimated to be between 85 – 125 ppbv using CO

657 measurements taken aboard the NOAA WP-3D aircraft off the LA coastline at altitudes less than

658 200 m (Latitude range: 32 to 35, Longitude range: -117 to -120). A concentration of 102 ppbv

659 was the minimum observed and concentrations below 110 ppbv were regularly observed.

660 Accordingly, the background CO was taken to be 105 ppb when calculating (OA/ΔCO), and the

661 error bars in Figure 8 represent the variability in the data if the background CO is taken to be

662 either 85 or 125 ppb. Given the observed CO values off the LA coastline this range represents a

663 conservative estimate of the uncertainty in background CO. The CO enhancement is assumed to

664 be a conservative tracer of urban combustion emissions that are also a source of aerosols and

665 aerosol precursors, and thus, normalizing the OA concentration to CO will remove the effect of

666 dilution. Photochemical formation of CO from VOCs or destruction of CO by OH reactions were

667 estimated to perturb CO concentrations minimally over these time and spatial scales [*Griffin et*

668 *al.*, 2007].

669 The grey region in Figure 8 represents (OA/ΔCO) versus photochemical age observations

670 from previous campaigns in Mexico City and the northeastern United States as summarized by

671 DeCarlo et al. [2010]. All the data sets display an increase in the OA/ΔCO ratios with

672 photochemical age due to secondary organic aerosol formation. The Pasadena OA/ΔCO versus

673 photochemical age plot follows the upper limit of the range of previously reported values,

674 although the differences should not be over interpreted given the uncertainties associated with

675 the background CO determination (indicated by the error bars) and the photochemical age

676 calculations. The photochemical age uncertainty has been discussed extensively in previous

677 papers and is due to, in part, the presence of mixed sources with different emission profiles and

678   spatial distributions [e.g. *Kleinman et al.*, 2007; *Parrish et al.*, 2007]. We evaluate this potential

679   source of error in Section E of the supporting material, and use sensitivity studies to determine

680   that photochemical age may be underestimated by approximately 10% in our analysis. This error

681   is in the accuracy rather than the precision, and thus, it does not impact relative comparisons for

682   Pasadena such as the weekday versus Sunday comparison described below. The underestimation

683   may impact comparisons with other campaigns though, and thus it is concluded that SOA

684   production per unit CO in the South Coast Air Basin is not different from other locations given

685   our estimated errors. (In Section E of the supporting material we also demonstrate that OH

686   radical chemistry dominates over Cl radical chemistry in the oxidation of the VOCs used to

687   calculate photochemical age.) The data in Figure 8 suggest that similar precursors are responsible

688   for SOA production in Pasadena, Mexico City, and the northeastern United States, and that the

689   precursors are emitted proportionally to CO. These conditions then imply a relatively constant

690   mix of the important SOA precursor and CO sources across the locations discussed.

691   To understand the similarity in OA/ΔCO it is important to consider the emission ratios for

692   SOA precursors (e.g., ΔVOC/ΔCO), especially given the long-term decrease of CO

693   concentrations in the United States [*Parrish et al.*, 2002] that could potentially influence

694   OA/ΔCO values. The emission ratios of aromatic, alkyne, and alkene VOCs with CO have

695   remained constant between 2002 and 2010, as has the ratio for acetaldehyde [*Warneke et al.*,

696   2012] a species that correlates strongly with OOA (R=0.81 in Pasadena) and is dominated by

697   secondary sources after sufficient photochemical processing of emissions. Furthermore, it has

698   been shown that urban VOC emissions at different locations in the US have similar composition

699   and emission ratios with CO (within a factor of 2) [*de Gouw et al.*, 2012; *Warneke et al.*, 2007].

700   The similarity of OA/ΔCO values described here for different campaigns spanning several years

701   is consistent with the lack of change in ΔVOC/ΔCO over spatial and temporal scales for the US.

702   However, in Mexico City the ΔVOC/ΔCO ratios are on average about a factor of 2 higher than in

703   the US [*Bon et al.*, 2011], but the OA/ΔCO values for Mexico City are not substantially higher

704   than in Pasadena or the northeastern US. This observation highlights the possibility that there

705   may be unmeasured organic compounds that are SOA precursors and do not follow the

706   ΔVOC/ΔCO emission trends discussed above. Lastly, we note that while plotting OA/ΔCO

707   versus photochemical age should account for differences in the amount of aging, the average

708   daily OH radical concentrations at the sites were fairly similar where measurements were

709   available: 1.3×10^6 molecules cm^{-3} for Pasadena, 1.5×10^6 molecules cm^{-3} for Mexico City

710   [*Hodzic et al.*, 2011].

711   Marked in Figure 8 is the sum of HOA, CIOA, and background LV-OOA (LVOOA$_{PCA=0}$)

712   divided by CO. The ratio of HOA+CIOA to CO is determined from the linear regression analysis

713   of the data in Figure 7B, and the background LV-OOA to CO ratio is the average of LV-OOA

714   divided by CO at photochemical ages less than 0.05 days (Figure 8 inset). Several explanations

715   are possible for the source of background LV-OOA. First, some very aged SOA may be present

716   due to recirculation in the LA basin, for which the photochemical tracers have mostly decayed

717   away. However, the similarity in calculated photochemical ages using either

718   (trimethylbenzene/benzene) or (NO$_x$/NO$_y$) suggests that this scenario is not the case, since the

719   high deposition velocity of nitric acid would lead to an observed discrepancy between the two

720   methods at high photochemical ages. A second plausible explanation is 'dark' SOA production

721   from ozone or nitrate radicals that will react with alkenes and PAHs. An important piece of

722   evidence to support this possibility would be an increase in OA/ΔCO at low photochemical ages

723   as the time-of-day approached sunrise, since the increase in morning traffic would lead to fresh

724 emissions that decrease photochemical age and react with ozone or nitrate radical to form SOA.

725 This phenomenon is not observed however, which indicates that 'dark' SOA is not an important

726 source of the background LV-OOA, consistent with the expected minor contribution of alkenes

727 to SOA in urban areas [*Dzepina et al.*, 2009; *Wood et al.*, 2010].

728   A third explanation is that marine OA may be contributing to the background LV-OOA.

729 However the very low OA concentrations, less than 0.2 μg m^{-3}, over the open ocean west of

730 California for periods with low pollution influence [P. K. Quinn, NOAA, personal

731 communication, 2012] indicate that this source is less important. In addition, low marine OA

732 concentrations, 0.5 μg m^{-3}, have been measured by an AMS in La Jolla, CA (located on the

733 California coast 170 km southeast of Pasadena) [*Liu et al.*, 2011], which is an amount similar to

734 other marine studies [*Russell et al.*, 2010], and would only account for a third of the background

735 LV-OOA.

736   The last and most likely explanation for the background LV-OOA is the influence of

737 biogenic sources that emit SOA precursors but relatively small amounts of 1,2,4-

738 trimethylbenzene, benzene, NO$_x$, and CO [*Slowik et al.*, 2010]. If the air mass above Pasadena

739 was influenced by a biogenic source, an increase in OA/ΔCO would be observed, but the

740 photochemical age as measured by the ratio of (1,2,4-trimethylbenzne/benzene) or (NO$_x$/NO$_y$)

741 would not be significantly altered. Back-trajectories for air reaching Pasadena during CalNex

742 often travel over the coastal California mountain ranges where biogenic VOC emissions are large

743 (see Figures A-3 through A-5 in the Supporting Material). Interestingly, at low photochemical

744 ages (less than 0.05 days) there is a general increase in OA/ΔCO with the sum of the

745 concentrations of the two isoprene oxidation products measured by the GC-MS. In particular,

746 when averaging the data into the three bins corresponding to low, medium, and high

747 concentrations of MVK plus methacrolein the binned OA/ΔCO increases from 21 to 26 μg sm^{-3}

748 ppmv^{-1} (standard errors are less than 0.5) from the lowest third to the highest third. This

749 observation indicates biogenic sources are influencing OA/ΔCO. Furthermore, ^{14}C measurements

750 for selected days during CalNex show that in the early morning hours when LV-OOA is

751 dominant (compared to other OA components and EC) about 50% of total carbon is non-fossil

752 (e.g. from modern sources) [*Bahreini et al.*, 2012]. These results are consistent with biogenic

753 sources influencing the OA/ΔCO ratio and substantially contributing to background LV-OOA

754 [Zotter et al., Manuscript in Preparation, 2012].

755   In the Figure 8 inset, the organic mass to ΔCO ratio is plotted for each PMF component.

756 The ratio increases for SV-OOA and LV-OOA with photochemical age consistent with both

757 components being dominated by secondary sources. In contrast, the ratios for HOA, CIOA, and

758 LOA do not vary substantially with photochemical age, which strongly supports that these three

759 components are dominated by primary sources. The data in Figure 8 also allow for estimating the

760 amount of background OA (i.e. OA from long range transport). As described above, the

761 concentration of LV-OOA at the lowest photochemical ages should approximately correspond to

762 background OA. Taking LV-OOA/ΔCO for the lowest age bin in Figure 8 and multiplying it by

763 the ΔCO for this bin yields a background OA concentration of 1.5 μg m^{-3}.

764   For HOA heterogeneous oxidation could potentially increase or decrease the magnitude

765 of HOA/ΔCO through either functionalization or fragmentation reactions, respectively. Given the

766 Van Krevelen diagram analysis described above in Section 3.2.2, fragmentations reactions

767 appear not to be the dominant oxidation pathway. This conclusion is consistent with the recent

768 work of Lambe et al. [2012] that showed for larger alkanes the onset of fragmentation occurs at

769 an O:C of about 0.3, which is much higher than the O:C of HOA reported here (0.14). For

770 functionalization reactions, based on the OM:OC ratio of 1.3 for HOA and an estimated OM:OC

771 of 1.2 for an un-oxidized alkane chain, it is calculated that the increase in HOA mass due to

772 oxidation is only 8%, which is smaller than the standard deviation (21%) of the data shown in

773 Figure 8. Condensation of primary semi-volatile organic compounds could also potentially

774 increase HOA/ΔCO since the averaged OA mass concentration increases with photochemical age

775 from 5 to 15 μg m^{-3} for the binned data shown in Figure 8. However, an increase in HOA/ΔCO

776 with photochemical age is not observed in Figure 8. This result is consistent with the calculated

777 change in HOA concentrations due to partitioning. Specifically, using the volatility distribution

778 for POA and primary semi-volatile organic compounds reported by Robinson et al. [2007] it is

779 calculated that the increase in HOA concentrations (and HOA/ΔCO) would be only 28% for an

780 increase of OA from 5 to 15 μg m^{-3}. This calculated increase is similar in magnitude to the

781 standard deviation of HOA/ΔCO, and hence, would be hard to discern. In addition, it is

782 substantially smaller than the increase observed for SV-OOA/ΔCO (540%) and LV-OOA/ΔCO

783 (300%). The considerations described in this paragraph also apply to CIOA and LOA but are

784 more difficult to quantify for these components given the lack of literature data (e.g.,

785 fragmentation reaction studies and volatility distributions).

786 **3.4.2. Correlation of oxygenated organic aerosols with the photochemical oxidation marker**

787 **odd-oxygen (O$_3$ + NO$_2$)**

788 Odd-oxygen, O$_x$, concentrations are closely linked to the extent of photochemical

789 oxidation in an air mass because O$_3$ production results from OH reactions with VOCs and CO.

790 Therefore, the ratios of OOA to odd-oxygen provide another metric for quantifying the

791   dependence of SOA concentration on photochemical oxidation. Following the work of Herndon

792   et al. [2008] and Wood et al. [2010], we examine the correlations of O_x instead of O_3 to account

793   for the titration of O_3 by fresh NO emissions which produces NO_2. When comparing the time

794   series of total OOA (SV-OOA + LV-OOA) versus O_x in Figure 9 similar temporal changes are

795   observed (R^2 = 0.53), but the correlation is stronger during the more polluted periods of high

796   OOA concentrations that occurred in June (R^2 = 0.72 for the June 2nd through 6th high pollution

797   period). It has also been observed that for long-range transported air the correlation vanishes due

798   to differing losses and ongoing chemistry of SOA and O_x [*Dunlea et al.*, 2009]. In Pasadena the

799   regression slope for OOA versus O_x is 0.146($\pm$0.001) µg sm^{-3} ppbv^{-1} (Figure 9 inset). The data in

800   the scatter plot is colored by time-of-day, and interestingly, the slope observed for the morning

801   (06:00 – 12:00 PDT) is steeper than the slope in the afternoon (12:00 – 18:00 PDT):

802   0.183($\pm$0.004) versus 0.163($\pm$0.002) µg sm^{-3} ppbv^{-1}. This trend has also been observed in other

803   field measurements [*Herndon et al.*, 2008; *Wood et al.*, 2010], and has been attributed to several

804   factors including increased evaporation of SV-OOA, mixing with air aloft that contains residual

805   OOA and O_x during boundary layer growth, and OOA production occurring on shorter

806   timescales than O_x. The slopes of identical analyses for Riverside, CA and Mexico City are

807   0.142($\pm$0.004) and 0.156($\pm$0.001) µg sm^{-3} ppbv^{-1} [*Aiken et al.*, 2009; *Docherty et al.*, 2011],

808   which are similar to the Pasadena ground site. This agreement indicates that the ratios of the

809   SOA to O_x production rates are remarkably constant for the different sites suggesting similar

810   SOA and O_x formation chemistries on average.   As discussed by Wood et al. [2010], changes

811   in the OOA/O_x ratio would be expected at locations where the relative concentrations of SOA

812   and O_x precursors are different. In Houston for instance, ratios as low as 0.030 µg sm^{-3} ppbv^{-1}

813   were found in correlation analyses during periods impacted by large petrochemical plant

814   emissions. This observation was explained by very high concentrations of light alkenes that

815   cause high ozone concentrations but are not expected to contribute greatly to SOA formation.

816   Contrastingly, in Riverside the relative concentrations of SOA and O_x precursors are expected to

817   be similar to Pasadena given that urban VOC emissions have similar composition and emission

818   ratios throughout the US [*Warneke et al.*, 2007] and have not changed over the past several years

819   [*Warneke et al.*, 2012]. In Mexico City, the emission ratios for VOCs (i.e., VOC/CO) are

820   generally higher by a factor of approximately 2 [*Bon et al.*, 2011], which would impact both

821   SOA and O_x production rates proportionally. An important exception is the emission ratios for

822   propane and butane, which were disproportionality high in Mexico City due to liquid petroleum

823   use [*Apel et al.*, 2010]. The contribution of these light VOC compounds was found to be small

824   for O_x production and zero for SOA production, however [*Wood et al.*, 2010]. Similar to the

825   OA/ΔCO discussion in the preceding section, the consistency in OOA/O_x for multiple field

826   campaigns suggests a relatively constant mix of different O_3 and SOA precursor sources, leading

827   to similar production ratios across multiple urban locations in North America. As also discussed

828   above, the insensitivity of OA/ΔCO to differences in VOC/CO suggests unmeasured precursors,

829   but if these unidentified species were emitted in proportion to other VOCs, then consistent

830   OOA/O_x values would be expected for the different locations.

831   Chlorine radicals are expected to play a larger role in ozone formation for Pasadena and

832   Riverside in comparison to Mexico City, since the first two locations are near the Pacific Ocean.

833   The contribution of chlorine radical chemistry to the total ozone concentration is a topic of

834   current research [*Young et al.*, 2012]. Still, published work [*Knipping et al.*, 2003] indicates that

835   in Pasadena and Riverside it is relatively small and, as a percentage, less than the 30%

836   uncertainty for AMS measurements [*Middlebrook et al.*, 2012], which is expected to dominate in

837   the OOA/O_x comparison. Thus, the similarity of OOA/O_x between the three locations is

838   consistent with previous work on chloride radical chemistry in the South Coast Air Basin. For

839   reference, average 24 hr OH radical concentrations in Mexico City and Pasadena were 1.3 x 10^6

840   and 1.5 x 10^6 molec. cm^{-3}, respectively.

841   Meteorological parameters could also influence OOA/O_x in a number of ways including

842   through changes in OOA partitioning with temperature or increases in the importance of aqueous

843   chemistry at high RH. These parameters do not appear to be important for the OOA/O_x analysis

844   presented here, however. The average temperatures and RHs for the different sites with similar

845   OOA/O_x were: 18°C and 83% (Pasadena), 27°C and 53% (Riverside), 16°C and 50% (Mexico

846   City). While higher temperatures in Riverside will favor partitioning of OOA to the vapor phase,

847   the measured volatility of OA for Riverside [*Huffman et al.*, 2009] indicates the amount of

848   evaporation will be small (less than 10%), and thus, will have little effect on OOA/O_x.

849   Additionally, the higher RH in Pasadena relative to Riverside and Mexico City may not

850   influence OOA concentrations given that aerosol water was not an important absorbing phase [*X

851   Zhang et al.*, 2012] as discussed in Section 3.1 above.

852   **3.5. Weekly cycles for organic aerosol components**

853   **3.5.1. Weekly cycles: Primary organic aerosols**

854   It is well-known that in California and the South Coast Air Basin a large decrease in on-

855   road diesel vehicle activity occurs on weekends, which leads to significant reductions in

856   atmospheric species associated with diesel vehicles such as NO_x, EC, specific VOCs, and

857   particulate nitrate [*Marr et al.*, 2002; *Millstein et al.*, 2008; *Pollack et al.*, 2012]. To explore if

858   primary organic aerosols show an analogous weekend effect in Pasadena during CalNex, the

859   diurnal cycles for HOA, EC, rBC, CIOA, CO, and benzene are plotted for weekdays and

860   Sundays separately in Figure 10. Included in the Sunday diurnal cycle is data from the Memorial

861   Day holiday, which occurred on a Monday and exhibited traffic patterns typical of Sundays

862   [*Caltrans*, 2010]. Thus, the 'Sunday' diurnal cycle combines data from six days. Saturday data is

863   not included in Figure 10 to avoid carryover effects from the preceding Friday. Carryover effects

864   on Mondays appear to have little impact on the weekday diurnal cycle with less than a 3%

865   change in the average daily concentrations when Mondays are omitted from averaging and no

866   qualitative change in the diurnal cycles. Thus, Monday data are included with the other weekday

867   data in Figure 10.

868   The EC (and rBC) concentration decreases on Sundays to 71($\pm$6)% of its weekday

869   average and has a very different diurnal cycle. A similar change is observed for HOA, which

870   decreases to 82($\pm$4)% of its weekday average. (Note: uncertainties are the standard errors of the

871   mean.) The decrease in concentrations is consistent with the weekend effect and the importance

872   of diesel vehicle emissions as a source for HOA and EC (and rBC). In contrast, CO

873   concentrations when integrated over the entire day are not substantially different on Sundays

874   versus weekdays, and the average concentration on Sundays is 99.4($\pm$0.3)% of the weekday

875   average.   The CO diurnal cycles are dissimilar probably due to changes in traffic patterns.

876   Benzene displays a similar lack of change on Sundays increasing to 105($\pm$3)% of the weekday

877   average. Since gasoline vehicles are an important source of CO and benzene [*Fruin et al.*, 2001;

878   *Schauer et al.*, 2002a], the lack of a weekend effect for these compounds is consistent with

879   previous studies that demonstrated similar overall activity for gasoline vehicles on weekends

880   compared to weekdays [*Marr and Harley*, 2002; *Pollack et al.*, 2012]. The CIOA concentrations

881   are elevated on Sundays by 161($\pm$4)% displaying a weekly cycle distinctly different from the

882 other species in Figure 10. An increase in barbecuing on weekends has been reported previously

883 for the South Coast Air Basin [*Chinkin et al.*, 2003], which is consistent with elevated CIOA

884 concentrations on weekends. However, given the limited corroborating evidence and lack of

885 previous long term observations of cooking emissions (to our knowledge), further studies are

886 needed to make a confident conclusion regarding the weekly variations in cooking organic

887 aerosol.

888   The observed decreases in HOA and EC concentrations on Sundays can be compared

889 against the expected decreases in their emissions, estimated from a combination of data on fuel

890 sales [*BOE*, 2011], emission ratios [*Ban-Weiss et al.*, 2008b], and traffic volume [*Caltrans*,

891 2010]. The first step to obtain the estimates is calculating the percentage of weekday EC and

892 HOA attributable to diesel emissions using Equation 2 below.

893
$$\frac{EC_{Diesel}}{EC_{Total}} = \frac{ER_{Diesel} \times FS_{Diesel}}{\left(ER_{Diesel} \times FS_{Diesel}\right) + \left(ER_{Gasoline} \times FS_{Gasoline}\right)} \quad (1)$$

894 In Equation 2, *ER* is the emission ratio for diesel and gasoline vehicles taken from Ban-Weiss et

895 al. [2008b], and *FS* is the gasoline and diesel fuel sales reported for the State of California during

896 May and June 2010 [*BOE*, 2011]. An analogous equation is used for HOA. The *ER* is defined as

897 the amount of EC (or HOA) emitted per unit fuel burned, and the values used in this work are:

898 0.022 (gasoline EC), 0.86 (diesel EC), 0.031 (gasoline HOA), 0.41 g kg^{-1} (diesel HOA). It is

899 assumed that the monthly fuel sales are representative of weekday fuel use in the South Coast

900 Air Basin. Following this method it is estimated that diesel emissions account for 87($\pm$3)% of EC

901 and 70($\pm$10)% of HOA. The second step utilizes daily vehicle miles traveled (VMT) data for Los

902 Angeles County to calculate that during the campaign truck traffic decreased 44% on Sundays

903 relative to weekdays [*Caltrans*, 2010]. This figure lies within the range of other estimates for

904   weekend reductions of heavy-duty vehicle traffic [*Chinkin et al.*, 2003]. Finally, an estimate of

905   EC concentrations on Sunday relative to weekdays, ΔEC_{sun} (%), can be calculated as follows (an

906   analogous equation can be used for HOA).

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

908   Using Equation 3 the Sunday concentrations of EC and HOA are estimated to be 64(±3)% and

909   72(±6)% of their weekday concentrations, respectively. To estimate these values the non-truck

910   VMT on Sundays versus weekdays was taken to be equal because of the similarity in the average

911   daily CO and benzene concentrations. In addition, the background EC is the average of the

912   values from Langridge et al. [2012], 40(±20) ng m^{-3}, and the background HOA, 70(±40) ng m^{-3},

913   was calculated from EC using the slope of HOA to EC reported in Figure 7. (Note: The

914   uncertainties for the calculated Sunday reductions in EC and HOA include the uncertainties in

915   the background concentrations reported in Langridge et al.) For comparison, the observed

916   average Sunday EC and HOA concentrations at the Pasadena ground site are 71(±6)% and

917   82(±4)% of the weekday averages, respectively. The agreement between the estimated and

918   observed values is good, given the need for several approximations to obtain the estimate. The

919   reduction in HOA is less than the reduction in EC for both the estimated and the observed values,

920   due to the greater portion of HOA emitted from gasoline vehicles. It is noted that in contrast to

921   HOA, the CIOA concentration is higher on Sundays as discussed above, and the combination of

922   the two opposite trends leads to a net increase of POA on the weekends.

923   An important assumption of this analysis is the only sources of EC are on-road diesel and

924   gasoline emissions, as well as the background from long range transport. Transport is the single

925 largest source of EC in the United States, and in the absence of biomass burning it accounts for

926 81% of emitted EC. Within the transport sector EC emissions are dominated by on-road and non-

927 road diesel [*EPA*, 2012]. Another question is whether commercial marine emissions may have a

928 substantial contribution to the EC budget. To address this consideration we examined the

929 correlation between EC and the oil combustion particles identified by the PALMS instrument,

930 which are presumably from shipping activities. We observed a low correlation (R^2=0.24), which

931 is consistent with commercial marine EC emission not substantially impacting the ground site.

932 Ultimately, accounting for only three sources of EC (on-road diesel, on-road gasoline, and a

933 background) is a simplifying assumption, but one that is consistent with emission inventories and

934 other observations. The reasonableness of this assumption is further supported by the closure

935 obtained between the calculated and measured weekly cycles.

936 **3.5.2. Weekly Cycles: Secondary organic aerosols and constraining the importance of diesel**

937 **emissions**

938 To evaluate the weekly cycle for secondary organic aerosols OA/ΔCO versus

939 photochemical age is plotted in Figure 11A for weekdays and Sundays. Also shown is the

940 analogous plot for total OOA (Figure 11B). The OOA plot is similar for weekdays versus

941 Sundays, and linear regression analyses of the data yield slopes of 108(±5) and 98(±8) µg sm^{-3}

942 ppmv^{-1} for weekdays and Sundays, respectively. (Note: the data fitted are averages resulting

943 from binning the raw data according to photochemical age, and the averages are weighted by the

944 standard errors of the x and y data.) After propagation of error these slopes correspond to a ratio

945 of 1.1(±0.1) for weekdays to weekends. Following the estimation method described by Bahreini

946 et al. [2012], and using a 44% decrease in diesel traffic on Sundays as determined above, this

947 ratio corresponds to diesel emissions accounting for 19(+17/-21)% of the OOA mass. Also, a

948   consistently higher photochemical age is observed on Sunday versus weekdays due to the higher

949   oxidant concentrations resulting from reduced NO_x emissions. These results are in good

950   agreement with other CalNex papers that address weekday/weekend effects [*Bahreini et al.*,

951   2012; *Pollack et al.*, 2012]. In particular, they are consistent with the conclusion reported by

952   Bahreini et al. [2012] that gasoline emissions are substantially more important than diesel

953   emissions in the formation of secondary organic aerosol mass within the LA Basin, since a large

954   decrease in the OOA/ΔCO ratio is not observed on weekends when there is less diesel traffic. It

955   should be noted as well that the results present here are better constrained than the Bahreini et al.

956   analysis because the PMF results are used to obtain OOA/ΔCO rather than relying on estimated

957   values of POA/ΔCO to calculate OOA/ΔCO, and because of the more precise binning by

958   photochemical age.

959   We note that for the diesel versus gasoline analysis presented in the preceding paragraph

960   three important assumptions are made. First, it is assumed that SOA precursors in the South

961   Coast Air Basin are dominated by motor vehicle emissions. While this is consistent with

962   measured VOC/CO ratios [*Warneke et al.*, 2012], the possibility of important and unidentified

963   SOA precursors from non-vehicular sources cannot be completely ruled out. Therefore, further

964   research is needed to constrain the contribution of non-vehicular sources to SOA.

965   The second important assumption is that some of the SOA measured may be due to long

966   range transport, which is not accounted for in the preceding analysis. To at least partially account

967   for this possible source of error, we repeat the analysis above but only for photochemical ages

968   above 0.1 days. Photochemical ages above 0.1 days generally occur during daytime when the

969   higher amount of SV-OOA versus LV-OOA indicates that SOA production is more local and

970   recent. The resulting slopes of the regression analyses are 121($\pm$7) and 115($\pm$10) µg sm^{-3} ppmv^{-1}

971 for weekdays and Sunday, respectively, and then the ratio of the slopes is 1.0(±0.1). This ratio

972 corresponds to diesel emissions accounting for -2(+21/-26)% of the OOA mass. The upper limit

973 of this range is less than that for the original analysis (36%) for all photochemical ages. Thus, we

974 report the 19(+17/-21)% result, since it is more conservative and represents the entirety of the

975 campaign.

976 The third assumption made in this analysis is that SOA yields do not change on weekends

977 when NO_x concentrations are lower. To test the impact of this assumption the branching ratios

978 for the high-NO_x and low-NO_x VOC oxidation channels were calculated following the same

979 method as described in Dzepina et al. [2011]. It is found that the high-NO_x channel dominates on

980 both weekdays and Sundays with mean branching ratios of 99% and 91%, respectively (see

981 Section F of the supporting material for box-and-whiskers plot). Using the NO_x-dependent

982 yields of Tsimpidi et al. [Tsimpidi et al., 2010] this difference in branching ratio would

983 correspond to an increase in weekend SOA yields of 1% (assuming a 7 $\mu g/m^3$ OA concentration)

984 for the aromatic precursors that dominate SOA formation from VOCs [Dzepina et al., 2011;

985 Dzepina et al., 2009]. This difference in yields would only change the determined diesel

986 contribution by about 2%, which is much smaller than our reported uncertainty. Thus, the

987 assumption that SOA yields do not change on weekends is robust. However, it should be noted

988 that primary semi-volatile and intermediate volatility compounds may have an important

989 contribution to SOA formation in the South Coast Air Basin [Robinson et al., 2007], but their

990 NO_x-dependent SOA yields are not well constrained.

991 **4. Conclusions**

Ambient aerosol measurements were made using a suite of aerosol composition instruments, including on- 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), semi-volatile 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.

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 ΔCO 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

1015   compared to other locations. Second, the OOA to odd-oxygen ratios for Pasadena are similar to

1016   those observed in Riverside and Mexico City, which indicates that SOA and odd-oxygen

1017   production rates are proportional across the different sites. Both HOA and EC exhibit weekly

1018   cycles with substantially lower concentrations on Sundays versus weekdays consistent with the

1019   well-known weekday/weekend effect in the South Coast Air Basin. The decreases in HOA and

1020   EC concentrations are quantitatively similar to those predicted for their emissions using fuel

1021   sales, traffic counts, and literature gasoline and diesel vehicle emission ratios. In contrast, OOA

1022   does not display a strong weekly cycle – after controlling for differences in photochemical ages

1023   and emission strengths – which is consistent with the dominance of gasoline emissions in SOA

1024   formation, insofar as non-vehicular emissions of SOA precursors are minor. In total, the findings

1025   reported here highlight several quantitative similarities in SOA properties observed in Pasadena,

1026   Riverside, Mexico City, and the northeastern United States including the ratios of SOA to odd-

1027   oxygen, the increases in OA/ΔCO with photochemical age, and the evolution of elemental

1028   composition (i.e. H:C versus O:C). These observations are consistent with a relatively constant

1029   mix of sources of CO, O_3 precursors, and SOA precursors across urban locations in North

1030   America.

1031

5. Appendix: Size Distributions, chemical aging of sea salt, and particulate charge balance

Displayed in Figure 12 are the AMS size distributions (Panel A), XRF size distributions (Panel C), and the contribution of all species to the total aerosol mass as a function of particle size (Panel D). 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 12D, 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 PM_1, and can have a tail due to slow evaporating particles [*Canagaratna et al.*, 2004] and should be interpreted accordingly. Also shown in Figure 12E 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.

Further information about the OA, nitrate, and sulfate size distributions can be inferred from comparisons of various PM_1 and $PM_{2.5}$ 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 PM_1 instrument, and several $PM_{2.5}$ OC time series taken from the GIT, EPA, and UNC filter samples results in slopes greater than 0.81, when the AMS data is plotted on the y-axis. (Supporting Material 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

46

1055   concentrations from the AMS and a $PM_{2.5}$ PILS-IC instrument results in slope of 1.01 leading to

1056   the conclusion that the sulfate mass above 1 μm is insignificant on average. The regression

1057   analysis of AMS and PILS-IC concentration data for nitrate results in a much different finding,

1058   and exhibits slope of 0.64 that is also dependent on sea salt concentrations measured by the

1059   PALMS instrument. These observations indicate that a substantial amount of nitrate mass is

1060   present above 1 μm, about 35%, and that the supermicron nitrate is at least partially comprised of

1061   sodium nitrate from chemical aging of sea salt by nitric acid although some supermicron

1062   ammonium nitrate may be present as well. The PILS-IC inlet was alternated between a PM_1 and

1063 $PM_{2.5}$ cyclone for a portion of the measurement period (6/12 – 6/16), which provides data that

1064   can also be used to assess the amount of sulfate and nitrate between 1 and 2.5 μm. The linear

1065   regressions of the PM_1 and linearly interpolated $PM_{2.5}$ data indicate that 34% and 80% of the

1066   nitrate and sulfate mass was present below 1 μm. (Note: Interpolation of the $PM_{2.5}$ data is

1067   necessary since only a single inlet and cyclone were used for the PILS-IC measurement

1068   preventing simultaneous measurements with different size cuts.) Similar to the AMS versus PILS

1069   comparison, these percentages indicate that the supermicron mass represents a greater fraction of

1070   the $PM_{2.5}$ mass for nitrate relative to sulfate. When using the PILS data with alternating cyclones

1071   a larger percentage of supermicron mass is found than in the AMS versus PILS comparison. This

1072   difference may be due to the stronger influence of sea salt during the portion of the campaign

1073   when the cyclones were alternated, as clearly seen in the PALMS time series (Figure 1E), which

1074   is consistent with substantial amounts of sodium nitrate, and to a lesser extent sodium sulfate,

1075   above 1 μm. The aging of sea salt upon exposure to pollution is described further in the next

1076   paragraph.

1077   Both the CalNex XRF and PALMS measurements provide quantitative information about

1078   non-EC refractory materials including sea salt. An important detail regarding the measurement of

1079   particulate chloride is that XRF is assumed to measure refractory chloride (rCl) since the XRF

1080   samples are placed under vacuum before measurements [*Johnson et al.*, 2008]. The non-

1081   refractory and refractory chloride fractions are thought to be predominately ammonium chloride

1082   [*Salcedo et al.*, 2006] and sodium chloride (from sea salt), respectively [*Malm et al.*, 1994;

1083   *Simon et al.*, 2011]. Sodium data is not available from XRF data due to measurement limitations,

1084   but the sodium mass concentration can be estimated from PALMS sea salt volume

1085   concentrations as described in the Figure 2 caption. For fresh sea salt the expected ratio of

1086   chloride to sodium mass concentrations is 1.8 [*Finlayson-Pitts et al.*, 2000]. However, a ratio of

1087   0.12 is observed for rCl to sodium at the Pasadena ground site indicating that the sodium

1088   chloride in sea salt aerosol has undergone a substantial amount of chemical processing by nitric

1089   and sulfuric acid, which depletes the amount of chloride ions in the sea salt aerosol by converting

1090   sodium chloride to sodium nitrate and sodium sulfate [*Gard et al.*, 1998]. For Pasadena, a

1091   fractional chloride depletion of 94% is calculated using the following equation described by

1092   Zhuang et al. [1999]. (In Equation 3 all concentrations are in units of moles m^{-3}.)

$$1093 \qquad Depletion = \frac{[Cl]_{original} - [Cl]}{[Cl]_{original}} \times 100\% = \frac{1.174[Na] - [Cl]}{1.174[Na]} \times 100\% \quad (3)$$

1094   This agrees with qualitative results from the PALMS mass spectra, which show significant

1095   displacement of chloride and accumulation of nitrate on individual sea salt particles that

1096   correlated with nitric acid concentrations.

1097   The acidity of the submicron aerosols in Pasadena can be evaluated by comparing the

1098   measured ammonium mass concentration against the amount needed to fully neutralize the

1099   measured sulfate, nitrate, and chloride, which is termed here 'NH$_4^+$ predicted'. The AMS

1100   measurements of non-refractory aerosol composition were used for this charge balance

1101   calculation. Particles are considered acidic if the measured ammonium concentration is

1102   substantially lower than the predicted values [*Q Zhang et al.*, 2007a]. As seen in Figure 13A,

1103   overall the particles appear to be bulk neutralized by ammonium with a majority of the data near

1104   the one-to-one line. It should be noted that the measured amines are not accounted for in the

1105   predicted ammonium, but even if it is assumed that the amines are all present as salts, the impact

1106   on the fit is minimal with the slope changing from 1.02 to 0.99 or 0.96 when AMS or FTIR

1107   measurements of amines are used, respectively. There are selected periods when the measured

1108   ammonium concentrations are not sufficient to neutralize the anions, especially at lower

1109   concentrations. These periods are more easily observed in the histogram shown in Figure 13B.

1110   The low ammonium measured-to-predicted ratios may be due to more acidic particles, but based

1111   on PALMS spectra only about 0.1% of particles contained sulfate that was highly acidic

1112   (NH$_4^+$:SO$_4^{2-}$ < 1) [*Froyd et al.*, 2009]. An alternative explanation then is the presence of sodium

1113   cations that are not accounted for in Figures 13A and 13B. Typically when using AMS data to

1114   evaluate particle acidity it must be assumed that ammonium is the only significant cation, and

1115   cations from sources such as sea salt are ignored [*Aiken et al.*, 2009; *Docherty et al.*, 2011; *Q

1116   Zhang et al.*, 2007a]. For Pasadena however, sodium concentration data can be estimated from

1117   PALMS measurements providing an opportunity to evaluate the role of sea salt in particle

1118   neutralization. (Note: The PALMS data was restricted to the submicron size range to match the

1119   AMS measurements.) In Figure 13C, there is a clear dependence of the ammonium measured-to-

1120   predicted ratios on the fraction of cations that are sodium (ratios are taken from molar units),

1121   which indicates that sodium plays a role in the charge balance.

1122   An important consideration when evaluating particle neutralization is whether the sodium

1123   cations are present as sodium nitrate or sodium chloride, and if those species can be vaporized by

1124   the AMS heater for detection. From the charge balance calculations above it appears that anions

1125   associated with sodium are detected by the AMS indicating that at least a fraction of the sodium

1126   nitrate evaporates rapidly (~1 s) in the AMS. The chloride depletion results and size distribution

1127   analysis discussed above indicate that a large majority of the sodium is present as sodium nitrate,

1128   which is more volatile than sodium chloride, and thus, more readily detected by the AMS, in

1129   which the vaporizer temperature was operated at approximately 600°C. Therefore, it appears that

1130   counter ions associated with sodium from sea salt do impact the AMS measurements of charge

1131   balance.

1132   Previously, Docherty et al. [2011] demonstrated that for Riverside during the SOAR-1

1133   campaign organonitrates and organosulfates impacted the charge balance calculation. These

1134   species add to the nitrate and sulfate mass measured by the AMS [*Farmer et al.*, 2010] due to

1135   fragmentation of the molecular parent, but do not contribute the expected amount of ionic

1136   charge, which leads to apparent particle acidity. An important contrast between Pasadena and

1137   Riverside is that the deviation between measured ammonium and NH_4^+ predicted occurs at low

1138   concentrations for Pasadena, but at high concentrations for Riverside. In addition, the measured

1139   versus predicted scatter plot for Pasadena has slope close to one, 1.02, whereas the analogous

1140   plot for Riverside has a lower slope of 0.86. (Note: sodium from sea salt is not accounted for in

1141   either slope.) For Riverside, the deviation in the slope from one was attributed to organosulfates

1142   and organonitrates. For Pasadena the charge balance calculation does not appear to be

1143 significantly impacted by organosulfates or organonitrates, which implies that the concentrations

1144 for these species are relatively low. This conclusion is supported by measurements from other

1145 instruments. The PALMS instrument observed that the isoprene-derived organosulfate, IEPOX

1146 sulfate ester, comprised <0.01% of submicron aerosol mass in Pasadena, which supports the

1147 negligible role of organosulfates in this location. (Note: The mass abundance for the IEPOX

1148 sulfate ester was determined using detailed laboratory calibrations that were performed for a

1149 previous study [*Froyd et al.*, 2010].) Furthermore, FTIR measurements of organonitrates [*Day et*

1150 *al.*, 2010] found that concentrations were less than 2% of the measured nitrate (by AMS) on

1151 average, which is much lower than the percentage estimated in Riverside (10%).

1152 　　　　Combining the discussions of size distributions and sea salt aging from above, in Figure

1153 12B the rCl to Mg ratio is shown as function of particle size for the period of high marine

1154 influence identified in Section 3.1 (5/20/2010 – 5/25/2010). During this period rCl and Mg are

1155 correlated in the larger XRF size bins (R > 0.62), and the ratio of the Mg PM_1 mass concentration

1156 to the PALMS sea salt PM_1 mass concentration is very close to the expected ratio for sea salt:

1157 0.044 vs. 0.039, respectively (R = 0.6) [*Finlayson-Pitts and Pitts*, 2000]. Thus, Mg is taken to be

1158 predominately from sea salt, which allows for calculating the amount of chloride depletion

1159 following an approach analogous to that described for sodium. (Data is not shown for smaller

1160 particle diameters since a strong correlation between rCl and Mg is not observed.) The rCl to Mg

1161 ratio is fairly constant with particle size from 660 to 3010 nm d_{va} indicating similar amounts of

1162 chloride depletion. Additionally, the average rCl to Mg ratio (2.0) corresponds to 86% chloride

1163 depletion, which is similar to 94% chloride depletion calculated using the estimated sodium data

1164 from the PALMS instrument. In general, the sea salt measured in Pasadena appears to be very

1165 aged mostly from chemical reactions with nitric acid. The extensive chloride depletion observed

1166 in Pasadena is consistent with previous work including modeling studies that predicted ~80%

1167 chloride depletion in Riverside, CA [*Knipping and Dabdub*, 2003], and single particle mass

1168 spectra of aged sea salt, also from Riverside, which showed extensive chloride depletion

1169 [*Hughes et al.*, 2000]. In addition, chloride depletions of 71 and 74% were reported for coarse

1170 mode aerosol in Upland and Rubidoux, CA, respectively [*Eldering et al.*, 1991]. These values

1171 are lower than observed for Pasadena in this study, which may be due to the Eldering et al.

1172 percentages corresponding to particles greater than 2.2 µm in diameter.

1173   The extensive depletion of chloride from sea salt suggests that appreciable amounts of

1174 chlorine radicals may be present due to the photolysis of photo-labile chlorinated gases such as

1175 HCl, $ClNO_2$, and Cl_2. Oxidation reactions of organics by chlorine radicals that produce

1176 organochlorines in the particle phase would then be possible. To investigate this possibility the

1177 concentrations of several organochlorine fragments were determined from the AMS

1178 measurements (CCl^+, C_2HCl^+, CCl_2^+, $C_2Cl_2^+$, $C_2HCl_2^+$, $CHOCl_2^+$). The relative concentration of

1179 these species compared to the total OA is very small, on average less than 0.1% and always less

1180 than 0.4%. In addition, the 2DTAG identified only one chlorine-containing OA compound,

1181 chlorophthalic acid, which represents less than 1% of the total phthalic acid concentration. These

1182 results are also consistent with FTIR spectra of filter samples collected during the CalNex

1183 campaign, which do not display vibrational resonances for acid chlorides (730-550 cm^{-1}) or alkyl

1184 chlorides (785-540 cm^{-1}). It is noted though that quantification of organochlorines by FTIR is

1185 difficult due to Teflon filter interferences in the same spectral region. In total, these

1186 measurements provide no evidence for organochlorines representing a substantial portion of the

1187 OA mass, but the methods utilized here are not optimal for the detection of organochlorines.

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6. Acknowledgements

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8. Figure Captions

Figure 1: **(A)** CO concentration. **(B)** The non-refractory aerosol concentrations sampled by the AMS. The measured species are organics (OA), nitrate (NO_3), sulfate (SO_4), ammonium (NH_4), and non-refractory chloride (nrCl). The elemental carbon (EC) concentration was measured *in-situ* by a Sunset analyzer. For completeness, the EC data includes occasional periods when a PM_1 cyclone was used instead of a $PM_{2.5}$ cyclone (6/12 – 6/16). **(C)** Refractory aerosol mass concentrations as measured by XRF (rCl: Refractory Chloride). **(D)** Particle type volume concentrations measured by the PALMS for PM_1, 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).

Figure 2: **(A)** Diurnal profiles for the non-refractory 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_1 mass concentration (in µg/m^3) for the ground site (5/15 00:00 – 6/16 00:00) including both refractory and non-refractory 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 $NaNO_3$ density of 2.1 g cm^{-3} [*Zelenyuk et al.*, 2005] and a sodium to sea salt mass ratio of 0.308 [*Hall et al.*, 1998]. All error bars indicate standard errors of the means.

Figure 3: Average volume concentration (in µm^3 cm^{-3}) of the different PALMS particle types for **(A)** PM_1 and **(B)** particles between 1 and 2.5 µm diameters at the Pasadena ground site during CalNex. Size ranges correspond to aerodynamic diameters.

Figure 4: **(A)** Mass spectra for the five factors 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 factors.

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_1 organic aerosol mass concentration.

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.

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).

Figure 8: The evolution of OA/ΔCO versus photochemical age for Pasadena during CalNex. The measured ratios are averaged into 25 bins according to photochemical age. The enhanced CO (ΔCO) is the ambient CO minus the estimated background CO (105 ppb). The standard error of OA/ΔCO 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); (2) Following Kleinman et al. [2008] and defining the photochemical age as $-\log_{10}(NO_x/NO_y)$ (red). All photochemical ages have been standardized to an OH radical concentration 1.5 x 10^6 molec. cm^{-3}, 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/ΔCO observed in the northeastern United States and the Mexico City area. The black horizontal line is the ratio of (HOA + CIOA + 'background LVOOA') to ΔCO. **(Inset)** Evolution of the PMF component concentrations normalized to ΔCO versus photochemical age. Data is binned according to photochemical age.

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.

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

Figure 11: (A) The evolution of OA/ΔCO versus photochemical age for Pasadena during CalNex separated by day of the week. The enhanced CO (ΔCO) 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.

Figure 12: (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 5/20 00:00 to 5/25 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.

Figure 13: (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.

Figure 1: **(A)** CO concentration. **(B)** The non-refractory aerosol concentrations sampled by the AMS. The measured species are organics (OA), nitrate (NO_3), sulfate (SO_4), ammonium (NH_4), and non-refractory chloride (nrCl). The elemental carbon (EC) concentration was measured *in-situ* by a Sunset analyzer. For completeness, the EC data includes occasional periods when a PM_1 cyclone was used instead of a $PM_{2.5}$ cyclone (6/12 − 6/16). **(C)** Refractory aerosol mass concentrations as measured by XRF (rCl: Refractory Chloride). **(D)** Particle type volume concentrations measured by the PALMS for PM_1, 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).

1

Figure 2: **(A)** Diurnal profiles for the non-refractory 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_1 mass concentration (in $\mu g/m^3$) for the ground site (5/15 00:00 – 6/16 00:00) including both refractory and non-refractory 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 $NaNO_3$ density of 2.1 g cm^{-3} [*Zelenyuk et al.*, 2005] and a sodium to sea salt mass ratio of 0.308 [*Hall et al.*, 1998]. All error bars indicate standard errors of the means.

Figure 3: Average volume concentration (in μm^3 cm^{-3}) of the different PALMS particle types for **(A)** PM$_1$ and **(B)** particles between 1 and 2.5 µm diameters at the Pasadena ground site during CalNex. Size ranges correspond to aerodynamic diameters.

Figure 4: **(A)** Mass spectra for the five factors 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 factors.

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_1 organic aerosol mass concentration.

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.

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).

Figure 8: The evolution of OA/ΔCO versus photochemical age for Pasadena during CalNex. The measured ratios are averaged into 25 bins according to photochemical age. The enhanced CO (ΔCO) is the ambient CO minus the estimated background CO (105 ppb). The standard error of OA/ΔCO 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); (2) Following Kleinman et al. [2008] and defining the photochemical age as $-\log_{10}(NO_x/NO_y)$ (red). All photochemical ages have been standardized to an OH radical concentration 1.5×10^6 molec. cm^{-3}, 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/ΔCO observed in the northeastern United States and the Mexico City area. The black horizontal line is the ratio of (HOA + CIOA + 'background LVOOA') to ΔCO. **(Inset)** Evolution of the PMF component concentrations normalized to ΔCO versus photochemical age. Data is binned according to photochemical age.
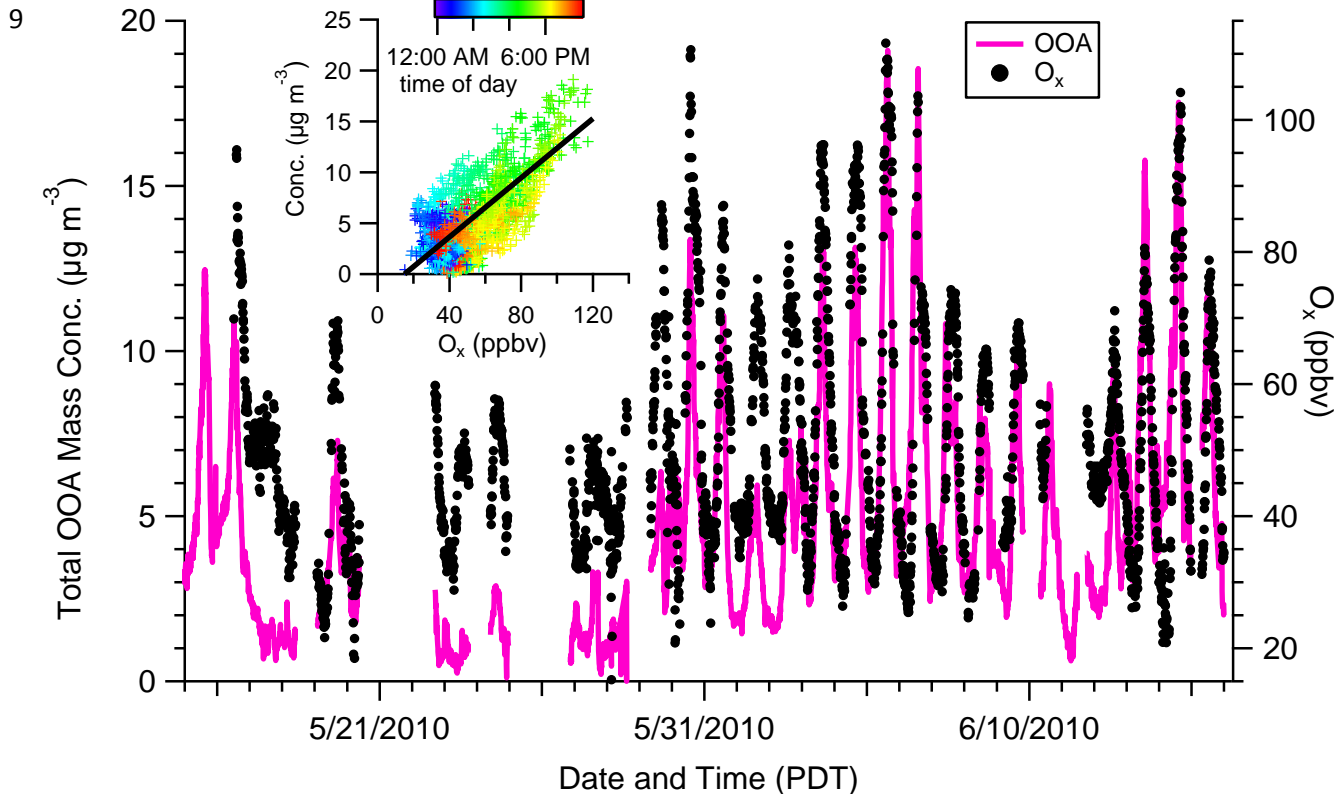
Figure 9: Time series for OOA (the sum of SV-OOA and LV-OOA), and O_x (the sum of O_3 and NO_2). **(Inset)** Scatter plot of OOA versus O_x with linear fit and colored by time-of-day. The best-fit slope is 0.146 ($R^2 = 0.53$). A fixed x-intercept of 15 ppmv O_x is used in the fitting procedure identical to previously published work.
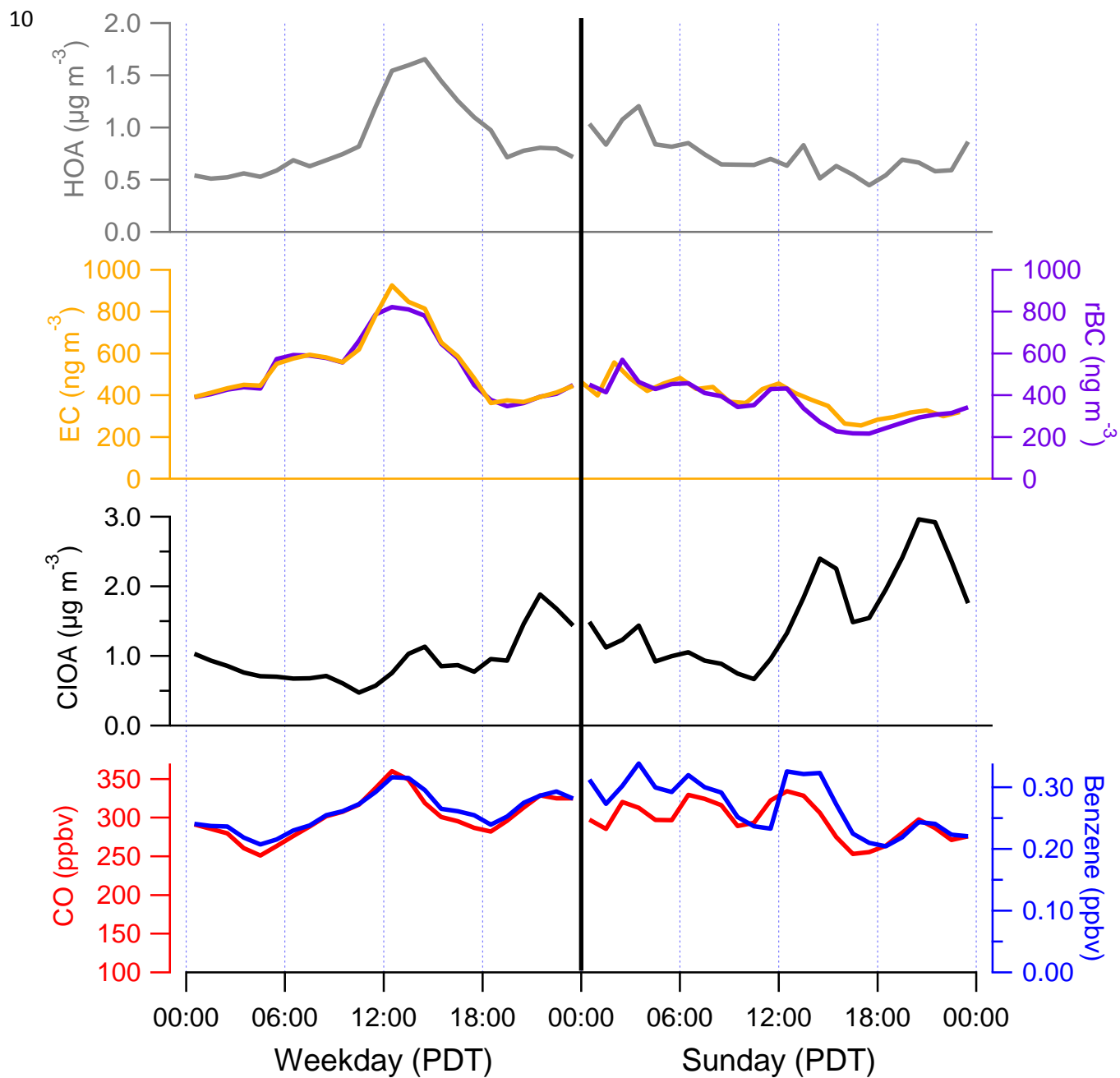
Figure 10: Diurnal profiles, calculated using means, of HOA, EC, rBC, CIOA, CO, and Benzene for weekdays and Sundays during CalNex.
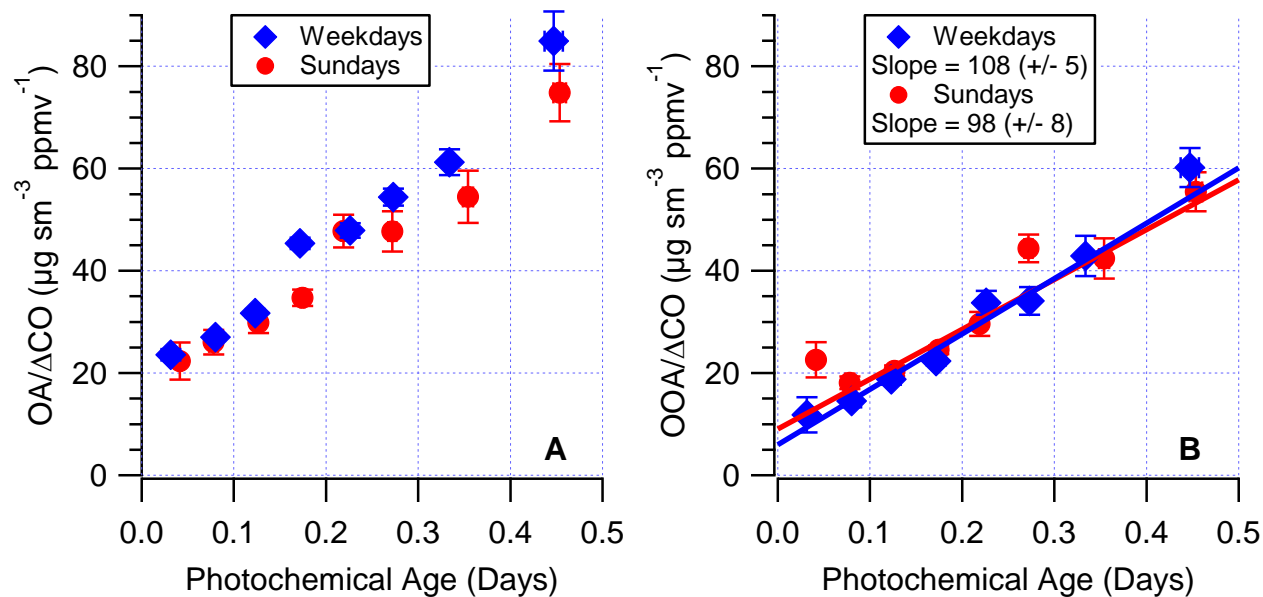
Figure 11: (A) The evolution of OA/ΔCO versus photochemical age for Pasadena during CalNex separated by day of the week. The enhanced CO (ΔCO) is the ambient CO minus the estimated background CO (105 ppb). Error bars indicate the standard errors. Photochemical age is determined using the method of Parrish et al. [2007]. **(B)** Also shown is the analogous plot for OOA with the linear ODR fits of the data.

Figure 12: (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 5/20 00:00 to 5/25 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.
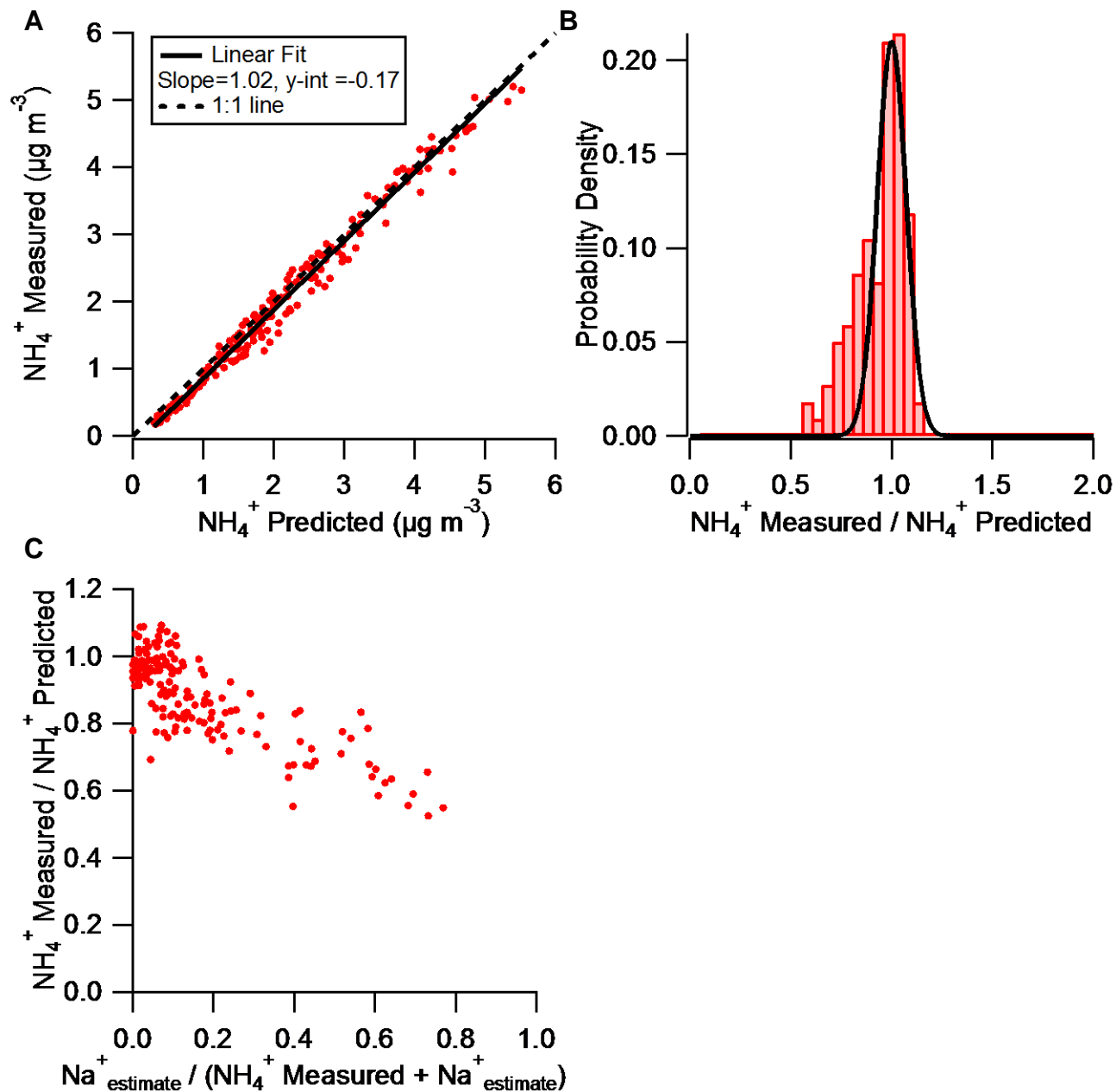
Figure 13: **(A)** Scatter plot of the measured ammonium versus 'NH$_4^+$ predicted', which is calculated using the concentrations of nitrate, sulfate, and chloride, as well as assuming full neutralization by ammonium (all data from AMS). **(B)** Histogram for the ratios of the measured ammonium to the 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.

Organic Aerosol Composition and Sources in Pasadena, California during the 2010 CalNex Campaign

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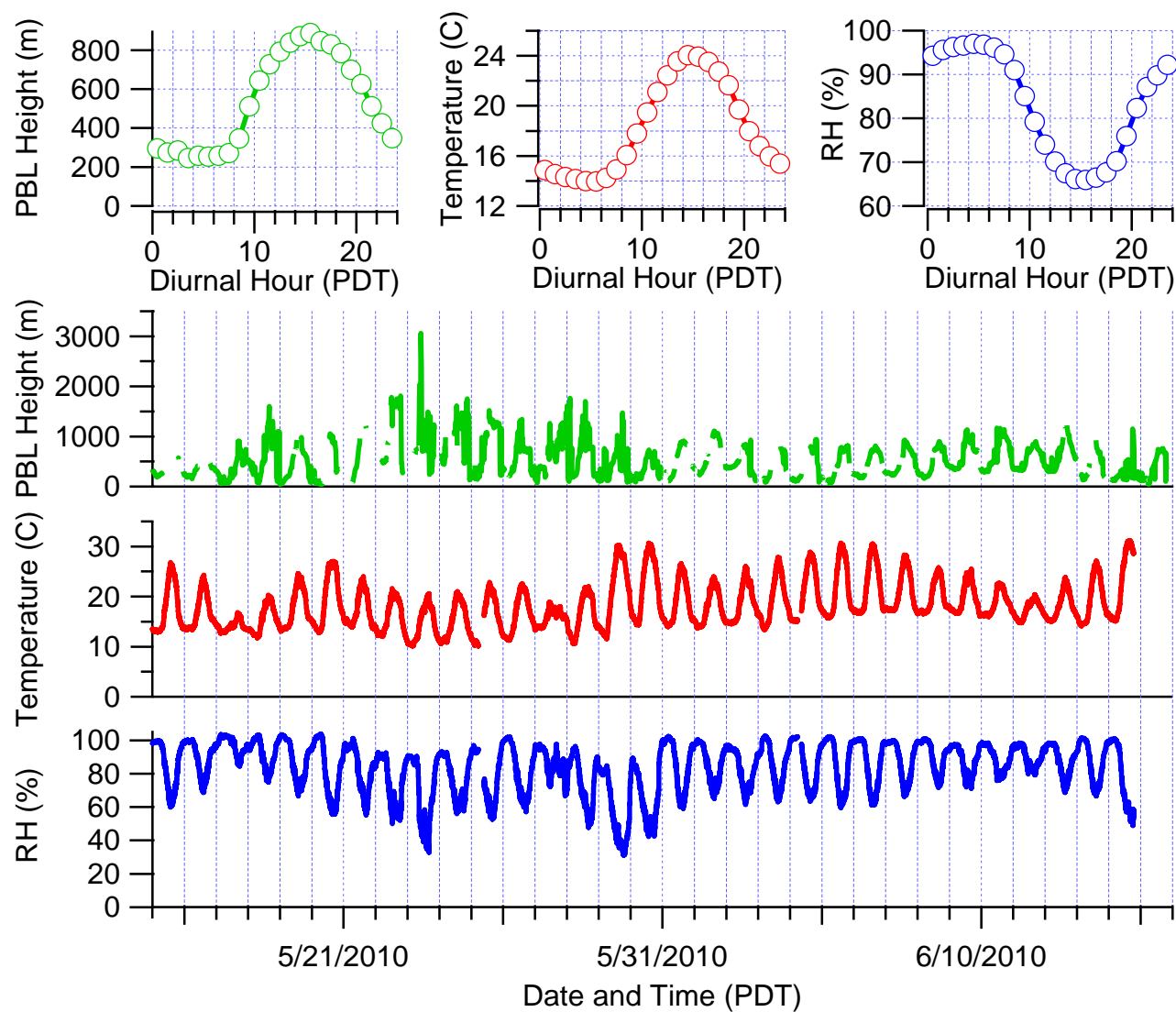
Figure A-1: Time series and diurnal profiles for planetary boundary layer height (PBL), temperature, and relative humidity at the Pasadena ground site during CalNex.
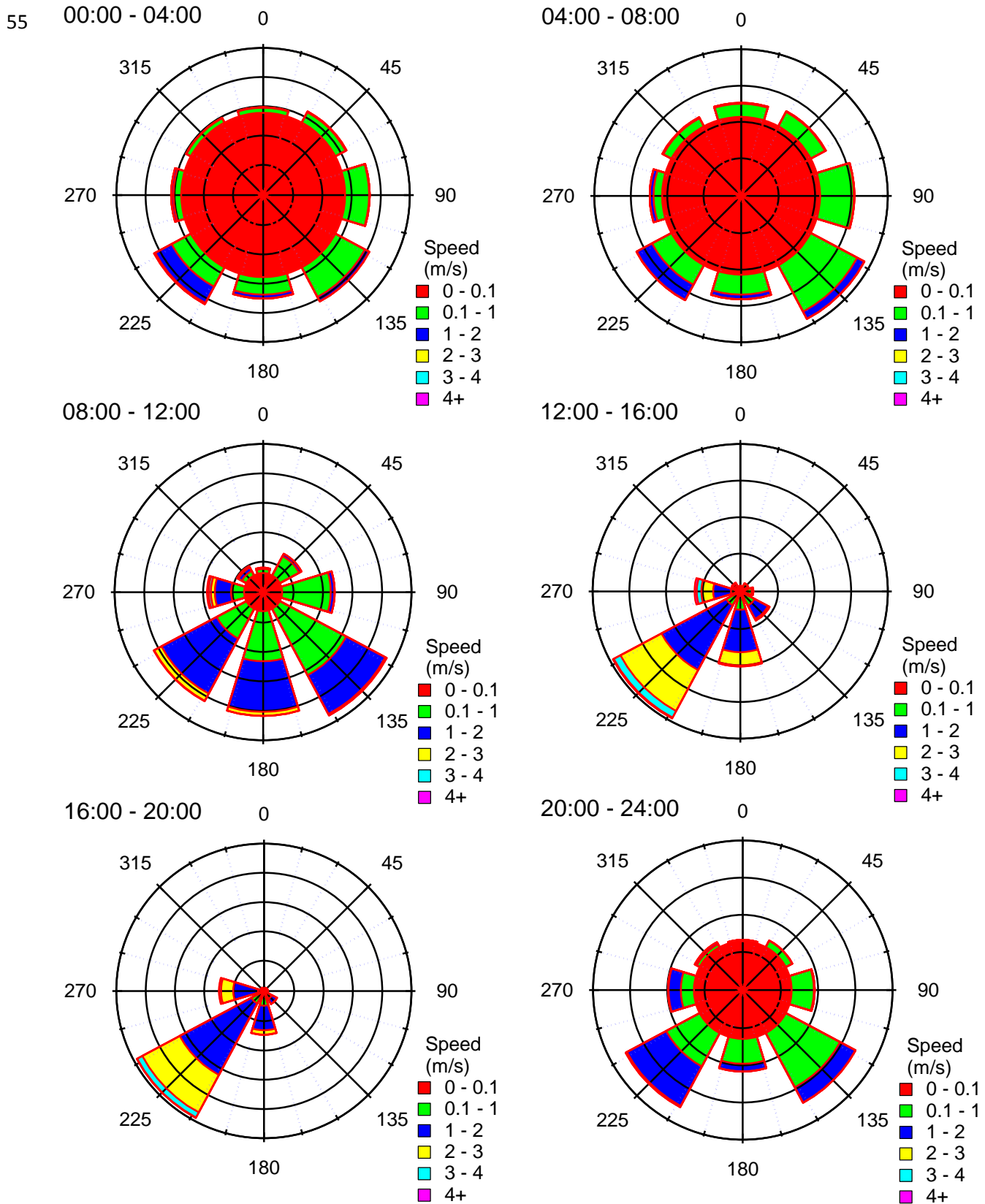
Figure A-2: Wind roses for the Pasadena ground site during CalNex organized by time of day (PDT). Zero on the polar coordinate is north and radial distance indicates relative frequency.

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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 2nd through June 6th. The grey triangle indicates the location of the Pasadena ground site.
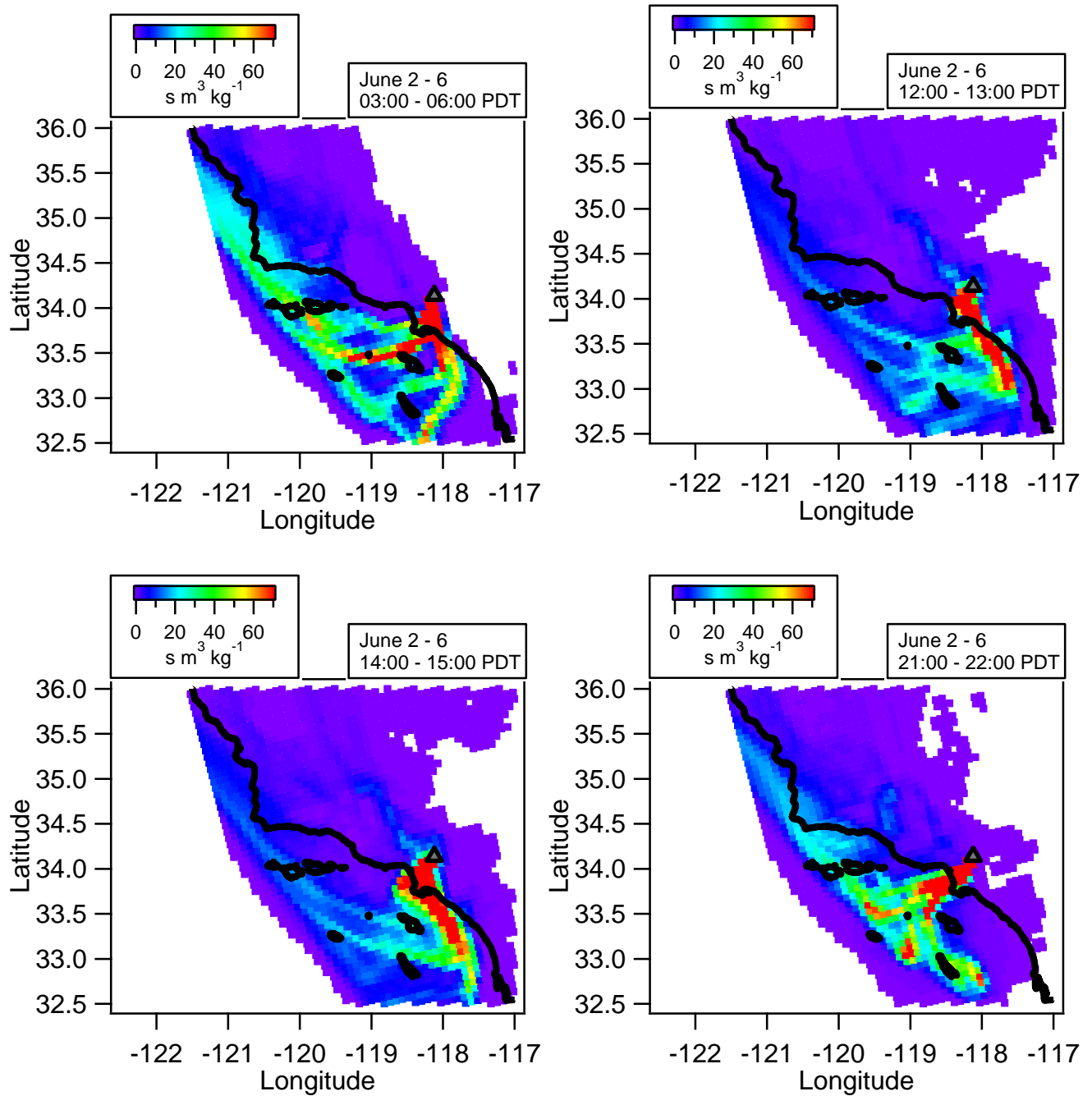
Figure A-4: Average 48 h FLEXPART back-trajectories for air masses arriving at the Pasadena ground site. Colors represent the footprint residence times. Each panel corresponds to a different time-of-day and is the average for June 9th through June 11th. The grey triangle indicates the location of the Pasadena ground site.
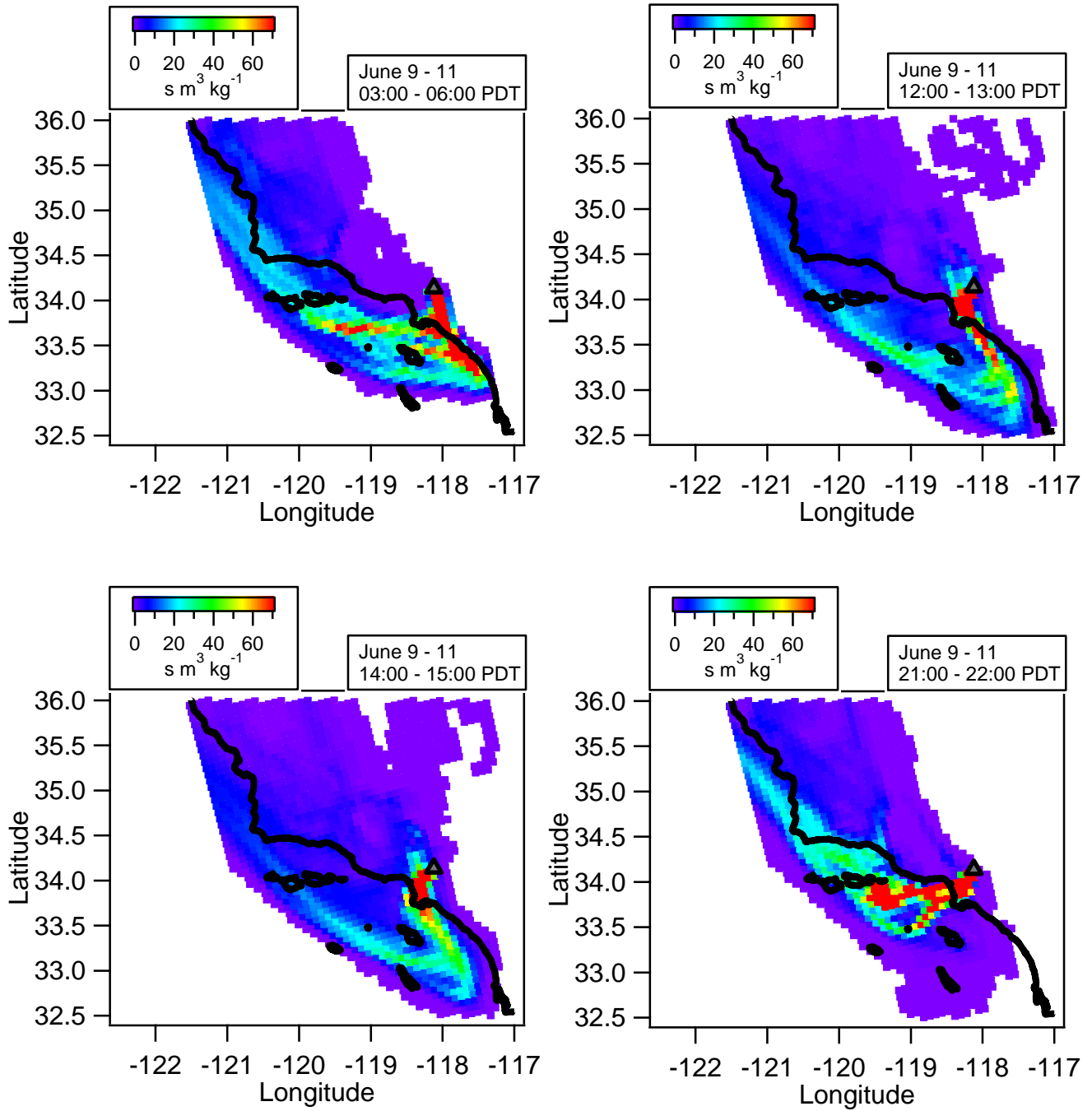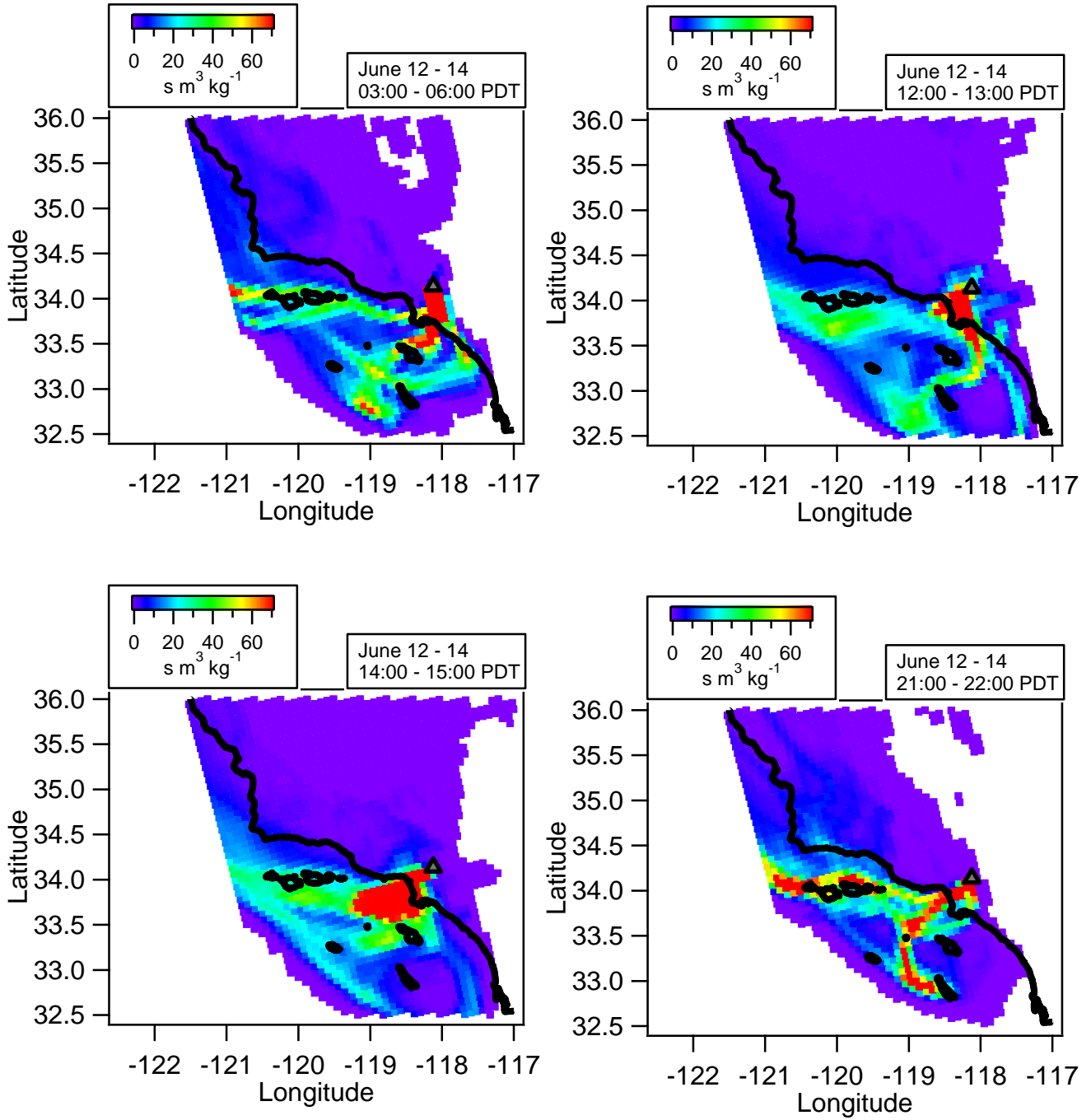
Figure A-5: Average 48 h FLEXPART back-trajectories for air masses arriving at the Pasadena ground site. Colors represent the footprint residence times. Each panel corresponds to a different time-of-day and is the average for June 12th through June 14th. The grey triangle indicates the location of the Pasadena ground site.

Section B: Instrument Comparisons & Selected Diagnostics

This section provides information that supports the validity of the AMS measurements. In Figure B-1 the time series of submicron aerosol mass concentration measured by the AMS and calculated from the SMPS and UHSAS number distributions are shown along with correlation plots for the various instruments. (Note: the UHSAS number distribution was determined using a refractive index of 1.515, which corresponds to dry ammonium sulfate at 1050 nm. A very brief discussion of refractive index and optical properties is contained in the next paragraph.) The AMS only measures non-refractory aerosol, and to partially compensate for this limitation the rBC concentration from the SP2 is added to the AMS time series. The AMS also does not measure mass from other refractory sources such as sea salt or mineral dust. These species are not expected to significantly impact the instrument comparison though, because the relative 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 salt to be 9% of total submicron volume (Figure 3A, main text). The AMS and SMPS instruments show good agreement, and a linear regression analysis of the two data results in a slope of 1.03 ($R^2 = 0.85$) as shown in Panel C. The agreement between the AMS and UHSAS is not as good (slope = 1.28, $R^2 = 0.84$) when the UHSAS data is truncated at 740 nm geometric diameter to approximate the 1 μm aerodynamic diameter size cut of the AMS (Panel D). Given the reasonable agreement between the AMS and SMPS as well as other instruments (see below), it appears that the UHSAS, including the uncertainties in the conversion to volume and the estimation of refractive index, may be responsible for this discrepancy. It is noted that from 6/4 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

82   (estimated geometric diameter, equivalent to an estimated vacuum aerodynamic diameter of

83   1080 nm using the average density of 1.46 g cm^{-3} calculated from the AMS and SP2 aerosol

84   composition measurements.) as measured by the UHSAS (Panel B). Similarly, PALMS

85   measurements show a large volume concentration of sulfate/OA/nitrate particles above 784 nm

86   geometric diameter during this period (Figure 1 in main paper). The discrepancy from 6/4

87   through 6/6 is therefore attributed to a period of unusually large particles, which are near and

88   above the 1 μm aerodynamic diameter size cut for measurement by the AMS.

89   The SMPS measurements are also validated by calculating the Mie scattering from the

90   number size distribution data, and then comparing the result against extinction measurements

91   (Figure B-2). The extinction measurements are from the CAPS instrument and were taken at 532

92   and 630 nm. Good agreement between the calculated scattering and measured extinction is

93   observed when using an index of refraction 1.54, which is the average for dry ammonium sulfate

94   and ammonium nitrate [*Kleinman et al.*, 2007]. The refractive index of OA will vary depending

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

9

105 generally good, and a linear ODR regression analysis of the two data sets results in a best-fit

106 slope of 1.01 ($R^2 = 0.84$). The same analysis for nitrate results in a slope of only 0.64 ($R^2 =$

107 0.85), however. A possible explanation for the discrepancy between the nitrate measurements is

108 the presence of super-micron sodium nitrate that is formed when sea salt reacts with nitric acid as

109 discussed in the Appendix of the main text. To test this hypothesis, the regression analysis for

110 nitrate was repeated using only periods with PALMS sea salt volume concentrations of less than

111 0.35 μm^3 cm^{-3}, which corresponds to the 5th percentile of the data. A substantial improvement in

112 agreement is observed with the slope increasing to 0.89 (from 0.64). For the sake of

113 completeness the same test was performed on the sulfate data, but there is only a small increase

114 in the slope to 1.09 (from 1.01). Interestingly, the excellent agreement between the PILS-IC and

115 AMS sulfate, as well as the weak dependence on PALMS sea salt concentrations in the sulfate

116 scatter plot, suggests that little sodium sulfate has been formed from the reaction of sea salt and

117 sulfuric acid. Despite the technical differences between the AMS and PILS-IC, after accounting

118 for the presence of sodium nitrate in the supermicron mode there is reasonable agreement

119 between these two instruments with respect to sulfate and nitrate concentrations.

120   The comparisons of the AMS organic mass (OM) with multiple other measurements of

121 organic aerosols at the Pasadena ground site exhibits reasonable agreement. The different OM

122 and OC measurements are listed in Table B-1, and the results of the OM and OC comparisons

123 are summarized Table B-2 and Figure B-4. In Panel A of Figure B-4 the AMS OM_1 (the

124 subscript indicates the size cut in μm) and the online Sunset organic carbon mass ($OC_{2.5}$) are

125 plotted together and a strong correlation between the two measurements is observed. The AMS

126 OM_1 and online Sunset $OC_{2.5}$ data (Panel B) yield an R^2 value of 0.76, but the regression slope of

127 3.3 is significantly higher than the expected range of 1.4 – 2.3 [*Aiken et al.*, 2008; *Turpin et al.*,

128   2001]. Such a large discrepancy is outside the AMS uncertainty bounds of ±30% [*Middlebrook*

129   *et al.*, 2012]. While the exact reason for this discrepancy is unclear it may be related, at least

130   partially, to the presence of a denuder upstream of the Sunset carbon analyzer. Specifically, the

131   denuder may cause volatilization of particulate OC from the collection filter that is induced by

132   re-equilibration of organic concentrations after removal of vapor-phase organics by the denuder

133   [*Grover et al.*, 2008].

134   A scatter plot of the AMS OM_1 versus the $OC_{2.5}$ measured from two sets of filter samples

135   collected by the Georgia Institute of Technology (GIT) and U.S. Environmental Protection

136   Agency (EPA) groups (Panel C) yields very reasonable slopes of 1.7 and 1.9 ($R^2 = 0.82$ and $R^2 =$

137   0.80, respectively). These slopes are similar to the $OM_1:OC_1$ of 1.7 that was determined from the

138   elemental analysis of the AMS mass spectra. The $OC_{2.5}$ concentration was also measured on a

139   third set of filter samples collected by the University of North Carolina (UNC) group. For the

140   UNC $OC_{2.5}$ measurement the slope obtained from the regression analysis (Panel D) is 1.4, which

141   is lower than the other filter samples. This difference seems to be related to the collection times

142   for the filter samples. The UNC samples included several intensive sampling periods of 6 h or

143   less, whereas the GIT and EPA filters were switched daily. If only the daily UNC samples are

144   included in the regression analysis a slope of 1.8 is obtained, which is similar to the GIT and

145   EPA samples. The AMS OM_1 and the FTIR $OM_{2.5}$ obtained from filter samples are compared in

146   Panel E resulting in a regression slope of 1.3 ($R^2 = 0.63$). Both the filters analyzed by FTIR as

147   well as the UNC filters exhibit higher amounts of organics relative to the 24 hr filters when the

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

150   where the filter samplers were located may have increased the influence of evaporation. It should

151   be noted that all the analyses are for $PM_{2.5}$ particles except the AMS, which is a PM_1 instrument.

152   The impact of the different size cuts on the comparison can be evaluated by estimating that 15%

153   of the $PM_{2.5}$ organic mass is present between 1 and 2.5 µm on average. This percent is

154   determined from online Sunset OC measurements that were performed while switching between

155   a $PM_{2.5}$ and PM_1 cyclone from 6/12 through 6/16. Accounting for this additional mass that is not

156   measured by the AMS would increase the slopes for the regression analyses, but the corrected

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 ±30% uncertainty range for the AMS, and

159   neglecting the uncertainty of the OC measurements).

160   For completeness, the slopes from linear ODR regression analyses for each possible

161   pairing of OM or OC measurements are summarized in Table B-2 along with R^2 values. The

162   AMS measurements of OM_1 are converted to OC_1 using the $OM_1:OC_1$ ratios determined from

163   the elemental analysis of the AMS mass spectra. In general, the AMS and all three of the filter

164     $OC_{2.5}$ measurements (GIT, EPA, UNC) are in agreement within the uncertainties, exhibiting

165   slopes between 0.81 and 1.14 and R^2 values higher than 0.60. The lowest correlations are for

166   comparisons with the UNC filter samples, which is likely due to different slopes observed in the

167   regression analyses for the 24 h versus intensive UNC sampling periods. If comparing only 24 h

168     $OC_{2.5}$ data from the UNC group against the AMS as well as the EPA and GIT filter samples, then

169   all the R^2 values are higher than 0.78. The online Sunset $OC_{2.5}$ measurement shows good

170   correlation with the AMS and the filter OC measurements ($R^2 \geq 0.75$), but it is systematically

171   lower by about a factor of two against all other measurements, which might be due to the

172   denuder utilized in the online Sunset $OC_{2.5}$ measurement as described in the preceding

173   paragraph. Alternatively, the un-denuded $OC_{2.5}$ filter samples may be impacted by a positive

174 artifact due to adsorbing volatile organic gases, although the agreement between the online AMS

175 OC_1 and offline filter $OC_{2.5}$ indicates that this positive artifact is not impacting other

176 comparisons. Lastly, when comparing the 24 h FTIR $OM_{2.5}$ against the 24 h GIT and EPA filter

177 $OC_{2.5}$ the slope is considerably lower than the expected OM:OC ratio, and the correlation

178 between the measurements is only moderate ($R^2 \geq 0.52$). One possible reason for the low FTIR

179 $OM_{2.5}$ concentrations and the lack of a strong correlation is that the evaporation of organics from

180 the FTIR samples was more extensive. The UNC filter $OC_{2.5}$ shows better agreement with the

181 FTIR $OM_{2.5}$ results (FTIR $OM_{2.5}$: UNC $OC_{2.5} = 1.29$, $R^2 \geq 0.76$), which is expected since these

182 samplers were located closer to each other on the Keck Building rooftop, and both analyses

183 included intensive samples. Selecting only the intensive periods slightly improves the best-fit

184 slope in the regression analysis (1.33 vs. 1.29). As discussed above the AMS OM_1 and FTIR

185 $OM_{2.5}$ agree reasonably well although the FTIR $OM_{2.5}$ is somewhat lower (AMS OM_1 : FTIR

186 $OM_{2.5} = 1.25$, $R^2 \geq 0.63$). This observation is consistent with previous comparisons that have

187 shown FTIR measurements tend to be lower than and less correlated with AMS measurements

188 when carried out in urban areas [*Russell et al.*, 2009a].

189 **Table B-1:** Summary of the different OM and OC measurements taken on the Caltech campus

190 during the CalNex campaign (GIT = Georgia Institute of Technology, EPA = U.S.

191 Environmental Protection Agency, UNC = University of North Carolina). Note: the intensive

192 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	$PM_{2.5}$
GIT Filter OC	Offline	Keck Roof	5/15-6/15	31	23 h	$PM_{2.5}$
EPA Filter OC	Offline	Keck Roof	5/15-6/15	32	23 h	$PM_{2.5}$
UNC Filter OC	Offline	Keck Roof	5/15-6/13	58	23 h, or 3-6 h	$PM_{2.5}$
FTIR OM (Scripps)	Offline	Keck Roof	5/15-6/15	57	23 h, or 3-6 h	$PM_{2.5}$

193

14

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

Slope	AMS OC_1	FTIR $OM_{2.5}$ (Scripps)	Online Sunset $OC_{2.5}$	GIT Filter $OC_{2.5}$	EPA Filter $OC_{2.5}$	UNC Filter $OC_{2.5}$	(y data)
AMS OC_1							
FTIR $OM_{2.5}$ (Scripps)	1.25[a]						
Sunset Online $OC_{2.5}$	1.95	3.13					
GIT Filter $OC_{2.5}$	0.99	0.83	0.48				
EPA Filter $OC_{2.5}$	1.13	0.99	0.56	1.14			
UNC Filter $OC_{2.5}$	0.81	1.29	0.41	1.12	0.88		
(x data)							

R^2	AMS OC_1	FTIR $OM_{2.5}$ (Scripps)	Online Sunset $OC_{2.5}$	GIT Filter $OC_{2.5}$	EPA Filter $OC_{2.5}$	UNC Filter $OC_{2.5}$
AMS OC_1						
FTIR $OM_{2.5}$ (Scripps)	0.63[a]					
Sunset Online $OC_{2.5}$	0.75	0.49				
GIT Filter $OC_{2.5}$	0.78	0.52	0.86			
EPA Filter $OC_{2.5}$	0.78	0.55	0.82	0.93		
UNC Filter $OC_{2.5}$	0.76	0.76	0.75	0.75	0.60	

199

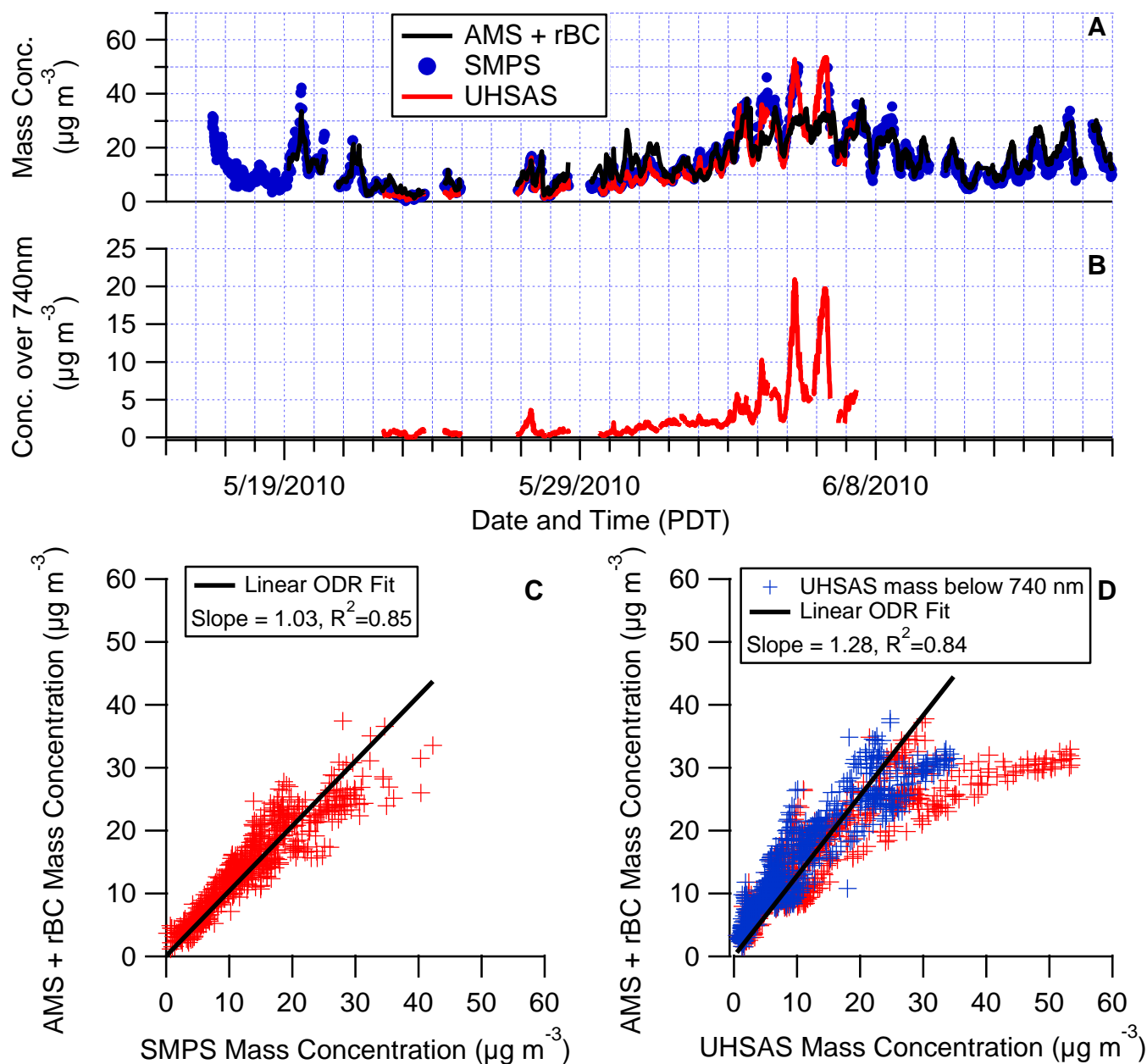200 [a]The AMS vs. FTIR comparison is for OM vs. OM.

201

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.
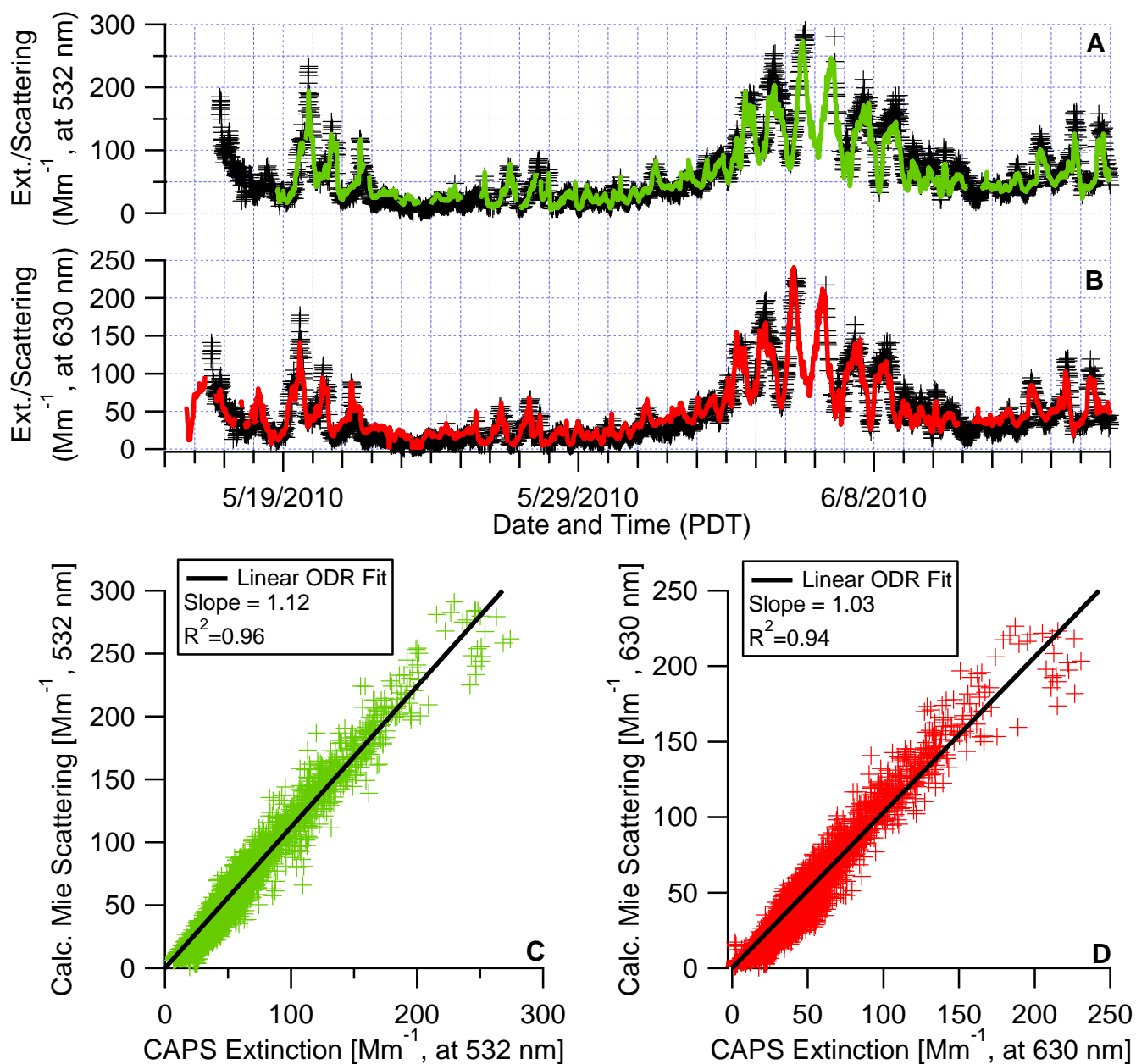
Figure B-2: (A) Time series of extinction measured by the CAPS instrument (green line) and Mie scattering calculated from SMPS data (black markers). Both traces correspond to a wavelength of 532 nm, and the Mie scattering was calculated using a refractive index of 1.54, which is the average for $(NH_4)_2SO_4$ 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.
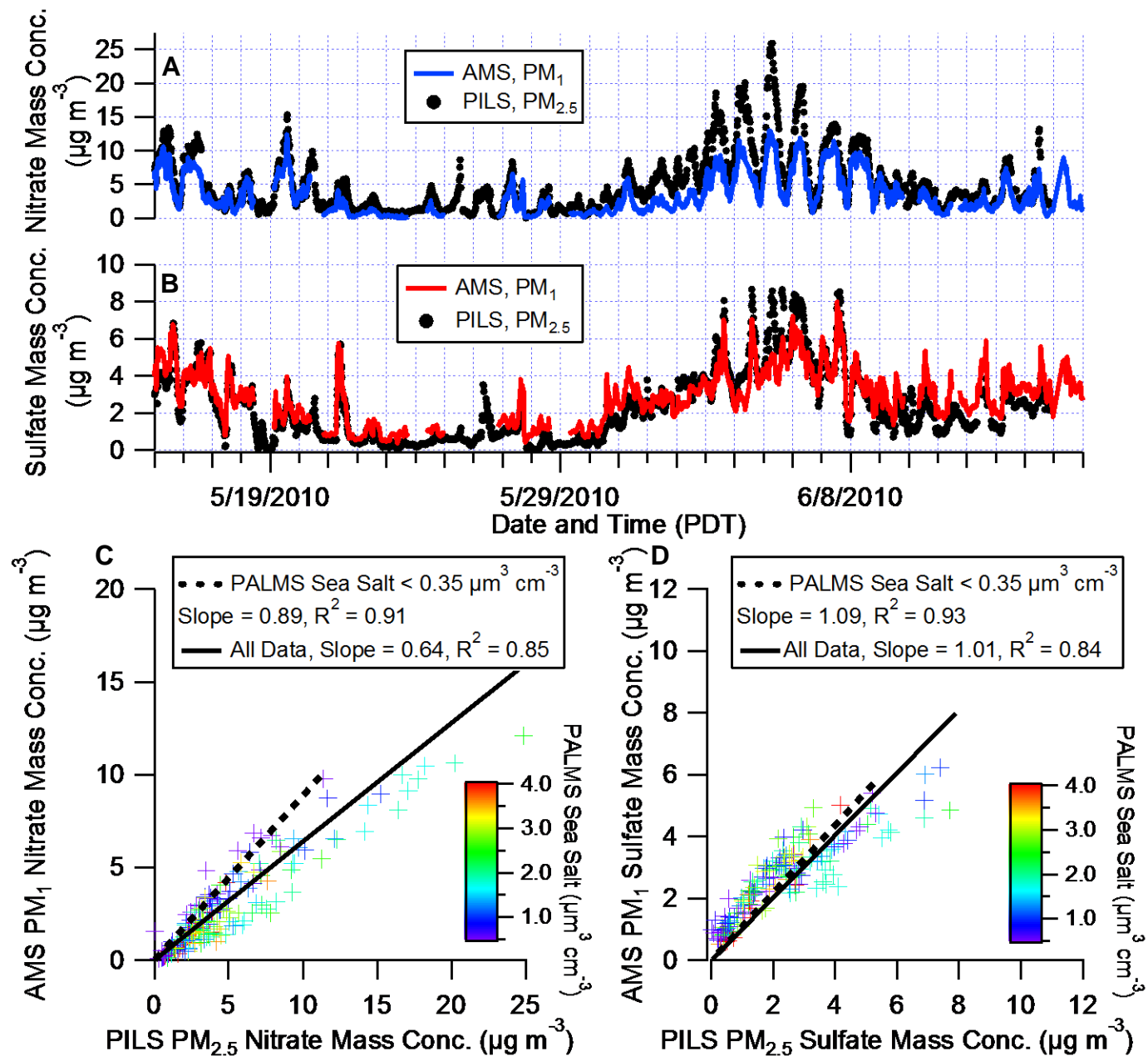
Figure B-3: **(A)** Time series of nitrate mass concentration measured by the AMS and the PILS-IC instrument. **(B)** Time series of sulfate mass concentration measured by the AMS and the PILS-IC instrument. **(C)** Scatter plot of the AMS and PILS-IC nitrate mass concentrations. Linear fits are shown 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 $PM_{2.5}$ size cut.
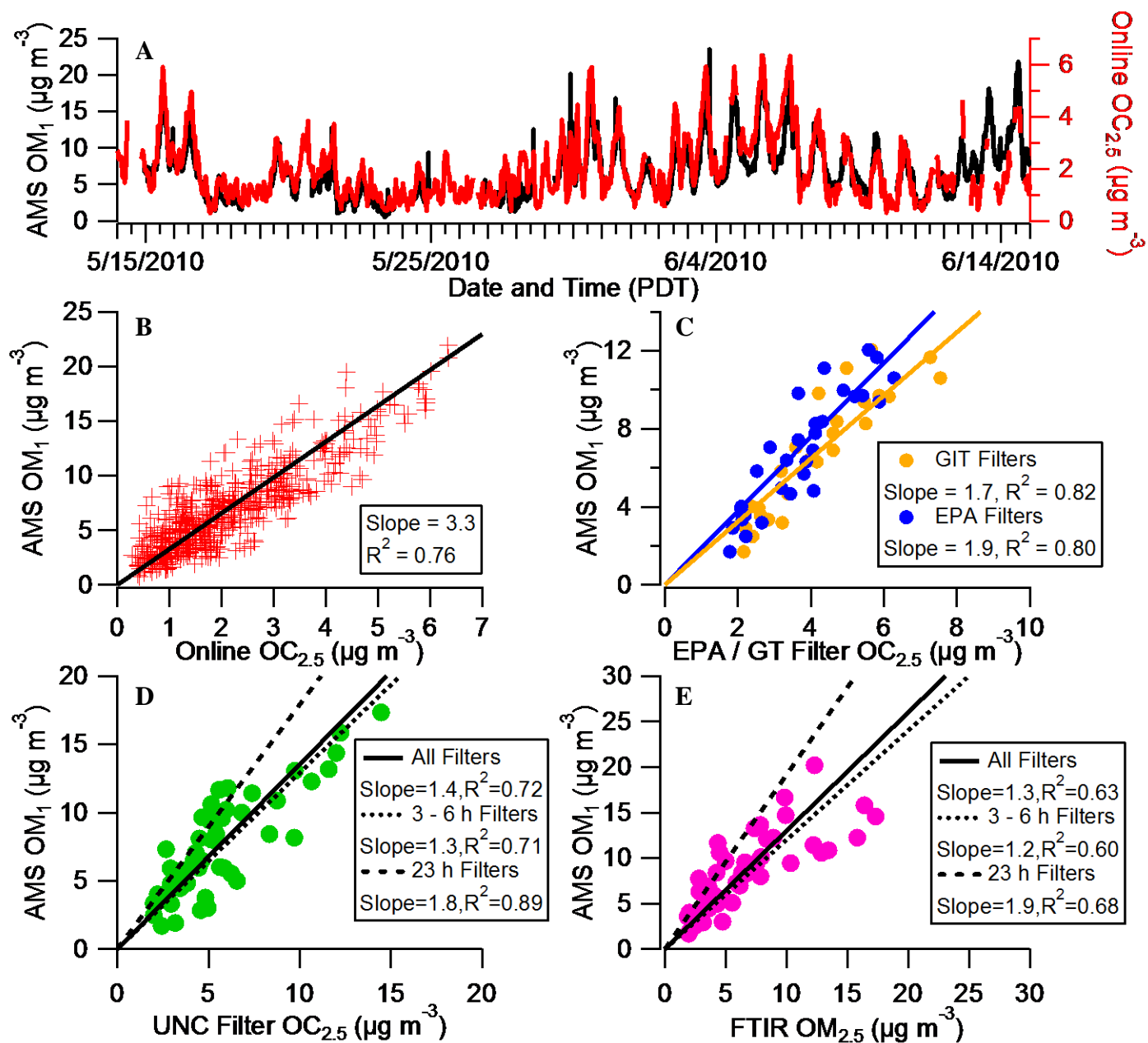
Figure B-4: **(A)** Times series of the OM_1 measured by the AMS and the $OC_{2.5}$ measured online by the Sunset Labs OC/EC analyzer. **(B)** Scatter plot of the AMS OM_1 versus the online Sunset $OC_{2.5}$. **(C)** Plot of the AMS OM_1 versus the $OC_{2.5}$ measured using two sets of filter samples collected by the Georgia Institute of Technology group (gold) and the EPA group (blue). **(D)** Plot of the AMS OM_1 versus the $OC_{2.5}$ measured from the UNC group filter samples. **(E)** Plot of the AMS OM_1 versus the $OM_{2.5}$ determined from FTIR measurements. The lines in Panels B – E represent linear fits of the data. Subscripts indicate measurement size cut in μm 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 compared against those from three previous campaigns that took place in the LA basin: SOAR-1 [*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 comparison the first and third periods were selected, since those portions of PACO took place at the same time of year as CalNex and SOAR-1, respectively. The fractional composition is similar between the sites despite the different locations and years for the campaigns, as well as 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 largest fractions ranging between 16 – 30% and 14 – 22% of the total mass, respectively. The 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 Pasadena, Riverside, and Burbank EC accounted for 3 – 6% of the aerosol mass concentration, respectively.

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_2^+ 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_2^+ was not separated using the high-resolution data for this figure, but on average CO_2^+ 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

229   are similar, which supports the validity of the AMS measurements for Pasadena and provides a

230   sample of the variability of the O/C to f_{44} relationship across different field sites and time

231   periods.

232   Shown in Figure C-2 is the relative contribution of each species to the submicron mass as

233   a function of the total mass. A probability density distribution of the submicron mass is displayed

234   as well (right axis). All data represent three hour averages. The relative composition does not

235   vary greatly between low and high concentration periods. Nitrate becomes more important with

236   increasing total concentrations (up to 29%). OA is important at all concentrations and is typically

237   40% of PM_1. The data in Figure C-2 illustrate that OA and ammonium nitrate contribute

238   substantially to the number of high PM_1 events. Shown in Figure C-3 is the relative contribution

239   of each PMF component to the OA mass as a function of the total OA mass (similar to Figure C-

240   2). A probability density of the OA mass is displayed as well (right axis). The relative OA

241   composition is increasingly dominated by OOA, and in particular SV-OOA, during high

242   concentration periods. As discussed previously, OA is an important contributor to the total

243   submicron mass at all concentrations. Combining the data shown in Figures C-2 and C-3, it can

244   then be concluded that freshly formed SOA, likely from photochemical production within the

245   basin, contributes substantially to the number of high PM_1 events along with nitrate. As

246   discussed in Section 3.1 many of the highest PM_1 concentrations occur during periods when

247   synoptic conditions (e.g., low boundary layer heights) trap pollution in the LA Basin.

248

249

250 **Table C-1:** Summary of campaign average mass concentrations as a percent of the total nrPM$_1$

251 and EC during CalNex, SOAR-1, PACO, and SCAQS. (Note: Campaign average EC

252 concentrations were not reported for PACO. Given the low concentrations of EC observed for

253 selected days during PACO however, the impact on the calculated percentages is likely to be

254 small.)

	CalNex[a]	SOAR-1[b]	PACO (I)[c]	PACO (III)[d]	SCAQS[e,f,g]
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

[a] May 15th to Jun 16th, 2010 (AMS and Sunset EC measurements)
[b] Jul 15th to Aug 15th, 2005 (AMS and Sunset EC measurement)
[c] May 22nd to Jun 12th, 2009 (AMS measurements)
[d] Jul 10th to Aug 4th, 2009 (AMS measurements)
[e] Jun 9th to Sept 3rd, 1987 (Selected Days)
[f] PM$_{2.5}$, OC measurement converted to OM using OM:OC of 1.7, water-soluble inorganics only
[g] Chloride, nitrate, and sulfate measured by ion chromatography, ammonium measured by colorimetry, OC measured by thermal manganese oxidation.
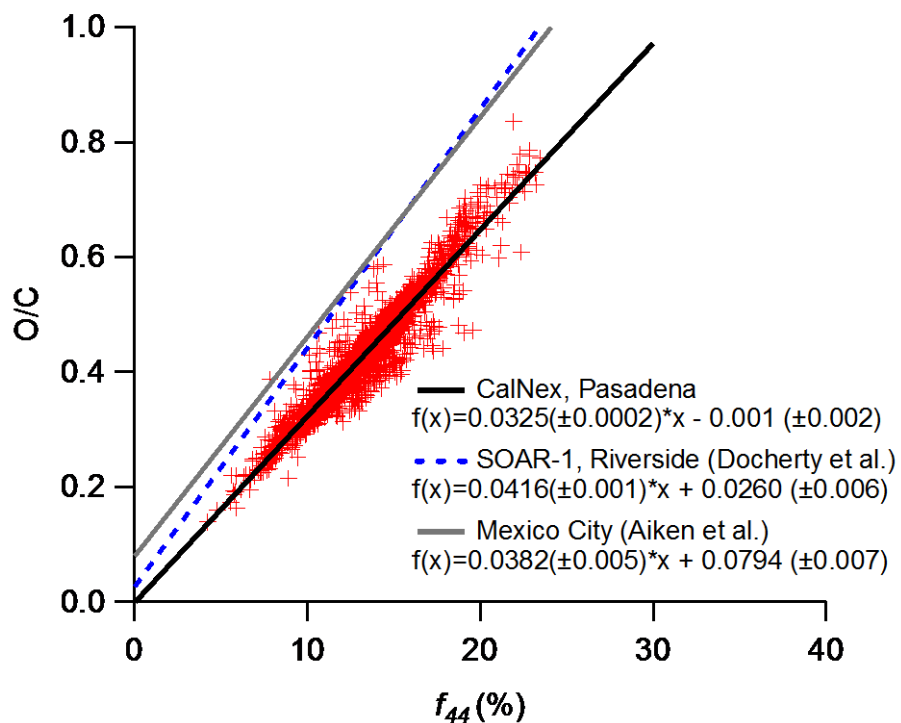
Figure C-1: Scatter plot of f_{44} versus O/C calculated from HR-ToF-AMS high resolution data. A linear ODR fit of the CalNex data is shown along with the similar results from Riverside, CA [*Docherty et al.*, 2011] and Mexico City [*Aiken et al.*, 2008].
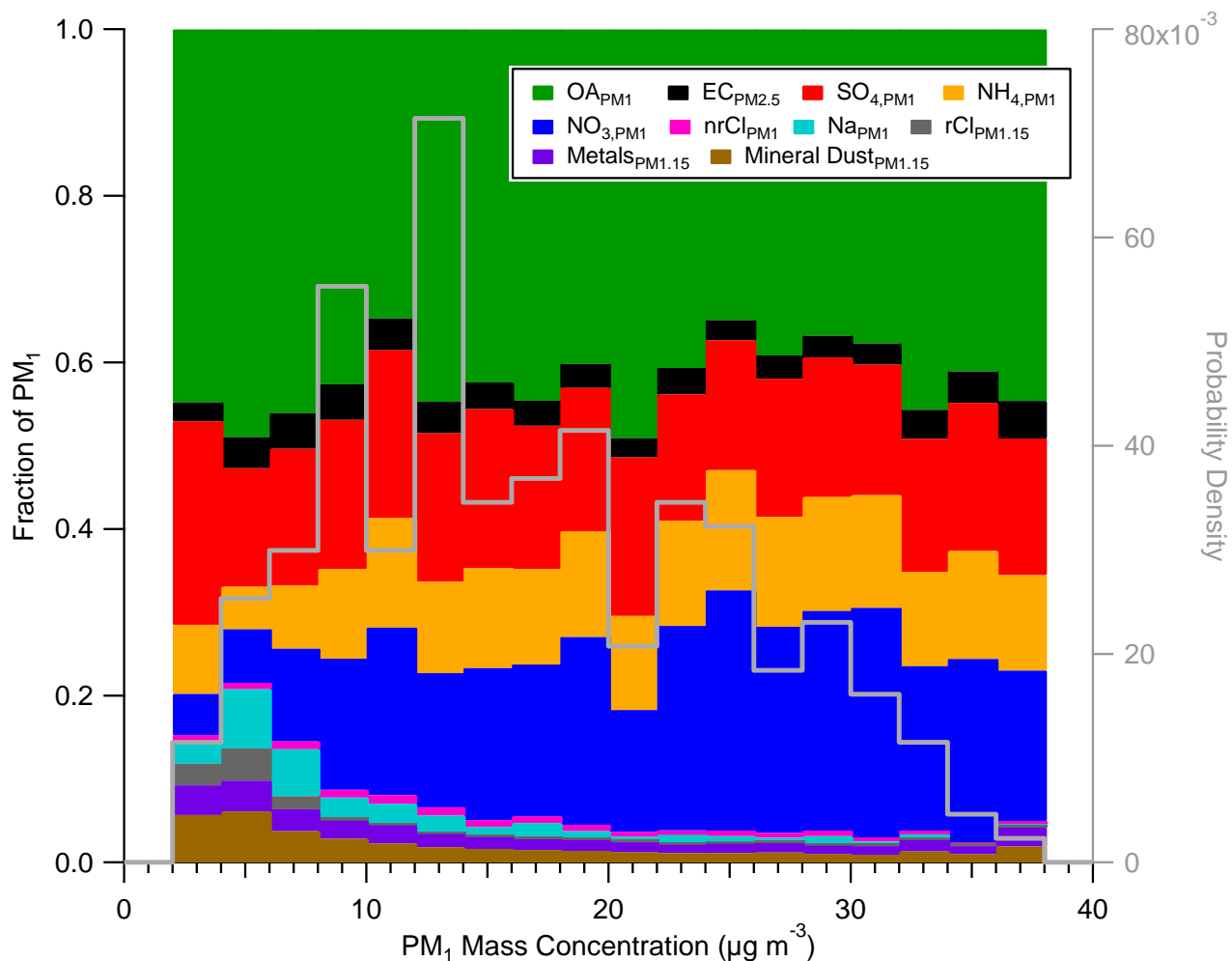
Figure C-2: The fraction of the total submicron aerosol mass contributed by different aerosol species as a function of the total mass. Also shown is a histogram of the total submicron aerosol mass for CalNex (right axis).
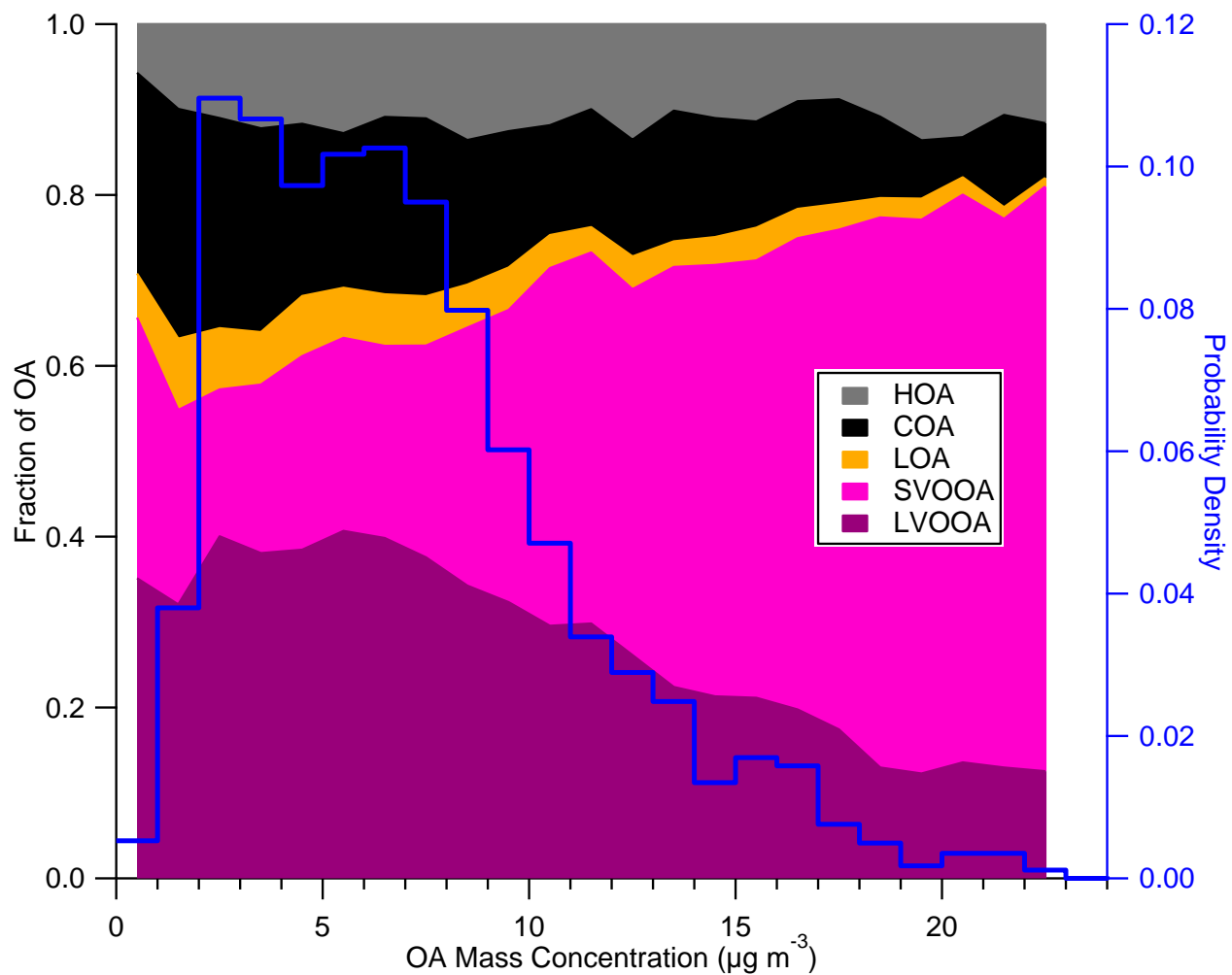
Figure C-3: The fraction of the OA mass contributed by different components as a function of the total OA mass. Also shown is a histogram of the total OA mass for CalNex (blue, right axis).

Section D: Selection of PMF solution & Additional PMF Figures

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 not included here as it has already been provided in previous publications [*Paatero et al.*, 1994; *Ulbrich et al.*, 2009], and instead we focus on the specific analysis of the CalNex data set. The 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 summarizes the types and mass fractions of the different components identified as the number of components is systematically increased from 3 to 10 (for FPeak=0). The 3-component solution is similar to that found for PMF analyses of other data sets with HOA, SV-OOA, and LV-OOA 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 compared to the 3-component solution. Furthermore, HOA in the 3-component solution exhibits 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 HOA in the 3-component solution. We conclude that the CIOA component is distinct from the other components, and in particular HOA, based on it substantially different diurnal cycle (Figure 5A, main text), and the dramatic improvement in the correlation of HOA with rBC (R 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.

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

284   LOA mass spectra is distinguished by prominent fragments that are characteristic of amines:

285   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),

286      $C_5H_{12}N^+$ (*m/z* 86). The sum of the absolute residuals associated with these amines is plotted

287   versus number of components in Panel B of Figure D-1. This residual decreases with the number

288   of components, but the decrease is largest between the five-component and six-component

289   solutions. In addition, there is only a slight decrease in the residuals when increasing the number

290   of components beyond six. Clearly, LOA in the 6-component solution is needed for PMF to

291   properly account for amines in OA measured at the Pasadena ground site.

292   For PMF solutions with more than 6 components interpretation becomes increasingly

293   difficult. Numerous oxygen-rich components are identified, which could be classified as OOA.

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

296   component. Thus, it is possible that the variable nature of the SOA spectrum with, for instance,

297   photochemical age leads to significant residuals in PMF, and when increasing the number of

298   components beyond six these residuals control the additional components in the PMF solution,

299   leading to more 'OOA' components [*Ulbrich et al.*, 2009].

300   Even in the 6-component solution it is unclear if the three OOA components represent

301   distinct sources or chemical types. Specifically, for the 6-factor solution two of the three OOA

302   components (OOA-2 and OOA-3) exhibit a high correlation in time (R=0.77) and very similar

303   correlations with tracers (Figure D-2), which suggests these two components may not be distinct.

304   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

307 from artificial "splitting" and/or "mixing" of distinct components that is observed when too

308 many components are requested in a PMF solution [*Ulbrich et al.*, 2009]. This artifact is likely

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

311 address this problem while at the same time resolving the LOA component, the PMF analysis is

312 repeated after subtracting out the contribution of LOA to the mass spectral matrix. The LOA

313 contribution is determined from the 6-component solution of the original PMF analysis, and is

314 included when summarizing the final PMF results. Thus, this method is equivalent to

315 constraining LOA to have a time series and mass spectrum that is invariant as the number of

316 component in increased similar to advanced factor analysis of Lanz et al. [2008]. It is also noted

317 that while selection of a PMF solution does require subjective 'user input', the exploration of

318 higher factor solutions and the recombination of factors that are indistinct has been previously

319 reported in the literature [e.g., *Docherty et al.*, 2011; *Liu et al.*, 2011; *Zhang et al.*, 2007].

320 It should be noted that the LOA contribution to the total OA mass is small. Also, LOA

321 exhibits a time series and mass spectra that contributes significantly to the PMF residual and is

322 quite different from the other components. Thus, it expected that subtracting the LOA

323 contribution only has a weak influence on the other PMF components. To verify this weak

324 influence, a correlation analysis was carried out that compared each component for the four

325 component solution without LOA subtracted against the five component solution in which the

326 LOA was subtracted. In other words, the 4-component solution (HOA, CIOA, SVOOA, and

327 LVOOA) in the original PMF analysis is compared against the 5-component solution in the PMF

328   analysis with a fixed LOA contribution (HOA, CIOA, SVOOA, LVOOA, and LOA). As can be

329   seen in Figure D-3 the time series and mass spectra of HOA, CIOA, SVOOA, and LVOOA for

330   the two PMF methods are almost identical. The correlation plot for the HOA time series exhibits

331   a slope of slightly lower than one (0.86) likely due to re-apportionment of HOA mass to LOA,

332   but the correlation is still very high (R=0.97). In total, Figure D-3 indicates subtracting the LOA

333   contribution does not substantially impact the other components in the PMF solution.

334   In Panel C of Figure D-1, the mass fraction and identities of the components are

335   summarized for the PMF analysis with the fixed LOA contribution. The 5-component solution is

336   the final solution described in the main text. Similar to the original PMF analysis, a dramatic

337   increase in the correlation of HOA and rBC is observed when the CIOA component is resolved

338   in the 5-component solution (Panel D), and subsequent increases in the number of components

339   either marginally increase or decrease this correlation. This observation is consistent with

340   concluding that CIOA is distinct from the other components. In addition, the 6-component

341   solutions for the two PMF analyses are similar, which is expected since the LOA contribution in

342   both analyses is identical. The similarity indicates that holding the LOA contribution fixed does

343   not create unforeseen changes in the PMF analysis. The Q/Q_{exp} values for the various PMF

344   solutions are shown in Panels C and D. (Note: Q is the total sum of the squares of each residual

345   divided by its expected error, and Q_{exp} equals the degrees of freedom in the fitted data, which is

346   approximately the product of the number of rows and columns for the input mass spectral matrix.

347   In addition, Fpeak is a parameter that explores different "rotations" of the PMF solution where

348   the component time series are made more different or the component mass spectra are made

349   more different [*Ulbrich et al.*, 2009].) For the final 5-component solution a reasonable Q/Q_{exp}

350   value of 1.9 is obtained (Panel D). A Q/Q_{exp} value near one indicates that the assumptions of the

351   bilinear PMF model are appropriate and that the estimation of the errors for the input data is

352   accurate.

353   Figure D-4 shows the value of Q/Q_{exp} as a function FPeak for the 5-component solution

354   with the fixed LOA contribution. Minimum Q/Q_{exp} values are observed for FPeak equal to zero.

355   In addition, the correlation of the HOA component time series with that of the external tracer

356   rBC does not improve for non-zero FPeak values. Thus, the 5-component solution corresponding

357   to FPeak = 0 is the final solution selected for further discussion in the main text. Additionally,

358   Figure D-5 summarizes an analysis of the residuals for the final 5-component solution (with

359   FPeak = 0).

360   It was recently shown by Mohr et al. [2011] that HOA and cooking organic aerosol can

361   be distinguished by their relative values of AMS f_{55} and f_{57}, which represent the fraction of the

362   total OA at m/z 55 and m/z 57, respectively. The differences in f_{55} and f_{57} between the two

363   components are driven by the relative prominence of the oxygenated fragments $C_3H_3O^+$ and

364    $C_3H_5O^+$ in the mass spectra of cooking organic aerosol. For the CalNex PMF solution, the mass

365   spectrum of the CIOA component (Figure 4A) shows the presence of these fragments, and they

366   represent a greater fraction of the signal at m/z 55 and m/z 57 for CIOA versus HOA. To further

367   explore if the mass spectra of HOA and CIOA for CalNex are consistent with previously

368   published studies, f_{55} versus f_{57} data for the two PMF components are plotted in Figure D-6A.

369   The lines in Figure D-6A are taken directly from Mohr et al. [2011] and represent linear fits of

370   f_{55} versus f_{57} data from previously reported cooking organic aerosol and HOA PMF components

371   as well as from cooking and traffic source emission studies. Also plotted in Figure D-6A is f_{55}

372   versus f_{57} for the total time-resolved organic mass spectra after subtracting out the contribution of

373   SV-OOA and LV-OOA (the axes are labeled with 'OOA sub' to indicate this subtraction) so the

374   data reflects only contributions from primary components. The resulting data points are colored

375   by the relative contribution of CIOA. The CIOA component lies along the line for cooking

376   source emissions, consistent with the description of CIOA as 'cooking-influenced' aerosol. The

377   HOA component at CalNex does not match the linear fits for HOA as well, but it does lie within

378   the range of the raw values used for the regression analysis in Mohr et al. [2011]. Since the

379   differences between CIOA and HOA in f_{55} versus f_{57} space are related to oxygenated fragments,

380   it is possible that the higher HOA oxidation in our study may lead to changes in the HOA data

381   points in this space and explain the difference between the CalNex HOA component and the

382   linear fits from Mohr et al. [2011]. For the time-resolved data, when CIOA has a large

383   contribution the data in f_{55} versus f_{57} space resembles cooking emission sources, whereas when

384   the CIOA contribution is low the data more closely resemble the expected HOA values. This

385   result supports the conclusion that the organic aerosol at the Pasadena ground site had substantial

386   contributions from both primary combustion and cooking sources. In addition, the CIOA and

387   HOA components contain spectral characteristics that are similar to analogous components and

388   primary emissions from previous studies.

389   The robustness of the PMF CIOA component is verified by comparing the CIOA time

390   series against the concentration predicted for cooking organic aerosol using the estimation

391   method presented in Mohr et al. [2011], which is derived from several previous source emission

392   and PMF studies. Briefly, this method calculates the amount of cooking organic aerosol by

393   scaling up the measured organic concentration at m/z 55 after accounting for possible

394   interferences from other primary and secondary OA. A scatter plot of PMF CIOA versus the

395   concentration calculated from m/z 55 is shown in Figure D-6B. For the entire CalNex data set

396   the slope is near one (0.98), but the correlation is not particularly strong (R=0.63). The data in

397   Figure D-6B are also colored by the amount of organic mass measured at *m/z* 44, which is an

398   indicator for the relative influence of SOA [*Aiken et al.*, 2009; *Mohr et al.*, 2011; *Ng et al.*,

399   2011]. It is observed that many periods with high *m/z* 44 exhibit a worse correlation, which is

400   expected given the known contribution of SOA compounds to *m/z* 55 as already mentioned.

401   Mohr et al. [2011] account for this interference by assuming the interference from SOA at *m/z* 55

402   is proportional to the amount of signal at *m/z* 44. This assumption may not hold in cases when

403   multiple SOA sources with different amounts of aging are contributing to the organic mass at *m/z*

404   44 and *m/z* 55 resulting in varying proportionalities. To minimize the impact of this interference

405   the data is fit a second time using only periods when *m/z* 44 is below its median value, which

406   results in a higher correlation (R=0.88) and lower slope (0.76). The difference of less than 25%

407   in average concentration represents reasonable agreement between the two methods, and can be

408   mostly explained by the 20% uncertainty in the scaling factor used in Mohr et al. [2011] to

409   calculate cooking organic aerosol from the organic mass measured at *m/z* 55. While the

410   possibility that PMF is apportioning non-cooking OA to the CIOA mass cannot be completely

411   ruled out, the comparison presented in this paragraph indicates a large majority of CIOA is from

412   cooking sources.

413   The time series of the PMF components can be further analyzed using an autocorrelation

414   plot in which the correlation of each factor with itself is calculated for various time offsets. In

415   this analysis species with high frequency fluctuations in concentrations (i.e., having many

416   'spikes' in their time series) will have a steep profile and vice versa. As seen in Figure D-7 the

417   autocorrelation profiles of SV-OOA and LV-OOA are the flattest, which is consistent with the

418   more regional nature of these components. Furthermore, the observation that the LV-OOA

419   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

422 times and a flatter profile at longer times indicating that this component has both local and

423 regional sources. This finding is not surprising given that some HOA is generated by local traffic

424 in the Pasadena area, but HOA is also advected to Pasadena from other areas in the LA Basin.

425 Interestingly, the CIOA component appears to be more dominated by local sources in

426 comparison to HOA, which may be related to the lower wind speeds and reduced advection in

427 the evenings when CIOA is highest in concentration. Alternatively, if the atmospheric lifetime of

428 CIOA was shorter than HOA, then that would also result in a relatively steeper profile for CIOA.

429 As described previously, the LOA component time series varies rapidly with time, and thus

430 displays the steepest profile in the auto-correlation plot, supporting the description of this factor

431 as 'local' organic aerosol.

432 The correlations of the PMF component time series with various other species measured

433 at the Pasadena ground site are summarized in Table D-1, and generally support the description

434 of the components discussed in the main text. For the readers convenience the correlations are

435 also summarized in a bar graph in Figure D-8. The most notable correlations are summarized in

436 this section. First, the primary combustion emissions tracers EC, rBC, NO_x, CO, and primary

437 hydrocarbons correlate with HOA. A correlation is also observed between HOA and $PM_{1.15}$ Zn.

438 The correlation with Zn may be explained by abrasion of tire-tread by road surfaces, which is

439 thought to be a major source of Zn in urban atmospheres [*Adachi et al.*, 2004; *Councell et al.*,

440 2004; *Hjortenkrans et al.*, 2007; *Salma et al.*, 2006], although a comparably strong correlation is

441 not observed for other metals that have been linked to brake wear or road dust. NO_x does not

442 exhibit as strong a correlation with HOA as the other primary combustion tracers, and this

33

443   observation is probably due to the short lifetime of NO_x and the multi-hour transport time for

444   advection of HOA from the more western portion of the LA basin to the Pasadena ground site.

445   Moreover, NO_y correlates better with HOA than NO_x (R of 0.63 versus 0.45) likely because

446   oxides of nitrogen emitted by vehicles have a longer atmospheric lifetime when measured as

447   NO_y. Taken together, the correlations of the various species with HOA suggest that primary

448   vehicular emissions are the dominant source for this component. The primary combustion tracers

449   do not correlate with CIOA with the exception of the moderate correlation with CO (R = 0.43).

450   The correlations of HOA and CIOA with CO, as well as the correlation of HOA with EC are

451   discussed in further detail in Section 3.2.3 of the main text. Previous work by Sun et al. [2011]

452   reported that the AMS fragments $C_5H_8O^+$ and $C_6H_{10}O^+$ showed high correlations specific to

453   cooking organic aerosols, and this correlation is also observed for the PMF results presented

454   here. However, these oxygenated fragments show an even stronger correlation with SV-OOA,

455   which suggests that these tracers are not highly specific to cooking OA.

456   The SV-OOA component correlates strongly with acetaldehyde and odd-oxygen.

457   Acetaldehyde is a well-known secondary photochemical product with direct emissions that are

458   quickly overwhelmed by secondary formation within hours of processing [*Sommariva et al.*,

459   2011; *Washenfelder et al.*, 2011], and odd-oxygen is a useful tracer for the oxidation of VOCs

460   [*Herndon et al.*, 2008; *Wood et al.*, 2010]. Thus, the strong correlation of these species with SV-

461   OOA is consistent with treating this component as a surrogate for 'fresh' SOA. Previous

462   publications have reported a correlation between nitrate and SV-OOA at some locations [e.g.

463   *DeCarlo et al.*, 2010; *Ulbrich et al.*, 2009], but a similar correlation is not observed at the

464   Pasadena ground site. The lack of correlation is likely due to the higher temperatures and

465   reduced RH in the afternoon at the ground site, which lead to the volatilization of ammonium

466 nitrate at the same time SV-OOA concentrations are typically increasing. For LV-OOA a strong

467 correlation with sulfate is observed that is consistent with other studies [*DeCarlo et al.*, 2010;

468 *Sun et al.*, 2011; *Ulbrich et al.*, 2009] and has been previously attributed to the non-volatile

469 nature of both sulfate and LV-OOA as well as the formation of these species from secondary

470 sources. The correlation of OOA with odd-oxygen is discussed in detail in Section 3.2.4 of the

471 main text.

472 PM$_{1.15}$ Ti exhibits a correlation with LOA (R = 0.63). A strong peak in LOA

473 concentrations occurred on the morning of June 5th (PDT), and a similar event is seen in the

474 PM$_{1.15}$ Ti time series. Paint-pigment has been identified as a source of titanium particles in the

475 atmosphere [*Alpert et al.*, 1981], and amines are often used in paint application and surface

476 coatings [*Unnikrishnan et al.*, 2006]. Still, a lack of corroborating evidence prevents assigning

477 LOA to any specific source with confidence.

478 Several other tracers are listed in Table 2. In particular, acetonitrile is a common tracer

479 for biomass burning emissions, and a lack of correlation with acetonitrile is initially observed (R

480 ≤ 0.1). In contrast, after filtering out the acetonitrile data with concentrations above 1.5 ppmv to

481 remove the possible influence of local solvent use, a moderately strong correlation is observed

482 with CIOA (R = 0.67) despite the relatively low acetonitrile concentrations that are near

483 background levels. This correlation may be due to barbequing with biomass fuels such as

484 charcoal. Indicators for marine influenced air masses used in this study are dimethyl sulfide

485 (DMS) and PALMS sea salt volume concentrations [*Malm et al.*, 1994; *Zorn et al.*, 2008], as

486 well as methanesulfonic acid (MSA) [*Gaston et al.*, 2010], which is measured by the PALMS as

487 a relative concentration [*Froyd et al.*, 2010]. However, the low correlations observed between

488   these indicators and all the PMF components provide little information about the role of marine

489   sources.

490   The concentrations for a variety of organic species were quantified by 2DTAG

491   measurements. The correlations between a selection of these species and the PMF components

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

494   strongest, which is not surprising given that these compounds are characteristic of primary

495   vehicle emissions [*Schauer et al.*, 1999a; 2002a; *Williams et al.*, 2010]. In addition, several

496   ketones and undecylbenzene exhibit a higher correlation with HOA than the other PMF

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

499   chrysene, a PAH, are clearly primary emissions, but show a similar level of correlation with both

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

502   the 2DTAG, which averaged samples over 85 minutes. Thus, periods of high HOA and SV-OOA

503   concentrations may appear to occur close to simultaneously on the time scale of the 2DTAG,

504   which unfortunately adds uncertainty to the comparison of the 2DTAG data against the PMF

505   components. This concern may also explain the apparent correlation of HOA with some

506   oxygenates. Considering only the compounds that have the highest correlation with SV-OOA,

507   this component tracks the concentrations of several phthalic acids and other compounds

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

510   [*Williams et al.*, 2010]. In contrast, the LV-OOA component exhibits weaker correlations with

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].

513   For CIOA, a weak correlation is observed with pentadecane. It should be noted that n-

514   alkanes have been identified in emissions from meat charbroiling [*Schauer et al.*, 1999b], but

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

517   sources. Using one-dimensional TAG Williams et al. [2010] observed in Riverside that several

518   alkanoic acids and alkylnitriles were the highest contributors to food cooking aerosols, although

519   it is recognized that some of these compounds can have secondary sources. For CalNex,

520   hexadecanoic acid correlates most strongly with SV-OOA rather than CIOA suggesting that

521   secondary sources of alkanoic acids are influencing the air mass above the ground site.

522   However, if the correlation analysis is limited to only periods with low SV-OOA concentrations

523   (less than the median) then CIOA does exhibit the strongest correlation with hexadecanoic acid.

524   The alkylnitriles correlate more strongly with other PMF components than CIOA, which

525   suggests that these compounds may not be good markers for cooking emissions in Pasadena

526   possibly because they are also associated with vehicle emissions [*Williams et al.*, 2010].

527   Cholesterol and oleic acid are known to be present in cooking emissions as well [*Schauer et al.*,

528   1999b; 2002b]. For cholesterol its size and alcohol functionality limits the sensitivity of 2DTAG.

529   Oleic acid can be measured by the 2DTAG, but in the field its mass spectrum is difficult to

530   distinguish from the background unresolved complex mixture.

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

534   similar in strength (e.g., Chrysene), which is likely due to the similar diurnal cycles of HOA and

535   SVOOA. Second, for CIOA a correlation with hexadecanoic acid is observed, but correlations

536   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.

Tracer	HOA	CIOA	LOA	SVOOA	LVOOA	
Campaign Avg. Conc. ($\mu g\ m^{-3}$)	0.82	1.21	0.34	2.43	2.26	
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_x	0.45	0.26	0.28	0.01	-0.07	Primary
Benzene	***0.71***	0.37	0.44	0.37	0.42	Primary
CO	***0.59***	0.43	0.41	0.49	0.41	Primary
Zn ($PM_{1.15}$)	***0.52***	-0.17	0.33	0.14	0.33	Primary
Acetonitrile[a]	0.47	***0.67***	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
n-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 ($PM_{1.15}$)	0.33	-0.08	***0.63***	0.05	0.11	Primary
NO_y	***0.63***	0.25	0.40	0.37	0.23	Primary + Secondary
O_x	0.28	0.10	0.04	***0.73***	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 Vol. Conc. (PM_1)	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	***0.70***	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	***0.86***	0.44	AMS
$C_6H_{10}O^+$	0.56	0.60	0.24	***0.71***	0.36	AMS

[a] 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
- 6/16. Only compounds with R > 0.5 are shown.

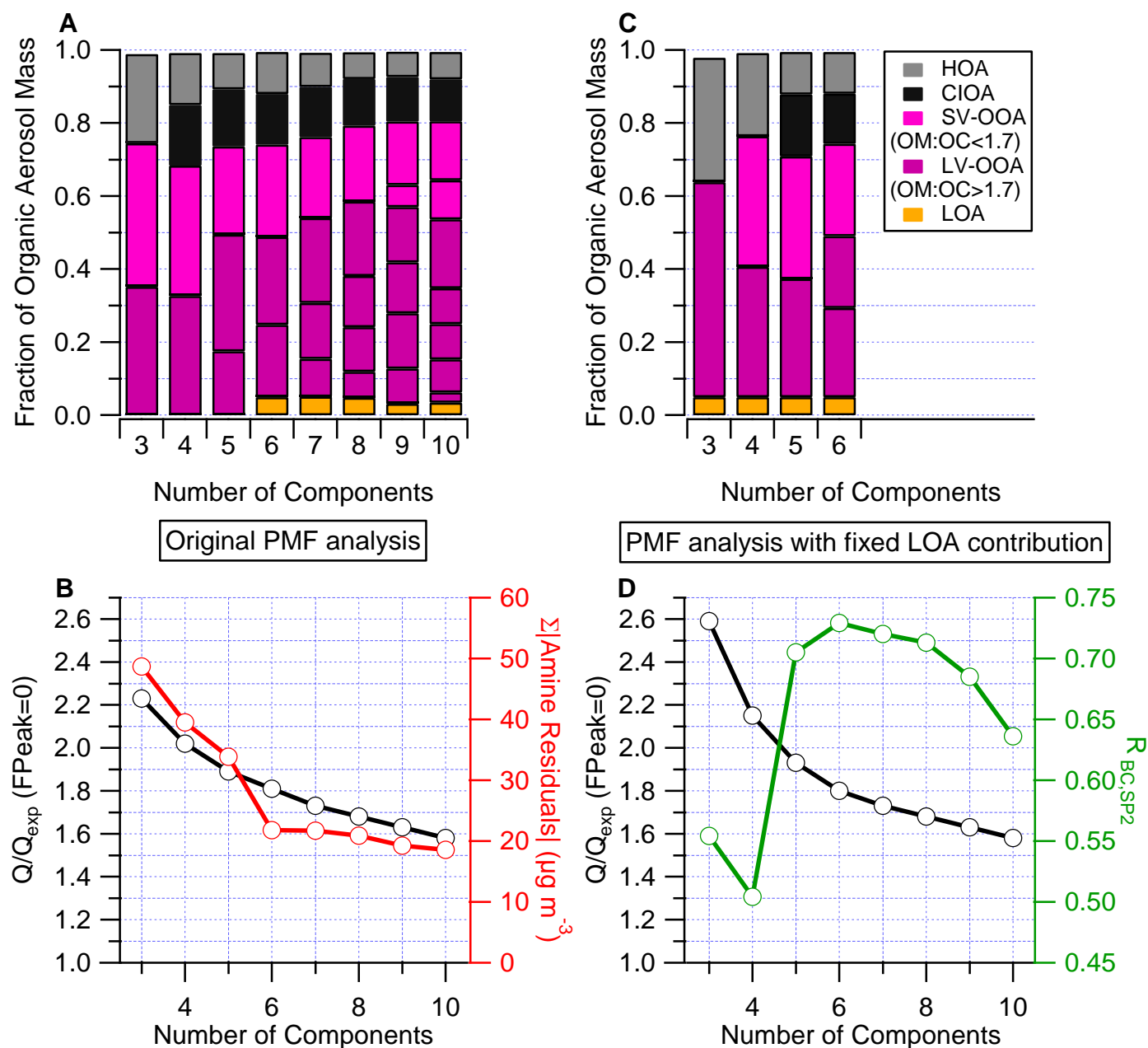| 2DTAG Compound	HOA	CIOA	LOA	SVOOA	LVOOA	
Phenanthrene	*0.60*	0.47	0.29	0.39	-0.01	H
1-Methylphenanthrene	*0.54*	0.48	0.22	0.46	0.03	Y
2-Methylphentanthrene	*0.56*	0.34	0.23	0.42	-0.10	D
1-Methylanthracene	*0.58*	0.41	0.26	0.46	-0.01	R
2-Methylanthracene	*0.54*	0.35	0.25	0.47	0.03	O
2-Phenylnaphthalene	*0.58*	0.28	0.36	0.48	0.14	C
Chrysene	0.58	0.27	0.24	*0.61*	0.21	A
Lowest-Volatility Hopane	*0.59*	0.38	0.41	0.49	0.15	R
Pentadecane	0.36	*0.52*	0.32	0.22	0.23	B
Octadecane	0.50	0.30	0.18	*0.51*	0.17	O
Phytane	*0.59*	0.29	0.31	0.45	0.15	N
Octacosane	0.46	0.05	0.08	*0.51*	0.10	S
Nonacosane	0.51	0.09	0.28	*0.71*	0.31	
Triacontane	0.52	0.05	0.22	*0.60*	0.25	
Hentriacontane	0.49	0.15	0.18	*0.61*	0.39	
Decylbenzene	0.54	0.34	0.27	*0.58*	0.20	
Undecylbenzene	*0.54*	0.36	0.25	0.48	0.11	
3-Methylphthalic Acid	0.51	0.03	0.12	*0.86*	0.20	O
4-Methylphthalic Acid	0.54	0.09	0.18	*0.81*	0.03	X
Dimethylphthalic Acids	0.53	0.03	0.13	*0.82*	0.13	Y
Chlorophthalic Acid	0.49	0.14	0.23	*0.74*	0.16	G
1H-Indene-1,3(2H)-dione	0.42	-0.05	0.06	*0.80*	0.24	E
delta-Decalactone	0.47	0.05	0.12	*0.72*	0.13	N
delta-Hexadecalactone	0.53	0.20	0.28	*0.76*	0.35	A
Pentadecanone	0.52	0.37	0.38	*0.54*	0.23	T
Hexadecanone	0.58	0.31	0.26	*0.64*	0.31	E
Heptadecanone	0.59	0.39	0.33	*0.64*	0.37	S
Octadecanone	*0.57*	0.21	0.31	0.54	0.07	
Nonadecanone	*0.50*	0.19	0.39	0.49	0.14	
Trimethylpentadecanone	*0.62*	0.22	0.39	0.59	0.36	
Fluorenone	0.47	0.21	0.10	*0.57*	0.24	
Hydroxyfluorenone	*0.54*	0.47	0.30	0.53	0.34	
Naphthalic Anhydride	0.49	0.11	0.17	*0.67*	0.17	
Benzophenone	0.66	0.37	0.36	*0.67*	0.43	
Benzyl Benzoate	0.68	0.35	0.38	*0.73*	0.30	
Isopropyl Myristate	*0.67*	0.00	0.62	0.45	0.15	
Dibenzofuran	*0.64*	0.39	0.32	0.47	0.05	
Hexadecanoic Acid (SV-OOA<2.4 µg/m3)	0.51	*0.66*	0.55	0.35	0.43	
Tetradecanenitrile	0.55	0.23	0.48	*0.59*	0.36	Nitrogen-
Hexadecanenitrile	0.46	0.34	0.28	*0.59*	0.47	Containing
Octadecanenitrile	0.44	0.35	0.28	*0.62*	0.48	
Phthalimide	0.56	0.23	0.22	*0.78*	0.36	
Homophthalimide	0.50	-0.01	0.13	*0.84*	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.
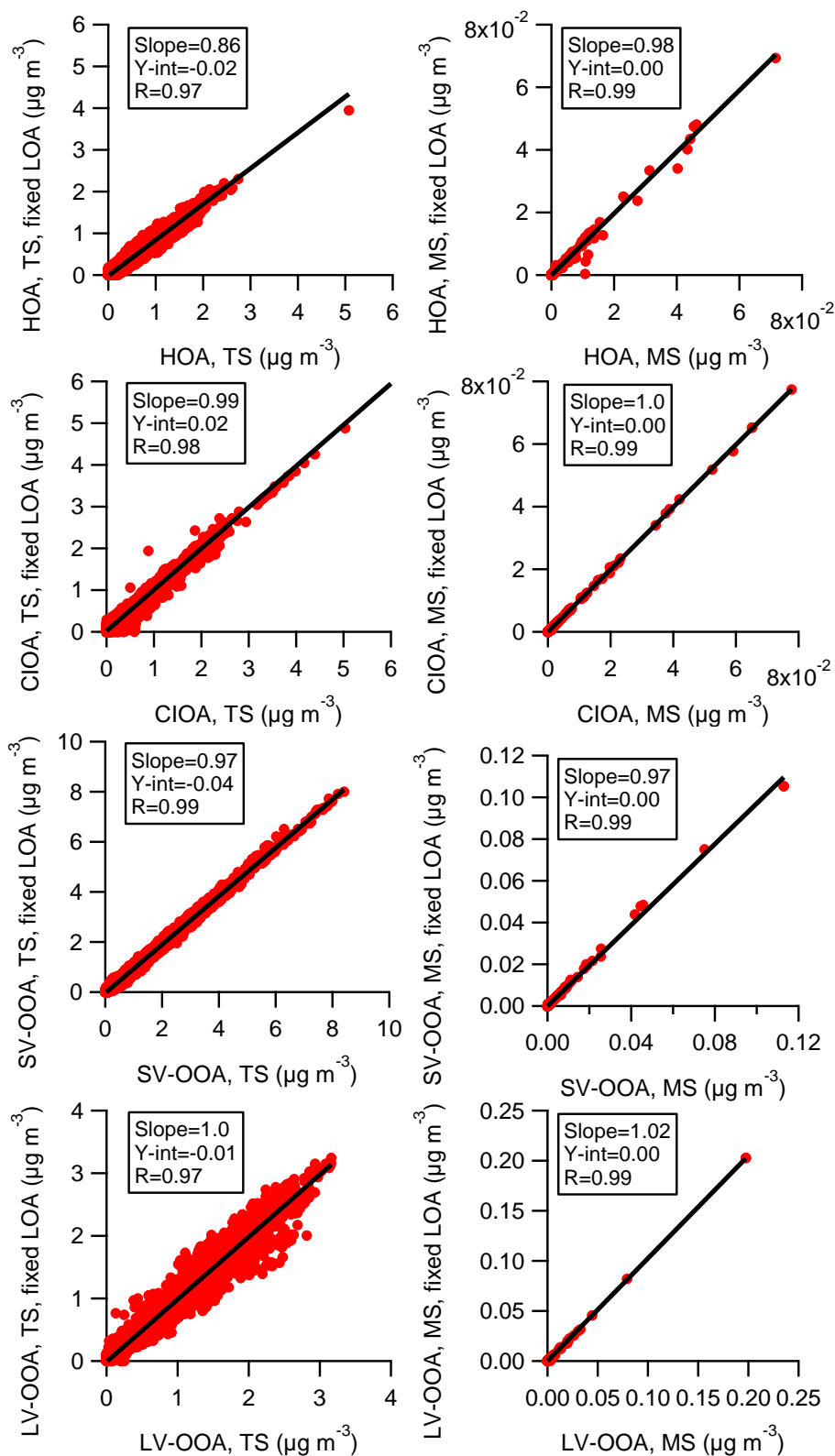
Figure D-3: Scatter plots of each component for the 4-component PMF solution and the 5-component PMF solution with a fixed LOA contribution. The left column contains plots for the time series and the right column contains plots for the mass spectra.
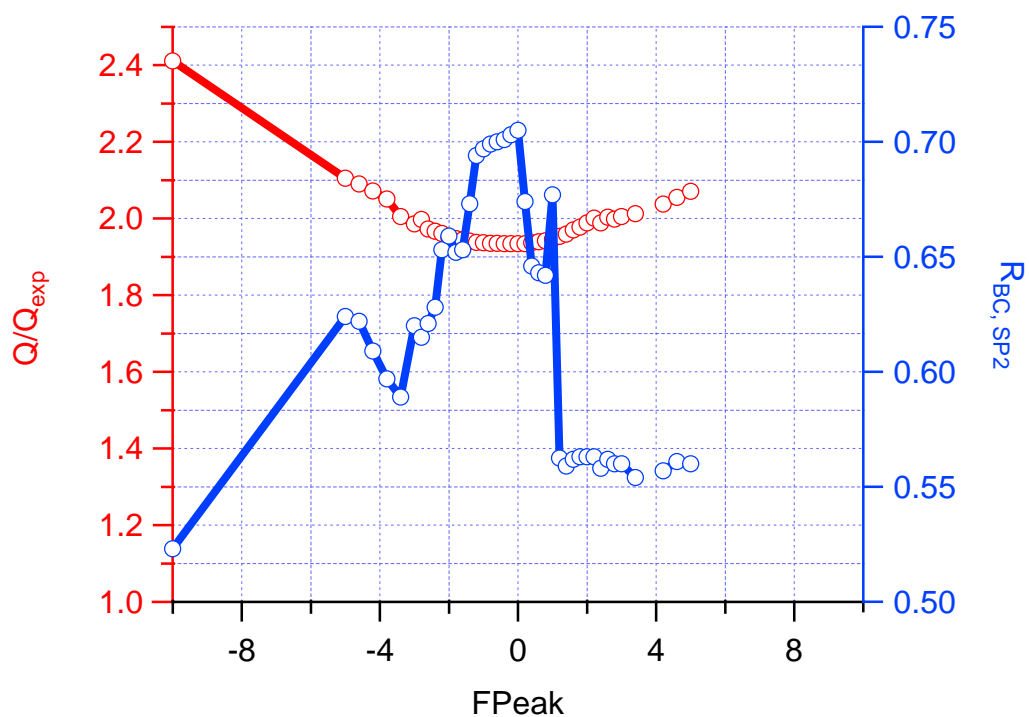
Figure D-4: (Left Axis) Q/Q_{exp} for the selected 5-component solution with the fixed LOA contribution plotted as a function of FPeak. **(Right Axis)** Correlation between HOA and rBC from the SP2 as a function of FPeak for the selected 5-component solution.

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 25th and 75th percentiles, and the whiskers represent the 5th and 95th percentiles. **(B)** Time series of the residual organic mass (= measured mass − reconstructed mass from PMF). **(C)** Time series of Q/Q_{exp} (i.e., the residual squared divided by the predicted error squared, which is then normalized to Q_{exp}).
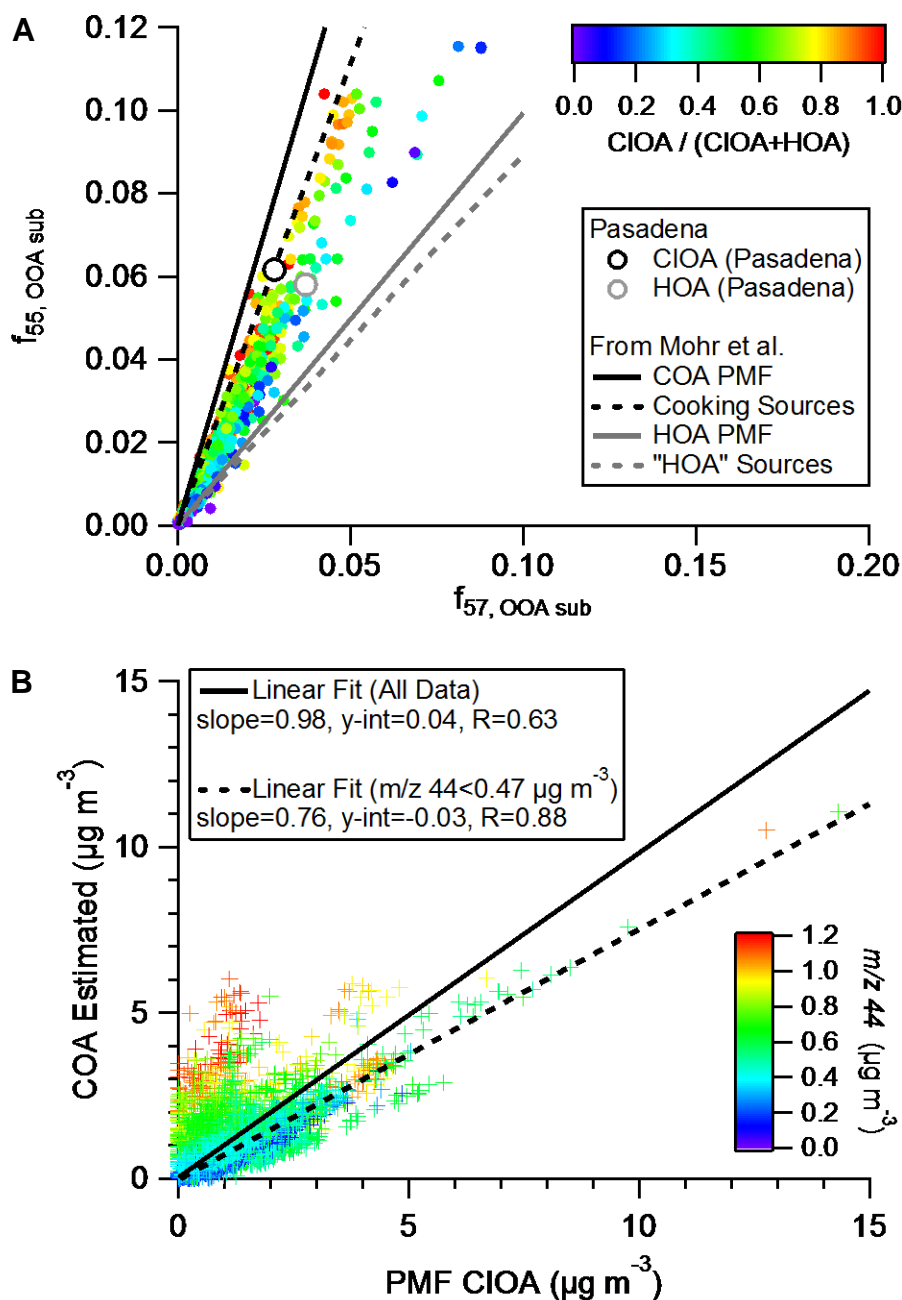
Figure D-6: **(A)** Scatter plot of $f_{55,\,OOA\,sub}$ versus $f_{57,\,OOA\,sub}$ colored by the relative amount of CIOA (markers). Also shown is f_{55} versus f_{57} for CIOA (black circle) and HOA (gray circle). The lines represent linear fits of f_{55} versus f_{57} data from previously reported 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 μg m^{-3} (dashed line).
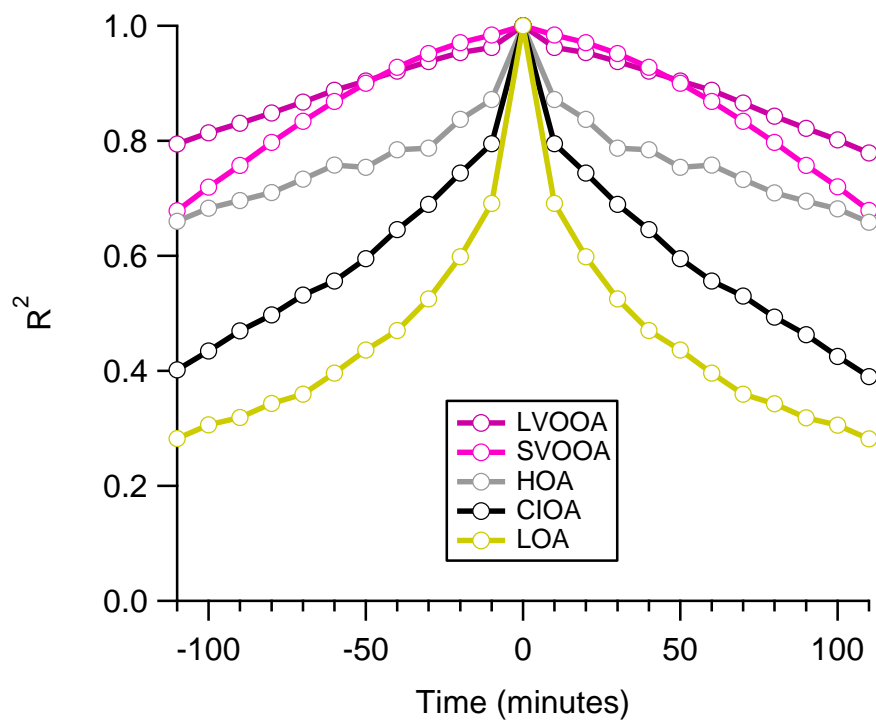
Figure D-7: Auto-correlations for the PMF component time series over +/-110 minutes.
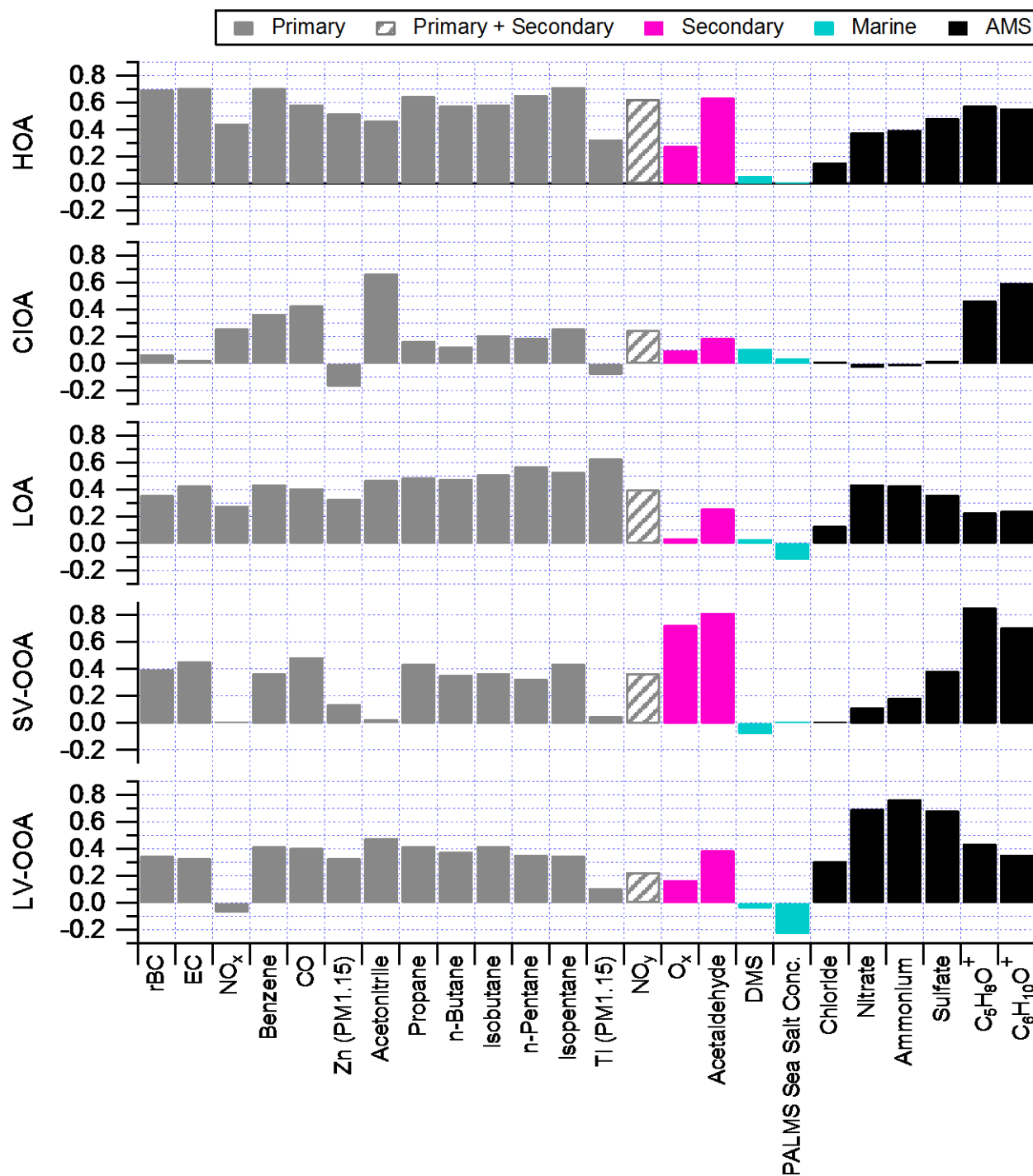
Figure D-8: Bar graph summarizing the correlations of the PMF factors with key tracer species. The correlations are taken from Table D-1. The bars are colored by the tracer classification. Note: Acetonitrile correlations correspond to only acetonitrile concentrations below 1.5 ppbv to eliminate potential contributions from nearby solvent use.

Section E: Evaluation of Photochemical Age Error

556

557   Photochemical age is a quantity developed as a metric for parcels of air arriving at remote

558   receptors sites, and it is derived by assuming that the parcel is decoupled from fresh emissions as

559   it is transported [*Kleinman et al.*, 2007; *Parrish et al.*, 2007]. However, the Pasadena ground site

560   is not a remote receptor site, and it is impacted by pollutants that have been emitted recently as

561   well as transported from more distant locations. The goal of this section is to evaluate the

562   potential errors that result from calculating the photochemical age for an air parcel that is

563   receiving continued additions of pollutants as it is transported to the measurement location.

564   A simple model was built that calculates the observed photochemical age based on a

565   given distribution of ages within an air parcel. For the dense urban region of Los Angeles it has

566   been assumed that emissions are constant as an air mass is advected from the coastline to the

567   Pasadena site [*Washenfelder et al.*, 2011]. Under this assumption the weights of the ages in the

568   distribution will be equal, and the distribution will range from zero to two times the chosen

569   photochemical age. Thus, the model has only one input parameter: photochemical age. It is

570   emphasized that in this analysis the flat distribution of ages assumed will not account for dilution

571   due to increasing boundary layer height, or diurnal cycles in emission rates and oxidant

572   concentrations. While different compounds could be used in the model, we specifically focus on

573   the case of photochemical age calculated from the ratio of 1,2,4-trimethylbenzene (1,2,4-TMB)

574   to benzene and utilize the emission ratios and OH reaction rates from Parrish et al. [2007]. The

575   model calculation involves: (1) calculating the concentrations of benzene and 1,2,4-TMB for

576   each age, (2) calculating the total contribution to benzene and 1,2,4-TMB concentrations from all

577   the age steps in the assumed age distribution, and (3) calculating the observed photochemical age

578   based on the VOC concentrations.

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

582   where $(Age)_{derived}$ is the photochemical age that would be derived from the observed VOC ratios,

583   and $(Age)_{input}$ is the age originally entered into the model. The error increases in magnitude with

584   photochemical age, and the age derived from the observed VOC ratios is systematically lower

585   than the actual average age. This trend can be explained by considering a hypothetical system

586   composed of a fresh and an aged air parcel of equal volumes. If each parcel started with the same

587   concentrations of emissions including benzene and 1,2,4-TMB, then when the two parcels are

588   mixed together the age of the mixed air should be simply the average of the ages of each

589   individual parcel. However, since both benzene and 1,2,4-TMB are depleted in the aged air

590   parcel due to chemical processing, in the photochemical age calculation the aged parcel has less

591   mathematical weight than the fresh parcel. This unequal weighting explains why observations, as

592   modeled here, will be systemically lower than the true average age of the mixed parcel.

593   The results reported here follow those previously published in Parrish et al. [2007], which

594   concludes that VOC ratios are a useful metric for determining photochemical ages even if mixing

595   of different air masses occurs. Based on the analysis presented here we estimate an error of

596   approximately 10%, corresponding to the mean photochemical age, which biases the observed

597   ages towards lower values. While this is a significant source of uncertainty, it should only impact

598   the accuracy of the observed photochemical ages and not relative comparisons for Pasadena (e.g.

599   weekday vs. Sunday), insofar as the distribution of ages is consistent. This requirement is likely

600   satisfied given the day-to-day similarity in meteorology and diurnal cycles at the ground site.
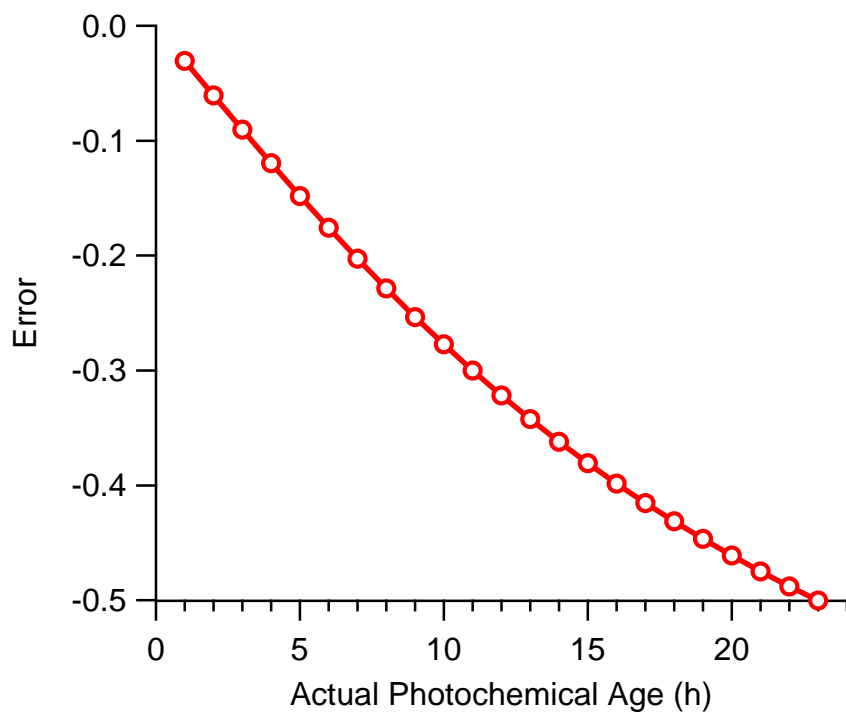
Figure E-1: The error in the photochemical age derived from the observed VOC ratios as a function of the actual photochemical age. The observed VOC ratios are simulated using the model described in Section E. The actual photochemical age is the mean of the different ages in the age distribution.
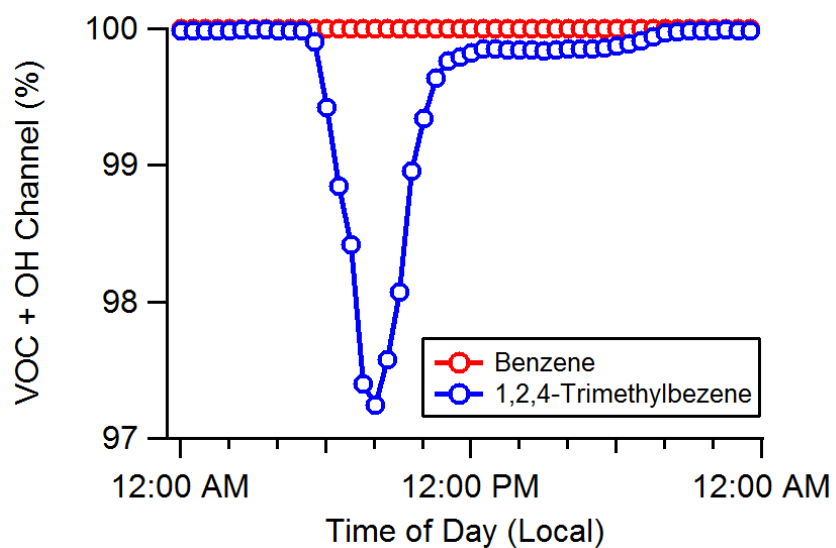
Figure E-2: Branching ratio between OH and Cl oxidation for benzene and 1,2,4-trimethylbenzene. The ratio was calculated using the relative OH to Cl concentrations as well as the corresponding rate constants from Young et al. [2013]. For both VOCs the oxidation chemistry is dominated by OH radicals, which is consistent with the method used to estimate photochemical age.
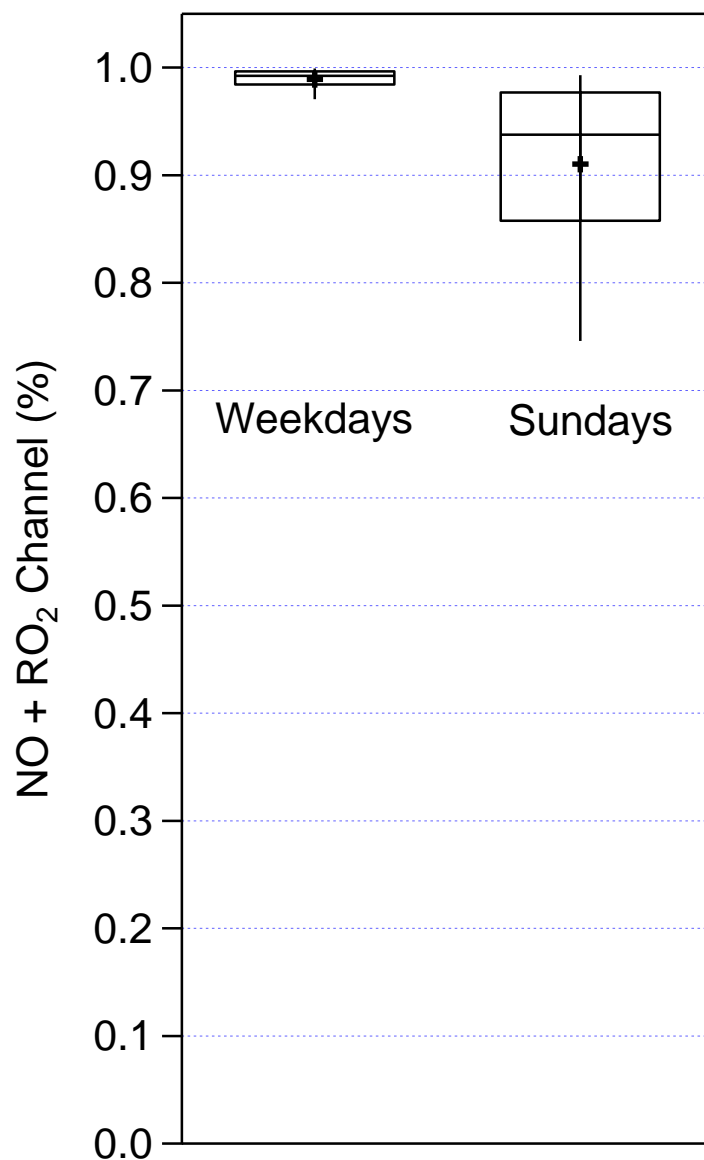
Section F: NO$_x$ Branching Ratios: Box-and-Whiskers Plot

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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