Oxidation of ketone groups in transported biomass burning aerosol from the 2008 Northern California Lightning Series fires

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1. Introduction

Globally the two largest sources of primary organic aerosol (POA) are fossil fuel combustion (2–28 Tg C yr⁻¹) and biomass burning (31–45 Tg C yr⁻¹) (Bond et al., 2004). Model estimates of secondary organic aerosol (SOA) range from 11.2 Tg yr⁻¹ (Chung and Seinfeld, 2002) to 79 Tg yr⁻¹ (Kanakidou et al., 2000), making SOA from fossil fuel combustion, biogenic, and biomass burning emissions a potentially important contributor to total organic mass (OM). The strengths of these sources are temporally and spatially inhomogeneous such that global organic carbon emissions cannot be attributed solely to one source, yet quantifying and characterizing organic aerosol components are essential for improving our understanding of aerosol–climate interactions, since the organic fraction of atmospheric particles is often greater than 50% (Zhang et al., 2007). However, Bond et al. (2004) estimate that 90% of combustion-related primary carbon emissions are from biofuel and biomass burning. Secondary biomass burning emissions cannot be neglected either (Gelencsér et al., 2007; Grieshop et al., 2009). Chamber studies have shown a doubling of biomass burning OM over only a few hours accompanied by chemical changes consistent with photochemical oxidation (Grieshop et al., 2009), indicating that the primary components of biomass burning aerosol represent only a portion of the potential particulate mass. This is especially noteworthy given that biomass burning emissions include both light-absorbing (elemental and organic carbon) and water soluble components and that biomass burning emissions are thought to be the single largest source of brown carbon, a poorly understood component of organic aerosols (Kirchstetter et al., 2004; Pósfai et al., 2004; Lukács et al., 2007; Gustafsson et al., 2009).

Previous characterization of biomass burning aerosol has focused on identifying tracer compounds in either the gas or particle phase (e.g. methylhalides, K, levoglucosan, and acetone).
Efforts to quantitatively characterize the remaining 90–95% of smoke-related aerosol particles are fettered by the diversity and complexity of organic molecules generated by the combustion process (Jacobson et al., 2000; Kanakidou et al., 2005). This complexity makes a complete, molecular-based characterization of biomass burning aerosol extremely difficult. As an alternative, solvent extraction techniques, including quantifying water soluble organic carbon (WSOC) fraction, have been used to estimate the contribution of multi-functional or oxygenated compounds to total OM (Mayol-Bracero et al., 2002; Saarikoski et al., 2007). However, in some cases, as much as 90% of the biomass burning WSOC is uncharacterizable (Graham et al., 2002; Fang et al., 1999) found that the solvent-extractable fraction of OM collected during Malaysian forest fires was dominated by n-alkanes, alkanolic acids, and polycyclic aromatic hydrocarbons (PAHs). Oros and Simoneit (2001) used dichloromethane filter extraction and derivatization coupled with GC–MS to analyze conifer smoke particles finding that straight-chain aliphatic compounds and diterpenoid acids composed over 60% of the solvent-extractable OM. While these measurements identify the presence of biomass burning aerosol, improve source attribution in regions with multiple organic aerosol sources, and provide some insight into the chemical composition of smoke particles, they are insufficient to provide a chemical characterization of the remaining aerosol mass.

Fourier transform infrared (FTIR) spectroscopy of ambient organic aerosol has been shown to quantify close to 100% of organic mass using the sum of measured organic functional groups and by calibrating the absorptivity of common organic bonds (Maria et al., 2002, 2003; Gilardoni et al., 2007; Russell et al., 2009b). In addition to providing quantitative OM concentration — without extraction or derivatization — and regardless of the number and diversity of compounds present, FTIR spectroscopy provides functional characterization of the aerosol including saturated and unsaturated aliphatic groups, carboxylic acid groups, organic hydroxyl groups, primary amine groups, and non-acid carbonyl groups (aldehydes and ketones). Non-acid carbonyl groups are particularly relevant for biomass burning and biogenic aerosol since they are characteristic of secondary organic aerosol (SOA) formed from the oxidation of biogenic volatile organic compounds (BVOCs) (Hatakeyama et al., 1991; Hakola et al., 1994; Calogirou et al., 1999; Capouet et al., 2004). Similarly, aerosol mass spectrometry (AMS) of organic aerosol can be used to estimate the non-refractory organic mass (nr-OM) and the contribution of individual mass fragments to nr-OM. The ratios of specific m/z fragments can be used to infer chemical properties, sources, and processes associated with organic aerosol (i.e. oxygenated vs. hydrocarbon-like fragments) (Jayne et al., 2000; Jimenez et al., 2003; Zhang et al., 2005a; Lanz et al., 2007).

Photochemical aging of biomass burning particles results in important chemical changes that reduce the number of chemical signatures available to identify aerosol sources, reducing the effectiveness of using organic tracer compounds to estimate the contribution of specific aerosol types to OM. Chamber studies have shown that at 1-amu resolution, the longer biomass burning particles are photochemically oxidized, the more similar the organic mass spectrum is to oxidized organic aerosol (OOA) from fossil fuels (Grieshop et al., 2009). This trend has been observed in ambient biomass burning aerosol over West Africa (Capes et al., 2008) where measurements in the smoke plume show increasing m/z 44 (CO2) and decreasing m/z 60 and 73 in aging smoke particles. Measurements of biomass burning in the Amazon rainforest indicate that detectable compositional changes can occur even on a diurnal time scale (Hoffer et al., 2006). These chemical changes can alter the direct and indirect effects of biomass burning particles by changing their size, shape, single scattering albedo, and hygroscopicity (Gelencsér et al., 2007; Capes et al., 2008) but are not captured without chemical characterization of a substantial portion of the particle mass.

In this study, we combine measurements from two organic characterization techniques for submicron particles collected at a coastal site (1) to separate contributions from forest fire and fossil fuel combustion to submicron organic mass by two independent methods (FTIR spectroscopy and AMS), (2) to characterize the chemical differences among these types of organic particles and the background (polluted marine) aerosol, and (3) to illustrate diurnal and multi-day changes in the forest fire particles that result from photochemical aging of a smoke plume.

2. Methods

2.1. Sample collection

Submicron particles were collected from 27 June to 17 September 2008 in La Jolla, California, as part of the Aerosol Scripps Coastal Observatory Pier Experiment (AeroSCOPE), which was designed to characterize and quantify sources of particles that contribute to aerosol in this coastal region. Day (0700–1900) and night (1900–0700) samples were collected through an inlet approximately 14 m above sea level (masl) on 37 mm Teflon filters ( Pall Corp., Ann Arbor, MI) located downstream of a 1-μm sharp-cut cyclone (SCE 2.229 PM1, BGI Inc., Waltham, MA) in an air conditioned housing located on the Scripps Pier. A flowrate of approximately 8.35 LPM was maintained through each filter set using one flow meter and one flow controller (Alicat Scientific, Tucson, AZ). A quadrupole aerosol mass spectrometer (Q-AMS, Aerodyne Research Inc., Billerica, MA) was also located downstream of the sharp-cut cyclone to quantify non-refractory sulfate, nitrate, ammonium, and organic mass at 1-amu resolution following standard calibration procedures (Jayne et al., 2000; Jimenez et al., 2003).

2.2. FTIR and XRF analyses

Filters for Fourier transform infrared (FTIR) spectroscopy and X-ray fluorescence (XRF) were transported back to the laboratory in air-tight bags and kept at 0 °C prior to FTIR spectroscopic analysis to
reduce evaporative losses of organic compounds. Duplicate back filters accompanied each sample filter for the entirety of the sampling and transportation process and were analyzed to quantify the adsorption of volatile compounds and other contamination. These back filters showed negligible infrared absorption.

FTIR absorbance spectra of each sample and back filter were obtained non-destructively using a Bruker Tensor 27 spectrometer with RT-DLATGS detector (Bruker, Billerica, MA) and were interpreted using calibration standards and a revised algorithm based on the linear response of absorption peak area to the number of moles of organic bond present on the Teflon filters (Maria et al., 2002, 2003; Gilardoni et al., 2007; Russell et al., 2009b). Quantified functional groups include saturated aliphatic C–CH (alkane), unsaturated aliphatic C=CH (alkene), aromatic C=CH, non-acid organic hydroxyl C–OH (alcohol, including phenol), primary amine C–NH2, non-acid carbonyl C=O (aldehyde and ketone), and carboxylic acid COOH. The C–O absorption peak near 1700 cm\(^{-1}\) can be attributed to aldehyde, ketone, and carboxylic carbonyl groups; however, stretching of the aldehydic hydrogen produces a pair of weak absorption bands between 2700 cm\(^{-1}\) and 2860 cm\(^{-1}\) that were not present in the spectra from ambient particles. Therefore all carbonyl absorption has been attributed to either carbonylic acid or ketone groups, depending on the estimated concentration of carbonylic COH groups. Aromatic C=C–H and alkene C=C–H groups were below detection limit in all samples and are omitted from the discussion. Organosulfate COSO\(_3^-\) groups absorb at 876 cm\(^{-1}\) in addition to carbonate and bisulfate; however, this peak was not above the organosulfate group detection limit in any sample and is omitted from this analysis.

Following FTIR spectroscopic analysis, a subset of filters were sent to Chester Labnet (Tigard, Oregon) for X-ray fluorescence (XRF) providing concentrations of Na and heavier elements (Maria et al., 2003; Gilardoni et al., 2007; Russell et al., 2009b). Elements present above detection limit in more than 25% of the analyzed subset include Na, Si, S, K, Ca, Ti, V, Fe, Ni, Zn, Se, and Br.

2.3. Aerosol mass spectrometry

The Q-AMS has been described in detail elsewhere (Jayne et al., 2000; Jimenez et al., 2003; Canagaratna et al., 2007). An aerodynamic lens focusses submicron particles into a narrow beam that either passes without interference from a spinning slotted wheel (in mass spectrum mode) or is aligned with the slotted spinning wheel to allow bursts of particles into the time-of-flight sizing chamber (in time-of-flight mode). In either mode, particles are then impacted onto a porous tungsten surface (600 °C), where the non-refractory components are vaporized and passed into the quadrupole mass spectrometer. Alternating between these modes every 30 s and taking a running average every 5 min provides high time resolution measurements of particle average mass spectra and average aerodynamic size distributions of the selected fragments. Particle losses resulting in a collection efficiency (CE) less than 1 can occur during transmission into the instrument, during beam focussing, and during impaction onto the heated filament. Laboratory experiments and ambient aerosol measurements indicate that particle phase is a significant factor controlling whether particles stick to the heated filament (and are collected) or bounce off the filament (and are missed) (Quinn et al., 2006; Matthew et al., 2008). For example, dry ammonium sulfate particles have a CE of 0.2 based on laboratory studies (Alfarra et al., 2004) though ambient ammonium sulfate CE is usually greater than 0.5 (Quinn et al., 2006; Bates et al., 2005, 2008).

The Q-AMS measurements were processed using Igor Pro software (Wavemetrics Inc.) and an algorithm designed for interpreting the measured signals (Allan et al., 2004). We have applied corrections to the measured AMS concentrations following Quinn et al. (2006) and assuming that the measured particles are internal mixtures of non-refractory components; for most measurements, the ammonium to sulfate ratio was equal to that of ammonium sulfate requiring the maximum correction (a factor of 2.2). The corrected AMS S from sulfate and filter XRF S measurements show mild agreement (\(r = 0.6\)), and the least-squares fit line has a slope of 1.16, which is within the 20% uncertainty associated with each method and indicates that non-sulfate S makes up only a small fraction of the total S, if present at all. For shorter periods, the correlation between AMS and XRF sulfur exceeds 0.8, suggesting that the mild correlation coefficient is likely caused by the intermittent contributions of non-sulfate S.

3. Results and discussion

3.1. Organic, inorganic, and elemental aerosol components

Panels in Fig. 1 show non-refractory submicron particle components from AMS, organic functional groups from FTIR, and potassium (K) and bromine (Br) from a subset of filters analyzed by XRF. From these measurements, two chemically distinct aerosol regimes are observable, suggesting that the Scripps Pier air masses were subject to two significantly different aerosol sources during summer 2008. From 27 June to 29 July, OM was the largest non-refractory component of the submicron aerosol (Fig. 1a) and ketone groups were above detection limit in nearly all samples (Fig. 1b). K and Br were elevated above 20 ng m\(^{-3}\) and 4 ng m\(^{-3}\) (Fig. 1c), respectively, consistent with forest fire emissions (Andreae, 1983; Andreae et al., 1996). This composition is very different from the composition observed during the period from 30 July to 9 September when SO\(_4^{2-}\) was the largest non-refractory component of the submicron aerosol and ketene groups were below detection limit in nearly all samples. During this time Br remained below 4 ng m\(^{-3}\) and K was below 20 ng m\(^{-3}\) with one exception. After 9 September, similar relative concentrations of organic and sulfate components to the first period were observed, with smaller contributions from ketene groups and lower K and Br concentrations.

3.2. Identified particle sources

HYSLIP back trajectories (Rolph, 2003) show most air masses arrived at the sampling location from the north having traveled south along the California coast, though occasionally sampled air masses arrived from central California, from northern Mexico, or from directly west of the Scripps Pier. Recent work has shown that the ports of Los Angeles and Long Beach are a major pollution source for the aerosol at the Scripps Pier, and air masses passing over the Long Beach region contain particles that include carbon, sulfate, vanadium and nickel originating from diesel trucks and large ships in port (Ault et al., 2009). However, shortly before sampling commenced (21 June 2008), approximately 2000 fires were ignited by lightning during a dry low-pressure system in northern California. By mid July, the Northern California Lightning Series fires burned over 3000 km\(^2\), severely impacting air quality in the Central Valley, the San Francisco Bay Area, Big Sur, and Santa Barbara county (visible in NASA Terra and Aqua MODIS images, http://www.nasa.gov/topics/earth/features/fire_and_smoke.html). By August 2008 most of the large fires were contained, the low-pressure system passed, and smoke-related air pollution in northern and central California subsided. Because of these extremely large, persistent wildfires, the largest organic aerosol source to the Scripps Pier during this study was forest fire emissions, though particles consistent with diesel and oil combustion
were also observed and dominated the submicron aerosol during non-fire periods.

On the basis of observed compositional patterns and the timing of the Northern California Lightning Series fires, we have designated 27 June–29 July as “fire period 1” (FP1), 30 July–9 September as the “non-fire period” (NFP), and 10 September–17 September as “fire period 2” (FP2). For some portions of the discussion we have combined FP1 and FP2 as the “fire periods,” recognizing that multiple types of particles were observed during all periods and that FP2 has a larger contribution from fossil fuel combustion sources than does FP1. Table 1 lists the average concentrations of each component for the entire campaign, for the two fire periods together, and for the non-fire period. Comparing the fire and non-fire periods, the former has a higher average OM (4.3 μg m⁻³ vs. 2.8 μg m⁻³) and a better agreement between the AMS and FTIR OM estimates. Fire periods also have lower sulfate (1.8 μg m⁻³ vs. 3.0 μg m⁻³) and a significantly higher ketone group concentration (0.67 μg m⁻³ vs. 0.032 μg m⁻³). K and Br are significantly higher during fire periods while S, V, and Ni are slightly lower.

For all measurements, FTIR OM shows mild agreement with the corrected AMS OM (Fig. 2, \( r = 0.62 \), slope = 1.1) although qualitative differences exist in the correlation during the three designated periods. FP1 has the lowest FTIR/AMS OM ratio (0.90) and a mild correlation (\( r = 0.55 \)) while FP2 has the highest FTIR/AMS OM ratio (1.5) and the strongest correlation (\( r = 0.62 \)). The NFP has the weakest correlation (\( r = 0.37 \)) and an average FTIR/AMS OM ratio of
1.3. These comparisons may result from chemical differences in the particle composition measured during all three periods and from applying a collection efficiency correction to all values assuming complete internal mixtures of organic mass and ammonium sulfate in all particles.

3.3. Positive matrix factorization of AMS and FTIR organic spectra

To quantitatively resolve the major factors that contribute to the measured mixtures of FTIR functional groups and AMS mass fragments, positive matrix factorization (PMF) was used to identify 3 factors for each data set separately and the resulting independently-derived factors were compared (Paatero and Tapper, 1994). For PMF of baseline FTIR spectra, only portions of the sample spectra with quantified peaks were included. The standard error of the absorbance for each wavenumber from all back filters was set as the measurement uncertainty. This error does not scale with absorption strength in the sample spectra. Using a signal-scaled error for PMF analysis resulted in solutions with little resemblance to ambient spectra that did not reproduce the measured OM. For low absorbance FTIR spectra, the standard error of the back filter absorbance – which includes substrate absorption, gas adsorption, and handling artifacts – is a more appropriate and accurate estimate of measurement error. Results for 2, 3, 4, 5, and 6 factor solutions were explored and although the Q-value (a normalized chi-square metric) was lowest for the 6-factor solution, factors in the 5 and 6-factor solutions were correlated to one another; to avoid this type of splitting, the 4-factor solution was identified as optimal, reproducing 107% of the measured OM and organic functional groups. The 3-factor solution over-estimated the measured OM by more than 10%, which was an unsatisfactory representation of the measured concentrations and variability. The 4-factor solution was subsequently reduced to 3 factors by combining the two smallest factors (each of which show no correlations to XRF elements) into a single minor background factor. Total OM from the summed 3-factor solution compared well with the measured FTIR OM (slope = 1.09, r = 0.96), demonstrating that three selected factors are sufficient to represent most of the features in the spectra. FPEAK (rotation) values from −0.4 to 0.4 were tested with the 4-factor solution but no significant difference in either Q-value or factor spectra was found among the rotations; FPEAK = 0 is presented here as a representative example. To test the robustness of the solution, the initialization seed was varied over 10 values; factor spectra showed only minute changes among the initializations seeds. Comparisons of factor strengths for the different seed values correlated with r = 0.99 or better and slopes of 0.99, showing that the solutions present here are robust.

Fig. 3 shows the FTIR spectra and the functional group composition of each of the three FTIR PMF factors. Table 2 summarizes the properties of each factor. Factor 1 consists of alkane (48%), ketone (25%), carboxylic acid (17%), primary amine (8%), and organic hydroxyl groups (2%) and correlates strongly with Br (r = 0.79) and mildly with K (r = 0.68). Factor 2 comprises alkane (86%), carboxylic acid (9%), organic hydroxyl (3%), and primary amine groups (2%) and correlates strongly to S (r = 0.82) and weakly to V (r = 0.46).
Factor 3 consists of organic hydroxyl (45%), alkane (35%), carboxylic acid (14%), and primary amine groups (6%) and does not correlate to any elemental markers measured by XRF. Panel (d) in Fig. 1 shows the time-dependence of the three factors as fractions of FTIR OM. Factor 1 is present mainly during FP1 and FP2 and is largely absent during the NFP. This trend, in addition the positive correlations with K and Br and the presence of significant ketone groups, suggests that Factor 1 is associated with biomass burning from forest fires (BBFTIR).

The spectrum for this factor in Fig. 3 shows two sharp peaks in the alkane absorption region at 2920 cm⁻¹ and 2850 cm⁻¹, consistent with sp³ C–H stretching absorption from methylene groups (−CH₂−) (Pavia et al., 2008). The sharpness of these peaks is due to a large number of repeating methylene units and may be derived from vegetative detritus (e.g. plant cuticle waxes), which is commonly observed as part of biomass burning emissions (Simoneit, 1985; Fang et al., 1999; Simoneit et al., 2004; Medeiros et al., 2006). Factor 2 makes up a significant portion of the OM during NFP, has consistent tracer correlations with diesel and residual oil combustion, and has a strong ammonium absorption signal suggesting it is associated with fossil fuel combustion (FFCFTIR, Fig. 3). Factor 3 shows no correlations to specific elements and is likely a combination of processed emissions and marine sources. The high organic hydroxyl fraction is consistent with previous measurements of marine organic aerosol in the southeastern Pacific (Hawkins et al., 2010), Arctic, and North Atlantic (Russell et al., 2010) oceans. In samples with little influence from FFCFTIR, m/z 79 fraction of AMS OM (a fragment associated with MSA in Phinney et al., 2006; Zorn et al., 2008) is strongly correlated to organic hydroxyl fraction of OM (r = 0.95 for samples with less than 20% FFCFTIR), supporting some influence of marine emissions on the composition of Factor 3. However, the small fractional contribution of this factor to the measurements during the project means that the marine emissions are likely not fully resolved from other pollution sources. Consequently, this factor is labeled “polluted marine.”

Table 2
Organic functional group composition, elemental correlations, and reference spectra correlations of PMF factors.

<table>
<thead>
<tr>
<th>FTIR factors</th>
<th>Biomass Burning</th>
<th>Fossil Fuel Combustion</th>
<th>Polluted Marine</th>
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<tr>
<td>FTIR Organic Functional Groups</td>
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<td></td>
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</tr>
<tr>
<td>Alkane</td>
<td>48%</td>
<td>86%</td>
<td>45%</td>
</tr>
<tr>
<td>Carboxylic acid</td>
<td>17%</td>
<td>9%</td>
<td>14%</td>
</tr>
<tr>
<td>Primary amine</td>
<td>8%</td>
<td>2%</td>
<td>6%</td>
</tr>
<tr>
<td>Organic hydroxyl</td>
<td>2%</td>
<td>3%</td>
<td>45%</td>
</tr>
<tr>
<td>Ketone</td>
<td>25%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Elemental Correlations (r, r &gt; 0.4 only)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>0.79</td>
<td></td>
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</tr>
<tr>
<td>S</td>
<td></td>
<td>0.82</td>
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<tr>
<td>V</td>
<td></td>
<td>0.46</td>
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Reference Spectra Correlations (r)

| All m/z | | |
| fir smoldering⁴ (0.99) | brush fire⁵ (0.95) | oak smoldering⁴ (0.89) |
| beech smoldering⁴ (0.99) | methylenecyclohexane SOA⁵ (0.94) | aged rural (high CO)⁶ (0.87) |
| OOA-etur (0.94) | cyclopentene SOA⁵ (0.94) | fir smoldering⁴ (0.87) |
| oxalic acid (0.90) | larch flaming⁶ (0.94) | beech smoldering⁴ (0.87) |
| m/z > 45 | urban Vancouver (high O₃)⁷ (0.98) | San Joaquin Valley⁸ (0.88) |
| terpinolene SOA (Q_018) (0.96) | OOA (0.96) | aged rural (high CO)⁶ (0.88) |
| myrcene SOA (0.95) | OOA (0.94) | above bovine⁸ (0.88) |
| OOA-etur (0.95) | terpinolene SOA (Q_025) (0.94) | downwind bovine⁸ (0.88) |
| terpinolene SOA (Q_025) (0.94) | aged rural (high CO)⁶ (0.88) | β-pinene SOA⁵ (0.87) |
| Elemental Correlations (r, r > 0.4 only) | | |
| K | 0.57 | 0.49 | 0.57 |
| Br | 0.9 | 0.49 | 0.46 |
| AMS sulfate (r) | | 0.64 | |

⁴ Weimer et al. (2008).
⁵ Lanz et al. (2007).
⁶ Takegawa et al. (2007).
⁷ Alfarra et al. (2004).
⁸ Bahreini et al. (2005).
⁹ Lanz et al. (2008).
₁₀ Sorooshian et al. (2008).
PMF analysis of AMS organic spectra was explored for 2, 3, 4, 5, and 6 factor solutions along with FPEAK values from –2 to 2 using fragments listed in Lanz et al. (2007). The signal and error matrices for organic spectra were prepared using ExtractWaves&Matrices, version 1.1 created by Q. Zhang [http://www.asrc.cstm.albany.edu/qz/ExtractWaves&Matrices%20v1.1.ipf]. This procedure was designed to work within the AMS processing algorithm (Allan et al., 2004) to produce organic-only mass spectra and the corresponding error (Allan et al., 2003). Signals at m/z 16, 17, 18, and 44 were down-weighted by increasing the corresponding error by a factor of 2 (Ulbrich et al., 2009). The matrices were averaged to 30-min resolution in preparation for comparing AMS factors to FTIR PMF factors, which have approximately 12-h resolution. We do not expect the 5-min resolution spectra to result in different factors given that the measured composition shows no significant changes on timescales less than 1 h. The factor spectra determined from PMF were correlated to all spectra available on the AMS spectral database (Ulbrich, I.M., Lechner, M., and Jimenez, J.L. AMS Spectral Database. URL: http://cires.colorado.edu/jimenez-group/AMSSd/) described in (Ulbrich et al., 2009) to determine which solutions produced spectra consistent with previous observations. Uncentered correlations were used for all mass spectra; correlations over m/z 10–300 and m/z 45–500 were explored (Table 2). Beyond 3 factors, additional factors showed correlations to one another indicative of factor splitting (Ulbrich et al., 2009). For the 3-factor solution, spectra from FPEAK = 0.4 had the highest correlations to literature spectra (Table 2) and a Q-value within 5% of the minimum observed Q. The most extreme FPEAK values (–2 and 2) FPEAK values corresponded to Q-values that were 20% larger than the minimum observed Q, and were therefore unsuitable. Therefore the 3-factor solution with FPEAK = 0.4 was selected to best represent the data chemically and quantitatively (reconstructed and measured OM had slope = 0.98 and r = 0.99). Fig. 4 shows the normalized spectra of AMS factors 1–3; correlations to reference spectra and inorganic components are included in Table 2. Again, the initialization seed was varied over 10 values as a test for robustness. The results showed no difference in factor spectra and comparisons of factor strengths agreed with r = 0.99 or better and slopes between 0.99 and 1.004.

The strength of Factor 1 is correlated to AMS sulfate (r = 0.64) and XRF Ni (r = 0.36) and is negatively correlated to BB\textsubscript{FTIR}, K, and Br. The spectrum for Factor 1 is correlated to wood smoldering spectra (r = 0.87–0.89) and OOA-I (r = 0.89). Despite the similarity of this factor to wood smoldering spectra, its contribution to OM during the two fire periods is minor. M/z 44 is a prominent fragment, with small contributions from m/z 43, 55, and 57 resulting in this factor’s assignment as OOA (Zhang et al., 2005b). The strength of Factor 2 is correlated to Br (r = 0.90), K (r = 0.57), and BB\textsubscript{FTIR} (r = 0.81). The spectrum for Factor 2 is correlated to fire smoldering emissions (r = 0.99), beech smoldering emissions (r = 0.99), and OOA-I (r = 0.94), when all m/z are considered. For m/z 45 and larger, the spectrum is correlated to terpinolene (r = 0.96) and myrcene (r = 0.95) SOA particles and OOA-I (r = 0.95). The strength of Factor 3 also correlates to Br (r = 0.46), K (r = 0.49), and BB\textsubscript{FTIR} (r = 0.48) though correlations are weaker than for Factor 2. The spectrum of Factor 3 correlates to brush fire and larch flame aerosol (r = 0.94–0.95), methylcyclohexane SOA particles (r = 0.94), and β-pinene SOA particles (r = 0.93). Factors 2 and 3 both have characteristics of biomass burning aerosol though Factor 2 is more similar to biogenic SOA and has a much larger contribution from m/z 44. Factor 3 is less oxygenated, resembles flaming phase smoke particles, and shares similar fragments (43, 55, 57) with urban fossil fuel emissions. Therefore, Factors 2 and 3 are labeled together as “BBOA” with one “oxidized biomass burning organic aerosol” factor (O-BBOA) and one “hydrocarbon biomass burning organic aerosol” factor (H-BBOA). Fig. 5a shows the difference between the normalized O-BBOA and H-BBOA spectra for each m/z that contributes more than 0.2% to the total organic signal. The largest differences are for m/z 17, 18, and 44 (positive) and m/z 27, 29, and 41 (negative). These differences support the assignment of O-BBOA as the more oxygenated of the two since m/z 18 (H\textsubscript{2}O\textsuperscript{+}) and 44 (COO\textsuperscript{-}) are associated with dehydration and oxygenated fragments, and m/z 27 (CH\textsubscript{2}CH\textsuperscript{+}) and 41 (CH\textsubscript{3}CH\textsubscript{2}CH\textsuperscript{+}) are associated with primary emissions from wood burning (Alfarra et al., 2007; Schneider et al., 2006). Small decreases in m/z 55, 56, and 58 also indicate oxidation or fragmentation of the larger hydrocarbon chains in O-BBOA. Recent comparisons between organic mass fragments and organic functional groups across multiple projects show general agreement on the assignments of m/z 44 and m/z 57 as carboxylic acid and alkane groups (Russell et al., 2009a). Fig. 5b shows an afternoon peak in the ratio of the two types of BBOA, consistent with photochemical oxidation causing some of the observed differences in the two AMS mass spectra.

Fig. 2b shows BB\textsubscript{FTIR} compared with the summed BBOA. The two independent estimates of biomass burning aerosol correlate more strongly using the sum of the two types of BBOA than either type.
alone with BB_{FTIR} (r = 0.89) and have a slope of 1.1. Similarities between H-BBOA and urban emissions indicate that H-BBOA may include local fossil fuel combustion emissions. However, BB_{FTIR} compared with only O-BBOA has a much weaker correlation (r = 0.52) and slope = 2.7 suggesting that, especially during BB events, H-BBOA is likely to have only a small amount of contamination from fossil fuel combustion. During NFP, the contribution of hydrocarbon fossil fuel combustion emissions to H-BBOA is potentially significant and may account for the negative intercept in the least-squares fit in Fig. 2b. To our knowledge, this is the first time organic mass from AMS has been compared, following factor analysis, with an independent measure of OM also separated by factor analysis. This level of agreement between two independent OM or OC measurements is higher than found previously in comparing two OC measurements using the same technique (Turpin and Lim, 2001). This good agreement suggests that the collection efficiency of BBOA is close to 1 and that the two methods of OM quantification perform similarly for the types of chemical mixtures that constitute forest fire aerosol. The apparent overlap of the two instrument size ranges also suggests low particle mass above 700 nm vacuum aerodynamic diameter (VAD).

3.4. Distinguishing forest fire from fossil fuel combustion organic aerosol

Forest fire emissions from fires in Northern California contributed an average of 40% of OM in fire periods of 2008, with characteristic correlations to elemental markers (K, Br) and a frequent contribution of ketone groups observed in previous woodsmoke (Russell et al., 2009b) and biomass burning aerosol (Liu et al., 2009). During NFP, fossil fuel combustion (FFC_{FTIR}) contributed 75% of OM and had distinctly different composition from both biomass burning and polluted marine aerosol. The traditional distinction of BBOA from HOA, OOA1, and OOA2 has rested on the presence of m/z 60 and 73 (Lanz et al., 2007; Zhang et al., 2007; Capes et al., 2008) although residual saccharides from cellulose combustion (levoglucosan) that produce those fragments and serve as tracers have been quantified as only a few percent of OM that may be lost in aging smoke plumes. The new result here is that BBOA is not just more or less oxygenated than fossil fuel combustion aerosol (Grieshop et al., 2009) but that it contains a significant fraction of ketone groups. The presence of ketone groups may result from more numerous alkene groups in non-aromatic ring structures present in biogenic VOCs that are co-emitted from forests during burning events (Greenberg et al., 2006) than in fossil fuel VOC emissions. For example, pinonaldehyde, pina ketone, 4-methyl-3-cyclohexenone, and limonon aldehyde have all been identified as major products of α-pinene, β-pinene, terpinolene, or limonene oxidation and all contain ketone groups — in addition to organic hydroxyl or aldehyde groups (Hatakeyama et al., 1991; Hakola et al., 1994; Calogirou et al., 1999).

PMF has been used with FTIR spectra in recent work to identify OM from oil combustion, woodsmoke, processed urban combustion, marine organic, and background aerosol (Russell et al., 2009b; Liu et al., 2009; Hawkins et al., 2010; Bahadur et al., 2010) based on the functional group composition of the factor, the sampling conditions and known sources, and the correlations to XRF tracer elements. Fossil fuel combustion particles identified in other regions typically include 40–70% alkane groups and 20–30% carboxylic acid groups (Russell et al., 2009b; Liu et al., 2009) while measurements in the Texas/Gulf of Mexico region resulted in a woodsmoke factor that was 12–32% non-acid carbonyl groups and 27–52% alkane groups, depending on the number of factors chosen for the solution (Russell et al., 2009b). This factor correlated mildly with K and Br in addition to several heavy metals. Because this factor was associated with urban wood burning, it is expected that it would be correlated to tracers commonly associated with fossil fuel combustion. Similarly, FTIR measurements in and around Mexico City also included a factor with significant non-acid carbonyl group contribution (26–47%) that was elevated during periods of elevated K, levoglucosan, and acetonitrile consistent with biomass burning (Liu et al., 2009; Gilardoni et al., 2009). The sharp methylene peaks in the biomass burning factor presented here are more prominent than the previously observed, consistent with the hypothesis that they are POA from plant cuticle wax detritus which has been associated with large wildfires but not necessarily with residential wood or trash burning or smaller fires (Simoneit, 1985; Fang et al., 1999; Medeiros et al., 2006).

3.5. Chemical and physical changes associated with aging forest fire aerosol

To investigate the chemical changes associated with aging of California wildfire aerosol, potential source contribution function (PSCF) analysis was applied to air masses sampled during FP1 for high ketone group fraction (>20%) and high carboxylic acid group fraction (>12%) (Fig. 6a,b). PSCF analysis combines a gridded geographical domain with air mass back trajectories and measured concentrations to determine the probability that each particular grid box contains a source of the measured component (Zeng and Hopke, 1989). In Fig. 6a, the high probability regions for ketone groups are located near the sampling site and off the coast of California between San Francisco and San Diego. This region experienced frequent intense plumes of smoke both from the fires in
northern California and in Big Sur (visible in satellite images obtained from MODIS on NASA’s Terra and Aqua satellites). Fig. 6c shows several examples of trajectories with high ketone group fractions that crossed smoke plumes within 2 days of arriving at the sampling site. Plume age was determined from the backward trajectory time to the first incidence of visible smoke in the satellite images (http://www.nasa.gov/topics/earth/features/fire_and_smoke.html). These particular trajectories crossed directly over the Basin Fire burning near Big Sur approximately 1–1.5 days before arriving at the pier. By contrast, the PSCF for high carboxylic acid group fractions shows high source probability near the far northern California coast and in the region southwest of the sampling site. The latter high probability region is due to trajectories like those shown in Fig. 6d that followed indirect paths from the fires to the pier or were forced south of the pier by strong offshore winds before being blown back to the pier. Trajectories in Fig. 6d reached the sampling site more than 3 days after crossing a fire or a smoke plume; trajectories from 10 to 11 July are examples of trajectories that were forced south before arriving at the pier. AMS time-of-flight mass distributions provide additional evidence that these air masses represent young (less than 2 days since emission) and aged (more than 4 days since emission) smoke particles (Fig. 7). Measurements of organic mass fragments (m/z 43, 44, and 55) from 1-day to 4-day old smoke particles show an increase in the peak diameter up to 80 nm (m/z 43) and a decrease in mass at 100 nm coinciding with an increase in mass at 400 nm (Fig. 7). Such a shift in the mean size has been observed in previous measurements of an aging biomass plume (Capes et al., 2008) where coagulation was determined to dominate the evolution of the particle number size distribution.

The submicron organic aerosol measurements presented here indicate that the ketone group signature of forest fire particles persists even in moderately aged particles but is weak or absent in measurements of highly aged smoke (greater than 4 days) (Fig. 8). The carboxylic acid to ketone group ratio increases from 0.35/0.11 for samples within 2 days of emission to 1.3 ± 0.6 for samples with greater than 4 days since emission. The increase in carboxylic acid/ketone group results from both a decrease in the ketone group fraction (Fig. 8b) and an increase in the carboxylic group fraction without an accompanying increase in BB_{FTIR} (Fig. 8a), consistent
with particle phase formation of carboxylic acid and loss of ketone groups rather than additional SOA formation. Table 3 gives the measured relationship between carboxylic acid to ketone groups and estimated smoke age, which are correlated mildly \( r = 0.72 \). A similar relationship was observed for the ratio of O-BBOA to H-BBOA. The ratio increases from 3.3 ± 1.2 for samples within 2 days of emission to 11 ± 0.77 for samples with more than 4 days since emission. Table 3 also shows the measured relationship between O-BBOA and H-BBOA and estimated smoke age, which also has a mild though lower correlation \( r = 0.55 \). By the same method, the hourly rate of oxidation of H-BBOA to O-BBOA can be estimated from the hourly average ratio of O-BBOA to H-BBOA, between 0900 and 1600 (Fig. 5b, Table 3).

The rate of increase in O-BBOA/H-BBOA from the diurnal average is more than 30 times the daily rate in Table 3; extrapolating the oxidation rate from diurnal measurements to 4-day old aerosol results in much higher O-BBOA to H-BBOA ratios than were observed in actual 4-day old smoke particles, indicating that dilution and losses play a significant role in the net chemical changes to the aging aerosol. Uniform marine stratocumulus clouds are visible in images from NASA’s Terra satellite along the coastal area near the sampling site during the measurement period increasing the likelihood that cloud processing is responsible for a significant fraction of the observed oxidation, though separating the contributions of photochemistry and cloud processing to the observed oxidation rates is not possible given the lack of airborne observations to characterize the meteorology.

The observed reduction in ketone groups simultaneously to the production of carboxylic acid groups in forest fire emissions during their processing in the atmosphere is consistent with the formation of carboxylic acid groups \( \text{O/C} = 2 \) coincident with loss of ketone groups \( \text{O/C} = 1 \) producing increasing \( \text{O/C} \) and \( m/z 44 \) fraction of OM. Ketone loss has previously been observed in controlled photochemical aging experiments (Mang et al., 2008), which demonstrate that photolysis of ketone groups in limonene SOA is a significant pathway for aging biogenic OM. Mang et al. (2008) attribute the simultaneous loss of ketone groups and production of CO to the Norrish type-I mechanism (Norrish and Bamford, 1936) that produces two alkyl radicals and one molecule of CO for each photolyzed parent ketone molecule. Grieshop et al. (2009) have shown that measurable chemical differences exist during oxidation of biomass burning particles, specifically increasing \( m/z 44 \) signal (up to 10% of the organic signal) and \( \text{O/C} \) (up to 0.5). Similarly, ambient measurements in West Africa following a smoke plume

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### Table 3

<table>
<thead>
<tr>
<th>Organic components</th>
<th>Oxidation Rate (days) Slope</th>
<th>Intercept</th>
<th>Correlation (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MCOCO}/\text{MC} )</td>
<td>0.2 ± 0.06</td>
<td>−0.03 ± 0.2</td>
<td>0.72</td>
</tr>
<tr>
<td>( \text{MO}_{\text{H.BBOA}}/\text{MC} )</td>
<td>2 ± 1</td>
<td>−0.5 ± 3</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Oxidation Rate (hours, 0900–1600 only)

| \( \text{MO}_{\text{H.BBOA}}/\text{MC} \) | 3 ± 0.3 | −30 ± 4 | 0.98 |

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**Fig. 7.** Normalized mass distributions for 1 (solid) and 4-day (dashed) old smoke plumes from AMS ToF measurements.

**Fig. 8.** (a) Carboxylic acid/ketone group ratio (left, black), O-BBOA/H-BBOA ratio (middle, pink), and carboxylic acid group fraction of OM (right, light green) for samples with estimated less than 2 days, between 2 and 4 days, and greater than 4 days since emission. (b) \( \text{BB}_{\text{FTIR}} \) (left, black) and ketone group fraction of OM (right, teal) for the same samples. Vertical error bars indicate one standard deviation of the average. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
show that the contribution of m/z 44 increased from 7.4% in fresh biomass burning spectra to 14% in aged spectra (Capes et al., 2008). It should be noted that O/C can also increase from a reduction in the alkane group fraction due to oxidation, fragmentation, and volatilization of newly formed VOCs. However, the measured alkane fraction actually increased from 0.42 ± 0.06 to 0.60 ± 0.04 between air masses with 2-day and 4-day old smoke particles due to mixing of fossil fuel combustion emissions (which have high alkane group fractions) with forest fire emissions. Measurements from Barrow, Alaska, show that in smoke plumes older than 5 days, ketone groups are below detection limit while carboxylic acid groups dominate the oxygenated OM (Shaw et al., 2010). Therefore, for very long range transport, ketone groups may not be the best indicator of forest fire emissions as the aerosol has aged sufficiently to look like OOA from fossil fuel combustion, consistent with Grieshop et al. (2009).

4. Conclusion

Measurements of organic functional groups and collocated measurements of non-refractory aerosol were used to separate contributions from forest fire and fossil fuel combustion aerosol to OM during summer 2008 in California. Similarities to previously reported woodsmoke and biomass burning aerosol are consistent with the compositions of the factors identified here. We report the first observations of substantial ketone groups (25%) in forest fire aerosol, which have both lower O/C and lower m/z 44/OM fraction than carboxylic acid groups. The similarity of the AMS spectrum of the dominant PMF-based factor to laboratory generated biogenic VOC oxidation products suggests that much of the measured organic aerosol is SOA from biomass burning sources rather than primary organic aerosol.

Changes in composition visible in FTIR spectra were complementary to diel changes observed in AMS mass spectra, including an increase in m/z 44 fraction and a decrease in m/z 27, 41, and 55 though the average daily increase in oxygenated BBOA was much greater than the rate estimated from observations of 2, 3, and 4-day old smoke particles. Atmospheric processing of these ketone-containing organic aerosol particles likely forms carboxylic acid groups and removes ketone groups, resulting in increased m/z 44 and O/C. These observations may provide an explanation for the observed increase in both O/C and m/z 44 in chamber studies of woodsmoke oxidation – by formation of carboxylic acid groups and loss of ketone groups – using quantitative measurements of organic functionality of ambient forest fire particles.

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References


