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Estimated contributions of primary and secondary organic aerosol from fossil fuel combustion during the CalNex and Cal-Mex campaigns

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HIGHLIGHTS

- Fossil fuel emissions contribute from 60% to 80% to the ambient particle OM.
- The identification of alkane group peaks by FTIR provides fuel-specific signatures.
- POM and SOM from fossil fuel sources accounted for 16–20% and 42–62%, respectively.

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ABSTRACT

Observations during CalNex and Cal-Mex field campaigns at Bakersfield, Pasadena, Tijuana, and on board the R/V *Atlantis* show a substantial contribution of fossil fuel emissions to the ambient particle organic mass (OM). At least two fossil fuel combustion (FFC) factors with a range of contributions of oxidized organic functional groups were identified at each site and accounted for 60–88% of the total OM. Additional marine, vegetative detritus, and biomass burning or biogenic sources contribute up to 40% of the OM. Comparison of the FTIR spectra of four different unburned fossil fuels (gasoline, diesel, motor oil, and ship diesel) with PMF factors from ambient samples shows absorbance peaks from the fuels are retained in organic aerosols, with the spectra of all of the FFC factors containing at least three of the four characteristic alkane peaks observed in fuel standards at 2954, 2923, 2869 and 2855 cm⁻¹. Based on this spectral similarity, we estimate the primary OM from FFC sources for each site to be 16–20%, with secondary FFC OM accounting for an additional 42–62%. Two other methods for estimating primary OM that use carbon monoxide (CO) and elemental carbon (EC) as tracers of primary organic mass were investigated, but both approaches were problematic for the CalNex and Cal-Mex urban sites because they were influenced by multiple emission sources that had site-specific and variable initial ratios to OM. For example, using the $\Delta\text{POM}/\Delta\text{CO}$ ratio of 0.0094 $\mu\text{g ppb V}^{-1}$ proposed by other studies produces unrealistically high estimates of primary FFC OM of 55–100%.

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1. Introduction

In California, as well as in much of the rest of the world, the organic fraction of particles constitutes 10–70% of the mass of fine aerosol (Turpin et al., 2000), but the quantity and composition of

the man-made contribution to atmospheric organic particles are not well characterized. Russell et al. (2011) used the spectral signatures of Fourier transform infrared (FTIR) spectroscopy measurements of carbonaceous particle mass to show that fossil fuel combustion (FFC) accounts for 62% of organic mass but ranges from 35% to 93%, although the sampled locations were biased toward coastal and marine locations. In highly populated urban regions such as southern California, most of the submicron organic mass (OM) is attributable to emissions of fossil fuel combustion, in particular to motor vehicles (Hayes et al., 2013; Liu et al., 2012).

Fossil fuel combustion processes produce organic compounds that can form particles before emission (primary organic mass,

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POM) and after emission (secondary organic mass, SOM) into the atmosphere. Models tend to track primary and secondary carbonaceous particles separately because of their different production mechanisms, but observations often have a difficult time separating these components, as some are chemically similar (Cass, 1998). For example, the loss of some mass of the carbonaceous particles due to increased volatility (Robinson et al., 2007) or reactivity (Molina et al., 2004) in changing ambient conditions means that using tracers will overestimate the primary OM associated with some sources. In addition, for some sources carbonaceous particles are accompanied by VOCs that can later add OM to the particle phase as secondary carbonaceous components. SOM has been estimated in several urban, polluted environments (de Gouw et al., 2005; Johnson et al., 2006; Takegawa et al., 2006; Volkamer et al., 2006), but there is significant disparity between laboratory simulations and SOM observations in areas with high anthropogenic activity (Gentner et al., 2012).

Several methods have been used to separate the contributions of POM and SOM to OM based on either temporal variation or the oxygenated OM composition (Liu et al., 2011). Comparisons of multiple methods have shown good agreement in some regions (Liu et al., 2011, 2012; Zhao et al., 2013) but such agreement may depend on local conditions since the types and mixtures of sources are different in each location as is their atmospheric processing.

Characterizing the main sources for POM and SOM in the California region was a major focus of the CalNex and Cal-Mex campaigns at the ground sites at Bakersfield, Pasadena, and Tijuana as well as for the shipboard observations on the R/V *Atlantis* during May and June of 2010. To assess the degree to which these short

campaigns are representative of the region and the summer season, we compare the organic carbon (OC) measurements from nearby monitoring sites of the IMPROVE and CARB networks. To separate primary and secondary contributions of fossil fuel combustion emissions (primarily from motor vehicles and shipping) to OM, we use organic functional group measurements to provide upper and lower bounds on the uncertainties associated with this separation. The results are used to evaluate the extent to which the relationship of OM components to CO and of OC components to EC can be used as indicators of primary and secondary organic sources.

2. Methods

2.1. OM, OC, EC, and CO measurements

The CalNex and Cal-Mex projects included three ground sites at Bakersfield (35° 21'0" N, 118° 58'12" W), Pasadena (34° 8'13" N, 118° 7'28" W), and Tijuana (32° 29'55" N, 116° 56'25" W). The sites are shown in Fig. 1. Measurements took place from 15 May to 30 June 2010 at Bakersfield and Tijuana, while at Pasadena the sampling period was 15 May to 16 June 2010. Coastal measurements were collected on board the R/V *Atlantis* from 15 May to 6 June 2010. Ambient particles were sampled at 18 m above sea level through a heated mast that controlled the relative humidity (RH) of the air masses to 60%, which partially dried the aerosol. Sector control for the flow was used to prevent sampling of emissions directly from the R/V *Atlantis*. The cruise track followed the California coastline and the Sacramento-San Joaquin River delta, with sampling in proximity to Los Angeles, Oxnard, Monterey Bay, San Francisco, and Sacramento.

Fig. 1. Density population map and the location of short-term and long-term sites. R/V *Atlantis* sampling points locations were divided into five off-coast regions according to proximity to urban locations: Sacramento, San Francisco, and Monterey Bay in the “NorCal” region and Oxnard and Los Angeles in the “SoCal” region. Note that the ship track also followed the Sacramento River from San Francisco Bay to Sacramento. Population map corresponds to the 2010 census (Source The U.S. Census Bureau, data available at <http://www.census.gov/2010census/>).

For comparison with the CalNex and Cal-Mex sites, we identified five IMPROVE (Interagency Monitoring of Protected Visual Environments, <http://views.cira.colostate.edu/web/DataWizard/>) and six CARB (California Air Resources Board, <http://www.arb.ca.gov/aqmis2/aqmis2.php>) sites with long-term measurements in nearby rural and urban locations. These sites, along with the distance to the intensive CalNex and Cal-Mex sites, are listed in Table 1 and shown on Fig. 1. For each intensive site, we identified both a nearby “background” site in a rural location from the IMPROVE network and a nearby “urban” site from the CARB network. At both IMPROVE and CARB sites, OC concentrations were measured in particles less than 2.5 μm in a 24-h basis every 3–6 days. The OC sampling and analysis protocols for the IMPROVE and CARB sites use the Thermal Optical Reflectance (TOR) method (with detailed protocols at ftp://ftp.arb.ca.gov/aqd/aqcd/web2011/pm25_speciation_desc.pdf, and <http://vista.cira.colostate.edu/improve/Publications/OtherDocs/IMPROVEDataGuide/IMPROVEDataGuide.pdf>).

For the CalNex and Cal-Mex measurements at Tijuana, Bakersfield and R/V *Atlantis*, particles were collected through a single 1- μm sharp-cut cyclone (SCC 2.229 PM1, BGI Inc., Waltham, MA) on 37 mm Teflon filters (Pall Corp., Ann Arbor, MI). The filters were loaded with constant airflow rate for 3 h–12 h. At Pasadena, similar sampling was carried out using a 2.5 μm sharp-cut cyclone during 23 h each day. After particle collection, the samples from all of the locations were sealed and stored below 0 °C to avoid evaporative losses before FTIR and X-ray fluorescence (XRF) analysis.

Four types of liquid fuels were selected to serve as standards. Gasoline, diesel, and motor oil were purchased in January 2012 at a Mobil gas station in La Jolla, California, and low-sulfur ship diesel was sampled from the tanks of the R/V *Point Sur* in July 2011. Each sample was atomized and collected on three 37 mm replicate Teflon filters.

Filters were scanned before and after aerosol loading by transmission FTIR spectroscopy using a Tensor 27 spectrometer with DTGS detector (Bruker Optics Inc., Billerica, MA; OPUS software). Initial spectra are obtained prior to sampling. After sampling, each ambient spectrum was calculated as the difference of the final and initial scan spectra. The OM and OC concentration of organic functional groups were determined using an automated baselining and peak-fitting algorithm (Day et al., 2010; Russell et al., 2009; Takahama et al., 2013b) that quantifies alkane (CH), hydroxyl (C–OH), carboxylic acid (COOH), non-acid carbonyl (C=O), amine (C–NH₂), and organonitrate (C–ONO₂) functional group concentrations based on the intensity of their characteristic infrared absorption band. Samples were analyzed for wavenumbers from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . Baselining and standard

compound calibrations for each organic functional group reported are provided in Gilardoni et al. (2007) and Liu et al. (2009). For the fuel standards, the average FTIR spectra of the three filters collected for each was used.

Refractory carbon concentrations were measured as a proxy for elemental carbon at the Tijuana and Pasadena sites. An 8-channel Single Particle Soot Photometer (SP2; Droplet Measurement Technologies, Inc.) was calibrated from the response to atomized, size-selected Aquadag (Aqueous Deflocculated Acheson Graphite, Acheson Inc., USA) particles in aqueous solution. The measurements were processed with PAPI, Probe Analysis Package for Igor, software modified from the work by Subramanian et al. (2010). The mass-based lower detection limit is ~ 0.7 fg, or 90 nm in mass-equivalent diameter (Schwarz et al., 2010). The SP2 measurements at the Pasadena supersite were using a 4-channel version of the instrument, calibrated using glassy carbon spheres (Type II, Alfa Aesar, Ward Hill, MA, USA) in the manner described by Liu et al. (2010) and McMeeking et al. (2010). Comparison to the NOAA SP2 calibrated with fullerene soot, showed agreement to within 10%. The SP2 also has two avalanche photodiode (APD) scattering detectors, which were calibrated with polystyrene latex spheres (PSLs; Duke Scientific, now Thermo Fisher Scientific, Waltham, MA, USA). ~~This deployment and data analysis and quality assurance methods is presented in more detail in Taylor (2013).~~

Carbon monoxide concentrations were measured at nearby monitoring sites in Tijuana (at La Mesa) and Los Angeles (at CARB site). At the Bakersfield location carbon monoxide was measured from the top of the tower using a gas filter correlation infrared spectrometer (Teledyne, API M300EU2).

3. Results and discussion

3.1. Comparison of CalNex and Cal-Mex OC with monitoring sites

At all four CalNex and Cal-Mex campaign sites discussed here (R/V *Atlantis*, Tijuana, Pasadena, and Bakersfield), the measured OC was above the nearby rural and below the urban OC concentrations from the long-term monitoring sites. Fig. 2 shows the comparison of the OC measurements at R/V *Atlantis*, Tijuana, Pasadena, and Bakersfield with the urban and rural monitoring sites. The urban sites typically have OC concentrations higher than the corresponding rural sites by factors of 2–5. Interestingly, the differences in OC concentrations are lower during the summer. This is consistent with a larger contribution from both biogenic and transported secondary OC in the summer and a smaller contribution from residential woodburning sources.

Table 1

Distances (km) between short-term CalNex and Cal-Mex sites (right) and long-term IMPROVE and CARB sites (top). The comparison of long-term and short-term monitoring sites only includes pairs of sites separated up to 216 km. Distances shown for R/V *Atlantis* correspond to the mean value of all sampled points at each sub-region, and the minimum and maximum distances of the sampled points are shown in parentheses.

Distance (km)		IMPROVE			CARB			
CalNex	Cal-Mex	Wrightwood	San Rafael	Point Reyes	Los Angeles	Simi Valley	San Jose	Vallejo
R/V Atlantis*	Los Angeles	101 (87–118)	181 (216–133)	–	45 (65–29)	64 (30–98)	–	–
	Oxnard	162 (144–199)	79 (43–103)	–	113 (154–91)	71 (53–109)	–	–
	Monterey Bay	–	–	155 (124–182)	–	–	59 (79–47)	–
	San Francisco	–	–	64 (51–71)	–	–	–	16 (12–23)
	Sacramento	–	–	119 (111–129)	–	–	–	19 (5–29)
Tijuana		Agua Tibia			El Cajon			
		107			32			
		Wrightwood			Los Angeles			
Pasadena		48			12			
Bakersfield		San Rafael	Dome Land Wilderness		Bakersfield			
		117	186		8			

The R/V *Atlantis* measured daily mean OC concentrations between $2 \mu\text{g C m}^{-3}$ and $0.3 \mu\text{g C m}^{-3}$ with a very uniform oxygen to carbon ratio (O/C) of 0.46 along its track. The highest OC concentrations were observed when the ship track was close to coastal southern California, and similar to Los Angeles and Simi Valley measurements (Fig. 2). As the ship moved northward, OC concentrations decreased to values below $0.6 \mu\text{g C m}^{-3}$ similar to the measurements at Vallejo and Sacramento sites during that period. The small difference in OFG (organic functional group) composition between southern California and northern California indicates that the two regions may have had similar mixtures of sources types. The significantly higher mass concentration in the more southern region indicates that the dilution of the OM loading in northern California was likely due to cleaner air brought from northwest offshore winds over the ocean.

The Cal-Mex measurements at Tijuana in Parque Morelos are comparable with both long-term sites, except from May 29 to June 7 when high local biomass burning emissions were detected. The

Agua Tibia (IMPROVE) and El Cajon (CARB) sites had similar OC concentrations during the summer. The similarity of OC concentrations among the three sites is consistent with the findings of Takahama et al. (2013b) that the majority (up to 80%) of the OM measured at Tijuana during Cal-Mex was transported from the Los Angeles area rather than produced by local sources (at least 20% of the total OM). The large contribution of transported OC also explains the similarity between the rural site at Agua Tibia and the urban site at El Cajon. In contrast, the wintertime concentrations at these two sites are very different, with El Cajon OC concentrations of more than $8 \mu\text{g C m}^{-3}$ exceeding those of Agua Tibia by a factor of 10 or more in December.

The OC concentrations at the CalNex Pasadena site ($3.6 \pm 1.3 \mu\text{g m}^{-3}$) were very similar in magnitude to the measurements at the long-term Los Angeles site. Daytime sea breeze transports emissions from the southwest to the northeast with an average transport time of emissions from Los Angeles to Pasadena of 3.25 h making the consistency in OC concentrations between Los

Fig. 2. Time series of OC concentrations at rural and urban locations at the four sites sampled by the ground and ship platforms of CalNex and Cal-Mex at a) northern California sites and R/V *Atlantis* (NorCal), b) Tijuana and surroundings, c) southern California sites including Pasadena and R/V *Atlantis* (SoCal), and d) San Joaquin Valley (SJV) sites including Bakersfield. Intensive organic carbon measurements during summer 2010 (black) are shown as 24 h averages for comparison purposes. Rural and urban continuous monitoring sites belong to IMPROVE (Point Reyes, Agua Tibia, Wrightwood, San Rafael, and Dome Land) and CARB (San Jose, Vallejo, Sacramento, El Cajon, Los Angeles, Simi Valley, and Bakersfield) networks, respectively. Organic Carbon was measured in fine particles (less than $2.5 \mu\text{m}$ or $\text{PM}_{2.5}$) at permanent locations and submicron particles at CalNex and Cal-Mex sites, except for Pasadena where only fine particles ($\text{PM}_{2.5}$) were collected.

Angeles and Pasadena reasonable (Hayes et al., 2013). The emissions in the Basin exit through passes in the San Gabriel (El Cajon Pass) and San Bernadino Mountains (Banning Pass) (Lu and Turco, 1995). Given that Wrightwood is located in the San Gabriel Mountains and is shielded from the high OC source regions of the Los Angeles Basin and its outflow pollution, such low OC concentrations are to be expected. The rural Wrightwood site had considerably lower OC concentrations than either Pasadena or Los Angeles, on average 5–10 times lower. Seasonal differences in OC were observed at the Los Angeles monitoring site, with higher concentrations in winter than in summer. One would expect similar seasonal differences at Pasadena, given the airflow patterns in the LA Basin. Wrightwood had fairly constant OC throughout the year, indicating no substantial biogenic or residential (or agricultural) burning sources.

The urban and rural OC concentrations near the CalNex Bakersfield site differed by less than a factor of 2 in summer 2010, with Dome Land and San Rafael rural concentrations of about $1 \mu\text{g C m}^{-3}$ and Bakersfield CARB site concentrations of $2 \mu\text{g C m}^{-3}$. Similar to Tijuana, wintertime OC concentrations showed a larger difference between urban and rural OC, consistent with lower contributions from local urban sources during summertime.

3.2. Factor analysis of FTIR spectra at CalNex and Cal-Mex sites

To assess the major sources that contribute to the total organic aerosol composition, the apportionment of measured OM using positive matrix factorization (PMF) (Paatero and Tapper, 1994) was determined for each site (R/V Atlantis, Tijuana, Pasadena and Bakersfield). This approach provides a framework that separates the organic mass into separate factors with distinctive functional group composition and magnitude. The complete description of PMF solutions and their association with specific sources is provided in Takahama et al. (2013a) and Liu et al. (2012) for Tijuana and Bakersfield, and in the Supplemental material for R/V Atlantis and Pasadena.

Five main source categories were identified based on factor spectra and organic composition similarities: less and more oxidized fossil fuel combustion (FFC), marine, vegetative detritus, and mixed FFC with biomass burning or biogenic SOM (Fig. 3).

The baselined FTIR spectra were separated by PMF, and ammonium is largely associated with the vehicular fuel factors in most of the PMF factor solutions that were produced. For comparison of only the organic functional group contributions, Fig. 3 also shows the factor spectra with the ammonium contribution removed.

Fig. 3. PMF factor spectra and organic composition for Bakersfield, Pasadena, R/V Atlantis, and Tijuana. The pie charts show the organic functional group composition for each factor: hydroxyl, alkane, non-acid carbonyl, and amine groups. Colors and patterns for each site and for the organic functional groups are as indicated in the legend. Factors are categorized into five main groups, based on their spectral features and sources: a) less oxidized FFC (high ammonium) for the FF Shipping factor (R/V Atlantis) and the PO (Petroleum Operations) SOA factor (Bakersfield), b) less oxidized FFC (low ammonium) for FF1 factor (Tijuana) and Aromatic SOA factor (Pasadena), c) more oxidized FFC for FF SOA (R/V Atlantis), Alkane SOA (Bakersfield), FF2 (Tijuana), and Alkane SOA (Pasadena) factors, d) marine factors, e) vegetative detritus factors, and f) other, including mixed FFC with biomass burning or biogenic SOM (Pasadena) and BB (Biomass Burning, Tijuana), Nighttime OA (Bakersfield), and Mixed SOA (Pasadena). Panels (a) and (b) have similar less oxidized organic mass but are separated here based on ammonium content. Right panels (g, h, i, j, k, and l) are the same as the corresponding left panels (a, b, c, d, e, f) but exclude the ammonium absorbance. For panel g, the reconstructed spectra are shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Two or more factors were identified as related to FFC based on both 1) the temporal correlations of the factor time series to measured elemental or molecular tracers of fossil fuel emissions or to PMF factors (from co-located online organic measurements) that were identified as associated with FFC and 2) the chemical similarities of the OFG composition and the FTIR spectra to PMF factors identified at other locations (Russell et al., 2011). At Tijuana, the FF1 and FF2 factors were identified as FFC related because of their correlation to higher time resolved ACSM (Aerosol Chemical Speciation Monitor) factors that had good correlations with benzene, toluene and heavier aromatic compounds (C8 and C9) (Takahama et al., 2013a). The FF1 factor was also correlated to V and S, suggesting some influence from shipping. Shipping was identified as the likely source of the small FF Shipping factor on the R/V *Atlantis*, since it had weak correlations to ammonium and sulfate but a weak anti-correlation to radon (a tracer for coastal influence). The FF SOA factor on the R/V *Atlantis* was identified as FFC-related and secondary because of its strong correlation to sulfate and oxalate (Sorooshian et al., 2006), but the correlation to radon indicated the more coastal origins of this OM (Hawkins et al., 2010). At Bakersfield, oxidation products of alkanes and polycyclic aromatic hydrocarbons were used as molecular tracers for the identification of the Alkane SOA and Aromatic SOA factors (Liu et al., 2012). Petroleum Operation SOA factor, denoted as PO SOA, at Bakersfield was correlated to V and S, which indicated the use of fuel that is similar to ship diesel in that it had not been refined but from back trajectories was identified with drilling processes that burn crude oil. In Pasadena, the Alkane SOA and Aromatic SOA factors were correlated with the sum of the first two FFC-related AMS factors (HOA and SV-OOA) and with the third FFC-related AMS factor (LV-OOA), respectively. The sum of the HOA and SV-OOA factors was associated with primary and “fresh” secondary combustion products because it was found to vary with BC, benzene, and EC, as well as with acetaldehyde and odd oxygen (Hayes et al., 2013). The LV-OOA factor was more oxidized and correlated mildly to sulfate, nitrate, and ammonium, consistent with a photochemically processed FFC source. Factors that were not primarily associated with FFC at each site included the Marine factor on the R/V *Atlantis* (see Supplemental material), Mixed SOA (including cooking as well as some FFC sources), Vegetative Detritus, and Marine factors at Pasadena (see Supplemental material), Vegetative Detritus and Nighttime OA factors at Bakersfield (Liu et al., 2012), and Biomass Burning (referred as BB factor) and Marine factors at Tijuana (Takahama et al., 2013a).

The multiple fossil-fuel-related factors had varying contributions from oxidized organic functional groups (non-acid carbonyl, hydroxyl, and carboxylic acid groups). The factors with lower oxidized organic functional groups concentrations may include both POM and first generation secondary OM (Fig. 3, panels a and b). Comparison of the left panels in Fig. 3 shows the large contribution of ammonium to the less oxidized FFC factors at Bakersfield and R/V *Atlantis*. The second FFC factor with a higher contribution of oxidized organic functional groups is dominated by secondary organic mass (panel c). An additional FFC factor dominated by SOM is observed only at Bakersfield (Fig. 3, panels f and i). This factor is attributed to oxidation products of aromatic hydrocarbons because of its large non-acid carbonyl content and its correlation with gaseous oxidation products of polycyclic aromatic compounds (Liu et al., 2012).

The contribution of organic mass related to total FFC sources accounts for more than half of the total OM in the inland and coastal sites (60–88%). Nevertheless, the relative contribution of two types of fossil fuel combustion sources varies considerably among R/V *Atlantis*, Tijuana, Pasadena and Bakersfield sites, with

the less oxidized FFC factors accounting for 8–42% and the more oxidized FFC factors accounting for 17–80% of the total OM. This wide range indicates that the OM contributions from fossil fuel combustion sources differ substantially by location. The composition of the more oxidized FFC factors are fairly consistent among all of the sites with 50% alkane, 12% hydroxyl, 35% carboxylic acid, and 4% amine groups by mass on average. The small range of slopes in the plot of the alkane group (CH) fraction to the sum of the oxidized groups (acid and non-acid C=O + C-OH) fractions of OM shows a narrow range from 0.8 to 1.3 as shown in Fig. 4a, indicating a fairly consistent composition among the four CalNex and Cal-Mex platforms with FTIR measurements (R/V *Atlantis*, Tijuana, Pasadena, and Bakersfield). Fig. 4a is analogous to a “van Krevelen diagram,” in that it provides the relationship between aliphatic functional groups and oxidized organic functional groups. The ratio of hydroxyl to acid and non-acid carbonyl functional groups also has a limited range from 0.2 to 0.5 (triangles in Fig. 4b), which is consistent with the similarities in the OFG shown in panel (c) of Fig. 3 despite local differences in oxidation conditions and primary source contributions. In contrast, there are significant composition differences among less oxidized FFC factors reflecting the different characteristic emission mixtures and processing conditions for the different sites.

The Marine factor identified by FTIR PMF is attributed to organic mass derived from ocean sources. The Marine factors are dominated by hydroxyl functional groups (70%) and have the highest values of hydroxyl (C-OH) to (acid and non-acid) carbonyl (C=O) group ratios (6.5–30, diamonds in Fig. 4b). The anti-correlation of the C-OH/OM to total C=O/OM is expected since a high fraction of

Fig. 4. Comparison of (a) unoxidized and oxidized functional group fractions of OM and (b) hydroxyl to carbonyl fraction of OM in ambient samples (circles) and PMF factors for each site. Sources identified by PMF solutions are categorized into five classes, less oxidized FFC (squares), more oxidized FFC (triangles), marine (diamonds), vegetative detritus (pentagons), and mixed FFC and biomass burning or biogenic SOM (stars).

hydroxyl group mass is characteristic of primary marine and vegetative sources whereas carbonyl group fraction increases with secondary aerosol formation. The Marine factors correlate well with sodium and chloride in submicron particles measured by XRF (Tijuana and R/V *Atlantis*). The organic hydroxyl groups found in the Marine factors are likely derived from polysaccharides concentrated on the ocean surface (Aluwihare et al., 1997; Russell et al., 2010). The similarity of the OFG composition of the Marine factor with the Vegetative Detritus factor found at Bakersfield is consistent with the saccharide-like composition of plant materials (Bianchi et al., 1993). Both the Marine and Vegetative Detritus factors have double peaks in absorbance at 2929 and 2855 cm^{-1} , characteristic of methylene peaks from longer chain hydrocarbons, which are present in waxes associated with plant materials (Hawkins and Russell, 2010).

The fifth factor found at three of the CalNex and Cal-Mex sites contains a large carbonyl or carboxylic acid group fraction and is related to mixtures of FFC emissions and biomass burning (Tijuana) or biogenic SOM (Pasadena and Bakersfield). The clear differences in OFG composition of these three factors reflects local influences of vegetation and anthropogenic activities, but the substantial alkane absorption at 2835–2980 cm^{-1} suggests a fossil fuel contribution to all of these factors. The similarities in the oxidized organic functional groups in these factors are evident in their proximity in Fig. 4.

3.3. Comparison of fuel standard and fossil fuel factor organic functional groups

Gentner et al. (2012) reviewed and quantified the similarities in individual molecular species identified in fuel and OM composition in tunnel studies, as well as Bakersfield, showing that total aliphatic compounds constitute the 58% and 68% carbon by weight of gasoline and diesel, respectively. Here, we use the alkane absorption region of FTIR spectra (2835–2980 cm^{-1}) to look for similarities between the composition of the observed OM and fuel standards. While FTIR spectroscopy cannot resolve the individual compounds, the spectral signature is characteristic of the mixture. Fig. 5 shows a comparison of the CalNex and Cal-Mex FFC factors to four fuel standards: gasoline, diesel, oil, and ship diesel. One interesting aspect of this comparison is that almost all of the fossil fuel OM factors at the four sites have at least three of the four characteristic peak locations (2954, 2923, 2869, and 2855 cm^{-1}) in common with the fuel standards. The ratios of the four common peaks differ in height, as summarized for the fuels and the factors in Table 2.

Comparing the peak ratios of the factors to the fuels, we see that the alkane region in the FF1 factor found at Tijuana is most similar to the motor oil signature. This local contribution is consistent with the older vehicle fleet in Tijuana than in the U.S. cities (Takahama et al., 2013a). The spectra of the Nighttime OA factor found at Bakersfield and the BB (mixed) factor at Tijuana are both quite

Fig. 5. FTIR spectra of PMF derived factors with fossil fuel contributions from CalNex and Cal-Mex compared with fossil fuel standards. The alkane absorption region is demarcated by two vertical lines at 2835 cm^{-1} (green), and 2980 cm^{-1} (blue), highlighting the four common peaks in the spectra of the fossil fuel standards. Only the fuel standards that best match with each factor are shown at each ambient factor panel. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Peak locations and relative heights in FTIR spectra of fuel standards and ambient factors related to fossil fuel (FF) emissions for each campaign. The table also shows the categories used for presenting the spectra in Fig. 3, where the less oxidized factors are shown in panels a) and b), the more oxidized factors in panel c) and other factors in panel f).

	Less oxidized	More oxidized	Other	Height at peak locations ^{a,b}			
				2954 cm ⁻¹	2923 cm ⁻¹	2869 cm ⁻¹	2855 cm ⁻¹
Fuel standards	Gasoline			0.80	1	0.50	0.60
	Diesel			0.50	1	0.50	0.70
	Ship diesel			0.80	1	0.70	0.80
	Motor oil			0.90	1	0.80	0.90
Bakersfield	PO (Petroleum Operations) SOA			1 ^b	–	0.71	0.60
		Alkane SOA		0.68	1	0.97	1.07
		Aromatic SOA		–	1	0.50	0.40
			Nighttime OA	0.51	1	0.45	0.59
Pasadena	Aromatic SOA			1.06	1	0.93	0.91
		Alkane SOA		0.83	1	1.01	1.09
			Mixed SOA	0.64	1	0.71	0.82
Tijuana	FF1			0.8	1	0.89	0.97
		FF2		1.32	1	1.18	1.32
			BB (Biomass Burning)	0.56	1	0.58	0.69
R/V Atlantis	FF Shipping			0.90	1	0.86	0.90
		FF SOA		0.90	1	1.12	1.14

^a Peak locations range from 2948 to 2956 cm⁻¹, 2921 to 2934 cm⁻¹, 2869 to 2877 cm⁻¹, and 2854 to 2858 cm⁻¹.

^b The height is relative to the peak located at 2923 cm⁻¹, except for the Petroleum Operation factor in Bakersfield which is relative to the peak located at 2948 cm⁻¹.

similar to the diesel fuel spectrum with an almost exact match in three of the four relative peak heights and widths and only a small difference at the 2855 cm⁻¹ peak, suggesting a large contribution from at least partially unreacted (primary) diesel. Since the San Joaquin Valley (SVJ), which encompasses the CalNex short-term site and the CARB long-term site at Bakersfield, has lower population density than the LA basin but a substantial amount of trans-valley transport of produce and other goods from San Francisco to LA, it is not surprising that diesel is a larger contributor in SVJ than LA. Using the fuel emission factors of non-combusted gas phase OC in vehicular exhaust of 0.38 gC L⁻¹, the yield of SOM formation per unburned fuel mass emission of 0.15 gSOM g⁻¹, and the total annual sales of diesel in Kern and LA county (Gentner et al., 2012), diesel was calculated to be responsible for 16.9% of FFC SOM formation in Kern county in contrast with 5.3% in LA basin. For Tijuana, the similarity may also arise from a nighttime contribution of unoxidized diesel traffic emissions, since this factor was frequently high at night; although it is also possible that diesel was used as part of trash burning activities. For the R/V Atlantis, the high peak at 2854 cm⁻¹ of the less oxygenated factor is consistent with a contribution from the ship-type diesel. The factors at Pasadena are generally more mixed so that the signature of a particular fuel is not clear, but the relative height of the peak at 2855 cm⁻¹ in the Mixed SOA factor certainly suggests that diesel emissions contribute part of the SOM formation. This is consistent with the small but non-negligible contribution of 5.3% estimated by Gentner et al. (2012) but contrasts with other studies that found that diesel contributions to SOM were below detection (Bahreini et al., 2011; Hayes et al., 2013).

3.4. Contributions of primary and secondary OM

Liu et al. (2011) reviewed methods used for attributing OM as secondary, showing that one of the most prevalent approaches is to define oxygen-containing mass fragments or oxidized functional groups as secondary. For FFC sources, there is little reason to doubt this is true, since oxidized organic functional groups in partially combusted, low-volatility (>C₃) carbonyls are less than 1/3 of the alkane group in OM identified in engine emissions (Jakober et al., 2008). However, primary marine and terrestrial biological sources, as well as biomass burning sources, may have substantial oxygen content (Jimenez et al., 2009; Takahama et al., 2011). For this

reason, the following discussion of separation of primary and secondary components has been applied only to the OM associated with the FFC sources.

There were twelve FFC factors identified at the four CalNex and Cal-Mex intensive campaigns (shown in Fig. 3). Only one of these factors (Nighttime OA factor at Bakersfield) had O/C close to 0.1, a frequently-used cutoff for identification of a purely primary, hydrocarbon-like OA (HOA), meaning that Tijuana, R/V Atlantis, and Pasadena had no factors that could be identified as POM and Bakersfield had only one POM-like factor that represented less than 10% of OM. Since PMF factors are identified by covariation of functional groups with each other, it is not surprising that rapid formation of SOM on time scales faster than captured by PMF of multi-hour filter samples may group the immediate POM with SOM that forms within a few hours – especially in an air basin with substantial mixing. This means that we cannot rule out that some fraction of the factors with O/C greater than 0.1 might be primary. To account for this possibility, we could identify the alkane group fraction of each FFC factor as primary. This calculation represents an upper bound (POM_{ub}), since most secondary organic products of alkanes contain 70%–90% (molar) alkane groups, and even aromatic products can retain up to 30% alkane groups (Russell et al., 2011). Then as a lower bound, we can calculate the primary OM (POM_{lb}) as the alkane group mass in excess of that expected for alkane-derived, second-generation SOA (mole fraction 0.73) (Russell et al., 2011). We consider this a lower bound because aromatic SOM and third and higher generation alkane SOM would have a lower mole fraction of alkane group.

Between these upper and lower bounds, we consider a value of 0.50 as the mole fraction of alkane group associated with FFC SOM to provide the best estimate of urban FFC SOM. This leads to a best estimate of POM (POM_{be}) as the alkane group in excess of 0.5 mole fraction of the FFC factor. Based on the best estimates, POM accounts for 16–20% of the OM at the CalNex and Cal-Mex urban sites (Table 3). The estimate for Pasadena of 16% (for particles smaller than 2.5 μm) is consistent with the 12–17% contributions of fossil fuel hydrocarbon-like organic aerosol (HOA) and local organic aerosol (LOA) identified by (Hayes et al., 2013) with AMS-based PMF (for particles smaller than nominal 1 μm cutoff). SOM from fossil fuel sources was calculated as the complement of the POM, i.e. the sum of all the oxygenated functional groups in the FFC OM factors. Since the ratio of OM to OC is different for primary and

Table 3Comparison of methods for estimating primary and secondary fossil fuel contributions to OM and OC (in $\mu\text{g m}^{-3}$ and percent of total OM and OC, respectively).

	PMF-based method (OM) ^a		CO-based method ^b		PMF-based method (OC) ^a		EC-based method ^c	
	POM ^d	SOM ^d	POM	SOM	POC ^d	SOC ^d	POC ^e	SOC ^e
Bakersfield	0.47 (19%) 0.29–0.86 (12–34%)	1.50 (62%) 1.09–1.68 (47–69%)	1.52 (90%)	0.84 (10%)	0.37 (30%) 0.23–0.69 (19–55%)	0.68 (58%) 0.37–0.83 (34–70%)	0.10 (11%) 0.09–0.11 (10–12%)	1.10 (89%) 1.09–1.11 (88–90%)
Pasadena	1.69 (16%) 0.53–4.23 (5–39%)	5.32 (49%) 3.15–6.31 (29–59%)	4.04 (55%)	5.85 (45%)	1.43 (25%) 0.44–3.57 (8–62%)	2.71 (47%) 0.88–3.78 (15–65%)	2.60 (60%) 3.23–1.97 (46–75%)	1.69 (40%) 2.05–3.31 (25–54%)
Tijuana	0.68 (20%) 0.44–1.22 (13–36%)	1.41 (42%) 0.87–1.65 (26–49%)	3.19 (100%)	0 (0%)	0.60 (32%) 0.38–1.09 (20–58%)	0.73 (39%) 0.24–0.95 (13–51%)	0.33 (25%) 0.22–0.44 (17–33%)	1.35 (75%) 1.24–1.46 (67–83%)

^a The PMF-based method uses the FFC factors at each site.^b The CO-based method uses regression to CO (Bahreini et al., 2011).^c The EC-based method uses regression to EC (Lim and Turpin, 2002).^d Ranges correspond to the upper and lower bounds. Non-fossil fuel OM are not listed, so sums are less than 100% (see Supplemental material).^e Ranges indicate the 95% interval of confidence.

secondary organic components, we used the functional group composition to calculate primary OC (POC) and secondary OC (SOC) for the PMF-based method. As expected, the POC fraction of OC is higher than the POM fraction of OM since the oxygen in oxidized organic functional groups (which are higher in SOM than POM) is excluded from SOC but not SOM.

Bahreini et al. (2011) used the ratio of $\Delta\text{OM}/\Delta\text{CO}$ as an indicator of secondary contributions to OM, since CO tracks emissions. Increases in the amount of OM per CO are inferred to be driven by post-emission (secondary) formation. Fig. 6 shows the relationship between OM, POM, and SOM with CO. Interestingly, the Tijuana campaign shows a very low ratio of either POM_{ub} or POM_{lb} to CO, consistent with the finding that most of the OM measured at this site on the northwestern edge of Tijuana was aged and transported (Takahama et al., 2013a). The slopes of POM_{ub} with CO for Bakersfield and Pasadena are more comparable to those reported in the literature (De Gouw and Jimenez, 2009), and their correlation coefficients are slightly higher although still weak ($0.47 < r < 0.52$). The wide scatter in $\Delta\text{OM}/\Delta\text{CO}$ is also consistent with the expected difference in diesel and gasoline usage on weekdays and weekends. However, if we use the ICARTT-based correlations of POM to CO to estimate POM as suggested by Bahreini et al. (2011), the primary contribution is 55% at Pasadena and 90% at Bakersfield, with no reasonable estimate possible for Tijuana since the CO is below the nominal range (making all OM appear to be primary).

Lim and Turpin (2002) proposed that POC could be quantified by its co-emission with EC, where this method was shown to be quite effective downwind of a single large urban area. We applied this approach to the CalNex and Cal-Mex ground sites in Fig. 6d, and for comparison we included the POC from the PMF-based approach. The EC-based results for Bakersfield (11%) and Tijuana (25%) indicate that POC is lower than PMF-based estimates (30% and 32%, respectively), but higher (60%) at Pasadena (compared to the PMF-based estimate of 25%). The EC-based and CO-based estimates are most similar for Pasadena, although both indicate primary FFC organic contributions that are much higher than can be accounted for by either FTIR or AMS-based PMF of organic composition (Liu et al., 2012; Hayes et al., 2013).

A clear result is that there are significant differences in the estimated relationship between primary organic contributions and either CO or EC at the three CalNex and Cal-Mex ground sites. Both methods require the ratio of primary organic components to combustion tracers (CO or EC) to be constant for all substantial sources in the region. Lim and Turpin (2002) noted this constraint and applied the approach to a case in which they were following a plume downwind of a city for quite some distance. It is consequently in keeping with their findings that the near-source urban measurements investigated here with multiple source regions and different emission profiles have different amounts of POM emitted

per CO and EC. However, in contrast to studies that have assumed that the POM to CO ratio is invariant for different locations (Bahreini et al., 2011), we find there is no evidence to support that approach even within the CalNex and Cal-Mex region (Fig. 4).

4. Conclusions

The four CalNex and Cal-Mex sites considered here (R/V Atlantis, Tijuana, Bakersfield, and Pasadena) provided intensive measurements of organic particle composition and sources. The OC concentrations were comparable to the measurements at nearby long term monitoring sites during the summer of 2010, which were typically lower than the wintertime concentrations, due to meteorological differences as well as the lower summertime contributions of biomass burning.

The CalNex and Cal-Mex sites (R/V Atlantis, Tijuana, Bakersfield, and Pasadena) showed similar OFG composition for the twelve FFC factors identified, with all reflecting contributions with both more and less oxidized organic components. The coastal measurements on the R/V Atlantis, Tijuana, and Pasadena also had primary marine biological contributions, while Bakersfield and Pasadena showed terrestrial biological vegetative detritus sources. The three land sites also had contributions from cooking (Pasadena, Bakersfield) and biomass burning activities (Tijuana). The similarity of the factor spectra for each source type across all four sites is striking, indicating that all four sites had similar types of sources, even though they contributed to ambient OM in different amounts. The similarities in the fossil fuel combustion factors are interesting in that they clearly include both more and less oxidized components at each site – with their spectral shapes indicating that different oxidized organic functional groups are associated with higher O/C. These differences are reflected in the higher fractions of hydroxyl groups in the less oxidized fossil fuel factors and in the higher fractions of carbonyl groups in the more oxidized fossil fuel combustion factors at all sites. The nearly linear alignment of the ambient samples in the functional group plot may be largely incidental, in that there is no direct evidence for progression from the less oxidized to the more oxidized factors. Such a result could also be explained by mixing primary and secondary organic components in different ratios.

Comparison of the FFC factors to FTIR spectra of diesel, gasoline, motor oil, and ship diesel shows interesting differences in the alkane group peaks. These differences may reflect either a primary contribution to the factors or the persistent FTIR absorbance signature of aliphatic hydrocarbon (alkane) precursors. In the Bakersfield Nighttime OA factor, the colder temperatures and lack of photochemical degradation produced a strong similarity between the factor alkane group absorbance and that of diesel fuel,

Fig. 6. Comparison of estimated primary and secondary organic component relationships to CO and EC. Panels (a), (b), and (c) show the estimated primary (POM) and secondary (SOM) organic mass plotted as a function of CO (carbon monoxide), for Bakersfield, Pasadena, and Tijuana. Panels (a), (b) and (c) show $\Delta OM/\Delta CO$, $\Delta POM/\Delta CO$, and $\Delta SOM/\Delta CO$ ratios, respectively. POM and SOM best estimate ratios ($\Delta POM_{be}/\Delta CO$, $\Delta SOM_{be}/\Delta CO$) are depicted in solid lines. POM upper boundary and SOM lower boundary ratios are shown in short-dashed lines, while POM lower boundary and SOM upper boundary ratios are denoted in long-dashed lines. Each pair of estimates account for the total FFC OM. Panel (d) shows OC/EC ratios (solid line) and POC/EC (dashed line) based on the lowest four OC/EC observed ratios. Inset shows only the lowest four OC/EC ratios, in circles, used to determine FFC POC.

suggesting a nighttime contribution of primary OM emissions from trucking in the San Joaquin Valley.

Using the functional group composition, we have estimated the primary contribution to the FFC factors from the alkane group mass contribution. These estimates indicate that 16–20% of OM (25–32% of OC) is from primary fossil fuel emissions at Bakersfield, Tijuana, and Pasadena (the CalNex and Cal-Mex ground-based sites). These estimates are two to five times lower than estimates based on a fixed ratio to CO emissions. While it is not surprising that the

Fig. 7. Comparison of methods for estimating primary and secondary organic carbon and organic mass at the CalNex and Cal-Mex ground sites at Bakersfield, Pasadena, and Tijuana. Bars on the right are based on Lim and Turpin (2002) in panel a and on Bahreini et al. (2011) in panel b. Bars on the left show estimates calculated from PMF-based FFC factors, whereas values suggested by Zhao et al. (2013) in Bakersfield are shown in the bar in the middle of panel a.

amount of POM associated with CO differs substantially at locations with different source emissions and vehicle fleets, this has important implications for using this ratio to separate primary and secondary sources. There is also a clear indication that in summer the secondary contribution from fossil fuel sources is 42–62% of OM (with the remaining 19–38% being from biological sources, including biogenic secondary components, vegetative detritus, biomass burning, and cooking activities). The fraction on an OC basis favors the primary fraction more since the non-carbon mass is excluded but still gives primary OC less than 25–32%.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2013.08.047>.

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