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Constraints on primary and secondary particulate carbon sources using chemical tracer and ^{14}C methods during CalNex-Bakersfield

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Abstract

The present study investigates primary and secondary sources of organic carbon for Bakersfield, CA, USA as part of the 2010 CalNex study. The method used here involves integrated sampling that is designed to allow for detailed and specific chemical analysis of particulate matter (PM) in the Bakersfield airshed. To achieve this objective, filter samples were taken during thirty-four 23-hr periods between 19 May and 26 June 2010 and analyzed for organic tracers by gas chromatography – mass spectrometry (GC-MS). Contributions to organic carbon (OC) were determined by two organic tracer-based techniques: primary OC by chemical mass balance and secondary OC by a mass fraction method. Radiocarbon (^{14}C) measurements of the total organic

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carbon were also made to determine the split between the modern and fossil carbon and thereby constrain unknown sources of OC not accounted for by either tracer-based attribution technique.

From the analysis, OC contributions from four primary sources and four secondary sources were determined, which comprised three sources of modern carbon and five sources of fossil carbon. The major primary sources of OC were from vegetative detritus (9.8%), diesel (2.3%), gasoline (<1.0%), and lubricating oil impacted motor vehicle exhaust (30%); measured secondary sources resulted from isoprene (1.5%), α -pinene (<1.0%), toluene (<1.0%), and naphthalene (<1.0%, as an upper limit) contributions. The average observed organic carbon (OC) was $6.42 \pm 2.33 \mu\text{gC m}^{-3}$. The ^{14}C derived apportionment indicated that modern and fossil components were nearly equivalent on average; however, the fossil contribution ranged from 32–66% over the five week campaign. With the fossil primary and secondary sources aggregated, only 25% of the fossil organic carbon could not be attributed. Whereas, nearly 80% of the modern carbon could not be attributed to primary and secondary sources accessible to this analysis, which included tracers of biomass burning, vegetative detritus and secondary biogenic carbon. The results of the current study contributes source-based evaluation of the carbonaceous aerosol at CalNex Bakersfield.

Keywords

primary organic aerosol; chemical mass balance; radiocarbon; secondary organic aerosol; CalNex

1. INTRODUCTION

Fine particulate matter (aerodynamic diameter $< 2.5 \mu\text{m}$; $\text{PM}_{2.5}$) is composed of a wide variety of organic and inorganic components of primary and secondary origin. The size range of particulate matter ($< 2.5 \mu\text{m}$) leads to physiochemical changes in the atmosphere, such as visibility degradation (Sisler and Malm, 2004), radiative forcing (Charleston et al., 1992; Haywood and Boucher, 2000), and cloud formation (Ramanathan et al., 2001). In addition, a number of studies have indicated that $\text{PM}_{2.5}$ exposure may be related to adverse health effects (Pope and Dockery, 2006; Pope et al., 2009). The regulation of $\text{PM}_{2.5}$ in the United States is based on aerosol mass. To formulate reliable control strategies to reduce $\text{PM}_{2.5}$ in any airshed, primary and secondary sources contributing to the composition of $\text{PM}_{2.5}$ must be understood. Organic aerosol is highly complex and represents a mixture of organic compounds from direct emissions and condensable gases. It typically comprises a substantial fraction of the $\text{PM}_{2.5}$ mass. A closely related metric for organic mass (OM) in $\text{PM}_{2.5}$ is the measured organic carbon (OC) mass.

In most air environments in highly industrialized countries, a considerable portion of $\text{PM}_{2.5}$ is composed of organic compounds leading to high values of OC of both primary and secondary origin. Considerable effort has been undertaken to apportion sources of primary organic carbon (POC) using molecular tracers together with a chemical mass balance (CMB) model (Schauer et al., 1996). Profiles have been developed for a number of primary sources, including wood burning (Fine et al., 2002), vehicle combustion (Schauer et al., 2002), natural gas combustion (Rogge et al., 1993a), vegetative detritus (Rogge et al., 1993b), and meat cooking (Schauer et al., 1999a). The results often show good agreement between apportioned primary sources and the measured OC during winter months (Zheng et al.,

2002). By contrast, during non-winter months, 20 – 70% of the OC is generally not accounted for by primary sources with the largest differences typically found in rural areas (Zheng et al., 2007). The difference is frequently assumed to be secondary organic carbon (SOC), and frequently taken to be the difference between OC and POC. However, recent research has suggested that POC can volatilize upon atmospheric dilution resulting in semivolatile organic compounds (SVOC) that can then reform OC. Thus, it is important to not only quantify fresh POC, but to also characterize and quantify the production of SOC from different sources (Robinson et al., 2007; Presto et al., 2009; Tkacik et al., 2012).

While several approaches have been used to estimate the secondary organic component of ambient aerosol by indirect means (e.g., EC-OC technique), recent methods have now been adopted that more directly associate sources of SOC (Docherty et al., 2008; Kleindienst et al., 2007). Aerosol mass spectrometry has also been used to examine the level of oxidation of ambient aerosol in an extensive number of locations. Tracer compounds from these studies are typically found as individual mass fragments for either primary or secondary sources. The extent of oxidation can be measured as an O:C ratio and regressed against the saturation concentration (Jimenez et al., 2009) to give a measure of so-called “aged” aerosol.

In another method for understanding the secondary organic component of ambient aerosol, a laboratory tracer-based technique has been used to estimate the contributions of individual secondary sources (Kleindienst et al., 2007; Lewandowski et al., 2008). In short, laboratory irradiations of hydrocarbon reactants (isoprene, α -pinene, β -caryophyllene, toluene, naphthalene, etc.) are conducted to quantify yields of molecular tracer compounds for possible atmospheric precursors. The laboratory determined mass fractions (MF) are applied to identical tracers detected in ambient air to estimate SOC contributions from the individual sources. This attribution approach has been shown to be successful when combined with CMB for POC in select regions. (Lewandowski et al., 2008; Kleindienst et al., 2010). The organic tracer-based CMB and MF can quantify the contribution of common POC sources including fresh motor vehicle exhaust and biomass burning, and SOC from oxidation of biogenic and aromatic precursors; with these sources quantified, the contribution from additional primary and secondary sources can be estimated. The addition of radiocarbon to CMB and MF allows the OC that is not attributed to these common urban sources to be constrained as fossil or contemporary. By constraining the unattributed carbon to fossil or contemporary, future efforts can be more effectively focused on studying unique fossil or contemporary (i.e. biogenic, in this case) in a given area.

The utility of combining molecular tracers with radiocarbon (^{14}C) measurements has already been demonstrated in the laboratory (Offenberg et al., 2007) and in the analysis of ambient aerosol in a 2009-10 study of Cleveland, Ohio (Piletic et al. 2013) as well as East Asia (Liu et al., 2013; Pavuluri et al., 2013; Zhang et al., 2015). In Cleveland, molecular tracer concentrations were used together with the modern carbon fraction as a constraint to the sources of carbonaceous aerosol using a PMF algorithm. A five factor solution was shown to best represent the data. The solution indicated four categories of combustion sources in addition to SOC as a fifth factor; mobile sources represented approximately one-quarter of the primary carbon emissions in the Cleveland study.

The California Research at the Nexus of Air Quality and Climate Change (CalNex) field study has been developed to help understand the sources of PM_{2.5} in the San Joaquin Valley Air Basin (SJV) and the South Coast Air Basin in Central California (Parish, 2014). This region has among the highest levels of PM_{2.5} in the U.S. and is regularly out of compliance with the Clean Air Act standard. The SJV was represented in the field study by a site in Bakersfield while the South Coast was represented by a site in Pasadena; these sites are not assumed to be impacted by the same emission sources. A number of studies have already reported on the organic aerosol composition, emission sources and atmospheric chemistry that lead to high levels of organic PM_{2.5} in Bakersfield (Liu et al., 2012; Chan et al., 2013; Gentner et al., 2014; Nallathamby et al., 2014; Baker et al., 2015). Liu et al. (2012) and Chan et al. (2013) have reported that alkanes and vehicle-emitted hydrocarbons appear to play an important role in OC concentration either as primary emissions or through secondary formation, while biogenic SOC was not a dominant contribution. If this is the case, then the fossil carbon would be expected to dominate over modern carbon in the composition of the aerosol.

In the present study, integrated samples taken during the CalNex Bakersfield study has allowed an examination of sources of organic aerosol from primary and secondary processes for a location with historically high fossil and motor vehicle contribution. The composition of this aerosol may differ from organic aerosol in the Eastern U.S. where there is a very large modern carbon component and may differ from Pasadena and the South Coast Air Basin where radiocarbon found an average fraction fossil of 0.51, with higher fossil in midday on select days during the CalNex Field Study (Zotter et al., 2014). Thus, one objective for this study is to conduct measurements that combine ¹⁴C and organic tracer methods for Bakersfield. Beyond understanding the contribution of OC sources, insight into the distribution of primary and secondary organic aerosol can also be gained with the constraint of a fossil and contemporary split by radiocarbon. These results can improve the carbon balance and potential source mitigation strategies for the Bakersfield airshed.

2. EXPERIMENTAL METHODS

2.1. Site Description and Sampling

The CalNex field experiment was conducted in 2010 at Pasadena and Bakersfield, CA. With extensive motor vehicle exhaust, industrial, fossil fuel extraction and production, and agricultural impacts, Bakersfield represents a unique opportunity to characterize carbonaceous aerosol at the urban-rural boundary. Additional site information is available in Liu et al. (2012) and Nallathamby et al. (2014). Ambient air samples were collected at the SJV ground site located in Bakersfield, CA (35.346033 N, - 118.965727 W) on the campus of the Kern County Agricultural Extension Office. Ambient sampling for the study occurred during the period 15 May – 26 June 2010. Daily integrated samples were collected for 23-h durations beginning at midnight (local daylight time, LDT). Sample collection was performed with two collocated Tisch Model 5200 PM_{2.5} Samplers (Tisch Environmental, Village of Cleves, OH) each operated at 226 l min⁻¹. The samplers collected particles onto 90-mm quartz-fiber filters with dual cyclone impactors to separate the sampled aerosol into a fraction of the proper size range. The collection of PM-coarse (PM between 2.5 and 10 µm)

was expected to be negligible. All filter handling – preparation, handling, transporting, and storage– were similar to those described previously by Lewis and Stiles (2006).

2.2. Analysis of Organic Compounds

Detailed organic analysis was completed for each sample for both primary and secondary organic tracers. The method for primary tracers will be described briefly first, followed by a brief description of the method for secondary tracers.

The primary tracer analysis has been described in Nallathamby et al. (2014) and elsewhere, but will be summarized here. An aliquot of each filter was spiked with an isotopically labelled internal standard including polycyclic aromatic hydrocarbons, alkanes, and a sterane (IS#6 (Wisconsin State Laboratory of Hygiene, WI, USA)). Each sample was extracted using accelerated solvent extraction (ASE; ASE 350, Thermo Scientific Dionex, CA, USA) using a sequential extraction of methanol followed by dichloromethane. These extracts were concentrated to 1 mL under nitrogen using a Turbopap (Zymark, Hopkinton, MA, USA) and then further reduced to about 250 μ L using a Techne Sample Concentrator (Bibby Scientific Limited, United Kingdom). Extracts were then analyzed by gas chromatography-mass spectrometry (GC-MS) as described in Nallathamby et al. (Nallathamby et al. 2014).

Quantification standards (PMSTD#12, Wisconsin State Laboratory of Hygiene, WI, USA) which included IS#6 were analyzed by GC-MS along with the aerosol extracts to enable quantification of primary organic tracers. All results have been blank subtracted using filter blanks collected during the field campaign. Field blanks were processed in the same manner as the sampled filters. For the primary organic tracers, most of the compounds utilized in the CMB were not present in the blanks (i.e. PAHs and alkanes with molecular weight greater than triacontane); the blanks represented 17 and 12% of norhopane and hopane, respectively, and 2, 8 and 1% of heptacosane, octacosane and nonacosane, respectively. The uncertainty of these measurements has been examined and typically found to be on the order of $\pm 20\%$ (Zheng et al., 2007). The National Institute of Standards & Technology Standard Reference Material® 1649b, Urban Dust was extracted and quantified with recovery of tracers utilized in the CMB as follows, PAHs at $96 \pm 33\%$, alkanes at $97 \pm 23\%$ and hopanes/steranes at $89 \pm 22\%$ (2016).

For the analysis of the SOA tracer compounds, filter and field blank samples followed the procedure described by Kleindienst et al. (2007). As with the primary tracers, internal standards were added to each sample before extraction. Cis-ketopinic acid and tetracosane- d_{50} were added as internal and recovery standards, respectively. The secondary tracers were extracted utilizing soxhlet extraction with 1:1 dichloromethane:methanol. Sample concentration was accomplished utilizing rotary evaporation followed by blow down with ultrazero nitrogen. Each sample extract was then derivatized with 250 μ L BSTFA (1% TMCS catalyst) and 100 μ L pyridine as described in Kleindienst et al. (2007). The GC-MS method for the silylated extracts is given in Jaoui et al. (2004). Discussion of the uncertainties associated with individual tracer measurement has been published previously (Jaoui et al., 2005; Kleindienst et al., 2012). Given the specificity of retention time and SIM masses, the blanks for the tracer values were all well below the detection limit of 0.1 ng m^{-3} (Kleindienst et al., 2012).

OC and EC analysis was performed on a 1.45-cm² punch taken from collocated quartz filters. Filters were analyzed using the NIOSH thermal-optical transmittance method as described by Birch and Cary (1996). Values for OC were corrected for filter background levels and averaged across collocated samples. The blank correction was less than 20%, on average, for OC during this campaign. There was no EC present on the filter blanks. The analysis corrects for instrumental response and values are given directly in $\mu\text{gC m}^{-3}$.

2.3. Method for POC Contributions

A CMB model was run for each sample using ambient concentrations of select primary organic tracers and daily OC to estimate contributions of primary sources of daily OC (POC) as in Lewandowski et al. (2008). Four source profiles were applied within the CMB 8.0 model for estimating source contributions to PM_{2.5} (Watson et al., 1991). For this study, the motor vehicle sources included exhaust emissions from compression ignition (diesel), spark ignition (light duty gasoline vehicles), and lubricating-oil impacted motor vehicles (Lough et al., 2007a and b). A single biogenically derived source, vegetative detritus (Rogge et al., 1993b) was also included in the CMB analysis. To account for the EC associated with each primary source, the source profiles were used to calculate the contribution to EC by multiplying the source EC:OC ratio by the OC attributed to each source for each day. This primary EC (PEC) was then added to the OC CMB for that source to estimate contribution of each primary source to total organic carbon (TOC).

2.4. Method for SOC Contributions

To estimate SOC contributions for each sample, an MF technique was employed as in Kleindienst et al. (2007). The MF technique is shorthand for mass fraction technique (or approach). The numerical values are experimentally derived values for the fraction of OC represented by the sum of tracers for a single SOA source. These laboratory-derived MF factors are then applied to the sum of the atmospherically measured tracer concentrations to give a measured OC source-specific value. Kleindienst et al. (2007; Table 1) presented MF data in a tabular form for each individual chamber experiment but also an average and uncertainty both for OC and OM. As noted above, tracer IDs have been updated from Kleindienst et al. 2007 and the corrected IDs (although in some cases, still tentative given the lack of standards) are given in Lewandowski et al. (2013; Table 2). Specific values for the MFs are provided in Lewandowski et al. (2013; Table 5) together with associated uncertainties. The following MF were utilized in the current study: isoprene (0.155 ± 0.039), α -pinene (0.231 ± 0.111) toluene (0.0079 ± 0.0026), and naphthalene (0.023 ± 0.0046). Uncertainties for the laboratory-generated mass fractions are represented by the standard deviations. Limitations to this method include the atmospheric time dependencies on the actual emission rates, processing times and other factors (Kleindienst et al., 2007).

2.5. Method for Carbon-14 Determination

Ambient air filter samples were submitted for Accelerator Mass Spectrometry (AMS) analysis to the National Ocean Science Accelerator Mass Spectrometry (NOSAMS) facility located at the Woods Hole Oceanographic Institute for ¹⁴C analysis (Pearson et al., 1998; Roberts et al., 2010). The radiocarbon represents the TOC, or the OC plus the EC. Prior to sample submission the outer non-aerosol loaded ring was removed and discarded to decrease

the potential filter blank. Results reported by the NOSAMS facility are in terms of “fraction modern carbon (f MC)” carbon, equivalent to

$$f MC_{\text{sample}} = (^{14}\text{C}/^{13}\text{C})_{\text{sample}} / (^{14}\text{C}/^{13}\text{C})_{1890\text{wood}} \quad (1)$$

The results include correction for ^{13}C fractionation using $\delta^{13}\text{C}$ measurements on each sample after Lewis and Stiles (2006). The reported f MC is used to be consistent with the notation found in previous articles (Lemire et al. 2002; Lewis et al. 2004; Lewis and Stiles, 2006). In prior assessments of AMS results, this technique for environmental trace analysis is extremely robust and is likely limited by the potential for contamination during the handling of filters (Sheffield et al., 1994; Lewis et al., 2004). To account for bomb-carbon in the assessment of the fraction contemporary (biogenic + biomass burning), a correction factor was used to adjust the f MC to F CC (Fraction Contemporary Carbon) and enable calculation of F FC (Fraction Fossil Carbon). The correction factor, or contemporary end member, utilized in the current study was previously published for the CalNex project (Zotter et al. 2014). The F CC is multiplied by the observed TOC to give TOC_{CC} . The F FC is multiplied by the observed TOC to give TOC_{FC} .

While the maximum value of f MC is defined by the diminishing curve of bomb radiocarbon impact, occasionally radiocarbon airborne contaminants can give an apparent value greater than bomb-corrected unity. For example, combustion of medical waste will contribute radiocarbon in excess of expected contemporary values. In the current study, in no sample did the observed ^{14}C exceed that of the maximum value.

3. RESULTS

3.1. Measurements of Individual Organic Compounds

Compounds serving as tracers for the contribution to the organic aerosol from primary sources are given in Table S1 (Supplemental Information) for the Bakersfield site. These tracers include four major classes of compounds: polycyclic aromatic hydrocarbons (PAHs), hopanes, steranes, and linear alkanes. Levoglucosan, a tracer for wood combustion, was below detection limits, indicating a minimal primary wood smoke contribution. The tracer compound concentrations typically range between 0.02 and 2.5 ng m^{-3} depending on the specific compound and the strength of the sources contributing to OC. 17 α -21 β hopane consistently had the highest concentration of the hopanes and steranes with a monthly average of $0.29 \pm 0.11 \text{ ng m}^{-3}$. Linear n-alkanes had significantly higher ambient loadings, with nonacosane and hentriacontane having average concentrations for the month of 4.5 and 4.4 ng m^{-3} , respectively. The carbon preference index (CPI for C24-34), averaged 8.55 ± 3.21 for the campaign, which indicates a high contribution of biogenic aliphatics. It is important to note here that the compounds used in this study for apportionment are low volatility and were originally recommended for tracking POC because of their lower reactivity during urban transport (Schauer et al, 1996). They will react/degrade in the atmosphere during transport, but they have been demonstrated to have a small negative bias for POC within urban areas (Roy et al, 2011, and Heo et al, 2013). Recent studies in

Bakersfield have conducted apportionment focused on higher volatility species (Zhao et al, 2013); the alkane series used in the current manuscript for inclusion in CMB was for carbon chainlengths of 27 to 34 carbons, while Zhao et al used carbon chainlengths of 16 to 21 carbons (2013). May et al (2012) has demonstrated that the volatility of organic molecular markers will have an impact on their atmospheric lifetime, for example reporting that *n*-triacontane (30 carbons) would be classified as “nonvolatile”. Therefore, a considerable difference would be expected between apportionment based on lower versus higher volatility organic compounds.

Concentrations for the individual secondary organic tracers for Bakersfield are also included in Table S1 (Supplemental Information). These including the tracer compounds for SOA generated from isoprene, α -pinene, toluene, β -caryophyllene, 2-ring PAH (as naphthalene), and 3-methyl-2-butene-3-ol (MBO). The MF approach uses the sum of the secondary tracers for an individual source rather than a CMB approach. The sum of the isoprene tracer concentrations ranged from 2.3 to 42.1 ng m⁻³. α -Pinene had total concentrations ranging from below the detection limit to 43.4 ng m⁻³. In this study, concentrations of 2,3-dihydroxy-4-oxopentanoic acid, the tracer for toluene SOC, were always less than 2 ng m⁻³. As noted by Kleindienst et al. (2007), this tracer is also found in SOC from other methyl benzene compounds, especially the xylene and trimethylbenzene isomers. Similarly, β -caryophyllinic acid was below the detection limit for each sample in the study.

3.2. Contributions of Primary and Secondary Sources to Organic Carbon in PM_{2.5}

Primary source contributions to OC concentrations in PM_{2.5} were estimated using CMB modeling. Contributions from four emission sources were determined, which include vegetative detritus, compression ignition, spark ignition, and lubricating oil impacted motor vehicle exhaust (Table 1 and Figure 1). The four primary emission sources when summed (POC) are found to contribute 0.76 – 5.57 $\mu\text{gC m}^{-3}$ (avg: 2.81 $\mu\text{gC m}^{-3}$) to measured OC. POC from lubricating-oil impacted motor vehicle exhaust was found to be the main contributor to OC in almost all instances, particularly after 23 May. The vegetative detritus contribution was a significant fraction of the attributed POC, with an average 0.63 $\mu\text{g m}^{-3}$ for the campaign. Average wood burning contributions were below the detection limit given that the levoglucosan concentrations were in all cases below the detection limits; the apportionment of primary wood smoke can be limited by the atmospheric lifetime of levoglucosan. Aged/oxidized biomass burning plumes or SOA from biomass burning plumes would not be traced by levoglucosan, a tracer for primary OC from biomass burning. These results are very similar to CMB reported for Central LA and Riverside for May–June 2009 (Heo et al., 2013), with the highest apportionment to mobile and primary biogenic and very little woodsmoke contribution. Heo et al. also validated these results by utilizing the same organic tracers in a positive matrix factorization model (PMF) where the mobile factor from the PMF very closely matched the combined mobile apportionment from the CMB (2013). Since the CalNex 2010 CMB study reported here was conducted at nearly the same time with the same CMB mobile source profiles, it is assumed that these profiles are adequate to apportion mobile sources in the CalNex campaign.

Of the SOC sources, only four were detected in the Bakersfield samples. Tracer concentrations representing secondary sources for β -caryophyllene and 3-methyl-2-butene-3-ol (MBO) were below the detection limit. Secondary contributions to the OC for each sample are given in Table 1 and combined with POC contributions in Figure 1. For SOC sources under consideration, the results generally show isoprene as having the highest average ($0.10 \mu\text{gC m}^{-3}$) followed by the other three measured sources (ca. $0.05 \mu\text{gC m}^{-3}$), which are within $0.01 \mu\text{gC m}^{-3}$ of each other. The total SOC carbon concentrations ranged between 0.03 and $0.56 \mu\text{gC m}^{-3}$ for individual days at this site. However, in virtually all cases the contributions from SOC in Bakersfield using this technique were minor during the study period.

3.3. Fraction of Contemporary Carbon of Total Organic Carbon

The radiocarbon apportionment provides constraining values for the composition of TOC, enabling a split between modern and fossil carbon. During the study period, f_{MC} was between 0.358 (5/26/2013) and 0.706 (6/13/2013) with an average and standard deviation for the 37 samples of 0.53 ± 0.09 . With end member correction for bomb carbon suggested for the CalNex study by Zotter et al (2014), there is very little difference between the measured f_{MC} and the corrected F_{CC} (0.509); the largest difference is with the highest f_{MC} (0.706) which translates to a F_{CC} of 0.676 . The average F_{CC} for the current Bakersfield study ($.51 \pm .08$) is nearly the same as the fraction nonfossil reported by Zotter et al. for the Pasadena site during seven days in the latter half of CalNex ($.51 \pm 0.15$; May 30, Jun 3-6, 13-14). However, the Pasadena site average did include anomalously high values for fraction nonfossil, including a value of nearly 1.0 on May 30, which made the average 6% more modern; thus Pasadena is likely more impacted by fossil sources on average than Bakersfield.

The F_{CC} together with the TOC values provide a numerical value for the contemporary and fossil carbon present in the samples in $\mu\text{g C m}^{-3}$ (Figure 2). The absolute carbon values can then be compared to contemporary and fossil contributions from POC and SOC estimates. The source components of contemporary carbon included in the CMB and MF for this study includes vegetative detritus for POC, and SOC from isoprene and α -pinene photooxidation. Additional contemporary carbon emission sources could include cooking, SOA from biomass burning, and agricultural emissions. The fossil sources of POC include the three forms of motor vehicle exhaust and the SOC produced from the photooxidation of toluene (and other monomethyl single ring aromatics), as well as naphthalene, the two-ringed representative PAH. Since motor vehicle emissions were the only substantial combustion source for this study, PEC is only added for the fossil mass balance.

Summary data from the contemporary and fossil carbon are given in Table 2 and Figure 2. The absolute values of the F_{CC} and F_{FC} together with the source contributions for each source permits a determination of a mass balance. An average of $3.57 \mu\text{gC m}^{-3}$ was found for contemporary carbon (TOC_{CC}), with $0.77 \mu\text{gC m}^{-3}$ accounted for by the sum of POC and SOC. While the average fossil carbon (TOC_{FC}) was $3.29 \mu\text{gC m}^{-3}$ for the campaign, with $2.21 \mu\text{gC m}^{-3}$ accounted for by the sum of POC and SOC and $2.62 \mu\text{gC m}^{-3}$ accounted for by the sum of POC, PEC and SOC.

4. DISCUSSION

POC and SOC distributions by sources have been summarized in Table 1. OC values ranged from $1.57 \mu\text{gC m}^{-3}$ to $10.6 \mu\text{gC m}^{-3}$ in Bakersfield; comparison with $\text{PM}_{2.5}$ will be discussed at the end of this section. The fraction of OC attributed to primary sources in this urban area are mostly dominated by motor vehicle emissions, with the lubricating oil-impacted dominating this contribution. On average, the spark and diesel emission fractions are respectively only 2.6% and 6.7% of the combined particle emissions from vehicles. The remaining 91% of the primary vehicle emissions is from the lubricating oil impacted component. Tracer concentrations in Bakersfield tended to be quite modest with a consistent measurement of hopanes and n-alkanes. Vegetative detritus, which is traced by n-alkanes, was a minor source component and the only measured primary component that contributes to the modern carbon; vegetative detritus makes up 23% of the total POC on average.

The gas-phase biogenic emissions in Bakersfield might be expected to drive the production of SOC given the high propensity for formation from isoprene and monoterpenes. However, isoprene was not found to be a major source of biogenic SOC in Bakersfield, likely due to the small contribution from deciduous tree vegetation. This situation is in stark contrast to emissions found in the eastern U.S. but very much in-line with findings from Riverside, CA during the 1995 SOAR campaign (Stone et al. 2009). Contributions to OC from toluene and two ring PAHs currently represent the only anthropogenic hydrocarbons for which MF information is available. Each of these sources of SOC was typically in the range of $0 - 0.3 \mu\text{gC m}^{-3}$. Possible explanations for the relatively low absolute levels of SOC compared to other sites (Lewandowski et al., 2008; Kleindienst et al., 2010) is given below. For Bakersfield, an urban site with many heavy industrial sources and nearby agricultural sources, 92% of the source identified OC was due to POC with 8% being due to source identified SOC (Table 2). However, the combined source identified OC (SOC + POC) averaged only 45% of the measured $\text{PM}_{2.5}$ OC, a result which is also similar to the SOAR campaign POC and SOC CMB analysis using similar organic tracers (Stone et al., 2009).

The combination of sources of POC and SOC from source attribution methods (CMB and MF) constrained by the ^{14}C values can be used to determine the degree to which missing carbon is more likely to be due to contemporary or fossil sources (Tables 1 and 2). The individual run-by-run determination of the TOC_{CC} is given in Table 1 and is found to range from 0.61 to $6.88 \mu\text{gC m}^{-3}$. The ^{14}C values indicate that the total OC fraction is at least 50% due to contemporary carbon sources. The contemporary carbon component from the tracer-based source attribution includes POC from vegetative detritus as a primary source, and SOC as secondary sources from biogenic emission of isoprene and α -pinene.

In a best case scenario, the undetermined OC for each type of carbon type (TOC_{CC} or TOC_{FC}) will be a positive value. The SOC contributions from biogenic emissions are extremely low and the undetermined fraction is high for the TOC_{CC} . Vegetative detritus, the only biogenic POC source, is also characteristically small. However, F CC correlates with vegetative detritus ($r^2 = 0.65$), with the next highest correlation for F CC with SOC from mono-terpenes ($r^2 = 0.5$); this may indicate that the n-alkanes measured here (which have a high odd-to-even predominance) are representing more biogenic carbon mass than is

included in the profile. This is in contrast with the results for CalNex Pasadena where the n-alkanes had a low correlation with the nonfossil OC (Pearson Correlation Coefficient of 0.09) (Zotter et al., 2013). For all samples, the undetermined TOC_{CC} was greater than the sum of the apportioned contemporary carbon sources. On average the concentration of TOC_{CC} that could not be attributed to a primary or secondary source was $2.80 \mu\text{gC m}^{-3}$. This is of significant interest, as it indicates a missing biogenic source of OC in the San Joaquin Valley. For example, dairy operations potentially produce TOC_{CC} , which most likely also include heteroatoms such as nitrogen or sulfur. Other vegetative agricultural emissions might also serve as unattributed primary sources of TOC_{CC} . While these may be some undetermined primary sources in addition to vegetative detritus, it is more likely that unknown sources are of secondary origin. There are several possible sources for this undetermined TOC_{CC} including oxidation products of dairy operation and agricultural emissions, food cooking and soil dust. Quantification of these sources will be required before source attribution methods can become more reliable in areas impacted by agricultural and cooking activities. Heo et al. reported higher contributions from a primary biogenic factor when estimated utilizing PMF apportionment, over 20% at two sites in the Los Angeles basin, as compared to CMB; Heo et al. was clear that this likely includes multiple agricultural and cooking components (2013).

A similar analysis was performed for the fossil carbon, TOC_{FC} , which is associated with anthropogenically-derived POC and PEC from motor vehicle exhaust and aromatic SOC. The TOC_{FC} includes contributions of POC and PEC resulting from the anthropogenically-derived inputs of compressed ignition (diesel), spark ignition, and lubricating oil-impacted motor vehicle exhaust combined with SOC produced from toluene and two-ring PAH products (Table 1 and 2) The three combustion derived motor vehicle exhaust source contributions are far more significant than the two secondary sources from aromatic and 2-ring PAH oxidation. The two secondary sources contribute only 3.5% on average to the total source attributed TOC_{FC} , which ranges from 0.09 to $5.29 \mu\text{gC m}^{-3}$ averaging $2.62 \mu\text{gC m}^{-3}$. The source attributed TOC_{FC} can then be compared to the daily values of the TOC_{FC} which range from 1.16 to $5.65 \mu\text{gC m}^{-3}$. When combined with the source attributed TOC_{FC} , the undetermined TOC_{FC} ranged from -1.40 to $3.00 \mu\text{gC m}^{-3}$. The negative value of undetermined TOC_{FC} results for cases when the sum of the fossil POC, PEC and SOC is greater than the radiocarbon-apportioned TOC_{FC} ; nine of 34 samples had negative undetermined TOC_{FC} fractions.

While the averages for the fossil and contemporary carbon components are nearly identical, the TOC_{CC} levels shows greater variability than the TOC_{FC} (3.6 ± 1.6 and $3.3 \pm 1.2 \mu\text{g m}^{-3}$, respectively). This may be due to a strong meteorological influence on eastern downslope air flow injecting biogenic emissions into the Bakersfield airshed. The TOC_{FC} has variability over the course of the campaign, but no discernable trend in the radiocarbon or tracer-based results. However, the TOC_{CC} is increasing over the course of the campaign, which is apparent in Table 1 and Figure 2 and has a slope of $0.12 \mu\text{g m}^{-3}$ per day ($r^2 = 0.63$). The beginning of the campaign is dominated by fossil carbon (5/19 through 5/28), while the end of the campaign is dominated by contemporary carbon (6/15-6/26). The slope for TOC_{FC} is lower over the course of the campaign, and does not have a strong correlation coefficient ($m = 0.05 \mu\text{g m}^{-3}$ per day; $r^2 = 0.26$). The slope for TOC_{CC} over the course of the campaign

was actually quite similar to the slope of increasing $PM_{2.5}$ over the same period ($m = 0.19 \mu g m^{-3}$ per day; $r^2 = 0.52$), which was reported by the California Air Resources Board for an air monitoring site at the Bakersfield airport (35.32464 N, -118.99763W; <https://www.arb.ca.gov/adam/weekly/weekly2.php>). The TOC_{CC} also had a higher correlation with $PM_{2.5}$ ($n=12$; $r^2 = 0.35$) than did TOC_{FC} ($n = 12$; $r^2 = 0.29$). This variability in the fossil and modern contributions highlights the need for longer campaigns: over the five weeks of the CalNex Bakersfield campaign, the fossil contribution ranged from 32 to 66%.

4.1. Internal consistency from comparison of similar methods in different locations

The present study is one of several studies to apportion primary and secondary sources from molecular tracers to establish the origin of organic carbon in ambient aerosol. The primary sources are apportioned using CMB or PMF approaches (Fujita et al., 1994; Jaekels et al., 2007). while the MF approach is used to apportion secondary sources of OC. The reliability of these apportioning methods depends on the representative nature of experiments determining profiles (POC) or mass fractions (SOC) for individual sources. This is especially true for SOC whereby the extent of the atmospheric processing time can be difficult to reproduce in the laboratory. Moreover, the formation of tracer species in many cases depends on specific conditions of the oxidants present in the atmosphere. As a result, the measurements generally are considered best estimates of sources present. For example, in the Western U.S., emissions from monoterpenes other than α -pinene (e.g., d-limonene) having substantially higher aerosol yields with similar GC-MS tracer masses (Jaoui et al., 2006) may dominate. In such a case, the monoterpene fraction may be substantially underestimated.

Limitations of the SOC tracer technique also apply to anthropogenic hydrocarbons. For aromatic hydrocarbons, the SOC contribution is derived from the mass fraction of a single aromatic hydrocarbon – toluene. In this case, the atmospheric oxidations of the three xylene isomers are known to lead to the same tracer compound (Kleindienst et al., 2007). In addition, tracer species for several compound classes like high molecular weight alkanes have not been examined to a significant extent.

Secondary sources also come from a biogenic component and anthropogenic component. In this case, the biogenic component comprises 60% of the total SOC with the anthropogenic component comprising the remaining 40%. However, the average SOC comprises only 8% of the total OC apportioned in this study. In several studies in the Eastern U.S. using the same method and analysis approach, the biogenic component of SOC has tended to dominate the total SOC attributed to secondary sources. In Lewandowski et al. (2008) during a similar period of the year (May–June), industrialized cities, such as E. St. Louis and Detroit, showed higher levels of POC than SOC, and in E. St. Louis, in approximately the same proportion. By contrast, Bondville, IL showed modestly higher SOC than POC. However, in the St. Louis study, the absolute levels of POC and SOC components were considerably higher.

Kleindienst et al. (2010) examined four sites in the southeastern U.S. in the SEARCH network during May 2008, and found again for an industrialized city (Birmingham, AL), POC was substantially higher than SOC due mainly to very high diesel exhaust levels. By

contrast, a rural site 30 miles southwest of Birmingham, Centreville, AL showed modestly greater SOC than POC (60:40) for atmospheric OC levels of $7.3 \mu\text{g m}^{-3}$ and approximately one-third of the carbon was not identified using these techniques. Notably, the regional background levels of SOC were essentially the same for the two sites. For the POC and SOC analysis in Riverside, CA during SOAR in 1995, the average POC contribution was 21%, the average SOC contribution was 26% and the undetermined OC was 53% on average (Stone et al., 2009); these results are for later in the summer in Southern California and have a similar undetermined fraction, but a higher contribution from α -pinene SOC. Finally, in a less constrained study, Kleindienst et al. (2007) found that the SOC component over the May–June period in Research Triangle Park, NC in 2003 showed approximately equal levels of SOC and ‘other’ OC. Again, absolute values of SOC had far higher absolute concentrations than in Bakersfield.

4.2. External consistency compared to independent techniques at CalNex Bakersfield

A great challenge in understanding sources of ambient aerosol is synthesizing results from numerous experiments and endpoints into a consistent view of ambient aerosol. This is especially challenging in atmospheres where a wide range of physical phenomena influence measurement metrics, e.g., aerosol composition, size distribution, etc. CalNex-Bakersfield provides a common air environment to test various hypotheses regarding the details of aerosol sources and composition. Thus, a number of other studies were conducted during CalNex Bakersfield and the constraints from the present study is expected to provide insight into the nature of sources leading to particulate organic carbon in $\text{PM}_{2.5}$.

The approach in the present work uses the ^{14}C data together with POC and SOC source attribution methods to determine the degree to which the anthropogenic and biogenic components contribute to the aerosol burden. If the anthropogenic component is considered first, Table 2 shows that the average of the TOC_{FC} is $3.29 \mu\text{g m}^{-3}$ of which $2.62 \mu\text{g m}^{-3}$ can be accounted for by the primary and secondary attributed total organic carbon. A simple mass balance thus yields $0.69 \mu\text{g m}^{-3}$ or 21% of the fossil carbon is undetermined.

Liu et al. (2012) during the same period in Bakersfield indicates from Fourier Transform Infrared (FTIR) measurements secondary organic aerosol dominates OC, with 80-90% estimated contribution; within that secondary fraction, OC from motor vehicle exhaust including primary and secondary products from alkane and aromatic hydrocarbons, were estimated to contribute 65% of OM. This high contribution from motor vehicles, is similar to our results indicating high lubricating oil impacted exhaust, however, our MF apportionment did not capture this SOC. It is possible that non-methylated and fused aromatic hydrocarbon, with naphthalene likely to be the greatest contributor, might make up a portion of the undetermined fossil TOC, but that cannot be determined with the source techniques in the current study. The undetermined TOC_{FC} is quite small on average ($0.69 \mu\text{g m}^{-3}$), however, it may be that the hopanes (the dominant tracer for lubricating oil-impacted motor vehicle exhaust) are not oxidized as rapidly as other fractions of motor vehicle exhaust and the fraction apportioned here to motor vehicle POC is actually representing some aged aerosol and SOC as well. It also may reflect a difference in apportionment based on lower versus higher volatility components. The current study in Bakersfield and the Heo et al. study in

Central LA and Riverside apportioned roughly 30% of the OC to mobile sources using CMB and PMF which were based off hopane and high molecular weight PAHs. Zhao et al. (2013) utilized higher volatility organic compounds, as mentioned earlier, and attributed 15% to local primary sources (likely mobile sources, oil and gas extraction activities and agricultural), 72% to SOA (the split between biogenic and anthropogenic could not be well defined) and 13% mixed organic aerosol. Zotter et al. had also measured hopanes and found a strong correlation with fossil OC ($r = 0.76$), indicating that hopanes could also strongly describe OC in CalNex Pasadena. The current study was not able to apportion the fossil SOC that was noted in other CalNex studies (Liu et al, 2012; Zhao et al. 2013).

Both Zotter et al. (2013) at Pasadena and Zhao et al. (2013) at Bakersfield indicated that secondary biogenic SOC maybe responsible for their measured nonfossil and SOA components, respectively, however, the current study does not measure significant contributions from isoprene or α -pinene SOC. Thus, the TOC_{CC} measured in the current study is most likely secondary, but from other contemporary sources potentially including aged/oxidized biomass burning emissions or SOC from other agricultural emissions. The Liu et al. (2012) study also reported a 10% contribution from vegetative detritus which is confirmed in the current study where vegetative detritus by CMB comprises 9.8% of the average OC for the campaign. The low contribution from biogenic SOC was also confirmed by Liu et al. (2012), which estimated less than 10% from nighttime oxidation of biogenic precursors.

Comparison of the present findings can also be made with other higher time resolution marker studies such as from measurements from the FTIR and Aerosol Mass Spectrometry (AMS) techniques. Previous studies, (Kleindienst et al., 2010; Blanchard et al., 2008) have shown that the secondary component of ambient organic aerosol is observed to be a regional component largely constant over urban and adjoining rural regions.

From a functional group analysis of the composition of $\text{PM}_{2.5}$, Liu et al. (2012) found an organic matter mass of $3.24 \pm 1.42 \mu\text{g m}^{-3}$. AMS mass data, adjusted for limitations in particle size cuts, give masses over the same period of $4.23 \pm 2.75 \mu\text{g m}^{-3}$. These masses are significantly lower than the average mass reported in this study. However, AMS measures $\text{PM}_{1.0}$ while the present study is $\text{PM}_{2.5}$.

5. CONCLUSIONS

1. The average OC measured during the CalNex-Bakersfield study was $6.42 \mu\text{g m}^{-3}$. The apportioned OC, which was 46% of the measured OC, was mostly of primary origin (92%) with SOC constituting a minor portion (8%). The major primary sources of OC were from vegetative detritus (9.8%), diesel (2.3%), gasoline (<1.0%), and lubricating oil impacted motor vehicle exhaust (30%); measured secondary sources resulted from isoprene (1.5%), α -pinene (<1.0%), toluene (<1.0%), and naphthalene (<1.0%, as an upper limit) contributions.
2. Constraints offered by radiocarbon apportionment together with primary and secondary OC sources based on molecular markers suggest that anthropogenic sources can be largely accounted for within 25% and are mostly primary by this

analysis. By comparison with other CalNex studies, the unapportioned fossil OC may be due to condensable products from aromatic and long-chained alkane oxidation products. These CalNex results highlight that additional organic tracers need to be developed for fossil SOC sources.

3. A majority of the contemporary TOC (>75%) is undetermined by either primary or secondary tracer apportionment. The dominant contemporary source by CMB and MF methods was vegetative detritus, but this only accounted for 10%, on average. The results from this study indicate that additional primary and secondary source assessment is needed in areas which could be impacted from additional contemporary carbon sources including agricultural activity, cooking, and SOA from biomass burning.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- Certificate of Analysis for Standard Reference Material 1649b Urban Dust. C. S. Division: 19.
- Ahlm L, Liu S, Day DA, Russell LM, Weber R, Gentner DR, Goldstein AH, DiGangi JP, Henry SB, Keutsch FN, VandenBoer TC, Markovic MZ, Murphy JG, Ren X, Scheller S. Formation and growth of ultrafine particles from secondary sources in Bakersfield, California. *J Geophys Res.* 2012; 117:1–13. DOI: 10.1029/2011JD017144
- Baker KR, Carlton AG, Kleindienst TE, Offenberg JH, Beaver MR, Gentner DR, Goldstein AH, Gilman JB, de Gouw JA, Hayes PL, Jimenez JL, Woody M, Pye HOT, Kelly JT, Jaoui M, Lewandowski M, Lin YH, Rubitschun CL, Surratt JD. Gas and aerosol carbon in California: comparison of measurements and model predictions in Pasadena and Bakersfield. *Atmos Chem Phys.* 2015; 15:5243–5258.
- Birch ME, Cary RA. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci Technol.* 1996; 25:221–241.
- Blanchard CL, Hidy CM, Tanenbaum S, Edgerton E, Hartsell B, Jansen J. Carbon in Southeastern U.S. aerosol particles: Empirical estimates of secondary organic aerosol formation. *Atmos Environ.* 2008; 42:6710–6720.
- Barrett TE, Robinson EM, Usenko S, Sheesley RJ. Source Contributions to Wintertime Elemental and Organic Carbon in the Western Arctic Based on Radiocarbon and Tracer Apportionment. *Environmental Science & Technology.* 2015; doi: 10.1021/acs.est.5b03081
- Chan AWH, Isaacman G, Wilson KR, Worton DR, Ruehl CR, Nah T, Gentner DR, Dallmann TR, Kirchstetter TW, Harley RA, Gilman JB, Kuster WC, deGouw JA, Offenberg JH, Kleindienst TE, Lin YH, Rubitschun CL, Surratt JD, Hayes PL, Jimenez JL, Goldstein AH. Detailed chemical characterization of unresolved complex mixtures in atmospheric organics: Insights into emission sources, atmospheric processing, and secondary organic aerosol formation. *J Geophys Res.* 2013; 118:1–14. DOI: 10.1002/jgrd.50533

- Charlson RJ, Schwartz SE, Hales JM, Cess RD, Coakley JA Jr, Hansen JE, Hofmann DJ. Climate forcing by anthropogenic aerosols. *Science*. 1992; 255:423–430. [PubMed: 17842894]
- Chow JC, Chen LWA, Watson JG, Lowenthal DH, Magliano KA, Turkiewicz K, Lehrman DE. PM_{2.5} chemical composition and spatiotemporal variability during the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS). *J Geophys Res*. 2006; 111(D10)
- Claeys M, Szmigielski R, Kourtchev I, Van Der Veken P, Vermaylen R, Maenhaut W, Jaoui M, Kleindienst TE, Lewandowski M, Offenberg JH, Edney EO. Hydroxydicarboxylic acids: Markers for secondary organic aerosol from the photooxidation of α -pinene. *Environ Sci Technol*. 2007; 41:1628–1634. [PubMed: 17396652]
- Docherty KS, Stone EA, Ulbrich IM, DeCarlo PF, Snyder DC, Schauer JJ, Peltier RE, Weber RJ, Murphy SM, Seinfeld JH, Grover BD, Eatough DJ, Jimenez JL. Apportionment of Primary and Secondary Organic Aerosols in Southern California during the 2005 Study of Organic Aerosols in Riverside (SOAR-1). *Environ Sci Technol*. 2008; 42:7655–7662. [PubMed: 18983089]
- Fine PM, Cass GR, Simoneit BRT. Organic compounds in biomass smoke from residential wood combustion: Emission characterization at a continental scale. *J Geophys Res*. 2002; 107:8349.
- Fujita EM, Watson JG, Chow JC, Lu ZQ. Validation of the chemical mass-balance receptor model applied to hydrocarbon source apportionment in the Southern California Air-Quality study. *Environ Sci Technol*. 1994; 28:1633–1649. [PubMed: 22176366]
- Gentner DR, Ford TB, Guha A, Boulanger K, Brioude J, Angevine WM, deGouw JA, Warneke C, Gilman JB, Ryerson TB, Peischl J, Meinardi S, Blake DR, Atlas E, Lonneman WA, Kleindienst TE, Beaver MR, St Clair JM, Wennberg PO, VandenBoer TC, Markovic MZ, Murphy JG, Harley RA, Goldstein AH. Emissions of organic carbon and methane from petroleum and dairy operations in California's San Joaquin Valley. *Atmos Chem Phys*. 2014; 14:4955–4978.
- Haywood J, Boucher O. Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: a review. *Reviews of Geophysics*. 2000; 38:513–543.
- Heo J, Dulger M, Olson MR, McGinnis JE, Shelton BR, Matsunaga A, Sioutas C, Schauer JJ. Source apportionments of PM_{2.5} organic carbon using molecular marker Positive Matrix Factorization and comparison of results from different receptor models. *Atmospheric Environment*. 2013; 73:51–61. <http://dx.doi.org/10.1016/j.atmosenv.2013.03.004>.
- Jaekels JM, Bae MS, Schauer JJ. Positive Matrix Factorization (PMF) analysis of molecular marker measurements to quantify the sources of organic aerosols. *Environ Sci Technol*. 2007; 41:5763–5769. [PubMed: 17874784]
- Jaoui M, Kleindienst TE, Lewandowski M, Edney EO. Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic and/or hydroxyl groups. 1. Method development. *Anal Chem*. 2004; 76:4765–4778. [PubMed: 15307788]
- Jaoui M, Kleindienst TE, Lewandowski M, Offenberg JH, Edney EO. Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic groups: Organic tracer compounds from monoterpenes. *Environ Sci Technol*. 2005; 39:5661–5673. [PubMed: 16124301]
- Jimenez JL, Canagaratna MR, Donahue NM, Prevot ASH, Zhang Q, Kroll JH, DeCarlo PF, Allan JD, Coe H, Ng NL, Aiken AC, Docherty KS, Ulbrich IM, Grieshop AP, Robinson AL, Duplissy J, Smith JD, Wilson KR, Lanz VA, Hueglin C, Sun YL, Tian J, Laaksonen A, Raatikainen T, Rautiainen J, Vaattovaara P, Ehn M, Kulmala M, Tomlinson JM, Collins DR, Cubison MJ, Dunlea EJ, Huffman JA, Onasch TB, Alfarra MR, Williams PI, Bower K, Kondo Y, Schneider J, Drewnick F, Borrmann S, Weimer S, Demerjian K, Salcedo D, Cottrell L, Griffin R, Takami A, Miyoshi T, Hatakeyama S, Shimono A, Sun JY, Zhang YM, Dzepina K, Kimmel JR, Sueper D, Jayne JT, Herndon SC, Trimborn AM, Williams LR, Wood EC, Middlebrook AM, Kolb CE, Baltensperger U, Worsnop DR. Evolution of organic aerosols in the atmosphere. *Science*. 2009; 326:1525–1529. [PubMed: 20007897]
- Kleindienst TE, Jaoui M, Lewandowski M, Offenberg JH, Lewis CW, Bhawe PV, Edney EO. Estimates of the Contributions of Biogenic and Anthropogenic Hydrocarbons to Secondary Organic Aerosol at a Southeastern US Location. *Atmos Environ*. 2007; 41:8288–8300.
- Kleindienst TE, Lewandowski M, Offenberg JH, Edney EO, Jaoui M, Zheng M, Ding X, Edgerton ES. Contribution of primary and secondary sources to organic aerosol and PM_{2.5} at SEARCH Network Sites. *J Air Waste Manage Assoc*. 2010; 60:1388–1399.

- Kleindienst TE, Jaoui M, Lewandowski M, Offenberg JH, Docherty KS. The formation of SOA and chemical tracer compounds from the photooxidation of naphthalene and its methyl analogs in the presence and absence of nitrogen oxides. *Atmos Chem Phys*. 2012; 12:8711–8726.
- Lemire KR, Allen DT, Klouda GA, Lewis CW. Fine particulate matter source attribution for Southeast Texas using $^{14}\text{C}/^{13}\text{C}$ ratios. *J Geophys Res*. 2002; 107:4613.
- Lewandowski M, Jaoui M, Offenberg JH, Kleindienst TE, Edney EO, Sheesley RJ, Schauer JJ. Primary and Secondary Contributions to Ambient PM in the Midwestern United States. *Environ Sci Technol*. 2008; 42:3303–3309. [PubMed: 18522110]
- Lewandowski M, Piletic IR, Kleindienst TE, Offenberg JH, Beaver MR, Jaoui M, Docherty KS, Edney EO. Secondary organic aerosol characterization at field sites across the United States during the spring-summer period. *Int J Environ Anal Chem*, SI. 2013; 93:1084–1103.
- Lewis CW, Klouda GA, Ellenson WD. Radiocarbon measurement of the biogenic contribution to summertime PM-2.5 ambient aerosol in Nashville, TN. *Atmos Environ*. 2004; 38:6053–6061.
- Lewis CW, Stiles DC. Radiocarbon content of PM_{2.5} ambient aerosol in Tampa, FL. *Aerosol Sci Technol*. 2006; 40:189–196.
- Liu D, Li J, Zhang YL, Xu Y, Liu X, Ding P, Shen CD, Chen YJ, et al. The Use of Levoglucosan and Radiocarbon for Source Apportionment of PM₂₅ Carbonaceous Aerosols at a Background Site in East China. *Environmental Science & Technology*. 2013; 47:10454–10461. DOI: 10.1021/es401250k [PubMed: 23957240]
- Liu S, Ahlm L, Day DA, Russell LM, Zhao Y, Gentner DR, Weber RJ, Goldstein AH, Jaoui M, Offenberg JH, Kleindienst TE, Rubitschun C, Surratt JD, Sheesley RJ, Scheller S. Secondary organic aerosol formation from fossil fuel sources contribute the majority of summertime organic mass at Bakersfield. *J Geophys Res*. 2012; 117:D00V26.doi: 10.1029/jgrd.018170
- Lough GC, Christensen CG, Schauer JJ, Tortorelli J, Mani E, Lawson DR, Clark NN, Gabele PA. Development of molecular marker source profiles for emissions from on-road gasoline and diesel vehicle fleets. *J Air Waste Manage Assoc*. 2007; 57:1190–1199.
- Lough GC, Schauer JJ. Sensitivity of source apportionment of urban particulate matter to uncertainty in motor vehicle emissions profiles. *J Air Waste Manage Assoc*. 2007; 57:1200–1213.
- May AA, Saleh R, Hennigan CJ, Donahue NM, Robinson AL. Volatility of Organic Molecular Markers Used for Source Apportionment Analysis: Measurements and Implications for Atmospheric Lifetime. *Environmental Science & Technology*. 2012; 46:12435–12444. [PubMed: 23013599]
- Nallathamby PD, Lewandowski M, Jaoui M, Offenberg JH, Kleindienst TE, Rubitschun C, Surratt JD, Usenko S, Sheesley RJ. Qualitative and quantitative assessment of unresolved complex mixtures in PM_{2.5} of Bakersfield, CA. *Atmos Environ*. 2014; 98:368–375.
- Offenberg JH, Lewis CW, Lewandowski M, Jaoui M, Kleindienst TE, Edney EO. Contributions of toluene and α -pinene to SOA formed in an irradiated toluene/ α -pinene/NO_x/air mixture: Comparison of results using ^{14}C content and SOA organic tracer methods. *Environ Sci Technol*. 2007; 41:3972–3976. [PubMed: 17612177]
- Parish, DD. Synthesis of Policy Relevant Findings from the CalNex 2010 Field Study. California Air Resources Board; 2014. p. 210
- Pavuluri CM, Kawamura K, Uchida M, Kondo M, Fu PQ. Enhanced modern carbon and biogenic organic tracers in Northeast Asian aerosols during spring/summer. *Journal of Geophysical Research-Atmospheres*. 2013; 118:2362–2371. DOI: 10.1002/jgrd.50244
- Pearson A, McNichol AP, Schneider RJ, von Reden KF. Microscale AMS ^{14}C measurement at NOSAMS. *Radiocarbon*. 1998; 40:61–75.
- Piletic IR, Offenberg JH, Olson DA, Jaoui M, Krug J, Lewandowski M, Turlington JM, Kleindienst TE. Constraining carbonaceous aerosol sources in a receptor model using combined ^{14}C , redox species, organic tracers, and elemental/organic carbon measurements. *Atmos Environ*. 2013; 80:216–225.
- Pope CA III, Dockery DW. Health effects of fine particulate air pollution: lines that connect. *J Air Waste Manage Assoc*. 2006; 56:709–742.
- Pope CA III, Ezzati MJ, Dockery DW. Fine-particulate air pollution and life expectancy in the United States. *N Engl J Med*. 2009; 360:376–386. [PubMed: 19164188]

- Presto AA, Miracolo MA, Kroll JH, Worsnop DR, Robinson AL, Donahue NM. Intermediate-volatility organic compounds: A potential source of ambient oxidized organic aerosol. *Environ Sci Technol*. 2009; 43:4744–4749. [PubMed: 19673260]
- Ramanathan V, Crutzen PJ, Kiehl JT, Rosenfeld D. Aerosols, climate, and the hydrological cycle. *Science*. 2001; 294:2119–2124. [PubMed: 11739947]
- Reff A, Bhawe PV, Simon H, Pace TG, Pouliot GA, Mobley JD, Houyoux M. Emissions Inventory of PM_{2.5} Trace Elements across the United States. *Environ Sci Technol*. 2009; 43:5790–5796. [PubMed: 19731678]
- Roberts ML, Burton JR, Elder KL, Longworth BE, McIntyre CP, von Reden KF, Han BX, Rosenheim BE, Jenkins WJ, Galutschek E, McNichol AP. A high-performance 14C accelerator mass spectrometry system. *Radiocarbon*. 2010; 52:228–235.
- Robinson AL, Donahue NM, Shrivastava MK, Weitkamp EA, Sage AM, Grieshop AP, Lane TE, Pierce JR, Pandis SN. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science*. 2007; 315:1259–1262. [PubMed: 17332409]
- Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of Fine Organic Aerosol. 5. Natural Gas Home Appliances. *Environ Sci Technol*. 1993a; 27:2736–2744.
- Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of Fine Organic Aerosol. 4. Particulate Abrasion Products from Leaf Surfaces of Urban Plants. *Environ Sci Technol*. 1993b; 27:2700–2711.
- Roy AA, Wagstrom KM, Adams PJ, Pandis SN, Robinson AL. Quantification of the effects of molecular marker oxidation on source apportionment estimates for motor vehicles. *Atmospheric Environment*. 2011; 45:3132–3140. DOI: 10.1016/j.atmosenv.2011.03.020
- Schauer JJ, Rogge WF, Hildemann LM, Mazurek MA, Cass GR. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos Environ*. 1996; 30:3837–3855.
- Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT. Measurement of Emissions from Air Pollution Sources. 1. C-1 through C-29 Organic Compounds from Meat Charbroiling. *Environ Sci Technol*. 1999a; 33:1566–1577.
- Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT. Measurement of emissions from air pollution sources. 5. C-1-C-32 Organic Compounds from Gasoline-Powered Motor Vehicles. *Environ Sci Technol*. 2002; 36:1169–1180. [PubMed: 11944666]
- Sheffield AE, Gordon GE, Currie LA, Reiderer GE. Organic, elemental and isotopic tracers of air pollution sources in Albuquerque, NM. *Atmos Environ*. 1994; 28:1371–1384.
- Sisler JF, Malm WC. The relative importance of aerosols to spatial and seasonal trends of impaired visibility in the United States. *Atmos Environ*. 2004; 28:851–862.
- Stone EA, Zhou J, Snyder DC, Rutter AP, Mieritz M, Schauer JJ. A comparison of summertime secondary organic aerosol source contributions at contrasting urban locations. *Environ Sci Technol*. 2009; 43:3448–54. [PubMed: 19544838]
- Tkacik DS, Presto AA, Donahue NM, Robinson AL. Secondary organic aerosol formation from intermediate-volatility organic compounds: Cyclic, linear, and branched alkanes. *Environ Sci Technol*. 2012; 46:8773–8779. [PubMed: 22823284]
- Watson JG, Cooper JA, Huntzicker JJ. The effective variance weighting for least squares calculations applied to the mass balance receptor model. *Atmos Environ*. 1984; 18:1347–1355.
- Yu J, Griffin RJ, Cocker DR, Flagan RC, Seinfeld JH. Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres. *Geophys Res Lett*. 1999; 26:1145–1148.
- Zhang Y, Sheesley RJ, Schauer JJ, Lewandowski M, Jaoui M, Offenberg JH, Kleindienst TE, Edney EO. Source apportionment of primary and secondary organic aerosol using Positive Matrix Factorization (PMF) of molecular markers. *Atmos Environ*. 2009; 43:5567–5574.
- Zhang YL, Huang RJ, El Haddad I, Ho KF, Cao JJ, Han Y, Zotter P, Bozzetti C, et al. Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013. *Atmospheric Chemistry and Physics*. 2015; 15:1299–1312. DOI: 10.5194/acp-15-1299-2015
- Zhao YL, Kreisberg NM, Worton DR, Isaacman G, Gentner DR, Chan AWH, Weber RJ, Liu S, et al. Sources of organic aerosol investigated using organic compounds as tracers measured during CalNex in Bakersfield. *Journal of Geophysical Research-Atmospheres*. 2013; 118:11388–11398.

- Zheng M, Cass GR, Schauer JJ, Edgerton ES. Source apportionment of PM_{2.5} in the Southeastern United States using solvent-extractable organic compounds as tracers. *Environ Sci Technol* 2002; 36:2361–2371.
- Zheng M, Cass GR, Ke L, Wang F, Schauer JJ, Edgerton ES, Russell AG. Source Apportionment of Daily Fine Particulate Matter at Jefferson Street, Atlanta, GA, during the Summer and Winter. *J Air Waste Manage Assoc.* 2007; 57:228–242.
- Zotter PI, El-Haddad I, Zhang YL, Hayes PL, Zhang XL, Lin YH, Wacker L, Schnelle-Kreis J, Abbaszade G, Zimmermann R, Surratt JD, Weber R, Jimenez JL, Szidat S, Baltensperger U, Prevot ASH. Diurnal cycle of fossil and nonfossil carbon using radiocarbon analyses during CalNex. *J Geophys Res.* 2014; 119:6818–6835. DOI: 10.1002/2013jd021114

Figure 1.

Contributions of primary and secondary organic carbon contributions (POC and SOC, respectively) to the total OC as estimated using chemical tracers by chemical mass balance (CMB) and mass fraction (MF). Spark ignition, compression ignition and lubricating oil impacted are the three types of motor vehicle exhaust (MVE).

Figure 2.

Fossil and contemporary total organic carbon (TOC) with summed source attribution during CalNex in Bakersfield, CA from 5/19 - 6/26/2010. Primary sources from chemical mass balance (CMB) and secondary sources from chemical mass fraction (MF) have been split into fossil and contemporary components. These components are compared to the fossil and contemporary TOC split based on the ¹⁴C data.

Table 1

Primary and secondary carbon sources to total organic carbon (TOC) during CalNex 2010 in Bakersfield, CA.

Sample	Veg detritus (POC)	CIMV (POC)	SIMV (POC)	LMV (POC)	Isoprene (SOC)	α -pinene (SOC)	Toluene (SOC)	2 ring PAHs (SOC)	TOC _{CC}	POC+SOC OC _{CC}	TOC _{FC}	POC+SOC OC _{FC}	POC+PEC+SOC TOC _{FC}
19-May-10	0.116	0.138	0.119	0.366	0.040	0.053	0.042	0.029	1.77	0.209	2.34	0.694	1.085
20-May-10	0.181	0.104	0.160	0.532	0.028	0.060	0.048	0.022	1.80	0.269	2.02	0.866	1.196
22-May-10	0.422	0.078	0.058	0.942	0.271	0.000	0.000	0.111	1.99	0.693	2.01	1.190	1.430
23-May-10	0.309	0.068	0.046	1.480	0.030	0.005	0.015	0.017	NA		NA		
24-May-10	0.536	0.112	0.102	3.221	0.052	0.013	0.042	0.024	2.16	0.601	2.48	3.500	3.881
25-May-10	0.436	0.127		3.202	0.072	0.012	0.027	0.005	1.69	0.520	2.68	3.362	3.751
26-May-10	0.192	0.059	0.052	1.226	0.016	0.003	0.007	0.002	0.61	0.211	1.16	1.346	1.536
27-May-10	0.353	0.076	0.132	1.792	0.044	0.003	0.007	0.003	1.08	0.400	1.81	2.010	2.280
28-May-10	0.338	0.071		1.259	0.015	0.006	0.014	0.002	1.32	0.359	1.74	1.345	1.545
29-May-10					0.056	0.020	0.061	0.028	3.19	0.076	3.09	0.089	0.089
30-May-10	0.268	0.092		2.343	0.076	0.049	0.115	0.063	4.18	0.393	3.85	2.613	2.904
31-May-10	0.442	0.098		3.018	0.115	0.051	0.046	0.027	3.28	0.608	3.46	3.189	3.499
1-Jun-10	0.438	0.145	0.002	1.105	0.019	0.005	0.014	0.020	2.31	0.462	2.51	1.286	1.677
2-Jun-10	0.399	0.127		1.241					3.38		2.63		
3-Jun-10	0.431	0.138		2.540	0.058	0.020	0.059	0.044	2.32	0.509	3.03	2.781	3.181
4-Jun-10	0.745	0.077		2.035	0.071	0.028	0.035	0.037	3.31	0.844	3.88	2.183	2.423
5-Jun-10	0.397	0.140	0.006	1.853	0.061	0.046	0.045	0.053	2.57	0.504	4.10	2.098	2.497
6-Jun-10	0.663	0.099		3.213	0.071	0.061	0.028	0.067	3.25	0.795	4.52	3.407	3.718
7-Jun-10	0.767	0.128	0.015	1.899	0.086	0.060	0.045	0.039	3.92	0.913	3.29	2.126	2.496
8-Jun-10	0.788	0.201		2.215	0.135	0.076	0.071	0.073	4.09	0.999	5.46	2.560	3.120
9-Jun-10	0.940	0.206		4.399	0.104	0.046	0.044	0.024	5.24	1.090	5.65	4.673	5.293
10-Jun-10	0.644	0.097		2.327	0.071	0.024	0.027	0.013	3.49	0.739	2.16	2.464	2.764
11-Jun-10	0.963	0.148		2.927	0.054	0.042	0.033	0.018	3.34	1.059	3.92	3.126	3.567
12-Jun-10	0.984	0.159	0.050	2.067	0.086	0.062	0.064	0.014	5.43	1.132	3.45	2.354	2.813
13-Jun-10	1.569	0.194	0.057	2.054	0.075	0.060	0.054	0.018	6.88	1.704	3.29	2.377	2.937
14-Jun-10	0.688	0.181	0.108	1.714	0.142	0.112	0.087	0.040	4.44	0.942	5.22	2.131	2.651
15-Jun-10	0.771	0.195	0.028	1.483	0.195	0.089	0.095	0.039	4.59	1.055	3.69	1.840	2.380
16-Jun-10	0.619	0.198	0.054	2.631	0.252	0.096	0.165	0.043	3.64	0.967	3.35	3.090	3.670

Sample	Veg detritus (POC)	CIMV (POC)	SIMV (POC)	LIMV (POC)	Isoprene (SOC)	α -pinene (SOC)	Toluene (SOC)	2 ring PAHs (SOC)	TOC _{CC}	POC+SOC OC _{CC}	TOC _{FC}	POC+SOC OC _{FC}	POC+PEC+SOC TOC _{FC}
17-Jun-10	0.883	0.185	0.071	2.501	0.126	0.071	0.054	0.035	5.59	1.080	3.21	2.846	3.386
18-Jun-10	0.898	0.208	0.043	2.235	0.143	0.080	0.078	0.043	4.85	1.121	3.42	2.607	3.187
19-Jun-10	0.887	0.129	0.022	1.330	0.127	0.050	0.055	0.018	3.49	1.064	2.30	1.554	1.924
20-Jun-10	0.553	0.104	0.027	1.677	0.087	0.067	0.065	0.024	3.94	0.707	2.37	1.898	2.208
21-Jun-10	0.621	0.178	0.051	1.737	0.196	0.150	0.152	0.063	4.26	0.967	3.99	2.181	2.681
22-Jun-10	0.841	0.293	0.050	1.288	0.108	0.113	0.077	0.060	6.67	1.062	3.65	1.768	2.548
23-Jun-10	1.191	0.268	0.052	1.607	0.151	0.188	0.137	0.089	6.28	1.530	5.12	2.152	2.882
24-Jun-10	0.502	0.219	0.002	1.021	0.122	0.095	0.080	0.041	4.67	0.719	4.32	1.364	1.944
25-Jun-10	0.713	0.201		1.737					5.26	0.713	3.86	1.938	2.488
26-Jun-10	0.851	0.170		2.638					4.97	0.851	3.72	2.809	3.299

¹POC is the primary organic carbon from chemical mass balance modeling.

²SOC is the secondary organic carbon from the mass fractions' apportionment.

³TOC_{CC} is ambient concentration of total organic carbon that is contemporary carbon.

⁴TOC_{FC} is ambient concentration of total organic carbon that is fossil carbon.

⁵PEC is the primary elemental carbon from chemical mass balance modeling
 Bold type indicates which source fraction dominated (fossil or contemporary).

Table 2

Summary statistics for organic carbon distribution for contemporary and fossil sources using ¹⁴C with primary and secondary tracer sources. All except F MC and F CC are given as ambient concentration (μg m⁻³).

	OC	EC	POC ¹	SOC ²	F MC ³	F CC ⁴	TOC _{CC} ⁵	POC+SOC OC _{CC}	Undeterm ⁶	TOC _{CC}	TOC _{FC} ⁷	POC+SOC OC _{FC}	POC+PEC ⁸ +SOC TOC _{FC}	Undeterm TOC _{FC}
Average	6.42	0.44	2.74	0.24	0.53	51%	3.57	0.77	2.8	3.29	2.21	2.62	2.62	0.69
Max	10.65	0.81	5.57	0.56	0.71	68%	6.88	1.7	5.61	5.65	4.67	5.29	5.29	3.0
Min	1.57	0.19	0.08	0.03	0.36	34%	0.61	0.08	0.4	1.16	0.09	0.09	0.09	-1.4
Std Dev	2.33	0.15	1.07	0.14	0.09	8%	1.57	0.37	1.3	1.1	0.92	0.99	0.99	1.04
Samples	38	38	39	35	37	37	35	34	34	35	34	34	34	34

¹ POC is the primary organic carbon from chemical mass balance modeling.

² SOC is the secondary organic carbon from the mass fractions apportionment.

³ F MC is fraction modern carbon.

⁴ F CC is the apportioned, bomb-corrected contemporary carbon.

⁵ TOC_{CC} is ambient concentration of total organic carbon that is contemporary carbon.

⁶ Undeterm is undetermined.

⁷ TOC_{FC} is ambient concentration of total organic carbon that is fossil carbon.

⁸ PEC is the primary elemental carbon from chemical mass balance modeling