Constraining Carbonaceous Aerosol Sources in a Receptor Model by Including $^{14}$C Data with Redox Species, Organic Tracers, and Elemental/Organic Carbon Measurements

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Keywords: source apportionment; primary organic aerosol; secondary organic aerosol; positive matrix factorization; $^{14}$C isotope; modern carbon fraction

Abstract

Sources of carbonaceous PM$_{2.5}$ were quantified in downtown Cleveland, OH and Chippewa Lake, OH located ~40 miles southwest of Cleveland during the Cleveland Multiple Air Pollutant Study (CMAPS). PM$_{2.5}$ filter samples were collected daily during July-August 2009 and February 2010 to establish the seasonal emission patterns from local and regional sources. Radiocarbon ($^{14}$C), redox species (NO$_x$, SO$_2$ and ozone), 28 primary and secondary organic aerosol tracers, elemental carbon (EC) and organic carbon (OC) measurements were analyzed using the EPA Positive Matrix Factorization (PMF) model to apportion carbonaceous aerosol sources. Five sources were identified at each site: mobile sources, fossil fuel combustion from fuels containing sulfur, local biomass combustion, other combustion (regional biomass, waste, meat, coal), and secondary organic aerosol (SOA). $^{14}$C data were incorporated in the PMF analysis as a novel method to obtain the modern carbon fraction ($f_{mod}$) of each source individually which aided all factor interpretations. SOA was the principal carbon source during summer as shown by the PMF analysis and a separate tracer based mass fraction method while biomass burning and other combustion sources were dominant in winter. Elevated levels of EC and fossilized carbon in downtown Cleveland are primarily attributed to increased mobile source and coal combustion emissions.
1. Introduction

Atmospheric fine particulate matter (PM$_{2.5}$ – particles with an aerodynamic diameter of less than 2.5 µm) is a criteria air pollutant that exerts detrimental effects on human health and affects the earth’s climate (Brook et al., 2010; Facchini et al., 1999). For regulatory purposes, it is important to understand PM$_{2.5}$ formation and evolution pathways from sources to receptors. One US airshed that has attracted considerable attention is Cleveland Ohio. Zhou et al. used data from the Speciation Trends Network site in Cleveland from 2001-2003 to source apportion PM$_{2.5}$ (Zhou et al., 2009). 8 sources were determined in this study with secondary sulfate being the dominant contributor to PM$_{2.5}$ mass. In 2008, Cleveland possessed two air monitoring sites reporting mass concentrations of PM$_{2.5}$ that exceeded the 24-hr and annual PM$_{2.5}$ standard (Ohio, 2008). In this work, data from the Cleveland Multiple Air Pollutant Study (CMAPS) was used to understand recent carbonaceous sources of PM$_{2.5}$ to assist air quality modelers and managers.

Carbon represents a major component of PM$_{2.5}$ (Jimenez et al., 2009). It may occur in elemental form as black carbon (EC) or in the form of low volatility compounds as organic carbon (OC) derived from biogenic or anthropogenic emissions. Alternatively, measurements of the carbon isotope $^{14}$C may be used to differentiate fossilized or old carbon mass derived from underground sources from the modern carbon obtained from the earth’s surface. In atmospheric applications, PM$_{2.5}$ is collected on filters and analyzed via accelerator mass spectrometry to quantify $^{14}$C content and the modern carbon fraction ($f_{\text{mod}}$). Like EC-OC measurements, $f_{\text{mod}}$ measurements have been used in numerous field studies to apportion aerosol carbon mass (Lewis et al., 2004; Schichtel et al., 2008; Sun et al., 2012; Szidat et al., 2006).

Further apportionment of the carbon content of PM$_{2.5}$ may be achieved via the detection of molecular tracer compounds. Primary organic aerosol (POA) emissions involve particles produced at the emission source that subsequently dilute in the atmosphere. During dilution, some semivolatile POA compounds may evaporate, oxidize further and repartition in ambient particles (Robinson et al., 2007). Secondary organic aerosol (SOA) is generated in the atmosphere via the photo-oxidation reactions of emitted volatile and semivolatile compounds. Some common POA tracers include cholesterol for meat cooking (Kleeman et al., 2008), levoglucosan for biomass burning (Simoneit et al., 1999), and hopanes and steranes for diesel, gasoline (Zielinska et al., 2004) and coal combustion (Oros and Simoneit, 2000). Polycyclic aromatic hydrocarbons (PAHs) are also used although they are generated in most combustion processes and are therefore difficult to interpret solely in source apportionment (Larsen and Baker, 2003). POA source estimations are further hampered by changes in gas-aerosol partitioning and photochemical aging (Grieshop et al., 2009). Despite these
challenges, studies have gone as far as resolving gasoline and diesel powered mobile sources (Kim et al., 2004), and SOA derived from different sources (Zhang et al., 2009).

SOA is considerably more difficult to quantify relative to POA, although it can play an equally significant role in aerosol loading particularly during summer. Indirect quantification of total SOA mass has been made using several experimental approaches such as the EC tracer method (Turpin and Huntzicker, 1995), organic tracer method (Edney et al., 2005; Jaoui et al., 2005), water soluble organic content (Weber et al., 2007), and factor analysis of Aerosol Mass Spectrometer (AMS) data (Docherty et al., 2008; Jimenez et al., 2009; Lanz et al., 2007). The organic tracer method (or empirical mass fraction method) is capable of apportioning the SOA with the use of data generated from smog chamber experiments simulating a variety of atmospheric oxidation reactions (Kleindienst et al., 2007; Lewandowski et al., 2008; Zhang et al., 2009).

Several types of receptor models have been implemented in recent source apportionment studies of aerosol particles. PMF is a type of receptor model that is based on a statistical multivariate factor analysis of aerosol constituent concentrations at the receptor site (Lee et al., 1999). The concentrations in the model are calculated using,

\[ c_{ij} = \sum_k a_{ik} b_{kj} + \tau_{ij} \]  

(1)

where \( c_{ij} \) represents the \( j^{th} \) species concentration (ppb or mass unit/m\(^3\)) from the \( i^{th} \) sample \( i \) typically represents time, \( a_{ik} \) is the apportioned airborne mass concentration of PM (or total carbon – TC in this work in units of \( \mu g/m^3 \)) from the \( k^{th} \) source during the \( i^{th} \) sampling period, \( b_{kj} \) is the \( j^{th} \) species concentration per TC mass concentration ((ppb or mass unit/m\(^3\))/\( \mu g/m^3 \)) from the \( k^{th} \) source and \( \tau_{ij} \) is the residual concentration (ppb or mass unit/m\(^3\)) of every measurement. Effectively, \( a_{ik} \) provides the factor contributions from each source while \( b_{kj} \) represents the source profiles.

PMF generates both source profiles and source contributions. By definition, it requires that all factor contributions are constrained to be non-negative as negative mass concentrations are forbidden. In PMF, the following residual function is minimized,

\[ Q = \sum_i \sum_j \left( \frac{r_{ij}}{u_{ij}} \right)^2 = \sum_i \sum_j \left( \frac{c_{ij} - \sum_k a_{ik} b_{kj}}{u_{ij}} \right)^2 \]

(2)

The residuals \( r_{ij} \) are scaled by the experimental uncertainties \( u_{ij} \) for every species \( j \) in each sample \( i \) in order to deemphasize the most uncertain measurements in the fitting procedure. PMF fits are generally more robust with larger datasets (> 100 samples) as correlations between species are more readily captured the longer they are observed. For intermediate sized datasets (such as for the CMAPS), factor mixing may occur because different sources may not decouple in a PMF analysis.
with a smaller sample size. However, the modern carbon fraction may then be used to decouple anthropogenic and biogenic mixed sources as described in further detail below.

In this paper, 34 gaseous and aerosol species sampled over 50 days during summer and winter in the CMAPS were compiled and analyzed using PMF to apportion the carbon component of PM$_{2.5}$. In particular, $^{14}$C measurements were included in the analysis to obtain the modern carbon fraction of each source individually which significantly aided the interpretation factors. This improvement has been observed in other studies employing $^{14}$C measurements with different source apportionment techniques (Gilardoni et al., 2011). In this manner, readily identifiable sources of local and regional origin were quantified in Cleveland, OH.

2. Materials and Methods

2.1 Sampling and Chemical Analysis.

PM$_{2.5}$ sampling and chemical analysis details are provided in the Supplementary Data and are briefly summarized here. Volatile species (NO$_x$, SO$_2$ and ozone) measurements and three PM$_{2.5}$ quartz filter samples were collected daily from 7/28/2009 – 8/27/2009 (summer) and 2/1/2010 – 2/28/2010 (winter) at two locations: the George T. Craig urban site in downtown Cleveland (referred to as the downtown Cleveland site) and the Chippewa Lake rural site in Medina County. The sites are shown on a map in Figure 1 in addition to wind speed and direction plots obtained from the downtown Cleveland site.

All three volatile redox species (NO$_x$, SO$_2$, ozone) were sampled using Thermo Environmental instruments (Thermo Fisher Scientific; Waltham, MA) at one minute temporal resolution. Daily values were obtained by averaging over 24 hour periods. The three volatile species were included in the PMF analysis because they help to identify sources of organic PM since they are involved in secondary oxidation and acid-base reactions that may produce semi-volatile or low volatility organic compounds. However, correlations between gas phase and aerosol compounds depend on all species exhibiting similar atmospheric lifetimes. PM$_{2.5}$ lifetimes range from days to weeks (Williams et al., 2002) which spans the lifetimes of NO$_x$ (Tie et al., 2001), SO$_2$ (Lee et al., 2011) and O$_3$ (Stevenson et al., 2006) in the troposphere.

Three sets of quartz fiber filters were collected at the G. T. Craig site in downtown Cleveland and the Chippewa Lake site. TE-1000 PUF Polyurethane Foam High Volume Air Samplers (Tisch Environmental Inc.; Cleves, Ohio) were used to sample the ambient air at 226 liters per minute. Filter collection times varied from 20 – 24 hours and the sampled air volumes (for concentration estimates) were determined by measuring the flow rates and time durations of daily experiments.
After collection, the filters were stored in a freezer prior to chemical analyses (EC-OC, $^{14}$C, POA tracers, SOA tracers).

One set of quartz fiber filters were used to quantify POA tracers. They were solvent extracted using a 1:1:1 mixture of hexane, methanol, and dichloromethane. Extracted samples were analyzed using a gas chromatograph (GC, Hewlett-Packard 6890N) having an inert mass selective detector (MSD, HP 5973N). Extraction and analysis procedures for POA compounds have been discussed in detail elsewhere (Olson and McDow, 2009; Turlington et al., 2010).

Another set of filters was used to quantify SOA tracer concentrations and sulfuric acid (Jaoui et al., 2010). The samples were mixed with 20 μg of cis-ketopinic acid (internal standard) and extracted using a 1:1 dichloromethane/methanol mixture in a Soxhlet extraction apparatus. The extracts were then concentrated and derivatized using bis(trimethylsilyl)trifluoroaceticimide (BSTFA) containing 1% trimethylchlorosilane.(Jaoui et al., 2004) All derivatized extracts were analyzed by GC-MS using a GC coupled with an ion trap mass spectrometer (ThermoQuest; Austin, TX).

Once the SOA tracers were quantified they were converted to SOC aerosol mass fractions using an empirical mass fraction method for five different types of precursors: isoprene, monoterpenes, sesquiterpenes, 2-methyl-3-buten-2-ol (MBO) and toluene. The conversion factors were empirically determined using an extensive series of smog chamber experiments (Kleindienst et al., 2007) and include: 6.5 (isoprene), 4.3 (monoterpens), 43.5 (sesquiterpenes), 6.3 (MBO) and 126.6 (toluene) in units of μg SOC/μg tracer compound. Ambient aerosol tracer compound concentrations multiplied by the appropriate precursor conversion factor give the SOC concentration due to that precursor. It is assumed that the laboratory derived tracer/SOC ratio is preserved for ambient samples and in this manner the SOA is source apportioned. This assumption introduces significant uncertainty in the apportionment of SOA because ambient aerosols may consist of other precursors, experience different partitioning depending on volatile species and aerosol concentrations and/or may have chemically aged significantly in the atmosphere.

The final set of filters was used in the EC-OC and $f_{mod}$ measurements. The analysis involved an OC/EC instrument (Sunset Laboratory Inc.; Tigard, OR) which is based on a thermal-optical method to determine the OC and EC masses on the filters (Birch and Cary, 1996). This procedure is consistent with the NIOSH method 5040 which has been shown to yield consistent OC and EC mass concentrations (Birch, 2002).

The remaining filters were sent to the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at the Woods Hole Oceanographic Institution in Woods Hole, MA.
Accelerator mass spectrometry is used to count $^{14}$C atoms to determine the fraction of modern carbon ($f_{\text{mod.}1950}$) present in the sample (TC = EC + OC). 1950 represents the year from which the reference compound (Oxalic Acid I with N.I.S.T. designation SRM 4990 B) was derived (Stuiver and Polach, 1977). No corrections to the $f_{\text{mod.}1950}$ values were made with regards to the $^{14}$C enrichment of biomass from nuclear bomb testing that predominantly occurred during the 1950’s and 1960’s prior to the PMF analysis (Hua and Barbetti, 2004). This correction is difficult to implement before a PM$_{2.5}$ source apportionment analysis because relative source contributions need to be known given that contemporary biomass was differentially enriched over the last several decades. For example, the $^{14}$C in leaves which generate SOA from volatile emissions during summer is expected to be in equilibrium with the $^{14}$C in the troposphere (Lewis et al., 2004). However, tree trunks (> 20 years old) have accumulated more $^{14}$C over the last several decades giving rise to an approximate 20% average increase in $^{14}$C relative to leaves (Lewis et al., 2004). Once the $f_{\text{mod.}1950}$’s were determined for every source (Figure 3), they were converted to the current fractions of modern carbon, $f_{\text{mod.current}}(\text{sample}) = f_{\text{mod.}1950}(\text{sample})/f_{\text{mod.}1950}(\text{biogenic})$ (3)

by scaling with the appropriate $f_{\text{mod.}1950}(\text{biogenic})$ value. For the biomass combustion of tree trunks $f_{\text{mod.}1950}(\text{biogenic}) = 1.20$ while for SOA emissions, $f_{\text{mod.}1950}(\text{biogenic}) = 1.06$ (Lewis et al., 2004).

The modern carbon fraction for all samples characterizes the total carbon contained in the sample (EC + OC). There were a total of four days at Chippewa Lake that an $f_{\text{mod.}1950} > 1$ was measured ($f_{\text{mod.}1950} = 2.46$: 8/10/2009, $f_{\text{mod.}1950} = 1.73$: 2/3/2010, $f_{\text{mod.}1950} = 1.20$: 2/4/2010, $f_{\text{mod.}1950} = 1.11$: 2/21/2010). The sources of the first two occurrences are likely due to $^{14}$C enriched hazardous/medical waste incineration or nuclear power plant effluents. Since this effect occurred relatively infrequently, these values were not included in the $f_{\text{mod.}1950}$ averages displayed in Figure 2.

Data for the CMAPS was obtained during the summer and winter seasons of 2009 and 2010 respectively. In 2009, the data range spanned from 7/28/2009 – 8/31/2009 while in 2010, the data ranged from 2/1/2010 – 2/28/2010. Not all species were detected over these entire ranges either due to instrument error or sample loss (see Supplementary Data). All interspersed missing data accounted for << 1% of the entire dataset and data interpolation (used in the subsequent PMF analysis) was therefore not expected to influence the results.

2.2 PMF Analysis.

The total dataset that was used in the PMF analysis consisted of summer and winter samplings in downtown Cleveland and at Chippewa Lake as mentioned above. The seasonal data at
both sites were compiled and two separate PMF fits were obtained for both sites. Source apportionment was conducted using EPA PMF 3.0 (Norris et al., July 2008).

In addition to species concentrations, the PMF program requires uncertainties for every measurement so that the residual function may be appropriately minimized (see equation 2). Uncertainties were estimated for all species (except bulk carbon measurements) using the following expression (Reff et al., 2007),

\[ u_{ij} = \sqrt{(MDL_j)^2 + (\%error_j \times c_{ij})^2} \]  

where \( u_{ij} \) denotes the uncertainty of the \( i \)th sample (day) from the \( j \)th species, \( MDL_j \) denotes the method detection limit for the \( j \)th species and \( \%error_j \) is the percent error for species \( j \) of the \( c_{ij} \) measurement. The units of the uncertainty are the same as the measurements (\( c_{ij} \)). The Supplementary Data detail the MDL’s and % errors for all detected species in the CMAPS.

While individual uncertainties provide the weighting factors used to minimize the residual function (equation 2) in PMF, they were fixed to the values described above. Further rescaling of specific samples may be required when different instrumentation is used for sampling (Slowik et al., 2010) and/or samples where poor signal to noise ratios are obtained for the species detected (Paatero and Hopke, 2003). In this work, down-weighting was implemented for the latter reason. Specifically, this was accomplished by labeling a species as ‘weak’ in EPA PMF, which increased the uncertainties by a factor of three (Paatero and Hopke, 2003). Table S1 of the Supplementary Data indicates what species were denoted as ‘strong’ (unmodified) and ‘weak’. A weak designation was earned if the signal to noise ratio was not high (< 2), if the data contained numerous zero values or if there were missing data that was interpolated (such as ozone at both sites). Some tracers were removed because the signal to noise ratio was quite poor (< 1) with sensitivity studies yielding inconsistent source profiles (such as specific SOA tracers showing up in factors dominated by POA). An inspection of Table S1 reveals that POA tracers were generally labeled as strong while SOA tracers were deemed weak although a majority of SOA tracers had a signal to noise ratio of ~1.75. Because this ratio is close to the cutoff value of 2, we also carried out PMF fits in the case where SOA tracers were labeled strong and the results are discussed in the following section. The total carbon (TC) was set as the total variable in the analysis so that all factor profiles are given relative to TC and factor contributions are measured in units of TC.

As all source profiles were normalized to the TC, inclusion of \( TC_{mod.1950,i} = f_{mod.1950,i} \ast TC \) for every sample \( i \) in the PMF analysis results in \( f_{mod.1950,k} = TC_{mod.1950,i} / TC \) for every source \( k \) in the factor profiles. After factorization, the factor profiles reveal what scaling factor is necessary to evaluate \( f_{mod. current,k} \) for every source \( k \). If levoglucosan, a biomass burning tracer is present in a
factor particularly during winter, then the $f_{\text{mod. 1950}} \cdot k$ is scaled by 1.20 as discussed above. If SOA tracers are present, then $f_{\text{mod. 1950}} \cdot k$ is scaled by 1.06 to determine $f_{\text{mod. current}} \cdot k$. This new fitting method greatly extends the significance of $^{14}$C measurements. Typically, $f_{\text{mod. 1950}}$ is determined for the bulk PM sample and is of limited use in source apportionment if not accompanied by other data because numerous sources may contain fossilized or modern carbon. Alternatively, if a factor analysis method such as PMF is applied, it is usually difficult to get a clean factorization for a variety of reasons. Poor signal to noise ratios (Paatero and Hopke, 2003), insufficient data samples where sources are more likely to be present concurrently (Henry, 2003), variable emissions from specific sources (Hildemann et al., 1991) and time-dependent photochemistry of POA and SOA (Jimenez et al., 2009) all hamper source apportionment studies by giving rise to mixed source factors that are difficult to interpret. By including $f_{\text{mod}}$ in the factor analysis, such ambiguities may be resolved by determining the modern carbon fractions for every source.

3. Results and discussion

3.1 CMAPS aerosol carbon content

Figure 2 displays the EC, OC, PAH, hopane, levoglucosan and the sum of the SOA tracer concentrations during the CMAPS. The downtown Cleveland site had higher time-averaged EC and OC levels by 100% and 15% respectively. Additionally, the $f_{\text{mod. 1950}}$ was significantly lower in downtown Cleveland indicating that fossilized carbon is more dominant at the urban site. Regional transport of combusted fossilized carbon from downtown Cleveland to Chippewa Lake is therefore not significant based on the differences in the two datasets. Figure 1 reinforces this view showing that the wind direction in downtown Cleveland is coming from the south-west (summer) or west (winter) during the field campaign.

The downtown Cleveland EC and OC concentrations are similar in magnitude to other US midwestern cities (Zhang et al., 2009) although considerably lower than larger cities in the US (Manchester-Neesvig et al., 2003), Europe (Gillardoni et al., 2011), South America (Cantanho and Artaxo, 2001) and Asia (Cantanho and Artaxo, 2001). Varying meteorological conditions, pollution control strategies and emissions all account for this disparity although it is the latter which is the principal driver of spatial PM$_{2.5}$ heterogeneity. Seasonal differences in the OC and EC concentrations were also observed at both sites although the variation does not appear as large as the site differences. The OC levels increased during the winter season which may be partly due to a lower mixing layer during winter. However with constant EC levels at both sites, the EC/OC ratio must
have changed to compensate for this effect. Without further chemical analysis, it is difficult to interpret all these changes occurring in PM$_{2.5}$.

As described above, PM$_{2.5}$ may be generated directly by a particular source (POA) or it may be produced via photochemical reactions of semi-volatile compounds that condense on growing particles in the atmosphere (SOA). In Figure 2, three groups of primary tracers are displayed: PAHs, hopanes and levoglucosan. PAHs and levoglucosan were significantly more prevalent in the winter at both sites. The high degree of correlation ($r^2 = 0.82$) between the winter PAH concentrations at both sites suggests that common source emissions are being regionally dispersed. The hopane concentrations were 3-4 times greater in downtown Cleveland during both seasons which is consistent with the greater number of mobile sources present at the urban site. However, some of the hopanes may be derived from coal combustion and are subsequently considered in the source apportionment analysis that follows.

SOA is a major source of carbon in summer PM$_{2.5}$. For this study, five classes of SOA precursors were considered: isoprene, monoterpenes, sesquiterpenes, MBO and aromatic compounds. Figure 2 displays the sum of all SOA tracer concentrations at each site. Winter SOA concentrations as estimated from the sum of all detected SOA tracers are minute at both sites. While the inventory of current SOA tracer compounds is not comprehensive (only one anthropogenic SOA tracer compound from toluene photo-oxidation was detected in this study), low winter SOA levels are consistent with other field studies (Anderson et al., 2003; Lewandowski et al., 2008; Szidat et al., 2006). A significant driving factor of decreased winter SOA levels is due to decreased solar intensity relative to summer that consequently gives rise to less photochemistry and biogenic emissions. The summer SOA tracer concentrations at both sites are strongly correlated ($r^2 = 0.91$) with larger isoprene tracer concentrations being detected at Chippewa lake. Like the correlated PAH concentrations in winter at both sites, much of the SOA is believed to be regional in extent due to this spatial correlation. While tracer compound concentrations reveal seasonal trends and correlations it is difficult to compare their relative contributions to the total OA mass without invoking some source apportionment model. Positive matrix factorization was used in this work to determine the relative source contributions.

### 3.2 PMF analysis

Five factors were used to fit the CMAPS dataset. The fits resulted in scaled residuals that were less than 2 for all except one species on 3 and 2 days in downtown Cleveland and Chippewa Lake respectively. If four factors are used, the fits were of poorer quality because the number of
days when species exceeded a scaled residual value of two increased to 10. Six factors did not significantly improve the quality of fit because the number of exceeding scaled residuals was the same as the five factor model in downtown Cleveland and one less at Chippewa Lake.

The source profiles expressed as percentages of species/source were determined relative to TC and are shown in Figure 3. Figure S1 in the Supplementary Data displays the source profiles expressed relative to TC mass. The first factor profile contained NO₃, hopanes and EC with low modern carbon fractions and is therefore attributed to mobile sources. The second factor contained predominantly SO₂, PAHs, hopanes and levoglucosan. Sulfur containing fossil fuel combustion giving rise to SO₂ emissions from coal-fired power plants (Reddy and Venkataraman, 2002; Zhao et al., 2008) and biomass burning are mixed in this factor at both sites. The $f_{\text{mod. 1950}}$'s at both sites confirm the mixing because the values of 0.63 and 0.87 are indicative of both anthropogenic and biogenic components. The third factor contained levoglucosan as well NO₀ and hopanes in downtown Cleveland and Chippewa Lake respectively. In this case, the $f_{\text{mod. 1950}}$'s also suggest that mobile sources are mixed with biomass burning. The fourth factor contains significant amounts of PAHs and was labeled 'other combustion'. Unfortunately, PAHs are not specific source markers as they arise from numerous combustion processes (Larsen and Baker, 2003). Some likely sources of PAHs that were not already mentioned include waste incineration, meat cooking and coal/coke combustion because hopanes were present in the profiles particularly in downtown Cleveland. Coal or coke combustion from industrial sources may account for the significantly lower modern carbon fraction in downtown Cleveland for this source relative to Chippewa Lake (Zhou et al., 2009). The final factor contained most SOA tracers and was therefore assigned to SOA. Biogenic sources such as isoprene, monoterpenes and sesquiterpenes comprise a large fraction of SOC at both sites because the modern carbon fractions were close to one.

An interesting component of the SOA factor profiles at both sites is the correlation of particle phase sulfuric acid with the SOA tracers. Sulfuric acid is produced in the atmosphere from the oxidation of SO₂ (Finlayson-Pitts and Pitts, 2000). In this analysis, the silylated derivative of sulfuric acid is detected which serves as an indicator of aerosol acidity (Jaoui et al., 2010). While the correlation observed here may be coincidental, a number of recent studies have shown reaction pathways linking SOA and acidic sulfate particles. Aqueous phase processing of organic compounds and sulfate (Yu et al., 2005), the production of organosulfates (Surratt et al., 2007) and acid catalyzed particle phase reactions (Barsanti and Pankow, 2004, 2005; Lin et al., 2012) may account for the correlation observed in this study. Further studies of aerosol acidity should elucidate the importance of its role in SOA formation.
Figure 4 displays the average factor contributions to TC mass at both sites during both seasons with error estimates. The error bars were determined by obtaining the standard deviations of factor contributions from a sampling of 20 randomly selected uncertainty weighting matrices (Christensen and Schauer, 2008). For each selection, one or two types of compounds were changed from ‘strong’ to ‘weak’ or vice versa relative to the original uncertainty weightings (see Table S1 in the Supplementary Data) to obtain sensitivity estimates. The data indicate that on average, greater than 90% of the TC was accounted for at both sites during both seasons when comparing the TC from Figure 4 with EC + OC in Figure 2.

The $f_{\text{mod.} \ 1950}$’s from the PMF fits displayed in Figure 3 may be used to unmix anthropogenic and biogenic sources to give pure source estimates to carbonaceous mass. Table 1 summarizes the sources attributed to the factors from inspection of the factor profiles as well as summer and winter TC concentrations. Each $f_{\text{mod.} \ 1950}$ for every factor was converted to an $f_{\text{mod.} \ \text{current}}$. The first four factors contained biomass burning contributions from the presence of levoglucosan in the factor profiles and so the $f_{\text{mod.} \ 1950}$’s were scaled by 1.20 while the SOA factor from plant foliage $f_{\text{mod.} \ 1950}$ was scaled by 1.06. The resulting $f_{\text{mod.} \ \text{current}}$’s were then multiplied with the TC summer and winter data to obtain the anthropogenic and biogenic contributions of each factor. The contributions from a particular source in different factors were then added together to give the final TC contributions of the pure sources. For example, factors 1 and 3 contained mobile sources as the fossilized carbon source at both sites whose contributions were extracted by multiplying the TC summer and winter concentrations by the associated percentage of fossilized carbon (1-$f_{\text{mod.} \ \text{current}}$) and then summed together. In this manner, the mixed factors 1 – 3 were resolved into mobile sources, sulfur containing fossil fuel combustion and biomass burning. The unmixed source contributions in Table 1 indicate that SOA dominates TC in summer while other combustion sources and biomass burning are the main sources in winter for both sites. Mobile sources also contribute a significant mass to TC at both sites during both seasons. Diesel emissions from heavy duty trucks contribute to a greater extent in downtown Cleveland given the higher EC/TC ratio (see Figure 3) and greater emissions during weekdays relative to weekends (see Figure S2 in the Supplementary Data) (Dreher and Harley, 1998). No such weekly dependence is observed at Chippewa Lake suggesting that the mobile sources contributions to PM$_{2.5}$ are from gasoline vehicles.

Table 1 reveals that the other combustion sources are responsible for half of the TC in winter with minimal contributions during summer. The $f_{\text{mod.} \ \text{current}}$’s in Table 1 designate at least half the carbon to biogenic sources at both sites with significantly more biogenic carbon being present in Chippewa Lake. If the biogenic component is not due to biomass burning, than waste incineration
(Lee et al., 2002) and meat cooking (Mohr et al., 2012) may account for the modern carbon mass. However, both waste incineration and meat cooking are expected to occur throughout the year and could give rise to considerable OC during summer if present in large concentrations during winter. Another possibility is that this source is due to the long range transport of primary biomass burning particles. This would account for the high $f_{\text{mod; current}}$, the strong correlation of PAHs at both sites ($r^2 = 0.82$), and its significant winter presence in PM$_{2.5}$ which is also seen in the levoglucosan dominant biomass combustion factor (see Figure S2 in Supplementary Data) in addition to other field studies (Gilardoni et al., 2011; Zhang et al., 2010). The loss of correlation between PAHs and levoglucosan as observed in the PMF analysis may occur because both are expected to exhibit different lifetimes in the atmosphere (Ananthula et al., 2007; Hennigan et al., 2010), with levoglucosan being particularly vulnerable to further oxidation (Cubison et al., 2011; Hennigan et al., 2010). Levoglucosan therefore may represent localized biomass burning PM while PAHs that contain mostly modern carbon in the winter may represent an aged biomass burning plume. The modern carbon fraction has therefore proved extremely useful in interpreting this mixed PMF factor at both sites.

The modern carbon fractions were also used to apportion the SOA mass into fossilized and biogenic components within the five factor PMF model. Figure 5 displays the apportioned SOA from the five factor PMF model in comparison with the empirical mass fraction method (Kleindienst et al., 2007). As mentioned in the previous section, the five factor model down-weighted the influence of SOA on the PMF fits because the data exhibited signal to noise ratios less than 2. Additional five and six factor PMF fits were carried out where SOA species were not down-weighted. In both cases, the overall fit quality was poorer and so only the six factor model is displayed. In this fit, species exhibited scaled residuals greater than 2 on 13 and 18 days in downtown Cleveland and at Chippewa Lake respectively (compared with 3 and 2 days in the original 5 factor fit). Despite the poorer fit quality, the results of the 6 factor fit are also displayed in Figure 5. In the 6 factor model, the original SOA component split into predominantly isoprene and monoterpane + sesquiterpane components. All models are fairly consistent in downtown Cleveland while only the 5 factor PMF solution at Chippewa Lake underestimates SOA relative to the other methods. The consistent data from the different models indicate that SOA precursor mass fractions determined from smog chamber experiments are sensible at this location with bounded uncertainties well below 100%. This estimate and validation of the mass fraction method would not have been possible without the incorporation of the modern carbon fractions in the PMF analysis.

4. Conclusion
In summary, carbonaceous aerosol sources were apportioned in Cleveland, OH using primary and secondary tracer compounds. EPA PMF 3.0 was used to apportion OC mass and 5 factors were resolved: mobile sources, fossil fuel combustion, biomass combustion, other combustion and SOA. SOA was observed to be dominant in summer at both sites while biomass burning and other combustion sources produced the most OC during winter. The lower modern carbon fraction in downtown Cleveland was primarily due to increased mobile source and industrial coal combustion emissions which were also present at the rural site although at lower concentrations. A novel aspect of the analysis was that the modern OC was included in the PMF analysis, which gave $f_{\text{mod}}$’s for every factor. Not only did this help to confirm factor interpretations but it also revealed the relative contributions of sources to mixed or unresolved factors. This analysis greatly improved the utility of $^{14}$C measurements in the source apportionment of carbonaceous aerosol particles.

Acknowledgements

The US Environmental Protection Agency through its Office of Research and Development funded and collaborated in the research described here under Contract EP-D-10-070 to Alion Science and Technology. The manuscript has been subjected to external peer review and has been cleared for publication. Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Supplementary Data

Additional input and results from the PMF analysis are given in the Supplementary material.

Supplementary data associated with this article can be found, in the online version, at

References


Table 1. Source attribution and factor unmixing using $f_{mod. \ current}$

### Downtown Cleveland

<table>
<thead>
<tr>
<th>Factor #</th>
<th>Source Contributions</th>
<th>TCsummer</th>
<th>TCwinter</th>
<th>f_{mod. \ 1950}</th>
<th>f_{mod. \ current}</th>
<th>Unmixed Sources</th>
<th>f_{mod. \ current \ unmixed}</th>
<th>TCsummer</th>
<th>TCwinter</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>Mobile Sources</td>
<td>0.58</td>
<td>0.34</td>
<td>0.00</td>
<td>0.00</td>
<td>Mobile Sources</td>
<td>0.00</td>
<td>0.79</td>
<td>0.89</td>
</tr>
<tr>
<td>2</td>
<td>Fossil Fuels a, Biomass Combustion</td>
<td>0.07</td>
<td>0.25</td>
<td>0.63</td>
<td>0.53</td>
<td>Fossil Fuels a</td>
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<td>0.03</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>Biomass Combustion, Mobile Sources</td>
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<td>0.64</td>
<td>0.53</td>
<td>Biomass Combustion</td>
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<td>0.76</td>
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<tr>
<td>4</td>
<td>Other Combustion b</td>
<td>0.21</td>
<td>1.54</td>
<td>0.68</td>
<td>0.57</td>
<td>Other Combustion b</td>
<td>0.57</td>
<td>0.21</td>
<td>1.54</td>
</tr>
<tr>
<td>5</td>
<td>SOA</td>
<td>1.32</td>
<td>0.00</td>
<td>0.86</td>
<td>0.81</td>
<td>SOA</td>
<td>0.81</td>
<td>1.32</td>
<td>0.00</td>
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</table>

### Chippewa Lake

<table>
<thead>
<tr>
<th>Factor #</th>
<th>Source Contributions</th>
<th>TCsummer</th>
<th>TCwinter</th>
<th>f_{mod. \ 1950}</th>
<th>f_{mod. \ current}</th>
<th>Unmixed Sources</th>
<th>f_{mod. \ current \ unmixed}</th>
<th>TCsummer</th>
<th>TCwinter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mobile Sources, Biomass Combustion</td>
<td>0.20</td>
<td>0.35</td>
<td>0.34</td>
<td>0.28</td>
<td>Mobile Sources</td>
<td>0.00</td>
<td>0.30</td>
<td>0.51</td>
</tr>
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<td>2</td>
<td>Fossil Fuels a, Biomass Combustion</td>
<td>0.10</td>
<td>0.36</td>
<td>0.87</td>
<td>0.73</td>
<td>Fossil Fuels a</td>
<td>0.00</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>Biomass Combustion, Mobile Sources</td>
<td>0.51</td>
<td>0.83</td>
<td>0.83</td>
<td>0.69</td>
<td>Biomass Combustion</td>
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<td>Other Combustion b</td>
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<td>0.97</td>
<td>0.81</td>
<td>Other Combustion b</td>
<td>0.81</td>
<td>0.00</td>
<td>1.59</td>
</tr>
<tr>
<td>5</td>
<td>SOA</td>
<td>0.95</td>
<td>0.00</td>
<td>0.88</td>
<td>0.83</td>
<td>SOA</td>
<td>0.83</td>
<td>0.95</td>
<td>0.00</td>
</tr>
</tbody>
</table>

a denotes fossil fuels containing sulfur  

b denotes combustion sources like aged biomass burning, industrial coal, meat cooking and waste incineration  

c calculated by $f_{mod. \ current} = f_{mod. \ 1950}/f_{mod. \ 1950(\ biogenic)}$ assuming $f_{mod. \ 1950(\ biomass \ burning)} = 1.20$ and $f_{mod. \ 1950(\ SOA)} = 1.06$
Figure Captions.

**Figure 1.** Map of the site locations for the CMAPS and wind speed and direction plots in downtown Cleveland during the two sampling periods.

**Figure 2.** Concentrations of EC, OC, PAHs, hopanes, levoglucosan and SOA tracer compounds respectively at both sites during both seasons. EC and OC data during summer in downtown Cleveland were missing (8/24 – 8/27). Average values of each species during a sampling period are placed on the graphs including the fractions of modern carbon ($f_{\text{mod. 1950}}$).

**Figure 3.** PMF profiles expressed as percentages of species over all factors in downtown Cleveland and Chippewa Lake. The fractions of modern carbon ($f_{\text{mod. 1950}}$) for each factor are listed. The factor profiles before being expressed as percentages have the following units: NOx, SO2, and ozone are in ppb/µg/m³ TC, PAHs and hopanes are in µg/µg TC, levoglucosan and SOA tracers are in ng/µg TC, EC and TC$_{\text{mod. 1950}}$ are in µg/µg TC. The SOA species name that is not fully shown is 3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid.

**Figure 4.** PMF contributions to TC from 5 sources in downtown Cleveland and Chippewa Lake over summer and winter sampling periods. The data point not displayed for the fourth factor in the winter dataset for Chippewa Lake has a value of 9.21 µg/m³. The average contributions to TC from each source expressed as an absolute value and percentage of TC are included on the graphs along with error bars.

**Figure 5.** Source apportioned SOC using the mass fraction method and the 5 and 6 factor PMF models. The 5 factor PMF model resolved the biogenic (dark green) and anthropogenic carbon components while the mass fraction method and 6 factor PMF model further resolved the biogenic component into isoprene (green), and monoterpenes + sesquiterpenes (lighter green).
Supplementary Data

Constraining Carbonaceous Aerosol Sources in a Receptor Model by Including $^{14}$C Data with Redox Species, Organic Tracers, and Elemental/Organic Carbon Measurements

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1. **PM$_{2.5}$ Sampling and Chemical Analysis**

Volatile species (NO$_x$, SO$_2$ and ozone) measurements and three PM$_{2.5}$ quartz filter samples were collected daily from 7/28/2009 – 8/27/2009 (summer) and 2/1/2010 – 2/28/2010 (winter) at two locations: the George T. Craig urban site in downtown Cleveland (referred to as the downtown Cleveland site) and the Chippewa Lake rural site in Medina County. The sites are shown on a map in Figure 1 in addition to wind speed and direction plots obtained from the downtown Cleveland site.

Wind data were collected using an RM Young Ultrasonic Anemometer Model 81000 (Traverse City, MI) located at the downtown Cleveland site. The instrument uses a 1-minute sampling frequency, though the data were later averaged to obtain daily values of wind speed and direction.

All three volatile redox species (NO$_x$, SO$_2$, ozone) were sampled using Thermo Environmental instruments (Thermo Fisher Scientific; Waltham, MA) at one minute temporal resolution. Daily values were obtained by averaging over 24 hour periods. NO$_x$ was sampled using a Model 42 chemiluminescent NO$_x$ analyzer with a precision of +/- 0.4 ppb. SO$_2$ was measured with a Model 43A sulfur dioxide analyzer with a precision of 1 ppb. O$_3$ was sampled using a Model 49 UV photometric ozone analyzer also with a precision of 1 ppb. The three volatile species were included in the PMF analysis because they help to identify sources of organic PM since they are involved in secondary oxidation and acid-base reactions that may produce semi-volatile or low volatility organic compounds. However, correlations between gas phase and aerosol compounds depend on all species exhibiting similar atmospheric lifetimes. PM$_{2.5}$ lifetimes range from days to weeks (Williams et al., 2002) which spans the lifetimes of NO$_x$ (Tie et al., 2001), SO$_2$ (Lee et al., 2011) and O$_3$ (Stevenson et al., 2006) in the troposphere.

Three sets of quartz fiber filters were collected at the G. T. Craig site in downtown Cleveland and the Chippewa Lake site. TE-1000 PUF Polyurethane Foam High Volume Air Samplers (Tisch Environmental Inc.; Cleves, Ohio) were used to sample the ambient air at 226 liters per minute. Filter collection times varied from 20 – 24 hours and the sampled air volumes (for concentration estimates) were determined by measuring the flow rates and time durations of daily experiments. After collection, the filters were stored in a freezer prior to chemical analyses (EC-OC, $^{14}$C, POA tracers, SOA tracers). The subsequent chemical analyses did not take into account any semi-volatiles that may have evaporated during the processing time. Estimates of this negative artifact are presumed to be less than 10% of the total carbon mass (Subramanian et al., 2004).
One set of quartz fiber filters were used to quantify POA tracers. They were solvent extracted using a 1:1:1 mixture of hexane, methanol, and dichloromethane. Extracted samples were analyzed using a gas chromatograph (GC, Hewlett-Packard 6890N) having an inert mass selective detector (MSD, HP 5973N). Extraction and analysis procedures for POA compounds have been discussed in detail elsewhere (Olson and McDow, 2009; Turlington et al., 2010).

Another set of filters was used to quantify SOA tracer concentrations and sulfuric acid (Jaoui et al., 2010). The samples were mixed with 20 μg of cis-ketopinic acid (internal standard) and extracted using a 1:1 dichloromethane/methanol mixture in a Soxhlet extraction apparatus. The extracts were then concentrated and derivatized using bis(trimethylsilyl)trifluoroaceticimide (BSTFA) containing 1% trimethylchlorosilane (Jaoui et al., 2004). All derivatized extracts were analyzed by GC-MS using a GC coupled with an ion trap mass spectrometer (ThermoQuest; Austin, TX).

Once the SOA tracers were quantified they were converted to SOC aerosol mass fractions using an empirical mass fraction method for five different types of precursors: isoprene, monoterpenes, sesquiterpenes, 2-methyl-3-buten-2-ol (MBO) and toluene. The conversion factors were empirically determined using an extensive series of smog chamber experiments (Kleindienst et al., 2007) and include: 6.5 (isoprene), 4.3 (monoterpenes), 43.5 (sesquiterpenes), 6.3 (MBO) and 126.6 (toluene) in units of μg SOC/μg tracer compound. Ambient aerosol tracer compound concentrations multiplied by the appropriate precursor conversion factor give the SOC concentration due to that precursor. It is assumed that the laboratory derived tracer/SOC ratio is preserved for ambient samples and in this manner the SOA is source apportioned. This assumption introduces significant uncertainty in the apportionment of SOA because ambient aerosols may consist of other precursors, experience different partitioning depending on volatile species and aerosol concentrations and/or may have chemically aged significantly in the atmosphere.

The final set of filters was used in the EC-OC and \( f_{mod} \) measurements. A 1.5 cm\(^2\) area was punched out of the 8.6 cm diameter filters for the EC-OC analysis. The analysis involved an OC/EC instrument (Sunset Laboratory Inc.; Tigard, OR) which is based on a thermal-optical method to determine the OC and EC masses on the filters (Birch and Cary, 1996). In this method, filter samples are placed in an oven and heated in inert (Helium) and oxidizing (oxygen) environments. The first temperature ramp to 575°C in helium is used to catalytically oxidize the OC to carbon dioxide which is then reduced to methane and subsequently detected using a flame ionization detector (FID). Continuous monitoring of filter transmittance to impinging laser radiation is used to subtract the
pyrolyzed char that is produced from OC reactions from the EC component. EC is then quantified during
the second phase of the temperature ramp in a He/O₂ environment where the sample is heated to
900°C. This procedure is consistent with the NIOSH method 5040 which has been shown to yield
consistent OC and EC mass concentrations (Birch, 2002). The area correction was used in conjunction
with the total air volume sampled to determine the final OC and EC ambient mass concentrations. This
procedure did not detect the amount of carbonate (inorganic carbon) in the samples although
carbonate concentrations are expected to be negligible in PM₂,₅ samples (Sillanpaa et al., 2005).

The remaining filters were sent to the National Ocean Sciences Accelerator Mass Spectrometry
(NOSAMS) facility at the Woods Hole Oceanographic Institution in Woods Hole, MA. Accelerator mass
spectrometry is used to count ¹⁴C atoms to determine the fraction of modern carbon (f₁₉₅₀) present
in the sample (TC = EC + OC). 1950 represents the year from which the reference compound (Oxalic Acid
I with N.I.S.T. designation SRM 4990 B) was derived (Stuiver and Polach, 1977). Specifically, the f₁₉₅₀
was determined by the following expression,

\[
f_{1950} = \frac{^{14}C_{\text{sample}} \div ^{12}C_{\text{sample}}}{^{14}C_{\text{reference}} \div ^{12}C_{\text{reference}}} = \frac{^{14}C_{\text{blank}} \div ^{12}C_{\text{blank}}}{^{14}C_{\text{blank}} \div ^{12}C_{\text{blank}}}
\]

(S1)

The ¹⁴C/¹²C ratio is determined for the field sample, a blank that measures background levels and a
reference standard that contained ‘modern carbon’. The reference is the National Bureau of Standards
(NBS) Oxalic Acid I standard (SRM 4990B) which is defined as 95% of the activity of oxalic acid in 1950
(Olsson, 1970). In order to accurately determine modern carbon fractions, differences in the uptake of
¹²C, ¹³C and ¹⁴C have to be accounted for. While the three carbon isotopes are chemically
indistinguishable, the order in which they are taken up in biological pathways is: ¹²C > ¹³C > ¹⁴C. An
assumption is used to determine the extent of fractionation for ¹⁴C: the fractionation of ¹⁴C relative to
¹²C is twice that of ¹³C, reflecting the difference in mass. ¹³C/¹²C ratios therefore quantify this differential
uptake of different carbon isotopes in the biosphere. The Oxalic Acid I standard is normalized to
δ¹³CVPDB=-19 per mil while all samples are normalized to δ¹³CVPDB=-25 per mil (mean value of terrestrial
biomass) as described by Stuiver and Polach (Stuiver and Polach, 1977). VPDB represents the Vienna -
Pee Dee Belemnite ¹³C standard. No corrections to the f₁₉₅₀ values were made with regards to the
¹⁴C enrichment of biomass from nuclear bomb testing that predominantly occurred during the 1950’s
and 1960’s prior to the PMF analysis (Hua and Barbetti, 2004). This correction is difficult to implement
before a PM₂,₅ source apportionment analysis because relative source contributions need to be known
given that contemporary biomass was differentially enriched over the last several decades. For
example, the $^{14}$C in leaves which generate SOA from volatile emissions during summer is expected to be in equilibrium with the $^{14}$C in the troposphere (Lewis et al., 2004). However, tree trunks (> 20 years old) have accumulated more $^{14}$C over the last several decades giving rise to an approximate 20% average increase in $^{14}$C relative to leaves (Lewis et al., 2004). Once the $f_{\text{mod.} \, 1950}$’s were determined for every source (Figure 3), they were converted to the current fractions of modern carbon,

$$f_{\text{mod. current}}(\text{sample}) = f_{\text{mod.} \, 1950}(\text{sample})/f_{\text{mod.} \, 1950}(\text{biogenic})$$

(S2)

by scaling with the appropriate $f_{\text{mod.} \, 1950}(\text{biogenic})$ value. For the biomass combustion of tree trunks $f_{\text{mod.} \, 1950}(\text{biogenic}) = 1.20$ while for SOA emissions, $f_{\text{mod.} \, 1950}(\text{biogenic}) = 1.06$ (Lewis et al., 2004).

The modern carbon fraction for all samples characterizes the total carbon contained in the sample (EC + OC). There were a total of four days at Chippewa Lake that an $f_{\text{mod.} \, 1950} > 1$ was measured ($f_{\text{mod.} \, 1950} = 2.46$: 8/10/2009, $f_{\text{mod.} \, 1950} = 1.73$: 2/3/2010, $f_{\text{mod.} \, 1950} = 1.20$: 2/4/2010, $f_{\text{mod.} \, 1950} = 1.11$: 2/21/2010). The sources of the first two occurrences are likely due to $^{14}$C enriched hazardous/medical waste incineration or nuclear power plant effluents (Uchrin et al., 1992; Vay et al., 2009). The latter two $f_{\text{mod.} \, 1950}$’s may also be caused by these sources or by extensive biomass burning of $^{14}$C enriched wood from nuclear bomb testing because they fall within the range of expected values from this effect (Lewis et al., 2004). Since this effect occurred relatively infrequently, these values were not included in the $f_{\text{mod.} \, 1950}$ averages displayed in Figure 2.

Data for the CMAPS was obtained during the summer and winter seasons of 2009 and 2010 respectively. In 2009, the data range spanned from 7/28/2009 – 8/31/2009 while in 2010, the data ranged from 2/1/2010 – 2/28/2010. Not all species were detected over these entire ranges either due to instrument error or sample loss. For instance, there were missing EC and OC data at the downtown Cleveland site (G.T. Craig) which restricted the range used in the PMF analysis from 7/31/2009 – 8/23/2009 at both sites. On 2/23/2010, an instrument extraction error occurred for the detection of PAHs and hopanes in downtown Cleveland. Consequently, this day was removed in the PMF analysis. For the volatile redox species, ozone had missing data on 8/18/2009 and 8/19/2009 in downtown Cleveland. At Chippewa Lake, data for NO$_x$, SO$_2$ and ozone were missing on 7/31/2009, 8/22/2009, and 8/23/2009. For these species, the data were linearly interpolated using measurements from adjacent days for the PMF analysis. All missing data after restricting the range accounted for << 1% of the entire dataset and data interpolation was therefore not expected to influence the results.
2. PMF Analysis

In addition to species concentrations, the PMF analysis requires uncertainties for every measurement so that the residual function may be appropriately minimized (see equation 2). Uncertainties were estimated for all species (except bulk carbon measurements) using the following expression (Reff et al., 2007),

\[ u_{ij} = \sqrt{(MDL_j)^2 + (\%error_j \times c_{ij})^2} \]  

(S3)

where \( u_{ij} \) denotes the uncertainty of the \( i \)th sample (day) from the \( j \)th species, \( MDL_j \) denotes the method detection limit for the \( j \)th species and \( \%error_j \) is the percent error for species \( j \) of the \( c_{ij} \) measurement. The units of the uncertainty are the same as the measurements \( c_{ij} \). Table S1 below illustrates that different classes of species were measured with different units which need to be tracked during the PMF analysis. MDL’s were estimated to be 0.5 ppb, \(~3 \) pg/m\(^3\) and 0.2 ng/m\(^3\) for the redox species, POA and SOA tracers respectively. Conservative estimates to the \% errors were used for POA and SOA tracers. For POA compounds, sample error estimates for polycyclic aromatic hydrocarbons (PAHs) and hopanes are determined to be less than 25% in the work by Turlington et al. (Turlington et al., 2010). For SOA tracer compounds, an upper bound error of 35% was estimated using data from Table 2 in the work of Kleindienst et al. (Kleindienst et al., 2007). In that work, pairs of filters were collected (same hydrocarbon and NO\(_x\) concentrations) for some of the listed smog chamber experiments involving \( \alpha \)-pinene, toluene and isoprene precursors (see Table 2). The largest percent difference in tracer concentrations occurred for an isoprene experiment where a relative difference of 34% was observed. Sampling biases such as extraction or reaction yields (95%) (Jaoui et al., 2004) and the use of gas chromatography standards that approximate the compounds contained within the aerosol affect the accuracy of the measurements although all are expected to be within the precision boundary.
### Table S1. List of species used in the PMF analysis with species categorizations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Type</th>
<th>Downtown Cleveland PMF</th>
<th>Chippewa Lake PMF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volatile Compounds (ppb)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOₓ</td>
<td>volatile oxidizer</td>
<td>strong</td>
<td>strong</td>
</tr>
<tr>
<td>SO₂</td>
<td>volatile reducer</td>
<td>strong</td>
<td>strong</td>
</tr>
<tr>
<td>ozone</td>
<td>volatile oxidizer</td>
<td>weak</td>
<td>weak</td>
</tr>
<tr>
<td><strong>POA Tracers (pg/m³)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chrysene</td>
<td>polycyclic aromatic hydrocarbon</td>
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<td>strong</td>
</tr>
<tr>
<td>3-methyl chrysene</td>
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<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>benzo[b]fluoranthene</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>benzo[k]fluoranthene</td>
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<td>&quot;</td>
</tr>
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<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
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<td></td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>perylene</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>ideno[1,2,3-c,d]pyrene</td>
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<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>benzo[g,h,i]perylene</td>
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<td>&quot;</td>
<td>&quot;</td>
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<tr>
<td>dibenz[a,h]anthracene</td>
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<td>Picene</td>
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<td>Coronene</td>
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<td>hopane</td>
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<td>&quot;</td>
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<tr>
<td>17α(H),21β(H)-hopane</td>
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<td>&quot;</td>
<td>weak</td>
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<tr>
<td>22S-17α(H),21β(H)-30-homohopane</td>
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<td>&quot;</td>
</tr>
<tr>
<td>levoglucosan</td>
<td>biomass burning tracer</td>
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<td>&quot;</td>
</tr>
<tr>
<td><strong>SOA Tracers (ng/m³)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methylglyceric acid</td>
<td>isoprene tracer</td>
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<td>weak</td>
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<tr>
<td>2-methylthreitol</td>
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<td>&quot;</td>
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<td>2-methylerythritol</td>
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<td>&quot;</td>
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<tr>
<td>3-acetyl pentanedioic acid</td>
<td>monoterpene tracer</td>
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<td>&quot;</td>
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<tr>
<td>3-acetyl hexanedioic acid</td>
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<td>&quot;</td>
</tr>
<tr>
<td>2-hydroxy-4-isopropylidic acid</td>
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</tr>
<tr>
<td>3-hydroxyglutaric acid</td>
<td></td>
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<tr>
<td>2-hydroxy-4,4-dimethylglutaric acid</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>removed</td>
<td>removed</td>
</tr>
<tr>
<td>pinonic acid</td>
<td></td>
<td>removed</td>
<td>removed</td>
</tr>
<tr>
<td>2,3-dihydroxysopentanol</td>
<td>2-methyl-3-buten-2-ol (MBO) tracer</td>
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<td>weak</td>
</tr>
<tr>
<td>β-caryophyllinic acid</td>
<td>sesquiterpene tracer</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2,3-dihydroxy-4-oxopentanoic acid</td>
<td>toluene (aromatic) tracer</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>sulfuric acid</td>
<td>acid tracer</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td><strong>Bulk Carbon (µg/m³)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>elemental carbon (EC)</td>
<td>black carbon</td>
<td>strong</td>
<td>strong</td>
</tr>
<tr>
<td>modern total carbon (TCmod. 1950)</td>
<td>surface carbon</td>
<td>weak</td>
<td>weak</td>
</tr>
<tr>
<td>total carbon (TC)</td>
<td>total carbon</td>
<td>weak (total variable)</td>
<td>weak (total variable)</td>
</tr>
</tbody>
</table>
Factor profiles expressed as percentages of a species over all sources is given in Figure 3 of the paper. The absolute profiles relative to TC are given in Figure S1. In Figure S1, the factor profiles have the following units: NO\textsubscript{x}, SO\textsubscript{2}, and ozone are in ppb/\mu g/m\textsuperscript{3} TC, PAHs and hopanes are in pg/\mu g TC, levoglucosan and SOA tracers are in ng/\mu g TC, EC and TC\textsubscript{mod. 1950} are in \mu g/\mu g TC. The sources attributed to these factor profiles are presented in Table 1.

**Figure S1.**

![Downtown Cleveland and Chippewa Lake source profiles expressed relative to TC. The factor profiles have the following units: NO\textsubscript{x}, SO\textsubscript{2}, and ozone are in ppb/\mu g/m\textsuperscript{3} TC, PAHs and hopanes are in pg/\mu g TC, levoglucosan and SOA tracers are in ng/\mu g TC, EC and TC\textsubscript{mod. 1950} are in \mu g/\mu g TC.](attachment:image.png)
The weekly and seasonal factor contributions are displayed in Figure S2. The mobile sources in downtown Cleveland display higher emissions during the week which is likely due to heavy duty diesel trucks that are absent from the roads on weekends. Several factors displayed strong seasonal dependences. SOA was present during the summer season while biomass burning and other combustion sources were mostly present in the winter at both sites.

**Figure S2.**

<table>
<thead>
<tr>
<th>Weekday vs. Weekend</th>
<th>Summer vs. Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mobile Sources</strong></td>
<td><strong>Mobile Sources</strong></td>
</tr>
<tr>
<td><strong>Fossil Fuel Combustion</strong></td>
<td><strong>Fossil Fuel Combustion</strong></td>
</tr>
<tr>
<td><strong>Biomass Combustion</strong></td>
<td><strong>Biomass Combustion</strong></td>
</tr>
<tr>
<td><strong>Other Combustion</strong></td>
<td><strong>Other Combustion</strong></td>
</tr>
<tr>
<td><strong>SOA</strong></td>
<td><strong>SOA</strong></td>
</tr>
</tbody>
</table>

Figure S2. Box plots showing the weekly and seasonal dependences of the five sources derived from PMF in downtown Cleveland and at Chippewa Lake.
References


