

Insights into the primary–secondary and regional–local contributions to organic aerosol and PM_{2.5} mass in Pittsburgh, Pennsylvania

R. Subramanian^{a,1}, Neil M. Donahue^b, Anna Bernardo-Bricker^c,
Wolfgang F. Rogge^c, Allen L. Robinson^{a,*}

^a*Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA*

^b*Department of Chemistry and Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA*

^c*Department of Civil and Environmental Engineering, Florida International University, Miami, FL 33199, USA*

Received 24 January 2007; received in revised form 27 May 2007; accepted 30 May 2007

Abstract

This paper presents chemical mass balance (CMB) analysis of organic molecular marker data to investigate the sources of organic aerosol and PM_{2.5} mass in Pittsburgh, Pennsylvania. The model accounts for emissions from eight primary source classes, including major anthropogenic sources such as motor vehicles, cooking, and biomass combustion as well as some primary biogenic emissions (leaf abrasion products). We consider uncertainty associated with selection of source profiles, selection of fitting species, sampling artifacts, photochemical aging, and unknown sources. In the context of the overall organic carbon (OC) mass balance, the contributions of diesel, wood-smoke, vegetative detritus, road dust, and coke-oven emissions are all small and well constrained; however, estimates for the contributions of gasoline-vehicle and cooking emissions can vary by an order of magnitude. A best-estimate solution is presented that represents the vast majority of our CMB results; it indicates that primary OC only contributes $27 \pm 8\%$ and $50 \pm 14\%$ (average \pm standard deviation of daily estimates) of the ambient OC in the summer and winter, respectively. Approximately two-thirds of the primary OC is transported into Pittsburgh as part of the regional air mass. The ambient OC that is not apportioned by the CMB model is well correlated with secondary organic aerosol (SOA) estimates based on the EC-tracer method and ambient concentrations of organic species associated with SOA. Therefore, SOA appears to be the major component of OC, not only in summer, but potentially in all seasons. Primary OC dominates the OC mass balance on a small number of nonsummer days with high OC concentrations; these events are associated with specific meteorological conditions such as local inversions. Primary particulate emissions only contribute a small fraction of the ambient fine-particle mass, especially in the summer.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Organic aerosol; Particulate matter; Source apportionment; Molecular markers; CMB; Regional transport; Secondary organic aerosol; Photochemical decay; Pittsburgh Air Quality Study

*Corresponding author. Tel.: +1 412 268 3657; fax: +1 412 268 3348.

E-mail address: alr@andrew.cmu.edu (A.L. Robinson).

¹Current address: Droplet Measurement Technologies, Boulder, CO 80301, USA.

1. Introduction

Organic carbon (OC) is a major component of fine particulate matter in all regions of the atmosphere. OC is directly emitted to the atmosphere from sources (primary OC); it is also formed in the atmosphere from low-volatility products produced by the oxidation of gas-phase anthropogenic and/or biogenic precursors (secondary OC or secondary organic aerosol—SOA). Although a number of approaches are used to estimate the primary–secondary split, each has its shortcomings, and the relative contribution of primary and secondary OC to the overall OC budget remains controversial.

One approach to investigate the sources of OC is chemical mass balance (CMB) analysis with organic molecular markers (Schauer et al., 1996; Watson et al., 1998a; Schauer and Cass, 2000; Zheng et al., 2002, 2006; Fraser et al., 2003b). This approach uses individual organic compounds such as hopanes, cholesterol, and levoglucosan as markers to estimate the contribution of emissions from major primary sources such as gasoline and diesel vehicles, food cooking, and wood combustion to ambient OC and fine-particle mass. Since CMB with molecular markers only considers primary sources, the OC not apportioned to these sources (the unapportioned OC) is commonly attributed to SOA.

The published CMB analyses of molecular-marker data indicate that the relative importance of primary sources varies widely with season and with location. Schauer et al. (1996) attributed 85% of the ambient OC in Los Angeles in 1982 to primary sources. Zheng et al. (2002) attributed essentially all of the wintertime ambient OC at both urban and rural sites in the Southeastern US to primary sources. During summer (Zheng et al., 2002) and photochemical smog episodes (Schauer et al., 2002a) the majority of the ambient OC often cannot be apportioned to sources in the model. In remote locations, very little of the OC is apportioned to primary sources (Sheesley et al., 2004). These trends are qualitatively consistent with spatial and temporal characteristics of SOA formation and reasonable correlation has been reported between the unapportioned OC and different indicators of secondary aerosol production (Schauer et al., 2002a; Zheng et al., 2002; Sheesley et al., 2004). Overall the published CMB results suggest a dominant contribution of primary sources to OC in urban areas, especially in winter. Such a conclusion is supported by estimates of SOA based on using EC

as a tracer for primary organic aerosol (Turpin and Huntzicker, 1995; Lim and Turpin, 2002; Cabada et al., 2004; Polidori et al., 2006). However, recent analyses of aerosol mass spectrometer (AMS) data suggest that SOA dominates OC levels, even in urban areas (Zhang et al., 2005; Volkamer et al., 2006; Zhang et al., 2007). In addition, a recent CMB study reports significant amounts of unapportioned OC in cities in the Southeastern US in the winter (Zheng et al., 2006).

A number of factors complicate the use of CMB analysis with molecular-marker data to quantitatively constrain the overall OC budget. OC is not fitted by the model because markers and source profiles do not exist for SOA. The CMB approach is sensitive to the selection of source profiles and fitting species (Robinson et al., 2006c,d; Subramanian et al., 2006a). Sampling artifacts—adsorption of organic vapors and evaporation of organic particles—influence filter measurements of OC both in the ambient atmosphere and from source emissions (Subramanian et al., 2004; Lipsky and Robinson, 2006). Photochemical decay of markers during regional transport may bias source contribution estimates (Robinson et al., 2006a). Finally, unknown sources of compounds fit by CMB—i.e., sources not included in the model—may bias source apportionment estimates (Robinson et al., 2006b).

This is the final paper in a series that uses a large database of organic molecular-marker data and CMB to investigate the sources of organic aerosol in Pittsburgh, Pennsylvania. Previous papers have considered in detail the contributions of motor-vehicle, biomass-burning, and food-cooking emissions to ambient OC (Robinson et al., 2006c,d; Subramanian et al., 2006a). Here we combine these earlier results with estimates for other primary sources to evaluate the overall OC budget and to examine the relative importance of local and regional primary sources. The analysis explicitly considers the uncertainty associated with source-profile variability and selection of fitting species. The CMB-unapportioned OC is compared to estimates of SOA based on the EC-tracer technique (Cabada, 2003; Cabada et al., 2004; Polidori et al., 2006) and ambient concentrations of organic compounds associated with SOA. Uncertainties due to unknown primary sources, photochemical decay, and sampling artifacts are discussed. Finally, we consider the contribution of primary emissions to $PM_{2.5}$ mass.

2. Methods

CMB analysis was performed on the dataset collected as part of the Pittsburgh Air Quality Study (PAQS) (Wittig et al., 2004), using the EPA's CMB8 model (<http://www.epa.gov/scram001/>). The analysis uses ambient concentrations of individual organic compounds, PM_{2.5} elemental carbon, and PM_{2.5} elemental composition measured on 100 days between July 2001 and July 2002 (Wittig et al., 2004). CMB analysis was performed using data for individual days; all reported averages were calculated from these daily estimates.

Daily 24-h samples were collected at the Pittsburgh Supersite in July 2001 and most of January 2002; during other periods 24-h samples were collected on a 1-in-6-day schedule. The Supersite was located in a large urban park next to the Carnegie Mellon University campus; it was not strongly influenced by any local sources (Wittig et al., 2004). Pittsburgh aerosol is dominated by regional transport (Tang et al., 2004). To characterize fine-particle concentrations in the regional air mass, a limited number of measurements were also made at a rural site in Florence, Pennsylvania (Wittig et al., 2004). This site was located 40 km west-southwest of Pittsburgh next to a large state park on a lightly traveled dirt road. There are no major roads or stationary sources within several kilometers of the Florence site. Florence is typically upwind of Pittsburgh, and the fine-particle mass and bulk constituents measured at the site are quite similar to those measured at other sites in the region (Tang et al., 2004). Thirteen sets of parallel 24-h samples were collected in Pittsburgh and Florence during January 2002 and four paired sets in July 2002.

PM_{2.5} and semivolatile organics were collected using medium-volume quartz-filter/polyurethane-foam-plug (PUF) samplers. Each quartz/PUF sample was solvent extracted and the extract was analyzed by high-resolution gas chromatography-mass spectrometry, providing a large dataset of daily organic composition (Robinson et al., 2006a). For the organic speciation measurements, identical samplers and procedures were used at both sites. At the Supersite, OC/EC samples were collected on quartz filters and analyzed using a thermal/optical transmission method (Subramanian et al., 2004; Subramanian et al., 2006b). Trace-metal data were measured by inductive coupled plasma-mass spectrometry (ICP-MS) analysis of samples collected on

cellulose filters (Pekney et al., 2006). EC and trace metal data for the Florence site were collected and analyzed as part of the EPA speciation trends network.

CMB results are sensitive to the specific combination of source profiles and fitting species (Robinson et al., 2006b–d; Subramanian et al., 2006a). For example, different combinations of source profiles typically yield well-correlated source-contribution estimates (especially if they are applied to the same set of fitting species), but biases between the estimates can exceed the uncertainties calculated by CMB. This underscores the fact that CMB-reported uncertainties are typically based on the measurement uncertainty and quality of the fit, and do not include the source profile variability.

To account for the uncertainty associated with selection of source profiles and fitting species, we present results for a large number of different CMB models, each of which was fit to the entire dataset using a different combination of source profiles and fitting species. The majority of the models use the same core set of fitting species: EC, iron, titanium, and 22 organic markers (individually or as groups of compounds): *n*-heptacosane, *n*-nonacosane, *n*-hentriacontane and *n*-trtriacontane; iso-hentriacontane, anteiso-dotriacontane; octadecanoic acid, hexadecanoic acid, 9-hexadecenoic (palmitoleic) acid, and cholesterol; syringaldehyde, sum of resin acids, acetosyringone, levoglucosan; 17a(H),21b(H)-29-norhopane, 17a(H),21b(H)-hopane, 22R + S-17a(H),21b(H)-30-homohopane, 22R + S,17a(H),21b(H)-30-bishomohopane; benzo[e]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, and coronene. Certain models used slightly different sets of species, as described in the online supporting material. OC is not included (“fitted”) by any model because molecular markers and source profiles for SOA are not known. Uncertainties for individual compounds are based on relative and absolute uncertainties determined from replicate analysis of samples from collocated samplers. Absolute uncertainties are based on multiples of the minimum detection limits, while relative uncertainties range from $\pm 10\%$ to $\pm 30\%$.

Each model fits source profiles for eight source classes: diesel vehicles, gasoline vehicles, road dust, biomass combustion, cooking emissions, coke production, vegetative detritus, and cigarette smoke. Source profiles for coke-oven emissions, vegetative detritus and road dust were developed as part of the PAQS (Robinson et al., 2006b, 2007b); the rest

of the profiles are taken from the literature. A complete list of the source profiles is provided in the online Supplementary Material.

Except for the addition of metallurgical coke production, our list of sources and marker species is based on the original CMB analyses of molecular marker data by Schauer et al. (1996) and Schauer and Cass (2000). Therefore, like previous studies, we assume that all major sources of each compound are included in the model and the marker species are conserved during transport from source to receptor. These assumptions are examined in detail later in this paper.

The sensitivity analysis considered different combinations of input species and source profiles. Eleven different combinations of motor-vehicle-specific source profiles and/or fitting species were used to apportion OC to motor vehicles (Subramanian et al., 2006a). Three different combinations of biomass-smoke-specific source profiles and/or fitting species were used to apportion OC to biomass burning (Robinson et al., 2006c). Three different combinations of cooking-specific source profiles and/or fitting species were used to apportion OC to food-cooking emissions (Robinson et al., 2006d). The variability in the contribution of metallurgical coke production is estimated using two different profiles developed from a series of samples collected at a fence-line site adjacent to a coke production facility (Weitkamp et al., 2005). The variability in the road-dust contribution is bounded by use of urban and rural road-dust profiles as well as by substituting calcium for iron as a fitting species. To investigate the uncertainty in the contribution of vegetative detritus, we fit both the PAQS and the Los Angeles profiles (Rogge et al., 1993), as well as different combinations of the higher odd *n*-alkanes.

The sensitivity analysis did not exhaustively evaluate every possible combination of source profiles and fitting species; for example, all eleven different motor vehicle scenarios were not evaluated with each of the three different food cooking scenarios. Instead we quantified the range of solutions for each source class using a few base sets of profiles and compounds for the other source classes. A more exhaustive analysis is not necessary because of the source-specificity of molecular markers. For example, the contribution of food-cooking emissions is determined by cholesterol, alkenoic acids and alkanolic acids, while motor-vehicle emissions are determined by hopanes and EC. Therefore, the estimated food-cooking contri-

bution changes minimally as we vary the motor-vehicle source profiles. There are some exceptions, most notably gasoline and diesel vehicles, which share markers (hopanes and EC). Therefore, we focus here on the total vehicle OC and not the gasoline–diesel split. Also, a number of sources contribute to ambient EC. We assessed this issue by running the different motor vehicle scenarios with various biomass smoke scenarios and found that it posed a problem on only a few days with high biomass smoke. The conclusions of this paper are based on the results of almost 100 different CMB models.

Our discussion of the overall OC mass balance focuses on the results from four CMB models: best estimate, maximum gasoline, maximum cooking, and maximum gasoline and cooking. As discussed below, the best-estimate model falls within the vast majority of the solutions, while the other models represent outlier solutions. These four models use the same set of profiles and fitting species for the non-vehicular and non-food-cooking source classes. For biomass smoke, one set of profiles is used for the fall/winter seasons and another set for the summer/spring seasons to account for the expected seasonal changes in the nature of biomass smoke sources. Three profiles are used in each season to account for the widely varying ratios of biomass smoke markers (Robinson et al., 2006c). The fall/winter data are fitted with the Fine et al. (2001) eastern hemlock, eastern white pine, and red-maple profiles. Of the viable combinations of space-heating profiles, this combination apportions the maximum amount of ambient OC to biomass smoke (Robinson et al., 2006c). The summer/spring data are fitted using three simulated open-burning profiles: the Hays et al. (2002) mixed hardwood forest foliage (MHFF) and Florida palmetto and slash pine profiles; and the Hays et al. (2005) wheat-straw profile. For the other source classes, we use Pittsburgh-specific vegetative-detritus and road-dust profiles (Robinson et al., 2007b), the Pittsburgh coke-production profile that yields the maximum OC contribution (Robinson et al., 2006b), and the Rogge et al. (1994) cigarette-smoke profile. The supporting online information provides more information on the CMB scenarios.

These four models use different combinations of fitting species and source profiles to estimate cooking and/or gasoline-vehicle emissions, the two source categories that exhibit the most variability (Robinson et al., 2006d; Subramanian et al., 2006a).

For cooking emissions, the best-estimate model fits three cooking profiles: average red-meat frying, Schauer et al. (1999a) charbroiling, and average seed-oil cooking; it provides the most plausible estimate of cooking emissions (Robinson et al., 2006d). The models that yield the maximum cooking estimate fit an average red-meat charbroiling profile and do not fit palmitic acid and stearic acid (Robinson et al., 2006d). For vehicle emissions, the best-estimate model fits the Northern Front Range Air Quality Study (NFRAQS, Watson et al., 1998a) heavy-duty diesel profile and a composite NFRAQS gasoline profile that assumes 6.8% of the fleet is high emitters and smokers, split evenly (Subramanian et al., 2006a). Of the 11 different combinations of vehicle profiles and fitting species we have considered, this scenario yields the median estimate of the total (gasoline+diesel) vehicular contribution to OC. The model that yields the maximum gasoline estimate used three source profiles: the Schauer et al. (2002b) catalytic and noncatalytic gasoline profiles fitted separately, and a composite of the Schauer et al. (1999b) and Fraser et al. (2002) diesel profiles. Two additional *n*-alkanes (C24 and C26) are included as fitting species in CMB to separate the two gasoline sources (Subramanian et al., 2006a).

On the vast majority of the days, all of the CMB solutions presented here meet the established goodness-of-fit criteria (Watson et al., 1998b). The regression coefficients (R^2) were 0.80 or higher for over 96% of all CMB runs, with median values above 0.90 for each solution set (CMB analysis for all samples with a given set of profiles and fitting species). The confidence levels (based on the χ^2 and degrees of freedom) on all solutions were 95% or better for 99.8% of the runs. The degrees of freedom for each CMB run were between 12 and 17 depending on the number of species fitted and the number of nonzero sources apportioned by CMB; the CMB specifications for a good fit require a minimum of 5. Over 90% of the fitted species in all runs were estimated by CMB to within a factor of two of the ambient concentration, i.e., the ratios of CMB-calculated concentrations to the measured values (C/M ratios) were between 0.5 and 2.0, another requirement for a good fit. The “percentage mass apportioned” criterion cannot be applied since SOA is a significant fraction of the ambient OC and is not included (“fitted”) in the CMB model. Excluding the days in which the models do not meet the CMB performance criteria does not alter

our conclusions. Table S1 in supporting online information lists R^2 and χ^2 values for the best-estimate model. More information on the statistical quality of the various solutions is also presented in the companion papers (Robinson et al., 2006b–d; Subramanian et al., 2006a).

3. Results and discussion

3.1. Source apportionment of primary OC and the regional–local split

We begin our discussion of the contribution of primary sources by considering the seasonal average CMB results shown in Fig. 1. The boxes represent the range of source-contribution estimates for all of the different CMB models, except for the maximum-cooking and the maximum-gasoline models. Table S2 in the supporting online material lists the seasonal-average amount of OC apportioned by the best-estimate, maximum and minimum models to each source class. Table S1 lists the daily source apportionment by the best-estimate model.

The CMB results are reasonably well constrained for four of the source classes—diesel vehicles, wood combustion, debris (vegetative detritus plus road dust), and coke production. For these sources, the seasonal average OC apportioned by the maximum and minimum models is within a factor of 2, which is comparable to the typical CMB-calculated uncertainty.

The CMB results for gasoline vehicles, total vehicles, and food cooking are not well constrained. For example, the maximum and minimum estimates of the average gasoline-vehicle contribution vary by more than a factor of 20 in the summer, which is much greater than the CMB-calculated uncertainties. This variability is primarily due to differences in markers-to-OC ratios of the different source profiles (Robinson et al., 2006d; Subramanian et al., 2006a). The large uncertainty in the contribution of motor vehicles and cooking significantly affects the overall OC mass balance, which is discussed in detail below.

Fig. 1 indicates that the contribution of some sources follows a seasonal pattern. Not surprisingly, biomass smoke exhibits the most striking seasonal pattern, with dramatically higher concentrations in the winter and fall when temperatures are colder. The contribution of coke-oven emissions is higher in the fall and spring when inversions are more common. The combined contribution of road dust

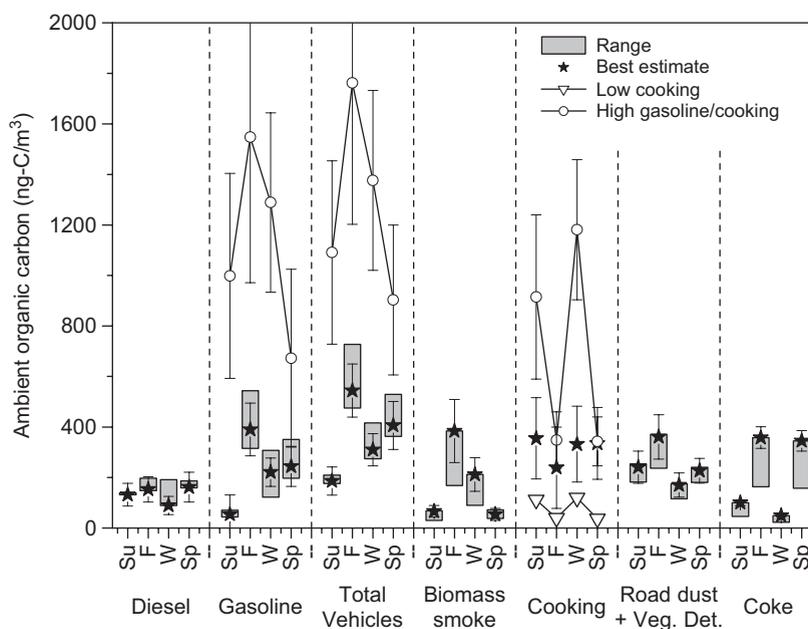


Fig. 1. CMB estimates of the seasonal average contributions of major primary sources of organic aerosol. Boxes show the range of the vast majority of the models (excluding the maximum gasoline and the maximum and minimum cooking). No range is indicated for cooking. The maximum gasoline and cooking scenarios, discussed in the text, are due to “outlier” profiles with relatively small marker-to-OC ratios. Error bars indicate CMB calculated uncertainty for selected results.

and vegetative detritus peaks in the fall and is at a minimum in the winter. Diesel vehicles exhibit essentially no seasonal variability.

All of the models indicate that the absolute and relative contributions of all source classes exhibit significant day-to-day variability, reflecting the changes in ambient molecular-marker concentrations. This variability is illustrated by the daily source-contribution estimates plotted in Fig. 2, in which results from the best-estimate model are grouped by season and then sorted by the ambient OC concentration. Although high concentration days occur episodically throughout the study, organizing the data by OC concentration allows one to compare days with similar concentrations. All of the models predict that motor vehicles, cooking, and debris contribute appreciable amounts of OC on essentially every day. Biomass smoke and coke production only contribute significant OC on a few days. The large variability in the contribution of coke production is due to the fact that it is a local point source, whose influence is strongly dependent on local meteorology. The day-to-day contribution of biomass smoke varies widely even in the winter when temperatures were consistently cold. This variability implies that biomass

was not an important fuel for space heating in Pittsburgh during this study (Robinson et al., 2006c).

Fig. 3 examines the relative contribution of regional versus local primary sources based on paired samples collected simultaneously in Pittsburgh and the upwind Florence sites. Fig. 3(a) plots the paired ambient OC measurements. OC concentrations in Pittsburgh are on average 30% higher than in Florence during the winter and 20% higher during the summer. Therefore, on a relative basis, local sources appear to be modestly more important in winter than in summer, but OC levels are also 40% lower in the wintertime compared to the summer. The ambient OC data places a hard constraint on the potential contribution of local sources, underscoring the significant contribution of regional transport to OC levels in the city (Tang et al., 2004).

Fig. 3 also presents scatter plots of CMB source contribution estimates for three major source classes: motor vehicles (Fig. 3(b)), biomass combustion (Fig. 3(c)), and cooking (Fig. 3(d)). The results are based on CMB analysis of paired speciation samples collected at the Pittsburgh and Florence sites using the best-estimate model. Our conclusions

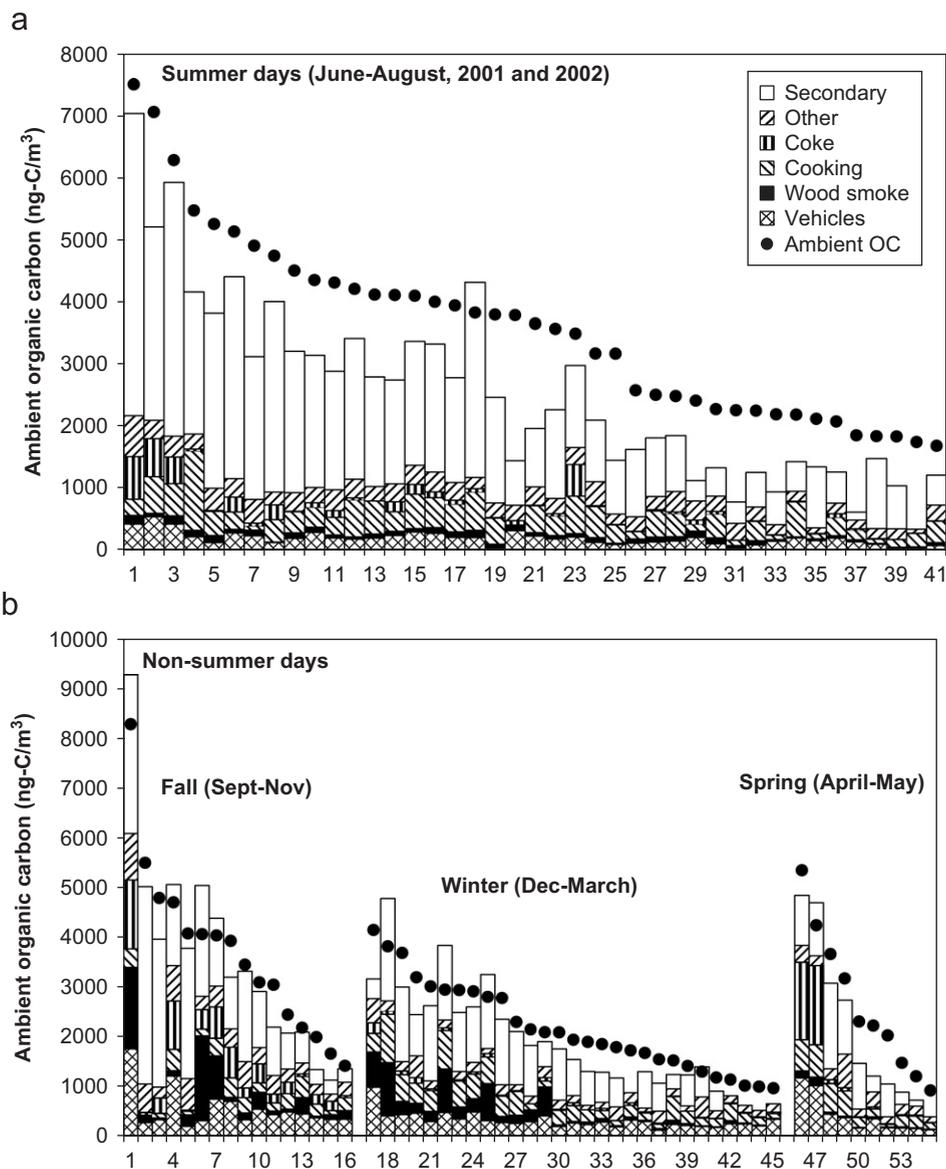


Fig. 2. Daily OC mass balance from the best-estimate CMB solution for (a) summer and (b) fall, winter and spring months. Data are first sorted by season and then by decreasing ambient OC concentration. The secondary OC is the upper bound for SOA using the EC-tracer technique (Cabada, 2003; Cabada et al., 2004). “Other” is the sum of vegetative detritus and road dust.

are not sensitive to the specific CMB model, as long as the data from both sites are analyzed using the same profiles and fitting species.

The wintertime CMB results shown in Fig. 3 indicate modestly higher levels of primary OC in the city than in Florence. For example, the average wintertime vehicular OC in Florence is $230 \pm 52 \text{ ng-C m}^{-3}$ versus $345 \pm 70 \text{ ng-C m}^{-3}$ in Pittsburgh (Fig. 3(b)). This implies that, on average, two-thirds of the wintertime primary vehicular OC in Pitts-

burgh is associated with regional transport and only one-third is due to local emissions. The wintertime cooking estimates shown in Fig. 3(c) indicate a similar regional–local split. The wintertime biomass-smoke contributions at the two sites are generally similar, except for a few days when biomass-smoke levels are enhanced at one of the two sites (Fig. 3(d)). The days with elevated biomass smoke in the city are associated with hardwood smoke, presumably due to local wood combustion

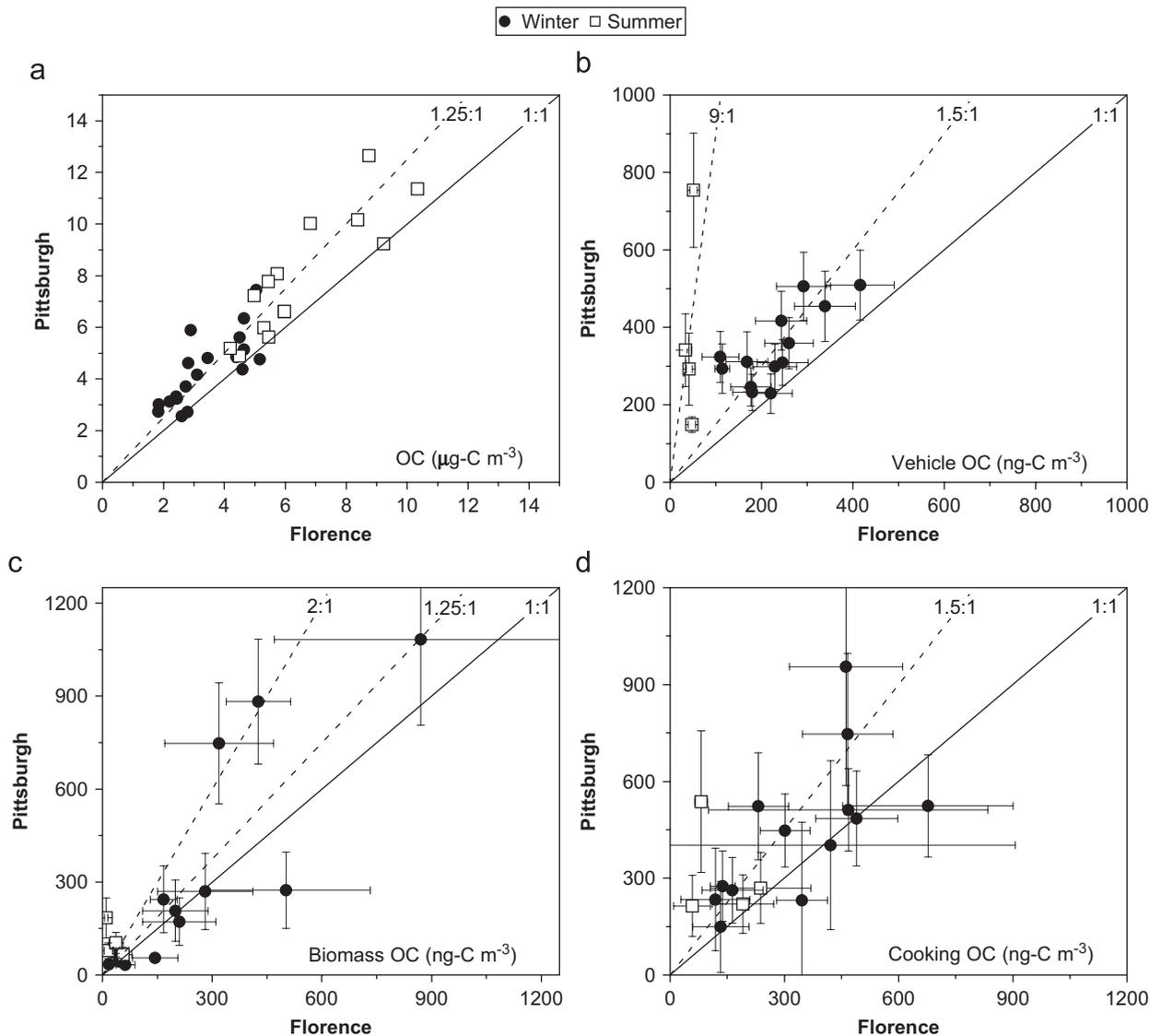


Fig. 3. Scatter plots of (a) measured ambient OC and (b)–(d) CMB source contribution estimates for Pittsburgh and an upwind, rural site in Florence, Pennsylvania. CMB results are shown for (b) motor vehicles (gasoline plus diesel), (c) biomass combustion, and (d) food cooking. The source apportionment results are based on the best-estimate CMB model. The lines indicate different ratios of the Pittsburgh-to-Florence results; for example, the 2:1 line in panel (c) indicates that CMB estimated biomass smoke contribution in Pittsburgh is twice that in Florence. Error bars are CMB-propagated uncertainties.

for space heating. During PAQS, high biomass smoke concentrations were typically observed on winter weekend days (Robinson et al., 2006c). On average, the wintertime CMB results indicate that 70% of the primary OC in Pittsburgh is emitted by regional and not local sources, consistent with the relatively uniform spatial distribution of ambient OC (Fig. 3(a)).

Interpretation of the summertime CMB data at the two sites is more complicated. During the

summer, biomass-smoke and meat-cooking contributions at the two sites are usually comparable, but the OC attributed to motor vehicles in Pittsburgh exceeds that in Florence by a factor of 9, as CMB apportions less than 50 ng-C m⁻³ of the ambient OC in Florence to motor vehicle emissions. In fact, the peak summertime concentration of vehicular OC in Florence is more than a factor of 2 smaller than even the lowest winter day. One interpretation of the Florence CMB results is that motor vehicles are

not a major source of OC in the regional air mass in the summer; however, this is inconsistent with the winter data. The underlying cause of this discrepancy is that in the summertime ambient hopanes concentrations are much lower in Florence than in the city; for example, summertime norhopane levels are three to twelve times higher in Pittsburgh than in Florence (Robinson et al., 2006a). The low summertime concentrations of hopanes in Florence severely constrain the OC apportioned to motor vehicles. Robinson et al. (2006a) argues that there is significant photochemical decay of hopanes in the regional air mass in the summer. If true, then the ambient hopanes in Pittsburgh during summer only represent local vehicular emissions because the hopanes in the regional air mass have been photochemically degraded. Photochemical decay of hopanes would violate one of the underlying assumptions of CMB and is discussed in more detail later.

3.2. Evaluation of the OC mass balance

We begin our discussion of the overall OC mass balance by considering the contribution of the four well-constrained source classes (diesel vehicles, biomass smoke, debris, and coke). The maximum CMB solution indicates that *together* these four classes contribute on average $23 \pm 11\%$ of the ambient OC (average \pm standard deviation of the daily source-contribution estimates). The relative contribution of these four source classes varies seasonally; it is lowest in the summer, $16 \pm 4\%$ of the daily OC, and highest in the fall, $35 \pm 13\%$ of the daily OC. However, the key point is that on essentially all days these well-constrained primary sources contribute relatively little ambient OC, even if one considers the maximum solution. Fig. 2 indicates that on only a handful of nonsummer days do any of the four well-constrained sources contribute large amounts of OC; for example the spikes in coke-oven emissions in the spring and spikes in biomass smoke in the fall.

The amount of OC not apportioned to primary sources therefore depends strongly on which model is used to represent the two poorly constrained source classes, gasoline vehicles and cooking. This is illustrated in Fig. 4, which compares seasonal-average results of four CMB models: the best-estimate, maximum-gasoline, maximum-cooking, and maximum-gasoline-and-maximum-cooking models. All of the models show a similar seasonal pattern with

a maximum primary contribution in winter and a minimum in summer, but they indicate very different splits between primary and unapportioned OC. On average these models apportion between 25% and 75% of the ambient OC to primary sources in summer and between 50% and 140% in winter. Of the four models shown in Fig. 4, the minimum estimate corresponds to the best-estimate model. The maximum primary estimate corresponds to the model that apportions the maximum OC to both food cooking and gasoline vehicles, the two poorly constrained source classes.

The maximum primary estimate shown in Fig. 4 is clearly implausible as it apportions more than 140% of the wintertime OC on average. The problems are even more apparent if one examines the daily source contribution estimates, as the maximum model overapportions the measured OC by as much as a factor of 3 on many individual days. Many of these problematic days are not low concentration days. Overapportionment of ambient OC by CMB analysis of molecular-marker data has been reported by other studies; it has been attributed to missing sources for specific markers (Sheesley et al., 2004) or sampling artifacts (Zheng et al., 2002). We believe that the problem is largely due to the specific combinations of sources profiles and fitting species, which maximize the contribution of cooking and gasoline vehicles. Fig. 1 indicates that, in comparison to the other solutions, models that apportion the maximum OC to cooking and/or vehicles appear to be outliers.

From the perspective of the seasonal-average OC mass balance, the other three solutions (maximum gasoline, best estimate, and maximum cooking) plotted in Fig. 4 appear plausible. In fact, models that apportion the maximum amount of OC to either meat cooking or gasoline vehicles attribute essentially all of the wintertime OC to primary sources, consistent with the conceptual model that primary sources are dominant in the winter. However, more detailed examination of these two solutions raises important concerns. For example, on one-fifth of the winter days, the maximum-gasoline and the maximum-cooking models apportion more than 120% of the ambient OC to primary sources. This exceeds the CMB-stipulated “allowable uncertainty” on the overall OC mass balance (the “percentage mass apportioned” criterion, $\pm 20\%$), assuming no missing sources. These models also apportion about 60% of ambient OC to a single source—either gasoline vehicles or meat

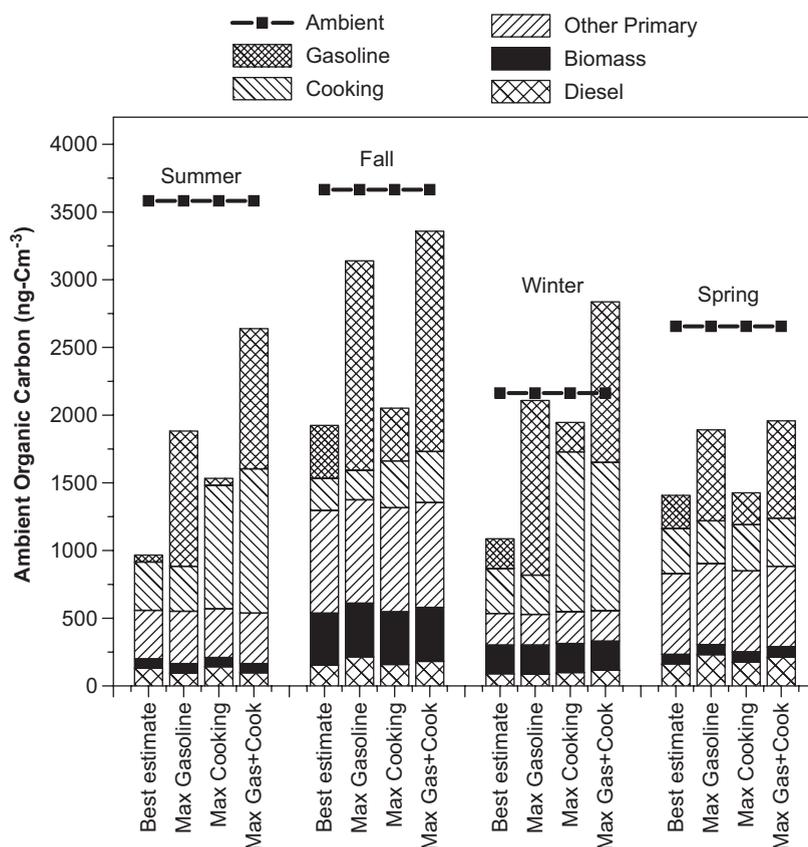


Fig. 4. Seasonal average contributions to the ambient OC from primary sources based on the four CMB models discussed in the text: best estimate, maximum cooking, maximum gasoline, and maximum gasoline and cooking. “Other primary” is the sum of coke, vegetative detritus, and road dust.

cooking—because of the specific combinations of profiles and fitting species. In the maximum-gasoline model the primary OC is dominated by the low-emitter Schauer et al. (2002b) catalytic gasoline profile which has extremely small marker-to-OC ratios (Subramanian et al., 2006a). One does not expect low-emitting gasoline vehicles to be the dominant pollutant source (Beaton et al., 1995). Combining the Schauer et al. (2002b) catalytic gasoline profile with any other gasoline vehicle profile dramatically reduces the amount of OC apportioned to gasoline vehicles (Subramanian et al., 2006a). Similarly, the maximum-cooking model is based on an average charbroiling profile with very small marker-to-OC ratios, which maximizes the amount of ambient OC apportioned to cooking sources (Robinson et al., 2006d). This model also overapportions stearic and palmitic acids by more than a factor of 3 in the winter (Robinson et al.,

2006d). These concerns diminish the probability that either of the maximum-gasoline and the maximum-cooking solutions is a reasonable explanation of the ambient data.

Fig. 1 indicates that the best-estimate model represents the vast majority of the solutions considered here. This and many other models only apportion on average 25% of the OC to primary sources in summer and about 50% in winter. While comparably large amounts of unapportioned OC have been reported by previous CMB studies, especially in rural areas (Zheng et al., 2002; Sheesley et al., 2004), the relatively small contribution of primary sources in an urban area, especially in winter, is surprising. Potential explanations include SOA, missing primary sources, sampling artifacts, and photochemical decay of tracers; these issues are considered in detailed in the next section.

We also examined the relative importance of primary emissions on a daily basis, focusing on the

days with above-average OC concentrations because of the association of adverse health effects with elevated PM concentration. Fig. 2 shows the daily source apportionment results for the best-estimate solution. The high-OC days in summer are not associated with primary emissions; however, Fig. 2(b) indicates that peak OC levels on the nonsummer days are generally associated with primary emissions. The highest OC occurred on a fall day with a strong local inversion; the best-estimate solution indicates that primary sources contributed 75% of the measured OC on that day. Metallurgical coke production, a local point source, contributed significant OC on several of these nonsummer high-OC days. Biomass smoke contributed a notable amount of OC on essentially all wintertime days with above-average OC concentrations but little OC on wintertime days with below-average OC concentrations. These conclusions hold across all of the solutions, even the maximum-gasoline and maximum-cooking models.

3.3. Sources of unapportioned OC

The major conclusion from our discussion of the CMB results is that the majority of the OC is not apportioned to any of the eight primary sources explicitly accounted for by the model. The vast majority of the models only apportion around 50% of the wintertime OC to primary sources and only 25% of it in the summer. The previous section illustrated how selection of source profiles and fitting species influences the amount of unapportioned mass. In this section we discuss a number of factors not explicitly considered by the CMB model that also influence the amount of unapportioned mass; these include SOA, unknown primary sources, decay of molecular markers, and sampling artifacts. Given the aforementioned concerns with the maximum gasoline and maximum cooking CMB models, we focus our discussion on the best-estimate model, which represents the vast majority of the solutions.

3.3.1. SOA

The OC not apportioned to primary sources by CMB is often attributed to SOA. The EC-tracer method provides an independent estimate of SOA and has been used to analyze the PAQS dataset (Cabada, 2003; Cabada et al., 2004; Polidori et al., 2006). The EC-tracer method requires estimating the aggregate OC/EC ratio for all

primary emissions, plus the OC contribution from primary sources that do not emit EC. For the PAQS dataset these parameters were derived from the ambient measurements made during periods with little evidence of photochemical activity.

Figs. 2 and 5(a) show the maximum SOA estimate derived by Cabada (2003) and Cabada et al. (2004) using the EC-tracer method. In the non-summer months, Fig. 2(b) indicates that the maximum EC-tracer SOA closes the OC mass balance, explaining most of the ambient OC not apportioned to primary sources by the best-estimate model. In the summer, EC-tracer SOA is strongly correlated with the unapportioned OC (R^2 of 0.81; Fig. 5(a)). The slope of the linear regression is 0.91 but there is a statistically significant intercept, indicating a persistent gap in the OC mass balance (Fig. 2(a)). This intercept could indicate unaccounted primary sources and/or photochemical decay of markers (the latter leading to an underestimate of the primary apportioned OC and an overestimate of the unapportioned OC). Lower estimates of SOA using the EC-tracer method (Cabada et al., 2004; Polidori et al., 2006) indicate zero secondary OC on many days for which CMB indicates substantial unapportioned OC, especially in winter. Regression analysis of the unapportioned OC with the lower EC-tracer estimates of SOA still yields good, but somewhat poorer, correlations. Therefore, all of the different EC-tracer estimates support the conclusion that much of the unapportioned OC, at least in summer, is SOA.

An argument for using the maximum EC-tracer estimate is that Pittsburgh is dominated by regional transport. If there is a consistent background of SOA in the regional air mass, the primary OC/EC ratio and/or intercept used in the EC-tracer method may be elevated above the actual values, reducing the SOA estimated by this technique. It is difficult to account for this *regional* SOA using the EC-tracer technique because *local* conditions are typically used to identify primary-dominated periods.

Ambient concentrations of organic compounds associated with SOA provide additional evidence that a large fraction of the unapportioned OC is SOA. For example, Fig. 5(b) shows reasonable correlation between the unapportioned OC and the sum of nopinone, norpinonic acid and pinonic acid (R^2 of 0.56). These species have been measured in smog chamber SOA experiments of α -pinene and β -pinene ozonolysis (Yu et al., 1999; Koch et al., 2000; Fick et al., 2003). Fig. 5(c) shows reasonable

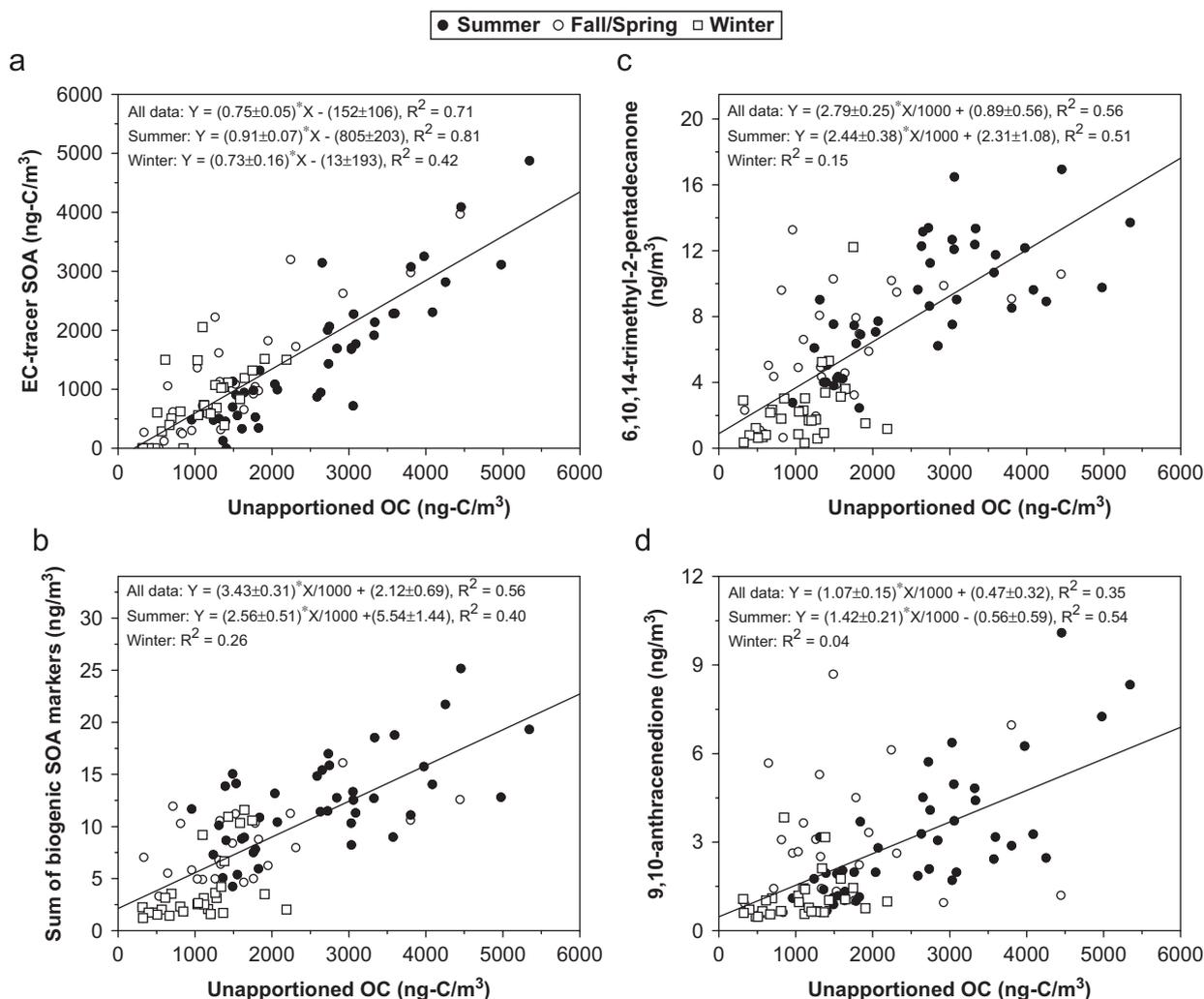


Fig. 5. Scatter plots of the ambient OC not apportioned by the best-estimate CMB model to primary sources with (a) SOA estimated using the EC-tracer method; (b) sum of three terpene oxidation products, nopinone, norpinonic acid and *cis*-pinonic acid; (c) 6,10,14-trimethyl-2-pentadecanone (a ketone associated with both biogenic or anthropogenic emissions); and (d) 9,10-anthracenedione (an oxy-PAH). Lines indicate linear regression of entire dataset. Results of linear regression for all of the data, summer data, and winter data given in each panel.

correlation between the unapportioned OC and 6,10,14-trimethyl-2-pentadecanone (R^2 of 0.56). This branched ketone has been used as an indicator of biogenic SOA formation in rural or remote areas (Simoneit and Mazurek, 1982; Simoneit et al., 1988; Alves et al., 2001; Engling et al., 2006). It is also formed from the incomplete combustion of pristane and phytane present in motor vehicle fuel (Simoneit, 1985); thus, its presence in urban areas cannot be uniquely attributed to SOA. The unapportioned OC is similarly correlated with 1,3-benzene dicarboxylic acid (R^2 of 0.55; not shown), which has been associated with primary vehicular emis-

sions (Fraser et al., 2003a). Finally, some correlation is observed between the unapportioned OC and oxy-PAHs such as 9-fluorenone and 9,10-anthracenedione ($R^2 > 0.4$, Fig. 5(d)). These PAH oxidation products can be formed in the atmosphere or during combustion (Ramdahl, 1983; Simoneit et al., 1991).

Previous studies have proposed 1,2-benzenedicarboxylic acid and aliphatic diacids as indicators of anthropogenic SOA (Schauer et al., 2002a; Fraser et al., 2003a; Sheesley et al., 2004). However, the unapportioned OC is not correlated with these compounds ($R^2 < 0.2$).

AMS data collected in Pittsburgh also suggest that SOA is the dominant component of the organic aerosol in Pittsburgh. Zhang et al. (2005) estimates that 50% of the OC in Pittsburgh in September 2002 was secondary (assuming an organic-mass-to-organic-carbon ratio of 2.2 and 1.2 for oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA), respectively). This is consistent with the results from the best-estimate solution shown in Fig. 2(b) for September 2001.

Overall these multiple independent indicators of SOA all provide strong evidence that the dominant component of the summertime unapportioned OC, and thus the ambient OC, is SOA. However, the potential contribution of SOA in winter is less clear. While the wintertime unapportioned OC is somewhat correlated with the maximum EC-tracer estimate of SOA ($R^2 = 0.45$; Fig. 5(a)), little correlation is observed with organic compounds commonly associated with SOA.

3.3.2. Unknown primary sources

Our CMB analysis only accounts for emissions from eight primary source classes. Except for the addition of metallurgical coke production, our list of sources is largely the same as that used in other studies. It includes major anthropogenic sources such as motor vehicles, cooking and biomass combustion as well as some primary biogenic emissions (leaf abrasion products). However, there are certainly other primary sources of OC. The fact that most of our CMB models do not apportion a significant fraction of the wintertime OC raises the possibility that unaccounted primary sources may be significant. In addition, Fig. 2(a) indicates that, even after including the maximum EC-tracer estimate of SOA in the OC mass balance, about $1 \mu\text{g-C m}^{-3}$ of the ambient OC remains unexplained in summer.

First we consider the potential contribution of unaccounted local sources. Not all local industrial sources are represented in the CMB model. The Allegheny County $\text{PM}_{2.5}$ point-source emission inventory is dominated by facilities related to steel production and coal-fired boilers (Hochhauser, 2004). The CMB analysis does include the largest point-source category, metallurgical coke production. The inventory estimates that coke production contributes 25% of the county-wide point-source emissions of $\text{PM}_{2.5}$ mass, and 40% of coke emissions are OC (Weitkamp et al., 2005). Although the CMB results indicate that coke production was

an important source on a few study days (Fig. 2), it only contributed $70 \pm 9 \text{ ng-C m}^{-3}$ or 2% of the study-average ambient OC. Therefore, one must carefully distinguish between the daily and long-term average contributions of a local point source. Given the fact that the Pittsburgh Supersite was not located close to any major local sources, it is highly unlikely that emissions from some unaccounted local point source strongly influenced the long-term average OC measurements at the site. In fact, highly time-resolved measurements made during PAQS reveal few periods with even modestly elevated OC spikes that would indicate strong influence of an OC-rich plume from a local source.

Another strong piece of evidence that unaccounted local sources are not strongly influencing OC concentrations at the Pittsburgh site is the ambient OC data shown in Fig. 3(a). As previously discussed, OC concentrations at the Pittsburgh Supersite are on average only 20–30% higher than levels in the regional air mass (Tang et al., 2004). This modest bump in urban OC concentrations represents the aggregate contribution of all local sources. Notably, this bump is substantially smaller than the amount of unapportioned OC. Furthermore, the CMB results from the Pittsburgh and Florence sites such as those shown in Fig. 3 indicate that about half of the bump can be accounted for by sources in the model. Therefore, a reasonable estimate for the contribution of unaccounted local sources is 10–15% of the long-term ambient OC, which is a small fraction of the unapportioned OC.

We cannot rule out an unaccounted, regional primary source. Fig. 2 indicates that after accounting for EC-tracer estimates of SOA, a larger fraction of the summertime OC remains unexplained compared to other seasons. This pattern is consistent with a primary biogenic source. Our CMB model does account for primary emissions from leaf abrasion, using the higher odd *n*-alkanes (C27, C29, C31, and C33) as markers. However, this is a minor source, contributing only $120 \pm 40 \text{ ng-C m}^{-3}$ or 3% of the study-average OC. Recent studies have suggested that biogenic materials such as fungal cells can contribute significant fine organic aerosol mass (Womiloju et al., 2003).

A potential explanation for the large amounts of unapportioned OC in winter is that we are systematically underestimating the contribution of biomass smoke. For example, our estimates of biomass smoke OC in Pittsburgh are much lower than

estimates made in the Southeast (Zheng et al., 2002). A challenge is that source profile levoglucosan-to-OC or levoglucosan-to-PM-mass ratios can vary widely depending on combustion conditions and fuel type (Hedberg and Johansson, 2006; Mazzoleni et al., 2007), which can create substantial variability in the CMB results. If one uses a source profile with a small levoglucosan-to-OC ratio one can attribute much more OC to biomass smoke. In fact on days when biomass smoke marker concentrations in Pittsburgh are high, a profile with a very small levoglucosan-to-OC ratio will attribute more than 100% of the ambient OC to biomass smoke.

Robinson et al. (2006c) examined in detail the contribution of biomass smoke to ambient OC in Pittsburgh using the PAQS dataset. The analysis considered a large number of fireplace, woodstove, and simulated open burning profiles and different combinations of molecular markers. A major challenge with the Pittsburgh dataset is the widely varying ambient ratios of different biomass smoke makers. This variability means that the composition (and the aggregate source profile) of the aged biomass smoke influencing Pittsburgh changes substantially from day to day, presumably because of the poorly controlled, highly variable nature of biomass combustion. In order to account for this variability one needs to use different profiles for each day, with little basis for selecting which profile to use. Alternatively, one can include multiple profiles simultaneously in the model. We have adopted the second approach. Therefore, on each day CMB calculates a weighted average contribution of three different source profiles, which ultimately better constrains the amount of biomass smoke OC compared to estimates based on a single (potentially outlier) profile. Another advantage of our approach is that CMB produces a solution of high statistical quality for the entire dataset with the same set of profiles. While different three-profile combinations yield different amounts of biomass smoke OC, much less variability is observed compared to solutions based on a single profile. Of the solutions derived by Robinson et al. (2006c), here we use the scenario that apportions the maximum OC to biomass smoke. Removing levoglucosan from the fitting dataset does not appreciably change the amount of OC apportioned to biomass smoke. Therefore, it seems unlikely that biomass OC explains the unapportioned wintertime OC.

3.3.3. Photochemical degradation of molecular markers

CMB analysis assumes that the compounds are conserved as source tracers during transport from source to the receptor. Therefore, any photochemical decay of molecular markers will reduce the CMB source-contribution estimates, increasing the amount of unapportioned OC. Schauer et al. (1996) concluded that most of the compounds used in CMB were stable in the context of Los Angeles. Robinson et al. (2006a) presented evidence for decay of molecular markers in the regional air mass in the summertime. Numerous lab studies have also reported rapid oxidation of individual organic compounds in simple mixtures (Rudich et al., 2007). Here we examine the solutions for evidence of photochemical decay and discuss whether such decay could strongly influence the amount of unapportioned OC.

Given the strong seasonal pattern of photochemical activity, significant marker decay should cause unexpected seasonal patterns in the source apportionment results. However, to attribute a seasonal pattern to photochemistry one needs to control for other factors that influence pollutant concentrations such as source strength and pollutant dispersion. Normalizing the source-contribution estimates using an inert tracer is one approach to control for variable dispersion. This tracer should be a condensed-phase compound so that it has a similar atmospheric lifetime as OC. EC is commonly used as the normalizing tracer to account for the effects of dilution.

Fig. 6 shows the monthly averages of the CMB results from the best-estimate model normalized by the monthly average ambient EC. This is an estimate of the primary OC/EC ratio. We consider monthly averages to smooth out the significant day-to-day variability in the solution. The primary OC/EC ratio varies seasonally with larger values in winter than in summer. Some of this variation is expected; for example, the largest OC/EC ratios are predicted in the winter and fall when wood smoke contributes significant OC but little EC.

Fig. 2 shows there is a strong seasonal pattern in the ratio of vehicular OC to ambient EC: 0.69 in summer versus 0.33 in winter. This shift is driven by seasonal changes in the ambient hopanes-to-EC ratios (Subramanian et al., 2006a). Assuming that the shift is due to photochemistry and not seasonally varying source profiles, Fig. 6 suggests that photochemistry reduces the CMB estimates of

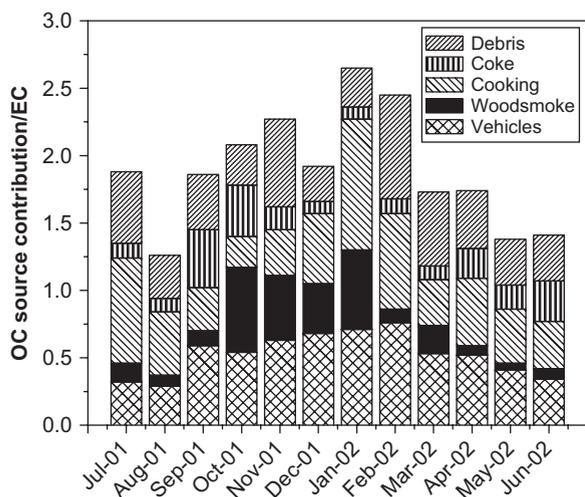


Fig. 6. Monthly average OC source contribution estimates from the best-estimate CMB model normalized by ambient EC.

motor vehicle OC in summer by about a factor of 2, on average, relative to the winter. However, average summertime vehicular OC based on the best estimate CMB solutions is only 186 ng-Cm^{-3} , which is less than a tenth of the unapportioned OC. Therefore even doubling the summertime vehicular contributions to account for any photochemical decay (as a rough estimate) only negligibly influences the overall OC mass balance.

Under the assumption that markers are stable in winter, the data shown in Fig. 6 suggests that the markers for other sources are not being severely depleted. Therefore, we conclude that the large amounts of unapportioned OC are not due to photochemical decay of molecular markers.

3.3.4. Sampling artifacts

OC measurements are often strongly influenced by sampling artifacts (Turpin et al., 2000) and previous studies have cited artifacts as explanation for unexpectedly high levels of unapportioned OC (Zheng et al., 2006). The effects of artifacts on the CMB results were not quantitatively explored because data are needed for both the source and the ambient samples. The sampling artifacts for the PAQS ambient samples were well characterized (Subramanian et al., 2004), but information on artifacts is not available for many source profiles. Therefore, our CMB results are based on noncorrected data from undenuded quartz filters for both source and ambient samples.

Subramanian et al. (2004) showed that there was a net positive organic sampling artifact of $\sim 0.5 \mu\text{g-Cm}^{-3}$ on the PAQS ambient samples, which corresponds to less than 20% of the measured OC. A positive artifact is due to adsorption of organic vapors by the filter, causing an overestimate of the particulate OC. Therefore, correcting the ambient measurements for a positive artifact reduces the amount of unapportioned OC.

Positive artifacts also appear to be the dominant artifact in emission measurements of OC (Hildemann et al., 1991; Schauer et al., 1999b, 2002b; Lipsky and Robinson, 2006; Robinson et al., 2006c). The effect of sampling artifacts on source profiles can be understood in terms of marker-to-OC ratios, which are used to convert CMB results to an OC basis. Correcting for a positive artifact increases the source profile marker-to-OC ratios, which decreases the amount of OC apportioned to the source. Therefore, correcting source profiles for a net positive artifact will increase the amount of unapportioned OC.

The key point is that the net effect of sampling artifacts on the unapportioned OC depends on the relative magnitude of the artifacts on both the source and the ambient samples. If they are comparable, the effects of artifacts will cancel out in the analysis. Given the relatively small positive artifacts of the Pittsburgh samples, this seems to be the best-case scenario (Subramanian, 2004). However, the published emissions data indicate that positive artifacts contribute 30% or more of the OC emissions measured with an undenuded quartz filter (Hildemann et al., 1991; Schauer et al., 1999b, 2002b; Lipsky and Robinson, 2006; Robinson et al., 2006c). They are therefore most likely larger than the artifacts on the PAQS ambient samples, and correcting both the source and the ambient samples for artifacts may modestly increase the amount of unapportioned OC. The bottom line is that sampling artifacts do not explain the high levels of unapportioned OC.

3.4. Source contributions to fine-particle mass

Fig. 7 presents the contribution of the primary sources considered by CMB to fine-particle mass in the context of the overall $\text{PM}_{2.5}$ mass balance. The figure only considers days with $\text{PM}_{2.5}$ concentrations greater than $25 \mu\text{g m}^{-3}$ —approximately 25% of the days with organic speciation data. Three-quarters of these high-PM days occur in summer,

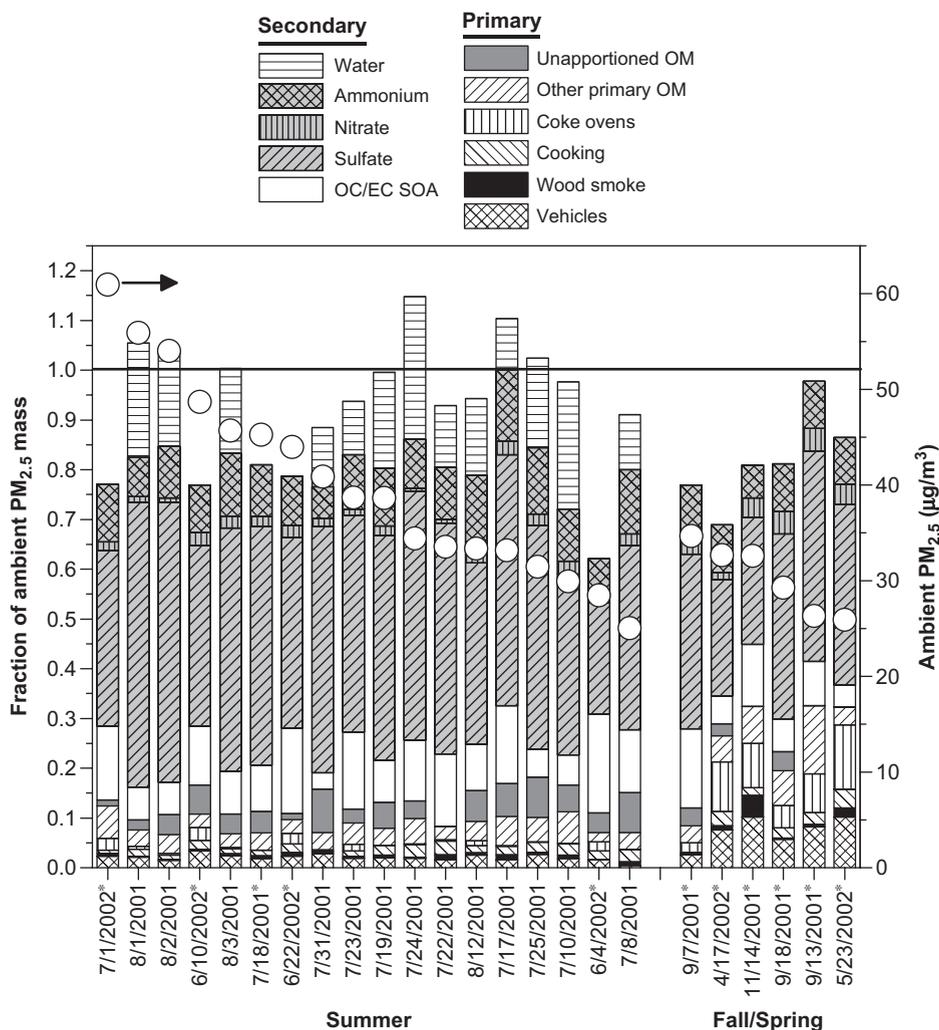


Fig. 7. Fine particle mass balance on days when ambient $PM_{2.5}$ mass was greater than $25 \mu\text{g m}^{-3}$. Ambient $PM_{2.5}$ levels measured using the Federal Reference Method are shown by the open circles and plotted against the right-hand y-axis. The bars indicate fractional contribution of primary sources calculated using CMB, SOA, other organics (unapportioned OM), inorganic ions, and water, as described in the text. Measurements of aerosol-bound water were not available on the dates indicated by the asterisks.

a fraction that is consistent with the entire PAQS dataset. The $PM_{2.5}$ mass did not exceed $35 \mu\text{g m}^{-3}$ (the revised 24-h standard proposed by the US EPA) on any of the non-summer days with organic speciation data; this level was only exceeded on three nonsummer days during the entire study.

In addition to the $PM_{2.5}$ mass apportioned to primary sources by the CMB model, Fig. 7 shows an estimate of SOA—either the maximum estimate from the EC-tracer method (Cabada 2003; Cabada et al., 2004) or the CMB-unapportioned OC, whichever is less, multiplied by an OM/OC ratio of 2.2. The OM/OC ratio for SOA was taken from the AMS results of Zhang et al. (2005). Any

remaining OC is multiplied by an OM/OC ratio of 1.8 and labeled “other primary OM”. This represents the organic aerosol not apportioned by CMB and not attributed to SOA, and its OM/OC ratio is that suggested by Rees et al. (2004) for the total Pittsburgh OC. Fig. 7 also shows the measured contribution of major inorganic ions (sulfate, nitrate, and ammonium). Fig. 7 does not account for crustal elements, which contribute a small fraction of the particle mass on high-concentration days (Rees et al., 2004). In order to close the mass balance, one must account for sampling artifacts and aerosol-bound water (Rees et al., 2004). Fig. 7 plots measurements of aerosol-bound water on the

days for which the data are available (Rees et al., 2004; Khlystov et al., 2005). The data are not corrected for potential sampling artifacts.

The major conclusion of Fig. 7 is that $PM_{2.5}$ concentrations in Pittsburgh on high-concentration days are dominated by secondary species. Inorganic ions alone contribute about 50% of the particulate mass on these high-PM days. Unapportioned organic PM, much of which is likely SOA, is the next biggest contributor, followed by aerosol-bound water. Water data were available for only 13 of the 18 summer days; on these days, water contributes an average of 17% of the $PM_{2.5}$ mass. The contribution of water is associated with acidic conditions common in summer (Rees et al., 2004).

Primary sources considered by CMB contribute only a small fraction of the ambient $PM_{2.5}$ on polluted days (Fig. 7). For example, the aggregate contribution from motor vehicles, biomass burning, cooking, coke ovens and other primary sources included in the CMB model is less than 15% of ambient fine PM on all high-concentration days in summer. Their aggregate contribution ranges between 10% and 39% of the fine-particle mass on non-summer “high-PM” days.

4. Conclusions

CMB analysis of molecular-marker data was performed to quantify the contribution of primary sources to organic aerosol concentrations in Pittsburgh, Pennsylvania. The model accounts for emissions from eight primary source classes, including major anthropogenic sources such as motor vehicles, cooking, and biomass combustion, as well as some primary biogenic emissions (leaf abrasion products).

Although our results demonstrate that the CMB results can depend strongly on the profiles and fitting species used in the model, the major conclusion of the study is that the eight primary sources included in the CMB model only contribute about 25% of the ambient OC in summer and about 50% of it in winter. Local sources not accounted for in the model are estimated to contribute at most another 10–15% of the ambient OC. A few solutions do apportion substantially more OC to primary sources, but these CMB models use gasoline and meat-cooking profiles that appear to be outliers relative to other published profiles.

Our estimates for the contribution of primary sources fall towards the low end of the range of

previous CMB analyses of molecular-marker data performed in urban areas (Schauer et al., 1996, 2002a; Schauer and Cass, 2000; Zheng et al., 2002, 2006). However, study-to-study differences may be due in part due to the sensitivity of the CMB results to the selection of source profiles and fitting species. These issues have not been routinely considered and can strongly influence the overall CMB solution and inferences regarding the overall OC mass balance. We have accounted for these issues by considering a large number of CMB models based on different combinations of source profiles and fitting species.

During the summertime, the dominant fraction of the unapportioned OC, and thus the total ambient OC, appears to be SOA. The summertime unapportioned OC is strongly correlated with SOA estimates using the EC-tracer method. The summertime unapportioned OC is also correlated with ambient concentrations of organic species associated with SOA and/or photochemical processing. Large amounts of SOA are also consistent with the fact that regional transport dominates fine-particle concentrations in Pittsburgh, which allows significant time for photochemical processing. While there is some evidence for photochemical decay of molecular markers in the summertime, this decay does not appear to significantly alter the CMB estimates of the total primary OC. Sampling artifacts and unaccounted local sources also appear to minimally influence the amount of unapportioned OC.

Our summertime results contribute to the growing body of evidence that SOA dominates OC ambient concentrations, even in urban areas. Factor analysis of aerosol mass spectrometer (AMS) measurements indicates that oxygenated organic aerosol that appears strongly associated with secondary production is the dominant component of OC in many urban areas (Zhang et al., 2005, 2007; Volkamer et al., 2006). Recent field studies have also observed rapid and substantial SOA production that cannot be explained by current SOA models (de Gouw et al., 2005; Volkamer et al., 2006). This unexpected SOA may be explained by oxidation of low volatility organic vapors that are not accounted for in current models (Robinson et al., 2007a). Accounting for SOA production from these vapors creates a regional organic aerosol dominated by SOA.

The vast majority of the CMB models attributed only about half of the wintertime OC to primary sources. Although EC-tracer estimates of SOA can

explain much of the wintertime unapportioned OC, little correlation is observed between the wintertime unapportioned OC and organic species associated with SOA. Therefore, the wintertime unapportioned OC cannot be definitively linked with SOA. Substantial amounts of SOA in winter may appear surprising, given the low levels of wintertime photochemical activity in a northern city such as Pittsburgh. A potential explanation might be regional transport of SOA produced in more-temperate areas of the country. Factor analysis of wintertime AMS data collected in New York City has indicated substantial amounts of oxygenated organic aerosol (Zhang et al., 2007). However, association of this wintertime oxygenated organic aerosol with SOA is complicated by the potential contributions of primary, oxygenated emissions from biomass combustion.

We also examined the contribution of primary emissions to fine-particle mass concentrations. Primary particulate emissions from motor vehicles, cooking, biomass burning and coke ovens only contribute a small fraction of the ambient fine-particle mass, especially in summer. On days with PM_{2.5} mass concentrations greater than 25 µg m⁻³, primary emissions contribute less than 20% of the mass in summer and less than 40% of the mass in winter. This underscores the importance of control strategies focusing on precursor emissions. In addition, human exposures on high concentration days in Pittsburgh are dominated by secondary aerosol. Primary OC dominates the OC mass balance on a small number of non-summer days with high OC concentrations; these events appear to be related to specific meteorological conditions such as local inversions.

Acknowledgments

This research was conducted as part of the Pittsburgh Air Quality Study, which was supported by US Environmental Protection Agency under Contract R82806101 and the US Department of Energy National Energy Technology Laboratory under Contract DE-FC26-01NT41017. This research was also supported by the EPA STAR program through the National Center for Environmental Research (NCER) under Grant R832162. This paper has not been subject to EPA's required peer and policy review, and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.atmosenv.2007.05.058](https://doi.org/10.1016/j.atmosenv.2007.05.058).

References

- Alves, C., Pio, C., Duarte, A., 2001. Composition of extractable organic matter of air particles from rural and urban Portuguese areas. *Atmospheric Environment* 35 (32), 5485–5496.
- Beaton, S.P., Bishop, G.A., Zhang, Y., Ashbaugh, L.L., Lawson, D.R., Stedman, D.H., 1995. On-road vehicle emissions—regulations, costs, and benefits. *Science* 268 (5213), 991–993.
- Cabada, J.C., 2003. Sources and physical characteristics of atmospheric carbonaceous aerosols. PhD thesis, Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA.
- Cabada, J.C., Pandis, S.N., Subramanian, R., Robinson, A.L., Polidori, A., Turpin, B., 2004. Estimating the secondary organic aerosol contribution to PM_{2.5} using the EC tracer method. *Aerosol Science and Technology* 38 (S1), 140–155.
- de Gouw, J.A., Middlebrook, A.M., Warneke, C., Goldan, P.D., Kuster, W.C., Roberts, J.M., Fehsenfeld, F.C., Worsnop, D.R., Canagaratna, M.R., Pszenny, A.A.P., Keene, W.C., Marchewka, M., Bertman, S.B., Bates, T.S., 2005. Budget of organic carbon in a polluted atmosphere: results from the New England Air Quality Study in 2002. *Journal of Geophysical Research* 110 (D16305), [doi:10.1029/2004JD005623](https://doi.org/10.1029/2004JD005623).
- Engling, G., Herckes, P., Kreidenweis, S.M., Malm, W.C., Collett, J.L., 2006. Composition of the fine organic aerosol in Yosemite National Park during the 2002 Yosemite Aerosol Characterization Study. *Atmospheric Environment* 40 (16), 2959–2972.
- Fick, J., Pommer, L., Nilsson, C., Andersson, B., 2003. Effect of OH radicals, relative humidity, and time on the composition of the products formed in the ozonolysis of alpha-pinene. *Atmospheric Environment* 37 (29), 4087–4096.
- Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2001. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. *Environmental Science and Technology* 35 (13), 2665–2675.
- Fraser, M.P., Lakshmanan, K., Fritz, S.G., Ubanwa, B., 2002. Variation in composition of fine particulate emissions from heavy-duty diesel vehicles. *Journal of Geophysical Research—Atmospheres* 107 (D21), [doi:10.1029/2001JD000558](https://doi.org/10.1029/2001JD000558).
- Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 2003a. Air quality model evaluation data for organics. 6. C-3-C-24 organic acids. *Environmental Science and Technology* 37 (3), 446–453.
- Fraser, M.P., Yue, Z.W., Buzcu, B., 2003b. Source apportionment of fine particulate matter in Houston, TX, using organic molecular markers. *Atmospheric Environment* 37 (15), 2117–2123.
- Hays, M.D., Geron, C.D., Linna, K.J., Smith, N.D., Schauer, J.J., 2002. Speciation of gas-phase and fine particle emissions from burning of foliar fuels. *Environmental Science and Technology* 36 (11), 2281–2295.

- Hays, M.D., Fine, P.B., Gerona, C.D., Kleeman, M.J., Gulletta, B.K., 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. *Atmospheric Environment* 39 (36), 6747–6764.
- Hedberg, E., Johansson, C., 2006. Is levoglucosan a suitable quantitative tracer for wood burning? Comparison with receptor modeling on trace elements in Lycksele, Sweden. *Journal of the Air and Waste Management Association* 56 (12), 1669–1678.
- Hildemann, L.M., Markowski, G.R., Cass, G.R., 1991. Chemical-composition of emissions from urban sources of fine organic aerosol. *Environmental Science and Technology* 25 (4), 744–759.
- Hochhauser, M.L., 2004. Point source emission inventory report for 2002. Air Quality Program 77, Allegheny County Health Department, Pittsburgh, PA.
- Khlystov, A., Stanier, C.O., Takahama, S., Pandis, S.N., 2005. Water content of ambient aerosol during the Pittsburgh air quality study. *Journal of Geophysical Research—Atmospheres* 110 (D07S10), doi:10.1029/2004JD004651.
- Koch, S., Winterhalter, R., Uherek, E., Koloff, A., Neeb, P., Moortgat, G.K., 2000. Formation of new particles in the gas-phase ozonolysis of monoterpenes. *Atmospheric Environment* 34 (23), 4031–4042.
- Lim, H.J., Turpin, B.J., 2002. Origins of primary and secondary organic aerosol in Atlanta: results of time-resolved measurements during the Atlanta supersite experiment. *Environmental Science and Technology* 36 (21), 4489–4496.
- Lipsky, E.M., Robinson, A.L., 2006. Effects of dilution on fine particle mass and partitioning of semivolatile organics in diesel exhaust and wood smoke. *Environmental Science and Technology* 40 (1), 155–162.
- Mazzoleni, L.R., Zielinska, B., Moosmuller, H., 2007. Emissions of levoglucosan, methoxy phenols, and organic acids from prescribed burns, laboratory combustion of wildland fuels, and residential wood combustion. *Environmental Science and Technology* 41 (7), 2115–2122.
- Pekney, N.J., Davidson, C.I., Robinson, A.L., Zhou, L., Hopke, P.K., Eatough, D., 2006. Identification of major sources of PM_{2.5} in Pittsburgh using PMF and UNMIX. *Aerosol Science and Technology* 40, 910–924.
- Polidori, A., Turpin, B.J., Lim, H.-J., Cabada, J.C., Subramanian, R., Pandis, S.N., Robinson, A.L., 2006. Local and regional secondary organic aerosol: insights from a year of semi-continuous carbon measurements at Pittsburgh. *Aerosol Science and Technology* 40 (10), 861–872.
- Ramdahl, T., 1983. Polycyclic aromatic ketones in environmental-samples. *Environmental Science and Technology* 17 (11), 666–670.
- Rees, S.L., Robinson, A.L., Khlystov, A., Stanier, C.O., Pandis, S.N., 2004. Mass balance closure and the federal reference method for PM_{2.5} in Pittsburgh, Pennsylvania. *Atmospheric Environment* 38 (20), 3305–3318.
- Robinson, A.L., Donahue, N.M., Rogge, W.F., 2006a. Photochemical oxidation and changes in molecular composition of organic aerosol in the regional context. *Journal of Geophysical Research—Atmospheres* 111 (D03302), doi:10.1029/2005JD006265.
- Robinson, A.L., Subramanian, R., Donahue, N.M., Bernardo-Bricker, A., Rogge, W.F., 2006b. Source apportionment of molecular markers and organic aerosol-1. Polycyclic aromatic hydrocarbons and methodology for data visualization. *Environmental Science and Technology* 40 (24), 7803–7810.
- Robinson, A.L., Subramanian, R., Donahue, N.M., Bernardo-Bricker, A., Rogge, W.F., 2006c. Source apportionment of molecular markers and organic aerosol-2. Biomass smoke. *Environmental Science and Technology* 40 (24), 7811–7819.
- Robinson, A.L., Subramanian, R., Donahue, N.M., Bernardo-Bricker, A., Rogge, W.F., 2006d. Source apportionment of molecular markers and organic aerosol-3. Food cooking emissions. *Environmental Science and Technology* 40 (24), 7820–7827.
- Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A.P., Lane, T.E., Pierce, J.R., Pandis, S.N., 2007a. Rethinking organic aerosols: semivolatile emissions and photochemical aging. *Science* 315 (5816), 1259–1262.
- Robinson, A.L., Subramanian, R., Lipsky, E.M., Rogge, W.F., Lucas, L.J., Wynne, D., 2007b. Speciated organic profiles for source-apportionment of the road-dust and vegetative detritus contribution to ambient fine particulate matter. *Aerosol Science and Technology*, in preparation.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. *Environmental Science and Technology* 27 (13), 2700–2711.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1994. Sources of fine organic aerosol. 6. Cigarette-smoke in the urban atmosphere. *Environmental Science and Technology* 28 (7), 1375–1388.
- Rudich, Y., Donahue, N.M., Mentel, T.F., 2007. Aging of organic aerosol: bridging the gap between laboratory and field studies. *Annual Reviews of Physical Chemistry* 58, 321–352.
- Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environmental Science and Technology* 34 (9), 1821–1832.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30 (22), 3837–3855.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999a. Measurement of emissions from air pollution sources. 1. C-1 through C-29 organic compounds from meat charbroiling. *Environmental Science and Technology* 33 (10), 1566–1577.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999b. Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks. *Environmental Science and Technology* 33 (10), 1578–1587.
- Schauer, J.J., Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 2002a. Source reconciliation of atmospheric gas-phase and particle-phase pollutants during a severe photochemical smog episode. *Environmental Science and Technology* 36 (17), 3806–3814.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002b. Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles. *Environmental Science and Technology* 36 (6), 1169–1180.

- Sheesley, R.J., Schauer, J.J., Bean, E., Kenski, D., 2004. Trends in secondary organic aerosol at a remote site in Michigan's upper peninsula. *Environmental Science and Technology* 38 (24), 6491–6500.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic-matter of the troposphere. 2. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmospheric Environment* 16 (9), 2139–2159.
- Simoneit, B.R.T., 1985. Application of molecular marker analysis to vehicular exhaust for source reconciliations. *International Journal of Environmental Analytical Chemistry* 22 (3–4), 203–233.
- Simoneit, B.R.T., Cox, R.E., Standley, L.J., 1988. Organic matter of the troposphere. 4. Lipids in Harmattan aerosols of Nigeria. *Atmospheric Environment* 22 (5), 983–1004.
- Simoneit, B.R.T., Sheng, G.Y., Chen, X.J., Fu, J.M., Zhang, J., Xu, Y.P., 1991. Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atmospheric Environment Part A—General Topics* 25 (10), 2111–2129.
- Subramanian, R., 2004. Sampling, Analysis, and Source-Appportionment of Ambient Carbonaceous Aerosols. PhD thesis, Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA.
- Subramanian, R., Khlystov, A.Y., Cabada, J.C., Robinson, A.L., 2004. Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations. *Aerosol Science and Technology* 38 (S1), 27–48.
- Subramanian, R., Donahue, N.M., Bernardo-Bricker, A., Rogge, W.F., Robinson, A.L., 2006a. Contribution of motor vehicle emissions to the ambient organic carbon and fine particle mass in Pittsburgh, Pennsylvania: effects of varying source profiles and seasonal trends in ambient marker concentrations. *Atmospheric Environment* 40 (40), 8002–8019.
- Subramanian, R., Khlystov, A.Y., Robinson, A.L., 2006b. Effect of peak inert-mode temperature on elemental carbon measured using thermal-optical analysis. *Aerosol Science and Technology* 40 (10), 763–780.
- Tang, W., Raymond, T., Wittig, A.E., Davidson, C.I., Pandis, S.N., Robinson, A.L., Crist, K., 2004. Spatial variations of PM_{2.5} during the Pittsburgh Air Quality Study. *Aerosol Science and Technology* 38 (S2), 80–90.
- Turpin, B.J., Huntzicker, J.J., 1995. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during Scaqs. *Atmospheric Environment* 29 (23), 3527–3544.
- Turpin, B.J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmospheric Environment* 34 (18), 2983–3013.
- Volkamer, R., Jimenez, J.L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L.T., Worsnop, D.R., Molina, M.J., 2006. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected. *Geophysical Research Letters* 33 (L17811), doi:10.1029/2006GL026899.
- Watson, J.G., Fujita, E.M., Chow, J.C., Zielinska, B., 1998a. Northern Front Range Air Quality Study Final Report and Supplemental Volumes. Desert Research Institute.
- Watson, J.G., Robinson, N.F., Fujita, E.M., Chow, J.C., Pace, T.G., Lewis, C., Coulter, T., 1998b. CMB8 Applications and Validation Protocol for PM_{2.5} and VOCs. US EPA, USA.
- Weitkamp, E.A., Lipsky, E.M., Pancras, P.J., Ondov, J.M., Polidori, A., Turpin, B.J., Robinson, A.L., 2005. Fine particle emission profile for a large coke production facility based on highly time-resolved fence line measurements. *Atmospheric Environment* 39 (36), 6719–6733.
- Wittig, A.E., Anderson, N., Khlystov, A.Y., Pandis, S.N., Davidson, C.I., Robinson, A.L., 2004. Pittsburgh Air Quality Study overview. *Atmospheric Environment* 38 (20), 3107–3125.
- Womilaju, T.O., Miller, J.D., Mayer, P.M., Brook, J.R., 2003. Methods to determine the biological composition of particulate matter collected from outdoor air. *Atmospheric Environment* 37 (31), 4335–4344.
- Yu, J.Z., Cocker, D.R., Griffin, R.J., Flagan, R.C., Seinfeld, J.H., 1999. Gas-phase ozone oxidation of monoterpenes: gaseous and particulate products. *Journal of Atmospheric Chemistry* 34 (2), 207–258.
- Zhang, Q., Worsnop, D.R., Canagaratna, M.R., Jimenez, J.L., 2005. Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols. *Atmospheric Chemistry and Physics* 5, 3289–3311.
- Zhang, Q., Jimenez, J.L., Canagaratna, M.R., Allan, J.D., Coe, H., Ulbrich, I., Alfarra, M.R., Takami, A., Middlebrook, A.M., Sun, Y.L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P.F., Salcedo, D., Onasch, T., Jayne, J.T., Miyoshi, T., Shimojo, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Weimer, S., Demerjian, K., Williams, K., Bower, K., Bahreini, R., Cotrell, L., Griffin, R.J., Rautiainen, J., Sun, J.Y., Zhang, Y.M., Worsnop, D.R., 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically influenced northern hemisphere mid-latitudes. *Geophysical Research Letters*, in press.
- Zheng, M., Cass, G.R., Schauer, J.J., Edgerton, E.S., 2002. Source apportionment of PM_{2.5} in the southeastern United States using solvent-extractable organic compounds as tracers. *Environmental Science and Technology* 36 (11), 2361–2371.
- Zheng, M., Ke, L., Edgerton, E.S., Schauer, J.J., Dong, M.Y., Russell, A.G., 2006. Spatial distribution of carbonaceous aerosol in the southeastern United States using molecular markers and carbon isotope data. *Journal of Geophysical Research—Atmospheres* 111 (D10S06), doi:10.1029/2005JD006777.