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Source Apportionment of Molecular Markers and Organic Aerosol. 3. Food Cooking Emissions

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The chemical mass balance model is applied to a large dataset of organic molecular marker concentrations to apportion ambient organic aerosol to food cooking emissions in Pittsburgh, Pennsylvania. Ambient concentrations of key cooking markers such as palmitoleic acid, oleic acid, and cholesterol are well correlated, which implies the existence of well-defined source profiles. However, significant inconsistencies exist between the ambient data and published source profiles. Most notably, the ambient ratio of palmitoleic-acid-to-oleic-acid is more than a factor of 10 greater than essentially all published source profiles. This problem is not unique to Pittsburgh. The reason for this discrepancy is not known but it means that both acids cannot be fit simultaneously by CMB. CMB analysis is performed using three different combinations of food cooking source profiles and molecular markers. Although all three solutions have high statistical quality, the amount of OC apportioned to food cooking emissions varies by a factor of 9. Differences in fitting species and source profile marker-to-organic-carbon ratios cause most of the large systematic biases between the different solutions. The best CMB model includes two alkanoic acids as fitting species in addition to other cooking markers, which helps constrain the source contribution estimates. It also includes two meat cooking source profiles to account for the variability in the ambient data. This model apportions 320 ± 140 ng-C m^{-3} or 10% of the study average ambient organic carbon to food cooking emissions. Although these results illustrate the significant challenges created by source profile variability, the strong correlations in the ambient dataset underscore the significant promise that molecular markers hold for source apportionment analysis.

Introduction

Food cooking has been shown to be an important source of the fine organic aerosol in urban environments (*1*−*5*). Organic molecular markers such as oleic acid, palmitoleic acid, and cholesterol have been used in conjunction with the chemical mass balance (CMB) model to estimate the contribution of meat-cooking emissions to primary organic aerosol (*1*, *5*, *6*).

Selection of source profiles and fitting species requires careful consideration when performing CMB analysis. Previous CMB analyses have used different combinations of source profiles and molecular markers to estimate the contribution of food cooking emissions to ambient particle concentrations (*1*−*5*). More than 10 food cooking source profiles have been published with speciated organics data (*6*−*10*); these profiles span a wide range in emission rates and emission composition depending on food type and cooking technique.

This paper is one of a series of papers that examines issues associated with CMB analysis of molecular marker data in Pittsburgh, Pennsylvania (*11*−*13*). The goal of this paper is to present source contribution estimates for food cooking and to examine the sensitivity of these estimates associated with the selection of source profiles and fitting species. First, a large data set of ambient molecular markers are examined for correlations among different compounds emitted by food cooking. Next, the data are compared to the available cooking source profiles using the approach described in Robinson et al. (*11*, *14*). Based on these comparisons, different scenarios for CMB analysis are defined and the results discussed. The paper concludes with a discussion of the strengths and challenges associated with using CMB analysis with molecular markers and approaches for better constraining source contribution estimates.

Materials and Methods

CMB analysis was performed to apportion ambient OC and fine particle mass in Pittsburgh, Pennsylvania to sources of primary organic aerosol. The analysis uses ambient concentrations of individual organic compounds, $PM_{2.5}$ elemental carbon, and $PM_{2.5}$ elemental composition measured on 96 days between July, 2001 and June, 2002 (*15*). Daily measurements were made in July 2001 and most of January 2002; during other periods 24-hr samples were collected on a 1-in-6-day schedule. Additional details of the dataset are provided in the Supporting Information.

CMB calculates source contribution estimates using a linear combination of source profiles to describe the ambient concentrations of a set of fitting species. The selection of compounds included in the CMB model is a critical issue—all major sources of each compound must be included in the model and the species should be conserved during transport from source to receptor (*16*). This work uses the basic set of compounds and source classes developed by Schauer et al. (*1*, *5*). In addition to the cooking-related markers discussed below, all calculations include four n-alkanes, iso-hentriacontane, anteiso-dotriacontane, syringaldehyde, sum of resin acids, acetosyringone, levoglucosan, four hopanes, four PAHs, titanium, iron, and elemental carbon. Source profiles for eight source classes are included in the model: diesel vehicles, gasoline vehicles, road dust, biomass combustion, cooking emissions, coke production, vegetative detritus, and cigarettes. A list of the specific profiles and fitting species used for each scenario is contained in the Supporting Information.

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This paper focuses on five important markers for cooking emissions: n-hexadecanoic (palmitic) acid, n-octadecanoic (stearic) acid, 9-hexadecenoic (palmitoleic) acid, 9-octadecenoic (oleic) acid, and cholesterol. Palmitoleic acid, oleic acid and cholesterol have all been used previously in CMB analysis as markers for meat cooking emissions (*1*, *5*, *6*). There are non-cooking related sources of these compounds: biomass smoke, motor vehicle exhaust and road dust all contain the four acids (*1*, *17*). Although cholesterol is thought to be a good marker for meat cooking emissions in urban environments (*6*), recent papers have reported unexpectedly high levels of cholesterol in a remote natural area (*18*) and in emissions from prescribed burns (*19*). All of these compounds are important constituents of plant and/or animal tissue, but the potential contribution of biogenic sources is not well defined. Palmitic and stearic acids are typically not fit by CMB because of concerns over unidentified sources.

CMB analysis is performed using different combinations of these five species with different food cooking source profiles (in addition to a standard set of non-food cooking source profiles and molecular markers). These scenarios are selected using ratio−ratio plots to compare ambient concentrations of different molecular markers with source profiles. Ratio−ratio plots are constructed using three species; one compound is selected as a reference to normalize the concentrations of the other two compounds, called target species. More details on the construction, interpretation, and mathematics of ratio−ratio plots are provided in Robinson et al. (*11*, *14*).

The calculations were performed using the computer program CMB8 distributed by the U.S. Environmental Protection Agency. Experimental uncertainties are estimated as ± 30% for cholesterol and as ± 20% for the alkenoic and alkanoic acids based on comparisons of results from collocated samplers. These uncertainties are applied to both the source profiles and the ambient data. Even though some of the five cooking markers are contained in non-cooking source profiles, CMB attributes the vast majority of them to the food cooking profiles. Therefore, the specific combination of non-food cooking profiles has little influence on the OC apportioned to food cooking emissions.

Previous CMB studies have used particle-phase nonanal as a marker for cooking emissions (*1*, *3*, *5*). We do not use nonanal as a fitting species in CMB because it is semivolatile, which raises a number of concerns. First, gas-particle partitioning of semivolatile species varies with atmospheric conditions, therefore the particle fraction of a semivolatile species is not a conserved during transport, violating one of the assumptions of CMB. Second, gas-particle partitioning inside of dilution samplers used for source tests can be significantly biased compared to more dilute atmospheric conditions (*20*). A better approach would be to use the total (gas + particle) concentration of a semivolatile species as a maker in CMB (assuming gas-phase reactions are slow). We measured the total ambient nonanal concentration using a quartz-PUF sampler, but most of the source tests only report quartz filter samples.

Results

Time series of ambient concentrations of cholesterol, palmitoleic acid, and palmitic acid are shown in Figure 1. The results are presented using box-plots constructed by grouping the data into one- or 2-month periods, depending on the number of samples. Ambient palmitoleic and oleic acid concentrations are well correlated (Figure 2a) so results for oleic acid are qualitatively similar to those shown in Figure 1b. Similarly ambient palmitic and stearic acid concentrations are well correlated (Figure 2d) so results for stearic acid are qualitatively similar to those shown in Figure 1c.

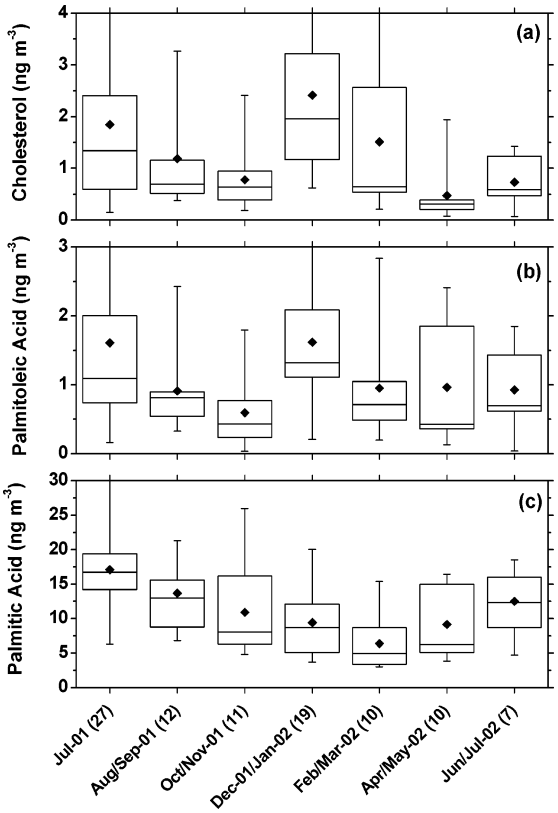

FIGURE 1. Box plots constructed from time series of 24-hr average concentrations of (a) cholesterol, (b) palmitoleic acid, and (c) palmitic acid. The boxes stretch from the lower quartile to the upper quartile values; median values are shown as lines across the boxes; filled diamonds indicate average values. The whiskers indicate the maximum and minimum values; whiskers that intersect upper boundary of the plot indicate that the maximum value is beyond the scale of the graph. The numbers in parentheses in *x*-axis labels indicate number of samples taken in the specified period.

The median ambient concentrations of cholesterol and the two alkenoic acids are around 1 ng m^{-3}. However, there is significant day-to-day variability in the ambient concentrations of these compounds as illustrated by the height of the boxes in Figure 1. There is no seasonal pattern in the concentrations of cholesterol or the two alkenoic acids, but relatively few high concentration days were observed in the spring and the fall. This may be due in part to only 20% of the samples being collected in the fall and spring versus 50% in summer and 30% in winter. Concentrations of the two alkanoic acids exhibit a distinct seasonal pattern, with wintertime concentrations being, on average, a factor of 3 smaller than summertime concentrations (Figure 1c).

The ambient concentrations of the different cooking markers in Pittsburgh are similar to those in other locations in the United States. For example, the Pittsburgh oleic acid levels are comparable to the "seasonal composite" concentrations in Houston, TX (*21*) but a factor of 2 or 3 lower than in Birmingham, AL and Atlanta, GA (*3*) The palmitoleic acid levels are a factor of 2 or 3 higher than other locations. The cholesterol levels in Pittsburgh are similar to average concentrations in Los Angeles (*22*).

A key consideration for CMB analysis is the relative distribution of different species fit by the model in both the ambient data and source profiles. These distributions can be visualized using both scatter and ratio−ratio plots (*11*).

Figure 2 shows scatter plots of ambient daily concentrations of the different cooking markers. Ambient oleic and palmitoleic acid concentrations are well correlated with a slope of roughly one (Figure 2a); in addition, most of the

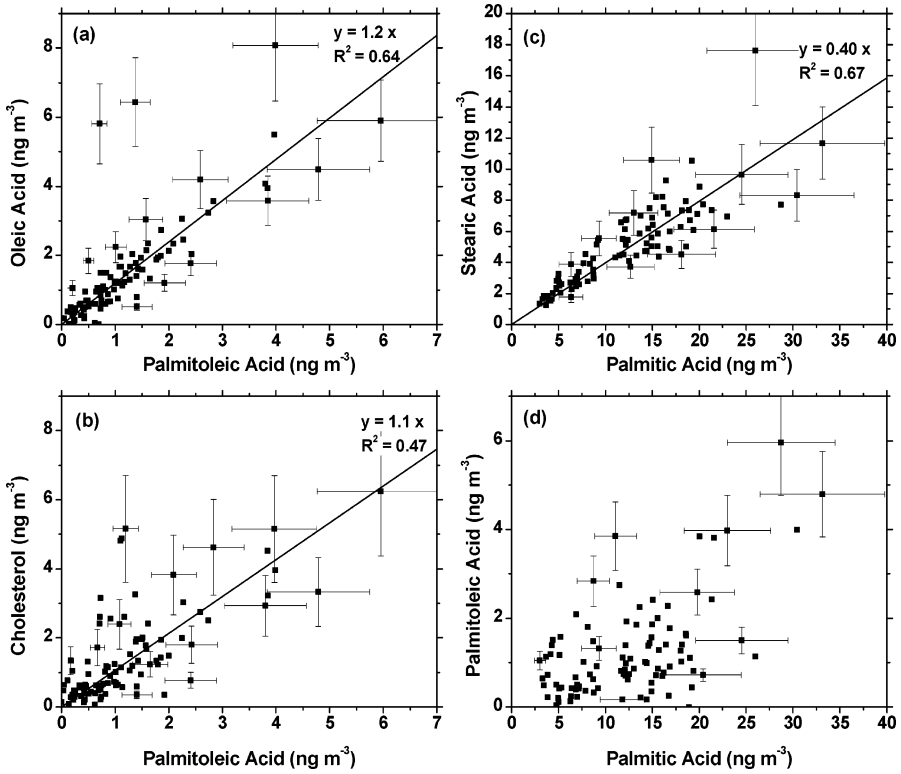

FIGURE 2. Scatter plots of the Pittsburgh ambient concentrations of the five cooking markers. Straight lines in (a)−(c) are linear regressions of the data which have been forced through zero. Excluding the three potential outliers in panel (a) improves the R^2 value of the regression to 0.92 and minimally influences the slope. Measurement uncertainty indicated for selected points; uncertainty on other points is comparable.

scatter in the data can be attributed to measurement uncertainty. This implies a single dominant source for the two alkenoic acids, presumably meat cooking. Cholesterol is also an important marker for meat cooking emissions (*6*). Figure 2b indicates only modest correlation between ambient palmitoleic and cholesterol data; however, much of the scatter is comparable to measurement uncertainty. Therefore, ambient concentrations of these three compounds are likely dominated by the same source. Ambient palmitic and stearic acid concentrations are well correlated (Figure 2c), but little correlation is observed between the two alkenoic and the two alkanoic acids (Figure 2d). If one assumes that these species are chemically stable in the atmosphere, then these saturated and unsaturated acids have different dominant sources.

Ratio−ratio plots provide additional insight into the ambient data, allowing one to infer potential source profiles (*11*, *14*). Figure 3a plots the two alkenoic acids normalized by cholesterol, while Figure 3b plots the two alkanoic acids normalized by cholesterol. The well organized ratio−ratio plots reflect the correlations in the ambient data. Within experimental uncertainty, the large majority of the data in Figure 3a can be explained by a single hypothetical source profile that is approximately 1:1:1 in palmitoleic acid:oleic acid:cholesterol. The modest scatter along the diagonal can be attributed to either the somewhat larger uncertainty of the cholesterol measurements and/or variability in the cholesterol emissions. Explaining the ambient alkanoic acid and cholesterol data in Figure 3b requires at least two source profiles: a profile rich in cholesterol located in the lower left-hand corner of the plot and a second source that emits alkanoic acids but little or no cholesterol (such as seed oil cooking or even motor vehicles) that is located in the upper right-hand corner of the graph. Such a profile pair creates a mixing line that passes through the ambient data.

The exact organization of data in a ratio−ratio plot depends on the reference species used to normalize the concentrations of the two target species. Changing reference species shifts the location of both the source profiles and ambient data in the plot, but does not alter conclusions drawn about viable source profile combinations. For example, using one of the alkenoic acids as the reference as opposed to cholesterol for the group of compounds presented in Figure 3a creates a plot with modest scatter parallel to one of the axes as opposed to along the diagonal, but the relationship with the source profiles is the same. In addition, the ratio plots are used to visualize the data; all source apportionment estimates are made using CMB, so these estimates do not depend on the choice of reference species. Cholesterol seems like a good choice as a reference for the food cooking markers given its importance as a tracer for meat cooking. In order to develop a thorough understanding of the ambient data and source profiles, one should examine ratio−ratio plots using different reference species and different combinations of source-specific markers. Figure 3 presents only two of the many plots examined as part of this research to illustrate important general conclusions.

Comparison of Ambient Data with Source Profiles. Relatively few cooking source profiles have been published that report alkanoic acid, alkenoic acid, and cholesterol data. Multiple profiles are available for commercial-scale frying and charbroiling of hamburger meat (*6*, *8*). Residential cooking profiles have been published for frying steaks, hamburgers, and breaded fish fillets using both electric and natural gas stoves (*23*). Profiles are also available for frying of vegetables in oil, which does not emit cholesterol (*7*). Not surprisingly, the fine particle emission rate and the composition of the emissions depend on type of food and cooking technique (*6*−*8*, *23*).

The published cooking source profiles are plotted in Figure 3. Source profiles appear as points in the ratio−ratio plots (*11*, *14*) and arrows are used to point toward sources of the different acids that do not emit cholesterol, such as seed oil cooking. The published cooking profiles organize along a

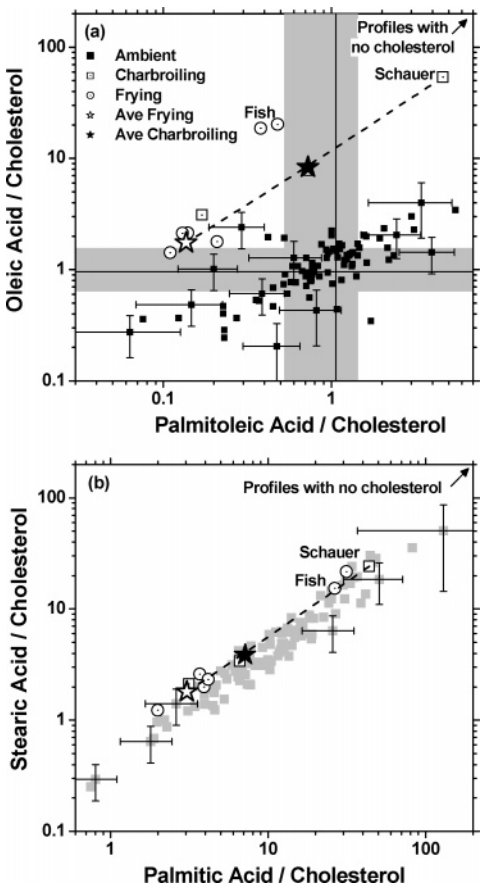

FIGURE 3. Ratio−ratio plots comparing ambient data for the five cooking markers to source profiles (*6*−*8*, *23*). The dashed line is a linear mixing line connecting the average frying and the Schauer et al. (*8*) charbroiling profile. The horizontal and vertical lines in (a) indicate the slopes of linear regressions of the oleic acid and the palmitoleic acid data versus cholesterol (e.g., Figure 2b). The gray areas in (a) indicate twentieth and eightieth percentiles of the data. The arrow in the upper right-hand corner of the plot points toward sources such as biomass combustion, motor vehicles, road dust, and seed oil coil cooking that emit the different acids but not cholesterol. Error bars are shown for a limited number of points to indicate typical level of measurement uncertainty. The label "fish" indicates the two fish frying profiles; the label "Schauer" indicates the Schauer et al. (*8*) charbroiling profile.

diagonal line in the ratio−ratio plots shown in Figure 3, indicating only modest profile-to-profile variability in the palmitic-to-steric-acid ratios compared to the almost two order of magnitude variability in relative emissions of cholesterol.

A comparison of the source profiles to the ambient data in Figure 3a reveals a large discrepancy in the palmitoleic-to-oleic-acid ratios. The ambient data have nearly equal loadings of these two acids compared to an average 20:1 dominance for oleic acid in the published meat cooking source profiles. Although there is some profile-to-profile variability in the ratio of these two acids, the cooking profile with the smallest oleic-to-palmitoleic acid ratio is still enriched by almost a factor of 10 in oleic acid compared to the ambient data.

Palmitoleic and oleic acid are also emitted by other, non meat cooking sources; however, emissions from these other sources cannot explain the unexpected oleic-to-palmitoleic acid ratios. Essentially all published source profiles are enriched in oleic acid. The only exceptions we have found are the Fine et al. (*24*) quaking aspen and softwood open-burn profiles (*25*). We explored including these profiles in CMB, but even on the limited number of days with significant biomass smoke, only a small fraction of the ambient alkenoic acids are apportioned to the non-cooking profiles. Consequently, CMB models that try to simultaneously fit both oleic and palmitoleic acid data have poor fitting statistics.

The unexpectedly small ambient ratios of oleic to palmitoleic acid are not unique to the Pittsburgh. Ratios of 1:1 to 3:1 (oleic:palmitoleic) have been reported in Houston, TX (*21*), Los Angeles (*26*), and rural sites in the Southeastern U.S. (*3*). Therefore, ambient data from all of these locations are inconsistent with the available profiles. Only in urban locations in the Southeastern U.S. do the ambient oleic-to-palmitoleic-acid ratios approach the available cooking source profiles (*3*).

Explaining the ambient alkenoic acid data requires a source rich in palmitoleic acid. In addition, the strong correlation shown in Figure 2a requires that the emissions from this unknown source must co-vary with the emissions of oleic acid. This constraint makes it very unlikely that the unknown source is a completely different (i.e., non-cooking) activity. Rather, it seems likely that the aggregate cooking profile characteristic of Pittsburgh differs from the published profiles, which points to the need to expand our knowledge of cooking emissions beyond the limited number of available profiles. An alternative explanation is that the alkenoic acid concentrations are altered during transport between the sources and the receptor. Although laboratory studies observe rapid oxidation of oleic acid (*27*), oleic acid would have to be oxidized at a much higher rate than palmitoleic acid to explain the ambient data. This would be unexpected given the chemical similarity of the two species. Laboratory measurements indicate the two alkenoic acids oxidize at essentially the same rate in model meat cooking aerosol mixtures (*28*). Preferential photochemical decay of oleic acid would also likely create seasonal patterns in the ambient palmitoleic-to-oleic-acid ratio; however, there is no such pattern in the Pittsburgh data.

CMB Analysis. In this section, we develop three CMB models to estimate the contribution of meat cooking emissions to ambient OC. First we consider two models in which the key markers for meat cooking emissions are cholesterol paired with either oleic or palmitoleic acid. As previously discussed, CMB cannot fit both acids simultaneously because of inconsistencies in the palmitoleic-to-oleic-acid ratios. Interestingly, almost all previous CMB analyses of molecular marker data have only fit one of these two alkenoic acids. Initially oleic acid was included in CMB (*1*), but it was replaced with palmitoleic acid because of concerns over emissions of oleic acid from seed oil cooking (*5*).

We used the ratio−ratio plot shown in Figure 3a to help identify the source profiles used in the CMB models. In order to fit the ambient oleic acid and cholesterol data the source profile must be in the horizontal gray band shown in Figure 3a, i.e., have the same oleic-acid-to-cholesterol ratio as the ambient data. Within experimental uncertainty, the red-meat frying profiles meet this criterion. Instead of using a profile from a single cooking experiment, we use the average frying profile indicated by the open star in Figure 3a in the CMB model that fits oleic acid and cholesterol. This profile is the OC-emission-rate weighted average of the individual red meat frying profiles. In order to fit the ambient cholesterol and palmitoleic acid data the cooking source profile must lie within the vertical gray band shown in Figure 3a. For this CMB model we use an average red meat charbroiling profile, which is indicated by the filled star in Figure 3a. Although using a single red-meat frying or charbroiling profile to represent the aggregate cooking emissions in CMB seems problematic given the diversity of cooking operations, the limited number of published profiles makes it impossible to construct a more realistic aggregate cooking profile based

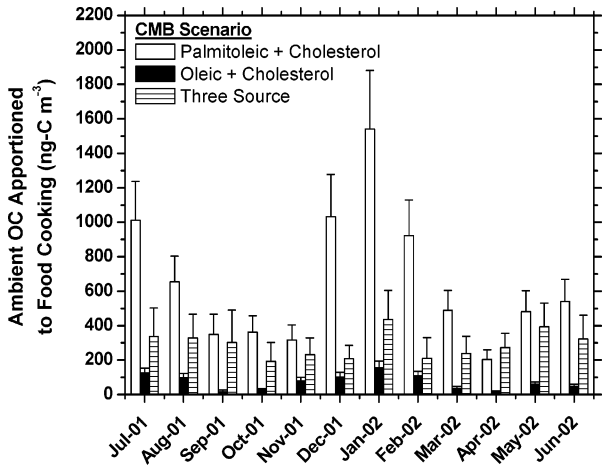

FIGURE 4. Time series of monthly average ambient OC apportioned to food cooking emissions by different CMB scenarios. As described in the text, the "palmitoleic + cholesterol" model uses an average red meat charbroiling profile; the "oleic + cholesterol" model uses an average red meat frying profile; and the "Three Source" model uses the Schauer et al. (*8*) charbroiling profile, an average frying profile, and an average seed oil cooking profile. Monthly average concentrations are the arithmetic average of the CMB results calculated for individual days.

on food consumption and cooking data. Most previous CMB analyses of molecular marker data have represented aggregate cooking emissions using a single red-meat cooking profile (*1*−*3*, *5*, *18*).

Figure 4 plots the monthly average ambient OC apportioned to meat cooking emissions. Both CMB models indicate widely varying meat smoke contributions that peak in the winter. The two solutions are strongly correlated; a linear regression of the daily source contribution estimates of meat cooking yields an R^2 value of 0.84. However, the model that fits cholesterol and palmitoleic acid apportions nine times more ambient OC to meat cooking than the model that fits cholesterol and oleic acid (e.g., 840 ± 190 ng-C m^{-3} or 27% versus 94 ± 24 ng-C m^{-3} or 3% of the study average ambient OC). This difference is much larger than the standard errors calculated by CMB.

The large bias between the ambient OC apportioned to meat cooking by the two CMB models is due to changes in both fitting species and source profiles. The effects of both of these changes can be understood in terms of the marker-to-OC ratios of the source profiles. These ratios are so important because OC is not included in the model as source profiles do not exist for secondary organic aerosol (SOA). Source contribution estimates to OC are determined using the actual fit of the species included in the model and the marker-to-OC ratio of the different source profiles. This second step is built into the analysis by using sources profiles normalized by OC. Differences in the cholesterol-to-OC ratio illustrate the strong effect that these ratios can have on the solution. The average charbroiling profile has a cholesterol-to-OC ratio that is 5.3 times smaller than the average frying profile (see Figure S-1 in the Supporting Information). This means that, for a given ambient cholesterol concentration, 5.3 times more meat cooking OC will be apportioned by the average charbroiling profile than by the average frying profile.

The actual bias is larger than a factor of 5.3 because the CMB model uses additional species to determine the meat cooking contribution, namely oleic or palmitoleic acid. Since all of the profiles are enriched in oleic acid, the oleic-acid-to-OC ratios of the source profiles are always larger than the palmitoleic-acid-to-OC ratios. This means that, in locations such as Pittsburgh where the ambient concentrations of these two acids are roughly equal, CMB models that fit palmitoleic acid will produce always significantly higher estimates of meat cooking OC than those that fit oleic acid. For example, the palmitoleic-acid-to-OC ratio of the average charbroiling profile is a factor of 12 smaller than oleic-acid-to-OC ratio of the average frying profile. The actual bias of a factor of 9 falls between these two limits.

Despite the widely divergent source contribution estimates of meat cooking emissions to ambient OC, on essentially all days the statistical quality of both solutions based on the performance measures calculated by CMB (R^2, χ^2, calculated over measured values, T-statistics, etc.) are similar and within the guidelines described in the CMB manual (*16*). For example, both solutions have average R^2 and χ^2 values of 0.92 and 2.0 respectively and both solutions have confidence levels greater than 96% based on the χ^2 values and the number of degrees of freedom. Therefore, the statistical parameters used to judge quality CMB solutions cannot be used to differentiate between the two CMB models. Additional information on the statistical quality of the solutions is presented in the Supporting Information.

Problems with the CMB model based on palmitoleic acid and cholesterol are apparent if one considers species not explicitly fit by CMB (non-fitting species). Similar to OC, CMB calculates the ambient concentrations of these non-fitting species using the marker-to-marker ratios of the source profiles and the optimum solution based on the specified set of target compounds. On winter days, the palmitoleic acid and cholesterol model over-predicts the ambient stearic acid concentrations by more than a factor of 3. On essentially all days it over-predicts the ambient oleic acid concentrations by almost a factor of 10. Although some over-prediction is acceptable, given measurement uncertainty, a target criteria for CMB analysis is that the calculated concentration of a fitted species should not be more than a factor of 2 greater than ambient data (*16*). This seems like a reasonable criterion for the non-fitting species that are atmospherically stable. Problems with over-predicting non-fitting species can be anticipated by examining the ratio−ratio plots; for example, Figure 3a shows that a reasonable fraction of the ambient data having alkanoic-acid-to-cholesterol ratios that are much smaller than the average charbroiling profile.

The oleic acid and cholesterol model does not have problems with over-predicting non-fitted species; however, it only apportions 3% of the study average OC to meat cooking, which is much less than previous CMB analyses using molecular marker data (*1*−*3*, *5*). In addition, this solution shows month-to-month changes in the contribution of meat cooking with almost no contribution in the fall and spring (Figure 4). Such changes are not expected given that cooking occurs on a reasonably consistent basis throughout the year.

The widely divergent results from the first two CMB models clearly indicate that additional information is needed to constrain the contribution of meat cooking emissions to ambient OC. Our approach is to include additional markers for meat cooking in the CMB model, namely stearic and palmitic acid. The final CMB model includes four meat cooking markers—cholesterol, palmitoleic acid, palmitic acid, and stearic acid—and three source profiles: the Schauer et al. (*8*) charbroiling profile, the previously discussed average red meat frying profile, and an arithmetic average of the three Schauer et al. (*7*) seed cooking profiles. We refer to this CMB model as the three-source model.

The ratio−ratio plots shown in Figure 3 provide insight into the rationale for selecting the Schauer et al. (*8*) charbroiling profile and the average frying profiles. These two profiles bracket the ambient palmitic- and stearic-acid-to-cholesterol ratios, and therefore, define a mixing line which passes through much of the ambient data (Figure 3b). These profiles also bracket the ambient palmitoleic-acid-to-cholesterol ratios (Figure 3a). Fitting both meat cooking

profiles requires including the two alkanoic acids in the model. Without these acids, a CMB model with the two meat cooking profiles finds essentially the same solution as the previously discussed palmitoleic acid and cholesterol model fit with the average charbroiling profile.

The average seed oil cooking profile is included as a third food cooking profile in the CMB model in order to avoid overapportioning meat cooking on days with high concentrations of palmitic and stearic acids because of unidentified sources. These acids are typically not included as fitting species in CMB because of this concern (*1*). Recall that the poor correlation between the alkenoic and alkanoic acids (Figure 2d) indicates that meat cooking is not the dominant source of alkanoic acids in Pittsburgh while the strong correlation of the ambient palmitic and stearic acid (Figure 2c) implies a single dominant source of these two alkanoic acids. The seed oil cooking profiles are highly enriched in alkanoic acids; for example, palmitic acid contributes 23% of the OC emissions of the average seed oil profile. This allows seed oil cooking to act as a sink for alkanoic acids in the model without CMB apportioning significant ambient OC to this source.

Time series of the monthly average OC apportioned to food cooking by the different CMB models are compared in Figure 4. The three-source solution falls between the other two previous CMB solutions and exhibits relatively little month-to-month variability in the amount of ambient OC apportioned to food cooking. On a study average basis, the three-source model apportions 320 ± 140 ng-C m^{-3} or 10% of ambient OC and 560 ± 240 ng m^{-3} or 3% of the $PM_{2.5}$ mass to cooking emissions. These estimates are comparable to results from CMB analyses with molecular markers performed in the Southeastern U.S. (*3*), but are a factor of 2 to 5 smaller than results from Houston (*2*), Los Angeles (*1*, *29*), and central California (*5*).

On most days, the three-source model provides a solution that meets the statistical guidelines outlined in the CMB manual (*16*). The average χ^2 and R^2 values are 2.1 and 0.92, respectively, and the minimum confidence level is 96% based on the χ^2 and number of degrees of freedom. However, the statistical quality is somewhat lower than the previous two models, especially in the winter. This is because adding alkanoic acids adds more constraints to the solution.

To help better understand the three-source model, Figure 5 presents the daily time series of the apportionment of ambient OC (Figure 5a), cholesterol (Figure 5b), and palmitic acid (Figure 5c) to the different cooking profiles. The Schauer et al. (*8*) charbroiling profile dominates the OC apportionment because it has by far the smallest marker-to-OC ratios of the three cooking profiles. The cholesterol-to-OC ratio of the average frying profile is a factor of 25 greater than the Schauer et al. (*8*) charbroiling profile. Therefore, it dominates the cholesterol apportionment but only modestly contributes to the ambient OC. As expected, given its large alkanoic-acid-to-OC ratios, seed oil cooking contributes little ambient OC—its maximum monthly average contribution is 28 ± 12 ng-C m^{-3}—but significant amounts of alkanoic acids. This reflects the role of the seed oil profile as a sink for alkanoic acids in the model.

A key feature of the three-source CMB model is that it includes two meat cooking profiles with very different marker-to-OC ratios. Figure 5 shows that, as the ambient concentrations of the cooking markers increase, the frying profile becomes more important. This allows CMB to explain the ambient cooking marker data on high concentration days without apportioning unrealistically large amounts of ambient OC to meat cooking (e.g., wintertime apportionment by the palmitoleic acid and cholesterol scenario shown in Figure 4). Conversely, on days when the ambient concentrations of the meat cooking markers are low, the Schauer et al. (*8*) charbroiling profile dominates, which avoids the unexpectedly small amounts of meat cooking OC apportioned by the oleic acid and cholesterol model in the fall and spring (Figure 4).

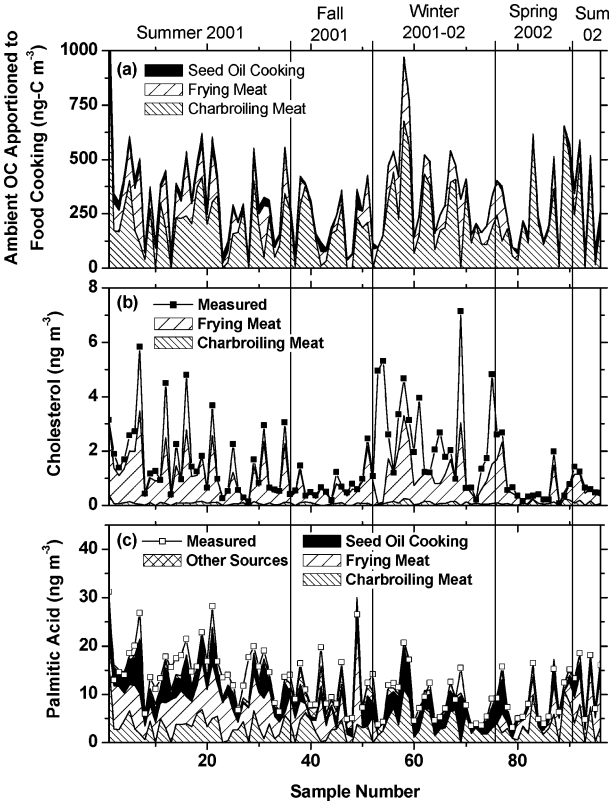

FIGURE 5. Time series of (a) food cooking OC, (b) measured and calculated cholesterol, and (c) measured and calculated palmitic acid for the three-source CMB scenario that fits the two alkanoic acids, palmitoleic acid, and cholesterol.

Despite its aforementioned advantages, there are a number of problems with the three-source scenario. First, it requires almost a factor of 10 higher ambient oleic acid concentrations than were actually measured as illustrated by the mixing line drawn in Figure 3a. Given the previously discussed inconsistencies between the source profiles and ambient data, this will be a problem with any CMB model that fits palmitoleic but not oleic acid. Second, the model cannot account for cholesterol and, to a lesser extent, palmitoleic acid (not shown) on days with very high ambient concentrations; see, for example, the first few winter days in Figure 5b. On these high concentration days the contribution of meat cooking is constrained by alkanoic acids.

The intermittent high concentration spikes in the cooking markers shown in Figure 5 suggest that there may be local cooking sources whose source contribution varies strongly with local meteorology and, therefore, only occasionally influences the site. There are both vans that prepare and sell food to students and picnic areas with barbeque pits within a kilometer of the site. Therefore, a potential explanation for the failure of CMB to close the mass balance for cholesterol and palmitoleic acid on high concentration days is that the emission profile for the very local sources is somewhat different than for the more regional sources.

Discussion

Our analysis of the Pittsburgh dataset in this and other papers in this series illustrates both strengths and challenges of using CMB and molecular markers to apportion organic aerosol. A major strength is the strong correlations in the ambient data for source-specific sets of markers, such as those shown

in Figure 2. These correlations reflect the source-specific character of molecular markers and imply the existence of a well-defined source profile for the aggregate cooking emissions. These are major advantages for using molecular markers in CMB or other source apportionment models, especially compared to using non-source specific bulk species such as metals, ions, or OC/EC. Previous molecular marker datasets have been much too small to directly probe for relationships in the ambient concentrations of source-specific sets of molecular markers.

A major challenge for constraining source contribution estimates is source profile variability, especially in marker-to-OC ratios used to convert the solution onto an OC basis. Ratios of specific markers such as cholesterol with OC vary by more than an order of magnitude across the set of cooking profiles (see Figure S-1 in the Supporting Information), which creates similar amount of variability in the CMB source contribution estimates. Source profile variability is also a problem if one normalizes emissions with $PM_{2.5}$ mass as opposed to OC because the marker-to-$PM_{2.5}$-mass ratios of the different source profiles exhibit as much variability as the marker-to-OC ratios. Source profile variability is also not unique to food cooking emissions profiles (*12*, *13*).

Given the sensitivity of the CMB solution to marker-to-OC ratios, these ratios must be carefully considered when selecting source profiles. Profiles with small marker-to-OC ratios will yield higher source contribution estimates than profiles with large ratios. In fact, profiles with very small marker-to-OC ratios can result in unrealistically large fractions of the ambient OC apportioned to a given profile. For example, on the 6 days with the highest cooking marker concentrations, more than 100% of the ambient OC is apportioned to the average charbroiling profile by the CMB model which fit palmitoleic acid and cholesterol. In the three-source model, the alkanoic acids constrained the source contribution estimates on these days. Unrealistically high meat cooking OC estimates have been reported by Sheesley et al. (*18*). They attributed the problem to an unknown source of cholesterol, but a significant factor may have been the very small cholesterol-to-OC ratio of the Schauer et al. (*8*) charbroiling profile used in the CMB model (see Figure S-1 in Supporting Information). In order to assess these issues, it is essential that CMB papers clearly identify the source profiles and fitting species included in the model so readers can assess these issues.

A second challenge facing the CMB calculations of cooking emissions is the factor of 10 or more inconsistency in the oleic-to- palmitoleic-ratio between the ambient data and the published source profiles. This means that CMB cannot fit both of these alkenoic acids simultaneously, even though the strong correlations of ambient concentrations indicate they come from the same source. In addition, as discussed previously, the amount of OC apportioned to meat cooking depends critically on which acid is included as a fitting species. Of the source-specific sets of molecular markers we have examined using the Pittsburgh dataset (*11*−*13*), the systematic inconsistency between ambient data and source profiles is unique to the cooking markers.

A final challenge is that the statistical measures calculated by CMB do not guarantee that you have found the true solution. For example, the three different CMB models presented here all have good statistical quality but widely divergent source contribution estimates. In fact, many other models based on different combinations of profiles and fitting species can be developed that all yield statistically acceptable but different solutions. The problem is that the statistical parameters calculated by CMB only assess the quality of the fit based on the subset of species included in the model. Thus, a good fit does not mean that the core assumptions underlying the CMB approach are valid because, for example, the statistical parameters do not account for problems such as variability in marker-to-OC ratios. Therefore, one cannot use the statistical parameters calculated by CMB to validate a solution. Instead, one should view the statistical parameters calculated by CMB as a necessary, but not sufficient, condition for the correct solution.

The net effect of these challenges is to create significant uncertainty in the CMB contribution estimates. In fact, the true uncertainty in the CMB solution is much larger than the typical uncertainty estimated by the model based on the fits and the analytical uncertainties of the data. This means that although food cooking emissions appear to be an important source of primary organic aerosol in Pittsburgh (our best estimate is 10% of study average ambient OC in Pittsburgh using the three-source model), its contribution is not well constrained by CMB analysis with molecular markers. These issues are not unique to Pittsburgh. Although previous CMB analyses with molecular markers typically report much more constrained source contribution estimates than the wide range of solutions reported here (*1*−*5*), these analyses are based on one set of profiles and markers and simply report the CMB-propagated uncertainty. Therefore, they have not considered the uncertainties associated with source profile variability and selection of fitting species discussed here.

An important question is how can we better constrain the CMB estimates given profile variability and other challenges? This requires adding more constraints to the model. In this paper we added species (two alkanoic acids) to the model to better constrain the CMB source contribution estimates of meat cooking emissions. Species such as high molecular weight alkanoic acids or n-alkanes provide useful constraints because they are present at ambient concentrations that can be measured with reasonable analytical precision and are not formed in the atmosphere. The problem with these species is unknown sources. In this paper, we addressed this concern by including a profile in the model that acts as a sink for the two alkanoic acids (the seed oil profile). An alternative approach is to account for additional species as a weaker, upper-bound constraint in the calculation using an approach such as that developed by Marmur et al. (*30*). By an upper-bound constraint, we mean that the CMB solution should not grossly overpredict the ambient concentration of any species (even those not explicitly fit by the model). Finally, one can simply examine the calculated-to-measured ratios of species not fit by the model to determine if the model estimates significantly exceed ambient concentrations.

Combining profiles to create an average profile for CMB analysis is another approach for reducing uncertainty created by source profile variability. A properly constructed average profile better represents the aggregate emissions of the many individual sources that make up a source class such as food cooking. The challenge is that one needs adequate activity data and source profiles to create realistic composite profiles. In addition, uncertainty assumptions used to combine profiles (e.g., activity data) are not accounted for in CMB, requiring sensitivity analysis using different profile combinations. We have used this approach for CMB analysis of motor vehicle emissions, a source category with numerous profiles and lots of activity data (*13*).

Another approach for reducing uncertainty associated with source profile variability may be to use factor-analysis models such as PMF to recover unknown sources directly from the data. The strong correlations in the ambient data indicate that molecular markers are ideally suited for factor analysis. We explore the strengths and weaknesses of the approach in an upcoming paper (*31*).

The systematic inconsistencies between the ambient molecular marker data and source profiles point to the need for additional source profiles. The need seems particularly

important for food cooking, an important source class, for which there are far fewer published profiles than for motor vehicles and biomass combustion. Finally, we must better understand the atmospheric transformation of the reduced organic compounds used as molecular markers, especially in locations like Pittsburgh that are strongly influenced by regional transport.

Acknowledgments

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Supporting Information Available

Additional details of our analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Source apportionment of molecular markers and ambient organic aerosol – 3. Food cooking emissions

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Description of ambient dataset

Samples for organic speciation were collected using a sampler operating at 145 lpm that consisted of a sharp cut $PM_{2.5}$ cyclone followed by a 102-mm quartz fiber filter and a 76.2-mm polyurethane foam (PUF) plug. The quartz filter and PUF plug were analyzed together so the data represent gas plus particle concentrations. The sampler is constructed of Teflon coated aluminum or glass and uses Teflon gaskets to minimize sample contamination. Samples were collected for 24-hr periods.

After sampling, filter-PUF pairs were stored in pre-cleaned glass jars in a freezer (-18 °C), and shipped in coolers with dry ice and synthetic ice packs overnight from Pittsburgh to Florida International University for analysis. Upon arrival, the temperature inside the coolers was determined and typically was well below -21°C. Until sample extraction, the samples were stored in freezers at temperatures well below -21°C.

Prior to each extraction, samples were spiked with an internal standard consisting of a suite of seven perdeuterated n-alkanes (C12, C16, C20, C24, C28, C32, C36). The samples were then extracted using dichloromethane. The extracts from each filter-PUF pair were combined and the volume of the combined extract reduced to about 1 ml by rotary evaporation; the volume was further reduced to about 250 μL using a gentle stream

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of pure N_2 prior to methylation using freshly prepared diazomethane. The methylated extracts were analyzed by gas chromatography-mass spectrometry (GC/MS) using electron impact ionization. Each analyte was quantified by reference to the internal standard and using a relative response factor which was determined using authentic standards. Authentic standards were used for almost all the compounds quantified.

Extensive preparation procedures were used to minimize sample contamination. Prior to sampling, the quartz filters were baked at 550°C in air for a minimum of 4 hours. PUF plugs were cleaned with repeated washing using a solutions of organic solvents. Extensive procedures were also used to clean filter holders, PUF canisters, glass storage jars containers, and tools that come into contact with the filters and PUFs.

Eight percent of all ambient samples available for analysis were field (handling) and solvent blanks. Blanks values were low. Sample concentrations for the species included in the CMB model were on almost all study days for almost all compounds well-above blank levels minimizing uncertainty associated with blank corrections.

Organic and elemental carbon were measured using quartz filters analyzed by a thermal-optical transmission method based on the NIOSH-5040 protocol (1). $PM_{2.5}$ elemental composition was measured using cellulose filters analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (2).

Description of CMB Analysis

Source contributions to ambient OC are determined by calculating the linear combination of source emissions needed to reproduce the ambient concentrations of a set of fitting species. The selection of compounds included in the CMB model is a critical issue; all major sources of each compound must be included in the model and the species should be conserved during transport from source to receptor (3). This work uses the basic set of compounds and source classes developed by Schauer et al. (4, 5).

Non-cooking markers: Twenty-one species are included in the CMB model (in addition to the cooking markers): n-heptacosane, n-nonacosane, n-hentriacontane and n-tritriacontane; iso-hentriacontane, anteiso-dotriacontane; 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, coronene; iron, titanium, and elemental carbon (EC).

Non-cooking profiles: An average gasoline profile based on the NFRAQS data (composed of 6.8% smokers/high-emitters) (6, 7); the NFRAQS heavy-duty diesel profile ("N048") (6); Pittsburgh-specific vegetative detritus, coke oven emissions and average road-dust profiles (8), and the Rogge et al. (9) cigarette smoke profile. For biomass smoke, we use the Space Heating #2 scenario (10) for the Oct-Mar samples, which consists of the Fine et al. (11) fireplace wood burning profiles for red maple, eastern white pine, and eastern hemlock. For the balance of the year we use the open burning scenario (10), which consists of the Hays et al. (12) MHFF and Florida Palmetto & Slash Pine profiles and the Hays et al. (13) wheat straw profile.

Scenarios for CMB analysis:

1. Average frying, Schauer et al. (14) charbroiling and an average seed oil cooking profile fitted with palmitic and stearic acids, palmitoleic acid, cholesterol (25 markers, 12 sources)
2. Average frying fitted only with oleic acid and cholesterol (23 markers, 10 sources)
3. Average charbroiling fitted only with cholesterol and palmitoleic acid (23 markers, 10 sources).

CMB statistical performance: The average R^2 is 0.92 or better, with a minimum R^2 of 0.75; the degrees of freedom vary between 11 and 17. The $\chi 2$ varies from 0.2 to 6.5 (these limits are quite similar for all solutions), and the minimum confidence for all three solutions is 96% based on the χ^2 and degrees of freedom.

Palmitoleic acid and oleic acid were measured as zero on four days and one day respectively. Excluding these days, the calculated-to-measured ratios for the fitted species on the 92 remaining days are as given below (target value between 0.5 and 2):

Average charbroiling fitting cholesterol and palmitoleic acid: cholesterol (palmitoleic) C/M < 0.5 on ten (seven) days, >2.0 on three (two) days.

Average frying fitting cholesterol and oleic acid: cholesterol (oleic) C/M < 0.5 on 32 (zero) days, >2.0 on zero (one) days.

Average frying, the Schauer charbroiling, and the average seed oil cooking profiles fitted with cholesterol, palmitoleic acid, palmitic acid, and stearic acid: cholesterol (palmitoleic) C/M < 0.5 on nine (28) days, >2.0 on zero (two) days. Palmitic (stearic) acid C/M <0.5 on one (zero) day, >2.0 on zero (zero) days.

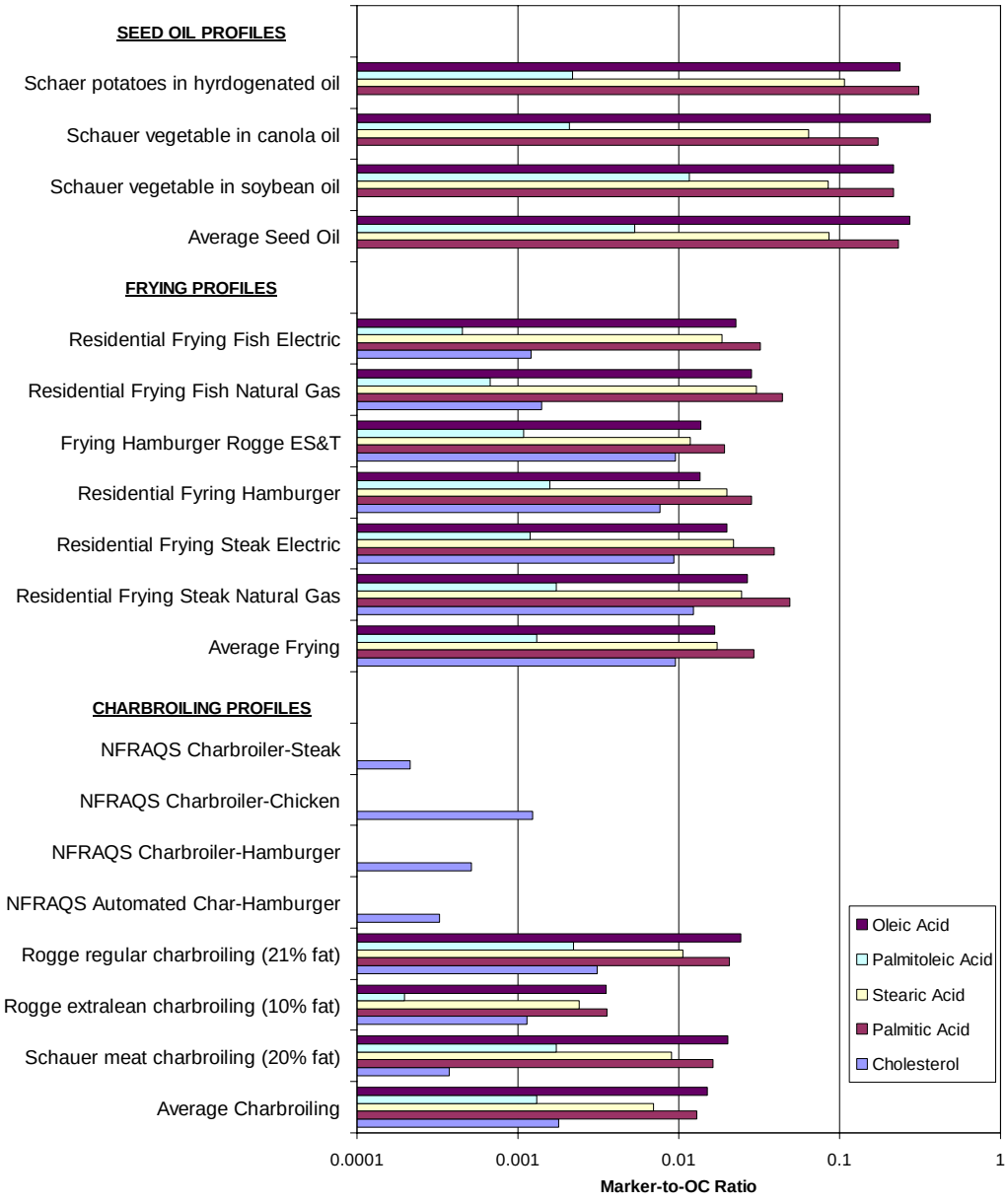

Figure S-1. Marker-to-OC ratio of meat cooking profiles. Profiles are from (6, 14-16). Residential cooking profiles have not yet been published.

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