RECEPTOR MODELLING OF FINE PARTICLES IN SOUTHERN ENGLAND USING CMB INCLUDING COMPARISON WITH AMS-PMF FACTORS

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ABSTRACT

$PM_{2.5}$ was collected during a winter campaign at two southern England sites, urban background North Kensington (NK) and rural Harwell (HAR), in January-February 2012. Multiple organic and inorganic source tracers were analysed and used in a Chemical Mass Balance (CMB) model, which apportioned seven separate primary sources, that explained on average 53% (NK) and 56% (HAR) of the organic carbon (OC), including traffic, woodsmoke, food cooking, coal combustion, vegetative detritus, natural gas and dust/soil. With the addition of source tracers for secondary biogenic aerosol at the NK site, 79% of organic carbon was accounted for. Secondary biogenic sources were represented by oxidation products of α-pinene and isoprene, but only the former made a substantial contribution to OC. Particle source contribution estimates for $PM_{2.5}$ mass were obtained by the conversion of the OC estimates and combining with inorganic components ammonium nitrate, ammonium sulphate and sea salt. Good mass closure was achieved with 81% (92% with the addition of the secondary biogenic source) and 83% of the $PM_{2.5}$ mass explained at NK and HAR respectively, with the remainder being secondary organic matter. While the most important sources of OC are vehicle exhaust (21% and 16%) and woodsmoke (15% and 28%) at NK and HAR respectively, food cooking emissions are also significant, particularly at the urban NK site (11% of OC), in addition to the secondary biogenic source, only measured at NK, which represented about 26%. In comparison, the major source components for $PM_{2.5}$ at NK and HAR are inorganic ammonium salts (51% and 56%), vehicle exhaust emissions (8% and 6%), secondary biogenic (10% measured at NK only), woodsmoke (4% and 7%) and sea salt (7% and 8%), whereas food cooking (4% and 1%) showed relatively smaller contributions to $PM_{2.5}$. Results from the CMB model were compared with source contribution estimates derived from the AMS-PMF method. The overall mass of organic matter accounted for is rather similar for the two methods. However, appreciably different concentrations were calculated for the individual primary organic matter contributions, although for most source categories the CMB and AMS-PMF results were highly correlated (r^2 = 0.69-0.91). In comparison with the CMB model, the AMS appears to overestimate the biomass burning/coal and food cooking sources by a factor of around 1.5 to 2 while estimates of the traffic source are rather similar for each model. The largest divergence is in the primary/secondary organic matter split, with the AMS estimating an appreciably smaller secondary component. Possible reasons for these discrepancies are discussed, but despite these substantial divergences, the strong correlation of the two methods gives some confidence in their application.

Keywords: $PM_{2.5}$; aerosol; source apportionment; CMB model; AMS; PMF model; urban site; rural site.

1. INTRODUCTION

Reduction of the airborne concentrations of particulate matter remains a high priority. The main drivers are European Union (EU) Limit Values and the health benefits to be gained from lower concentrations. In particular, the exposure reduction targets of the EU for fine particle $PM_{2.5}$ (a 15% reduction to be achieved by the UK by 2020 from 2009-2011 average concentrations) provide tough challenges for abatement measures. Cost-effective abatement depends upon a clear knowledge of the contributions of individual sources and source sectors to airborne concentrations. Currently in the UK, components of $PM_{2.5}$ for which data are particularly weak are woodsmoke (or solid fuel burning smoke more generally) (Harrison et al., 2012), cooking aerosol (especially in city centres with a high concentration of restaurants) (Allan et al., 2010), abrasion particles from road vehicles (Thorpe and Harrison, 2008; Pant and Harrison, 2013) and secondary organic fractions, which need additional research in order to fully understand their source contributions.

It has been established that significant amounts of the fine particulate matter ($PM_{2.5}$) are comprised of organic matter at sites within and outside Europe, representing around 25-31% in the UK West Midlands (Harrison et al., 2004), 21-33% in Ireland (Yin et al., 2005), 27-47% in Australia (Chan et al., 1997), 38-47% in France (Bressi et al., 2013) and 50% in Michigan, USA (Pancras et al., 2013). Organic matter is derived from both primary sources from which it is directly emitted to the atmosphere, and secondary production through oxidation of volatile organic compounds (VOCs) in the atmosphere. While numerous studies have been carried out upon the primary organic compounds in terms of their speciation and sources (e.g. Schauer et al., 1996; Stone et al., 2008; Yin et al., 2010; El Haddad et al., 2011a; Hasheminassab et al., 2013), the contribution of secondary organic aerosol to the total organic carbon and particle mass remains less clear due to its complex origins, composition and formation mechanisms in the atmosphere (Turpin et al., 2000; Hallquist et al., 2009). A number of studies have been carried out over mainland Europe on secondary organic aerosols formed through oxidation of biogenic volatile organic compounds (BVOCs) (Böge et al., 2006; Plewka et al., 2006; Wagener et al., 2012a,b), since their global emissions have been estimated to be 10 times higher than those of anthropogenic VOCs (Guenther et al., 1995). The major molecular markers for biogenic secondary organic aerosol constituents identified/used include a) pinic and pinonic acid (the major oxidation products of α-pinene) (Presto et al., 2005), and b) 2-methyltetrols (i.e., 2-methylthreitol and 2-methylerythritol: oxidation products of isoprene) (Claeys et al., 2004; Kourtchev et al., 2005; Clements and Seinfeld, 2007; Stone et al., 2009).

Receptor modelling methods have been used for quantitative source apportionment of both primary and secondary particulate matter using chemically discriminated composition to provide source attribution. The widely used receptor models include Principal Component Analysis with Multiple Linear Regression (PCA-MLR), Positive Matrix Factorization (PMF), UNMIX and Chemical Mass Balance (CMB). The molecular marker-based CMB model requires aerosol chemical composition data from both the pollution sources and the receptor site, and has proved able to distinguish different primary sources of carbonaceous aerosols (Schauer et al., 1996; Zheng et al., 2002; Fraser et al., 2003; Stone et al., 2008; Yin et al., 2010; El Haddad et al., 2011a).

The contribution of secondary organic aerosol (SOA) has been estimated based simply upon laboratory-derived ratios of secondary organic carbon (SOC) mass to individual secondary organic marker compounds from the precursors isoprene, α-pinene, β-caryophyllene and toluene (Kleindienst et al., 2007; Lewandowski et al., 2008; Kourtchev et al., 2009; El Haddad et al., 2011b), although this method is subject to considerable uncertainties due to the simplification of replacing the complex atmospheric chemical reactions responsible for SOA formation with a laboratory-derived single-value mass fraction. The CMB model has also been used to apportion both primary and secondary sources (e.g. Stone et al., 2009) by the addition of specific secondary organic molecular markers derived from isoprene, α-pinene, β-caryophyllene and toluene, with the highest ambient concentrations observed for derivative species of isoprene and α-pinene (Lewandowski et al., 2008; Stone et al., 2009).

Our previous study at two sites in the West Midlands area of the UK (Yin et al., 2010) identified eight primary sources that contribute about 56-85% on average to fine particulate organic carbon, including vehicular emissions (diesel engines, gasoline engines, smoking engines), wood smoke, vegetative detritus, natural gas combustion, coal combustion and road dust/soil. Vehicle exhaust emissions from all engines contributed up to 57% of the fine OC, with a relatively smaller amount up to 14% from other known sources, whilst a large amount (up to 34%) of the OC remained unexplained (termed as Other-OC), and was inferred to be mostly associated with secondary organic compounds.

A further study, reported here, has been carried out in southeast England at urban background and rural sites in order to obtain updated and extended information. Ambient aerosol samples have been analysed for multiple organic and inorganic source tracers, specifically including a number of additional markers for food cooking and secondary biogenic aerosols, in addition to the primary molecular markers previously analysed in the earlier study (Yin et al., 2010). This new dataset, particularly the food cooking and biogenic secondary markers, has allowed further evaluation of the concentration and sources of those components and the possibility for the first time to estimate, with the CMB method, the contributions of the main groups of biogenic VOC to secondary organic aerosol in the UK atmosphere. The CMB results have been compared with source contribution estimates derived from an Aerosol Mass Spectrometer (AMS), with an emphasis on sources of food cooking and secondary particles.

The comparison of CMB and AMS-PMF results is very challenging as the two techniques are very different. The CMB method takes measured chemical source profiles and constructs linear combinations to give a best fit to the composition of the ambient particles. It thus requires prior knowledge of the contributing sources. On the other hand, the application of Positive Matrix Factorization (PMF) to AMS mass spectral data is a multivariate statistical fitting method which identifies covariations within the mass spectral data itself, and outputs mass spectral profiles of contributing sources without any *a priori* assumptions about the contributing sources. The CMB model will work best when the contributing sources are well characterised in terms of a constant chemical composition of each. If any source is omitted, or has a different chemical profile to that used to describe it in the model, or varies in composition, uncertainties and errors are introduced. The AMS method does not depend upon known source profiles (although use of ME-2 rather than PMF for data analysis allows them to be introduced), but achieving a reliable separation of factors with PMF requires considerable skill, and attribution to sources relies upon subjective judgements. The AMS-PMF method is also subject to other uncertainties, such as those introduced by rotational ambiguities, discussed in the body of the paper. Hence both have their own strengths and weaknesses, with intercomparisons being a useful means of evaluating performance with a view to their optimisation.

2. Methodology

2.1 Site Location and Aerosol Sampling

Sampling was carried out during the winter ClearfLo campaign in January-February 2012 in southeast England, UK at two sites, an urban background site, North Kensington, (NK) London and a rural site, Harwell, (HAR), Oxfordshire. The NK site (51º, 31”N, 0º 12”W) is situated in the grounds of a school in a residential area, 7 km to the west of central London and is widely accepted as representative of air quality across a large part of London. The air pollution climate at the NK site has been previously analysed in detail by Bigi and Harrison (2010). The HAR monitoring station (51^{o} 34”N, 1^{o} 20”W) is situated to the west of London. The nearest road is a minor road located approximately 140 metres from the station and the surrounding area is generally open with agricultural fields, with the nearest trees at a distance of approximately 25 metres.

There were two collocated instruments at NK and HAR sites, a dichotomous Partisol 2025 sampler and a Digitel DHA-80 sampler for the purpose of both chemical and physical analyses. The Partisol sampler was used to collect 24-hour fine ($PM_{2.5}$) particles onto 47 mm PTFE filters used for gravimetric and metal analyses. The Digitel was used for collecting also 24-hour fine particles on 150 mm diameter quartz fibre filters, which were analysed for organic molecular markers, total organic carbon (OC), elemental carbon (EC), anions and cations. In addition to the samplers at NK, an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer was deployed. The sampling record, instrument/filter media used for ambient sampling, chemical and physical properties analysed and the methodologies/instrumentation used in the laboratory are summarised in Table 1. Most of the detailed procedures have been outlined in previous studies (Harrison and Yin, 2010; Yin et al., 2010) and are briefly described here along with the new procedures which are described in greater detail.

2.2 Methodologies

2.2.1 $PM_{2.5}$mass and metals

The Partisol PTFE filters collected at NK and HAR were conditioned and weighed in a controlled environment room (20±2ºC and 35-45% R.H.) before and after exposure to obtain the gravimetric mass of $PM_{2.5}$. After gravimetric analysis, those samples were analysed for elements Fe, Si and Al using a Bruker S8 Tiger WD-XRF (X-ray Fluorescence Spectrometer) instrument, and then for metals Ti, Mn, Ni, Cu, Zn and Ba by Agilent 7500ec ICP-MS, after extraction using an aqua regia acid solution (Harper et al., 1983; Allen et al., 2001; Birmili et al., 2006).

2.2.2 Ions, OC, EC and organic markers

The Digitel $PM_{2.5}$ samples on quartz filters at NK and HAR were analysed for ions SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+ using a Dionex ion chromatograph, OC and EC by Sunset Laboratory thermal-optical OC/EC analyser and organic markers (Table S1) by GC-MS, including 12 n-alkanes C_{24} – C_{35}, 9 hopanes, 10 PAHs, 2 sterols (cholesterol and levoglucosan), 6 fatty acids and 4 secondary biogenic molecular markers (at NK only), i.e. oxidation products of α-pinene (pinonic acid, pinic acid) and isoprene (2-methyltetrols: 2-methylthreitol and 2-methylerythritol). Similar methods to those reported by Yue and Fraser (2004) and Yin et al. (2010) have been applied for the sample extraction and analysis procedures, but a modified derivation/quantification method from Wagener et al.(2012a) was used for the secondary biogenic markers. In brief, one quarter of the Digitel sample was spiked with internal standards octacosane-d_{58}, aaa-20R-cholestane-d_4, dibenz(ah)anthracene-d_{14},cholesterol-2,2,3,4,4,6-d_6, methyl-beta-D-xylopyranoside, heptadecanoic acid-$d_{33}$and meso-erythritol and extracted with DCM and methanol (2:1) by undergoing mild ultrasonic treatment at room temperature. The combined extract was reduced in volume to approximately 5mL using a turbo evaporator, then filtered/dried and further concentrated down to 300μL. One aliquot of the extract was analysed directly using an Agilent GC-MS system for non-polar compounds, n-alkanes, hopanes and PAHs, whilst the polar organics needed to be derivatised before the GC-MS analysis. For fatty acids, one aliquot of the extract was evaporated to near dryness and derivatised by addition of methanol and 2.0M trimethylsilyldiazomethane (TMS-DM) in diethyl ether. For sterols and biogenic markers, another aliquot of the extract was concentrated down to near dryness and derivatised by addition of N,O-bis(trimethylsilyl)trifluoroacetamide plus 1% trimethylchlorosilane (BSTFA + 1% TMCS) and pyridine at 70^{o}C for 1h, and finally cooled in a desiccator before being run on the GCMS. The analytical precision and detection limit for individual compounds calculated using repeated measurement of the lowest standard are listed in Table S2. Blank values higher than the DL were subtracted from the sample results.

2.2.3 The CMB model

The US EPA CMB8.2 software was used for CMB modelling, with mostly similar source profiles to our earlier work, including vegetative detritus (Rogge et al., 1993a), natural gas combustion (Rogge et al., 1993b), wood smoke/biomass burning (Fine et al., 2004), dust/soil (Schauer, 1998) and coal combustion (Zhang et al., 2008). For traffic, the split of source profiles for gasoline, diesel and smoking engines may be incorrect as it is based on old engine source profiles from Los Angeles in 2001 (Lough et al., 2007) and tends to overestimate the emissions from the UK traffic fleet (Yin et al., 2010; Pant et al., 2014). Therefore they were not applied here, and instead a single traffic source profile was generated from a twin site measurement from London (roadside site minus background site) (Pant et al., 2014). Additional source profiles used were food cooking (Zhao et al., 2007b) and secondary biogenic emissions, which was generated from ambient measurements in Germany (Wagener et al., 2012a,b). Selected fitting species used in the model are elemental carbon, silicon, aluminium, levoglucosan, C_{29}–C_{35}*n*-alkanes, 17a(H)-22,29,30-trisnorhopane, 17a(H)-21b(H)-hopane, 17b(H)-21a(H)-30-norhopane, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene, picene,*n*-hexadecanoic acid, *n*-octadecanoic acid, 9-octadecenoic acid, 9,12-octadecadienoic acid, pinonic acid, pinic acid, 2-methylthreitol and 2-methylerythritol. Detailed model performance measures can be found in Yin et al. (2010).

2.2.4 AMS data analyses

The chemical composition of non-refractory PM_1 species was measured by an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, hereafter AMS), which operated in the standard configuration at NK, taking both MS and PToF data. A detailed description of the instrument can be found elsewhere (DeCarlo et al., 2006; Canagaratna et al., 2007). As the AMS sampled in an alternating sequence with other black carbon and aerosol volatility measurements, 5-minute averaged ambient samples in ‘V mode’ were only obtained every 30 minutes. Full details of the measurements are given in Young et al. (2014).

Data were analysed within Igor Pro (Wave metrics) using the standard analysis software packages, SQUIRREL v1.52J and PIKA v1.11J. A time and composition dependent collection efficiency (CE) was applied to the data based on the algorithm by Middlebrook et al. (2012) and was validated by comparing the volume concentration with that of the DMPS measurements. The AMS was calibrated using 350nm monodisperse ammonium nitrate particles.

Positive matrix factorization (PMF) (Paatero, 1997) was performed on the organic data matrix from the ‘V-mode’ data, permitting analysis of peaks according to elemental composition (Sun et al., 2011). While the ‘W-mode’ data could in theory provide a more detailed analysis, too low a fraction of peaks were consistently fit by PIKA (due to the lower signal-to-noise) to permit a meaningful PMF analysis. A front-end for using the related ME-2 algorithm (Lanz et al., 2008; Paatero, 1999) is currently available (Canonaco et al., 2013), which in some circumstances can produce more accurate data. However, the benefits of this approach are most significant when applied to unit mass resolution (UMR) data (from the Q-AMS, C-TOF-AMS and ACSM), where key peaks (such as $C_3H_7^+$ and $C_2OH_3^+$) cannot be explicitly separated and therefore contribute to rotational ambiguity under normal PMF analysis. As this is not an issue with the HR-TOF-AMS data presented here, it was decided that it would be most appropriate to use PMF, so the results would not be influenced by a priori assumptions regarding the aerosol’s behaviour.

The data were pre-processed in the recommended method of practice as described by Ulbrich et al. (2009). Isotopes were not included in the organic matrix and nitrogen-containing peaks were not deemed to have been successfully retrieved using PIKA. Five factors were identified: oxygenated OA (OOA), cooking OA (COA), hydrocarbon-like OA (HOA) and two solid fuel OA (SFOA 1 and

SFOA 2), which had the appearance of 'split' factors. While the 4-factor solution (which contained only one SFOA factor) seemed to be valid, the 5-factor solution gave improvements to diagnostics (e.g. Q) and correlations with ancillary data (e.g. NO_x, BC and CO), so it was deemed that the 5-factor solution with the split SFOA factors was the most appropriate. The 6-factor solution was discarded due to its significant dependency on initialisation seed (unlike the solutions with 5 or fewer factors) and as well as the production of a factor that did not appear physically meaningful. Further details are presented in Young et al. (2014).

2.2.5 Rotational ambiguity

Ambiguity due to rotational freedom within the solutions is a problem inherent to PMF, in common with many multivariate analyses; subtle changes in the mass spectral profiles can alter the mass concentrations of the factors, while still producing mathematically viable solutions (Paatero et al., 2002). This ambiguity was explored through varying the 'fpeak' parameter and it was found that values between -0.6 and 1.0 produced solutions that could be considered valid (see Table S3). Outside of this range, solutions produced nonphysical factors or failed to converge properly. It was found that between these values, the concentrations of HOA and COA showed some variation, however the ambiguity was not a direct rotation between the two factors as would be expected for factors derived from UMR data. Because the high-resolution data is good at distinguishing HOA (which is mainly hydrocarbons) from COA (which contains oxygenated peaks), the HOA profile was consistent between all values of fpeak. Instead, the exchange of signals between profiles seemed to involve the COA and two SFOA factors, with HOA variance accounting for changes in the hydrocarbon peaks in the SFOA.

This range of variation can been seen as indicative of the amount of rotational ambiguity present in the solutions (Allan et al., 2010). However, the solution for fpeak=0 is used for further analysis, as this is most likely to be physically meaningful according to the recommendations of Paatero et al. (2002), which does not advocate the use of nonzero values of fpeak for environmental data.

3. RESULTS AND DISCUSSION

3.1 Measured Ambient Concentration Levels at NK and HAR

Average concentration statistics are shown in Table 2 for the measured components that are used in the CMB modelling. The mean concentrations of $PM_{2.5}$ and its chemical components were mostly higher at the NK urban site than at the HAR rural site except for woodsmoke (levoglucosan) and vegetative detritus (n-alkanes) marker compounds which showed the opposite, whilst similar concentrations were observed for chloride, nitrate and sulphate.

3.1.1 Secondary organic marker components at NK

Quantifiable concentration levels of the secondary biogenic compounds were detected (0.19-1.3 ng m^{-3}) (Table 2) at the London NK urban background site, but these levels are lower than those measured from other European sites (Table 3). Wagener et al. (2012a) conducted measurements at three sites (HV – high vegetation influenced site, LV – low vegetation influenced site and regV – regional vegetation influenced site) in Berlin, Germany, and reported higher levels of those molecular markers for PM_{10} and $PM_{1.0}$ at HV, PM_{10} and $PM_{1.0}$ at LV and PM_{10} at regV. Regardless of the different particle size fraction measured, the concentration levels in Berlin are roughly 2-10 times higher than those at the London site, presumably due to influences from the surrounding forest area at the Berlin sites. Higher levels were also found for pinonic and pinic acids in the PM_{10} fraction at a background station in southern Sweden, , with higher levels in summer than in winter (Hyder et al., 2012), and for 2-methylthreitol and 2-methylerythritol in PM_{10} at a rural background site at Hyytiälä, Finland(Kourtchev et al., 2005). It is interesting to note that similar concentrations have been observed at the rural background site, Hyytiälä, Finland in autumn

2004 for the two isoprene-oxidation products to those at the UK NK site, although the former is surrounded by forests. Clearly meteorological/seasonal effects as well as source proximity can influence the levels of the biogenic secondary organic markers, which explain the low concentrations detected at our site in the winter months. In particular, the isoprene-derived compounds show much higher levels in summer than in winter, whilst similar concentrations were observed for α-pinene derived products (Wagener et al., 2012a), which may explain the higher concentrations of pinic and pinonic acids than 2-methyltetrols at our NK site. Another study in summer 2002, in a coniferous forest in Germany (Plewka et al., 2006) indicated very different day and night concentrations, with higher night-time levels for pinic acid, but higher daytime levels for pinonic acid, 2-methylthreitol and 2-methylerythritol.

Apart from the European data, sampling has also been reported from four sites in a heavily wooded region in the south-eastern US in June 2004, and also showed higher average concentrations of 2-methylthreitol and 2-methylerythritol of 4.8 and 11.9 ng m^{-3} at the inland sites, and 1.6 and 4.9 ng m^{-3} at the coastal site (Clements and Seinfeld, 2007). It is noticeable that the concentrations of 2-methylerythritol are always higher than those of 2-methylthreitol at both our NK site and in the published work, whilst higher levels of pinonic acid than pinic acid were observed at NK and in Berlin, Germany (Wagener et al., 2012a) but not at the background station in Southern Sweden (Hyder et al., 2012) where similar mean concentrations were observed.

3.1.2 Primary organic components at NK and HAR

Concentrations of both biogenic and anthropogenic primary molecular marker compounds were mostly similar or higher in comparison with those of secondary marker compounds at the UK NK site, where anthropogenic sources such as traffic emissions, wood smoke and food cooking markers play an important role. Higher levels were found for levoglucosan (Levo) (73.9 ng m^{-3} and 94.5 ng m^{-3}), hopanes (0.25-0.50 ng m^{-3} and 0.079-0.36 ng m^{-3}) and PAHs (0.10-0.67 ng m^{-3} and 0.044-0.51

ng m^{-3}) at the current southeast England sites NK and HAR in winter 2012 than that measured at the UK West Midlands urban background monitoring site, EROS, (Levo: 9.2 ng m^{-3}; hopanes: 0.08-0.18 ng m^{-3}; PAHs: 0.06-0.27 ng m^{-3}) and rural site CPSS (Levo: 7.7 ng m^{-3}; hopanes: 0.07-0.15ng m^{-3}; PAHs: 0.05-0.21ng m^{-3}) in 2007-2008 (Harrison and Yin, 2010), but lower levels were observed for n-alkanes from the current study (0.58-2.1 ng m^{-3} and 1.2-3.7 ng m^{-3} for NK and HAR), presumably due to a seasonal effect, since earlier results (1.0-5.2 ng m^{-3} and 1.8-4.7 ng m^{-3} for EROS and CPSS) cover both summer and winter periods. Similar or higher n-alkane concentration levels can be found from the current study if compared with winter periods only for EROS (0.73-1.9 ng m^{-3}) and CPSS (0.47-1.7 ng m^{-3}).

3.2 CMB Model Results

Source contributions to fine particulate OC and $PM_{2.5}$ were calculated with the CMB model for the averaged samples for the whole sampling periods and for the individual daily samples for NK and HAR sites (Table 4 and Figures 1-4).

3.2.1 Source contributions to fine OC from the CMB model

Seven primary pollution sources were apportioned initially using the average concentration data (Table 4 and Figure S1) that contribute on average about 53% at NK and 56% at HAR of the particulate organic carbon including traffic, wood smoke/biomass burning, food cooking, vegetative detritus, coal combustion, natural gas combustion and road dust/soil. The most significant sources identified are vehicle exhaust and woodsmoke emissions contributing about 21% and 15% of organic carbon (OC) at the London urban background NK site, and 16% and 28% at the rural HAR site. Other sources together contribute a relatively smaller amount of about 18% for NK and 12% for HAR respectively, including a significant amount of food cooking particularly at NK (NK: 11% and HAR: 3%), coal combustion (NK: 2% and HAR: 2%), vegetative detritus (NK: 2% and HAR: 5%), natural gas combustion (NK: 1% and HAR: 2%) and dust/soil (NK: 1% and HAR: 1%). As expected, most of the source contribution estimates, such as traffic, food cooking, coal combustion, dust/soil were larger at the urban site NK than that at the rural site HAR, where dust/soil (in bold figures) was not statistically significant over the winter period. The unidentified sources, referred to as 'Other-OC', calculated as the difference between the measured total organic carbon and the sum of all source contribution estimates has been considered as being mostly secondary organic aerosol (SOA) (Yin et al., 2010) and any unidentified primary sources that are not accounted for in the CMB modelling. These represent about 47% at NK and 44% at HAR of the measured particulate OC over the whole sampling period. Daily source contributions fluctuate at both sites with a tendency that higher percentage mass explained by the model mostly occurred when ambient OC levels were low, and on the other hand, a large un-apportioned Other-OC component was often associated with high OC levels, indicative that secondary sources played an important role in these samples.

In order to apportion the Other-OC component, a source profile of the secondary biogenic component was generated using the mean ambient measurement data from Berlin, Germany (Wagener et al., 2012a). Both PM_{10} and $PM_{1.0}$ fractions were available, but the $PM_{1.0}$ was used since previous data obtained by Wagener et al. (2012a) suggested that those biogenic markers were present mostly in the fine rather than the coarse fraction. The newly measured data on secondary biogenic molecular markers at NK, the 2-methyltetrols and the α-pinene-oxidation products, pinonic and pinic acid was combined with those source markers used earlier, and the CMB calculation was repeated to estimate an OC source contribution from secondary biogenic sources. Table 4 and Figure S1 show the mean results with (NK2012b) and without (NK2012a) the addition of these new molecular markers.

On average, organic carbon was much better accounted at NK (79%) with the addition of the secondary biogenic components than without (54%). In addition to the major primary source components, traffic (0.73μg m^{-3}), wood smoke (0.54 μg m^{-3}) and food cooking (0.39 μg m^{-3}), the secondary biogenic concentration was estimated at 0.90 μg m^{-3}, representing about 26% of the total organic carbon mass for North Kensington in winter 2012. Similar concentration estimates were obtained using a PMF model in Berlin with ranges for PM_{10} of 0.34-0.84 μg m^{-3} and $PM_{1.0}$ of 0.43-1.03 μg m^{-3} in the colder months, and as 0.9-1.5 μg m^{-3} for PM_{10} and 1.1-1.2 μg m^{-3} for $PM_{1.0}$ in the warmer months (Wagener et al., 2012b). Relative source contributions to OC in Berlin were mostly similar to the UK site for the colder months (6.3-32.2%), but higher values were obtained for the warmer period (20.0-54.5%) in Berlin. Daily CMB results (Figures 1 and 2) showed, as expected, fluctuations for the source contribution, with a few days when more OC was apportioned by the model than was measured (Figure 2). Over 30% of the OC was attributed to Other-OC on the days starting January13th, 17th, 30- 31st and February 3-5th when higher pollution levels of OC occurred, which is likely due to other biogenic and anthropogenic primary or secondary sources that are not accounted for on those days. Air mass back trajectories (Figure S2) over those periods indicated that the high OC levels were strongly influenced by pollutants transported from mainland Europe on January 17th, 30th and 31st, whilst during January 13th local or regional sources within the UK were dominant as the air mass travelled across the Atlantic Ocean and passed through southern England before reaching the site. On February 3-5th, both sources from mainland Europe and UK regional/local may have contributed.

3.2.2 Source contributions to $PM_{2.5}$ from the CMB model

Source contribution estimates were calculated by multiplication of the fine OC source apportionment concentrations by the ratios of $PM_{2.5}$ mass to fine OC obtained from the same source profiles used for the primary OC apportionment (Pant et al., 2014; Rogge et al., 1993a,b; Fine et al., 2004; Zhang et al., 2008; Schauer, 1998; Zhao et al., 2007b). Whilst the aerosol mass to OC ratio is not available for the secondary biogenic sources, a ratio of 1.8 was used to obtain this source contribution estimate for the NK site (Utembe et al., 2009). In addition to the seven/eight source components calculated from OC source contribution estimates, other organic matter (Other-OM) was estimated by multiplying the ‘Other-OC’ by a factor of 1.8 (Utembe et al., 2009), sea salt calculated as 1.65*Cl^- , ammonium sulphate as 1.38*SO_4^{2-} and ammonium nitrate as 1.29*NO_3^- were added into the $PM_{2.5}$ source apportionment (Harrison et al., 2003).

The output of the CMB model is critically dependent upon the source profiles used. The starting point was those used by Yin et al. (2010) which were mostly derived from earlier work in North America. A sensitivity study was conducted in which three ways were used of estimating the profile for road traffic following the work of Pant et al. (2014). The first two methods used dynamometer data, one using profiles of gasoline and diesel exhaust from dynamometer tests reported by Schauer et al. (1999; 2002). Secondly, more recent dynamometer data, reported by Lough et al. (2007), were utilised. Thirdly, a profile for road traffic created from measurements in a heavily-trafficked street canyon in London after subtraction of the local urban background as reported in Pant et al., (2014) was tested. This profile seems more likely to be reflective of the current vehicle fleet in London as the data are relatively recently collected. For each of these three traffic profiles, CMB was run with two different woodsmoke profiles, both taken from the USEPA SPECIATE database, one for USEPA Region 4 and the other for USEPA Region 5. In order to judge which source profiles gave the best results, the estimate for road traffic exhaust from CMB was compared with an estimate based on elemental carbon using an OC/EC ratio of 0.63 as measured in recent London data as well as an OC/EC ratio of 0.35 as reported for roadside sites in Europe by Pio et al. (2011). The derivations from elemental carbon concentration gave estimated traffic OC of 0.96 $\mu g\ m^{-3}$ and 0.54 $\mu g\ m^{-3}$ from the two OC/EC ratios. The CMB estimate of traffic exhaust OC from the application of the traffic source profile derived from data collected in London by Pant et al. (2014) of 0.73 $\mu g\ m^{-3}$ lay comfortably between these values, and hence the measured London profile was our final choice.

There was also some sensitivity of the model output to the choice of woodsmoke profile, with the EPA Region 5 profile giving an estimate for woodsmoke OC of 0.53 µg m^{-3} and that for EPA Region 4, giving 0.78 µg m^{-3} of organic carbon. The estimate for woodsmoke organic carbon based upon mean levoglucosan for the campaign times a factor of 7.35 (Puxbaum et al., 2007) gave an OC concentration of 0.54 µg m^{-3} which lay very much closer to the estimate using the USEPA Region 5 source profile and therefore this profile was adopted for the final runs of the model.

Once the optimal source profiles had been selected using the campaign averaged dataset, source contribution estimates to OC and $PM_{2.5}$ were run both on the averaged dataset and on the data for each separate day of the campaign. Since the model needs to be separately optimised for each measurement day, the average of the daily model runs presented in Table S4 is slightly different from that derived from the overall campaign averaged concentration data which is reported in Table 5. Unless stated otherwise, source contribution estimates reported are derived from the overall average dataset.

Concentrations of woodsmoke $PM_{2.5}$ were found by the CMB model to be an average of 0.64 µg m^{-3} at North Kensington in the winter 2012 campaign and 0.77 µg m^{-3} at Harwell during the same campaign (from daily data). These concentrations are slightly higher but comparable in magnitude to those measured in London in the winter of 2011 (Harrison et al., 2012). As they were measured at the coldest time of the year, it can be anticipated that annual average concentrations of woodsmoke would be appreciably lower than from those measured during the winter campaign and probably no more than 50% of these concentrations.

$PM_{2.5}$ source apportionment results for both mean and daily samples at NK and HAR sites are shown in Table 4 and Figures 3 and 4. $PM_{2.5}$ mass was well explained by those source components which represented about 81%/92% without/with the addition of secondary biogenic component at the urban NK site over the winter period. This comprised on average of 37% ammonium nitrate, 14% ammonium sulphate, 8% exhaust emissions, 10% secondary biogenic, 7% sea salt and 24% of all other identified/unidentified source components (vegetative detritus, wood smoke, natural gas, coal, dust/soil, food cooking, Other-OM and the unidentified component). The rural HAR site, with 83% total explained $PM_{2.5}$ mass, showed similar relative source contributions from ammonium salts (37% ammonium nitrate and 19% ammonium sulphate) but a smaller relative contribution from vehicle exhaust emissions (6%). In comparison, ammonium salts were also predominant in the UK West Midlands sites for both winter (urban background: 33.6%, rural: 37.7%) and summer (urban background: 52.5%, rural: 44.2%) periods (Yin et al., 2010), with much higher estimated contributions from vehicular emissions in the winter months (urban background: 29.0%, rural: 23.7%), due to apportionment with separate traffic source profiles for diesel, gasoline and smoking engines which lead to an overestimation (Pant et al., 2014). In addition, the source contribution estimates from food cooking (previously not apportioned) were not large but significant particularly at the urban NK site (OC: 0.39 $\mu g\ m^{-3}$, $PM_{2.5}$: 0.69 $\mu g\ m^{-3}$) representing about 11% of the OC and 4% of the $PM_{2.5}$ mass. As discussed for OC above, the secondary biogenic source contribution, 26% for OC and 10% for $PM_{2.5}$ at the UK site NK, cannot be ignored, particularly as during summer months this component may be significantly larger (Wagener et al., 2012b). Heal et al. (2011) studied the carbon-14 content in $PM_{2.5}$ samples from a UK West Midlands urban background site (EROS) in 2007/2008, and found that the fraction of contemporary total carbon f_c (TC) was positively correlated to the ratio SOC/TC, which were both related to airmass origin, suggesting that secondary organic aerosol is substantially associated with the oxidation of biogenic VOC emissions from terrestrial contemporary carbon sources from continental Europe. An average estimate of about 40% of the total carbon and 9-29% of the $PM_{2.5}$ was attributed to biogenic SOC or biogenic SOA (Heal et al., 2011). Those contribution estimates were higher in comparison with the current CMB estimates from the NK site (26% and 10% for OC and $PM_{2.5}$), which is likely due to (a) use of a different sampling season, i.e. the study at NK only involve winter months while both winter and summer months were included in the study by Heal et al. (2011), and (b) estimates of contemporary carbon using carbon-14 also contain sources of non fossil OC/OA other than biogenic SOC/SOA, whilst the estimates from the current study include only those components which correlate with the oxidation products of α-pinene or isoprene.

The results from NK indicate an average secondary/Other-OC organic component of $PM_{2.5}$ mass of 2.95 µg m^{-3}, of which 1.63 µg m^{-3} (55%) is accounted for by the inclusion of oxidation products of α-pinene and isoprene. The CMB method can address the composition and origin of this material, but does not explicitly consider its mechanism of formation. It seems very probable that production of other biogenic VOC and their oxidation products would correlate strongly with α-pinene and isoprene, which are recognised as two of the main precursors of biogenic secondary organic aerosol. This leads to the tentative conclusion that at least 55% of the secondary organic aerosol (SOA) is biogenic in origin, even during winter, consistent with the conclusions of both Heal et al. (2011) and Charron et al. (2013) that SOA in the south and Midlands of the UK is dominated by the biogenic component. By inference, up to 45% of SOA may arise from anthropogenic precursors such as toluene.

4. COMPARISON BETWEEN CMB AND AMS-PMF ESTIMATES

The AMS data collected at NK during winter 2012 has been analysed and apportioned using the PMF (Positive Matrix Factorisation) model based on the method used by Allan et al. (2010). Full details of the methods are available from Young et al. (2014). The results identified five source emission components that contribute to organic aerosols/matter (OA/OM), including one secondary component (OOA) and four primary components, two biomass burning/solid fuel burning organic aerosol (SFOA) factors, cooking organic aerosol (COA) and traffic related/hydrocarbon-like organic aerosol (HOA). Estimates of OC from the CMB model are then converted into source contribution estimates to $PM_{2.5}$ (Table 4) using conversion factors established in earlier work (Yin et al., 2010 and references therein). The conversion of organic carbon to $PM_{2.5}$ mass is to allow for other elements (H, N, O) associated with carbon in the organic compounds, as well as other chemical constituents associated with that source. For example, in the case of road traffic exhaust, there is a component of elemental carbon which is included, and for dust/soil, major contributions from inorganic constituents of soil (Si, Al etc.) are included. For comparison with the AMS results, OC values calculated from the CMB modelling have been converted to OM by applying OM/OC ratios considered appropriate to the source, as illustrated in Table 6 and Figure 5. The two SFOA factors have been summed as this gave the strongest correlation to both the woodsmoke and woodsmoke plus coal contributions derived from the CMB. Table 6 used OC average estimates calculated from the daily CMB results, shown in Table S4, in order to be consistent with Figure 5. The conversion of OC to $PM_{2.5}$ in Table 4 used factors taken from earlier CMB studies (see Section 3.2.2). Different factors were used to estimate values of OM in Table 6 based upon extensive literature. These may be derived from the ratio of OM for CMB in Table 6 to OC for that source in Table S4.

4.1 Woodsmoke Particles

The mean concentration of SFOA (1.63 $\mu g\ m^{-3}$) derived from AMS-PMF was almost 2 times the CMB woodsmoke (CMB-WS) concentration estimate (0.85 $\mu g\ m^{-3}$) (Table 6), possibly due to the SFOA factor also including particles from other solid fuel combustion apart from wood burning. The AMS-SFOA value remained larger at 1.7 times the CMB value when the CMB coal combustion component was also included (CMB-WS + Coal: 0.97$\mu g\ m^{-3}$). The conversion to OM in Table 6 used an OM/OC ratio of 1.6 which is smaller than some literature values, although larger than that in Table 4. This is broadly consistent with the estimated OM/OC ratios of 1.69 and 1.33 derived using the high-resolution profiles of SFOA1 and SFOA2 respectively, using the method described by Aiken et al. (2007) and also consistent with the values of 1.91 and 1.40 respectively if the modified algorithm proposed by Canagaratna et al. (2014) is used. Using a larger factor would obviously reduce the divergence between the CMB and AMS estimates from woodsmoke. Turpin and Lim (2001) suggest an OM/OC ratio as high as 2.2-2.6 for an aerosol heavily impacted by woodsmoke, which would have contributed significantly to reducing the divergence of OM masses. Nevertheless good correlation was observed between CMB-WS and AMS-SFOA ($r^2 = 0.75$) (Table 5 and Figure 5a), indicating that the SFOA component is closely related to woodsmoke. It is notable that a slightly stronger correlation is observed between the AMS-SFOA and the CMB component (WS+Coal) ($r^2 = 0.78$), which may indicate other sources in the AMS component SFOA apart from woodsmoke. It is interesting to note that both CMB-WS and CMB-(WS+Coal) are correlated more closely to SFOA at low levels of those components (CMB-WS/WS+Coal <0.9/1.2 and SFOA < 3.0) as compared to high levels when data points are more scattered from the regression line (Figures 5a and b). This seems most likely to relate to a change in composition at higher concentrations.

Previous work in the UK has obtained lower biomass smoke OC values for Birmingham EROS 2009-2010 (0.23 $\mu g\ m^{-3}$), London NK 2010/2011 (0.33 $\mu g\ m^{-3}$) and Budbrooke, Warwickshire 2009-2010 (0.42 $\mu g\ m^{-3}$) (Harrison et al., 2012), whilst six European sites showed biomass smoke OC concentrations in the range of 0.039-3.1 $\mu g\ m^{-3}$ annually and 0.048-7.7 $\mu g\ m^{-3}$ for winter months (Gelencsér et al., 2007).

Based on the CMB-WS estimates, woodsmoke can represent on average about 15% and 28% of the OC, and 4% and 7% of the $PM_{2.5}$ for NK and HAR respectively. The relative contributions of woodsmoke to OC are similar to those measured in Belgium by Maenhaut et al. (2012), and the woodsmoke contributions to $PM_{2.5}$ are in line with the lower range calculated by Zhang et al. (2010) who conducted measurements at 15 urban/rural sites in the south-eastern US and estimated that the relative contribution of biomass burning to $PM_{2.5}$ were 13% annually, 27% in winter and 2% in the summer months.

4.2 Food Cooking Particles

Many studies have indicated that food cooking is one of the most important aerosol emission sources in the indoor environment (Kamens et al., 1991; Zhao et al., 2007a; Buonanno et al., 2009; Wan et al., 2011; Massey et al., 2012). A detailed review has shown that cooking aerosol is a significant PM source for both indoors and outdoors (Abdullahi et al., 2013), and may arise from both residential and commercial food cooking. The AMS has been used to characterise PM and identify organic aerosols from cooking by means of application of PMF to mass spectral data (Kleeman et al., 2008; Allan et al., 2010; Huang et al., 2010; Williams et al., 2010; He et al., 2010 and 2011; Sun et al., 2011; Zhang et al., 2011; Mohr et al., 2009 and 2011; Clougherty et al., 2011), whilst CMB is able to calculate the food cooking concentration estimate using appropriate molecular markers (Zheng et al., 2002; Fraser et al., 2003; Schauer et al., 1996; Robinson et al., 2006; Wang et al., 2009). Food cooking estimates were calculated for the first time in the UK using a CMB model with this source profile at both sites NK and HAR. Earlier work (Yin et al., 2010) used only cholesterol as a tracer of meat cooking, suggesting much lower concentrations. AMS-PMF method data were available for the NK site only, for which the results were compared.

The CMB-derived mean food cooking concentration estimates for OC and OM/$PM_{2.5}$ from averaging the daily CMB results are 0.32 and 0.56 μg m^{-3} at NK (Tables S4 and 5), representing about 9% of the fine OC and 4% of the $PM_{2.5}$ mass. In comparison, the PMF apportioned results from the AMS data gave a value of 0.87μg m^{-3} for cooking organic aerosol, which is about 1.6 times the value of the $PM_{2.5}$ CMB estimate. A strong correlation ($r^2 = 0.80$, Pearson) was found for the daily food cooking estimates between the AMS-PMF and CMB datasets, with a gradient of 2.40 (the gradient is 1.76 with a small intercept of -0.13 after removing the high value point) (Table 5 and Figure 5c). A much lower food cooking contribution was obtained from the CMB method for HAR (0.12 μg m^{-3} or 1% of $PM_{2.5}$), where no immediate local sources were present.

Similar food cooking concentration estimate ranges have been observed in many previous studies for outdoor measurements from both CMB and AMS-PMF source apportionment. Fraser et al. (2003) conducted source apportionment using CMB for both urban and background sites in Houston, Texas, and identified a $PM_{2.5}$ source component of meat cooking of 0.9-1.3 $\mu g\ m^{-3}$ at an urban and 0.7 $\mu g\ m^{-3}$ at a background site. Robinson et al. (2006) used CMB to apportion ambient fine OC, and indicated that 10% or 0.32 $\mu g\ m^{-3}$ of the OC is attributable to food cooking in Pittsburgh, Pennsylvania. Zheng et al. (2002) estimated that about 5-12% of the fine OC arose from meat cooking emissions in the South-eastern US, whilst Lee et al. (2008) estimated that 12% of the $PM_{2.5}$ mass was from meat cooking in Korea. Sun et al. (2011) apportioned $PM_{1.0}$ AMS data using PMF and obtained 1.02 $\mu g\ m^{-3}$ of cooking organic aerosol in New York City, which contributes 30% to the primary OA. Williams et al. (2010) analysed the AMS data collected in Southern California with PMF source apportionment, which identified 10.4% or 0.98 $\mu g\ m^{-3}$ of cooking emissions from the organic aerosol in summer. Huang et al. (2010) concluded that about 24.4% of the OA was related to cooking emissions during the Beijing 2008 Olympic Games. There appears to be a trend, with AMS studies estimating larger contributions to OM and $PM_{2.5}$ than CMB studies. Summertime concentrations for cooked meat-related air particles are normally higher than in wintertime, presumably due to increased outdoor cooking activities and open kitchen windows.

4.3 Traffic Related Particles

The CMB mean concentration estimates (Table 4) of total traffic are 0.73$\mu g\ m^{-3}$ for OC and 1.26 $\mu g\ m^{-3}$ for $PM_{2.5}$ at North Kensington, while about a half of these levels were observed at rural Harwell (OC: 0.36 $\mu g\ m^{-3}$ and $PM_{2.5}$: 0.61$\mu g\ m^{-3}$). The relative contribution of total traffic to OC and $PM_{2.5}$ at the urban site is about 21% and 8%, and at the rural site about 16% and 6% respectively. Very strong correlations (r^2 = 0.90-0.99) have been observed for the CMB traffic component and other related variables such as aethalometer BC, measured EC and calculated primary organic carbon (obtained based on the method of Castro et al., 1999) at both urban and rural sites (Pant et al., 2014). The AMS-PMF derived component HOA is also strongly correlated with the CMB OM traffic component (r^2 = 0.80) for NK, and if the two outlying points are removed, the correlation improves (r^2 = 0.86) and the gradient reduces to 0.98. The absolute OM concentration levels are very similar from the two methods, showing a CMB traffic estimate of 0.98 μg $m^{-3}$and an AMS value of 0.86 μg m^{-3} (Table 6).

4.4 Secondary Particles

The CMB component Other-OC/Other-OM is regarded as mostly secondary OC/OM (Yin et al., 2010). The Other-OM, with concentration estimates of 2.92 μg m^{-3} at North Kensington and 1.85 μg m^{-3} at Harwell (Table S4), represented about 46% and 45% of the total organic aerosol (OA) mass, and 19% and 17% of the $PM_{2.5}$ mass at those two sites. The secondary component derived from the AMS-PMF results (OOA) is 0.99 μg m^{-3} for the same period at NK, which is well below the CMB Other-OM level. Docherty et al. (2008) studied secondary organic aerosol (SOA) at Riverside, Southern California in the summer period using different methods, and showed very similar proportions of SOA/OA estimated by the CMB (77%) and AMS-PMF (74±19%) methods, but with much higher relative contributions of SOA comparing with our UK NK site. However, the study also summarised results from previous studies in the Eastern LA Basin area with different methods, found that the SOA/OA ratios were mostly less than 50% (range: about 15-50%), with only one exception (75%) by Schauer et al. (2002), and attributed those large differences to variations in sampling season, location, duration and methodology.

The CMB Other-OC/OM is strongly correlated with the calculated Sec-OC (obtained based on the elemental carbon tracer method of Castro et al., 1999) at both sites (r^2 = 0.84 and 0.62 for North Kensington and Harwell respectively), confirming that this component is mainly secondary organics, and lesser but still significant correlations were observed for Other-OM with secondary inorganic components, sulphate and nitrate. A strong relationship was found for AMS OOA with the CMB Other-OM (r^2 = 0.68), Sec-OC (r^2 = 0.64) and inorganic components SO_4^{2-} and NO_3^- (r^2 = 0.79 and 0.80) as expected (Table 5).

Regression analyses showed low to moderate correlation between the measured biogenic secondary marker 2-methyltetrols and the calculated Sec-OC/CMB Other-OC (r^2 = 0.25-0.41), whilst higher correlations were found between the measured α-pinene oxidation products and Sec-OC/CMB Other-OC (r^2 = 0.31-0.82). Pinic acid particularly showed strong correlation with Sec-OC/CMB Other-OC (Figure 6). In comparison, no correlation was found between 2-methyltetrols and AMS OOA showing close to zero coefficients, whilst pinic acid again exhibited a good relationship with the AMS OOA component (r^2 = 0.55) (Figure 6). The results of Kleindienst et al. (2007) from measurements of VOC oxidation products at a US site attribute far greater importance to α-pinene than isoprene as an SOA precursor during the cooler months of the year. The species of trees and shrubs present locally will also be influential.

4.5 Overview of CMB Comparison with AMS-PMF Results

There are few previous published studies that have compared the results between the AMS-PMF and the CMB methods, and this first comparison study in the UK at the NK site has shown some inconsistent results for individual primary component estimates, and a different split between the total primary and secondary source components. In a study in Mexico, Aiken et al. (2009) found similar average OA/OM apportionment values from the two methods AMS-PMF and CMB for HOA/Vehicle (4.5 $\mu g\ m^{-3}$, 28%/4.5 $\mu g\ m^{-3}$, 29%), BBOA/Woodsmoke (2.7 $\mu g\ m^{-3}$, 17%/1.7 $\mu g\ m^{-3}$, 12%) and OOA/Other-OM (7.4 $\mu g\ m^{-3}$, 46%/9.2 $\mu g\ m^{-3}$, 58%), but the source components calculated were different to our study.

Generally speaking, overall correlations between the CMB and PMF based estimates here are very good, but the quantitative agreement is lacking, with PMF estimates generally greater than CMB for the primary species (in particular, cooking and solid fuel burning) and CMB assigning a much larger proportion of organic matter to secondary aerosol. Agreement between the methods is relatively good for the traffic source, and fair for food cooking (Table 6). Measurements of levoglucosan and fine potassium made during the campaign (Crilley et al., 2014) give an estimate for biomass burning particles consistent with the CMB results, and other work based upon elemental carbon data (arising mostly from diesel emissions) suggests that the traffic estimate in the CMB model is reasonable (Pant et al., 2014). The AMS estimates of SFOA and HOA also correlate very well with a Single Particle Soot Photometer (SP2) -based apportionment of the black carbon particles present, based on the mass of individual particles and coating thicknesses (Liu et al., 2014).

It is important to remember that the CMB model is applied to organic carbon, which is apportioned into the eight categories listed at the top of Table 4. Table 6 shows a comparison of the CMB with the AMS data, attempting where possible to express the CMB results as solely the organic matter content so as to be comparable with the AMS data. The AMS factors do not include vegetation, natural gas and dust/soil in their apportionments, however this is not unexpected; vegetation and dust/soil particles are generally too large to be detected by the AMS and natural gas does not contribute a sufficient mass of particulate organics to the overall loading.

There are also a number of technical reasons why both techniques may deliver inaccurate estimates. In the case of the CMB model, uncertainties arise from the concentration measurements, the source profiles and the amount of colinearity amongst the source profiles. This is expressed quantitatively as a standard deviation in Table 4, and varies substantially in proportion to the Source Contribution Estimate between source categories. The uncertainties in AMS source apportionment results are more difficult to quantify, and possible sources of error in both techniques are discussed below. The sum of the two sets of measurements when expressed as organic matter is greater for the CMB than the AMS (Table 6). The CMB model is applied to samples of $PM_{2.5}$ whereas the AMS samples particles up to around 0.8 µm, and consequently fails to sample larger particles, which are possibly of different composition. It is conceivable that the larger estimate of SOA by CMB may be caused in part by condensation of secondary material onto supermicron particles.

One issue that may affect the AMS is an ambiguous collection efficiency (CE). A time-dependent and composition-dependent parameterisation of CE was used, with a value of 0.5 used for most of the data, in line with the parameterisation of Middlebrook et al. (2012). However, it is possible that if a certain particulate population is externally mixed with the inorganic fraction in the accumulation mode, it may exhibit a different collection efficiency. While the overall CE was validated against a DMPS, it is possible that if a fraction makes a low enough contribution to the total volume concentration, it may not be picked up through this test. In the event that cooking particles are liquid, which is deemed likely given that many of the constituents such as oleic acid are of this phase at room temperature, their concentration could be overestimated by the AMS by up to a factor of 2. Note that this will only apply to particles that have not diffused onto the accumulation mode, so the level of overestimation could be less than 2, even if the true CE of pure-component particles is unity. However, this could account for the majority of the discrepancies with the primary particles.

PMF analysis is subject to inherent uncertainties associated with rotational ambiguity (Allan et al., 2010) referred to in Section 2.2.5. This can result in an amount of the mass being misattributed between factors and it is conceptually possible that some secondary material could be wrongly interpreted as solid fuel burning; indeed, there is evidence for this occurring to an extent in the CTOF instrument, which suffers from this phenomenon more than the HR-AMS used here (Young et al., 2014). Dall'Osto et al. (2014) showed that the COA factor from AMS data in Cork, Ireland exhibited an association with other urban aerosol sources, possibly indicating that it contained a contribution from these rather than cooking. These issues should be manifested as rotational freedoms within the solution sets and by varying the fpeak parameter, a tangible amount of uncertainty in the PMF outputs can be attributed to this (see Table S3) but this in itself is not large enough to explain the discrepancies. It is worth noting in particular that the ambiguity identified using this method consists mainly of a redistribution of mass between the primary factors, so would not explain in isolation an overestimation of both SFOA and COA. Nevertheless, it could be that this might explain at least part of the discrepancies reported.

There are a number of problems that may cause the CMB model to be inaccurate. Firstly, there is a general uncertainty surrounding how representative the source profiles assumed are of the aerosols encountered in this environment, but the sensitivity study of CMB profiles discussed above was intended to probe and minimise such effects. That said, it is recognised that the application of CMB to the secondary fraction is inherently highly uncertain, owing to the broad range of precursors and the complexity of the chemistry. It is also possible that some of the marker compounds are being lost from the aerosols between emission and measurement, either through repartitioning to the gas phase as the aerosol undergoes dilution in the atmosphere, chemical reactions through atmospheric processing, or evaporating from the filter during or after sampling. Levoglucosan could be an example, contributing to a CMB underestimate of woodsmoke mass. The Partisol sampler used to collect samples for the CMB estimation is subject to both positive (adsorption of vapour on the filter) and negative (evaporation of semi-volatile material from the filter) artefacts.

5. CONCLUSIONS

The CMB and AMS-PMF methods use entirely different processes to apportion organic carbon and organic matter respectively to source categories. The CMB method is able to attribute carbon to a larger number of sources, but depends upon prior knowledge of source profiles, which must add a significant element of uncertainty. The AMS-PMF method makes no *a priori* assumptions, but depends upon the PMF to separate components with many similarities in their mass spectra, and is able to apportion into a smaller number of classes.

The use of other marker elements/compounds to estimate source contributions from biomass burning and road traffic gives some confidence in the estimates from the CMB approach. It also attributes carbon to sources not recognised by AMS-PMF, which must be in some way included in the factors output by this method.

Although the average mass estimates for primary components differ appreciably between the CMB and AMS-PMF results, the estimated daily average concentrations for each generic source category show generally good correlations. In summary, the PMF estimations were higher than CMB by over a factor of two for solid fuel burning and cooking, slightly higher for traffic and lower for the secondaries. While no single issue with either technique can explain the discrepancies, they are within the scope of a combination of known problems and ambiguities (such as AMS collection efficiency, PMF rotation, inhomogeneous distribution of components across size fractions, Partisol collection artefacts and uncertainties in CMB profiles). Work needs to be performed to better constrain all of these issues. This would include obtaining further local source profiles for use in the CMB model, and designing air sampling so that the bulk chemical data used in the CMB model derive from the same particle size range as is sampled by the AMS.

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TABLE LEGENDS

Table 1	Air sampling and analytical instrumentation.
Table 2	Concentration summary of measured components at NK and HAR.
Table 3	Comparisons data for mean concentrations of secondary biogenic molecular markers.
Table 4	Source contribution estimates (SCE) (µg m^{-3}) and standard deviation (S.D.) for fine particulate OC and $PM_{2.5}$ at NK and HAR from the CMB model.
Table 5	RMA regression results for CMB and AMS-PMF OM estimates and related variables.
Table 6	Comparison of apportionment of organic matter by the AMS-PMF and CMB method at NK (µg m^{-3})

FIGURE LEGENDS

Figure 1	Daily OC source contributions at NK and HAR (without secondary biogenic component identified separately).
Figure 2	Daily OC source contribution estimates with secondary biogenic components at NK.
Figure 3	Daily $PM_{2.5}$ source contribution estimates with secondary biogenic components at NK.
Figure 4	Daily $PM_{2.5}$ source contribution estimates at HAR.
Figure 5	Primary component comparison between the AMS-PMF and CMB methods at NK.
Figure 6	Secondary component comparison at NK showing relationships between pinic acid concentrations and estimated secondary OC from the elemental carbon tracer method (Sec-OC) and the CMB model (Other-OC), and with the AMS OOA factor.

Table 1: Air sampling and analytical instrumentation

Site	Instrument/ Filter media	Particle size	Chemical analyses /Measurements	Analyser/ Methods	Sample intervals
NK	Partisol/ PTFE filter	$PM_{2.5}$	PM mass	Balance	Daily
			Al, Si, Fe	XRF	
			Ti, Mn, Ni, Cu, Zn, Ba	ICP-MS	
	Digitel/ Quartz filter	$PM_{2.5}$	Organic markers (including secondary)	GCMS	Daily
			OC & EC	OCEC analyser	
			SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+	Dionex	
	TOF-AMS	$PM_{0.8}$	Mass size segregated Organic aerosol OOA, BBOA, HOA, COA	PMF	1-10 minutes
HAR	Partisol/ PTFE filter	$PM_{2.5}$	PM mass	Balance	Daily
			Al, Si, Fe	XRF	
			Ti, Mn, Ni, Cu, Zn, Ba	ICP-MS	
	Digitel/ Quartz filter	$PM_{2.5}$	Organic markers (not including secondary)	GCMS	Daily
			OC & EC	OCEC analyser	
			SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+	Dionex	

Table 2: Concentration summary of measured components at NK and HAR

	NK			**HAR**		
Components	**Mean**	**Median**	**10%ile/90%ile**	**Mean**	**Median**	**10%ile/90%ile**
PM2.5 (µg m^{-3})	15.7	12.6	4.9/29.8	11.0	10.2	3.1/19.6
OC	3.5	2.6	1.3/6.7	2.3	2.1	0.46/5.0
EC	1.5	1.2	0.67/2.7	0.68	0.56	0.12/1.3
Cl^-	0.67	0.60	0.33/1.3	0.50	0.45	0.23/0.76
SO_4^{2-}	1.8	1.3	0.58/3.8	1.7	1.3	0.46/4.4
NO_3^-	3.5	2.6	0.69/7.6	3.2	2.7	0.42/6.3
Al	0.044	0.035	0.017/0.086	0.027	0.019	0.008/0.060
Si	0.14	0.12	0.056/0.25	0.077	0.056	0.023/0.15
Levo (ng m^{-3})	73.9	69.5	42.7/118	94.5	99.0	27.2/152
C29	2.1	1.7	1.2/4.0	3.7	3.6	1.6/5.4
C31	1.7	1.3	0.84/3.1	2.9	3.0	0.93/4.3
C33	0.95	0.75	0.43/2.0	1.2	1.2	0.54/2.0
C35	0.58	0.47	0.28/1.1	3.1	3.5	0.4/4.3
17αTNohop	0.25	0.19	0.14/0.36	0.079	0.075	0.042/0.12
17βαNohop	0.50	0.41	0.24/0.84	0.36	0.36	0.25/0.47
17αβHop	0.33	0.26	0.20/0.39	0.17	0.16	0.14/0.22
B(k)F	0.67	0.50	0.15/1.4	0.49	0.38	0.053/1.0
B(b)F	0.54	0.39	0.15/1.1	0.51	0.48	0.12/0.94
B(e)P	0.48	0.35	0.14/0.94	0.33	0.29	0.048/0.66
IP	0.40	0.28	0.11/0.84	0.29	0.23	0.041/0.62
PIC	0.10	0.081	0.045/0.17	0.044	0.034	0.005/0.10
B(ghi)PER	0.47	0.35	0.15/0.94	0.25	0.20	0.039/0.52
PalmA	60.2	50.1	29.0/110	19.0	13.7	7.2/34.5
LinoA	7.9	2.0	0.17/14.2	6.7	0.66	0.31/6.3
OleiA	11.8	2.3	1.1/22.4	3.0	1.6	0.66/3.2
SteaA	26.6	22.7	12.6/43.1	10.7	7.3	5.4/18.7
MethT	0.19	0.13	0.05/0.27	-	-	-
MethE	0.31	0.26	0.12/0.39	-	-	-
PinoA	1.3	0.96	0.55/2.7	-	-	-
PinicA	0.94	0.56	0.11/2.5	-	-	-

Note: PM$_{2.5}$ mass and inorganic constituents in µg m^{-3}; Organic markers in ng m^{-3}

Table 3: Comparison of data for mean concentrations of secondary biogenic molecular markers

Site	Season/ Fraction	2-Methyl -threitol	2-Methyl -erythritol	2-Methyl -tetrols	Pinonic acid	Pinic acid	Pinonic + Pinic acids	References
NK, London, UK, urban background	Jan-Feb2012/ $PM_{2.5}$	0.19	0.31	0.50	1.3	0.94	2.3	-
HV (high vegetation site), Berlin, Germany	Feb-Oct2010/ PM_{10}	0.8	1.4	2.2	13.2	3.9	17.1	Wagener et al., 2012a,b
LV (roadside, low vegetation), Berlin, Germany	Feb-Oct2010/ PM_{10}	0.6	1.2	1.8	8.4	2.2	10.6	Wagener et al., 2012a,b
RegV (background, regional influence), Berlin, Germany	Feb-Oct2010/ PM_{10}	0.8	1.2	2.0	15.3	5.6	20.9	Wagener et al., 2012a,b
HV (high vegetation site), Berlin, Germany	Feb-Oct2010/ PM_1	0.6	1.1	1.7	11.9	3.1	15.0	Wagener et al., 2012a,b
LV (roadside, low vegetation), Berlin, Germany	Feb-Oct2010/ PM_1	0.3	0.8	1.1	6.9	2.3	9.2	Wagener et al., 2012a,b
Vavihill, background, southern Sweden	2008-2009/ PM_{10}	-	-	-	3.02	3.03	6.1	Hyder et al., 2012
Hyytiälä, Finland, rural with forests surrounded	summer2004/ PM_1	5.1	21.2	26.3	-	-	-	Kourtchev et al., 2005
Hyytiälä, Finland, rural with forests surrounded	autumn2004/ PM_1	0.18	0.29	0.47	-	-	-	Kourtchev et al., 2005
Southeastern US, urban & urban background	June2004	4.8	11.9	16.7	-	-	-	Clements and Seinfeld, 2007
Southeastern US, rural	June2004	1.6	4.9	6.5	-	-	-	Clements and Seinfeld, 2007

Table 4: Source contribution estimates (SCE) (µg m^{-3}) and standard deviation (S.D.) for fine particulate OC and PM$_{2.5}$ at NK and HAR from the CMB model

		OC			**PM$_{2.5}$**			**OC/PM$_{2.5}$**
Source Name		**NK**[a]	**NK**[b]	**HAR**[a]	**NK**[a]	**NK**[b]	**HAR**[a]	
Vegetation	*SCE*	0.069	0.069	0.11	0.21	0.21	0.35	0.324
	S.D.	0.010	0.010	0.015	0.030	0.030	0.048	-
Woodsmoke	*SCE*	0.53	0.53	0.64	0.64	0.64	0.76	0.836
	S.D.	0.11	0.11	0.14	0.14	0.14	0.16	-
Natural Gas	*SCE*	0.046	0.046	0.042	0.054	0.054	0.049	0.849
	S.D.	0.009	0.009	0.007	0.011	0.011	0.008	-
Dust/Soil	*SCE*	0.044	0.044	***0.016***	0.34	0.34	***0.12***	0.131
	S.D.	0.036	0.036	0.015	0.27	0.27	0.11	-
Coal	*SCE*	0.074	0.074	0.041	0.17	0.17	0.094	0.432
	S.D.	0.020	0.020	0.009	0.046	0.046	0.021	-
Food Cooking	*SCE*	0.39	0.39	0.072	0.69	0.69	0.13	0.566
	S.D.	0.066	0.066	0.013	0.12	0.12	0.023	-
Total Traffic	*SCE*	0.73	0.73	0.36	1.26	1.26	0.61	0.579
	S.D.	0.35	0.35	0.16	0.86	0.86	0.29	-
Biogenic Secondary	*SCE*	-	0.90	-	-	1.63	-	0.556
	S.D.	-	0.17	-	-	0.31	-	-
Other-OC/OM	*SCE*	1.64	0.73	1.02	2.95	1.32	1.84	0.556
	S.D.	-	-	-	-	-	-	-
Sea Salt	*SCE*	-	-	-	1.1	1.1	0.82	-
	S.D.	-	-	-	0.020	0.020	0.020	-
Ammonium Sulphate	*SCE*	-	-	-	2.2	2.2	2.1	-
	S.D.	-	-	-	0.028	0.028	0.028	-
Ammonium Nitrate	*SCE*	-	-	-	5.8	5.8	4.1	-
	S.D.	-	-	-	0.072	0.072	0.072	-
Measured OC/PM$_{2.5}$	*Mass*	3.5	3.5	2.3	15.7	15.7	11.0	-

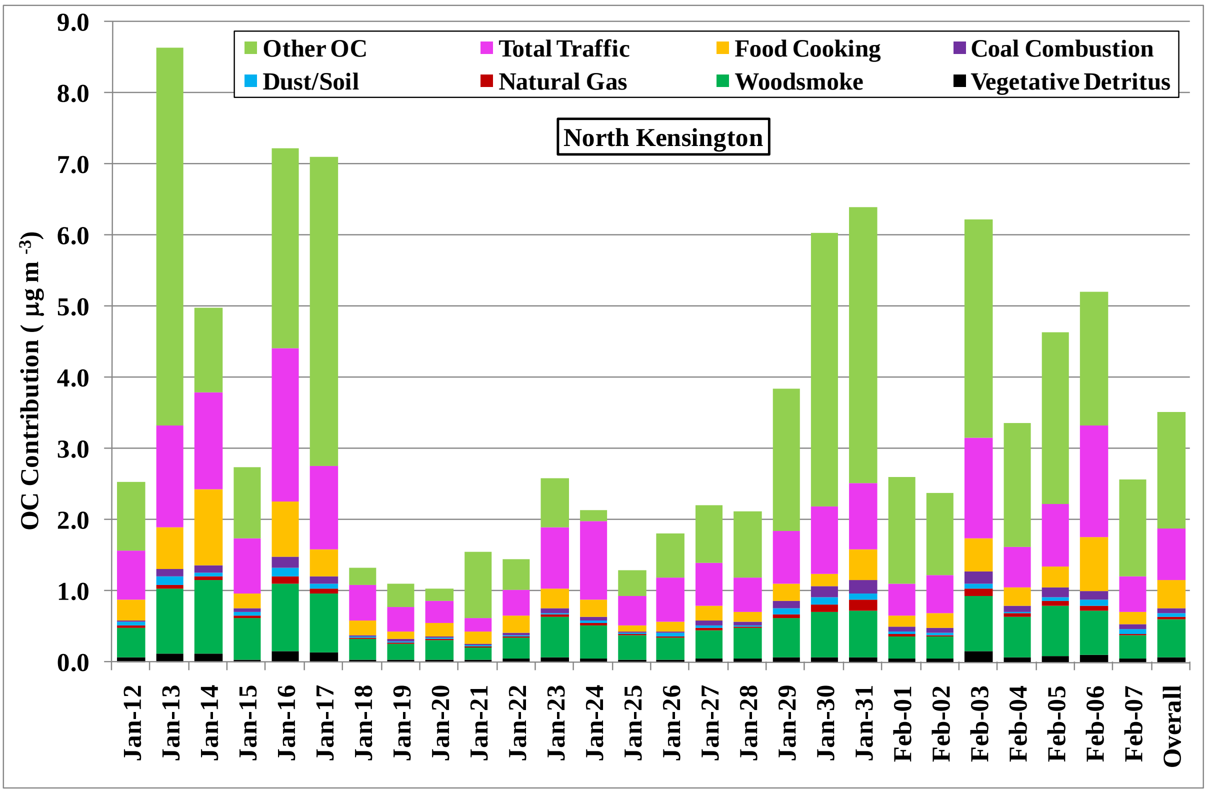
Note: Figures in bold were not statistically different from zero; *a* - Modelled without biogenic secondary source profile; *b* – Modelled with biogenic secondary source profile; *c* – Conversion factor

Table 5: RMA regression results for CMB and AMS-PMF organic matter estimates and related variables

	NK2012		
Pair of Variables	***Slope***	***Intercept***	r^2
AMS-SFOA/CMB-WS	2.81	-0.69	0.75
AMS-SFOA/CMB-(WS+Coal)	2.40	-0.64	0.78
AMS-COA/CMB Food Cooking	2.24	-0.33	0.80
AMS-HOA/CMB Traffic	1.24	-0.32	0.80
AMS (SFOA+COA+HOA)/CMB (WS+Coal+Food+Traffic)	1.85	-1.14	0.91
AMS-OOA/CMB Other-OM	0.39	-0.06	0.69
AMS-OOA/Sec-OC	0.81	0.18	0.64
AMS OOA/Measured SO_4^{2-}	0.71	-0.27	0.79
AMS OOA/Measured NO_3^-	0.33	-0.16	0.80
CMB Other-OC/Sec-OC	0.99	0.66	0.84
CMB Other-OM/Measured SO_4^{2-}	1.13	0.78	0.39
CMB Other-OM/Measured NO_3^-	0.58	0.84	0.42

Table 6: Comparison of apportionment of organic matter by the AMS-PMF and CMB method at NK (μg m^{-3})

Source	**CMB Estimate**	**AMS-PMF Estimate**
Woodsmoke	0.85	1.63
Coal	0.12	-
Food cooking	0.56	0.87
Traffic	0.98	0.86
Vegetation	0.11	-
Natural gas	0.055	-
Dust/soil	0.10	-
Primary-total	2.77	3.36
Secondary	2.92	0.99
TOTAL	5.69	4.35



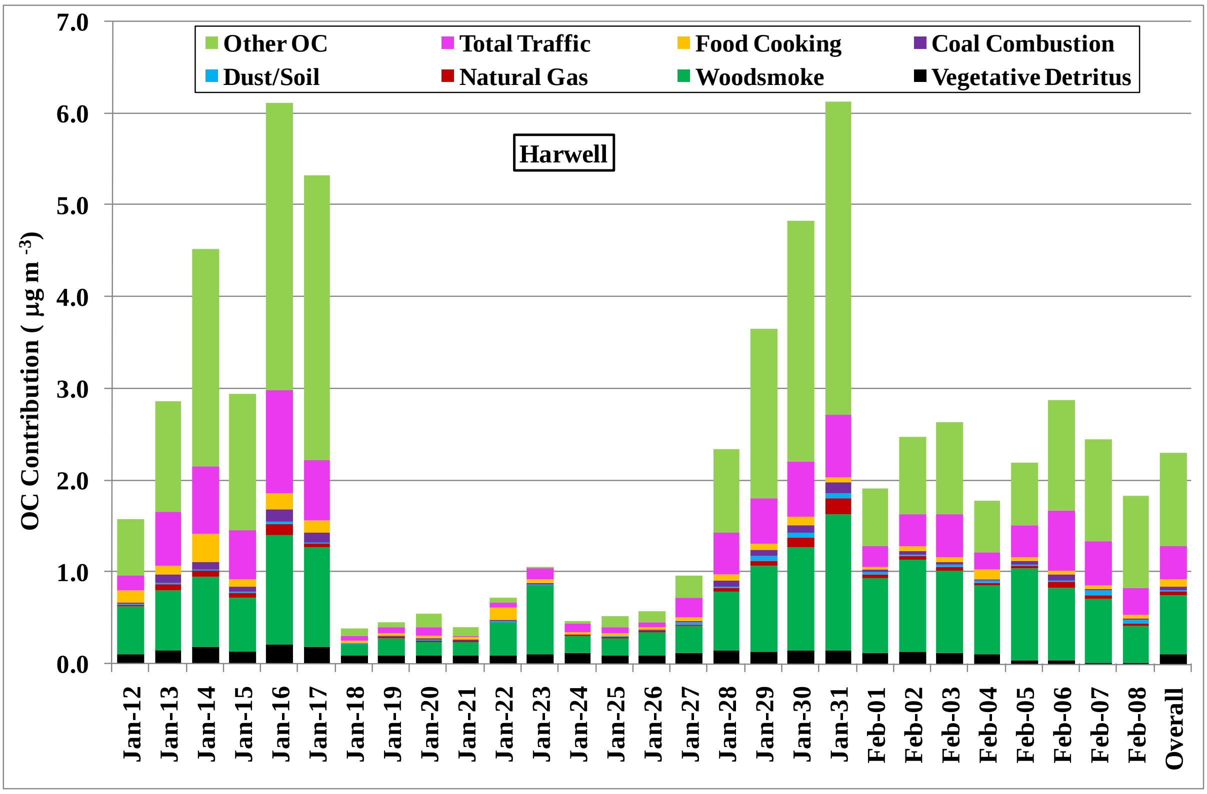


Figure 1: Daily OC source contributions at NK and HAR (without secondary biogenic component identified separately)

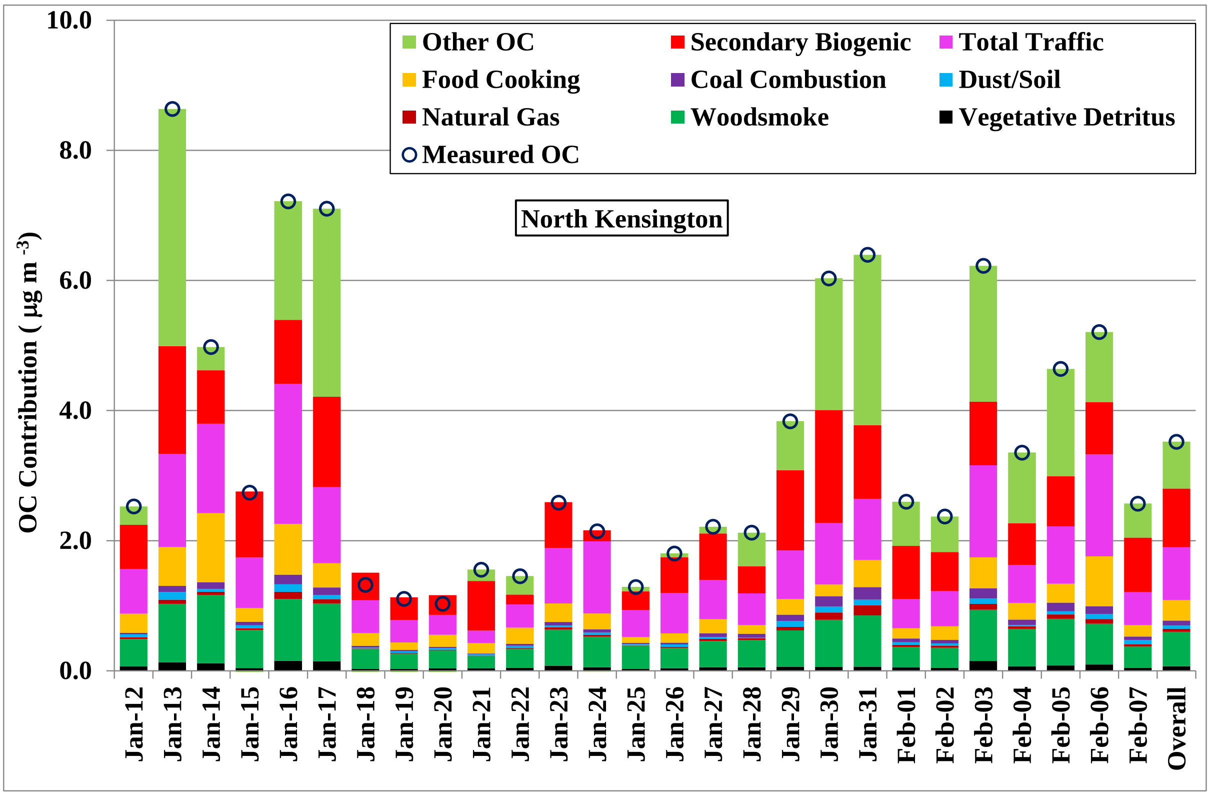


Figure 2: Daily OC source contribution estimates with secondary biogenic components at NK

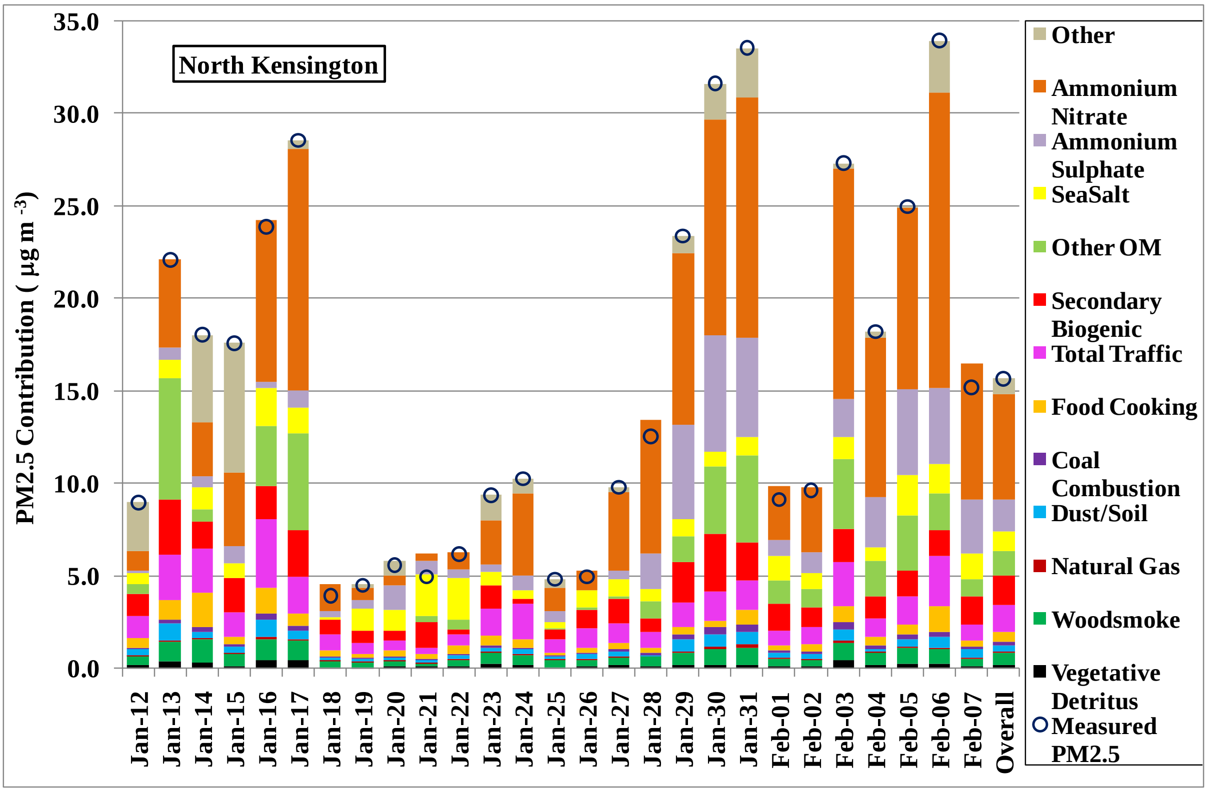


Figure 3: Daily $PM_{2.5}$ source contribution estimates with secondary biogenic components at NK

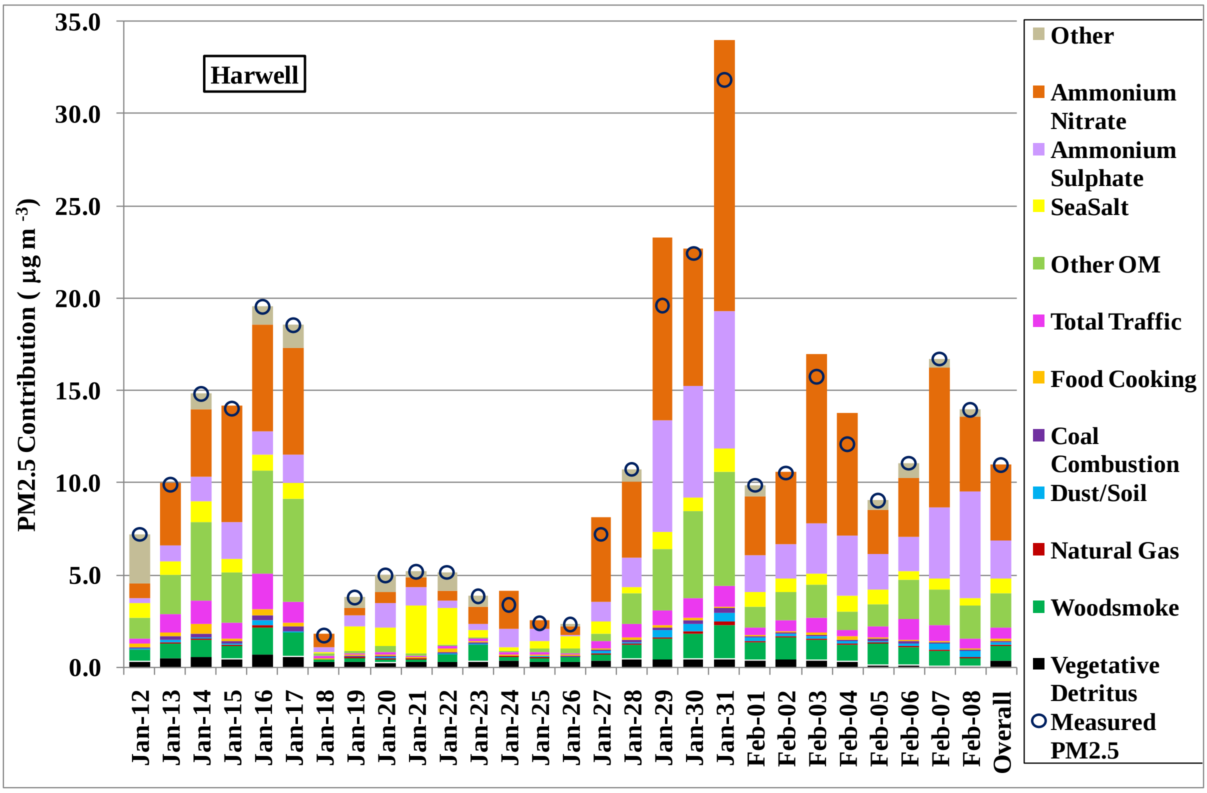
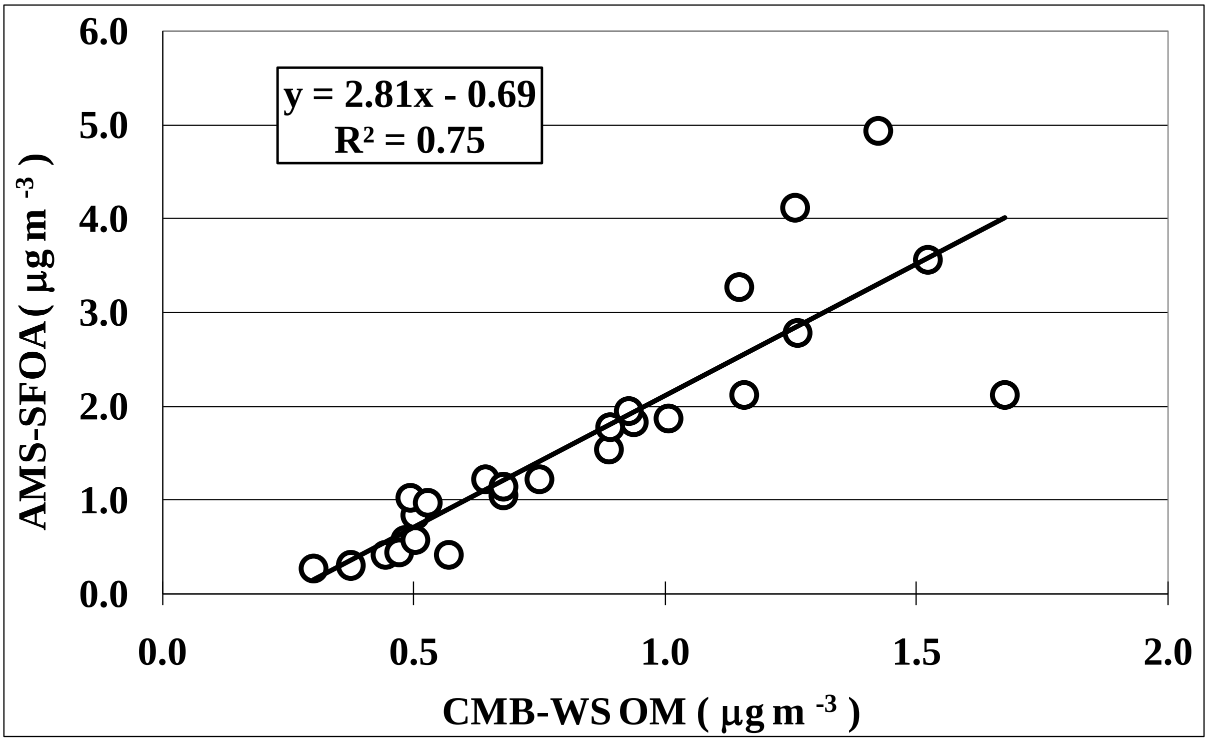
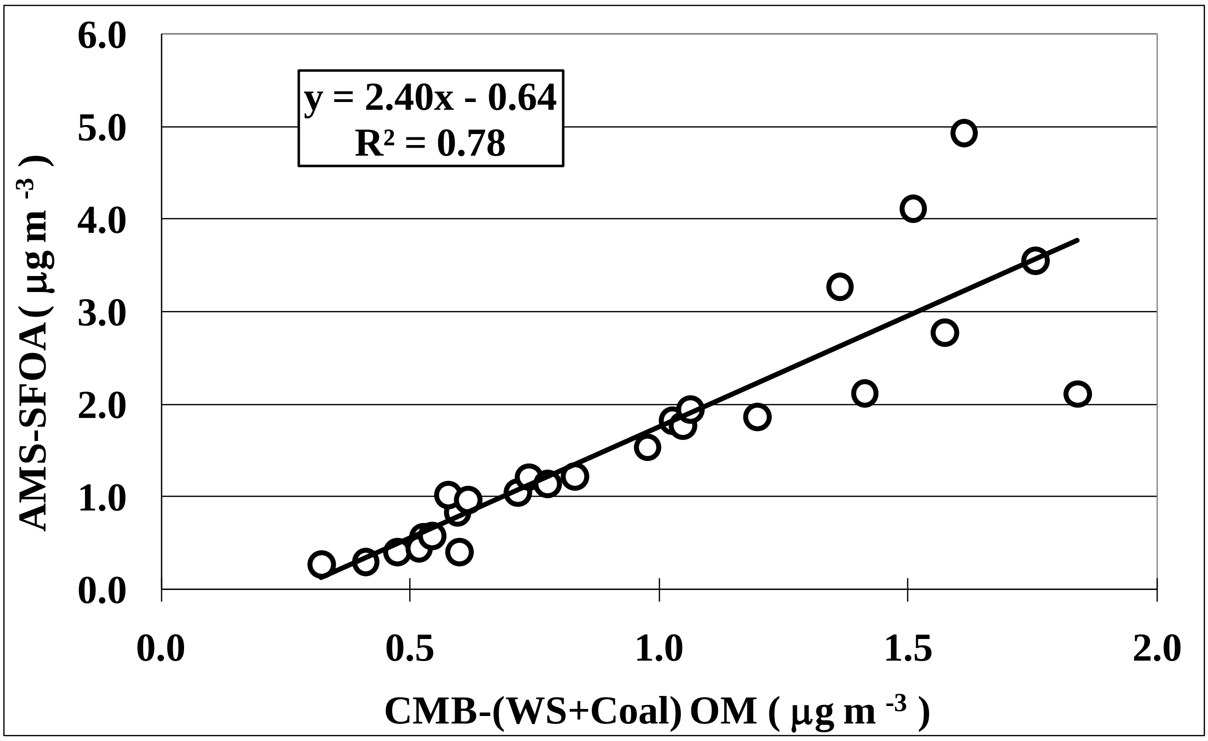


Figure 4: Daily $PM_{2.5}$ source contribution estimates at HAR

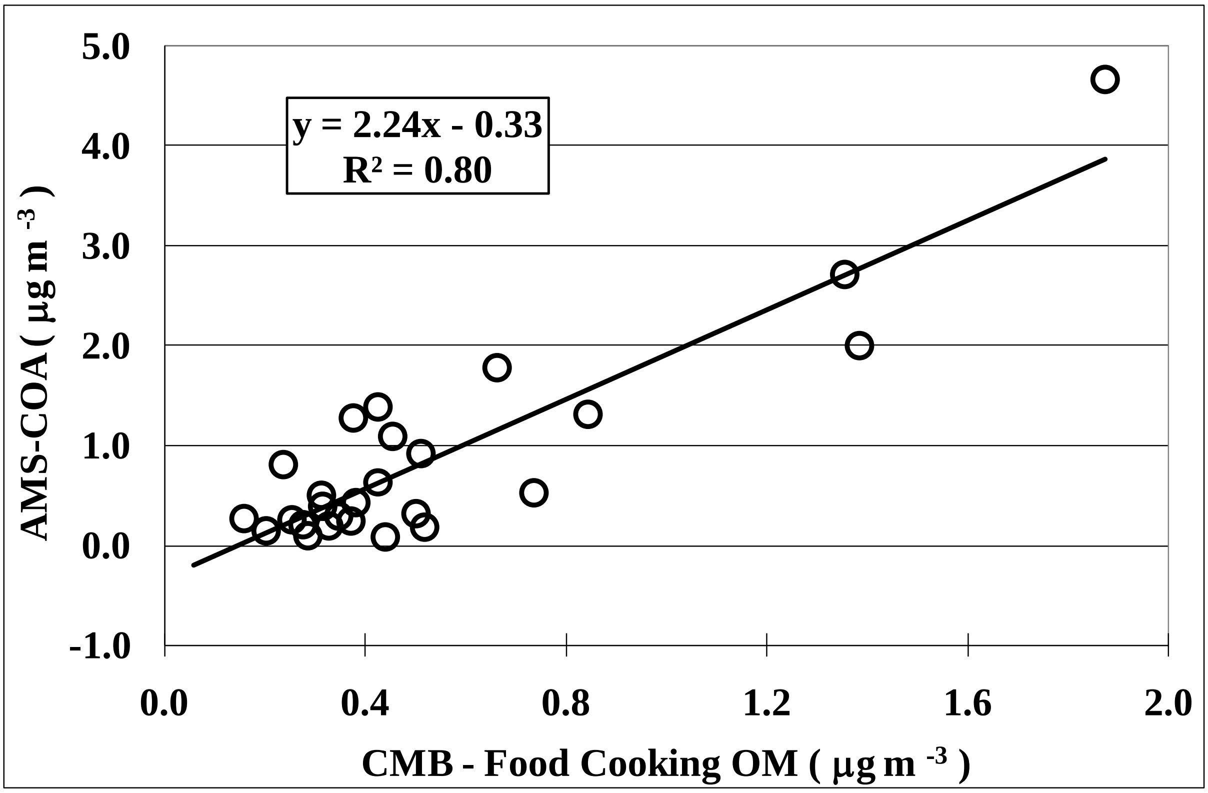
(a)


y = 2.81x - 0.69
R² = 0.75
AMS-SFOA (μg m -3)
CMB-WS OM (μg m -3)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0
0.5
1.0
1.5
2.0

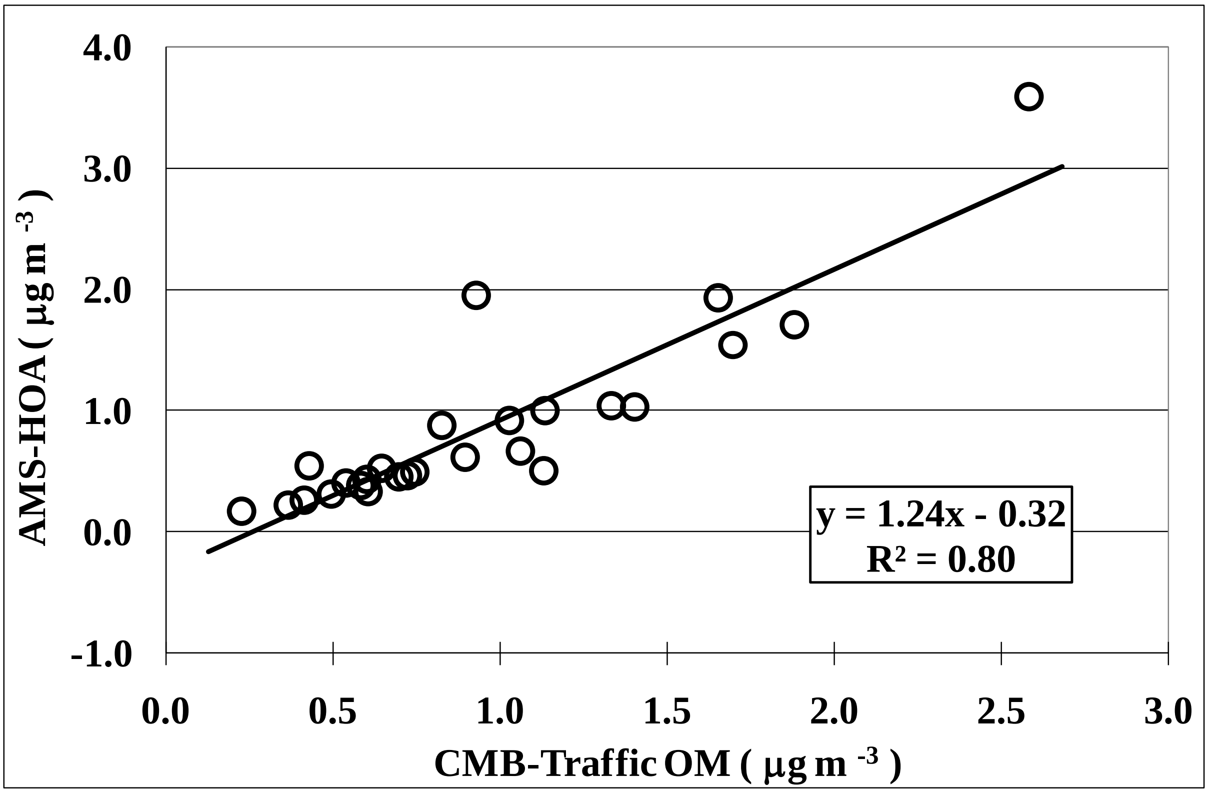
(b)


y = 2.40x - 0.64
R² = 0.78
AMS-SFOA (μg m -3)
CMB-(WS+Coal) OM (μg m -3)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0
0.5
1.0
1.5
2.0

(c)


y = 2.24x - 0.33
R² = 0.80
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
0.0
0.4
0.8
1.2
1.6
2.0
AMS-COA (μg m -3)
CMB - Food Cooking OM (μg m -3)

(d)


y = 1.24x - 0.32
R² = 0.80
4.0
3.0
2.0
1.0
0.0
-1.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
AMS-HOA (μg m -3)
CMB-Traffic OM (μg m -3)

(e)

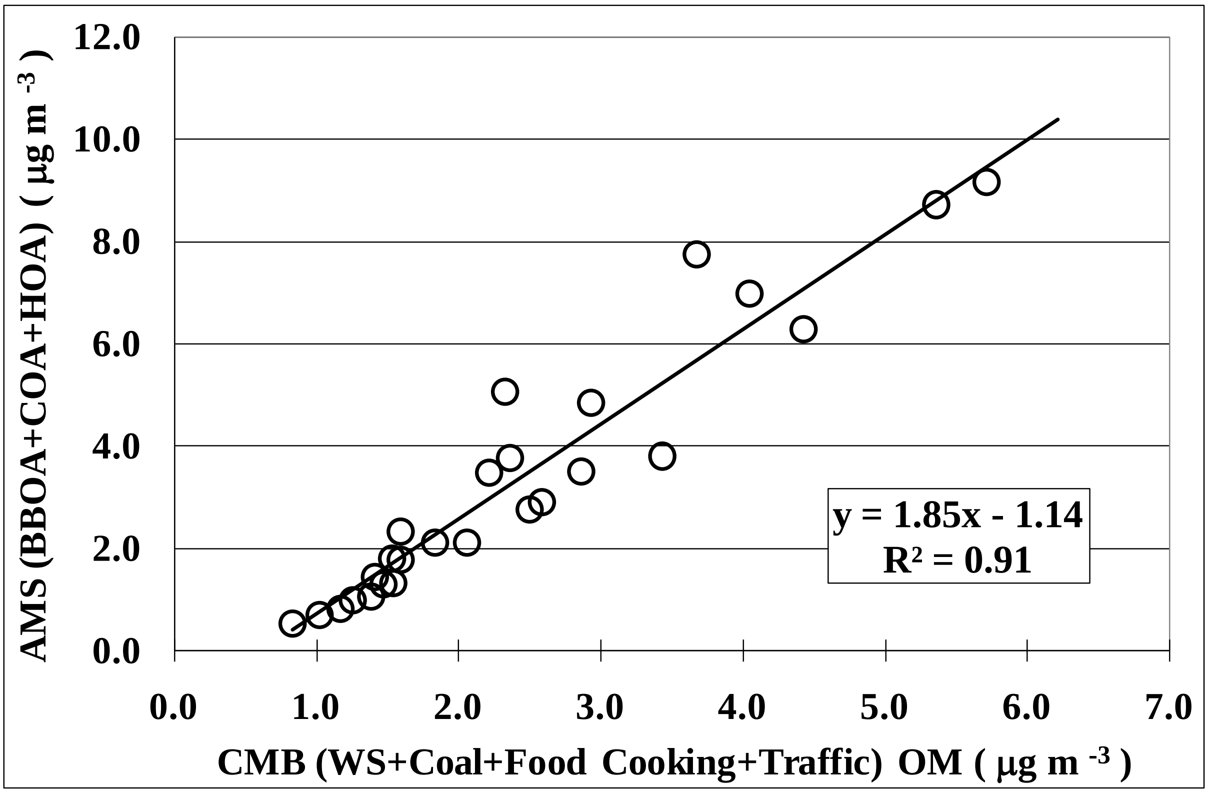


Figure 5: Primary component comparison between the AMS-PMF and CMB methods at NK

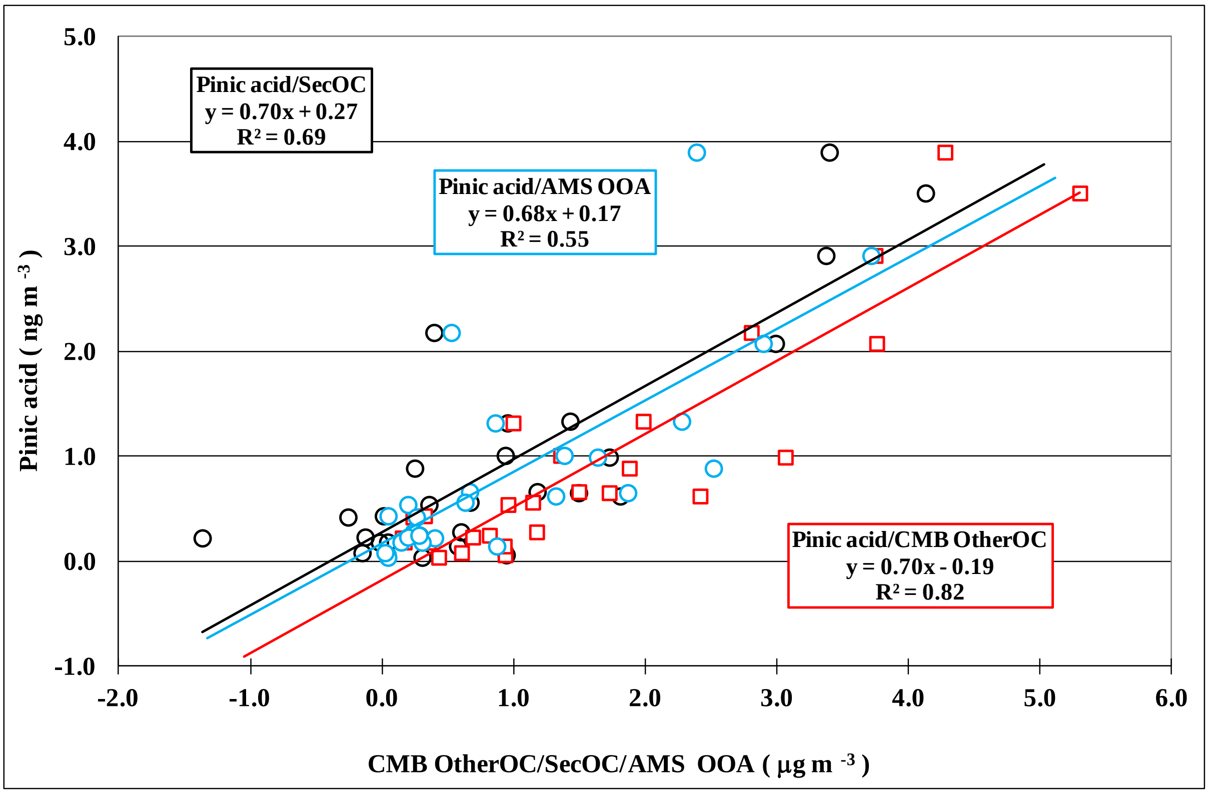


Figure 6: Secondary component comparison at NK showing relationships between pinic acid concentrations and estimated secondary OC from the elemental carbon tracer method (Sec-OC) and the CMB model (Other-OC), and with the AMS OOA factor