Sensitivity of a Chemical Mass Balance Model to Different Molecular Marker Traffic Source Profiles

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ABSTRACT

Use of the Chemical Mass Balance (CMB) model for aerosol source apportionment requires the input of source profiles of chemical constituents. Such profiles derived from studies in North America are relatively abundant, but are very scarce from European studies. In particular, there is a lack of data from European road vehicles. This study reports results from a comparison of road traffic source profiles derived from (1) US dynamometer studies of individual vehicles with (2) a traffic profile derived from measurements in a road tunnel in France and (3) new data derived from a twin-site study in London in which concentrations at an urban background site are subtracted from those measured at a busy roadside to derive a traffic increment profile. The dynamometer data are input as a diesel exhaust, gasoline exhaust and smoking engine profile, or alternatively as just a diesel exhaust and gasoline exhaust profile. Running the CMB model with the various traffic profiles together with profiles for other sources of organic carbon gives variable estimates of the contribution of traffic to organic carbon and to PM$_{2.5}$ concentrations. These are tested in two ways. Firstly, unassigned organic carbon in the output from the CMB model, assumed to be secondary organic carbon, is compared to secondary organic carbon estimated independently using the elemental carbon tracer method. Secondly, the estimated traffic contribution to organic carbon and PM$_{2.5}$ is compared with an estimate derived simply from the measured elemental carbon concentrations, and the effect on aerosol mass closure is investigated. In both cases the CMB model results correlate well with the independent measures, but there are marked differences according to the traffic source profile employed. As a general observation, it appears that the use of dynamometer data with inclusion of a smoking engine profile has a tendency to over-estimate traffic emissions at some sites whereas the tunnel profile shows a tendency to under-estimate. Overall, the traffic profile derived from the twin-site study gives probably the best overall estimate, but the quality of fit with independent estimates of secondary organic carbon and traffic particle mass depends upon the site and dataset for which the test is conducted.

Keywords: Receptor models; CMB; source profile; traffic emissions; particulate matter
1. INTRODUCTION

Road traffic is one of the key urban air pollution sources, and in the last few decades a significant amount of research has been undertaken in order to understand the emission characteristics as well as processes that govern vehicular emissions (Shi and Harrison, 1999; Charron and Harrison, 2003; Lough et al., 2007; Phuleria et al., 2007; El Haddad et al., 2009; Pant and Harrison, 2013). A good understanding of the relative contribution of traffic to ambient air pollutant concentrations, especially particulate matter (PM) is vital for policy action. Source apportionment techniques are used widely for quantitative estimation of the contribution of different sources to ambient PM concentrations and can be implemented in many different ways, receptor modelling being one of the methods. Watson and Chow (2007) describe receptor models as models that “interpret measurements of physical and chemical properties taken at different times and places to infer the possible or probable sources of excessive concentrations and to quantify the contributions from those sources” and this category of source apportionment techniques includes microscopic and chemical models (Pant and Harrison, 2012). With the assumption that the concentrations of chemical species are preserved between sources and receptors, receptor models use the principle of mass conservation for apportionment of PM mass to different air pollution sources. Thus, the concentration of a species measured in a sample of particulate matter can be described as (Hopke, 1991):

\[
X_{ij} = \sum_{p=1}^{P} g_{ip} f_{pj}
\]

where \(X_{ij}\) is the species concentration of \(i\) in the sample \(j\), \(g_{ip}\) is the fractional mass of species \(i\) in source \(p\) and \(f_{pj}\) is the mass contribution of source \(p\) to particulate matter in ambient air in sample \(j\).

There are several receptor models such as the Chemical Mass Balance (CMB) model, multivariate statistical models such as Principal Component Analysis (PCA) including factor analysis models such as Positive Matrix Factorization (PMF), Multilinear Engine (ME), and UNMIX) and hybrid...
models such as Constrained Physical Receptor Model (COPREM) (Watson et al., 2002; Viana et al., 2008). Different models use different approaches to solve equation 1, for e.g., the CMB model uses the effective-variance least squares method whereas UNMIX uses eigenvector analysis.

1.1 CMB Model

The CMB model uses the ambient measurement data for chemical species together with the associated uncertainty and source profiles for different sources as inputs, and the output consists of estimates of the contribution of each source to the total mass. The model has several assumptions including non-reactivity of the chemical species and non-co-linearity of the source profiles (Watson et al., 2002). In addition, the number of species should be greater than the number of sources in order to derive results from the model. This model has been used extensively for source apportionment of PM mass (Schauer et al., 1996; Bi et al., 2007; Sheesley et al., 2007; Chelani et al., 2008; Lambe et al., 2009; Stone et al., 2010; Yin et al., 2010; El Haddad et al., 2011; Hanedar et al., 2011; Rutter et al., 2011; Guo et al., 2012; Perrone et al., 2012). A large number of markers can be used for source apportionment including elemental carbon (EC), organic carbon (OC), trace metals and organic molecular markers. However, trace metals such as Fe, Cu, Zn and Ni are often emitted from several key sources, and in some cases, it is difficult to apportion PM mass to the sources based on the trace metals alone (Lin et al., 2010). In addition, with removal of species such as Br and Pb from fuels, such markers cannot be used conclusively for source apportionment analyses. With the idea that molecular marker compounds are emitted by specific sources and can be used to distinguish between PM sources, Schauer et al. (1996) proposed CMB modelling using organic molecular markers (hereafter referred to as CMB-MM). A number of source-specific organic molecular markers have since been proposed for use in CMB modelling. Key molecular markers include levoglucosan for wood burning, hopanes and steranes for vehicular emissions, higher n-alkanes for vegetative detritus, benzothiazoles for tyre wear and cholesterol and lactones for cooking (Rogge et al., 1993a,b; Schauer et al., 1996; Lough et al., 2007; Heo et al., 2013).
detailed description of various organic markers for different sources has been compiled by Lin et al. (2010).

1.2 Source Profiles

Selection of appropriate source profiles is one of the critical steps towards obtaining a good fit with the CMB model. Source profiles are defined as “the mass abundances, i.e. fraction of total mass of chemical species in source emissions, and such profiles are generally representative of source categories rather than individual emitters” (Watson et al., 2002). Such profiles are created using emission samples from a range of emitters of a particular source category and conducting physical and chemical analyses to arrive at the contributions of each tracer element/compound (Watson et al., 2002). Source profiles are used for identification and quantification of contributions of different sources to PM using the CMB model as well as to compare and validate results obtained from factor analysis models (e.g. PMF) and to a large extent the model relies on the accuracy of the source profiles used as an input. However, in the absence of locally relevant source profiles, the Source Contribution Estimates (SCE) can be prone to erroneous results. In recent years, significant differences have been observed between laboratory-tested and real world mixed source traffic emissions (Gertler et al., 2002; Yan et al., 2009; Ancelet et al., 2011). While the typical components of any source profiles are found to be more-or-less similar, the relative mass abundances vary based on location and emitter characteristics. As a result, different combinations of source profiles can provide statistically valid yet completely different solutions (Robinson et al., 2006a).

Traffic emission profiles can be generated using several different methods including lab-based dynamometer studies, tunnel studies and twin-site studies (Rogge et al., 1993a; Lough et al., 2007; He et al., 2008; El Haddad et al., 2009; Yan et al., 2009). Since the twin site/tunnel measurements are carried out in the ambient environment, and for a mixed fleet, they are seen to be more representative of real-world emissions. A number of papers have reported the estimation of the
contribution of traffic emissions to total PM or a component of PM using twin-site studies (Yan et al., 2009; Bukowiecki et al., 2010; Gietl et al., 2010; Oliveira et al., 2010; Pey et al., 2010). With the assumption that all sources other than traffic (including any local or regional sources) have the same impact at both roadside and a nearby background site, the increment at the roadside site obtained using the equation 2 is used as a local traffic increment estimate (Harrison, 2009; Yan et al., 2009; Wang et al., 2010).

\[
\text{Concentration of } X_{\text{traffic}} = \text{Concentration of } X_{\text{roadside}} - \text{Concentration of } X_{\text{background}} \quad (2)
\]

The aim of this paper is to assess the response of the CMB model to molecular marker profiles for traffic derived using different sampling approaches. Tests of the model are summarised in Figure 1. Traffic source contribution estimates (SCEs) of PM$_{2.5}$ OC as well as PM$_{2.5}$ mass generated from CMB using different traffic profiles were compared with the traffic estimates obtained using elemental carbon as a tracer (Pio et al., 2011). The estimated Secondary Organic Carbon (SOC) derived from CMB was compared to SOC calculated using the method proposed by Castro et al. (1999).

2. METHODS

2.1 Air Sample Collection and Analysis

PM$_{2.5}$ samples were collected in Birmingham in 2007-2008 and in London (United Kingdom) in the years 2010 (summer) and 2011 (winter) respectively. The urban background site in Birmingham was located in an open field within the University of Birmingham campus. The site is about 3.5 km southwest of the centre of Birmingham and the nearest anthropogenic sources are a nearby railway and some moderately trafficked roads. The rural site is located about 20 kilometres west of Birmingham at a distance of about 200 metres from the A451, a moderate to heavily-trafficked road. The site is surrounded by unused land/grass. The urban background site in London was located in a residential area in West London at a distance of 10 metres from the road. The site is
located 7 kilometres to the west of central London and is located in a cabin within a school campus
where equipment from the national Automatic Urban and Rural Network is also hosted. The
roadside site was located on the kerbside of a heavily trafficked (ca. 80,000 vehicles per day) six
lane highway (Marylebone Road) running through a street canyon in central London. The sampling
station is located at a distance of 1 metre from the road at height of 3 metres. The site is located
opposite the Madame Tussauds Museum and is surrounded by residential and commercial
buildings. Further site details for Birmingham and London are available in Yin et al. (2010) and
Gietl et al. (2010) respectively. PM$_{2.5}$ samples were collected on 150 mm quartz fibre filters using
Digitel high volume samplers (DHA-80) in summer and winter seasons for a period of 24 hours in
London. In Birmingham, 24 hour PM$_{2.5}$ samples were collected for the first 5 days of every month
on 20 cm x 25 cm quartz fibre filters using a Tisch TE-6070 high volume sampler. In addition, 24
hour PTFE filter samples (PM$_{10}$ and PM$_{2.5}$) were also collected at all sites using a collocated
dichotomous Partisol sampler. OC and EC were measured using the Sunset Laboratory Thermal-
Optical Carbon Analyser, molecular markers including hopanes, straight-chain alkanes, PAHs and
levoglucosan were measured using GC-MS (Agilent GC-6890N plus MSD5973N) and Al and Si
were measured using WD-XRF (Philips® MAGIX-PRO automatic sequential wavelength dispersive
X-ray Fluorescence spectrometer). Ions (SO$_4^{2-}$, NO$_3^-$, Cl$^-$) were measured using ion chromatography
(Dionex ICS-2000). The detailed sampling and chemical analysis methodology is presented in Yin
et al. (2010) and Harrison and Yin (2010). Only PM$_{2.5}$ samples were used for this study.

2.2 CMB Model

The CMB 8.2 model from USEPA was used for the estimation of source contribution to PM$_{2.5}$-OC.
Six key sources were included in the model runs including vegetative detritus (Rogge et al., 1993b),
wood smoke (Fine et al., 2004; Sheesley et al., 2007), natural gas (Rogge et al., 1993c), coal
combustion (Zhang et al., 2008), road dust (Chow et al., 2003) and traffic. Species used in the data
analysis include elements (Al, Si), n-alkanes (C25-C35), hopanes (trisnorhopane, hopanes,

Winter samples from the roadside and urban background sites in London were used for preparation of the source profile while the samples from the Birmingham sites (n= 28 for each site) and the summer samples from the urban background site (n= 30) in London were used for the CMB analysis.

Model outputs were evaluated using several different parameters. As a first step, goodness-of-fit parameters, $r^2$ and chi$^2$ values were checked and a chi-square value less than 4 and $r^2$ value between 0.8-1.0 were considered acceptable. T-stat values (ratio of the source contribution estimate and standard error) were used to determine the significance of a particular source and a value less than 2 indicates that the source is at or below detection limit. Other parameters included the species’ C/M ratio (i.e. ratio between calculated and measured concentration) and R/U ratio (i.e. ratio of signed difference between calculated and measured concentration, i.e. residual divided by standard error, i.e. uncertainty) with acceptable values ranging between 0.75-1.5 and -2 to +2 respectively. Species that did not fit within the range were removed from subsequent runs but a base number of species were always included to ensure that the number of species is more than the number of sources. The MPIN (modified pseudo inverse normalized) matrix was used as a diagnostic tool to identify the influential species for each source type with influential species showing values between 0.5 to 1 (Chow et al., 2007).

2.3 Source Profiles
Profile derived from twin-site data

To prepare a dimensionless profile for PM requires calculation of the ratio of each of the species with respect to PM concentration for the same location (Landis et al., 2007). In this study, a similar approach was used, and since we are assuming the difference between the roadside and background site to be the traffic increment (as in equation 2), the formula has been modified accordingly (equation 3).

\[
Source \ profile \ value(X) = \frac{X_{\text{roadside}} - X_{\text{background}}}{OC_{\text{roadside}} - OC_{\text{background}}}
\]  

Table 1 presents the source profile that was prepared using this approach derived from measurements at the heavily-trafficked Marylebone street canyon site (Galatioto and Bell, 2013) and the typical urban background site of North Kensington (Bigi and Harrison, 2010). The species mean value represents the species source profile value and standard deviation refers to the profile uncertainty. Daily winter campaign samples (n = 26) were averaged to obtain the profile and the average standard error was used as source profile uncertainty. A similar approach has been reported by Yan et al. (2009) for preparation of a traffic profile for Georgia, USA. The traffic mix on Marylebone Road is broadly representative of UK traffic (see Table S1 in Supplementary Information). It is important to note that this profile was generated based on a select group of organic markers, and the unique site characteristics at the roadside site (Marylebone Road) in London might have introduced some bias in the results.

Uncertainty for the various organic species in the profile was observed to be much higher compared to other published real-world and lab-based profiles. Similar observations of high uncertainties in ambient data have been reported by Yan et al. (2009) and Peltier et al. (2011) and may reflect in part, different traffic mixes on different days as well as higher uncertainties associated with ambient sampling.

Tunnel profile
This was derived from measurements in a road tunnel in France reported by El Haddad et al. (2009). The profile (Table 1) was prepared by normalizing the species concentration in PM$_{2.5}$ against OC concentration in PM$_{2.5}$ to get concentration in terms of species/µg of organic carbon.

Dynamometer profiles

Separate source profiles for gasoline, diesel and smoking engines were taken from the work of Lough et al. (2007) derived from measurements of emission from US vehicles made using dynamometers.

3. RESULTS AND DISCUSSION

3.1 Comparison of Source Profile with other Published Profiles

Concentrations of most of the organic markers are broadly similar across the ambient data profiles with the exception of PAHs for which the tunnel profile from France reported lower PAH concentrations than roadside profiles from the UK and USA (Figure 2). This may be related to the very high uptake of diesels in France. However, the freeway measurement of Phuleria et al. (2007) appear to suggest higher emissions from diesel vehicles. The dynamometer gasoline profile was observed to be very similar to the profiles derived from ambient data.

Ambient concentration data for hopanes from London and Birmingham were compared with a wide range of traffic profiles using ratio-ratio plots. Such plots are defined as ‘scatter plots of ratios constructed with data from three species, i.e. two species (which are the target species) whose values are normalized using the third reference species’ (Robinson et al., 2006a). While the aggregation of the ambient data around a point signifies that CMB can produce a good result with a single source profile, distribution of data along a diagonal line indicates the need for at least two distinct profiles for good results. Plotting the source profiles with ratio-ratio plots using specific markers can be useful for determination of the most relevant source profiles and such plots have
been used previously for comparison of ambient data with source profiles (Subramanian et al., 2006; Dutton et al., 2009; Gao et al., 2011).

Ambient data for hopanes and EC from London and Birmingham were plotted together with source profiles derived from laboratory dynamometer studies, as well as real-world mixed traffic emissions collected from the literature (Schauer et al., 1999; Watson et al., 1998; Schauer et al., 2002; Lough et al., 2007; El Haddad et al., 2009; Yan et al., 2009) in Figure 3. The composite traffic profile was found to be significantly different from lab-generated source profiles for both the background and roadside sites, while the comparison with other ambient traffic profiles revealed a similarity between ambient measurement data and ambient profiles, although the uncertainty (expressed as standard deviation of daily data) is typically much higher for ambient profiles (Figure 3). The differences between the profiles were smaller in the case of homohopanes and bishomohopanes. Differences among the various profiles can be attributed to changes in vehicle technology over time and the dynamic fleet mix. Significant differences in the source profiles have been reported for different vehicle categories (Kim Oanh et al., 2010). Use of different sampling and analytical protocols may also have an influence.

The ambient air data in the case of hopane-EC plots generally fit to a straight line, suggesting a variable mixture of two sources, presumably reflecting gasoline and diesel vehicles. However the huge difference in concentrations between the ambient air data and the majority of the dynamometer profiles is unexplained. The diesel dynamometer profiles generally appear to be to the left of the gasoline profiles, but lie in a totally different region of the plot to the ambient air data. This may relate to the rapidly evolving technology of diesel vehicles, and the different vehicle types studied. In particular, the reductions in smoke emissions, and hence EC, from diesels will have led to increased hopane/EC ratios in newer vehicles.

3.2 CMB Sensitivity Analysis
3.2.1 Estimation of traffic particle mass and mass closure

Chemical profiles measured in London (2010 summer data) and Birmingham (2007 data) were analysed using the CMB model to calculate source contributions to PM$_{2.5}$ OC with the aim of comparing the sensitivity of the model to different types of traffic profiles. Three different traffic profiles were tested, i.e. dynamometer profiles for diesel, gasoline and smoking engines (hereafter referred to as DYN) (Lough et al., 2007), a twin-site London profile (hereafter referred to as TWIN) and a France tunnel profile (hereafter referred to as TUN) (El Haddad et al., 2009). The smoking engine profile used in the analysis includes off-road engines and Lough and Schauer (2007) reported smoker profiles to impact the estimation of source contribution from gasoline, diesel and smoker vehicles. In order to understand the contribution from the smoking engine profile, two analyses were conducted for the DYN profile: gasoline and diesel engine only (DYN-GD) and gasoline, diesel and smoking engines (DYN-A). For comparison, the average data from each of the sites was also run with a traffic profile consisting of 80% of the concentrations of the chemical species measured at the roadside site in London (hereafter referred to as R80). For coal combustion, wood combustion and road dust, a number of source profiles were tested initially to choose the best profile for the ambient measurement data and the selected profiles were then used together with different traffic profiles to obtain final results. A number of different source profiles were run and the statistical outputs such as standard error and the ratio between calculated/measured values were assessed for each profile.

Based on equation 4, “Other OC” was calculated which is the OC unaccounted for by primary sources, and taken to represent secondary OC (SOC) (Yin et al., 2010).

\[
\text{Other OC} = \text{Measured OC} - \sum \text{SCFs (primary sources)}
\]  

Several other authors have also used the same approach and have also assumed the “Other OC” to be SOC (Subramanian et al., 2007; Docherty et al., 2008; Stone et al., 2009). Source contributions
to PM$_{2.5}$ mass were then calculated using ratios of PM$_{2.5}$ mass/PM$_{2.5}$ OC for each source applied to the PM$_{2.5}$-OC SCEs obtained using CMB modelling as detailed in Yin et al. (2010). These were added to estimates of contributions from other sources (marine aerosol, sulphates, nitrates) using factors from the Pragmatic Mass Closure Model (Harrison et al., 2003) to test overall PM$_{2.5}$ mass closure.

In the CMB model, $r^2$ and $\chi^2$ values were observed to be between 0.96-1.00 and 0.02- 2.70 respectively. Only the species with C/M ratio (ratio between calculated and measured concentration) between 0.75-1.5 and R/U ratio (ratio of signed difference between calculated and measured concentration, i.e. residual divided by standard error, i.e. uncertainty) between -2- +2 were used for the model runs. In addition, any profiles with a negative source contribution or a $t_{\text{stat}}$ <1 were removed from subsequent runs and markers for the different sources were monitored using the MPIN matrix available in the CMB model runs and were cross-validated with published marker data (Table S2, Supplementary Information).

In the case of the daily data, although overall correspondence was observed between CMB runs using DYN and TWIN and TUN in terms of identification of sources and OC mass attribution, there were variations in certain cases with higher or lower attribution of a source. In some cases, however, while for one model, a source was deemed insignificant (t-stat value < 2), the other models showed it as a significant source. It is important to note that a $t_{\text{stat}}$ value >2 indicates 95% or more confidence in the estimates.

Results for apportionment of OC appear in Figure 4. Across all scenarios, the total traffic contribution to OC varied as DYN-A > TWIN > DYN-GD > TUN. The DYN-A profile attributed more OC to vehicles (including off-road engines) than the DYN-GD, TWIN and TUN profile. However, at both the urban background and rural sites in Birmingham, the results were comparable.
between DYN-A and TWIN profiles and DYN-GD and TUN profiles. Interestingly, while the TWIN profile used benzo(ghi)perylene as the key marker for traffic, the TUN profile used EC as the key marker. In the case of DYN profiles, EC, hopanes and benzo(ghi)perylene were observed to be the key markers for diesel, smoking and gasoline engines respectively. In the case of the London data, the DYN-A scenario causes the primary sources in the model to account for > 100% of OC without any SOC, which is clearly implausible. In the Birmingham data, the choice of profile does not impact greatly on the outcome. The R80 profile produced very similar results to the TWIN profile (Table 2; Figure 4). The traffic SCEs using TUN and DYN-A and DYN-GD were also compared against the traffic SCE using TWIN profile, and while good correlation was observed for urban background sites ($r^2 > 0.75$), the correlation was much weaker in case of the rural site ($r^2 \sim 0.25-0.35$).

When mass closure of PM$_{2.5}$ is attempted including other major sources using the coefficients reported by Harrison et al. (2003), closure is generally good, especially for the Birmingham data (Figure 5). The DYN-A attributes a larger PM$_{2.5}$ mass to road traffic than the other profiles, especially in the London data. Predictably, as for OC results, the total PM$_{2.5}$ mass apportioned to traffic varied as DYN-A > TWIN > DYN-GD > TUN. Overall mass closure is good for both urban and rural sites and winter and summer seasons (Table 2). Results for the R80 profile are not discussed for PM$_{2.5}$ since very similar SCEs were observed for this profile compared to the TWIN profile.

The CMB/Pragmatic Mass Closure Model resolved the PM mass reasonably well with all profiles with 89.8-129.7% of PM$_{2.5}$ mass resolved across all data sets (Table 2, Figures 4 and 5) and the DYN-GD profile models the highest percentage mass across all sites. In general, all the CMB models (based on dynamometer profiles and the composite profiles) were able to apportion approximately similar OC mass, although dynamometer-based profiles apportioned a higher
percentage of OC mass to traffic. Subramanian et al. (2007) postulated that over-apportionment of OC mass can occur either due to missing primary sources or due to sampling artifacts. Between the three profiles, the lowest total OC mass was attributed by the TUN profile runs across all sites. In terms of resolution of the traffic source, CMB runs with dynamometer and composite profiles showed some differences. If only gasoline and diesel sources are considered (i.e. using DYN-GD), the TWIN profile had the maximum mass apportioned to the traffic source and the TUN profile had the minimum mass apportioned to traffic. However, with the inclusion of the smoking engine profile in DYN set of profiles, DYN-A apportioned the highest mass to the traffic source. Further, the \( t_{\text{stat}} \) values for the DYN-A (\( t_{\text{stat}} > 5 \) across all cases for diesel and smoking engine profiles) and TUN (\( t_{\text{stat}} > 6 \) across all cases) profiles were consistently higher than the TWIN model (\( t_{\text{stat}} \) between 2-3 in most cases). The lowest standard error was recorded for the DYN profiles (A & GD) which correlates with the lower uncertainties associated with these profiles. Higher uncertainties in the case of TWIN and TUN profiles can be attributed to the errors associated with ambient measurements. Between the TWIN and TUN profiles, the standard error was lower in the case of the TUN profile. In some cases, the \( t_{\text{stat}} \) for the traffic and gasoline had a value of less than 2 in the case of TWIN and DYN (A & GD) profiles respectively rendering the traffic source insignificant. No runs had \( t_{\text{stat}} < 2 \) for traffic in the case of the TUN profile. The R80 profile, run as a test yielded results very similar to the TWIN profile (Table 2; Figure 4).

The MPIN matrix data for runs was also analysed to assess and cross-compare the influential species (defined as species with a value >0.7 in the matrix) for the different traffic profiles. While in the case of DYN profiles (A & GD), the same markers (EC for diesel engine, hopanes for smoking engine and benzo(ghi)perylene for gasoline engine, value = 1 across all runs) were consistently found to be influential across all runs, different species were recorded as influential in the case of the TWIN and TUN profiles. Overall, the TWIN profile showed a value of 1 for benzo(ghi)perylene across the runs and the TUN profile showed a value of 1 for EC. In both cases, the other key sets of
markers, i.e. EC and hopanes were found to be influential across most runs. Similar results were reported by Chow et al. (2007). There were cases, however, where EC and/or trisnorhopane were over- or underestimated, and in those cases, the key marker varied. Benzo(ghi)perylene and hopane were estimated correctly in most cases. For the TUN profile, n-alkanes (A25 and 26) were also recorded as influential species in some cases. Interestingly, in the case of TUN profile runs, interference between the vegetative detritus and traffic profile was observed, and in many runs, the vegetative detritus SCE was insignificant or zero although positive SCEs were recorded using TWIN and DYN (A & GD) profiles. In a CMB sensitivity study, Sheesley et al. (2007) observed the biomass profile to impact the contribution estimate for traffic. Test runs were then conducted with the TUN profile excluding the n-alkane data, but the SCEs for traffic were found to be more or less similar to the original runs. The Other OC mass and the total mass apportioned, however, changed slightly as a result of positive SCEs for vegetative detritus. Lower percentages of mass were apportioned to traffic during the summer season by the model with both types of profile. Similar observations have been reported for the USA (Subramanian et al., 2007; Bullock et al., 2008) and Europe (El Haddad et al., 2011) where SOC has been reported to be higher in the summer season due to increased photochemical activity. Also, a higher percentage of SOC was estimated for the rural site compared to the urban background sites, which is also reflected in the higher OC/EC ratio for the rural site.

### 3.3.2 Comparison of CMB traffic estimates with an estimate based upon EC

Assuming road traffic to be the dominant source of EC, traffic emission estimates were obtained for PM$_{2.5}$-OC and PM$_{2.5}$ mass using EC*0.35 and EC*1.35 respectively based on Pio et al. (2011). The traffic SCE outputs for PM$_{2.5}$-OC and PM$_{2.5}$ from the CMB model with different traffic profiles were compared against the EC traffic emission estimates (Table 3). The most similar estimates for primary vehicular emissions were observed for DYN-GD with the estimates being highly correlated ($r^2 > 0.85$) with the traffic estimates obtained using EC for the Birmingham sites. For DYN-A, the
dynamometer profiles produced a much higher estimate for the traffic contribution and this was due
to a high SCE for the smoking engine profile. However, not all of that SCE is necessarily derived
from road traffic as the source profile for the smoking engine includes off-road vehicles which are a
significant contributor to PM$_{2.5}$ in the UK (AQEG, 2012). Poor correlation was observed for all the
profiles at the rural Birmingham site with correlation coefficients ranging between 0.26-0.41. The
estimates obtained using the TWIN profiles showed similar correlation with the EC estimate
compared to the estimates from the TUN profile.

3.2.3  Comparison of estimates of SOC

Organic carbon can be present in the atmosphere as primary organic carbon (POC) (directly
emitted) or SOC (formed by atmospheric chemistry). Generation of SOC source profiles is rendered
difficult due to the complex chemistry of secondary organic aerosol formation (Bullock et al., 2008)
and diversity of composition. As a result, while the CMB model works well for attribution of POC
sources such as biomass combustion and traffic, it is not able to apportion SOC due to lack of
availability of appropriate source profiles (Stone et al., 2009; Guo et al., 2012; Schauer and Sioutas,
2012). Consequently, as in Yin et al. (2010), the CMB model was run to account for known
primary sources of OC, and the difference between the sum of POC and measured total OC was
attributed to SOC.

EC is released directly into the atmosphere and can be used to estimate relative amounts of primary
and secondary OC. One of the simplest approaches involves use of the ratio between OC and EC.
Higher OC/EC ratios are expected in the conditions where SOC is dominant and the highest OC/EC
ratios are reported in rural and remote sites (Pio et al., 2011). The EC-tracer method involves the
use of EC as a tracer for POC, allowing SOC to be calculated (Turpin and Huntzicker, 1995; Castro
et al., 1999; Lee and Russell, 2007; Sheesley et al., 2007; Pio et al., 2011). Minimum ratios of
OC/EC are taken as representative of primary OC (although they may be an over-estimate (Pio et
al., 2011)) and OC above that ratio is taken to be SOC. The method as outlined by Castro et al. (1999) was used (equation 5) and estimates of daily SOC were made for each of the sites.

\[
\text{Secondary OC} = \text{Total OC} - (\text{EC} \times \frac{\text{OC/EC}}{\min})
\]

The quality of fit between the estimates of SOC from the CMB model and the EC tracer method was evaluated by regression analysis (Table 4). Given that the EC tracer method is liable to underestimate SOC (Pio et al., 2011), an excess of “Other OC” over SOC might be expected, but in most cases the “Other OC” is similar to, or less than the SOC. In the Birmingham (urban background), London (urban background-summer) and Birmingham (rural) datasets, the three estimates are in broad agreement.

4. CONCLUSIONS

It is evident from Figure 2 that traffic profiles of molecular markers measured in the field show generally broad agreement. However, as Figure 3 shows, where plotted as normalised abundance (marker/EC), the field data can differ by orders of magnitude from dynamometer data, and the variation between dynamometer studies is typically greater than that between field measurements. Perhaps surprisingly, both, however, give broadly similar estimates of traffic PM$_{2.5}$ mass. Those from the composite profile (TWIN) are probably better, as judged from the estimates from the EC tracer method, and the mass closures. Correlations of the traffic estimates using the TWIN profile against those obtained using EC were broadly similar to those obtained using the DYN (A & GD) profiles. The estimates from TUN profile, however, were much more weakly correlated, particularly at the rural site. This could be due to the interference between the traffic and vegetative detritus sources for TUN model runs as explained in the previous section. It is possible that other tunnel profiles more representative of the UK might perform better. It was also observed that selection of species for inclusion in the profile can determine the overall modelling output, both for estimation of the traffic source and the overall model output.
Based on the current analysis, it can be concluded that both the dynamometer and composite (twin-site) profiles can provide reasonable estimates of the traffic contribution. In cases where dynamometer profiles are not available, composite profiles can be used to estimate traffic contribution to OC or PM mass. However, it is important to bear in mind that the high uncertainty associated with the composite traffic profile can impact upon CMB model output since the model takes into account both the profile uncertainty and the ambient data uncertainty. Further, traffic source profiles based on ambient data can cause mis-apportionment of other sources since similar compounds are often reported from different sources, for e.g. PAHs from different combustion sources. Thus, it is important to select species for the profile in such a way that interference with other sources would be minimal. Another consideration for the use of ambient data for preparation of source profiles is the impact of oxidation of marker species in the atmosphere (Robinson et al., 2006b). This can also impact the model output as it is assumed that the species are chemically stable.

**ACKNOWLEDGEMENTS**

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REFERENCES


Environmental Science and Technology, 42, 5068-5073.
TABLE LEGENDS

Table 1: Source composition profile for traffic based on twin sites from London (this study), tunnel site from France (El Haddad et al., 2009) and 80% of concentration data from the roadside site in London (this study) (all values in µg/µg of OC)

Table 2: Traffic mass estimate (µg/m³) and total percentage (%) explained using different traffic profiles for (a) OC and (b) PM₂.₅

Table 3: Comparison of the traffic estimates from the CMB model with the traffic estimate obtained using EC

Table 4: Comparison of the other OC estimate from the CMB model with the SOC estimate obtained using EC tracer method

FIGURE LEGENDS

Figure 1: Assessment of model performance using different metrics.

Figure 2: Comparison of London profile with other traffic and dynamometer profiles (TWIN-Our profile; TUN-El Haddad et al. (2009); TWIN US-S&W-Yan et al., 2009; DYN-D, G&S-Lough et al., 2007).

Figure 3: Comparison of source profiles derived from ambient air measurements and dynamometer studies using ratio-ratio plots.

Figure 4: Source contribution estimates for organic carbon at different sites.

Figure 5: Source attribution of PM₂.₅ mass based on CMB results.
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<table>
<thead>
<tr>
<th>Compound</th>
<th>TWIN (mean ± s.d.)</th>
<th>TUN (mean ± s.d.)</th>
<th>R80 (mean ± s.d.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>1.600±1.440</td>
<td>2.72±0.49</td>
<td>1.620±1.440</td>
</tr>
<tr>
<td>Trisnorhopane</td>
<td>0.0005±0.00004</td>
<td>0.00010±0.00001</td>
<td>0.00007±0.00004</td>
</tr>
<tr>
<td>Norhopane</td>
<td>0.000200±0.00017</td>
<td>0.00036±0.0005</td>
<td></td>
</tr>
<tr>
<td>Hopane</td>
<td>0.00014±0.00012</td>
<td>0.00027±0.0005</td>
<td>0.00016±0.00010</td>
</tr>
<tr>
<td>(S+R) Homohopanes</td>
<td>0.00020±0.00018</td>
<td>0.00028±0.00004</td>
<td>0.00026±0.00015</td>
</tr>
<tr>
<td>(S+R) Bishomohopanes</td>
<td>0.00030±0.00025</td>
<td>0.00010±0.00002</td>
<td>0.00036±0.00021</td>
</tr>
<tr>
<td>(S+R) Trishomohopanes</td>
<td>0.00028±0.00022</td>
<td>0.00008±0.00002</td>
<td>0.00029±0.00018</td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>0.000080±0.000055</td>
<td>0.000003±0.000002</td>
<td>0.00011±0.00006</td>
</tr>
</tbody>
</table>
Table 2: Traffic mass estimate (µg/m³) and total percentage (%) explained using different traffic profiles for (a) OC and (b) PM$_{2.5}$

(a) OC

<table>
<thead>
<tr>
<th>Site (season)</th>
<th>OC mass apportioned to traffic</th>
<th>Total % OC mass apportioned</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DYN-A</td>
<td>DYN-GD</td>
</tr>
<tr>
<td>Urban background site, London (Summer)</td>
<td>1.87</td>
<td>0.73</td>
</tr>
<tr>
<td>Urban background site, Birmingham</td>
<td>1.63</td>
<td>0.80</td>
</tr>
<tr>
<td>Urban background site, Birmingham (Summer)</td>
<td>1.43</td>
<td>0.69</td>
</tr>
<tr>
<td>Urban background site, Birmingham (Winter)</td>
<td>1.91</td>
<td>0.89</td>
</tr>
<tr>
<td>Rural site, Birmingham</td>
<td>1.33</td>
<td>0.55</td>
</tr>
<tr>
<td>Rural site, Birmingham (Summer)</td>
<td>1.34</td>
<td>0.44</td>
</tr>
<tr>
<td>Rural site, Birmingham (Winter)</td>
<td>1.26</td>
<td>0.66</td>
</tr>
</tbody>
</table>

(b) PM$_{2.5}$

<table>
<thead>
<tr>
<th>Site (season)</th>
<th>PM$_{2.5}$ mass apportioned to traffic</th>
<th>Total % PM$_{2.5}$ mass apportioned</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DYN-A</td>
<td>DYN-GD</td>
</tr>
<tr>
<td>Urban background site, London (Summer)</td>
<td>2.98</td>
<td>1.61</td>
</tr>
<tr>
<td>Urban background site, Birmingham</td>
<td>2.61</td>
<td>1.61</td>
</tr>
<tr>
<td>Urban background site, Birmingham (Summer)</td>
<td>2.39</td>
<td>1.50</td>
</tr>
<tr>
<td>Urban background site, Birmingham (Winter)</td>
<td>2.93</td>
<td>1.70</td>
</tr>
<tr>
<td>Rural site, Birmingham</td>
<td>2.06</td>
<td>1.13</td>
</tr>
<tr>
<td>Rural site, Birmingham (Summer)</td>
<td>1.97</td>
<td>0.89</td>
</tr>
<tr>
<td>Rural site, Birmingham (Winter)</td>
<td>2.07</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Table 3: Comparison of the traffic estimates from the CMB model with the traffic estimate obtained using EC

<table>
<thead>
<tr>
<th>Site (season)</th>
<th>OC</th>
<th>PM$_{2.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r$^2$</td>
<td>r$^2$</td>
</tr>
<tr>
<td>Urban background, London (Summer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DYN-GD</td>
<td>0.99</td>
<td>1.00</td>
</tr>
<tr>
<td>DYN-A</td>
<td>0.94</td>
<td>0.98</td>
</tr>
<tr>
<td>TWIN</td>
<td>0.71</td>
<td>0.71</td>
</tr>
<tr>
<td>TUN</td>
<td>0.84</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>y = 1.28x + 0.01</td>
<td>y = 0.75x + 0.01</td>
</tr>
<tr>
<td></td>
<td>y = 1.45x + 1.04</td>
<td>y = 0.80x + 1.24</td>
</tr>
<tr>
<td></td>
<td>y = 1.55x + 0.37</td>
<td>y = 0.66x + 0.60</td>
</tr>
<tr>
<td></td>
<td>y = 0.61x + 0.29</td>
<td>y = 0.26x + 0.48</td>
</tr>
<tr>
<td>Urban background, Birmingham (Summer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DYN-GD</td>
<td>0.87</td>
<td>0.95</td>
</tr>
<tr>
<td>DYN-A</td>
<td>0.78</td>
<td>0.89</td>
</tr>
<tr>
<td>TWIN</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>TUN</td>
<td>0.73</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>y = 1.31x + 0.00</td>
<td>y = 0.76x - 0.03</td>
</tr>
<tr>
<td></td>
<td>y = 2.37x + 0.33</td>
<td>y = 1.09x + 0.37</td>
</tr>
<tr>
<td></td>
<td>y = 1.93x + 0.14</td>
<td>y = 0.83x + 0.23</td>
</tr>
<tr>
<td></td>
<td>y = 0.79x + 0.14</td>
<td>y = 0.34x + 0.23</td>
</tr>
<tr>
<td>Rural, Birmingham (Summer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DYN-GD</td>
<td>0.97</td>
<td>0.92</td>
</tr>
<tr>
<td>DYN-A</td>
<td>0.41</td>
<td>0.61</td>
</tr>
<tr>
<td>TWIN</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>TUN</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>y = 1.21x - 0.00</td>
<td>y = 0.73x - 0.10</td>
</tr>
<tr>
<td></td>
<td>y = 1.12x + 0.88</td>
<td>y = 0.71x + 0.91</td>
</tr>
<tr>
<td></td>
<td>y = 1.00x + 0.55</td>
<td>y = 0.43x + 0.91</td>
</tr>
<tr>
<td></td>
<td>y = 0.32x + 0.37</td>
<td>y = 0.14x + 0.62</td>
</tr>
</tbody>
</table>

Note: $y =$ CMB model estimate; $x =$ estimate derived from EC concentration

Table 4: Comparison of the Other OC estimate from the CMB model with the SOC estimate obtained using EC tracer method

<table>
<thead>
<tr>
<th>Site (season)</th>
<th>r$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban background, London (Summer)</td>
<td></td>
</tr>
<tr>
<td>DYN-A</td>
<td>0.81</td>
</tr>
<tr>
<td>TWIN</td>
<td>0.70</td>
</tr>
<tr>
<td>TUN</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>y = 0.92x - 0.69</td>
</tr>
<tr>
<td></td>
<td>y = 0.83x + 0.07</td>
</tr>
<tr>
<td></td>
<td>y = 0.80x + 0.74</td>
</tr>
<tr>
<td>Urban background, Birmingham (Summer)</td>
<td></td>
</tr>
<tr>
<td>DYN-A</td>
<td>0.92</td>
</tr>
<tr>
<td>TWIN</td>
<td>0.91</td>
</tr>
<tr>
<td>TUN</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>y = 0.86x - 0.52</td>
</tr>
<tr>
<td></td>
<td>y = 0.86x - 0.10</td>
</tr>
<tr>
<td></td>
<td>y = 0.90x + 0.49</td>
</tr>
<tr>
<td>Rural, Birmingham (Summer)</td>
<td></td>
</tr>
<tr>
<td>DYN-A</td>
<td>0.76</td>
</tr>
<tr>
<td>TWIN</td>
<td>0.69</td>
</tr>
<tr>
<td>TUN</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>y = 0.79x - 1.22</td>
</tr>
<tr>
<td></td>
<td>y = 0.73x - 0.71</td>
</tr>
<tr>
<td></td>
<td>y = 0.88x - 0.67</td>
</tr>
</tbody>
</table>

Note: $y =$ CMB model estimate; $x =$ estimate from EC tracer method
Figure 1: Assessment of model performance using different metrics
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(a) Hopane-EC ratio-ratio plot

(b) Hopane-hopane ratio-ratio plot
Figure 3: Comparison of source profiles derived from ambient air measurements and dynamometer studies using ratio-ratio plots

- o ambient data from current study; □ other ambient profiles; ♦ gasoline profile from dynamometer; ∆ diesel profile from dynamometer; + smoking engine profile from dynamometer
Measured OC (µg/m³)

Source Contributions to OC (µg/m³)

- Vegetative Detritus
- Wood Smoke
- Natural Gas
- Coal Combustion
- Road Dust
- Diesel
- Gasoline
- Smoking Engine
- Traffic: Mixed

(a) London
(b) Birmingham

1. Urban background

2. Rural
Figure 4: Source contribution estimates for organic carbon at different sites

(a) London
Source contributions to PM$_{2.5}$ (µg/m$^3$)

Vegetative Detritus  Wood Smoke  Natural Gas  Coal Combustion  Road Dust  Diesel  Gasoline
Smoking Engine  Traffic- Mixed  Sea Salt  Ammonium Sulphate  Ammonium Nitrate  SOC  Measured PM$_{2.5}$
(b) Birmingham

1. Urban background

![Graph showing PM2.5 contributions and measured PM2.5 concentrations across different sources and seasons.](image)

Legend:
- Vegetative Detritus
- Wood Smoke
- Natural Gas
- Coal Combustion
- Road Dust
- Diesel
- Gasoline
- Smoking Engine
- Traffic-Mixed
- Sea Salt
- Ammonium Sulphate
- Ammonium Nitrate
- SOC
- Measured PM2.5
Figure 5: Source attribution of PM$_{2.5}$ mass based on CMB results