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Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities

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Abstract

Organic matter frequently represents the single largest fraction of fine particulates in urban environments and yet the exact contributions from different sources and processes remain uncertain, owing in part to its substantial chemical complexity. Positive Matrix Factorisation (PMF) has recently proved to be a powerful tool for the purposes of source attribution and profiling when applied to ambient organic aerosol data from the Aerodyne Aerosol Mass Spectrometer (AMS). Here we present PMF analysis applied to AMS data from UK cities for the first time. Three datasets are analysed, with the focus on objectivity and consistency. The data were collected in London during the Regent's Park and Tower Environmental Experiment (REPARTEE) intensives and Manchester. These occurred during the autumn and wintertime, such that the primary fraction would be prominent. Ambiguities associated with rotationality within sets of potential solutions are explored and the most appropriate solution sets selected based on comparisons with external data. In addition to secondary organic aerosols, three candidate sources of primary organic aerosol (POA) were identified according to mass spectral and diurnal profiles; traffic emissions, cooking and solid fuel burning. Traffic represented, on average, 40% of POA during colder conditions and exhibited a hydrocarbon-like mass spectrum similar to those previously reported. Cooking aerosols represented 34% of POA and through laboratory work, their profile was matched with that sampled from the heating of seed oils, rather than previously-published spectra derived from charbroiling. This suggests that in these locations, oil from frying may have contributed more to the particulate than the meat itself. Solid fuel aerosols represented 26% of POA during cold weather conditions but were not discernable during the first REPARTEE experiment, when conditions were warmer than the other campaigns. This factor showed features associated with biomass burning and occurred mainly at night. Grid-scale emission factors of the combustion aerosols suitable for use in chemical transport models were derived relative to CO and NO_x. The traffic aerosols were found to be 14.4 µg m^{-3} ppm^{-1} relative to CO for Manchester and 28 µg m^{-3} ppm^{-1} relative to NO_x

for London. Solid fuel emissions were derived as 17.3 µg m^{-3} ppm^{-1} relative to CO for Manchester. These correspond to mass emission ratios of 0.012, 0.021 (as NO) and 0.014 respectively and are of a similar order to previously published estimates, derived from other regions or using other approaches.

1 Introduction

There has long been an association between fine particulate pollution and adverse effects on human health (Pope and Dockery, 2006; Dockery et al., 1993; Fenger, 1999; Künzli et al., 2000). Most official regulation is founded on mass-based metrics such as the PM_{10} and $PM_{2.5}$ standards (European Union, 2008). However, these particles are known to be composed of a variety of different chemical components, each with their own sources, behaviours and impacts (Pio et al., 2007). Of particular interest are organic aerosols (OA), which can constitute a large fraction of the mass of fine particulates and are known to be composed of a highly complex mixture of many tens of thousands of species or more (Hamilton et al., 2004; Jacobson et al., 2000; Saxena and Hildemann, 1996). These are known to originate from a variety of different sources, often broadly categorised as either primary or secondary.

While primary aerosols do not necessarily represent the greatest fraction of the mass of particulate matter, they are the controlling factor of the ultrafine fraction, i.e. those of less than 100 nm in size. These are present in very large numbers in urban environments and are potentially very important because they are small enough to travel deep into the lungs and additionally, have the potential to penetrate into tissues beyond the lungs and cause more physiological damage (Ibald-Mulli et al., 2002; Maudgalya et al., 2008; Kreyling et al., 2006). The transport sector is known to be a major source of primary organic aerosols (POA) in urban environments (Colvile et al., 2001), but others such as cooking (Robinson et al., 2006) and the burning of solid fuels such as biomass (Simoneit, 2002) are also known to be significant in some locations. At distances removed from the sources of POA, secondary organic aerosols (SOA) begin to dominate as POA is diluted and SOA is produced (Alfarra et al., 2004; de Gouw et al., 2005).

In recent years, the Aerodyne Aerosol Mass Spectrometer (AMS) has proven itself to be a powerful tool in the study of submicrometer aerosols (Canagaratna et al., 2007; Jayne et al., 2000). As well as being able to quantify the mass concentration of organic matter (Takegawa et al., 2005), information on the functional nature of the organics can be gleaned by inspecting the mass spectra after the inorganic contributions have been removed (Allan et al., 2003a; Allan et al., 2004). The AMS has been shown to generate distinctive spectra from the analysis of organic test aerosols generated from model compositions such as lubricating oil and fulvic acid and the features have been found to be present in ambient and laboratory generated spectra (Canagaratna et al., 2004; McFiggans et al., 2005; Schneider et al., 2006).

Quantitative analysis of organic functionality is possible if factor analysis is employed to analyse the entire AMS organic mass spectrum. The first technique to be widely used was the two-component method introduced by Zhang et al. (2005a), which separated the measured signal as either hydrocarbon-like or oxygenated organic aerosol (HOA or OOA), which can be broadly attributed to POA and SOA respectively in polluted environments. This technique was subsequently modified to a three-component version (multicomponent anlaysis or MCA) and been shown to be applicable to many different polluted environments and able to discern variations in OOA composition (Zhang et al., 2007). More recently, the application of positive matrix factorisation (PMF) (Paatero, 1997) has become widespread. This technique has been successfully applied to other sources of atmospheric aerosol data (e.g. Paatero et al., 2003; Jaeckels et al., 2007; Eatough et al., 2008) and was first used in conjunction with AMS data by Lanz et al. (2007), who showed that in an urban environment (Zurich), the OA quantified by the AMS can be separated into many more sources that go beyond the simple primary and secondary model. In that work, the primary fraction was divided into HOA, charbroiling and wood burning. In common with Zhang et al. (2007), the secondary fraction was further split into so-called type 1 and type 2 OOA, which exhibited subtle differences in their mass spectra. Type 1, which is dominated by a peak at m/z 44 (CO_2^+ from decarboxylation on the vaporiser surface), has been shown to be typical of highly processed organic aerosols in remote environments (McFiggans et al., 2005). Type 2 had a base peak at m/z 43 ($C_2H_3O^+$ and $C_3H_7^+$) and a greater fraction of signal in minor peaks. This is thought to be less oxygenated and therefore chemically younger secondary material.

The quality of the organic data produced by the AMS has also been improved greatly in recent years by the use of a Tofwerk AG (Thun, Switzerland) orthogonal extraction compact time-of-flight (C-TOF) mass spectrometer (Drewnick et al., 2005), resulting in a much better sensitivity and signal-to-noise (Drewnick et al., 2009) that has improved the overall quality of the PMF outputs. More recently, the high resolution time-of-flight (HR-TOF) AMS was developed (DeCarlo et al., 2006). This is capable of operating in a dual reflectron configuration (W mode), which has sufficient mass resolution ($m/\mathrm{d}m>10^5$) to allow the elemental composition of peaks within the mass spectrum to be quantitatively evaluated and estimates made of the chemical functionality of the aerosol, such as the O/C and H/C elemental ratios and the organic mass (OM) to organic carbon (OC) mass ratio (Aiken et al., 2007; Aiken et al., 2008). However, the signal to noise ratio is greatly reduced in this mode, so a single reflectron configuration (V mode) is used for producing unit mass resolution data.

With these tools, it is possible to quantitatively attribute various fractions of the organic aerosol burden to different generalised sources. It would be expected that the relative significance of each of these sources would vary according to location and season, due to differences in meteorology and sources, so it is important to compare a number of different datasets. Here, for the first time, we present a PMF attribution study of organic aerosols measured in UK cities, specifically Manchester and London. These are much larger cities compared to Zurich; the populations within their respective administrative areas were estimated to be 2.6 and 7.6 million in 2007 (Wroth and Wiles, 2009) and if the surrounding areas are included, the overall London agglomeration can be considered a megacity, having a population in excess of 13 million. The focus in this study is the primary fraction, so measurements were performed in autumn and winter, when the organic aerosols will be biased towards this fraction due to reductions in the photochemistry, mixing layer height and emissions of biogenic volatile organic compounds (VOCs). Attempts are made to derive estimates of regional emission factors that could be utilised in regional chemical models.

2 Experimental

2.1 Sites and instrumentation

The London measurements took place as part of the Regent's Park and Tower Environmental Experiment (REPARTEE). More details regarding the overall experiment and the measurements sites are given elsewhere in this special issue (e.g. Dall'Osto et al., 2009a). As part of two intensive measurement campaigns (hereafter referred to as REPARTEE 1 and 2), measurements of background aerosol composition were made in Regent's Park in central London. The measurements were conducted in the "Inner Circle" of the park (51.528° N, –0.153° E), which is a 300 m diameter area surrounded by a lightly-used park road and at a minimum distance of 500 m from urban street traffic. It is assumed that at this location, the measurements are representative of the urban background atmosphere in an inner city location. The instruments were housed inside a shipping container during REPARTEE 1 and a smaller trailer during REPARTEE 2. Aerosols were sub-sampled from a sampling stack via a 2.5 µm cutoff cyclone. REPARTEE 1 took place during October 2006 and REPARTEE 2 during October-November 2007. While both strictly took place during the calendar autumn, the air temperatures were colder during REPARTEE 2 compared to REPARTEE 1 (a mean of 11.6 compared to 15.6°C), and as will be shown, this resulted in changes in the aerosol phenomenology.

In Manchester, a separate set of measurements were also performed at roof level on the Sackville Street Building at The University of Manchester (53.476° N, –2.234° E), which is the same site that has been used in some previous studies (Allan et al., 2003a;

Williams et al., 2000). The aerosols were sub-sampled from the flow through a standard PM_{10} inlet, located on the northeastern side of the building at a height of approximately 35 m, above a street canyon and with no significantly taller buildings in the immediate vicinity. While this site is much closer to the primary sources, it is again assumed to be more (but not perfectly) representative of the urban background air, due to its location above the urban canopy (Longley et al., 2004). Measurements took place during January–February 2007.

During REPARTEE 1 and the Manchester measurements, a compact time-of-flight AMS was used, while in REPARTEE 2 a high resolution time-of-flight AMS was used, alternating between V and W modes. During the Manchester sampling, the instrument was run alongside one of the older quadrupole-based instruments for validation purposes. The linear regression outputs are shown in Table 1 and show errors on the slopes of 13% or less for all species and r^2 values of 0.94 or more. The intercepts of 0.13 $\mu g\,m^{-3}$ or less were very small compared to the mass loadings reported during the study. A speculative reason for why the C-ToF-AMS measured slightly more organics may be due to an improvement in the transmission of smaller particles in the newer instrument. The organic fraction tends to dominate particles of these sizes in urban environments (Allan et al., 2003a).

The instruments operated in the standard configuration, taking both mass spectrum (MS) and particle time of flight (pToF) data. The instruments were calibrated using 350 nm monodisperse ammonium nitrate particles and based on previous experience in urban environments, a collection efficiency (CE) of 0.5 was assumed, in line with the parameterised treatments of Matthew et al. (2008) and Crosier et al. (2007). In the case of REPARTEE 1, this was validated by estimating the ambient volume concentration using the densities reported by Cross et al. (2007) and comparing with that derived using a differential mobility particle sizer (DMPS), as shown in Fig. 1. The volume concentration of the AMS was found to be equal to or less than that of the DMPS. A slightly greater volume as reported by the DMPS would be expected if a fraction of the volume was made up of refractory material such as elemental carbon or dust.

Collocated measurements of carbon monoxide were performed using a fast response fluorescence instrument, (Aero-Laser GmbH model AL5002, Garmisch-Partenkirchen, Germany), fitted with a Nafion dryer to remove water vapour. A two-point calibration of the instrument was performed automatically every 6 h, using a primary gas standard containing 21.6±5% ppmv CO in compressed air (BOC gases, Guildford, Surrey, UK) and catalytically scrubbed (SOFNAFIL) laboratory air. The linearity range of the instrument was 0–100 ppm and was verified through a multi-point span check using a Thermo Fisher Scientific Inc. model 146 gas calibration unit for dilution (Waltham, MA, USA).

During REPARTEE 1, NO_x was measured using a Thermo model 42C chemiluminescence analyser. The instrument was calibrated using a NO standard in compressed air (BOC) and a gas dilution system (Environics Inc. model 6103 multigas calibrator, Tolland, CT, USA). In all experiments, optical absorption was measured using a collocated Thermo model 5012 Multi-Angle Absorption Photometer (MAAP) (Petzold et al., 2005), using its factory default mass specific absorption of $6.67\,m^2\,g^{-1}$ to derive equivalent black carbon (EBC) concentrations.

2.2 Analysis of aerosol mass spectrometer data

The data analysis was performed using SQUIRREL, the standard ToF-AMS analysis suite developed by the Universities of Manchester and Colorado and Aerodyne Research and hosted electronically at the University of Colorado at Boulder.[1] The high-resolution data was processed to generate quantitative peak areas according to elemental composition using the Peak Integration by Key Analysis (PIKA) software. These data were then used to estimate elemental ratios within the parent molecules using the Analytic Procedure for Elemental Separation (APES) software. These tools were developed and hosted at the University of Colorado.

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[1] http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html

The unit mass resolution data from the C-TOF and the V mode of the HR-TOF were analysed using the “fragmentation table” method described by Allan et al. (2004). This separates signals within the mass spectra according to chemical source by performing weighted subtractions and substitutions based on key identification peaks in the form of matrix operators. For error estimation, the model described by Allan et al. (2003b) was applied to the unit mass resolution data, propagated through the matrices.

The factorisation of unit mass resolution data was performed using the PMF2 executable version 4.2, as provided by the University of Helsinki, running in robust mode. While it would be possible to perform this analysis on the high resolution data from the REPARTEE 2 experiment, this technique is still in its relative infancy and considered outside the scope of this paper. The AMS PMF toolkit developed at the University of Colorado and introduced by Ulbrich et al. (2009) was employed. This provided the facility to run the analysis in batches, varying the number of factors, “fpeak” (rotationality) parameter and initiation seed, and the diagnostic tools to evaluate the solutions derived. The default conversion criteria were used, whereby 5 consecutive iterations result in changes of less than 0.5 in Q (the total weighted and squared residual) for the first two iteration stages and 0.3 in the final stage. The maximum cumulative number of iterations was 300.

In order to make the analysis of the three datasets comparable, the emphasis on the approach used in this work was on consistency and objectivity, rather than seeking to thoroughly evaluate all of the variance within each dataset. The choice of number of factors chosen is covered in detail in the supplementary material http://www.atmos-chem-phys-discuss.net/9/19103/2009/acpd-9-19103-2009-supplement.pdf, but generally speaking, the main criteria were the uniqueness of the factors and numerical stability of the solutions. While the 3 and 4 factor solutions presented here may not explain all of the variance within the datasets, higher order solution sets produced were regarded as unreliable and inconsistent results, so were rejected for the purposes of this work.

Only the signals up to m/z 200 were used, as those of a greater mass were not deemed to be significant due to their low signal-to-noise. The signal at *m/z* 18 (H_2O^+) contains contributions from many sources, so when the organic mass spectrum is extracted using the fragmentation tables, the organic signal at this *m/z* is estimated based on the signal at *m/z* 44 (CO_2^+). This renders the inclusion of the *m/z* 18 peak unsuitable for PMF analysis as it will explicitly covary with the *m/z* 44 peak, which would cause artificially strong weighting of both peaks. Therefore, the *m/z* 18 peak is removed prior to PMF execution and the derived mass concentrations are fractionally scaled up according to the derived peak sizes at *m/z* 44 (this is an alternative method to the downweighting approach used in other works). At times, certain other peaks were considered problematic (based primarily on inspection of their residuals) and had to be excluded from the analysis and these are mentioned in the results section.

Discrete plumes and spikes can have a negative effect on the applicability of the PMF outputs, so these were manually removed through multiple runs of the analysis. Spikes (caused by local emissions or instrumental glitches) were identified through inspection of the time series of summed residuals and it was found that they typically lasted only one data point, although on occasion up to three consecutive points were removed. The removal of larger plumes was a little more subjective but was done on the basis of identifying parts of the datasets that could be considered atypical of the overall sampling periods. These are described in more detail on a case-by-case basis below or in the supplementary material http://www.atmos-chem-phys-discuss.net/9/19103/2009/acpd-9-19103-2009-supplement.pdf.

3 Results

3.1 Basic analysis

Figure 2a–c shows the non refractory mass concentrations encountered during these projects. Generally speaking, organics dominate with contributions from sulphate, nitrate, ammonium and chloride. This behaviour could be considered fairly typical of measurements in urban environments (Zhang et al., 2007). A more detailed analysis of the inorganic aerosol fraction is presented in Nemitz et al. (this special issue).

One event that is of note during REPARTEE 2 is the spike around the night of the 4–5 November 2007, which is probably due to Guy Fawkes' night bonfires and fireworks. While 5 November is the traditional date for this event, this fell on a Monday in 2007, so most public displays took place over the preceding weekend. However, it is possible that some events took place on other nights, although these are not as distinct in the data. Similarly high concentrations were observed around Guy Fawkes' night in 2006, following the main REPARTEE 1 period presented here (Nemitz et al., this special issue).

The dominance of the organics in the Manchester dataset was particularly evident during the latter part of the measurements, beginning 2 February 2007, where the region came under the influence of an anticyclone and synoptic wind speeds dropped. This resulted in reduced mixing and elevated primary emission concentrations, especially at night when shallow inversions formed over the city. Under these conditions, concentrations typically fell around midday, when the height of the boundary layer rose and the pollutants were diluted through mixing.

The high resolution instrument used during REPARTEE 2 permitted the elemental analysis of the individual organic peaks. For the sake of comparison with the previously published results from Mexico City presented by Aiken et al. (2008), the same calibration factors for H/C, O/C and N/C were used (0.91, 0.75 and 0.96 respectively) and the results are shown in Fig. 3. The mean OM/OC ratio was found to be 1.53 with a standard deviation of 0.14. This would correspond to the lower end of the range of values reported from the Mexico City dataset. The O/C ratio was similarly low at 0.27±0.11 and the H/C ratio high at 1.62±0.10. This is all entirely consistent with the organic aerosol being heavily dominated by primary emissions. The estimated N/C ratio (not shown) was very low at 0.03±0.01. There was very little if any evidence to support the presence of organic sulphur.

For the PMF analysis of REPARTEE 2, the data corresponding to the activity that occurred after midday on 9 November 2007 was removed, as this seemed to cause its own unique factor to be generated in the higher order solutions and large, structured residuals in the lower order solutions (see Sect. 2.1 of the supplementary material http://www.atmos-chem-phys-discuss.net/9/19103/2009/acpd-9-19103-2009-supplement.pdf). This would indicate that the reported organics during this period were different to the 4 factors from the rest of the experiment, due to the aerosol having a chemical composition unique to this event. The exact nature of this event was not resolved but irrespective of this, the fact it is clearly distinct from the majority of the campaign renders it unsuitable for analysis. Similarly, the large bonfire peak that occurred between 01:00 to 06:00 LT on 5 November 2007 was removed as this event was almost certainly unique, although this particular removal did not significantly alter the solution profiles and time series outside of this period. Note that additional firework and bonfire contributions would be expected outside this period, but would be harder to identify.

3.2 Classification of PMF factors

In the experiments presented here, 4-factor solutions were derived for REPARTEE 2 and Manchester and a 3-factor solution for REPARTEE 1. While higher order solutions gave improvements to diagnostics such as Q/Q_{exp}, common features appeared within the time series and profiles of the factors that could be taken as indicative of factor splitting and it was not possible to validate the factors derived with the supporting data available. The solutions chosen also showed a good degree of stability when subjected to bootstrapping analysis, unlike the higher order solutions. These analyses are covered in detail in the supplementary material http://www.atmos-chem-phys-discuss.net/9/19103/2009/acpd-9-19103-2009-supplement.pdf. Therefore, in each instance, the results should be seen as the “best estimate” of a 4 or 3 component assignment, although it is inevitably possible that certain minor fractions and variabilities within fractions are being overlooked.

In the solutions derived, the factor profiles tended to show similarities between the different experiments and could be classified according to previously published mass spectra (AMS Spectral Database, 2009). The four types and the criteria used to classify these are described below. The example spectra, time series and diurnal profiles from each experiment shown in Figs. 4–6 originate from the solutions described at the end of Sect. 3.3. The diurnal profiles are shown using the medians and 25th and 75th percentiles.

3.2.1 Oxidised organic aerosol (OOA)

These spectra have a strong base peak at *m*/*z* 44 and do not contain significant contributions from marker peaks of other organic aerosol classes such at *m*/*z* 57 or 60 (Fig. 4a). This spectrum has been widely reported as "type 1" OOA, which is taken to represent well-aged secondary organic aerosols (Lanz et al., 2007; McFiggans et al., 2005; Zhang et al., 2007). This factor does not show a strong diurnal cycle in any of the experiments (Fig. 6a), which is consistent with a regional source and domination by atmospheric transport rather than local meteorology, although a slight dip around midday is seen in all three campaigns. "Type 2" OOA did not feature in any of the solutions derived here; this would indicate that there was not sufficient variance within the OOA fractions (relative to the estimated errors) such that a two-factor model could be reliably applied.

3.2.2 Hydrocarbon-like organic aerosol (HOA)

This is again very similar to previously reported spectra, showing characteristic peaks at *m*/*z* 41, 43, 55 and 57 with little or no signal at 44 and the largest peaks at 43 and 57 (Fig. 4b). This is entirely in keeping with the previously-reported HOA spectra associated with hydrocarbons in vehicle exhaust emissions (Canagaratna et al., 2004; Schneider et al., 2005). In each experiment, the strongest peak in the diurnal cycle occurred in the late morning, which corresponds to the morning rush hour (Fig. 6b). The afternoon rush hour was sometimes present, but was often smaller, presumably due to the elevated boundary layer height and mixing volume typically seen later in the day.

3.2.3 Cooking organic aerosol (COA)

This has a very similar sequence of peaks to HOA, however unlike the other spectrum, has its largest peaks at *m*/*z* 41 and 55 (Fig. 4c). This has been previously reported by Lanz et al. (2007) and was associated with charbroiling. This also exhibits a distinctly different diurnal profile to HOA, with a large peak occurring in the late evening and a smaller peak around midday (Fig. 6c). These probably correspond to mealtimes, modulated by the boundary layer height.

3.2.4 Solid fuel organic aerosol (SFOA)

REPARTEE 2 and Manchester showed a factor with a notable signal at *m*/*z* 60 with (in the case of REPARTEE 2) an associated peak at 73 (Fig. 4d), which is usually taken to be due to levoglucosan (in the Manchester dataset, the 73 peak was removed due to excessively large residuals at this *m*/*z* caused by an unknown interference). A thermal decomposition product of cellulose, levoglucosan is often used as a tracer for biomass burning organic aerosol (BBOA) (Jordan et al., 2006; Simoneit, 2002) and has been seen with the AMS in both ambient and laboratory spectra (Capes et al., 2008; Schneider et al., 2006; Alfarra et al., 2007). Peaks were also observed at *m*/*z* 43 and 55, with minor peaks at 41 and 57, which is consistent with combustion HOA. An appreciable signal was also seen at *m*/*z* 44, which implies a degree of oxygenation that would be consistent with humic-like substances (HULIS) that can be produced by biomass burning (Dinar et al., 2006) and have previously been seen with an AMS during the smouldering phase of wood burning (Weimer et al., 2008). The peak in the diurnal profiles tends to occur in the evening, going into the night (Fig. 6d), which would be consistent with domestic space heating. Wood is often used as fuels in the UK, however other solid fuels such as wood-derived smokeless fuels, coal, coke and anthracite are also in use (NAEI, 2009) and it may be expected that if these are contributing to the organic aerosol produced from this sector, they may covary and also contribute to this factor, warranting the more general classification as “solid fuel” rather than “biomass”.

If a 4-factor solution was derived from REPARTEE 1, a factor was sometimes derived that exhibited some of these features. However, the fractional contribution of the *m*/*z* 60 peak was less than half of those of the SFOA factors derived from other campaigns (0.6 as opposed to 1.4 and 2.2%), so its assignment as SFOA was questionable. Given the fact that the 4 factor solution also exhibited major instabilities when subjected to bootstrapping analysis (see supplementary material http://www.atmos-chem-phys-discuss.net/9/19103/2009/acpd-9-19103-2009-supplement.pdf), the SFOA factor was deemed unreliable in this campaign, so the 3 factor solution, which did not feature a factor with features that could be interpreted as SFOA, was used instead.

3.3 Rotational ambiguity

The factors produced by the PMF2 algorithm are not completely unambiguous and many valid solutions can be derived from a range according to “rotations” of the output vectors within solution space. To facilitate exploration within these solution sets, PMF2 allows for variations of a parameter known as “fpeak”, which causes the algorithm to skew the optimisation process, giving alternative solutions that while typically not the most optimal, also satisfy the convergence criteria (Ulbrich et al., 2009). The setting of a nonzero value often results in the favouring of the numerical separation of the factors in mass spectral space at the expense of separation in time series space, or vice versa. To explore the solution dependency according to the fpeak parameter, the fractional contributions of the factors were compared after the factors were classified according to the above criteria and shown in Fig. 7a–c. In each case, only the range of fpeak under which the fit converged is shown. In the case of the REPARTEE experiments, values less than -1.5 still resulted in successful convergence, but fractional contributions remained roughly constant. The Q/Q_{exp} values are also shown and consistently minimum at fpeak=0, which is the expected behaviour. The values of Q/Q_{exp} are much greater than would be considered optimal for a perfect characterisation of the data, however as stated before, it would not be possible with the data available to constrain or validate solutions with the greater number of factors needed to reduce Q further, so this contribution to Q could be considered "model error".

Upon inspection of the mass spectra, the solutions for positive values of fpeak for REPARTEE 2 and Manchester were discounted, as the SFOA factor began to take on an unrealistic mass spectral profile with many of the characteristic peaks becoming small or zero; in REPARTEE 2, m/z 41, 43, 44, 55 and 57 were diminished and in Manchester, m/z 55. The mass spectra are shown in Fig. 8. As the fractional contribution of SFOA began to decrease for positive values in each case, it was clear that some of the mass that would otherwise have been assigned to SFOA was being assigned to the other factors.

Within the other convergent solutions, there was a certain amount of redistribution between the factors. While they could still be assigned according to the criteria above, there were subtle changes in their mass spectral profiles. The derived time series changed little in their qualitative structure, however the magnitude of the specific events varied, which was reflected in variations in the mean contributions to the total mass concentrations.

Within these solutions, it would seem that many of the convergent solutions could be considered acceptable. Without a more definitive and objective method of validation, the range of variability within these solutions can be considered the confidence interval of the analysis method. To investigate the stability of the solutions, bootstrapping analysis was performed, resampling in the time dimension (Ulbrich et al., 2009), and the variability in the solutions was found to be small compared to the rotational ambiguity (see supplementary material http://www.atmos-chem-phys-discuss.net/9/19103/2009/acpd-9-19103-2009-supplement.pdf).

In order to further assess how physically meaningful the solutions are, the factors were compared with inorganic gas phase tracers. In the case of REPARTEE 1, the collocated NO_x measurement was used and in Manchester CO was used. For REPARTEE 2, a collocated measurement was not available, so NO_x data from an automated London Air Quality Network background monitoring site in North Kensington (51.521° N, −0.213° E) was used. While the distance between the two sites is by no means ideal (4.3 km), closer network monitoring sites such as Marylebone Road are considered unsuitable due to their proximities to busy roads. It could be expected that there will be general agreement of the temporal trends if not the absolute concentrations of NO_x at North Kensington and Regent's Park, as they will both be controlled by the boundary layer mixing and general traffic activity. This assumption is supported by a comparison of NO_x concentrations measured at the two sites during REPARTEE 1, which yields a Pearson's r value of 0.88.

Both NO_x and CO have been shown to bear a very strong relationship with HOA measured by the AMS as both are emitted by traffic activity (Zhang et al., 2005b). The Pearson's r values derived between these and the HOA factor are shown in Fig. 7a–c. However, it could also be expected that some of the gases may also originate from other local combustion sources. To address this, a bilinear fitting was performed using both the HOA and SFOA factors using the following function:

$$f\,(\mathrm{HOA},\ \mathrm{SFOA}) = A\,[\mathrm{HOA}] + B\,[\mathrm{SFOA}] + C \tag{1}$$

A, B and C are arbitrary fitting parameters and are optimised to minimise the squared difference between f(HOA, SFOA) and the combustion tracer. The Pearson's r value between the optimised function and the gas phase concentration are shown in Fig. 7a–c alongside the value associated with the HOA comparison. The A and B parameters were constrained to be non-negative and some fits resulted in B equalling zero, so the derived r was, in effect, the same as if only HOA had been included.

This approach yielded greater values of r for the CO comparison in Manchester, but did not improve the NO_x values in all of the REPARTEE 2 solutions. This may be because traffic NO_x dominates over its solid fuel counterpart at this measurement site; if there is a big enough mismatch in the atmospheric lifetimes of SFOA and NO_x such that their ratio is not conserved and the correlation breaks down over regional scales, so the variance in the NO_x concentrations will be more representative of the more local source in central London, i.e. traffic.

It could be postulated that there may be some covariance between combustion tracers and COA, given that natural gas is frequently used as a heat source in cooking in the UK, however no discernable improvement to the fits was found when it was included as a third component in Eq. (1). This is most likely because the emissions from this sector are dwarfed by those from other combustion sources.

For each experiment, a "best estimate" solution was chosen for further analysis. For REPARTEE 1, fpeak=−0.5 was used. Generally speaking, the NO_x correlation improved with decreasing fpeak but the value at −0.5 was considered close to the asymptote, whereas Q/Q_{exp} began to rise sharply for more negative values. An fpeak of 0 was chosen for REPARTEE 2 as this gave the optimal values for both Q/Q_{exp} and the NO_x comparison. For Manchester, −0.5 was used as this gave the best CO comparison result for a minimal increase in Q/Q_{exp} relative to fpeak=0. A better CO correlation was obtained for 0.5, however this gave an unrealistic SFOA spectrum, as described above. Table 2 gives a summary of the fractional contributions of the factors and the range associated with the rotational ambiguity.

4 Discussion

4.1 Secondary organic aerosols

PMF analysis on all of the datasets gave mass spectra that could be described as type 1 OOA using the criteria of previous studies, with a large peak at *m*/*z* 44 and with minor peaks at 43 and 55. Note that this does not mean that type 2 OOA was chemically absent in each case, but that there was not enough variation within the OOA during the individual experiments such that a distinct factor could be reliably discerned. In effect, both factors are combined as a single OOA factor. None of the datasets yielded particularly high fractions of OOA, which assuming it is secondary in nature, is in line with the time of year that the experiments were conducted and also reflects the island location of the UK, which often receives relatively clean background air from the Atlantic. The results gleaned from REPARTEE 1 contrast with the other two experiments in that the fractional OOA contributions were slightly larger. At the same time, sulphate concentrations were lower during REPARTEE 1 than during REPARTEE 2 (Nemitz et al., this special issue), which may indicate that in terms of airmass history, advection of secondary pollution was less pronounced. Thus a likely reason for the larger OOA during REPARTEE 1 could be the fact that it took place earlier in the year, when there is likely to be more photochemistry taking place and stronger emissions of biogenic VOCs due to the increased temperature (Fehsenfeld et al., 1992). The campaign also showed the greatest 44/total ratio (Table 3), which is a proxy for the level of oxidation in the organics.

Many previous studies have noted correlations between OOA and other aerosol species attributed to secondary sources, notably sulphate and nitrate. This would indicate a similarity in the emissions of precursors and formation of such species (Lanz et al., 2007; Lanz et al., 2008; Zhang et al., 2007), which given that these can be photochemical products of anthropogenic emissions, would seem reasonable. Furthermore, a relationship between nitrate and type 2 OOA has sometimes been reported in other studies, with both anticorrelated with ambient temperature. The behaviour with respect to nitrate is due to a temperature and humidity driven partitioning with gas phase ammonia and nitric acid (Morino et al., 2006). It is possible that if a significant fraction of the less-oxidised SOA is semivolatile (Grieshop et al., 2007; Robinson et al., 2007), it could follow a similar modulation related to temperature. It is possible that temperature may be modulating the SOA concentrations in REPARTEE 2 and Manchester; both show a slight dip just after midday in their diurnal profiles.

No variation within the OOA factors was found to be strong enough to warrant multiple factors for any of the campaigns presented here. However, variations in the behaviour of the single OOA factor were noted between campaigns and showed in Table 3. During REPARTEE 1, the greatest correlation was found to be with sulphate. In contrast, the OOA in REPARTEE 2 and Manchester were found to have lower levels of oxidation and to have the greatest correlations with the total inorganics, with nitrate showing a better correlation than sulphate. This behaviour was most pronounced in the wintertime Manchester dataset, which had by far the lowest oxidation levels and the reported mass spectrum that bore the closest similarity to type 2 OOA. This behaviour would be consistent with more photochemistry taking place during the REPARTEE 1 campaign, producing a more oxidised SOA on the same timescale as the production of sulphate on regional scales. This is consistent with the evidence supporting regional production reported by Dall'Osto et al. (2009b).

4.2 Combustion factors

The observations of HOA related to traffic in both cities is in common with many previous observations in other cities worldwide and the average mass fractions would be considered typical according to the urban studies presented by Zhang et al. (2007). The significantly greater fraction and reduced rotational ambiguity observed in Manchester is probably due to its closer proximity to the sources.

As part of air quality controls, solid fuel burning that produces smoke is legislated against in most metropolitan areas in the UK, which includes most of the Greater London and Greater Manchester areas (Smoke Control Areas, 2009). Smokeless fuels can be used in open fires and seasoned wood can be burned in approved burners. The practice of burning smoking fuels such as wood in open fires is widespread in the rural areas surrounding Manchester. An intensive field study in November 2006 at Holme Moss, a rural site to the southeast of Manchester, showed that locally-produced solid fuel aerosols were a major contributor to the bulk optical absorption properties of the aerosol (Corris, 2008).

During the Manchester sampling, the solid fuel was most prevalent during the stagnant conditions in the latter part of the experiment and very low at other times. Most burning will occur during the late evening and will become trapped within the nocturnal inversion at night, being released when the height of the boundary layer rises during the day. It is possible that the SFOA factor is originating from smokeless burners and fuels within the cities, although it is also possible that burning of smoking fuels was taking place regardless of legislation. While bonfires may be contributing during REPARTEE 2 this would have been limited to a few specific nights over the 5 November weekend.

Something that should also be considered is whether the solid fuel emissions are purely limited to factors that contain levoglucosan. Weimer et al. (2008) reported such AMS spectra under laboratory conditions when sampling high-efficiency domestic wood burners, the lack of a levoglucosan marker being due to the higher combustion temperatures. The spectra featured an OOA-like peak at *m*/*z* 44 (probably from biomass burning HULIS), and also featured strong signals at *m*/*z* 55 and 57, which are more typical HOA. Because of this, it is possible that some of the signal may be exchanged with the OOA and HOA factors within the rotations.

When comparing the two REPARTEE experiments, the lack of detectable SFOA during REPARTEE 1 is consistent with the expectation that this would be a weaker source; there would have been less of a requirement for space heating during the warmer temperatures. The Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS, TSI, Shoreview MN, USA) deployed by the University of Birmingham (Dall'Osto et al., 2009a b) also did not record any particle classes with features indicative of biomass burning during REPARTEE 1 (M. Dall'Osto, School of Physics, National University of Ireland, Galway, Ireland, Personal communication, June 2009). Regrettably, this measurement was not available during REPARTEE 2. Inspection of *m*/*z* 60 in the raw AMS spectra would concur with SFOA being less significant, as this represented 0.3% of the total organic signal in REPARTEE 1, compared with 0.7% during REPARTEE 2.

4.3 Quantitative comparisons with combustion tracers

In order to budget for the production of POA from traffic within chemical transport models, emission factors can be employed. The most appropriate factors to use are those derived on the scales of the resolution of the simulation so as to eliminate sub-grid processes such as deposition and repartitioning that may alter the perceived factors after the initial emission. As a result, these measurements would lend themselves best to those using kilometre-scale grids. Note that for the purposes of the conclusions reached here, a CE of 0.5 was used, as verified by DMPS closure. However, in a number of previous studies (discussed below) other values have been used. While it is possible that a liquid organic coating on soot particles may mitigate particle bounce (the primary cause of CE suppression), it is also likely that a certain amount of primary material in urban atmospheres will be internally mixed with secondary species deposited between emission and detection (Shiraiwa et al., 2007), causing the CE to revert to that of the overall aerosol. In absence of direct evidence to support the use of a greater value, a CE of 0.5 is used here, in line with the bulk of the aerosol. This resulting caveat is that the reported values may prove to be an overestimate if the "true" CE is greater.

The most desirable reference to use for the emission factors would be carbon dioxide, as a direct relationship can be made between this and fuel consumption. This usually forms the basis of factor derivation by direct source sampling and flux measurement. However, this is an unsuitable tracer for these atmospheric measurements as its background concentrations are too high. For these measurements, carbon monoxide provides a more suitable tracer, as variations due to regional and local sources are much more discernable over the background. Factors derived relative to this can then be used to estimate OA source functions through comparison with existing carbon monoxide inventory data. Recent independent assessment of the UK emission totals of both CO and CO_2 through country-level boundary layer budget measurements suggested that the UK National Atmospheric Emissions Inventory for these compounds is robust (Polson et al., 2009). NO_x can also be used for near-field sources in an equivalent manner. This has a much smaller background, but a shorter atmospheric lifetime, so will not be suitable for emissions on regional scales.

A previous analysis using this method by Allan et al. (2003a) used a time series of total organic mass concentration of particles below sizes of 200 nm in vacuum aerodynamic diameter and through linear regression with gas phase data from a roof-level network monitoring site 0.75 km away, a POA emission factor of 2.29 µg m^{-3} ppm^{-1} (at STP) compared to CO and 21.1 µg m^{-3} ppm^{-1} compared to NO_x were derived. These were subsequently revised to 3.74 and 34.2 µg m^{-3} ppm^{-1} respectively (assuming a CE of 1) as quantification techniques improved (Allan, 2004).

The measurements presented here offered a number of improvements of the previous results and an opportunity to quantify the emission factor much more reliably. Because of the improved sensitivity of the instrument and the collocation with the gas measurements, a much improved fit to the data would be expected. By way of comparison, the calculation performed previously by Allan et al. (2003a) was repeated using the new dataset, comparing the mass concentration of organics contained within particles smaller than 200 nm with the gas phase CO. An increased Pearson's r value was found (0.84, as compared to 0.65) and an emission factor of 10.30 µg m^{-3} ppm^{-1} derived for a CE of 0.5. This equates to an increase of 37% over the previous estimate after taking account of the different CE values used. This difference may be due to a change in the overall fleet emission profile in the intervening time, however it may be that there was a systematic error in the previous estimate due to the physical separation in the measurements and resulting differences in their source footprints.

It is expected that a much more robust evaluation of the emission factor can be derived when using the outputs of the PMF analysis, as this separates the organic fractions more explicitly than simple sizing. Performing a linear regression fit using the "best estimate" HOA data generates an emission factor of 11.5 µg m^{-3} ppm^{-1} (CE=0.5). However, as shown above, the quality of the fit improves if the SFOA is included and the emission factors of the two fractions are, in effect, the reciprocals of the A and B parameters in Eq. (1). Using this, the emission factors of HOA and SFOA are estimated as 14.4 and 17.3 µg m^{-3} ppm^{-1} respectively (equivalent to mass emission ratios of 0.012 and 0.014). Somewhat counter-intuitively, the derived emission factor for HOA is greater using this method. Because the diurnal cycles of the two fractions are mismatched, destructive interference occurs between the two patterns.

By comparison, using Q-AMS data collected during REPARTEE 1 on top of the BT Tower, Phillips et al. (this special issue) derived an HOA emission factor relative to CO of 8.8 µg m^{-3} ppm^{-1} from concentration measurements and an emission factor of 5.6 µg m^{-3} ppm^{-1} from flux measurements, which show a wide spread. This was based on a two-component PMF split into HOA and OOA; at the elevated measurement height and using a quadrupole-based AMS, the PMF analysis failed to identify the COA component. The lower emission factors derived from the elevated measurement height during REPARTEE 1 (compared with the REPARTEE 2 ground-level results) may reflect lower emission factors during the warmer 2006 measurement period or the evaporation of some semi-volatile HOA components during transport to the top of the tower.

While CO_2 background concentrations are too large to quantify the urban increment and thus the ratio of HOA to CO_2 concentrations (and thus fuel consumption) directly, urban CO_2 emissions could nevertheless be derived from flux measurements on the BT Tower (Helfter et al., this special issue), together with fluxes of CO (Phillips et al., this special issue). Molar flux ratios averaged over central London of CO relative to CO_2 (during REPARTEE 1) were fairly constant over the day at 8.9×10^{-3}. If this ratio is applied to the emission factor of HOA relative to CO derived from Manchester, an emission factor of HOA relative to CO_2 can be estimated as 0.128 µg m^{-3} ppm^{-1}, which corresponds to a mass emission ratio of 6.5×10^{-5} (1.8×10^{-5} relative to mass of fuel carbon burned).

A similar comparison can be made using the collocated measurements of NO_x during REPARTEE 1 (the physical separation of the measurements during REPARTEE 2 renders this unsuitable for that campaign). The factor derived is 28 µg m^{-1} ppm^{-1} (a mass emission ratio of 0.021, assuming NO_x is emitted as NO), which is 51% less than the CE-equivalent value estimated by Allan (2004). While this could be partly due to an increase in accuracy (as discussed above), it is also possible that this reflects a difference in the fleet emission profiles between the two cities.

The OM factors derived here are about 2.4 times greater for CO and 50% less for NO_x compared to the CE-equivalent values derived from Pittsburgh sampling by Zhang et al. (2005b), which could be a reflection of differences in the fleet emission profiles. Taken as wholes, the USA and UK are very different in terms of sources of CO and NO_x from the transport sector. The breakdowns from recent data from the relevant national inventories (EPA, 2009; NAEI, 2009) are shown in Fig. 9. The majority of CO emissions in both countries originate from petrol engines, although in the USA a large fraction of the total (49%) is from petrol-driven goods vehicles. A much bigger fraction of UK CO emissions originates from diesel engines (9.4 as opposed to 1.9%) and within these diesel CO emissions, a substantially larger fraction is made up of light duty goods vehicles and cars (47 as opposed to 1.8%). The contribution to NO_x emissions from heavy duty diesel is more similar between the two countries (51 and 44% for the UK and USA respectively), as is that from petrol-driven cars (28 and 24%). However, in the USA, the majority of the remaining NO_x emissions originate from petrol-driven goods vehicles whereas in the UK, it mainly originates from diesel-powered cars and light duty goods vehicles. Given that these vehicle types are highly likely to have greatly different OM emission profiles, this will directly translate to different fleet OM/CO and OM/NO profiles between the two countries. In addition, it is also possible that within these vehicle classifications, differences in engine sizes may also be playing a role. In either case, the values derived here should be considered more representative of the UK urban fleet as a whole.

The NO_x factor derived here is around 5 times greater than the equivalent derived by Schneider et al. (2008) based on chasing heavy duty diesel vehicles in Germany, although it must be noted that their estimate is a reflection of a specific vehicle type and driving conditions rather than a fleet average. It may be that the OM/NO ratio changes for this engine type for urban driving and also the emission factors reported by NAEI (2009) show light duty diesel goods vehicles emit 3.8 times more PM_{10} relative to NO_x during equivalent driving conditions when compared with heavy duty equivalents, so when comparing overall city traffic with this, the difference is perhaps not surprising.

Emission factors for solid fuel burning have been found to be highly variable in direct source sampling experiments, with the emission profiles depending on the temperature of the burn, the fuel used and oxygen availability. Khalil and Rasmussen (2003) reported an OC/CO mass emission ratio of 0.0178 for smouldering wood burning, which assuming an OM/OC ratio of 1.6 (Turpin and Lim, 2001), would equate to an organic matter emission factor of 35 $\mu g\,m^{-3}\,ppm^{-1}$, around double the value of 17.3 $\mu g\,m^{-3}\,ppm^{-1}$ derived here, although it must be noted that that work was more representative of wild fires. The simulations of domestic wood burning presented by Alfarra et al. (2007) gave organic emission factors relative to CO for open burning ranging from 5 to 21.25 $\mu g\,m^{-3}\,ppm^{-1}$ for the flaming phase and 1.3 to 2.5 $\mu g\,m^{-3}\,ppm^{-1}$ for the smouldering phase (S. Weimer, Internal Combustion Engines Laboratory, EMPA Materials Science & Technology, Dübendorf, Switzerland, Personal communication, April 2009). Interestingly, the ratio derived for an automatic domestic burner (fuelled with beech chips) was much greater at 106 $\mu g\,m^{-3}\,ppm^{-1}$. Given that the value derived here is an average of burning within the local region which will involve many different types of burners, this agreement seems reasonable.

In all three campaigns, collocated measurements of equivalent black carbon were made and used to conduct a numerical comparison with the combustion aerosols. It is not prudent to optimise a linear combination as was performed with the gas phase tracers, as there is a complex relationship between the mass specific absorption and mixing state (Bond et al., 2006; Fuller et al., 1999). It has been found that a coating of organic material can drastically enhance the reported equivalent black carbon (Lack et al., 2008; Slowik et al., 2007) and as such, only qualitative comparisons can be made without modelling the optical properties of the particles explicitly.

The Pearson's r values comparing the factors with the reported equivalent black carbon is shown in Table 4. In all experiments, the closest relationship is found with HOA, which is not unexpected due to the high elemental carbon content of aerosols from the traffic sector (Bond et al., 2004). The next best r value was found with SFOA in REPARTEE 2 but Manchester is slightly different in that a slightly better correlation with OOA is derived in comparison to SFOA. However, much of the variability in that dataset is driven by the transition between the non-stagnant and stagnant conditions.

When the analysis is repeated using only the data after 2 February 2007, all of the relationships weaken, but the relationship with SFOA becomes stronger than that for OOA, in line with REPARTEE 2.

4.4 Cooking aerosols

In all three datasets, a robust factor was derived that can be associated with cooking aerosols, based on the diurnal profile and the similarity of the mass spectral profile to that reported by Lanz et al. (2007). At around 34%, the fractional contribution to POA is greater than the estimate of a 5–20% contribution to primary PM for the USA reported by Simon et al. (2008). Cooking is known to release a complex combination of different chemical species, depending on the food being cooked and the method of cooking (Schauer et al., 1999; Schauer et al., 2002). Many other sources of these species exist within the atmosphere and they are subject to many transformation processes, making marker-based estimates of sources difficult (Robinson et al., 2006).

As part of general work to help identify factors derived from ambient AMS measurements, various laboratory experiments were conducted by Mohr et al. (2009), which involved the charbroiling of various foodstuffs such as chicken, fish and processed meat. These produced spectra that bore some similarities with the profiles of the cooking factors derived here in that the *m*/*z* 55 and 41 peaks were very prominent, however there are differences in that the Mohr et al. spectra also had very large peaks at *m*/*z* 43 (greater than 41) and 57.

While charbroiling is undoubtedly a significant source of particulates it will not be representative of all cooking processes and the prevalence of different practices will vary geographically. One significant alternative source of OA will be oils used during frying; when a body of oil is heated, a fraction will vaporise (after the breakdown of glycerides where present) and subsequently recondense as the air carrying them cools (Schauer et al., 2002). To investigate whether this process may represent a factor in the data presented here, a laboratory experiment was conducted where 200 ml of cooking oil was heated in a metallic container and the air immediately above was sampled continuously with a C-ToF-AMS. The three cooking oils used in this experiment were supermarket brand oils of rapeseed (canola), sunflower and groundnut (peanut).

In each case, OA mass concentrations in excess of 1 mg m^{-3} were quickly generated after the heat was applied, with a monomodal size distribution peaking below 100 nm. This would suggest that the oils were becoming supersaturated in the space immediately above the heated liquid and were nucleating new particles. The mass spectral profiles are shown in Fig. 10. In contrast to the meat cooking spectra previously reported by Mohr et al. (2009), these spectra feature a peak at *m/z* 41 that is greater than that at 43, which while not identical in proportion, is more in keeping with the profiles reported from the ambient data. Some slight variation was noted with oil type, most significantly with *m/z* 44 in the rapeseed oil.

This would indicate that the ambient cooking aerosols in these studies bear more resemblance to those produced from seed oils used in frying rather than those from meat cooking. When comparing the laboratory and ambient spectra with previously derived laboratory spectra, the laboratory and field spectra show a strong similarity to those reported for oleic (9-octadecenoic) acid by Katrib et al. (2004) and Alfarra (2004). This is a monounsaturated fatty acid present in many plant oils. In contrast, the meat cooking spectra of Mohr et al. (2009) bear a strong resemblance to the spectrum of palmitic (hexadecanoic) acid as reported by Alfarra (2004), a saturated fatty acid. That is not to say that these results indicate the presence of pure-component aerosols, as cooking produces a complex mixture of species in varying proportions which will all be detected by the AMS. Indeed, both oleic and palmitic acids have been shown to be present in both charbroiling and frying emissions (Schauer et al., 1999; Schauer et al., 2002). Instead, variations in the AMS spectra will be representative of a bias towards particular groups of organic species within the mixture, which in turn may indicate a prevalence of a particular cooking activity.

Based on the comparisons of ambient AMS spectra with those from laboratory simulations of cooking, it would imply that with regards to the total particulate organics, emissions from frying oils are highly significant within ambient measured COA, at least within London and Manchester. Particles of the sizes found in the laboratory study (<100 nm) could be small enough to penetrate through the extraction systems of commercial kitchens, however the exact sizes of the particles at emission will be entirely dependent on nucleation and coagulation rates, which are difficult to predict.

To evaluate cooking as a factor further, more work is needed to characterise the various cooking sources with an AMS. However, even if sources were to be more comprehensively profiled, it would be difficult to make quantitative estimates of source types based on mass spectral profiles alone, as the emissions will be subject to atmospheric processing that may alter the mass spectral profile. For instance, some species may react heterogeneously with ozone (Zahardis and Petrucci, 2007). The rates of this processes will vary greatly according to the molecular weight and level of saturation of the species. Given the ensemble nature of AMS data, effects such as this would be difficult to model. The most effective way of more accurately constraining the relative prevalence of different cooking types at a given location would be if the ensemble organic data from an AMS could be combined with chemical marker-based data. This would preferably be from an online system such as the Thermal Desorption Aerosol Gas Chromatograph (TAG) (Williams et al., 2006), which would allow the diurnal profiles to be studied.

The relationship between COA and equivalent black carbon (as shown in Sect. 4.3) is positive but weak in all of the experiments except for REPARTEE 2 and in this instance, its r value is still smaller than those of the combustion sources. While elemental carbon can be associated with charbroiling emissions (Kleeman et al., 2008), this might not be expected with direct emissions from cooking oils during frying. Either way, these particles are not a significant factor in optical absorption in an urban environment compared to the other OA types.

5 Conclusions

Presented here is the first PMF attribution study on the organic fraction of urban background AMS data in large European conurbations, studying autumn and wintertime data from two field studies in two UK cities (London and Manchester) covering three intensive measurement campaigns. Given the times of year, the data are biased towards the primary fraction and this work shows this to be highly significant; at times, the summed primary organic aerosols would represent over half of the 25 $\mu g\,m^{-3}$ limit for $PM_{2.5}$ mass concentration that will be enforced in the UK after 2020 (DEFRA, 2007). Given that the primary particles tend to dominate the ultrafine fraction, these may be a highly significant factor when considering effects of particulates on human health.

Furthermore, this study shows that the primary organic fraction can be split into three factors that can be attributed to known sources, namely transport, cooking and solid fuel burning, based on diurnal profiles and comparisons with previously published mass spectra. While rotational ambiguity introduces a significant amount of uncertainty associated with these assignments, this work indicates that each source is of high significance in UK urban environments; on average, traffic, cooking and solid fuel emissions represent 40, 34 and 26% of POA respectively during the studies in colder conditions. During the experiment in warmer conditions (REPARTEE 1), the solid fuel contribution is not significant enough to be reliably discernable as a separate factor using PMF. This is thought to be due to the increased ambient temperatures and associated reduced requirement for space heating.

The combustion factors showed strong relationships with collocated CO and NO_x measurements. Kilometre-scale emission factors relative to these gases suitable for use in regional chemical models in conjunction with existing inventory data. The mass emission ratios for traffic-based HOA emissions were derived to be 14.4 $\mu g\,m^{-3}\,ppm^{-1}$ relative to CO for Manchester and 28 $\mu g\,m^{-3}\,ppm^{-1}$ relative to NO_x for London. Solid fuel emissions were derived as 17.3 $\mu g\,m^{-3}\,ppm^{-1}$ relative to CO for Manchester. These correspond to mass emission ratios of 0.012, 0.021 (as NO) and 0.014 respectively. These are of a similar order to previously published estimates. Estimates for national emissions can be made by applying mass emission ratios to inventory data if it is assumed that the ratios derived here are representative of the country as a whole. Using 2007 inventory data (NAEI, 2009), the national emission rate of OM from the transport sector is estimated as 9.43 and 9.27 $\mathrm{kT\,y^{-1}}$ using the Manchester and London factors respectively. The national OM emission rate from domestic burning can be estimated using the same method as 3.9 $\mathrm{kT\,y^{-1}}$.

The mass spectral profile of the cooking factor was found to bear a strong resemblance to previously published spectra and its diurnal profile was consistent between the three studies, giving peaks that could be associated with lunch and evening meal time. Comparisons between the derived mass spectral profile with laboratory spectra suggest that a significant source of the organic matter in the cooking aerosols may be from plant oils used in frying rather than the food itself. More work is needed to study these sources further so that their influence on the UK aerosol budget can be evaluated.

This work highlights how much rotational ambiguity there is within the 4 factor solutions. If more accurate assessments of the organic aerosol fractionation are to be gleaned using this method, a greater range of collocated measurements will be required to constrain the solutions, particularly if the organic fraction is to be separated into a greater number of factors. The Multilinear Engine may also be of much use in applying these constraints more systematically and basing factor profiles on a prioi spectra from laboratory and other field studies (Lanz et al., 2008; Paatero, 1999). However, this will intrinsically be at the expense of objectivity in the analysis. More chemical information could also be gleaned if the technique is applied to the outputs from the analysis of W mode data from the high resolution AMS datasets (Aiken et al., 2009). While potentially very powerful, this technique is entirely dependent on the reliable separation of the peaks during data analysis, so extreme care must be taken when fitting and quantifying peaks to avoid artefacts.

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Table 1. Linear regression outputs comparing the data products of the C-ToF-AMS with the Q-AMS during the Manchester sampling.

Species	Slope	Intercept (µg m^{-3})	r^2
Sulphate	1.053	0.130	0.942
Nitrate	1.049	0.121	0.971
Organics	1.130	0.113	0.968
Ammonium	0.972	−0.049	0.978
Chloride	0.883	−0.062	0.977

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Table 2. Summary of attributed mass fractions based on the "best" solutions. The range of fractions derived from other non-rejected solutions is shown in brackets (those that converged and produced realistic mass spectra).

Campaign	"Best" fpeak	OOA	HOA	COA	SFOA
REPARTEE 1	−0.5	53% (43–54%)	25% (22–26%)	22% (22–31%)	N/A
REPARTEE 2	0	28% (28–29%)	23% (15–23%)	30% (29–30%)	19% (19–28%)
Manchester	−0.5	28% (24–28%)	35% (33–37%)	19% (17–27%)	18% (13–23%)

Table 3. The m/z 44 fractions and Pearson's r values derived for the different "best estimate" OOA factors derived from the three campaigns. The summed inorganics included sulphate, nitrate, ammonium and chloride.

Campaign	44/total	$r(SO_4)$	$r(NO_3)$	$r(NH_4)$	$r(\Sigma$ Inorganics)
REPARTEE 1	16.9%	0.905	0.752	0.903	0.897
REPARTEE 2	16.6%	0.652	0.786	0.802	0.843
Manchester	12.3%	0.673	0.900	0.919	0.926

Table 4. Pearson's *r* values comparing the derived factors to equivalent black carbon concentrations measured using a MAAP. The "Manchester stagnant" is the same calculation only using data after 2 February 2007, when meteorological conditions caused measured concentrations to be much greater.

Campaign	HOA	SFOA	OOA	COA
REPARTEE 1	0.88	N/A	0.61	0.27
REPARTEE 2	0.91	0.74	0.46	0.70
Manchester	0.82	0.72	0.73	0.38
Manchester stagnant	0.74	0.41	0.35	0.23

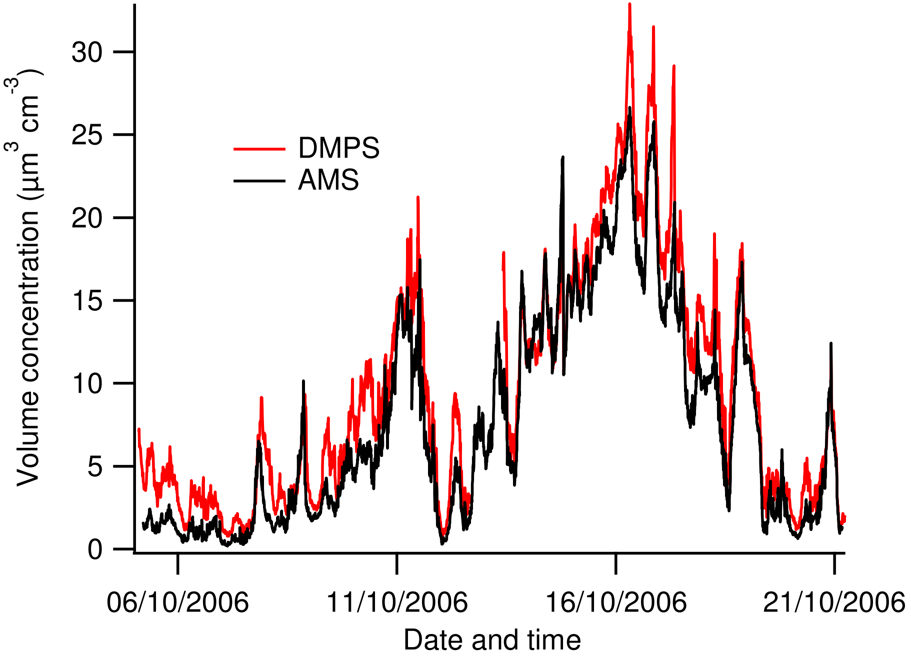

Fig. 1. Volume closure with a DMPS during REPARTEE 1, assuming densities of 1.27 and 1.77 g cm^{-3} for organics and inorganic contributions respectively. All dates and times are local (GMT).

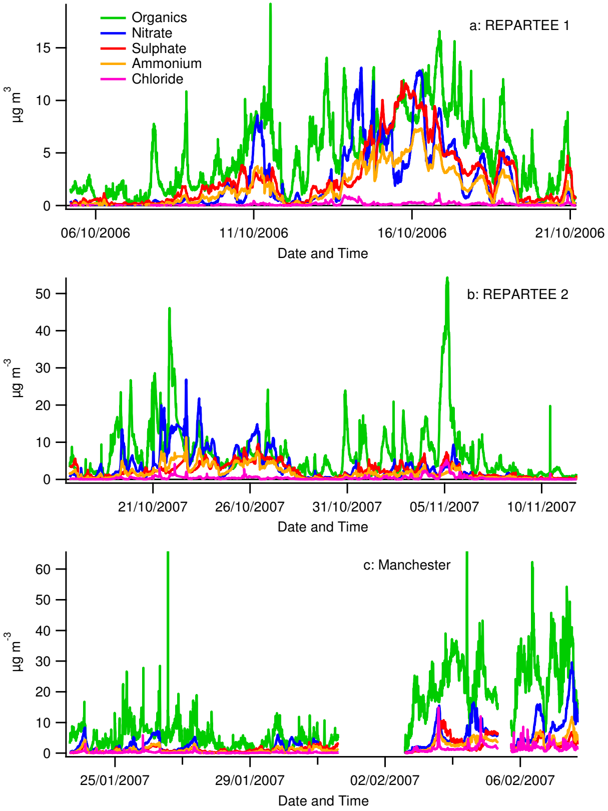

Fig. 2. Reported mass concentrations from REPARTEE 1, REPARTEE 2 and Manchester respectively.

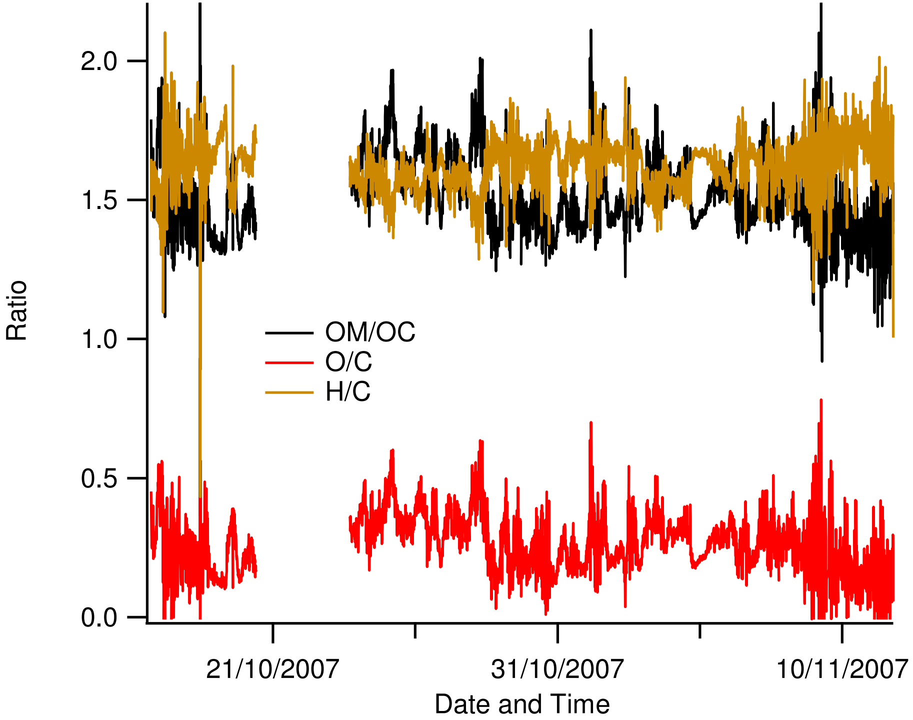

Fig. 3. Elemental ratio analysis of the REPARTEE 2 study.

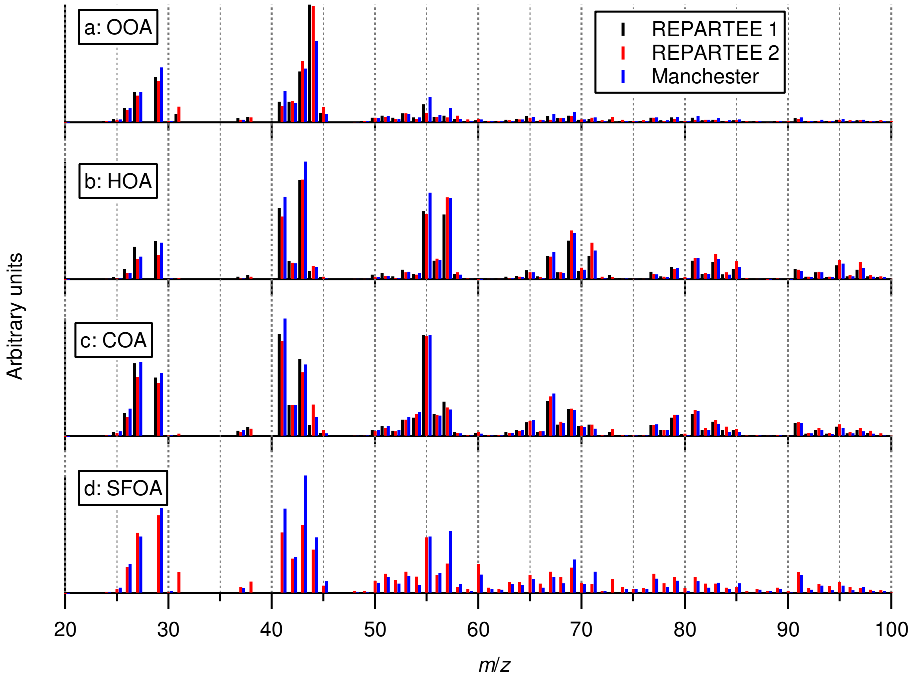

Fig. 4. The averaged mass spectra for the "best estimate" solution sets for each experiment, showing oxygenated organic (OOA), hydrocarbon-like (HOA), cooking (COA) and solid fuel (SFOA) organic aerosol fractions. fpeak=0 was used for REPARTEE 2 and fpeak=−0.5 for REPARTEE 1 and Manchester. Only *m*/*z* 20 to 100 are shown for clarity.

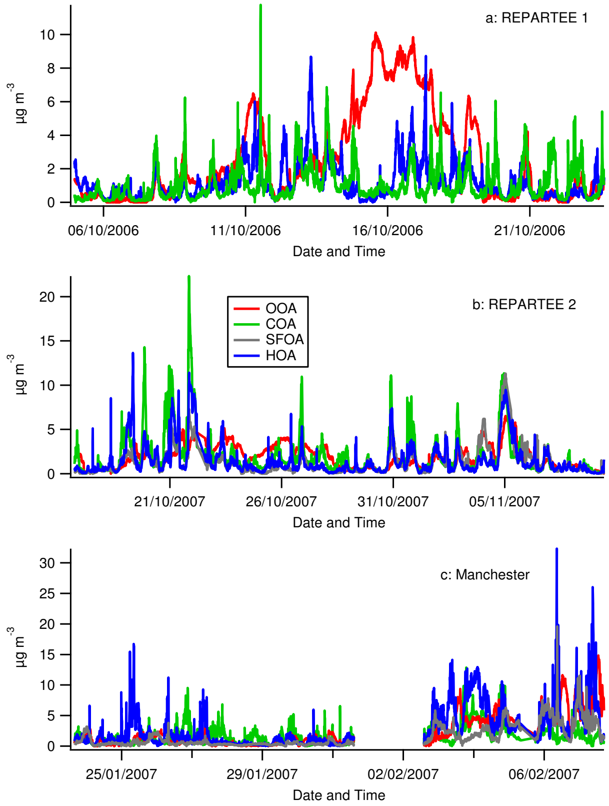

Fig. 5. Time series of the factors from the "best estimate" solutions for REPARTEE 1, REPARTEE 2 and Manchester respectively.

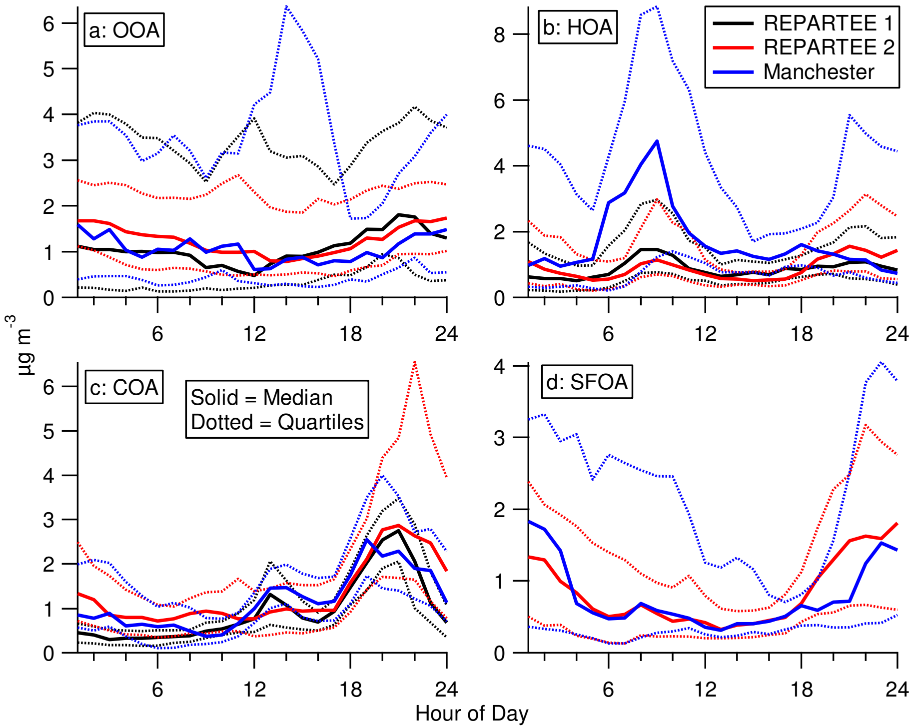

Fig. 6. Median diurnal profiles of the factors from the three campaigns, with the quartiles shown as dotted lines.

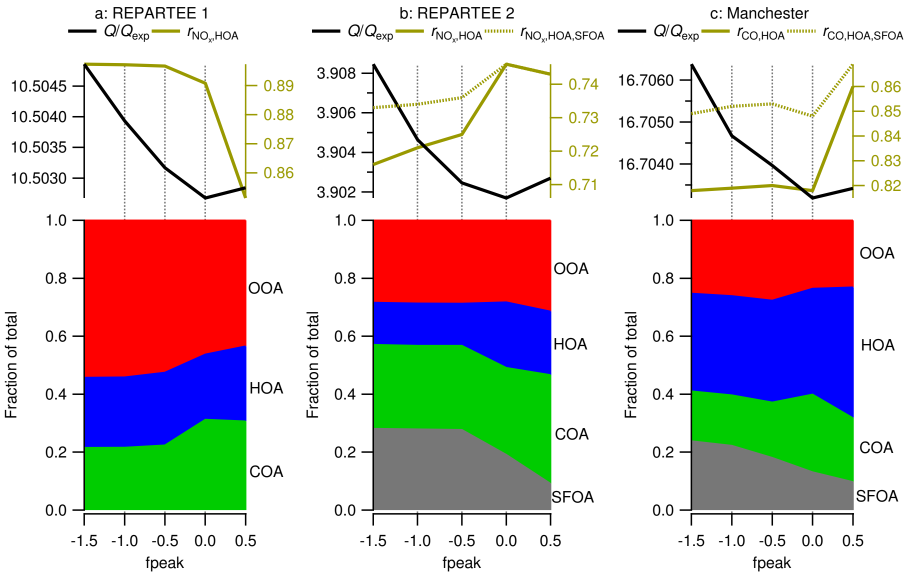

Fig. 7. Variations in the mean mass attributions with varying values of fpeak and Pearson's *r* values of comparisons of the pyrogenic factors with combustion tracers for **(a)** REPARTEE 1, **(b)** REPARTEE 2, **(c)** Manchester.

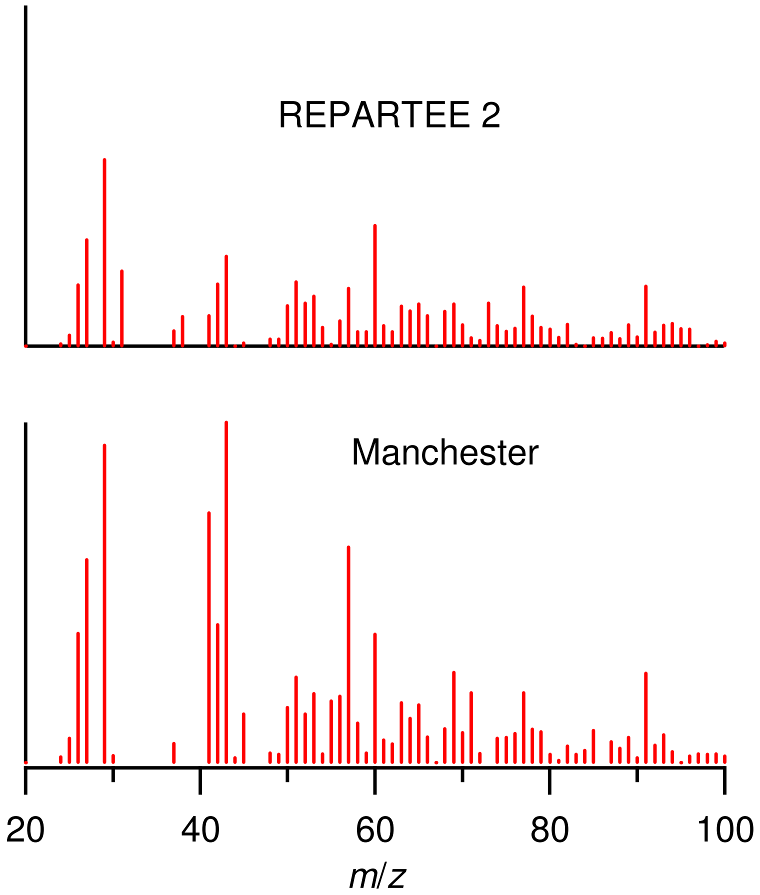

Fig. 8. The mass spectral profiles for SFOA at fpeak=0.5 for REPARTEE 2 and Manchester, which were considered unphysical due to the lack of expected significant peaks such as *m*/*z* 55 and in the case of REPARTEE 2, 41 and 57.

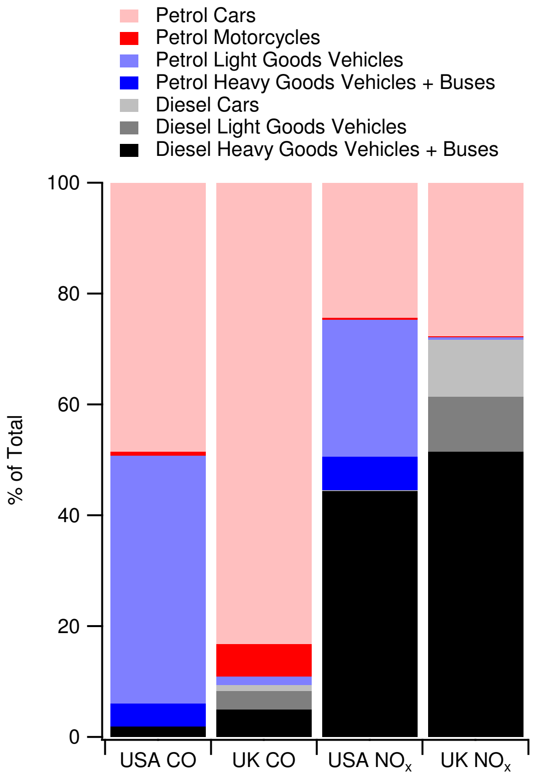

Fig. 9. Percentages of transport CO and NO$_x$ for the USA and UK according to vehicle and fuel type. USA data is taken from the 2005 Environmental Protection Agency Atmospheric Emissions Inventory. UK data is taken from the 2006 Department of the Environment, Fisheries and Rural Affairs National Atmospheric Emissions Inventory.

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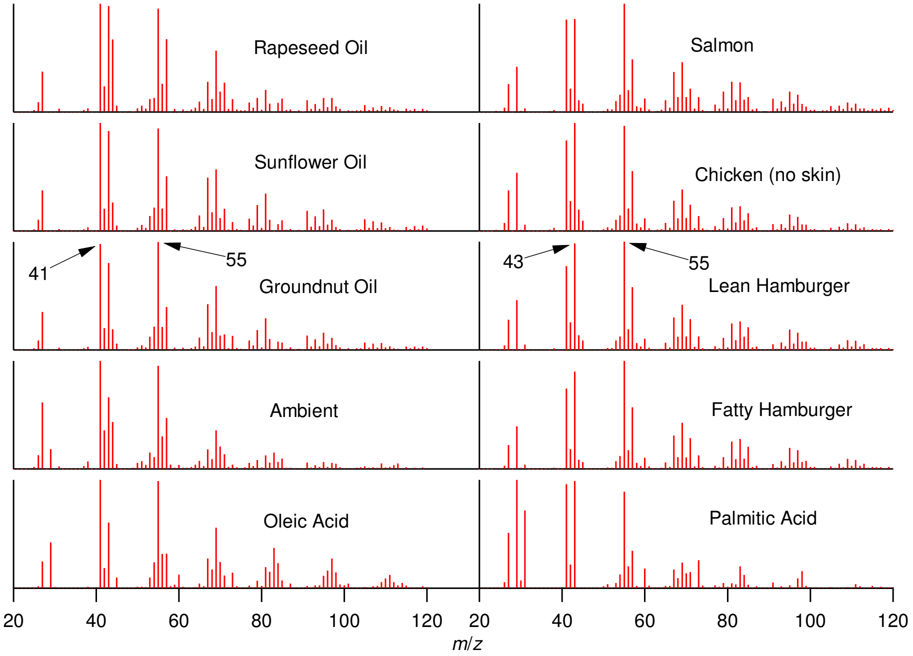

Fig. 10. Mass spectra of various candidates for cooking aerosols. The oil spectra were obtained by sampling aerosols over heated cooking oil baths. The ambient mass spectrum was taken during a period of REPARTEE 2 postulated to be dominated by cooking aerosols. The laboratory-derived spectrum of oleic acid was reported by Katrib et al. (2004) and retrieved via the AMS mass spectral database. The palmitic acid is as reported by Alfarra (2004). The meat cooking spectra are as reported by Mohr et al. (2009).