

**INTERPRETATION OF PARTICULATE
ELEMENTAL AND ORGANIC CARBON
CONCENTRATIONS AT RURAL, URBAN AND
KERBSIDE SITES**

Alan M. Jones and Roy M. Harrison*

**Division of Environmental Health & Risk Management
The University of Birmingham
Edgbaston, Birmingham B15 2TT
United Kingdom**

*To whom correspondence should be addressed
(R.M.Harrison@bham.ac.uk)

ABSTRACT

Concentration measurements are reported for particulate organic and elemental carbon, measured using a R&P 5400 ambient particulate carbon monitor at four sites in the United Kingdom, one roadside (London, Marylebone Road), two urban (London, North Kensington and Belfast, Centre) and one rural (Harwell). Whilst data recovery was by no means complete, the measurements were collected on a continuous three hourly average basis between January 2002 and mid-2004. The concentrations show no obvious seasonal cycle, except for an increase in OC/EC ratio at London, North Kensington during the summer months consistent with a possibly greater relative contribution of secondary organic aerosol. Perhaps surprisingly this is not, however, seen at the rural Harwell site. At Belfast, both organic and elemental carbon show elevated winter concentrations, consistent with important local primary sources. Only at the roadside Marylebone Road site, is there a high correlation ($R^2 = 0.59$) between organic carbon and elemental carbon concentrations which persists when simultaneously measured urban background concentrations from the nearby North Kensington site are subtracted; the ratio of OC to EC in the traffic related concentration increment, is 0.88, well below the ratios typical of the urban background. Directional analysis of the data from the Marylebone road street canyon show that whilst elemental carbon concentrations are determined primarily by on-road traffic emissions, both organic carbon and PM_{10} derive primarily from inputs from outside the street canyon. It therefore appears that at all times of year non-traffic sources of particulate organic carbon, be they primary or secondary, are dominant over traffic emissions in the urban background.

1. INTRODUCTION

In recent years there has been increased interest in the specific components of airborne particulate matter due the debate as to whether any particular component(s) of the particles are responsible for ill health effects (Harrison and Yin 2000) and to assist in source apportionment. The carbon fraction of the particulate matter has been suggested as a possible contributor to adverse health effects due to its reductive potential, and due to specific organic species present. Because of its radiative properties, elemental carbon may also play a significant role in global warming. Carbonaceous material can make up a substantial proportion of the total mass of particulate matter. For example, Harrison et al. (2004) found that in London and Birmingham elemental carbon accounted for on average 26% and 10% of the total PM₁₀ at kerbside and urban background sites respectively, and that organic compounds were 23% (equivalent to 18% organic carbon) and 21% (equivalent to 15% organic carbon) of mass respectively at the two types of site.

Particulate carbon consists of both elemental carbon, from the incomplete combustion of fossil fuels and the pyrolysis of biological material during combustion, and organic carbon which may be either primary or secondary. Sources of primary organic carbon are the incomplete combustion of organic materials and the degradation of carbon containing products such as vehicle tyres (Rogge et al., 1993a) and of vegetation (Rogge et al., 1993b). Degradation of any material is likely to give rise to particles with larger sizes than those resulting from combustion. Secondary organic carbon is formed through the condensation, or sorption onto other particles of organic carbon gases. Sources of organic carbon gases may be from the combustion of organic material, the evaporation of fuels, or the natural emission of volatile organic compounds from vegetation. The resuspension of road dust due to traffic movement may result in increased concentrations of both primary and secondary organic carbon particulate matter (Rogge et al., 1993a). The concentration of secondary organic carbon may also be dependent on the temperature and vapour pressure which will determine whether the material is in the vapour or particle phase at the time of measurement.

In order to assess both organic and elemental carbon, several similar thermo-optical methods have been developed (Chow et al., 2001) in which a sample collected on a filter is heated at temperatures of up to 850 °C in the absence of oxygen to liberate organic carbon compounds which are then converted into methane for quantification. The sample is then heated again at high temperature in the presence of oxygen to combust and quantify the elemental carbon. These methods require a correction procedure to take account of the pyrolysis of organic

carbon to elemental carbon on the filter during analysis, which if uncorrected is likely to result in overestimation of the elemental carbon (Schmid et al., 2001). Any procedure involving the collection of material on a filter may be affected by the adsorption of organic carbon vapours onto the sampling filter.

Other thermal methods for determining the organic and elemental carbon collected on filters heat the filter in oxygen to a lower temperature (typically 350 °C) to assess the organic carbon, and then take the carbon released at higher temperatures to be elemental carbon (Schmid et al., 2001; Harrison et al., 2003). An instrument has been developed by Rupprecht et al. (1995) which measures the quantities of both organic and elemental carbon deposited on an impactor by heating the sample in oxygen at temperatures of 340 °C and 750 °C, combusting the resultant gases, and measuring the carbon dioxide produced, to quantify the organic and elemental carbon. It is recognised (Rupprecht et al., 1995) that using a temperature of 340 °C to distinguish between organic and elemental carbon will result in some of the less volatile organic carbon being classified as elemental carbon. The misallocation of organic carbon to elemental carbon due to the use of a lower dividing temperature is most likely to occur in the case of wood smoke (Chow et al, 2001).

This paper reports measurements of organic and elemental carbon using Rupprecht and Patashnick Type 5400 Ambient Particulate Carbon Monitors co-located with PM₁₀ and gaseous pollutant monitors at four different types of site in the UK.

2. SAMPLING SITES AND DATA MEASURED

2.1 Sampling Sites

Carbon particulate monitors were co-located with other ambient particulate and gaseous monitors at four sites of different types across the UK over a two and a half year period between January 2002 and mid 2004. The site locations are described below.

Harwell: *Rural site* 80 km to the west of London, near the south western corner of a business and science park but otherwise surrounded by agricultural land. Over much of the monitoring period building work was taking place approximately 300 metres to the east of the monitoring location. (Grid reference SU474863; met station, Benson).

North Kensington: *Urban background site* in the grounds of a school in a residential area 7 km to the west of central London. (Grid reference, TQ240817; met station, Heathrow).

Belfast Centre: *Urban centre* site in a pedestrianised area of a provincial city surrounded by typically five story retail and office premises. (Grid reference, 339744; met station, Aldergrove).

Marylebone Road: *Kerbside site* on the southern side of a busy London arterial route in a street canyon aligned on an axis of 75° to 255° . The road carries an average of 75,000 vehicles a day, with the nearside lane in each direction being restricted to use by buses and taxis. Vehicle numbers, speeds and types are counted by means of induction loops buried in the carriageway alongside the monitoring position. Details of the make up of the vehicle population are given in Table 1, making the assumption that all ‘cars’ in the bus lane are taxis, and that no taxis travel in the other lanes. (Grid reference, TQ281820; met station, Heathrow). A pedestrian light controlled crossing 50 metres to the west of the sampling site (and a light controlled junction a further 100 metres to the west) result in frequent interruptions to the flow of traffic to the west of the site. The effect of this is that hourly averaged vehicle speeds in the west-bound direction (towards the traffic lights) are reduced at times of high traffic flow and pedestrian movement, while the east-bound traffic remains free flowing. West-bound vehicle speeds are at a minimum during the late afternoon period.

2.2 Instrumentation for the Measurement of Particulate Carbon

Particulate carbon was measured on a semi-continuous basis using Rupprecht and Patashnick Series 5400 Ambient Carbon Particulate Monitors (Rupprecht et al., 1995). These instruments collect particulate matter on an impactor over a set period of time and then analyse the carbon content of the particulate matter collected while continuing to sample on a second channel. The amount of organic carbon present is determined by oxidising the collected particles at a temperature of 340°C and measuring the resultant CO_2 . The sample is then oxidised again at a temperature of 750°C and the resultant CO_2 is measured to determine the quantity of elemental carbon present. The instrument temperature was maintained at 50°C while sampling, with a PM_{10} sampling inlet. Sampling was carried out over three hour periods. The use of an impaction system to collect the sample is intended to reduce the problem of sampling artefacts due to the absorption of volatile carbonaceous gases that frequently occurs when sampled material is collected on a filter, resulting in erroneously high results for the particulate organic carbon (Kirchstetter et al., 2001). The use of an impactor will however result in loss of material below the impactor cut-off diameter. Trials of co-located R&P 5400 monitors operated under the same conditions have shown consistent results for both the

organic carbon and elemental carbon components (Even et al., 1998; Cowen et al., 2001), with the ratio of the results between the instruments close to unity, and with a degree of correlation (r^2) between the instruments of 0.9 or better. The Licor sensor within the instruments was periodically calibrated by passing through first nitrogen, then nominally 5 ppmV CO₂ in nitrogen, and the slope and intercept were updated in the sensor as necessary. Generally, the slope was seen to be stable; however there were occasional drifts in the intercept. As the instrument calculates the high and low temperature carbon fractions via subtracting the ambient CO₂ concentration, this phenomenon was not seen to affect the quality of the data capture.

Correlations of the results of R&P 5400 monitors with reference samplers, where the sample is collected on a filter and later analysed, are frequently much poorer. Measurements of elemental carbon made by Cowen et al. (2001) showed the R&P 5400 monitor recording 0.36 to 0.89 (depending upon the time of day) of that measured by the reference sampler, although the more extreme differences may in part be a result of the use of linear regression techniques which fail to take account of the uncertainty in the measurements by the reference instrument (Ayers, 2001). A similar under-recording of elemental carbon as measured by a R&P 5400 monitor when compared with other samplers was found by Even et al. (2000), Tohno and Hitzenberger (2000) and ten Brink et al. (2004). Conversely, Rattigan et al. (2004) and Lim et al (2003) found good agreement when comparing the measurements of elemental carbon by a R&P 5400 monitor with a reference sampler.

Due to the impaction system used in the R&P 5400 monitor less than 50% of particles with aerodynamic diameters below 140 nm are collected. At sites with local combustion sources approximately half of the mass of elemental particulate carbon may have diameters of less than 140 nm (Tohno and Hitzenberger, 2000; Holler et al., 2002) resulting in a significant underestimate of the concentration of elemental particulate carbon present by the R&P 5400 monitor. Even et al. (2000) found an improved relationship between elemental carbon particulate measured by a R&P 5400 monitor and other instruments when the impactor of the R&P 5400 monitor was replaced by a filter. Good agreement was found (Tohno and Hitzenberger, 2000) between R&P 5400 measurements of elemental carbon particulate and those of a 12 stage impaction sampler after those stages of the sampler collecting particles with diameters less than 140 nm were excluded.

Trials of R&P 5400 monitors alongside reference samplers have also shown significant under recording of particulate organic carbon concentrations by the R&P 5400 monitors (Cowen et al., 2001). Trials by Rattigan et al. (2004), while not showing a general under measurement of organic carbon particulate by the R&P 5400 monitor, did show highly scattered data with a poor correlation between the two measuring systems. Ten Brink et al. (2004), when measuring total particulate carbon, found the R&P 5400 monitor to have a positive offset which they ascribed to an adsorption artefact in the sampling of organic carbon particulate. Lim et al (2003) found quite good comparability of the R&P instrument with a reference thermal-optical method.

Even et al. (1998) compared the measurement of organic particulate carbon by two R&P 5400 monitors, one of which was fitted with an absolute filter in front of the inlet. They found that there was a positive artefact in the measurement of organic carbon particulate by the unfiltered R&P 5400 monitor of, on average, $1.1 \mu\text{g C m}^{-3}$. Two R&P 5400 monitors, with one instrument preceded by an organic vapour denuder, were operated by Matsumoto et al. (2003), who found that lower concentrations of organic carbon particulate were measured by the instrument fitted with the denuder, implying a positive artefact of around $2 \mu\text{g C m}^{-3}$ on the instrument without the denuder. It should however be noted that there is likely to be greater volatilisation from particles collected on a filter downstream of a denuder due to the changed gas-particle equilibrium (Turpin et al., 2000).

In conclusion, while the results obtained by pairs of R&P 5400 monitors may be consistent, there are problems in making comparisons with the results obtained by other sampling systems. In addition to any consequences of different definitions of organic and elemental particulate carbon, there is in most cases a substantial underestimation of concentration of the elemental particulate carbon by the R&P 5400 monitor due to the low collection efficiency of particles with aerodynamic diameters below 140 nm. While organic particulate carbon is generally associated with particles larger than 140 nm (Holler et al., 2002), some organic particulate carbon will be lost due to the 50°C operating temperature of the instrument causing the vaporisation of the more volatile material (Rattigan et al., 2004). There may also be a small positive artefact (Even et al., 1998; Matsumoto et al., 2003).

2.3 Other Pollutants

Hourly measurements of PM₁₀, NO_x and (in some cases CO) were obtained from co-located instruments. The mean concentrations of these pollutants were calculated over the 3 hourly sampling periods of the R&P 5400 monitors to allow comparison with the particulate carbon concentrations. The PM₁₀ concentrations were obtained from TEOM instruments in which mass measurements are automatically adjusted by multiplying the measured mass by 1.03 and adding 3 µg m⁻³. The TEOMs were operated at a temperature of 50 °C.

2.4 Meteorological Data

Meteorological data were obtained from 3 airfield sites within approximately 20 km of each of the sampling sites. Mean values of the meteorological data were calculated over the 3 hourly sampling periods of the carbon particulate monitors, using vector averaging in the case of the wind direction data.

3. RESULTS AND DISCUSSION

3.1 Total Concentrations

The mean, standard deviation and geometric mean of all the organic and elemental carbon particulate measurements made at each site are presented in Table 2. The distributions of concentrations for organic and elemental carbon at each site were generally log-normal. In the case of elemental carbon there is an increasing trend in concentration from rural, to urban background, to urban centre to kerbside sites. There is a similar trend between sites in the organic carbon particulate concentrations with the exception that the urban background and urban centre sites are reversed. The mean monthly concentrations of organic and elemental particulate carbon at each site are shown in Figures 1a and 1b. Due to instrumentation problems no data were collected during the months of January, November and December at Harwell, October at Belfast, and November at North Kensington. The trend of increasing organic and elemental carbon concentrations from rural to kerbside sites (Table 2) is as would be expected for pollutants with anthropogenic sources, although it is notable that the difference between the rural and kerbside sites is much greater for elemental carbon than for organic carbon.

Measurements of elemental and organic carbon using R&P 5400 monitors reported by other authors are presented in Table 3. Most of these studies were of carbon within the PM_{2.5} fraction and are therefore likely to record lower concentrations than the present study which was of carbon within the PM₁₀ fraction. However in the case of elemental carbon, which is known to be dominated by fine particulate matter, the difference should be small. The mean

values of elemental carbon reported here are similar to the range of values reported by the other authors (Table 3), with the exception of Avino et al. (2000). It should be noted that while the Marylebone Road site is on the kerbside of a heavily trafficked road, the proportion of vehicles with heavy duty diesel engines (lorries and buses) at 12% is relatively low compared to inter-urban routes. The values of particulate organic carbon concentration reported here are low compared to those reported by the majority of other authors (Table 3) despite the inclusion of material in the PM_{2.5-10} size fraction in the present measurements.

There is no consistent seasonal trend across the sites in the concentrations of either organic or elemental carbon (Figures 2a and b). In the work listed in Table 3 there is similarly no evidence of seasonal trends in organic and elemental carbon concentrations, with the possible exception of Prosmittis et al. (2004), who over an eight month period found higher organic carbon particulate concentrations during the summer months, consistent with increased recording OC in the summer months. The seasonal patterns of OC/EC ratios revealed a distinct increase in ratio during the summer months only at the London, North Kensington site. The reason why this is observed at only one site not known. At Belfast, higher concentrations of both EC and OC are observed in the winter, consistent with the influence of primary source emissions.

3.2 Relationship between Particulate Organic and Elemental Carbon

Concentrations of organic particulate carbon are plotted against the corresponding concentration of elemental particulate carbon for each site in Figures 2a-d. Correlations are generally low ($r^2 < 0.5$) except at the kerbside site (Marylebone Road) where higher elemental carbon values resulted in a reduced gradient of organic carbon to elemental carbon.

All of the plots show an intercept of organic carbon a little below $1 \mu\text{g C m}^{-3}$, strongly suggestive of the artefact reported by Even et al (1998). The OC/EC gradients at the two urban background sites (London, North Kensington and Belfast) are 2.09 and 1.54 respectively, but with much scatter. Castro et al (1999) reported an OC/EC ratio of 1.1 at urban background sites as apparently reflective of primary aerosol, ratios above this reflecting incorporation of secondary OC. A line of gradient 1.1 in Figure 2 for London, North Kensington and Belfast would be consistent with the lower points in the clusters of data, if only a few outlying points are ignored. The data are therefore broadly consistent with those of Castro et al (1999), perhaps surprisingly given the difference in sampling and analytical procedures (Castro et al used filter sampling and a more conventional EC/OC separation).

Ratios of OC/EC at London, Marylebone Road, are significantly lower than at the other sites, and far more constant. The lower ratio at this site is consistent with the roadside site data from Rome reported by Avino et al (2004). When simultaneously collected London, North Kensington data were subtracted from the London, Marylebone Road data and one extreme outlying point excluded, the following relationship representative of traffic emissions was found.

$$\text{OC} = 0.88 \text{ EC} - 0.42 \mu\text{g m}^{-3} \quad (r^2 = 0.50)$$

3.3 Diurnal Concentration Profiles

The mean diurnal profiles obtained over weekdays (Monday – Friday) and Sundays, of both the organic and elemental particulate carbon concentrations were plotted. At the rural site (Harwell) there is not a significant difference between the measurements made during the weekdays or on Sundays. The trends in organic and elemental particulate carbon are similar, with rising concentrations during daylight hours. The peak concentration of both organic and elemental carbon occurs earlier on Sundays than on weekdays, with a greater range of concentration over the day on Sundays.

At the urban background site of London, North Kensington the weekday concentrations rise compared to the Sunday concentrations from 06:00 onwards. This is more significant in the case of elemental than of organic carbon. The diurnal profiles of both organic and elemental particulate carbon on Sundays show lower concentrations around midday in contrast to the results obtained at the rural site. The diurnal profiles of particulate carbon concentration from the urban centre site (Belfast) show significantly higher values on weekdays compared to Sundays for samples obtained between 06:00 and 21:00. On Sundays both the organic and elemental carbon concentrations were lower during the middle part of the day in a similar, but more pronounced, pattern to that at North Kensington.

The diurnal profiles of particulate carbon at the roadside site (Marylebone Road) show substantial increases in both organic and elemental carbon between 06:00 and 18:00 on weekdays compared to Sundays. On Sundays the trend of both organic and elemental carbon concentrations is similar, with a minimum at 03:00 and a maximum at 18:00. Subtraction of the simultaneous London, North Kensington data from the Marylebone Road data had little

effect on the average diurnal profiles, which were very strongly correlated with the NO_x traffic increment calculated in the same manner.

Morning peaks in the elemental carbon concentration have also been observed in Athens by Prosmittis et al. (2004), and in New York by Rattigan et al. (2004). Prosmittis et al. (2004) observed a bimodal diurnal profile of organic carbon particulate with peaks around 08:00 and 23:00 hours. The late evening peak was particularly prominent during warm periods. There is some evidence of elevated organic carbon concentrations during the evening periods in our data from the urban sites.

3.3 Effect of Wind Direction on Concentration

The mean concentrations of organic and elemental carbon at each wind direction, normalised against the mean concentration over all wind directions, are shown for each of the four sites in Figures 3a-d. The error bars indicate the standard error in the means normalised by the mean concentrations over all wind directions. Also shown are the corresponding data for PM_{10} and NO_x , and for carbon monoxide in the case of Marylebone Road.

At the rural site, Harwell (Figure 3a), the normalised concentrations of both PM_{10} and NO_x are at a maximum when the wind is from the east, the direction of London and the European mainland, and concentrations are generally raised when the most developed part of the business park is upwind (when the wind is from north to east). Lower concentrations in winds from the south west may also be a consequence of the higher mean wind speeds from this direction resulting in increased dispersion. While the plots of normalised PM_{10} and NO_x (Figure 3a) appear to be significantly different, regression of PM_{10} on NO_x shows these pollutants to be closely correlated ($r^2 = 0.90$).

The normalised concentration of organic carbon generally follows the trend of PM_{10} and is moderately correlated with both the PM_{10} and NO_x concentrations ($r^2 = 0.55$ and 0.47). Conversely, elemental carbon is poorly correlated with both PM_{10} and NO_x ($r^2 = 0.16$ and 0.11) although there is a reasonably good correlation with organic carbon ($r^2 = 0.60$). The profile of normalised elemental carbon concentration with wind direction (Figure 3a) shows large variations in the normalised concentration over small changes in wind direction in easterly and south easterly winds, but with these exceptions normalised concentrations of elemental carbon are similar at all wind directions. Values of the standard error are also large.

It is likely that these peaks in the normalised concentration are due to intermittent local sources of elemental carbon. It was noted that there were a number of construction operations on the southern side of the business park and it may be that construction equipment is emitting large quantities of elemental carbon.

At North Kensington, the urban background site, the normalised concentrations for all pollutants (Figure 3b) show higher values in easterly winds, the direction of central London, and are lower when the wind is from the south west when mean wind speeds are likely to be higher and dispersion greater. The normalised concentrations of both organic carbon and PM₁₀ show a smaller range of values than elemental carbon and NO_x. Elemental carbon concentrations are better correlated with those of NO_x than with PM₁₀ concentrations ($r^2 = 0.90$ vs. 0.73). The correlation coefficients between organic carbon concentration and the concentrations of PM₁₀ and NO_x are similar.

The normalised concentration profiles of all pollutants at Belfast (Figure 3c) are similar with maximum values in easterly winds and minimum values when the wind is from the north west. All pollutant concentrations correlate well with each other and neither fraction of carbon shows closer correlation with either PM₁₀ or NO_x.

At Marylebone Road the normalised pollution concentration profiles against wind direction (Figure 3d) are quite different from those at the other urban sites. All instruments at Marylebone Road are located on the southern side of the road within a street canyon, the height of which is approximately 0.8 times its width. The street is aligned on an axis of 75° to 255° (approximately east to west). In a street canyon of the relative dimensions of Marylebone Road a cross canyon wind will induce a vortex in the canyon resulting in the direction of the airflow at street level being reversed (Nakamura and Oke, 1988; Vardoulakis et al., 2003). The consequence of such a vortex is seen in Figure 3d with the mean normalised concentrations of all pollutants being greater when the wind direction above the canyon (as measured at Heathrow) is from a southerly direction and the reversed flow at street level draws polluted air across the traffic lanes to the north onto the sampler.

It is clear from Figure 3d that the profiles of normalised concentration of different pollutants against wind direction can be ascribed to two distinct classes. The profiles for PM₁₀ and organic carbon are symmetrical about the 165° wind direction (i.e. directly across the canyon), while the profiles for NO_x, CO and elemental carbon are asymmetric. The standard errors of

each value (indicated by the error bars) show that there is generally little significant difference between the profiles within each class, but a significant difference between the classes. Similar profiles have been reported previously (Harrison and Jones, 2004) where the normalised particle number concentration profile was asymmetric while the normalised concentration profile of $PM_{2.5}$ was symmetric. There is some evidence in Figure 3d of small differences between the profiles in each class with the normalised concentrations of organic carbon being less than those of PM_{10} at wind directions between 60° and 260° and greater at other wind directions.

In order to examine this phenomenon more closely, the roadside pollutant increment was calculated by subtracting simultaneously measured background concentrations from London, North Kensington from the London, Marylebone Road data. The resultant traffic increment should reflect only the influence of traffic emissions on Marylebone Road itself. The outcome was that the directional profiles of NO_x , CO, PM_{10} , OC and EC, all became very similar in appearance reflecting the influence of the street canyon vortex upon concentrations. This is interpreted as implying that in the raw Marylebone Road concentration data, elemental carbon has a common source with NO_x and CO in emissions from road traffic, predominantly that of Marylebone Road. On the other hand, the predominant source of particulate organic carbon is in PM_{10} derived from the background outside of Marylebone Road. This is an important finding as it emphasises the fact that elemental carbon and organic carbon have substantially different sources even in the polluted urban atmosphere as represented by London, North Kensington, which explains their relatively weak degree of correlation. It appears that in fresh vehicle emissions at Marylebone Road, elemental carbon typically exceeds the concentration of organic carbon whilst in the background urban atmosphere, organic carbon strongly predominates. It would appear therefore, that secondary organic carbon or primary non-traffic sources play a major role in determining OC:EC ratios in all months of the year in London.

The different protocols for distinguishing between organic and elemental carbon differ as to where to set the boundary between allocating material to the organic or the elemental fraction. At the Marylebone Road site the R&P 5400 monitor separates the carbon into two distinct fractions which conform with the two types of normalised concentration profile which are seen for other pollutants, and which can be associated with the different sources. At the rural site, where particulate carbon concentrations are lower, the correlation between organic and elemental carbon is stronger than the correlations between the carbon and either PM_{10} or NO_x .

It may be that this stronger correlation between the organic and elemental particulate carbon is a result of some degree of misclassification of the carbon.

3.4. CONTRIBUTION OF ORGANIC CARBON TO PM₁₀ CONCENTRATION

The mean organic carbon concentration measured at each wind direction is plotted against the corresponding value of PM₁₀ for each site in Figure 4. Error bars indicate the standard error in the mean of each value. The line is fitted by the reduced major axis technique (Ayers, 2001) but excludes data with PM₁₀ values greater than 34 $\mu\text{g m}^{-3}$. This effectively excludes data from the direction of the road at Marylebone Road. There is seen to be a consistent relationship between organic carbon and PM₁₀ measured in the background air at Marylebone Road and the other three sites with organic carbon making up fourteen per cent of the PM₁₀ mass. The ratio of organic carbon to PM₁₀ is lower when the airflow at Marylebone Road is from the road than when it is towards the road. This is contrary to what would be expected if organic carbon from tyre debris was a significant part of the organic carbon particulate in the airflow from the road. If a typical conversion factor between OC and organic compound mass of 1.6 is applied, organic compounds are seen to contribute 22.4% of measured PM₁₀, a substantial proportion.

4. CONCLUSIONS

The mean concentrations of elemental particulate carbon measured ranged from 0.6 $\mu\text{g m}^{-3}$ at the rural site to 3.4 $\mu\text{g m}^{-3}$ at the kerbside site and are similar to the values measured by most other authors using Rupprecht and Patashnick Type 5400 Ambient Carbon Particulate Monitors. The mean concentrations of organic particulate carbon measured ranged from 1.8 $\mu\text{g m}^{-3}$ at the rural site to 4.5 $\mu\text{g m}^{-3}$ at the kerbside site. These values are towards the lower end of the range of measurements of organic carbon concentrations made by other authors using Rupprecht and Patashnick Type 5400 Ambient Carbon Particulate Monitors. This is despite the fact that the measurements reported here were made using a PM₁₀ pre-impactor whereas most other work made use of a PM_{2.5} pre-impactor. This difference should have no significance in the case of elemental carbon where the particles are all expected to be within the PM_{2.5} fraction. There was no evidence of a systematic seasonal variation across all sites in the concentrations of either organic or elemental particulate carbon. There was a positive, but with the exception of the kerbside site, weak correlation between the concentrations of organic and elemental carbon.

The diurnal profiles of organic and elemental carbon show increased concentrations of both on weekdays (Monday – Friday) during the main working hours compared to concentrations on Sundays at the urban sites confirming the importance of anthropogenic sources for both fractions of the carbon.

While there was a limited association between the directional profiles of elemental and organic carbon at the rural site, at the urban sites the elemental and organic carbon concentrations were more closely related to the NO_x and PM_{10} concentrations respectively. At the kerbside site concentrations of pollutants could be associated with two distinct directional profiles. This phenomenon is explained by elemental carbon at Marylebone Road deriving predominately from on-road emissions, whilst organic carbon derives largely from the urban background. Therefore, primary non-traffic sources and secondary sources of organic carbon play an important role in determining concentrations in the atmosphere of London.

At all sites, with the exception of the kerbside site when the air flow was from the direction of the road, the mean organic carbon particulate comprised around 14% of the PM_{10} at each wind direction, and 22.4% when converted to organic matter mass. When the air flow was from the road at the kerbside site, organic carbon concentrations were a smaller proportion of the PM_{10} concentration than when the wind was from the opposite direction, indicating that abrasion of tyres is not a significant source of organic particulate carbon at the site, but that larger particles with organic carbon adsorbed on their surface may be.

5. ACKNOWLEDGEMENTS

This work was funded by The Department for Environment, Food and Rural Affairs and the Devolved Administration under Contract number EPG 1/3/184 The operation of the R&P 5400 monitors and ratification of carbon particulate data was carried out by S Moorcroft, J Booker, J Alexander and D Harrison of Casella Group. Traffic data from Marylebone Road was provided by David Green of King's College, London. Meteorological data is from the British Atmospheric Data Centre. Other pollutant data is from the UK National Air Quality Information Archive.

6. REFERENCES

- Avino P, Brocco D, Lepore L and Ventrone I (2000) Distribution of elemental carbon (EC) and organic carbon (OC) in the atmospheric aerosol particles of Rome. *J Aerosol Sci* **31S** S364-S365
- Ayers GP (2001) Comment on regression analysis of air quality data. *Atmos Environ.* **35** 2423-2425
- ten Brink H, Maenhaut W, Hitzenberger R, Gnauk T, Spindler G, Even A, Chi X, Bauer H, Puxbaum H, Putard J-P, Tursic J and Berner A (2004) INTERCOMP2000: the comparability of methods in use in Europe for measuring the carbon content of aerosol. *Atmos Environ* **38** 6507-6519
- Castro LM, Pio CA, Harrison RM and Smith DJT, *Atmos. Environ.*, 33, 2771-2781 (1999).
Carbonaceous Aerosol in Urban and Rural European Atmospheres: Estimation of Secondary Organic Carbon Concentrations
- Chow JC, Watson JG, Crow D and Lowenthal DH (2001) Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Sci Tech* **34** 23-34
- Cowen K, Kelly T, Coutant B and Riggs K (2001) Environmental Technology Verification Report: Rupprecht and Patashnick, Co. Series 5400 Ambient Particulate Carbon Monitor. Battelle, Columbus, OH
- Even A, Khlystov A and ten Brink HM (1998) Performance of two ambient carbon particulate monitors in background air. *J Aerosol Sci.* **29S** S873-S874
- Even A, Khlystov A, Kos GPA, ten Brink HM, Hoek G, Oldenwening M and Hartog J. (2000) Improvement of BC measurement with the Ambient Carbon Particulate Monitor RP5400. *J Aerosol Sci* **31S** S897-S898
- Harrison RM (2004) Key pollutants – airborne particles. *Sci Total Environ* **334-335** 3-8
- Harrison RM and Yin J (2000) Particle matter in the atmosphere: which particle properties are important for its effects on health ? *Sci Total Environ* **249** 85-101
- Harrison RM, Jones AM and Lawrence RG, (2003) A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. *Atmos Environ* **37**, 4927-4933
- Harrison RM, Jones AM and Lawrence RG (2004) Major component composition of PM₁₀ and PM_{2.5} from roadside and urban background sites. *Atmos Environ* **38** 4531-4538.
- Harrison RM and Jones AM (2004) A multi-site study of processes influencing particle number concentrations in urban air, *Environ. Sci. Technol.*, submitted.
- Holler R, Tohno S, Kasahara M and Hitzenberger R (2002) Long-term characterisation of carbonaceous aerosol in Uji, Japan. *Atmos Environ* **36** 1267-1275

- Kirchstetter TW, Corrigan CE and Novakov T (2001) Laboratory and field investigation of the adsorption of gaseous and organic compounds onto quartz filters. *Atmos. Environ.* **35** pp 1663-1671
- Lim H-J, Turpin BJ, Edgerton E, Hering SV, Allen G, Maring H and Solomon P (2003) Semi continuous aerosol carbon measurements: comparison of Atlanta supersite measurements. *J Geophys Res – Atmos.* **108** No. D7 8419
- Matsumoto K, Hayano T and Uematsu M (2003) Positive artifact in the measurement of particulate carbonaceous substances using an ambient carbon particulate monitor. *Atmos Environ* **37** 4713-4717
- Molnar A, Meszaros E, Hasson HC, Karlsson, Gelencser A, Kiss GY and Krivacsy Z (1999) The importance of organic and elemental carbon in the fine atmospheric aerosol particles. *Atmos Environ* **33** 2745-2750
- Nakamura Y and Oke TR (1988) Wind, temperature and stability conditions in an east-west orientated urban canyon. *Atmos Environ* **22** 2691-2700
- Promitis AB, Diapouli E, Grivas G, Chaloulakou A and Spyrellis N (2004) Continuous filled measurements of organic and elemental carbon concentrations in Athens, Greece. *J Aerosol Sci* **35S** S1077-S1078
- Rattigan OV, Felton D, Schwab JJ and Demerjian KL (2004) Measurements of PM_{2.5} in New York City. Organic Carbon Speciation April 2004 Las Vegas.
ocs.fortlewis.edu/Aerosols/SPECIATION/VegasOC_2004_Rattigan.pdf
- Rogge WF, Hildemann LM, Mazurek MA and Cass GR (1993a) Sources of fine organic Aerosol. 3. Road dust, tire debris and organometallic brake lining dust: Roads as sources and sinks *Environ Sci Technol* **27** 1892-1904.
- Rogge WF, Hildemann LM, Mazurek MA and Cass GR (1993b) Sources of fine organic Aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. *Environ Sci Technol* **27** 2700-2711.
- Rupprecht G, Patashnick H, Beeson DE, Green RN, and Meyer MB (1995) A new automated monitor for the measurement of particulate carbon in the atmosphere. In: *Particulate matter: health and regulatory issues. Proceedings of an international specialty conference, April 1995, Pittsburgh, PA.* Air and Waste Management Publications, Pittsburgh, PA pp 309-319
- Schmid H, Laskus L, Abraham HJ, Baltensperger U, Lavanchy V, Bizjak M, Burba P, Cachier H, Crowe D, Chow J, Gnauk T, Even A, ten Brink HM, Giesen K-P, Hitzenberger R, Hueglin C, Maenhaut W, Pio C, Carvalho A, Putard J-P, Toom-Sauntry D and Puxbaum H (2001) Results of the “carbon conference” international aerosol round robin test stage I. *Atmos Environ* **35** 2111-2121.
- Tohno S and Hitzenberger R (2000) Comparison of Ambient Carbon Particulate Monitor and filter sampling for black carbon measurement. *J Aerosol Sci* **31S** S315-S316
- Turpin BJ, Saxena P and Andrews E (2000) Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmos Environ* **34** 2983-3013

Vardoulakis S, Fisher BEA, Pericleous K and Gonzalez-Flesca N (2003) Modelling air quality in street canyons: a review. *Atmos Environ* **37** 155-182

LIST OF TABLES

- 1 Average daily traffic volumes at Marylebone Road
- 2 Mean particulate carbon concentrations measured at each site
- 3 Measurements of elemental and organic carbon using R&P 5400 monitors by other authors

LIST OF FIGURES

- 1 Monthly mean carbon particulate concentrations at each site (a) organic carbon; (b) elemental carbon
- 2 Regression of organic carbon particulate on elemental carbon particulate at each site (a) Harwell – rural; (b) North Kensington – urban background; (c) Belfast – urban centre; (d) Marylebone Road – kerbside
- 3 Directional profiles of the normalised concentrations of organic and elemental carbon particulate, PM_{10} and NO_x at each site (a) Harwell – rural; (b) North Kensington – urban background; (c) Belfast – urban centre; (d) Marylebone Road – kerbside (including CO)
- 4 The variation of organic carbon particulate concentration with PM_{10}

	west bound	east bound
Motor cycles	630	796
taxis (cars in bus lane)	5086	3918
buses	659	617
cars (excl bus lane)	26270	29917
lorries	3903	3263
All traffic	36548	38512

Table 1: Average daily traffic volumes at Marylebone Road

Site	Type of site	Organic carbon				Elemental carbon			
		Number of samples	Mean concentration [$\mu\text{g m}^{-3}$]	Standard deviation concentration [$\mu\text{g m}^{-3}$]	Geometric mean concentration [$\mu\text{g m}^{-3}$]	Number of samples	Mean concentration [$\mu\text{g m}^{-3}$]	Standard deviation concentration [$\mu\text{g m}^{-3}$]	Geometric mean concentration [$\mu\text{g m}^{-3}$]
Harwell	Rural	3641	1.79	2.26	1.27	3510	0.64	1.61	0.31
North Kensington	Urban background	2149	2.75	1.62	2.37	2149	0.86	0.78	0.65
Belfast Centre	Urban centre	4659	2.47	2.33	1.94	4665	1.10	1.51	0.69
Marylebone Road	Kerbside	4558	4.51	2.57	4.10	4558	3.38	2.26	2.69

Table 2: Mean particulate carbon concentrations measured at each site

Location	Site description	Particle size fraction	Organic carbon [$\mu\text{g m}^{-3}$]	Elemental carbon [$\mu\text{g m}^{-3}$]	Type of data	Reference
Melpitz, Germany	rural	<2.5 μm	-	0 – 1	range	ten Brink et al (2004)
New York, USA	urban	<2.5 μm	1.83 – 2.96	0.54 – 0.77	monthly means	Rattigan et al (2004)
Uji, Japan	urban	<2.5 μm	1.48 – 2.58	1.54 – 3.66	monthly means	Holler et al (2002)
K-puszta, Hungary	forest	<2.5 μm	7.1	0.5	mean	Molnar et al (1999)
Athens, Greece	urban	unspecified	4.96 – 8.32	1.52 – 3.91	monthly means	Prosmittis et al (2004)
Atlanta, USA	industrial /residential	<2.5 μm	7.93	2.0	mean	Lim et al (2004)
Rome, Italy	roadside	unspecified	5.7 – 10.6	7.6 – 11.8	monthly means	Avino et al (2000)

Table 3: Measurements of elemental and organic carbon using R&P 5400 monitors by other authors

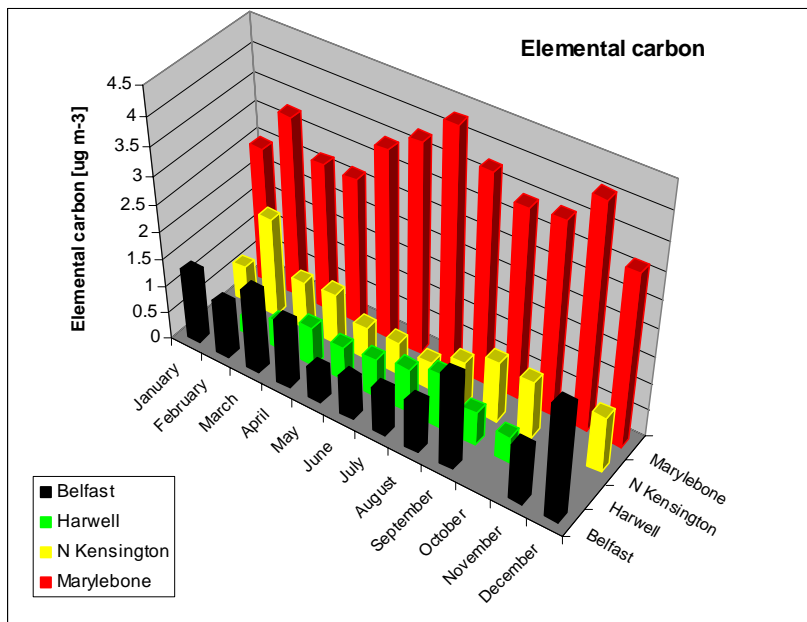
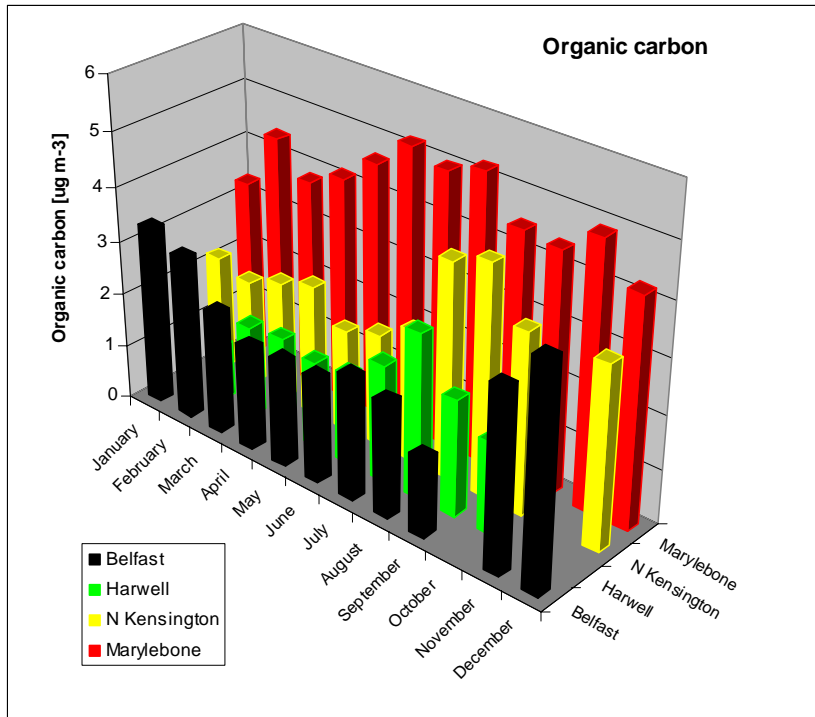


Figure 1: Monthly mean particulate carbon concentrations at each site (a) organic carbon; (b) elemental carbon

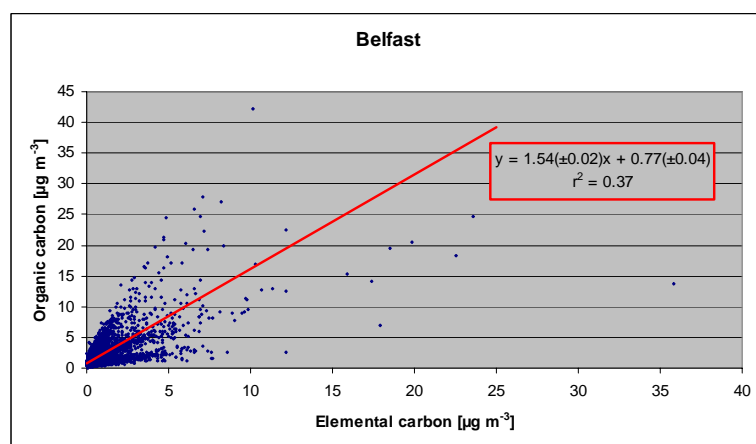
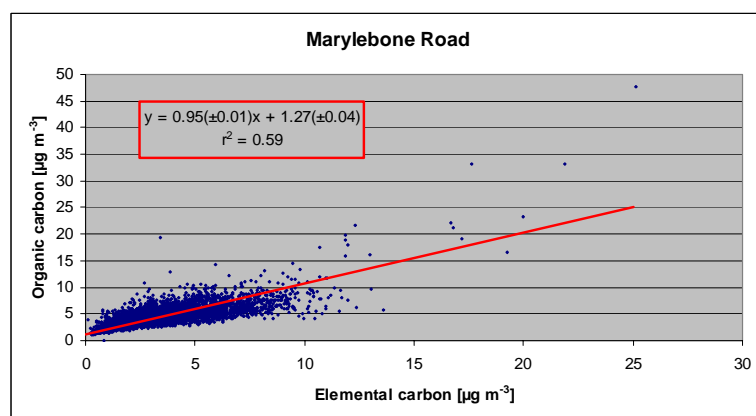
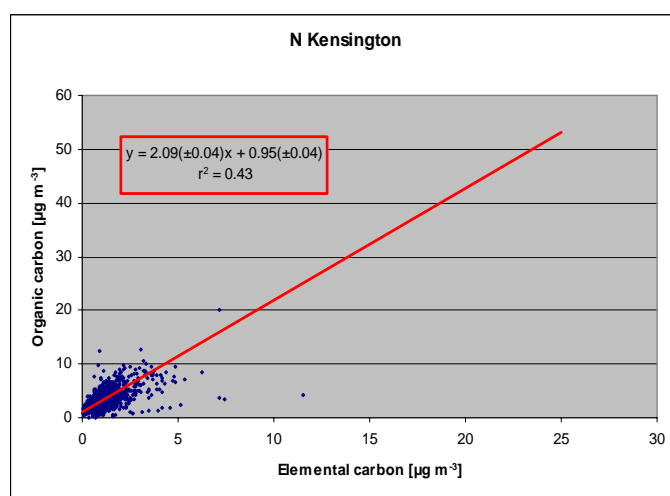
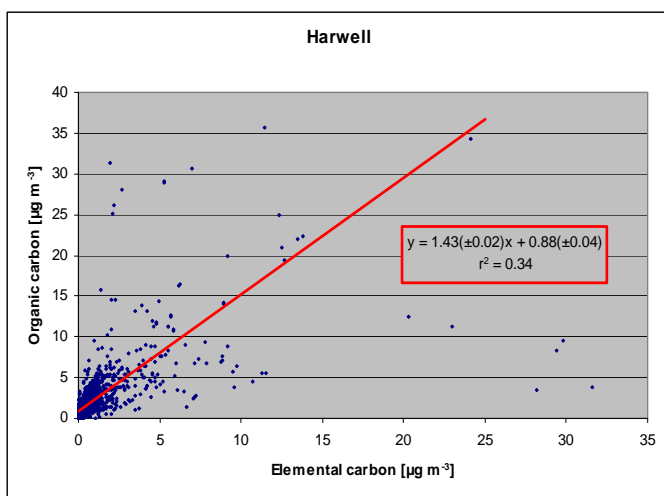


Figure 2: Regression of organic carbon particulate on elemental carbon particulate at each site (a) Harwell – rural; (b) North Kensington – urban background; (c) Belfast – urban centre; (d) Marylebone Road – kerbside

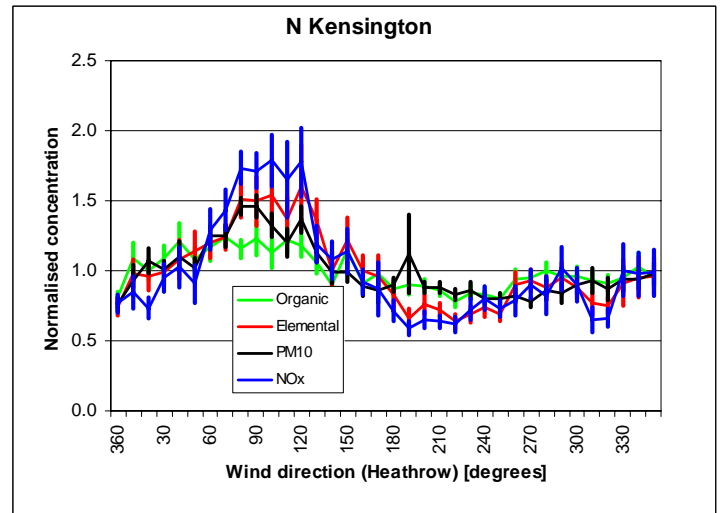
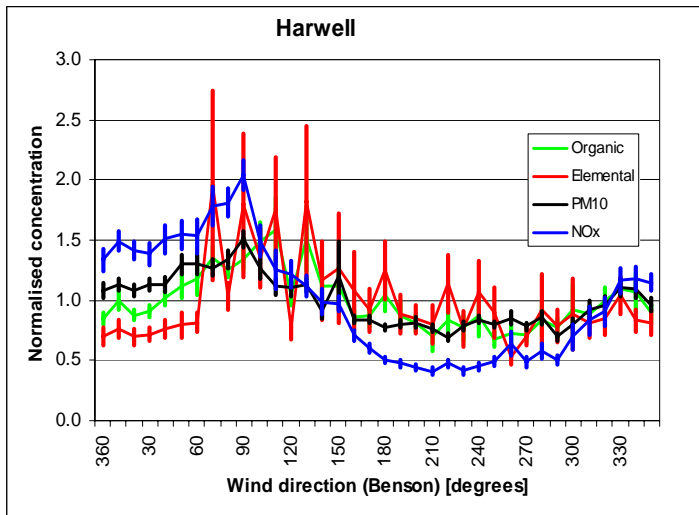
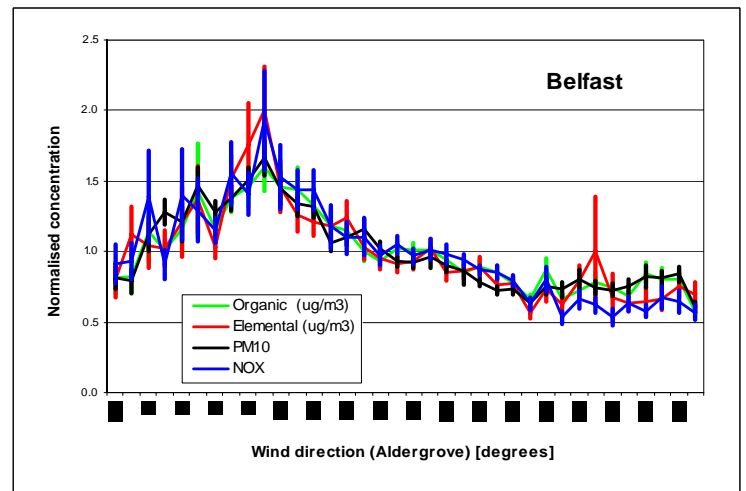
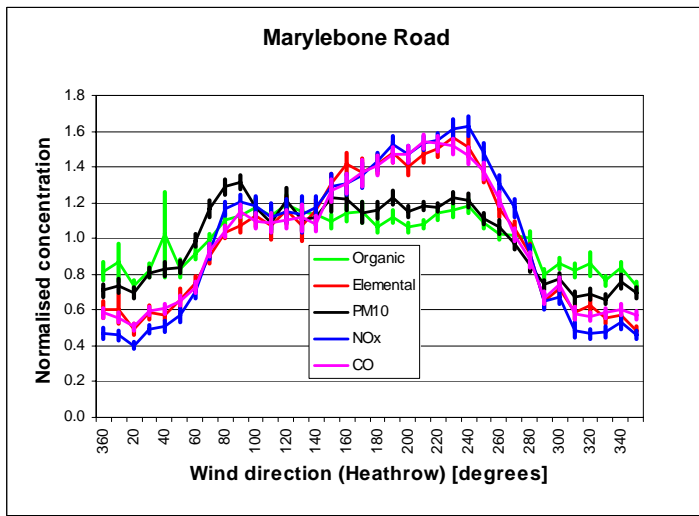


Figure 3: Directional profiles of the normalised concentrations of organic and elemental carbon particulate, PM_{10} and NO_x at each site (a) Harwell – rural; (b) North Kensington – urban background; (c) Belfast – urban centre; (d) Marylebone Road – kerbside (including CO)

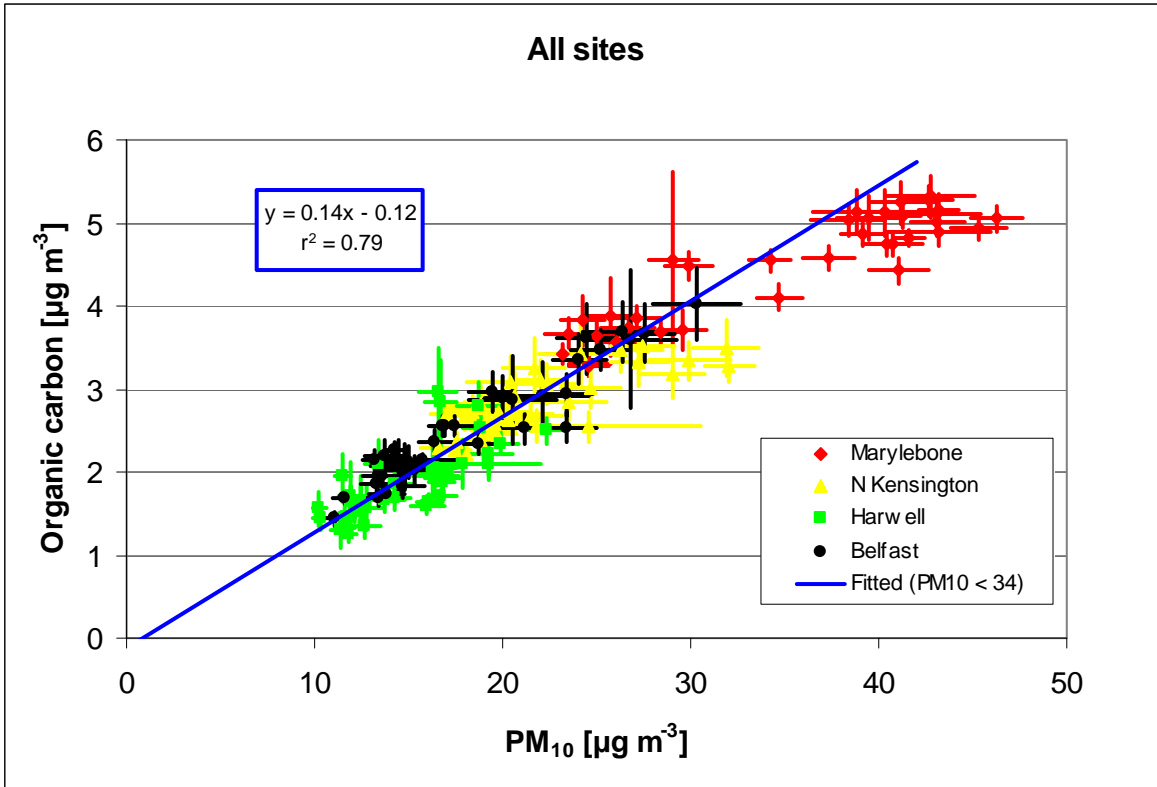


Figure 4: The variation of particulate organic carbon concentration with PM₁₀