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Application of ^{14}C analyses to source apportionment of carbonaceous PM[2.5] in the UK

Mathew R. Heal[1] *, Philip Naysmith[2], Gordon T. Cook[2], Sheng Xu[2],

Teresa Raventós Duran[3 †], Roy M. Harrison[3]

[1] *School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK*
[2] *Scottish Universities Environmental Research Centre, Scottish Enterprise Technology Park, East Kilbride, G75 0QF UK*
[3] *Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK*

[†] *Present address: Laboratoire Interuniversitaire des Systèmes Atmosphériques UMR 7583, Faculté des Sciences, Université Paris Est, 61 Avenue du Général Charles de Gaulle, 94010 Créteil Cedex, France*

* Corresponding author:
    Dr. M.R. Heal
    School of Chemistry,
    University of Edinburgh,
    West Mains Road
    Edinburgh,
    EH9 3JJ, United Kingdom
    Tel: 0131 6504764
    m.heal@.ed.ac.uk

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Abstract

Determination of the radiocarbon (^{14}C) content of airborne particulate matter yields insight into the proportion of the carbonaceous material derived from fossil and contemporary carbon sources. Daily samples of $PM_{2.5}$ were collected by high-volume sampler at an urban background site in Birmingham, UK, and the fraction of ^{14}C in both the total carbon, and in the organic and elemental carbon fractions, determined by two-stage combustion to CO_2, graphitisation and quantification by accelerator mass spectrometry. OC and EC content was also determined by Sunset Analyzer. The mean fraction contemporary TC in the $PM_{2.5}$ samples was 0.50 (range 0.27-0.66, $n = 26$). There was no seasonality to the data, but there was a positive trend between fraction contemporary TC and magnitude of SOC/TC ratio and for the high values of these two parameters to be associated with air-mass back trajectories arriving in Birmingham from over land. Using a five-compartment mass balance model on fraction contemporary carbon in OC and EC, the following average source apportionment for the TC in these $PM_{2.5}$ samples was derived: 27% fossil EC; 20% fossil OC; 2% biomass EC; 10% biomass OC; and 41% biogenic OC. The latter category will comprise in addition to BVOC-derived SOC other non-combustion contemporary carbon sources such as biological particles, vegetative detritus, humic material and tyre wear. The proportion of total $PM_{2.5}$ at this location estimated to derive from BVOC-derived secondary organic aerosol was 9 – 29%. The findings from this work are consistent with those from elsewhere in Europe and support the conclusion of a significant and ubiquitous contribution from non-fossil biogenic sources to the carbon in terrestrial aerosol.

Introduction

Organic carbon (OC) and elemental carbon (EC) together constitute a substantial fraction of airborne particulate matter, at least one-third on average in background fine particulate matter, $PM_{2.5}$, in the UK and elsewhere (AQEG, 2005; Harrison et al., 2003; Harrison and Yin, 2008; Putaud et al., 2004; Sillanpaa et al., 2006; Yin et al., 2010). This carbonaceous material is hard to characterise, not only because it comprises a vast array of individual chemical components and condensed material that are hard to separate and identify, but because even its apportionment into fractions labelled EC and OC is methodologically dependent (Chow et al., 2004a).

An important issue in both scientific and policy terms is the relative contributions of anthropogenic and biogenic sources to this carbonaceous component, in particular to the secondary organic aerosol (SOA) component for which there is currently least understanding. Natural and/or biogenic sources will not be readily amenable to control through deliberate policy action. Numerical modelling studies suggest that >80% of SOA in the UK atmosphere derives from biogenic precursors (Derwent and Malcolm, 2000; Whyatt et al., 2007) but this prediction has not been tested through any kind of atmospheric measurements. On the other hand, the modelling study of Johnson et al. (2006b; 2006a) found contributions of biogenic precursors to SOA to vary over the range 16–85% for a series of case studies in the TORCH 2003 campaign in the southern UK, with important contributions from both anthropogenic and biogenic precursors simulated for the majority of conditions.

The radioisotope of carbon (^{14}C) is an ideal tracer for distinguishing between fossil and contemporary carbon since the latter contains ^{14}C at a relatively known concentration (in excess of 226 Bq kg^{-1} of carbon) whereas the former, on account of its age far exceeding the half-life of ^{14}C, contains none. Thus, in principle, determination of the ratio of ^{14}C abundance in a sample of PM to its contemporary abundance directly yields the proportions of contemporary and fossil carbon in that sample. A challenge is the very high level of accuracy and precision to which the very low abundances of ^{14}C need to be determined. This requires the use of accelerator mass spectrometry (AMS) which is now being applied in this context to samples of atmospheric PM (Bench et al., 2007; Endo et al., 2004; Gelencser et al., 2007; Hodzic et al., 2010; Lewis et al., 2004; Schichtel et al., 2008; Szidat et al., 2004a; Szidat et al., 2006; Szidat et al., 2009). The vast majority of these AMS measurements have been

applied to the total carbon (TC) content only. In this work, the first of its kind in the UK, the contemporary/fossil split has been determined in the TC, and OC and EC, components of samples of $PM_{2.5}$ collected at an urban background location in Birmingham. Such data has previously been determined only for two locations: Zürich (Szidat et al., 2006) and Göteborg (Szidat et al., 2009). A subsequent mass balance approach permits a top-down apportionment of the broad categories of origin of the $PM_{2.5}$ carbon.

Methods

Sample collection
Seventy-five samples were collected during two periods, 11 Jun – 1 Sep 2007 and 21 Jan – 9 May 2008, at an urban background site at the University of Birmingham (52° 27′ N, 1° 56′ W). Birmingham is the second largest city in the UK (population 1.0 million) and lies within the West Midlands conurbation of 2.2 million. The University campus has a suburban setting in the south east of the city (Figure S1, supplementary information). 24-hour samples of $PM_{2.5}$ were collected by high-volume sampler (Tisch Environmental TE-6001 fitted with TE-230-QZ impactor), at flow rates of 1.137 m^3 per minute, onto 20.3 × 25.4 cm quartz microfiber filters (Whatman QM-A sheets) pre-heated at 550 °C for 12 hours. Following exposure, filters were folded in half, exposed side inwards, and stored wrapped in Al foil at −20 °C.

OC and EC analysis
Punches from each filter (1.5 cm^2) were analysed for OC and EC content by Sunset Analyzer (Tigard, USA) using the temperature protocol detailed in supplementary information Table S1.

Determination of ^{14}C content
One-quarter portions of the filters from a sub-set of 26 of the $PM_{2.5}$ samples (2, 3 & 8 from Jun, Jul and Aug 07, respectively, and 1, 3, 4, 3 & 2 from months Jan to May 08, respectively) were analysed for their 'fraction modern carbon' (f_M). This is an international convention that expresses sample ^{14}C activity relative to the activity of wood growing in the northern hemisphere in 1890, prior to the significant changes in atmospheric concentrations of ^{14}C that occurred in the 20th century from the worldwide increase in fossil-fuel burning and nuclear

weapons detonation. Fraction modern values can be converted into more useful fraction contemporary carbon, f_c, using knowledge of recent variations in atmospheric ^{14}C abundance and assumptions regarding the age of material contributing to the ^{14}C in the sample. This is discussed in more detail later. It is assumed that inorganic carbonates make negligible contribution to carbon in UK $PM_{2.5}$ compared with OC and EC (AQEG, 2005).

Samples were prepared for AMS analysis using two combustion steps (Figure 1), similar to the methodology developed by Szidat and co-workers (Szidat et al., 2004a; 2004b; 2004c). In the first step the filter was heated in a sealed quartz chamber with pure O_2 for 20 min at 340 °C. The evolved CO_2 was collected and purified offline, first by combustion at 850 °C in the presence of CuO and Ag, then by passage through an ethanol/solid CO_2 cold trap (−80 °C) to remove water vapour followed by a liquid nitrogen trap (−196 °C) in tandem with cryogenic pumping to remove any non-condensing contaminants. The purified CO_2 was quantified manometrically. The CO_2 was then reduced to graphitic C and pressed into aluminium holders (AMS target) for AMS measurement. For samples of CO_2 >3 mL the method of Slota et al. (1987) was employed for graphitisation and $\delta^{13}C$ values were measured off-line on a sub-sample of CO_2 using a VG SIRA 10 isotope ratio mass spectrometer. For samples smaller than 3 mL the method of Xu et al. (2007) was employed for graphitisation and $\delta^{13}C$ values were measured on-line on the AMS. The f_M value from this first step is taken to represent the overall OC activity as demonstrated by Szidat et al. (2004c). In the second step, the filter was combusted in O_2 for 4 h at 850 °C and the evolved CO_2 subject to the same cryogenic purification and graphitisation procedures for generation of the AMS target. The f_M value from this step is the contribution of any remaining OC activity and the EC activity.

The f_M value in each graphitic target, relative to the international Oxalic Acid II (OXII) standard (SRM-4990C), was determined using either the SUERC National Electrostatics Corporation tandem-accelerator mass spectrometer which is based on a 5 MV Pelletron or the single-stage accelerator mass spectrometer. The instruments differ in their ion optics (including source geometries), ion energies and molecular interference removal, but produce similar data (Freeman et al., 2010) and long-term QA documentation indicates no significant difference in ^{14}C results from the two instruments (Naysmith et al., 2010). Each batch of samples (typically around 130) run on the AMS is split into sub-groups of 10 targets. Samples are measured to completion in groups of 10 in only a few hours, with OXII primary standards spanning groups for inter-group consistency. Each group of 10 samples contains

one OXII primary standard, one wood secondary standard of just less than one half-life in age, either a modern secondary standard material or a background standard (i.e. a zero ^{14}C activity sample derived from either calcite mineral or interglacial wood with an age in excess of 100,000 years) and 7 unknowns. Each sample is automatically repeatedly measured in intra-group rotation until the sample total counting statistics and the scatter of the repeat ^{14}C/^{13}C measurements exceeds a quality threshold of typically 3‰□, disregarding early inconsistent measurements as necessary. Any time trends remaining in the completed data sets can be compensated for in subsequent data reduction and normalization.

Blank quartz filters (both direct from the packet and passed through the PM$_{2.5}$ sampler) processed in the same manner contained insignificant amounts of carbon compared with sample filters so no filter blank adjustment was required.

The value of f_M for total carbon was derived by mass and activity balance (Equation 1), where the F quantities are the mass fractions of TC evolved at each combustion step.

$$f_M(TC) = f_M(340^0 C) \times F(340^0 C) + f_M(850^0 C) \times F(850^0 C) \qquad \text{Eqn. 1}$$

In this study, two independent quantifications of the TC content of each PM$_{2.5}$ sample are available, from the CO_2 evolved during preparation for AMS analysis and from the Sunset Analyzer. The scatter plot shown in Figure 2 demonstrates excellent quantitative agreement between the two sets of measurements ($R^2 = 0.94$, gradient 1.0, non-significant intercept) and provides additional assurance in the cumulative combustion approach used for the determination of ^{14}C in TC.

A value for $f_M(EC)$ was determined by the mass and activity balance in Equation 2, where $F_{Sunset}(OC)$ and $F_{Sunset}(EC)$ are the mass fractions of TC defined as OC and EC, respectively, according to the Sunset Analyzer determinations.

$$f_M(EC) = \frac{f_M(TC) - f_M(340^0 C) \times F_{Sunset}(OC)}{F_{Sunset}(EC)} \qquad \text{Eqn. 2}$$

Analysis of standard reference material

Results from analysis of NIST urban dust standard reference material SRM-1649a by the same procedures are given in Table 1. This is the only PM material for which there are published ^{14}C data against which to compare. The $f_M(TC)$ values of 0.515 and 0.570 obtained

here (via single and double combustion, respectively) are within the range 0.505–0.61 provided by NIST (Currie et al., 2002; NIST, 2007), as is the value 0.522 presented by Szidat et al. (2004c).

The assignment of the split between OC and EC for particulate matter carbon remains a methodologically-defined quantity (Chow et al., 2004a). The extent to which this is so is illustrated by the greater than 6-fold range in EC/TC mass ratios (0.075 to 0.52) from 19 different methods or research groups which have been collated for SRM-1649a (Currie et al., 2002; NIST, 2007). Consequently it must be accepted that the two-staged combustion separation of OC and EC used in this work (Figure 1) represents one approach only to defining an OC-EC divide. The approach adopted here was guided by the work of Szidat et al. (2004c) who reported that whilst the OC/TC mass ratio increased as the first combustion temperature (or time) was increased the $f_M(OC)$ value remained unchanged. Presumably as a consequence of the inherent methodological differences, NIST do not provide a value for $f_M(OC)$ in SRM-1649a, so the only available comparison for the value of 0.66 ± 0.02 obtained in this work is with the value 0.70 ± 0.05 reported by Szidat et al. (2004c) (Table 1). Although the two research teams have used similar methods, the extremely good agreement between the two values nevertheless provides considerable confidence in the consistency of measurements. NIST do provide values for $f_M(EC)$ in SRM-1649a (Table 1) although the mean values for groupings of similar measurement methods span the range 0.065 to 0.153. In this work, combining the ^{14}C determinations from the two combustion stages with data on OC-EC split from the Sunset Analyzer yields a value of $f_M(EC) = 0.15$. This is within the range provided by NIST, somewhat higher than the value of 0.066 reported by Szidat et al. (2004c), but uncertainty estimates are large.

Results and discussion

Secondary organic carbon
The $PM_{2.5}$ TC concentrations varied between 1.2 and 26.2 µg m^{-3} ($n = 75$) and exhibited no seasonality. Apportionment of the OC content of each sample into primary organic carbon (POC) and secondary organic carbon (SOC) was undertaken using the assumption that the minimum OC/EC ratio observed across all sample data indicates the (OC/EC)$_{primary}$ value applicable to that sampling location, as demonstrated in Figure 3 (Castro et al., 1999;

Harrison and Yin, 2008). The individual sample SOC/TC ratios varied between 0 and 0.68, and likewise exhibited no temporal pattern (Figure S2, supplementary information).

Four-day air-mass back trajectories corresponding to arrival at the sampling location at the mid-time of each sample collection were calculated using the trajectory facility at the British Atmospheric Data Centre (www.badc.ac.uk). Sampling days were divided into groups according to the four geographical sectors from which the air mass had originated, with days on which air-mass origin was in the westerly sector (SW to NW) being further sub-divided into 'Atlantic fast' and 'Atlantic slow' to separate long-range westerlies from trajectories of slower, circulating air in the near-Atlantic vicinity of the British Isles. Illustrative trajectories for each group are shown in Figure S3, supplementary information. Both TC concentration and SOC/TC ratio differed significantly with air-mass trajectory grouping (Figure 4), with both metrics being higher on average for the easterly and southerly trajectories travelling extensively over land. TC concentration and SOC/TC ratio were also greater for northerly trajectories passing over the UK than for Atlantic westerlies.

^{14}C data

f_M values were converted to fraction contemporary carbon (f_c) by dividing by 1.08. The ratio of ^{14}C activity relative to 'modern' in organic material photosynthesised around the time of sample collection is about 1.05 (Levin et al., 2008), which will apply to PM carbon derived from biogenic VOC emissions or from biofuel blends derived from recent-grown crops. The ratio is about 1.15 for tree wood ~30-50 years old (Szidat et al., 2009) since past atmospheric $^{14}CO_2$ levels were much higher (maximum atmospheric $^{14}CO_2$ value occurred in 1963). The value 1.08 was chosen as between these two, but weighted based on the expectation from previous similar studies (Szidat et al., 2006; Szidat et al., 2009) that the majority of the non-fossil carbon in these samples is derived from truly contemporary sources rather than from 50 y old biomass. The sensitivity of the results to this choice is discussed later.

The values for fraction contemporary total carbon, $f_c(TC)$, in the $PM_{2.5}$ samples analysed ranged from 0.27 to 0.66 ($n = 26$) with mean 0.50 (median 0.51). Again there was no seasonality to the data. However, $f_c(TC)$ was positively associated with the SOC/TC ratio, and consequently also (as described above) with air-mass origin (Figure 5); larger values of $f_c(TC)$ were associated with samples collected on days with slower air masses from the east and south continental regions. These observations are consistent with the hypothesis that

secondary organic aerosol generation relies on substantive contribution from terrestrial contemporary carbon sources, e.g. BVOC emissions.

The mean non-fossil fraction TC of ~50% for these urban background $PM_{2.5}$ samples from Birmingham are entirely in line with the few comparative studies elsewhere in Europe: $f_c(TC)$ ~50−60% for urban background PM_{10} in Zürich (Szidat et al., 2004b; 2006), and mean $f_c(TC)$ ~50% for urban background PM_{10} and $PM_{2.5}$ in Göteborg (Szidat et al., 2009). For samples of $PM_{2.5}$ collected at five remote and rural sites in the European CARBOSOL project, $f_c(TC)$ values were higher, in the range ~57-82% (Gelencser et al., 2007), presumably reflecting greater contribution of biogenic carbon at these non-urban locations. In the US, Schichtel et al. (2008) similarly report $f_c(TC)$ values of ~50% for $PM_{2.5}$ collected at urban sites within the IMPROVE network, rising to 70-97% at non-urban locations. Altogether, these studies confirm a ubiquitous presence of contemporary carbon in PM.

For all samples $f_M(EC) < f_M(OC)$, indicating greater fossil-fuel contribution to the more recalcitrant, soot-like carbonaceous material. Mean $f_M(OC)$ was 0.76 ($n = 26$), with range 0.57−0.99 (not including one low outlier). These are consistent with the few other published data: $f_M(OC)$ values in the range 0.55−0.95 ($n \approx 8$) for PM_{10} in Zürich (Szidat et al., 2006), and in the range 0.59−0.78 ($n = 7$) for PM_{10} and $PM_{2.5}$ in Göteborg (Szidat et al., 2009). A general observation from these studies is for $f_M(OC)$ to be fairly constant (i.e. generally in excess of ~0.6) over wide variations in OC concentration and OC/TC or SOC/TC ratios. Mean $f_M(EC)$ was 0.11, or 0.087 if excluding one sample with a high value of 0.64. As discussed later $f_M(EC)$ values are subject to particular uncertainty and where negative $f_M(EC)$ values were derived these were set to zero. Values were generally lower than the mean $f_M(EC)$ of 0.31, 0.14 and 0.07 for winter, spring and summer PM_{10}, respectively, in Zürich (Szidat et al., 2006) and of 0.12 for PM_{10} and $PM_{2.5}$ in Göteborg (Szidat et al., 2009), indicating low contributions of contemporary carbon to EC at the Birmingham location.

Source attribution
Contributions of five broad categories of carbon sources to individual samples were attributed as illustrated in the following example application to data for the sample from 22nd February 2008. The EC and OC concentrations for this sample were 0.59 and 1.47 μg m^{-3}, respectively, and it was assigned to the 'Atlantic fast' grouping of air mass origin. Fraction contemporary

carbon values were $f_c(TC) = 0.543$, $f_c(OC) = 0.733$ and $f_c(EC) = 0.064$. The contemporary-fossil split for the EC component can be assigned directly from the ^{14}C data as follows:

$$EC_{biomass} = 0.064 \times 0.59 = 0.038 \ \mu g \ m^{-3}$$

and

$$EC_{fossil} = 0.55 \ \mu g \ m^{-3}$$

Here, the designation 'biomass' in the subscript encompasses EC emanating from deliberate combustion of solid and liquid biofuels as well as from natural wildfires. If it is assumed the latter source generally makes negligible contribution to UK EC, then the $EC_{biomass}$ component derives from primary anthropogenic sources.

The OC component can be sub-divided into three broad categories,

$$OC_{total} = OC_{fossil} + OC_{biomass} + OC_{biogenic}$$

where OC_{fossil} is most likely POC from fossil-fuel combustion but could include SOC formed from emissions of fossil-derived VOC, $OC_{biomass}$ designates POC from combustion of biofuels/biomass, and $OC_{biogenic}$ designates SOC formed from biogenic VOC oxidation (and other unaccounted for contemporary carbon – see later discussion). The OC_{fossil} contribution is calculated directly from the ^{14}C data:

$$OC_{fossil} = (1 - 0.733) \times 1.47 = 0.39 \ \mu g \ m^{-3}$$

The concentration of $OC_{biomass}$ can be estimated using an assumed $(OC/EC)_{biomass}$ primary emission ratio. Using a value of 5 here (Chow et al., 2004b) gives

$$OC_{biomass} = 0.038 \times 5 = 0.19 \ \mu g \ m^{-3}$$

The $OC_{biogenic}$ concentration is then derived by mass balance of contemporary OC:

$$OC_{biogenic} = (0.733 \times 1.47) - 0.19 = 0.89 \ \mu g \ m^{-3}$$

The attribution is illustrated in the pie-chart of Figure 6a. A contrasting example apportionment for 31st Jan 2008, for which EC = 0.75 $\mu g \ m^{-3}$, OC = 0.74 $\mu g \ m^{-3}$, fc (TC) = 0.380, $f_c(OC) = 0.684$ and $f_c(EC) = 0.082$ is shown in Figure 6b.

The mean % apportionment of TC across all 26 samples into the five categorisations described above is, to nearest integer value: 2% biomass EC; 27% fossil EC; 20% fossil OC; 10% biomass OC; 41% biogenic OC (Figure S4, supplementary information). This mean relative apportionment for the Birmingham samples is compared in Figure 7 with that for Zürich (Szidat et al., 2006) and Göteburg (Szidat et al., 2009), derived using similar methods.

The apportionments are broadly similar, although the two mainland European cities are strongly influenced by wood burning in winter, not present in the summer samples, nor in the Birmingham data which do not show seasonality. Little seasonality in wood-smoke contribution to $PM_{2.5}$ at this site was also reported by Yin et al. (2010). The Birmingham samples have highest EC/TC ratios on average (0.30), as anticipated for the larger and more-heavily trafficked city, and again consistent with other measurements at this site (Yin et al., 2010).

The above source attributions must be interpreted in the context of a number of caveats and uncertainties. As described in the methods section, the apportionment of TC into OC and EC fractions is highly method dependent as evidenced by a >4-fold variation in EC/TC ratios and EC ^{14}C abundances presented for the airborne PM SRM-1649a (Currie et al., 2002). To proceed with any apportionment of OC and EC fractions requires some decision to be made on the OC-EC division which means that all such studies such derive f_M values that are linked to their method. In this work the Sunset Analyzer protocol (Table S1) was used to assign OC-EC split, with mass activity Equation 2 used to derive $f_M(EC)$, coupled with the information from Szidat et al. (2004c) that $f_M(OC)$ remain unchanged with first combustion temperature (or time). Following a method similar to that pioneered by Szidat and co-workers ensures a basis for comparability between the studies shown in Fig. 7. In the majority of cases the fraction OC-EC assignments via Sunset or AMS preparative protocols were similar. While this appeared to work well for SRM-1649a the calculation yielded negative values for some EC which is not possible. The $f_M(EC)$ is subject to large uncertainty because it is a small value difference between two much larger values. However, because $f_M(EC)$ is generally considerably lower than $f_M(OC)$ its higher uncertainty actually has reduced practical consequence; i.e. since average proportion TC assigned as $EC_{biomass}$ through use of $f_M(EC)$ is only 2%, even fairly large uncertainty does not alter the overall picture that $EC_{biomass}$ is a very minor component of TC.

The instrumental uncertainty in the AMS-derived values of f_M is small but uncertainty is introduced in the correction to f_c values. A conversion factor of 1.08 was used here, for the reasons given above. The relatively large 'biogenic' source from the source-apportionment modelling justifies the choice of a factor close to the value 1.05 for wholly contemporary carbon. It is not possible to know the exact correction value since this depends on the mix of non-fossil carbon sources to the $PM_{2.5}$ which is not known and will vary from sample to

sample. Varying the conversion factor between 1.08 and its possible range of 1.05 to 1.15 (the extremes that all non-fossil carbon is entirely contemporary or entirely mature tree-wood, respectively) corresponds to uncertainty factors in the point estimate of proportion contemporary ranging from 0.94 to 1.03, i.e. to uncertainty ranges of 1.9-2.1% for the 2% average $EC_{biomass}$ portion, and of 26.9-27.1% forthe 27% average EC_{fossil} portion, entirely negligible compared with other uncertainties. Similarly, applying the same uncertainty in f_M to the 20% average OC_{fossil} assignment yields an uncertainty range of 18.5-23.1%.

The assignment to $OC_{biomass}$ is defined to be a fixed multiple of the derived $EC_{biomass}$ value. Whilst a single value for an $(OC/EC)_{biomass}$ primary ratio must be chosen for this analysis, it is clearly highly unlikely that a single value for this ratio is applicable for all conditions. Chow et al. (2004b) report a range 2.5–10 for this ratio. Use of other values for this ratio in the above analysis would alter the assigned split between what is classified as $OC_{biomass}$ and $OC_{biogenic}$ although the sum of the two contributions would be unchanged. Since $EC_{biomass}$ (and hence $OC_{biomass}$) are minor contributions to TC, the uncertainty in this ratio, whilst certainly important, does not fundamentally alter the general pattern of source attribution. Combining the worse cases from the uncertainties in $EC_{biomass}$ due to uncertainty in f_M and in $(OC/EC)_{biomass}$ ratio, gives a lower uncertainty for $OC_{biomass}$ of $1.9\% \times 2.5 = 4.8\%$ and an upper uncertainty of $2.1\% \times 10 = 21\%$. The $OC_{biogenic}$ portion is calculated by difference so again combining the worse cases of both uncertainties gives a lower uncertainty for $OC_{biogenic}$ of $71\%-23.1\%-21\% = 26.9\%$ and an upper uncertainty of $71\%-18.5\%-4.8\% = 47.7\%$.

To summarise, the point estimate and uncertainty ranges for the mean apportionments into the 5 categories presented in Figs. S4 and 7 are $EC_{biomass}$ 2% (1.9-2.1%), EC_{fossil} 27% (26.9-27.1%), OC_{fossil} 20% (18.5-23.1%), $OC_{biomass}$ 10% (4.8-21%) and $OC_{biogenic}$ 41% (26.9-47.7%). As with any similar work, these values are based on the methodological split of TC into OC and EC used. The ranges represent the extreme ends of estimated uncertainty from the two sources discussed, and will only come about if analyses of all 26 samples were subject to identical bias. In practice, there will be some tendency for uncertainties to cancel when averaging across 26 samples, so the extremes in these uncertainty ranges for mean apportionments are much less likely than values closer to the central estimate. It should also be noted that apportionments between individual samples vary and that it is not possible to quantify any bias due to the 26 samples analysed not being representative of the long-term

average contributions of these sources to $PM_{2.5}$ at this sampling location. This latter comment applies to all studies involving relatively few samples.

If there is a 'wildfire' biomass burning contribution to $EC_{biomass}$ then the current assignment to $EC_{biomass}$ could be further subdivided into $EC_{biomass}$(biofuel) and $EC_{biomass}$(wildfire). The current $OC_{biomass}$ assignment would also be subdivided into $OC_{biomass}$(biofuel) and $OC_{biomass}$(wildfire). Whether the latter two sub-divisions would still sum to the magnitude of the current $OC_{biomass}$ assignment would depend on assumed OC/EC primary emission ratios for the anthropogenic combustion of biomass/biofuel and wildfire burning of biomass. These ratios are unlikely to be universally-applicable single values, as already discussed. However, it is not anticipated that natural wildfire contributes significantly to UK PM carbon on average.

It is not possible from the data to subdivide the assignment to OC_{fossil} between primary and secondary. The latter would encompass SOC derived from atmospheric oxidation of, for example, fossil-derived toluene. Its presence would mean that the current assignment to OC_{fossil} would be divided into POC_{fossil} and SOC_{fossil} components: no other assignments would be altered. However, EC_{fossil} and POC_{fossil} are likely to have a common local source, particularly for an urban sampling location. Previous measurements in Birmingham have inferred primary OC/EC ratios in the $PM_{2.5}$ size fraction of 0.4 at a roadside location and 0.65 at a city centre background location (Harrison and Yin, 2008). The $(OC/EC)_{primary}$ ratio inferred from this work at a more suburban background location in Birmingham is 1.1 (Figure 3), similar to the ratio 1.0 derived from other $PM_{2.5}$ measurements at the same site (Yin et al., 2010). These data show a gradient of increasing $(OC/EC)_{primary}$ on moving away from the immediate roadside. It is therefore reasonable to anticipate that the POC_{fossil}/EC_{fossil} ratio at this sampling location is also in the approximate range 0.7–1. Comparison of the magnitudes of the EC_{fossil} and OC_{fossil} contributions in Figure 7 with this estimated POC_{fossil}/EC_{fossil} ratio therefore suggests that the bulk of the contribution assigned to OC_{fossil} is comprised of POC_{fossil} rather than SOC_{fossil} at this site. However, the atmospheric processing of semi-volatile emissions in moving away from roadside sources to background sites leads to a blurring of distinction between POC and SOC anyway (Robinson et al., 2007).

The category designated $OC_{biogenic}$ will include, in addition to BVOC-derived secondary organic carbon, other sources of non-fossil OC not explicitly allocated to biomass/biofuel

combustion. These may include primary biological material such as viruses, spores, pollen plant detritus and particle-bound carbohydrates, amino acids and endotoxin, as well as particles derived from vehicle tyre wear (where tyres are composed of natural rubber) and cigarette smoke. The category may also include some OC from food cooking although this latter may form part of the category assigned as 'biomass.' The magnitudes of the contributions of these sources to individual size fractions of PM OC remains highly uncertain, and their determination requires identification and quantification of specific marker components. Despite this, it is reasonable to anticipate that the portion of TC in these Birmingham samples that is BVOC-derived SOC, although still likely a significant component, is somewhat lower than the 41% on average shown in Figure 7. Using chemical markers and a chemical mass balance model based on USEPA source profiles Yin et al. (2010) estimated a few % contribution each from 'vegetative detritus' and 'soil/dust' humic material to other samples of $PM_{2.5}$ from the same location. Thus, even if $OC_{biogenic}$ were in reality split into, say, 29% $OC_{BVOC\text{-}SOC}$ and 12% $OC_{other\text{-}contemporary}$ (using rough estimates provided also by Hodzic et al. (2010)), the BVOC-derived SOC still comprises $29/71 \cong 40\%$, on average, of all OC at this Birmingham location. This is comparable to the estimated 33% contribution to OC, on average, ascribed by the chemical mass balance model to 'other organic matter' – assumed to be secondary organic aerosol – in the Yin et al. (2010) study. Biogenic SOC therefore appears to dominate anthropogenic SOC, in support of earlier model studies for the UK (Whyatt et al., 2007). Szidat et al. (2006), using additional evidence from ^{14}C analyses of water-soluble OC, also concluded that biogenic SOC considerably exceeded anthropogenic SOC in Zürich.

Overall, therefore, this and other studies cited confirm the ubiquitous presence of background SOC (Zhang et al., 2007) and the predominance of biogenic SOC over anthropogenic SOC, particularly for air masses passing over land where, in addition to sources of BVOC precursors, anthropogenic emissions of NO_x facilitate its formation (Carlton et al., 2010).

A pertinent policy issue is to express the component assigned as BVOC-derived SOC as a proportion of total $PM_{2.5}$. To do so requires both the $PM_{2.5}$ mass and an appropriate scaling factor from mass of SOC to mass of secondary organic matter (SOM). The former was not determined directly from the hi-vol filter samples collected in this study. However, a co-located FDMS TEOM with $PM_{2.5}$ inlet was operating during the first period of the sample collection (Jun-Aug 2007). For the 13 dates during this period for which apportionment via

[14]C was made, the average ratio of BVOC-derived SOC to $PM_{2.5}$ was 0.09. In their pragmatic mass closure model, Harrison et al. (2003) assumed an OM/OC ratio of 1.4 for urban background PM_{10} in Birmingham. However, recent literature suggests earlier values used for OM/OC may be rather too low, particularly for the more heavily oxidised secondary organic aerosol component, for which OM/OC ratios in the approximate range 1.5-2.4 have been reported (e.g. Aiken et al., 2008; Chan et al., 2010; El Zanan et al., 2009; Polidori et al., 2008; Simon et al., 2010). Taking the mid-point of this range (2.0) as the OM/OC ratio for this SOC component yields a proportion ~18%, on average, of the total mass of $PM_{2.5}$ at this location comprising BVOC-derived secondary organic aerosol. Note this 18% proportion excludes the estimated contribution to $PM_{2.5}$ from other non-combustion sources of contemporary carbon such as vegetative detritus, humic material, tyre particles. It is also derived from only half the samples analysed, although other analyses presented here have not demonstrated systematic difference in average apportionment with season of sampling. An alternative estimate for proportion of $PM_{2.5}$ that is BVOC-derived secondary organic aerosol can be obtained by expressing the average concentration of BVOC-derived SOC from all 26 analysed samples (1.0 $\mu g\ m^{-3}$) relative to the long-term mean $PM_{2.5}$ of 11.6 $\mu g\ m^{-3}$ determined by Yin et al. (2010) from the same site for the immediately preceding year. Applying, as before, a value 2.0 to scale OC to OM yields ~16% as the proportion of $PM_{2.5}$ mass estimated to be attributable, on average, to BVOC-derived secondary organic aerosol.

Whilst both these estimates are consistent it should be remembered that they are averages and that proportions in individual daily samples will vary considerably around this average. In addition, the values are clearly subject to the same source attribution assumptions that are discussed at length in this paper. Varying the assumed OM/OC scaling between 1.5 and 2.4 gives an uncertainty range of 13–21 % for the contribution of BVOC-derived SOA to $PM_{2.5}$. Including uncertainty in the split of non-combustion contemporary carbon between BVOC-derived SOC and other types (vegetative detritus, etc.) over the range from 50:50 to 100:0 (earlier calculations assumed 70:30 as an average point-estimate) increases the uncertainty range for the contribution of BVOC-derived SOA in $PM_{2.5}$ to 9–29 %. As with other estimates of uncertainty ranges the true average is more likely to be towards the centre of this range than the extremes.

Finally, it is worth noting again the problem of OC-EC distinction and its consequence that attempting to assign a single value of f_c to a single entity called OC (and likewise for EC) is

both uncertain and of limited interpretive use. If it is recognised that the ideal of a 'clean' binary physical separation into OC and EC is not possible, an alternative methodological approach to gain insight into the contemporary carbon contributions to different components within TC might be more fruitful. This could be achieved by solvent extraction of the PM with staged combustion, to yield f_c values of the components of TC categorised quasi 2-dimensionally according to volatility and polarity.

Conclusions

This study has shown that a substantive proportion (~50% on average) of UK urban background $PM_{2.5}$ carbon is of contemporary origin. The largest component of this contemporary carbon has been ascribed to BVOC-derived SOC, although a proportion has been assigned as contemporary POC from anthropogenic combustion of biofuel/biomass and a further portion to other non-combustion contemporary sources such as biological particles, vegetative detritus, humic material and tyre-wear resuspension. The study confirms the ubiquitous presence of background biogenic SOC, particularly for air masses passing over land. It is proposed that separation of the $PM_{2.5}$ according to polarity and volatility may provide more useful and less method dependent information than is gained from attempting an OC-EC split.

References

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., et al , 2008. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. Environmental Science & Technology 42, 4478-4485.

AQEG, 2005. Particulate Matter in the United Kingdom. Second report of the Air Quality Expert Group, UK Department for Environment, Food and Rural Affairs, PB10580, London.

Bench, G., Fallon, S., Schichtel, B., Malm, W., McDade, C., 2007. Relative contributions of fossil and contemporary carbon sources to PM 2.5 aerosols at nine Interagency Monitoring for Protection of Visual Environments (IMPROVE) network sites. Journal of Geophysical Research 112, D10205, doi:10.1029/2006JD007708.

Carlton, A. G., Pinder, R. W., Bhave, P. V., Pouliot, G. A., 2010. To What Extent Can Biogenic SOA be Controlled? Environmental Science & Technology 44, 3376-3380.

Castro, L. M., Pio, C. A., Harrison, R. M., Smith, D. J. T., 1999. Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. Atmospheric Environment 33, 2771-2781.

Chan, T. W., Huang, L., Leaitch, W. R., Sharma, S., Brook, J. R., Slowik, J. G., Abbatt, J. P. D., Brickell, P. C., Liggio, J., Li, S. M., Moosmuller, H., 2010. Observations of OM/OC and specific attenuation coefficients (SAC) in ambient fine PM at a rural site in central Ontario, Canada. Atmospheric Chemistry and Physics 10, 2393-2411.

Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., Moosmuller, H., 2004a. Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. Environmental Science & Technology 38, 4414-4422.

Chow, J. C., Watson, J. G., Kuhns, H., Etyemezian, V., Lowenthal, D. H., Crow, D., Kohl, S. D., Engelbrecht, J. P., Green, M. C., 2004b. Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol Visibility and Observational study. Chemosphere 54, 185-208.

Currie, L. A., Benner, B. A., Kessler, J. D., et al , 2002. A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in the carbonaceous particle reference material, NIST SRM 1649a. Journal of Research of the National Institute of Standards and Technology 107, 279-298.

Derwent, R. G., Malcolm, A. L., 2000. Photochemical generation of secondary particles in the United Kingdom. Philosophical Transactions of the Royal Society of London Series A-Mathematical Physical and Engineering Sciences 358, 2643-2655.

El Zanan, H. S., Zielinska, B., Mazzoleni, L. R., Hansen, D. A., 2009. Analytical Determination of the Aerosol Organic Mass-to-Organic Carbon Ratio. Journal Of The Air & Waste Management Association 59, 58-69.

Endo, M., Yamamoto, N., Yoshinaga, J., Yanagisawa, Y., Endo, O., Goto, S., Yoneda, M., Shibata, Y., Morita, M., 2004. C-14 measurement for size-fractionated airborne particulate matters. Atmospheric Environment 38, 6263-6267.

Freeman, S. P. H. T., Cook, G. T., Dougans, A. B., Naysmith, P., Wilcken, K. M., Xu, S., 2010. Improved SSAMS performance. Nuclear Instruments & Methods in Physics Research Section B- Beam Interactions with Materials and Atoms 268, 715-717.

Gelencser, A., May, B., Simpson, D., Sanchez-Ochoa, A., Kasper-Giebl, A., Puxbaum, H., Caseiro, A., Pio, C., Legrand, M., 2007. Source apportionment of PM2.5 organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and fossil/biogenic origin. Journal of Geophysical Research 112, D23S04, doi:10.1029/2006JD008094.

Harrison, R. M., Jones, A. M., Lawrence, R. G., 2003. A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. Atmospheric Environment 37, 4927-4933.

Harrison, R. M., Yin, J. X., 2008. Sources and processes affecting carbonaceous aerosol in central England. Atmospheric Environment 42, 1413-1423.

Hodzic, A., Jimenez, J. L., Prévôt, A. S. H., Szidat, S., Fast, J. D., Madronich, S., 2010. Can 3-D models explain the observed fractions of fossil and non-fossil carbon in and near Mexico City? Atmospheric Chemistry and Physics 10, 10997-11016.

Johnson, D., Utembe, S. R., Jenkin, M. E., 2006a. Simulating the detailed chemical composition of secondary organic aerosol formed on a regional scale during the TORCH 2003 campaign in the southern UK. Atmospheric Chemistry and Physics 6, 419-431.

Johnson, D., Utembe, S. R., Jenkin, M. E., Derwent, R. G., Hayman, G. D., Alfarra, M. R., Coe, H., McFiggans, G., 2006b. Simulating regional scale secondary organic aerosol formation during the TORCH 2003 campaign in the southern UK. Atmospheric Chemistry and Physics 6, 403-418.

Levin, I., Hammer, S., Kromer, B., Meinhardt, F., 2008. Radiocarbon observations in atmospheric CO2: Determining fossil fuel CO2 over Europe using Jungfraujoch observations as background. Science Of The Total Environment 391, 211-216.

Lewis, C. W., Klouda, G. A., Ellenson, W. D., 2004. Radiocarbon measurement of the biogenic contribution to summertime PM-2.5 ambient aerosol in Nashville, TN. Atmospheric Environment 38, 6053-6061.

Naysmith, P., Cook, G. T., Freeman, S. P. H. T., Scott, E. M., Anderson, R., Xu, S., Dunbar, E., Muir, G. K. P., Dougans, A., Wilcken, K. M., Schnabel, C., Russell, N., Ascough, P. L., Maden, C., 2010. [14]C AMS at SUERC: Improving QA data with the 5 MV tandem and 250 kV SSAMS. Radiocarbon 52, 263-271.

NIST, 2007. Certificate of analysis for Standard Reference Material 1649a, Urban Dust. Revised Certificate, National Institute of Standards and Technology, Gaithersburg, MD. https://www-s.nist.gov/srmors/view_cert.cfm?srm=1649A.

Polidori, A., Turpin, B. J., Davidson, C. I., Rodenburg, L. A., Maimone, F., 2008. Organic PM2.5: Fractionation by polarity, FTIR spectroscopy, and OM/OC ratio for the Pittsburgh aerosol. Aerosol Science and Technology 42, 233-246.

Putaud, J. P., Raes, F., Van Dingenen, R., et al , 2004. European aerosol phenomenology-2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmospheric Environment 38, 2579-2595.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., Pandis, S. N., 2007. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. Science 315, 1259-1262.

Schichtel, B. A., Malm, W. C., Bench, G., Fallon, S., Mcdade, C. E., Chow, J. C., Watson, J. G., 2008. Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States. Journal of Geophysical Research 113, D02311, doi:10.1029/2007JD008605.

Sillanpaa, M., Hillamo, R., Saarikoski, S., et al , 2006. Chemical composition and mass closure of particulate matter at six urban sites in Europe. Atmospheric Environment 40, S212-S223.

Simon, H., Bhave, P. V., Swall, J. L., Frank, N. H., Malm, W. C., 2010. Determining the spatial and seasonal variability in OM/OC ratios across the US using multiple regression. Atmospheric Chemistry and Physics Discussions 10, 24651-24698.

Slota, P. J., Jull, A. J. T., Linick, T. W., Toolin, L. J., 1987. Preparation of small samples for C-14 accelerator targets by catalytic reduction of Co. Radiocarbon 29, 303-306.

Szidat, S., Jenk, T. M., Gaggeler, H. W., Synal, H. A., Fisseha, R., Baltensperger, U., Kalberer, M., Samburova, V., Reimann, S., Kasper-Giebl, A., Hajdas, I., 2004a. Radiocarbon (C-14)-deduced biogenic and anthropogenic contributions to organic carbon (OC) of urban aerosols from Zurich, Switzerland. Atmospheric Environment 38, 4035-4044.

Szidat, S., Jenk, T. M., Gaggeler, H. W., Synal, H. A., Fisseha, R., Baltensperger, U., Kalberer, M., Samburova, V., Wacker, L., Saurer, M., Schwikowski, M., Hajdas, I., 2004b. Source apportionment of aerosols by C-14 measurements in different carbonaceous particle fractions. Radiocarbon 46, 475-484.

Szidat, S., Jenk, T. M., Gaggeler, H. W., Synal, H. A., Hajdas, I., Bonani, G., Saurer, M., 2004c. THEODORE, a two-step heating system for the EC/OC determination of radiocarbon (C-14) in the environment. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 223-24, 829-836.

Szidat, S., Jenk, T. M., Synal, H. A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., Baltensperger, U., 2006. Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by [14]C. Journal of Geophysical Research 111, D07206, doi:10.1029/2005JD006590.

Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H. A., Hallquist, M., Shannigrahi, A. S., Yttri, K. E., Dye, C., Simpson, D., 2009. Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Goteborg, Sweden. Atmospheric Chemistry and Physics 9, 1521-1535.

Whyatt, J. D., Metcalfe, S. E., Nicholson, J., Derwent, R. G., Page, T., Stedman, J. R., 2007. Regional scale modelling of particulate matter in the UK, source attribution and an assessment of uncertainties. Atmospheric Environment 41, 3315-3327.

Xu, X. M., Trumbore, S. E., Zheng, S. H., Southon, J. R., McDuffee, K. E., Luttgen, M., Liu, J. C., 2007. Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: Reducing background and attaining high precision. Nuclear Instruments & Methods in Physics Research Section B- Beam Interactions with Materials and Atoms 259, 320-329.

Yin, J., Harrison, R. M., Chen, Q., Rutter, A., Schauer, J. J., 2010. Source apportionment of fine particles at urban background and rural sites in the UK atmosphere. Atmospheric Environment 44, 841-851.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., et al , 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. Geophysical Research Letters 34, L13801, doi:10.1029/2007GL029979.

Tables

Table 1: Values of fraction modern ^{14}C determined in NIST urban dust SRM-1649a.

f_M(TC)	f_M(EC)	f_M(OC)
This work		
0.515 (single combustion)		
0.570 ± 0.014 (two-step combustion)	0.15 ± 0.08	0.66 ± 0.02
NIST (2007) certificate		
0.61 ± 0.08 (combustion manometry)	0.065 ± 0.014 (thermal oxidation)	no value given
0.505 ± 0.006 (H_3PO_4-combustion-manometry)	0.153 ± 0.004 (chemical oxidation)	no value given
0.517 ± 0.007 (combustion-GC)	0.038 ± 0.024 (thermal kinetic oxidation)	no value given
Szidat et al. (2004c)		
0.522 ± 0.018	0.066 ± 0.020	0.70 ± 0.05

Figure captions

Figure 1: Schematic of determination of ^{14}C in the TC, OC and EC of samples of $PM_{2.5}$.

Figure 2: Scatter plot of individual sample total carbon determined independently from the cumulative CO_2 evolved during the two combustions for preparation of AMS targets and by Sunset Analyzer.

Figure 3: Methodology for assigning OC content of individual samples into POC and SOC for all $PM_{2.5}$ samples collected and analysed by Sunset Analyzer ($n = 75$). One exceptional sample (18th Feb 08) for which OC was 21.9 μgC m[-3] (EC = 4.3 μgC m[-3]), see Figure 2, is not illustrated on this figure since to do so would require substantial compression of the remaining data.

Figure 4: Box-whisker distributions of $PM_{2.5}$ TC concentrations (upper panel) and SOC/TC ratios (lower panel) grouped according to incoming air-mass back trajectory direction at the sampling location. Boxes show interquartile ranges; whiskers extend to maximum (minimum) value within 1.5 times the IQR above (below) the upper (lower) quartile. Groups annotated with a common letter have significantly different median values. Sample date 18th Feb 08 with the exceptionally high carbon loading (see Figure 2) is an off-scale outlier of group 'East' in the upper plot.

Figure 5: Fraction contemporary carbon in TC plotted as a function of both SOC/TC ratio and the geographical classification of the incoming air-mass direction at the sampling location.

Figure 6: Source attribution of EC and OC, as described in the text, for the sample of $PM_{2.5}$ collected on 22nd Feb 2008 (upper) and 31st Jan 2008 (lower). Values are concentrations in units of μgC m[-3].

Figure 7: Mean 5-source apportionment of TC in Birmingham (this work) compared with similar work from Zurich (Szidat et al., 2006) and Göteburg (Szidat et al., 2009). $OC_{biomass}$ is POC from combustion of biofuels/biomass, OC_{fossil} is both fossil-derived POC and any SOC from fossil-derived VOC, and $OC_{biogenic}$ is SOC formed from BVOC oxidation together with any other contemporary OC material not explicitly accounted for elsewhere, for example

spores, vegetative detritus, tyre rubber, etc. Uncertainties in the values presented from this work are discussed in the text.

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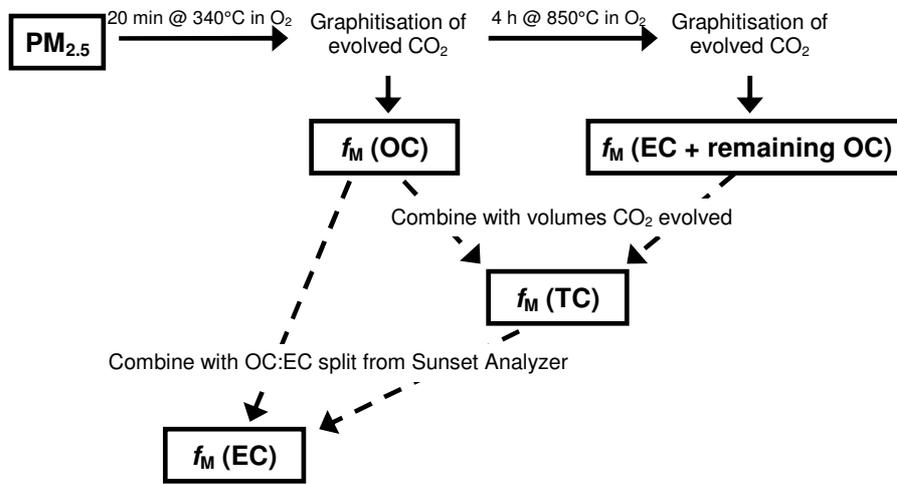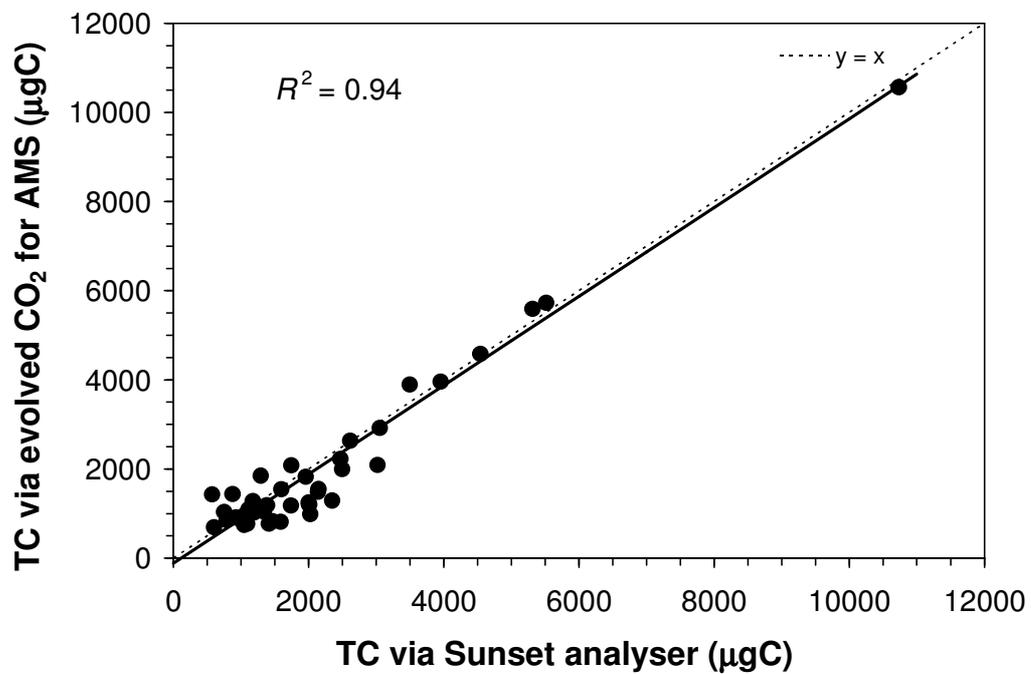
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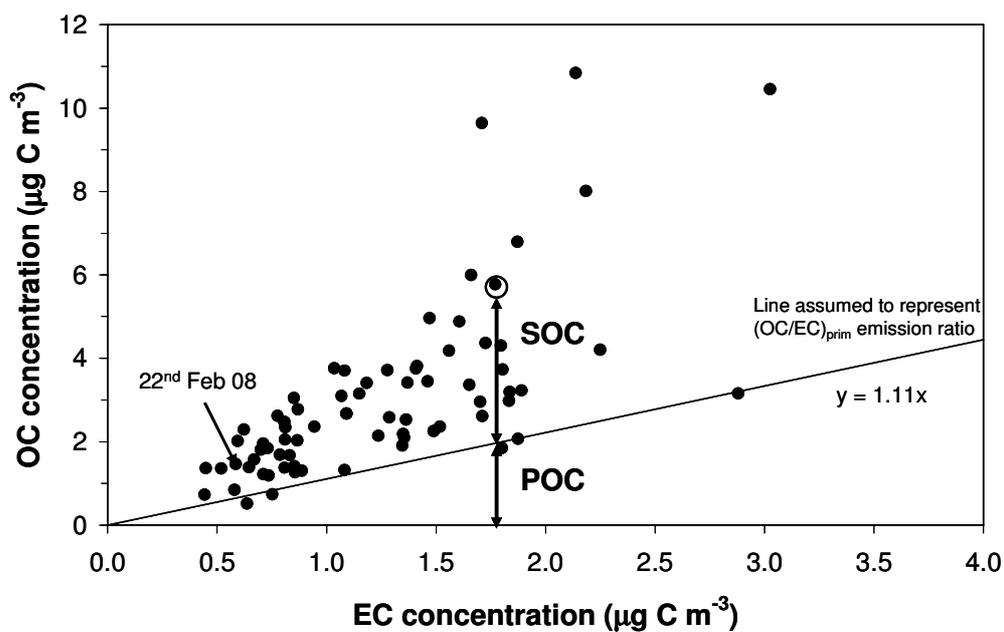Figure 4: Box-whisker distributions of $PM_{2.5}$ TC concentrations (upper panel) and SOC/TC ratios (lower panel) grouped according to incoming air-mass back trajectory direction at the sampling location. Boxes show interquartile ranges; whiskers extend to maximum (minimum) value within 1.5 times the IQR above (below) the upper (lower) quartile. Groups annotated with a common letter have significantly different median values. Sample date 18th Feb 08 with the exceptionally high carbon loading (see Figure 2) is an off-scale outlier of group 'East' in the upper plot.
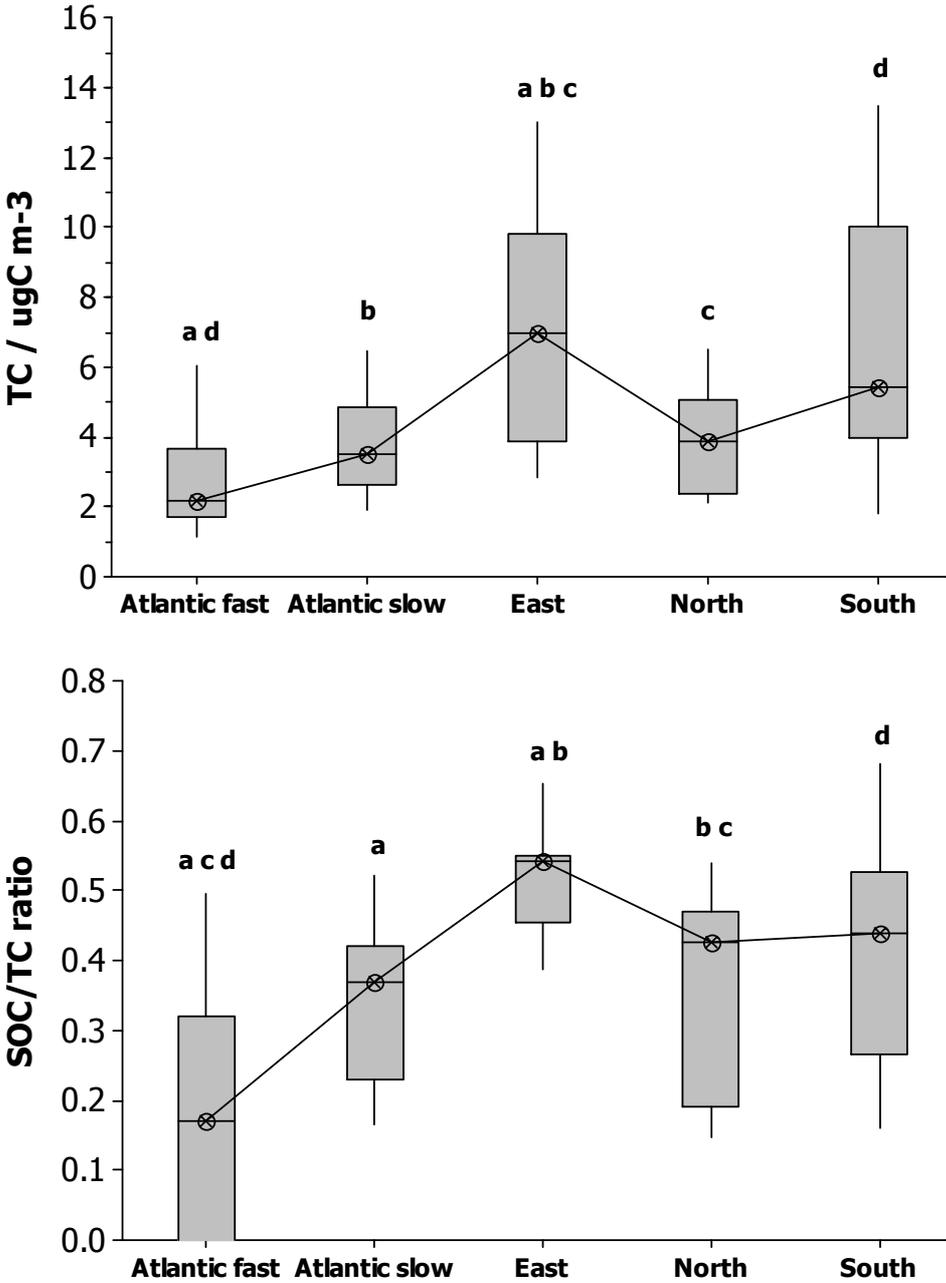
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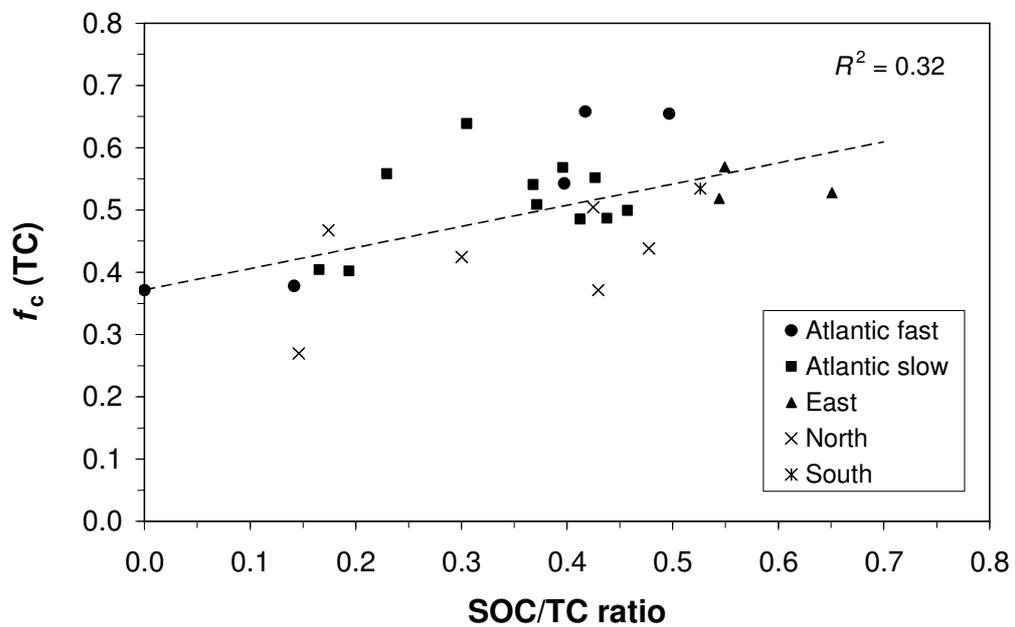
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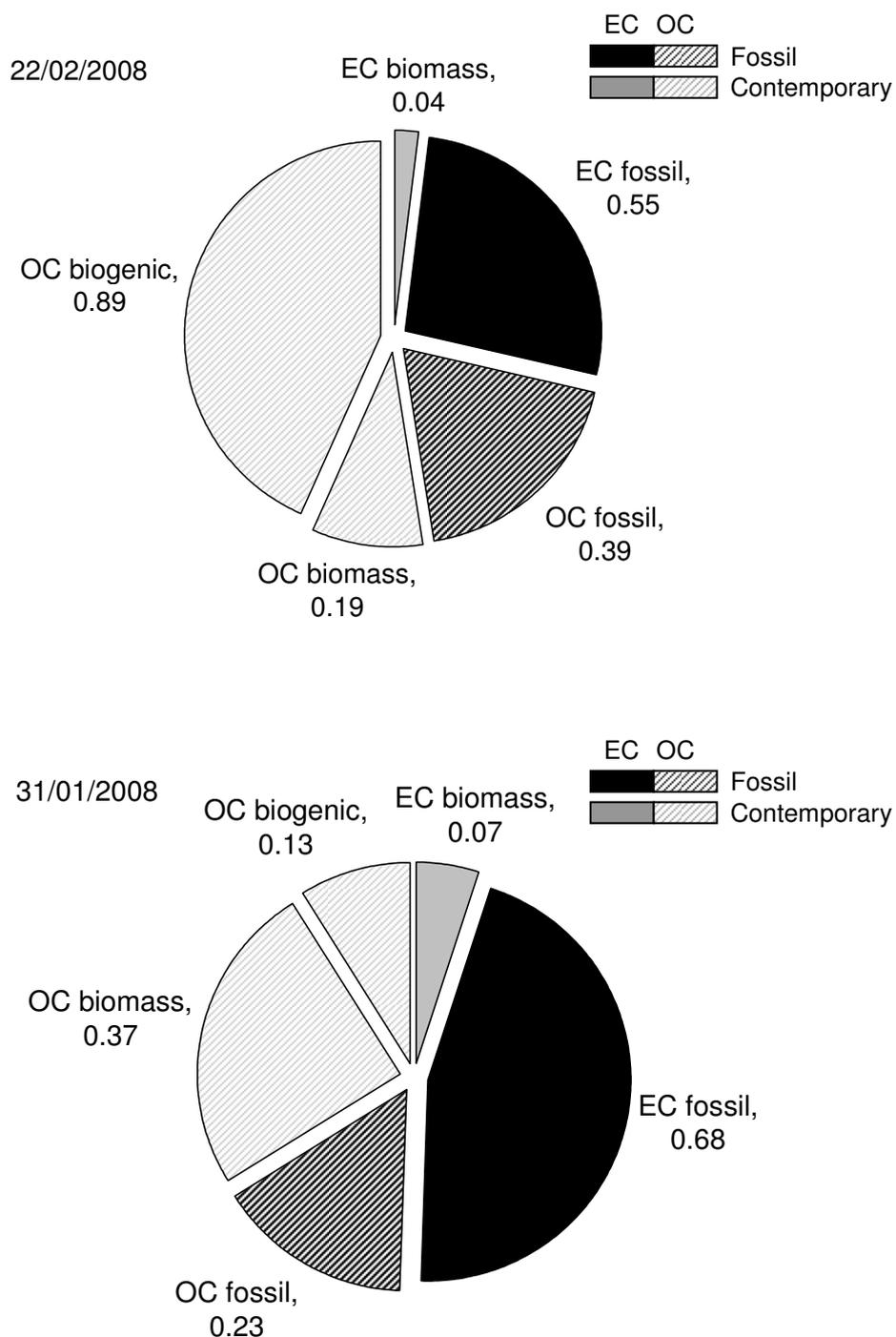
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