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The application of carbon-14 analyses to the source apportionment of atmospheric carbonaceous particulate matter: a review

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Abstract

Organic carbon (OC) and elemental carbon (EC) together constitute a substantial proportion of airborne particulate matter (PM). Insight into the sources of this major contributor to PM is important for policies to mitigate the impact of PM on human health and climate change. In recent years measurement of the abundance of the radioisotope of carbon (carbon-14 or ^{14}C) in samples of PM by accelerator mass spectrometry has been used to help quantify the relative contributions from sources of fossil carbon and contemporary carbon. This review provides an introduction to the different sources of carbon within PM and the role of ^{14}C measurements, a description of the preparation of PM samples and of the instrumentation used to quantify ^{14}C , and a summary of the results and source apportionment methods reported in published studies since the mid-2000s. All studies report a sizable fraction of the carbonaceous PM as of non-fossil origin. Even for PM collected in urban locations proportions of non-fossil carbon generally exceed 30%; typically the proportion in urban background locations is around 40-60% depending on the local influence of biomass burning. Where values have been measured directly, proportions of non-fossil carbon in EC are lower than in OC, reflecting the greater contribution of fossil-fuel combustion to EC and the generally small sources of contemporary EC. Detailed source apportionment studies point to important contributions from biogenic-derived secondary organic carbon, consistent with other evidence of a ubiquitous presence of heavily oxidised background SOC. The review concludes with some comments on current issues and future prospects, including progress towards compound-class and individual compound specific ^{14}C analyses.

Keywords: carbon-14; accelerator mass spectrometry; atmospheric particulate matter; organic carbon (OC); elemental carbon (EC).

List of acronyms

AMS	accelerator mass spectrometry
BVOC	biogenic volatile organic compound
CARBOSOL	name given to the EU project <i>A study of the present and retrospective state of the organic versus inorganic aerosol over Europe</i>
CPI	carbon preference index
EC	elemental carbon
HULIS	humic-like substances
IMPROVE	the US Interagency Monitoring of Protected Visual Environments program
IQR	inter-quartile range
MS	mass spectrometry
MW	molecular weight
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
OC	organic carbon
OM	organic matter
PAH	polycyclic aromatic hydrocarbon
PM	particulate matter
PM ₁₀ , PM _{2.5}	particulate matter fraction consisting of particles with aerodynamic diameter <10 µm or <2.5 µm, respectively
pMC	percent modern carbon
POC	primary organic carbon
SOA	secondary organic aerosol
SOC	secondary organic carbon
SRM	standard reference material
TC	total carbon
TSP	total suspended particles
VOC	volatile organic compound
WHO	World Health Organisation
WINSOC	water-insoluble organic carbon
WSOC	water-soluble organic carbon

1 Introduction

Ambient airborne particles have extremely diverse physicochemical properties, sources and impacts – the latter including effects on transport, transformation and deposition of chemical species, on radiative forcing and on human health [1;2]. The magnitude of the net direct and indirect radiative forcing induced by particles is the most uncertain component in estimation of anthropogenic global warming [3]. Part of this uncertainty derives from lack of detailed knowledge of the chemical composition of particles that affects optical scattering and hygroscopicity. The deleterious impact of ambient particulate matter (PM) on human health is well established in the literature and the World Health Organisation (WHO) publishes advisory air quality guidelines for mass concentrations of PM in the PM₁₀ and PM_{2.5} size fractions (particles with aerodynamic diameters <10 µm and < 2.5 µm, respectively) [4]. A recent WHO review reports a strengthening of the evidence for the association between PM and a number of adverse health outcomes [5]. It has been estimated that 89% of the world's population live in areas where ambient PM_{2.5} exceeds the WHO guideline of 10 µg m⁻³ [6] and outdoor PM air pollution is ranked ninth in the list of risk factors contributing to the global burden of disease (indoor air pollution is ranked fourth) [7]. Given the lack of unequivocal evidence for either a threshold concentration for adverse health effects or of differential toxicity for different components, current air quality legislation and policies to limit and reduce health effects from PM put equal emphasis on all PM mass reductions [8].

The major chemical constituents contributing to bulk ambient PM are well known – elemental carbon, organic carbon, ammonium sulphate, ammonium nitrate, sodium nitrate, sea-salt, other inorganic dusts – but the exact composition varies markedly with particle size range and locality. The elemental and organic components comprise a substantial proportion of total

particle mass, at least one third on average [9-13]. However, the characterisation and source apportionment of these components remains a major challenge [14-18]. The organic component may comprise hundreds or thousands of individual organic species, the majority of which are individually present at ultra-trace concentrations. The difficulty even of demarcating between organic and elemental carbon is well known and methodologically defined [19-21].

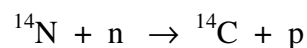
An important issue in both scientific and policy terms is the relative contributions of anthropogenic and biogenic sources to the carbonaceous component. Natural biogenic sources will not be readily amenable to control through policy action. The radioisotope of carbon (^{14}C) is an ideal tracer for distinguishing between fossil and contemporary carbon. Living material is in equilibrium with CO_2 in the atmosphere containing a known abundance of ^{14}C . On death, the ^{14}C isotope decays with a half-life of 5370 years [22] which is negligible in comparison with the age of fossil carbon sources. Thus, in principle, determination of the ratio of ^{14}C abundance in a sample of PM to its contemporary abundance directly yields the proportion of contemporary to fossil carbon in the sample. However, it is important to recognise that division between fossil and contemporary sources of carbon is not equivalent to a division between anthropogenic and natural sources. Data from ^{14}C analyses are therefore usefully combined with other information to inform a source apportionment of carbonaceous PM.

An analytical challenge is the very high level of accuracy and precision to which the very low abundances of ^{14}C (of the order of 10^{-12} atom ratio) need to be quantified. This requires the use of accelerator mass spectrometry (AMS), a technique that is becoming more widespread. Consequently, the last decade or so has seen increasing application of ^{14}C analysis to atmospheric PM. The aim of this article is to summarise this methodology, highlighting

advantages and disadvantages, to review the state-of-the-art of recent studies and to comment on current issues and future prospects.

2 The origin of ^{14}C in the environment

Cosmic rays passing through the atmosphere generate neutrons which on capture by nitrogen in the air produce ^{14}C at a relatively stable rate,



where n and p are, respectively, a neutron and proton. This cosmogenic ^{14}C is rapidly oxidised to $^{14}\text{CO}_2$ which in turn becomes equilibrated within the carbon of all living material through the balance of photosynthesis and respiration fluxes. Therefore all living material has a constant characteristic abundance of ^{14}C . On death, the uptake of ^{14}C ceases and the amount of ^{14}C present at death starts to decrease exponentially with a half-life of 5370 years. Consequently, the carbon in fossil fuels, which are millions of years old, effectively contains zero ^{14}C .

Two global anthropogenic effects perturb this neat picture. One is an atmospheric ^{14}C dilution effect caused by the increasing amount of CO_2 released by the burning of fossil fuels since the start of the industrial revolution. The second is the significant release of ^{14}C into the atmosphere from nuclear bomb tests in the middle of the last century. The correction for these effects is described in Section 4.3. In addition, there are instances of local controlled release of ^{14}C into the air via, for example, the incineration of medical or biological material where ^{14}C has been used as an isotopic tracer (Section 6.1).

3 An overview of the broad sources of carbonaceous PM and the role of ^{14}C data

Figure 1 illustrates a heuristic ‘top down’ apportionment of PM total carbon (TC) into broad categories: first into EC and OC, which are further sub-divided according to anthropogenic or contemporary sources and into direct primary emissions to the atmosphere or within-atmosphere secondary formation. These divisions lead to the following 8 broad categories of carbonaceous PM:

- anthropogenic primary fossil EC (burning of fossil fuels);
- anthropogenic primary contemporary EC (deliberate burning of contemporary biomass/biofuel);
- natural primary contemporary EC (natural burning of contemporary biomass, e.g. wildfires);
- anthropogenic primary fossil OC (burning of fossil fuels);
- anthropogenic primary contemporary OC (deliberate burning of contemporary biomass, and sources such as cooking, cigarette smoke and natural rubber tyre wear);
- natural primary contemporary OC (natural burning of contemporary biomass (wildfires); primary biological material derived from pollen, spores and mechanical attrition from living and detritus vegetation; suspended soil humic material, etc.);
- anthropogenic secondary fossil OC (in-atmosphere production of secondary organic aerosol (SOA) from emissions of fossil-fuel derived VOC precursors such as toluene, xylene, 1,3-butadiene, etc.);
- natural secondary contemporary OC (in-atmosphere production of SOA from emissions of biogenic VOC precursors, principally from vegetation, such as isoprene, pinene, limonene, etc.).

It is assumed the EC fraction only has primary sources, and that all fossil carbon is anthropogenic. (The latter may not be strictly true where genuinely natural burning of seams

of fossil fuel contribute to measured PM.) It is also assumed impractical to distinguish between natural and anthropogenic contemporary SOC, i.e. between biogenic SOC derived from BVOC emissions from truly natural land cover or from BVOC emissions from human-influenced land cover.

Many localities may experience negligible contribution from natural contemporary EC and POC if natural wild fires are not an issue, although long-range transport from further afield may still be important.

The aim of ^{14}C measurements is to help constrain the broad source apportionments, principally between fossil and contemporary sources. Whilst initially this apportionment was applied only to the TC content, a two-step preparative combustion approach can, in principle, allow the fossil-contemporary split to be determined in the OC and EC components separately [23;24]. The categories then directly quantifiable by ^{14}C determination are highlighted in Figure 1. This figure, and the above discussion of contributing sources to carbonaceous PM, illustrate the point that a fossil-contemporary apportionment is not equivalent to an anthropogenic-natural apportionment; for example, POC from the combustion of biomass/biofuels or from cooking, or natural rubber tyre wear are all anthropogenic activities releasing contemporary carbon. Likewise, deliberate land-use change that alters BVOC emissions and SOA production is an anthropogenic rather than a natural source.

4 Determination of ^{14}C abundance by AMS

The essence of the methodology is that the PM sample is combusted to convert all (or particular components) of the carbon to CO_2 , which is then reduced to a graphite target for the

accelerator mass spectrometer. A general description of the sample preparation and mode of operation of an AMS is given here; individual approaches and instrumentation will vary, as described in individual studies.

4.1 Sample preparation

Samples of PM (size fractionated as required) are collected onto quartz filters, usually with hi-vol samplers so as to collect a few hundred $\mu\text{g C}$ within a 24 h period. Filters are pre-baked (typically at temperatures $> 500\text{ }^\circ\text{C}$ for $> 12\text{ h}$) to remove any contaminant carbon. Prior to combustion, the filter sample may be pre-washed in dilute HCl to remove any carbonate (CO_3^{2-}) [25;26]. Many studies assume negligible CO_3^{2-} in comparison to the organic and elemental carbon and exclude this step. Filters are sealed in a quartz combustion tube. In the general case of determination of ^{14}C in TC only, the tube typically contains CuO as oxidizer, plus Ag to remove any liberated halogen, and is combusted for at least 4 h at $800\text{ }^\circ\text{C}$. The evolved gas, principally CO_2 , is released into a gas-handling line for purification. This may consist, first, of further combustion at $850\text{ }^\circ\text{C}$ in the presence of e.g. CuO and MnO_2 , to ensure complete oxidation of any CO to CO_2 , followed by passage through an ethanol/solid CO_2 cold trap ($-72\text{ }^\circ\text{C}$) to remove water vapour and a liquid nitrogen trap ($-196\text{ }^\circ\text{C}$) in tandem with cryogenic pumping to remove any non-condensing contaminants [27]. The volume of CO_2 is measured by capacitance manometer.

For the reduction step an aliquot of CO_2 is transferred to a further combustion tube containing a few tens mg Zn powder and a few mg of Fe powder and is heated to $450\text{-}550\text{ }^\circ\text{C}$. The Zn reduces the CO_2 to CO, and the Fe reduces the CO to a graphite coating on the Fe powder

[28]. The Fe/graphite is then compressed into a small-diameter hole in an Al target holder to form the target for the AMS.

4.2 AMS instrumentation

In accelerator mass spectrometry the abundance of the ^{14}C nuclei is measured directly, rather than via counting of radioactive β -decays [29]. Key features of AMS which facilitate the high discrimination required to quantify ^{14}C at sub 10^{-12} atom ratio include:

- initial production of negative ions to eliminate isobars with low electron affinity (e.g. ^{14}N);
- acceleration of ions to high energy to increase sensitivity during m/z and m/E selections;
- stripping of electrons to dissociate molecular isobars and produce multiply-charged positive ions;
- energy-loss detection that is sensitive to atomic number.

A general schematic of the components of an AMS instrument is shown in Figure 2. Individual instrument set-ups may differ from this figure and from the following description. Sputtering of the graphite target, usually with Cs^+ ions, gives an intense, short pulse of negative sample ions. This includes molecular anions such as hydrides of carbon (CH^-). The first magnet performs initial mass separation. The m/z 14 ions enter an accelerator which generates voltages up to 5 MV and accelerates ions through a low pressure gas (e.g. Ar) or a thin metal foil ‘stripper’ that removes electrons from the ions to yield multiply-charged positive ions with energies of several tens MeV. Any molecular ions are destroyed since these are not stable with greater than +1 charge. A subsequent electrostatic deflector with a narrow

exit slit separates ions by energy and charge. The selected multiply-charged carbon ions then pass through a further magnetic selector before reaching an energy-loss detector. This consists of a gas path with a longitudinal series of electrical sensors that determines the rate at which the incoming ion loses energy as it passes down the gas path. Although all ions arriving at the entrance of the detector have the same kinetic energy, the rate at which the energy of a particular ion loses energy in collision with the gas in the detector is dependent on the atomic number of the incoming ion. Therefore by only counting ions that have an energy-loss profile in the detector that matches the profile for an ion with the atomic number of carbon it is possible to discriminate between ions from ^{14}C and, for example, ^{14}N . The ability of the energy-loss detector to discriminate between atomic number very approximately requires ~ 1 MeV of energy per atomic number, i.e. distinguishing between ^{14}C and ^{14}N requires an incoming ion energy of ~ 14 MeV. This is another reason why large initial accelerator voltages are required.

The use of AMS rather than β -decay counting gives greater precision overall, and a large reduction in measurement time. Of particular relevance to the application to samples of ambient PM is the considerably smaller size of sample required.

4.3 Calibrations and determination of fraction contemporary

The abundance of ^{14}C is expressed relative to the abundance of ^{12}C and the value of this ratio for a sample, $F^{14}\text{C}_{\text{sample}}$ is expressed relative to the equivalent ratio for a standard called the Modern Carbon standard, $F^{14}\text{C}_{\text{Modern}}$. The ratio of $F^{14}\text{C}_{\text{sample}}$ to $F^{14}\text{C}_{\text{modern}}$ is the fraction modern carbon, f_M , of the sample:

$$f_M(\text{sample}) = \frac{\frac{^{14}\text{C}}{^{12}\text{C}}(\text{sample})}{\frac{^{14}\text{C}}{^{12}\text{C}}(\text{Modern})} = \frac{F^{14}\text{C}_{\text{sample}}}{F^{14}\text{C}_{\text{Modern}}}$$

An alternative nomenclature to f_M is percent modern carbon, pMC, where $\text{pMC} = 100 \times f_M$. The extensive release of fossil CO_2 from burning of fossil fuels, and of ^{14}C from nuclear bomb tests, have significantly perturbed the value of $F^{14}\text{C}$ in the last century or so. The latter led to an almost doubling of atmospheric ^{14}C in the northern hemisphere in the 1960s. Following the ban on above-ground bomb tests the abundance of ^{14}C in the atmosphere has been declining, as illustrated in Figure 3, as it gets taken up by the oceans and terrestrial biosphere [30;31]. The recent variability in ^{14}C is why measured abundances are reported against a defined standard value of $F^{14}\text{C}_{\text{Modern}}$ that is related to the equilibrium ^{14}C content of living material in an atmosphere (largely) unaffected by anthropogenic perturbations.

The primary radiocarbon standard is the international Oxalic Acid II (HOXII) standard (SRM-4990C). Each batch of samples analysed by AMS will typically also contain targets produced from the HOXII primary standard, a secondary standard of known near-contemporary age and/or a secondary old-age standard (e.g. ancient wood sample), and a ‘blank’ standard of zero ^{14}C activity derived from either calcite mineral or interglacial wood with an age in excess of 100,000 years. A typical AMS blank value might be $f_M \sim 0.0002$ (pMC = 0.02) or better.

If the potential contribution of carbon from the filter material on which the PM samples are collected is a concern then f_M values from loaded sample filters ($f_M(\text{loaded})$) can be corrected for positive organic artifacts using $f_M(\text{blank})$ values derived from analysis of blank filters:

$$\begin{aligned}
f_M(\text{sample}) &= \frac{F^{14}\text{C}_{\text{sample}}}{F^{14}\text{C}_{\text{Modern}}} = \frac{F^{14}\text{C}_{\text{loaded}}}{F^{14}\text{C}_{\text{Modern}}} \frac{L_{\text{loaded}}}{(L_{\text{loaded}} - L_{\text{blank}})} - \frac{F^{14}\text{C}_{\text{blank}}}{F^{14}\text{C}_{\text{Modern}}} \frac{L_{\text{blank}}}{(L_{\text{loaded}} - L_{\text{blank}})} \\
&= f_M(\text{loaded}) \frac{L_{\text{loaded}}}{(L_{\text{loaded}} - L_{\text{blank}})} - f_M(\text{blank}) \frac{L_{\text{blank}}}{(L_{\text{loaded}} - L_{\text{blank}})}
\end{aligned}$$

where L_{loaded} and L_{blank} are the carbon masses in the analysed regions of, respectively, the loaded sample filters and the blank filter [32;33].

In a simple two-member model, in which it is assumed the carbon in the sample comprises only of fossil carbon ($F^{14}\text{C} = 0$) and of contemporary carbon from a single source with a single age of carbon, then the fraction of contemporary carbon, f_c , that is present in the sample is derived directly by dividing $f_M(\text{sample})$ by the value for the ^{14}C excess prevalent at the point in time when the contemporary carbon was living. For example, if the contemporary carbon source was derived only from material from an annual crop growing in 2010 then f_M would be divided by the factor $F^{14}\text{C} = 1.04$, which is the ^{14}C excess in living material in 2010 (see Figure 3) [31]. In practice, the non-fossil carbon in PM will derive from multiple ‘contemporary’ sources spanning the range from truly contemporary, e.g. SOC derived from BVOC emissions from the year in which the sample was collected, to mature tree-wood laid down several decades ago when atmospheric ^{14}C abundance was substantially higher. Estimates of $F^{14}\text{C}$ for wood biomass are usually based on tree-growth models [34] and depend on assumptions about the age profiles of the trees contributing to the wood stock. Values used in the literature have ranged from 1.08 to 1.30 [35-40], which shows that this correction can be important otherwise f_M is a substantial overestimate of the true fraction f_c contributed by the biomass-derived carbon. Unfortunately, circularity arises in that the ^{14}C analyses are undertaken to help constrain proportions of fossil and contemporary carbon but the appropriate correction to apply to f_M requires knowledge of the contributing sources of contemporary carbon. Sensitivity analyses to certain assumptions are often undertaken [27;40;41].

4.4 Preparation of samples for determination of ^{14}C in OC and EC separately

Figure 1 illustrates the benefit of determining the fractions of contemporary carbon in the OC and EC fractions of TC separately. The methodology to apportion TC into its OC and EC fractions has been subject to much debate, and still remains essentially a methodologically-defined split [19-21;42]. The physical separation of samples of PM into OC and EC fractions for ^{14}C determination was pioneered by Szidat and co-workers [23;24;35;43]. In their original procedure ('THEODORE': two-step heating system for the EC/OC determination of radiocarbon in the environment), combustion of the sample in a stream O_2 for 10 min at 340°C was used to evolve CO_2 from a fraction assigned as OC [24]. These workers reported that although the OC/TC ratio increased with temperature between 340 and 440°C the f_M value remained unchanged, indicating that whilst additional OC was combusted at higher temperatures there was negligible interference to f_M from EC at temperatures up to 440°C , i.e. the chosen temperature of 340°C was sufficient to determine an accurate value of $f_M(\text{OC})$ even if some OC remained non-combusted. A sequential combustion in O_2 for a further 10 min at 650°C yielded further CO_2 . Mass balance with the volumes and f_M values for the CO_2 evolved from the two combustions provided $f_M(\text{TC})$. To determine the $f_M(\text{EC})$ value required >4 h combustion at 375°C performed off-line in a muffle furnace on a parallel sample.

Szidat et al. [23;35] refined the above technique to provide further distinction between water-soluble and water-insoluble components of OC (WSOC and WINSOC) and to recognise that EC may also contain high MW, low volatility organic species. Some classes of organic compounds associated with WSOC include polyols, polyethers and mono-, di- and polycarboxylic acids, whilst organic compounds associated with WINSOC include n-alkanes,

aromatic compounds (e.g. PAHs) and long-chained carboxylic acids. Figure 4 reproduces the flow procedure for determining mass and ^{14}C in each fraction.

- TC was obtained by combustion for 10 min at 650 °C in a stream of O_2 . Mass of C and ^{14}C content in this fraction are determined directly from the sample.
- OC was obtained by combustion for 10 min at 340 °C in a stream of O_2 . Mass of C and ^{14}C content in this fraction are determined directly from the sample.
- WINSOC was obtained by first soaking a filter overnight in 10 mL of high-purity water and then drying it prior to the OC combustion. Mass of C and ^{14}C content in this fraction are determined directly from the sample.
- WSOC was determined by difference: $\text{WSOC} = \text{OC} - \text{WINSOC}$. Thus mass of C and ^{14}C content in this sample are determined indirectly by subtraction.
- ‘EC+polymerizable_WSOC’ was determined by first heating the filter for 4 h at 375 °C in a muffle furnace to eliminate OC and then combusting for 10 min at 650 °C in a stream of O_2 . Mass of C and ^{14}C content in this fraction are determined directly from the sample. The ‘polymerizable_WSOC’ (or pyrolizable OC) represents ‘polymeric polar OC’ (e.g. polyacids, HULIS) which chars and remains on the filter rather than being driven off in the prior heating at 375 °C, and which often interferes with OC-EC separations.
- EC was obtained by first soaking a filter overnight in 10 mL of high-purity water prior to the elimination of OC at 375 °C and the subsequent combustion in O_2 at 650 °C. This fraction is most readily equated to ‘true EC’. Mass of C and ^{14}C content in this fraction are determined directly from the sample.
- ‘Polymerizable_WSOC’ was determined by difference: ‘Polymerizable_WSOC’ = ‘EC+polymerizable_WSOC’ – EC. Thus mass of C and ^{14}C content in this sample are determined indirectly by subtraction.

Zhang et al. [44] conducted further extensive evaluations towards a protocol for the isolation of OC and EC fractions from filter samples of PM for ^{14}C determinations. They present a four-step protocol that minimises the positive and negative artefacts associated with the charring of OC and the premature combustion of OC. However, these authors also acknowledge the continuum that exists in reality between refractory OC and non-refractory EC such as derived from wood-burning. Zhang et al. [44] stress the importance of pre-treatment of filters destined for EC analysis with acidified ultrapure water to remove high molecular-weight polyacidic species; otherwise the non-fossil contribution may be overestimated due to the positive bias from charring. The four consecutive steps are:

- (1) combustion at 375 °C in pure O_2 of untreated filters for separation of OC, and of water-extracted filters for separation of WINSOC. The WSOC fraction is determined by the subtraction of the water-soluble fraction of TC from the untreated TC;
- (2) combustion at 475 °C in O_2 of the latter filter, immediately followed by
- (3) combustion at 650 °C in He for 2 min, for the complete removal of OC prior to EC isolation;
- (4) combustion at 760 °C in O_2 for recovery of EC.

The authors recommend that ^{14}C results of EC should be presented together with a description of the methodology employed and of the EC recovery. Bernardoni et al. [45] similarly report that an additional high temperature combustion in He (corresponding to step (3) above) prior to the final combustion in O_2 for the isolation of the EC is effective at removing the refractory OC, although these workers' choice of temperature was 750 °C. Both these latter studies emphasise the pre-washing of filters prior to EC isolation.

4.5 Reference PM material and ^{14}C values

The only PM reference material for which certified ^{14}C values are available is the USA National Institute of Standards and Technology (NIST) 1649a urban dust standard reference material (SRM), originally collected in 1976-77 [46]. This is a total suspended particle size fraction. The original certificate for this SRM [47] has been revised twice [48;49], the latter to coincide with the re-issue of samples of this SRM in 2007. The revisions relate principally to provision of additional data on proportion of individual carbon fractions and additional f_M values. NIST have created a $\text{PM}_{2.5}$ sub-fraction of the original 1649a bulk TSP reference material which has been dispersed onto quartz filters [50] and is now being issued as RM 8785 [51]. Whilst the TC, OC and EC mass contents of this filter-based $\text{PM}_{2.5}$ matrix have been issued as information values, the ^{14}C content of these fractions has not.

Aside from the NIST certificate values themselves, there are almost no other published data for the f_M values of the SRM-1649a urban dust. Table 1 summarises the data. The f_M values for TC are fairly consistent, since the preparation of a sample of TC for ^{14}C is relatively straightforward. No certified data for $f_M(\text{OC})$ are presented by NIST but the two values reported by Szidat et al. [24] and Heal et al. [27] are in good agreement. In contrast, the f_M values for the EC fraction in Table 1 vary by a factor 4, even on the NIST certificate [49]. This highlights the considerable method-dependent issues in defining and isolating an EC fraction already discussed, as also manifest by the range of EC/TC values quoted for this SRM. The NIST [49] certificate reports the results of EC/TC determinations by several methodologies in three clusters of values: cluster 1 has mean EC/TC = 0.075 (IQR 0.071-0.78, $n = 4$), cluster 2 has mean EC/TC = 0.28 (IQR 0.27-0.29, $n = 4$), and cluster 3 has mean EC/TC = 0.46 (IQR 0.44-0.50, $n = 5$); the mean EC/TC ratios in these 3 clusters vary by more than a factor 6. For the $\text{PM}_{2.5}$ NIST 8785 SRM, mean EC/TC is reported as 0.279 for determination using the

NIOSH thermal optical transmittance method originally developed by Birch and Carey [42], or 0.490 using the IMPROVE thermal optical reflectance method [52].

5 A review of published studies

5.1 Fraction non-fossil in TC

Table 2 summarises the fraction of particulate matter TC of contemporary (non-fossil) origin, f_c , reported in studies published since about the mid-2000s. Meta-data on geographical location, site type and PM size fraction are included. Values of f_c , for OC and EC are also presented in Table 2, where these are available. These latter values may derive from measurement on the carbonaceous fraction itself, or be inferred by mass balance or a source apportionment approach. In some instances, f_M rather than f_c values are presented in Table 2. In some studies it is difficult to interpret whether data presented are f_c or f_M .

The studies listed in Table 2 are from all over the world, except South America, with data from Europe predominating. It is important to note that the number of individual samples analysed in some studies is very low, which reflects the considerable resource requirements associated with collecting sufficient PM onto filter media, its preparation for AMS analysis, and the AMS analyses themselves.

The principal observation from Table 2 is that all studies report a sizable fraction of the carbonaceous PM to be of non-fossil origin, on average, even for PM collected in urban locations. Even the lowest $f_c(\text{TC})$ values in Table 2 indicate non-fossil contributions in the range 0.3-0.4. These lower non-fossil contributions tend to be associated with east Asia, e.g.

Tokyo [53;54], Beijing [55] and Lhasa [26] and at kerbside in Marseille and Geneva [56]. At the other extreme, contemporary carbon fractions approaching unity are reported at rural sites well away from urban centres in the USA [32;33;57] or where residential wood-burning completely dominates, e.g. Launceston, Tasmania [25]. $f_c(\text{TC})$ values in the range 0.4-0.8 are typical, with PM in urban areas having $f_c(\text{TC})$ values at the lower end of this range (except where residential biomass burning makes a substantial contribution to urban emissions) and PM at suburban, rural and coastal locations having values at the higher end.

5.2 Fraction non-fossil carbon in EC and OC

Where direct ^{14}C measurements have been made, the fraction non-fossil in EC is universally lower on average than in OC. In their original OC-EC separation work, Szidat et al. [23] report average $f_c(\text{OC})$ and $f_c(\text{EC})$ values of 0.75 and 0.30 for PM_{10} in Zürich. Subsequent measurements in the same city gave $f_c(\text{OC})$ values in the range 0.68-0.72 and $f_c(\text{EC})$ values in the range 0.06-0.25, varying with season [35]. In Göteborg, $f_M(\text{OC})$ and $f_M(\text{EC})$ values were 0.59-0.78 and 0.05-0.17, respectively [36], whilst in Birmingham (UK), they averaged 0.76 and 0.11, respectively [27], and in Barcelona they were 0.52-0.75 and 0.09-0.34, respectively [39]. These findings show that fossil-fuel burning is, in most areas, the predominant source of EC.

5.3 Examples of more detailed source apportionment

Measurements of ^{14}C in EC and OC separately, alongside appropriate conversions of f_M values into f_c values, permits direct apportionment of TC into five source categories [27;35;36]. Refer also to Figure 1 and Section 3.

Biogenic emissions do not give rise to EC, so $f_c(\text{EC})$ directly yields the division between fossil and biomass combustion contributions to total EC:

$$\text{EC}_{\text{biomass}} = f_c(\text{EC}) \times \text{EC}$$

$$\text{EC}_{\text{fossil}} = (1 - f_c(\text{EC})) \times \text{EC}$$

Sources of $\text{EC}_{\text{biomass}}$ include burning of biomass in residences or for power generation, biofuel blends in transport fuels and long-range transport of EC from vegetation fires. With the exception of genuinely natural wild fires, all these sources are anthropogenic, even though the radiocarbon signature is contemporary.

The OC can likewise be apportioned between fossil-fuel and biomass combustion, and also to secondary organic aerosol products of biogenic VOC emissions:

$$\text{OC} = \text{OC}_{\text{fossil}} + \text{OC}_{\text{biomass}} + \text{OC}_{\text{biogenic}}$$

It must be noted that this $\text{OC}_{\text{biogenic}}$ component also includes other contemporary OC material not explicitly accounted for elsewhere, for example spores, plant detritus, tyre rubber, etc. This is discussed further later. The contribution of $\text{OC}_{\text{fossil}}$ is obtained directly from the measurement of $f_c(\text{OC})$:

$$\text{OC}_{\text{fossil}} = (1 - f_c(\text{OC})) \times \text{OC}$$

The $\text{OC}_{\text{fossil}}$ component is both fossil-derived POC and any SOC from fossil-derived VOC. A value for $\text{OC}_{\text{biomass}}$ can be estimated from the $\text{EC}_{\text{biomass}}$ value already derived using an assumed OC/EC emission ratio for biofuel burning, $(\text{OC}/\text{EC})_{\text{ER}(\text{biomass})}$, from the literature:

$$\text{OC}_{\text{biomass}} = \text{EC}_{\text{biomass}} \times (\text{OC}/\text{EC})_{\text{ER}(\text{biomass})}$$

The value for $\text{OC}_{\text{biogenic}}$ is determined by mass balance of OC:

$$\text{OC}_{\text{biogenic}} = \text{OC} - \text{OC}_{\text{fossil}} - \text{OC}_{\text{biomass}}$$

Figure 5 shows an example application of this source apportionment approach to TC in samples of PM_{2.5} collected at an urban background site in Birmingham, UK [27]. The average apportionment (2% biomass EC; 27% fossil EC; 20% fossil OC; 10% biomass OC; 41% biogenic and other contemporary OC) is similar to that in Zürich [35] and Göteborg [36] although the two continental European cities are more strongly influenced by wood-burning sources.

The category OC_{fossil} will comprise both primary and secondary OC_{fossil}, the latter derived from atmospheric oxidation of fossil-derived VOC emissions, e.g. toluene (Figure 1). It can be sub-divided using an assumed POC_{fossil}/EC_{fossil} ratio for the sampling site, with the remainder of OC_{fossil} assumed to be SOC_{fossil}. Recent values of this ratio for traffic emissions are reported in the range 0.3-0.4 [58;59] and 0.65 for a background site in Birmingham [58]. Table 3 shows the division of OC_{fossil} for measurements in Birmingham using a ratio of 0.35.

As noted already, the category designated OC_{biogenic} in this 5-source apportionment approach includes, in addition to BVOC-derived SOC, 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, etc., as well as particles derived from vehicle tyre wear (where tyres are composed of natural rubber) and cigarette smoke. Sources of contemporary OC from cooking may be incorporated within the OC_{biomass} category. The magnitudes of the contributions of these sources to individual size fractions of PM OC is highly uncertain, but information can be derived from identification and parallel quantification of specific marker compounds in the PM. The most widely used are levoglucosan, as a marker for wood burning, and cellulose, as a marker for primary particles from vegetation. With these data it is possible to devise an apportionment into similar source

categories as described above even when f_M has been determined only for TC, as has been described by Gelencser et al. [41] for $PM_{2.5}$ from the European CARBOSOL sites.

As before, EC is assumed to derive only from two sources,

$$EC = EC_{\text{biomass}} + EC_{\text{fossil}}$$

where EC_{biomass} is again derived from $OC_{\text{biomass}}/EC_{\text{biomass}}$ mass emissions ratios reported for wood burning in the literature, and EC_{fossil} is obtained by difference from EC. The OC is divided into three primary and two secondary sources,

$$OC = POC_{\text{fossil}} + POC_{\text{biomass}} + POC_{\text{primary_bio}} + SOC_{\text{fossil}} + SOC_{\text{biogenic}}$$

where

- POC_{fossil} from fossil-fuel combustion is derived from EC_{fossil} by using $(POC_{\text{fossil}}/EC_{\text{fossil}})_{\text{prim}}$ mass emission ratios for fossil-fuel combustion taken from the literature;
- POC_{biomass} from biomass burning is calculated from measured levoglucosan concentrations and reported OC/levoglucosan mass emission ratios;
- $POC_{\text{primary_bio}}$ derives from plant debris and is calculated from measured cellulose concentrations and an assumed $POC_{\text{bio}}/\text{cellulose}$ mass ‘emission’ ratio;
- SOC_{biogenic} (secondary PM carbon derived from plant VOC emissions such as isoprene and pinene) is derived from:

$$SOC_{\text{biogenic}} \times f_{M(\text{nonfossil})} = TC \times f_M(\text{TC}) - OC_{\text{biogenic}} \times f_{M(\text{biogenic})} - (OC_{\text{biomass}} + EC_{\text{biomas}}) \times f_{M(\text{biomass})} - (OC_{\text{fossil}} + EC_{\text{fossil}} + SOC_{\text{fossil}}) \times f_{M(\text{fossil})}$$

The value $f_M(\text{TC})$ is as measured in the sample; the value of $f_{M(\text{biogenic})}$ is assumed to be that of contemporary atmospheric CO_2 at the time of sampling, the value of $f_{M(\text{biomass})}$ is more uncertain ranging from the value at sampling for burning of contemporary agricultural residues to 1.25 for burning of old trees, the value of $f_{M(\text{fossil})} = 0$ by

definition, the value of $f_{M(\text{nonfossil})}$ is taken to be the value at sampling, i.e. that $\text{SOC}_{\text{nonfossil}}$ is derived from contemporary biomass VOC emissions.

- The final source contribution term, $\text{SOC}_{\text{fossil}}$, (secondary PM carbon derived from emissions of fossil-fuel derived VOC precursors) is derived as the residual after subtraction of all other terms from TC. There is no circularity in deriving $\text{SOC}_{\text{fossil}}$ because the parameter $f_{M(\text{fossil})} = 0$ so the term containing $\text{SOC}_{\text{fossil}}$ in the above equation is in fact zero.

Because several assumptions are made regarding appropriate emissions and concentration ratios, and for f_M values, Gelencser et al. [41] undertook a comprehensive Latin hypercube sampling approach to provide a Monte-Carlo type probability distribution for concentration and contribution of each source based on the estimated ranges and uncertainties attributed to each contributing parameter.

Other studies have also measured concentrations of arabitol and mannitol as specific markers for fungal spores, enabling a further separation of contemporary POC between this source and the vegetation detritus estimated from cellulose concentrations [37;60;61]. Details of extension of the apportionment of TC into seven [61] or even eight [37] carbonaceous sources have been described. These latter studies all also investigate the impact of uncertainties in assumptions through Latin hypercube sampling approaches.

5.4 Scaling up from carbon to PM mass

A pertinent output is to scale the mass of OC in each source to determine the contribution of each to total PM mass (EC has unity scaling factor). In their pragmatic mass closure model, Harrison et al. [62] assumed an average 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 [63-67]. The scaling factors assumed by AQEG [13] for the PM_{2.5} data from Birmingham are given in Table 3, and range from 1.2 for biogenic POC to 2.0 for biomass burning POC. It is emphasised that all values for ratios and scaling factors used in Table 3, and in other studies, are subject to uncertainty and to inter-site variability.

It is clear from all studies apportioning OC into fossil and non-fossil POC and SOC sources is that carbonaceous PM, even in many urban areas, is substantially influenced by both biomass burning and by BVOC-derived SOA. The latter is consistent with other evidence for a ubiquitous presence of heavily oxidised regional/hemispheric background SOC presumed to derive in large part from BVOC emissions [68].

6 Issues and prospects

6.1 Sample contamination

The unintended sampling of PM that derives from, or has been contaminated by, emissions from incinerators combusting medical or biological wastes containing ¹⁴C used as a radioactive tracer can significantly bias the derived f_M and consequently cause overestimation of the true proportion of contemporary carbon in the rest of the sample. Measured values of f_M substantially greater than 1 could be indicative of contamination unless a substantial proportion of the carbon in the PM is assumed to derive from tree-wood several decades old. From data for two monitoring sites in the USA where ¹⁴C contamination is apparent, Bukholz

et al. [69] suggest that such contamination is uncommon but is also not rare (~10%) for PM sampling sites. The extent to which contamination may be an issue more widely is not possible to gauge because the vast majority of authors do not comment on this. However, the possibility of the occasional artificially inflated value for fraction modern needs always to be borne in mind.

6.2 Improvements in AMS analyses

Sputtering a CO₂ gas sample directly, rather than a graphitized target, gives a lower intensity ion beam but, with additional time, it is possible to utilize the entire source in order to acquire sufficient ions. It is then possible to work with samples down to a few tens µg C [70] which opens the way for shorter durations of sample collection (e.g. sub-diurnal) or analyses of different classes of organic compounds, or even individual compounds (Section 6.4). The facility to analyse filters with shorter sampling duration is also an advantage from the perspective that the OC fraction can be prone to losses during sampling. The increased sensitivity comes at extra cost because of the additional beam time required.

The Cs⁺ sputter source that is normally used in AMS instruments can have some chemical effects on analytes. Use of other ions such as Kr⁺ and Xe⁺ that avoid these interferences has been proposed [29]. Another development is the insertion of an additional reaction cell between the initial electric analyser and the accelerator to separate out some rare and stable anions with energies of about 20 keV that interfere with isobar separation [29].

6.3 Separation of OC-EC

The distinction and isolation of fractions of carbon into OC and EC will likely remain a methodologically-defined process. In reality anyway, a sample of PM containing material derived from many sources will contain a continuum of carbonaceous material spanning elemental graphitic carbon, non-refractory and partially functionalised elemental and ‘brown’ carbon, polymeric (and ‘humic-like’) organic material and individual organic compounds with a wide range of functionality and hygroscopicity [14-17;71]. Considerable progress has been made in refining protocols for OC-EC demarcation for application to ^{14}C studies that can form the basis for reporting to standard analyses [44;45]. An alternative, or parallel, approach is to subdivide the carbonaceous material according to gradations in external properties such as polarity and solubility in different solvents, or to pursue compound-class or individual compound isolation for ^{14}C determination (Section 6.4).

The determination in parallel to ^{14}C of marker compounds in the PM, such as levoglucosan for wood burning, and cellulose, mannitol and arabitol for primary biological material, has been shown invaluable in helping discriminate and quantify different carbon sources [37;38;60;61;72]. Other potential source markers include PAH ratios, which are diagnostic of different combustion sources, and the carbon preference index of n-alkanes (organic matter of recent biogenic origin shows pronounced predominance towards n-alkanes with odd carbon numbers (CPI >1), whilst n-alkanes of fossil-fuel origin typically show CPI of one or less) [73;74]. The introduction of high-resolution MS techniques (e.g. orbitraps) will push forward the identification and quantification of marker compounds, particularly for the more complex highly oxidized OC components.

6.4 Compound-specific ^{14}C determinations

A few studies have investigated fossil/non-fossil contributions to classes of organic compounds isolated from ambient PM, or even at the level of an individual compound. Aside from the time consuming nature of such studies, the major limiting factor is the collection of sufficient material from which can be extracted sufficient mass of the component of interest to prepare as an AMS target. Work to date has focused on polycyclic aromatic hydrocarbons (PAH).

Mandalakis et al. [75] combined several hi-vol samples from 3 background sites in Sweden, Greece and Croatia into a single sample per site, and used extensive preparative GC clean-up and pre-concentration to obtain sufficient material (14 to 68 μg total) for ^{14}C analysis on a combined sample of the 9 most abundant PAHs in each sample. They found that biomass burning contributes nearly 10% of the total PAH burden in the two southern European sites (with fossil fuel combustion making up the 90% balance) but contributed about 50% of total PAHs at the Swedish site. In a similar study, sampling at a number of sites across the western Balkans, Zencak et al. [76] reported significantly higher non-fossil contributions to atmospheric PAH, even in urban and industrialized areas, than for the previous single measurement at a remote Croatian site [75].

In suburban Tokyo, compound-class specific ^{14}C analysis revealed that biomass burning contributed 17-55% of the PAH burden, and that the increase in the biomass PAH accounted for ~27% and 22% of winter-time elevation of low molecular weight PAH and high molecular weight PAH, respectively [77]. For $\text{PM}_{2.5}$ samples collected in North Birmingham, Alabama, USA, compound-class ^{14}C determinations showed that only 3-8% of the PAHs were of non-fossil origin, and that the non-fossil contribution was greater in winter than in summer, which was attributed to increased contribution of PAHs from biomass burning [78]. Biomass burning

contributed more to heavier PAHs (modern source accounting for 6–8%) than lighter ones with a modern contribution of 3%.

Sheesley et al. [79] claim the first compound-specific radiocarbon analysis of atmospheric PAHs, for a set of samples collected in Lycksele, Sweden. Five individual/paired PAH isolates from three pooled fortnight-long filter collections were analyzed: phenanthrene, fluoranthene, pyrene, benzo[b+k]fluoranthene and indeno[cd]pyrene plus benzo[ghi]perylene. A simple isotopic mass balance model was applied to estimate the fraction biomass, which was constrained to 71–87% for the individual PAHs. Indeno[cd]pyrene plus benzo[ghi]perylene had a fraction biomass of 71%, while fluoranthene had the highest biomass contribution at 87%. The authors concluded that residential wood combustion is the dominating source of atmospheric PAHs to this region with some variations in contribution to specific PAHs.

These studies reveal wide variation in the relative contributions of fossil and biomass sources to atmospheric PAHs with geographic region, and with season. It is anticipated that as the capability to utilize smaller masses of carbon in ^{14}C determinations improves additional studies of other compound classes, e.g. organic acids, will be undertaken.

7 Summary

Carbon-14 (^{14}C) is an ideal tracer for distinguishing between contemporary and fossil carbon since carbonaceous material derived from sources of contemporary carbon (e.g. biomass burning, cooking, SOA from biogenic VOC emissions) contains a known abundance of ^{14}C whereas carbonaceous material derived from fossil-fuel source contains none. In principle, measurement of the abundance of ^{14}C in a sample directly yields the relative proportions of

each. To measure accurately the very low abundances of ^{14}C in the small amounts of carbon available in filters samples of PM requires accelerator mass spectrometry. The PM sample is combusted in O_2 to CO_2 and the carbon reduced to graphite. AMS derives high sensitivity through a number of instrumental features, including the acceleration of ions through a stripper to dissociate molecular isobars and produce multiply-charged elemental ions, and atomic-number-sensitive detection.

The increasing availability of AMS facilities (albeit that it remains a specialist and expensive technique) has led to a number of investigations of its application to atmospheric PM. All studies report a sizable fraction of the carbonaceous PM as of non-fossil origin. Even for PM collected in urban locations proportions of non-fossil carbon generally exceed 30%; typically the proportion in urban background locations is around 40-60% depending on the local influence of biomass burning. A number of studies have sought to thermally isolate the carbon in the PM into CO_2 derived from OC and EC and to measure the ^{14}C in each fraction separately. Issues remain with unambiguously achieving such a separation, but where this speciation has been undertaken, proportions of non-fossil carbon in EC are lower than in OC, reflecting the greater contribution of fossil-fuel combustion to EC and the generally small sources of contemporary EC.

Sophisticated source apportionment work has been undertaken incorporating data from parallel determinations of other organic tracers such as levoglucosan for wood burning, cellulose for primary plant material, and mannitol or arabitol for fungal spores, together with assumptions of ratios for the concentrations of these markers to bulk mass emissions from these sources. An important contribution from BVOC-derived SOC is identified, consistent with other evidence of a ubiquitous presence of heavily oxidised background SOC. The best prospects for maximizing information from application of ^{14}C analyses to PM are in

conjunction with other source markers, facilitated through application of high-resolution MS techniques, and through increases in AMS sensitivity enabling ^{14}C determinations in compound-class specific and individual compound components of PM.

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Tables

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

$f_{\text{M}}(\text{TC})$	$f_{\text{M}}(\text{EC})$	$f_{\text{M}}(\text{OC})$
<i>NIST [49] certificate</i>		
0.61 ± 0.08 (combustion manometry)	0.065 ± 0.014 (thermal oxidation)	no value given ^a
0.505 ± 0.006 (H_3PO_4 -combustion-manometry)	0.153 ± 0.004 (chemical oxidation)	no value given ^a
0.517 ± 0.007 (combustion-GC)	0.038 ± 0.024 (thermal kinetic oxidation)	no value given ^a
<i>Szidat et al. [24]</i>		
0.522 ± 0.018	0.066 ± 0.020	0.70 ± 0.05
<i>Heal et al. [27]</i>		
0.515 (single combustion)		
0.570 ± 0.014 (two-step combustion)	0.15 ± 0.08	0.66 ± 0.02

^a No information value(s) are supplied on the certificates for f_{M} of the OC fraction, although the associated paper [46] provides the following f_{M} values for certain organic fractions: polar carbon, $f_{\text{M}} = 0.43$; aromatic carbon, $f_{\text{M}} = 0.17$; aliphatic carbon, $f_{\text{M}} = 0.024$;

Table 2: A summary of studies reporting the fraction non-fossil carbon in atmospheric PM published since the mid-2000s. The focus is on data relating to the fraction non-fossil carbon in PM total carbon (TC) but data for non-fossil carbon in the OC and/or EC components are also presented where these were measured. Data are for fraction contemporary, f_c , except where stated to be fraction modern, f_M . The emphasis is on summarising reported f_c (or f_M) values but some data in this table are from source apportionment calculations presented by the study authors or has been inferred by this author. In some instances reported data were difficult to interpret exactly. Abbreviations: KERB – kerbside; URB – urban; SUB – suburban; RUR – rural; COAST – coastal; MAR – marine; sum – summer; win – winter; spr – spring; aut – autumn (fall). All site and season assignments as presented by study authors.

Reference	Location	Site type	PM fraction	Approx. period during which samples collected	Fraction non-fossil TC (mean and/or range)	Fraction non-fossil OC	Fraction non-fossil in EC	Comments
Bench [32]	Yosemite NP, USA	RUR	TSP	Jul-Sep 2002	$f_M = 0.801-1.04$ ($n=23$)	-	-	
Lewis et al. [34]	Nashville, USA	AIRPORT	PM _{2.5}	Jun-Jul 1999	0.60 – 0.80	-	-	
Endo et al. [80]	Tokyo, Japan	URB	5 fractions from <1.1 μm to >7.0 μm	Apr 2002	~0.60 for largest size to 0.40 for smallest size	-	-	Increasing contribution of fossil carbon in smaller size fraction
Szidat et al. [23]	Zürich, Switzerland	URB	PM ₁₀	Aug 2002	0.63 ($n=3$)	0.75 ($n = 4$)	0.30 ($n = 4$)	
Szidat et al. [43]	Zürich, Switzerland	URB	PM ₁₀	Aug 2002 (day and night)	-	0.69 (0.51-0.80) ($n = 13$)		
Szidat et al. [35]	Zürich, Switzerland	URB	PM ₁₀	Aug-Sep 2002 (sum); Feb 2003 (win); Mar 2003 (spr)	-	0.70 (sum); 0.68 (win); 0.72 (spr);	0.06 (sum); 0.25 (win); 0.12 (spr);	
Jordan et al. [25]	Launceston, Tasmania	SUB	TSP & PM ₁₀	May 2002 - Dec 2003 (win)	0.86-1.0	-	-	Very large contribution from wood burning stoves
Gelencser et al. [41]	5 \times European 'CARBOSOL' sites	RUR	PM _{2.5}	Oct 2002- Jul 2004	0.57-0.82	-	-	Fossil carbon dominates EC; consistency in relative source apportionment across the 5 sites.
Yamamoto et al. [53]	Tokyo, Japan	URB	PM _{1.3}	Jun 2002 – Feb 2003	0.30-0.40	-	-	
Zencak et al. [81]	Stockholm, Sweden	URB, RUR	TSP	Oct - Dec 2005	-	-	URB 0.70 RUR 0.88	
Bench et al. [33] & Schichtel et al. [57]	12 \times USA 'IMPROVE' sites	URB, NEAR-URB, RUR	PM _{2.5}	Various Jun-Aug (sum) & Dec-Feb (win) periods 2000-2006	URB ~0.50; NEAR-URB 0.70-0.97; RUR ~0.82-1.0.	-	-	At RUR sites non-fossil C generally lower in winter than summer, although still the major component

Szidat et al. [36]	Göteborg, Sweden	URB	PM ₁₀ (win) PM _{2.5} (sum)	Feb - Mar 2005 Jun-Jul 2006		f_M OC = 0.69 (0.59-0.78 (n=7))	f_M EC = 0.12 (0.05-0.17 (n=7))	No sig. difference with season or PM fraction. Apportionment model gives mean f_c (TC) = 0.54 (sum), = 0.45 (win)
Gustafsson et al. [82]	Singahad, India & Maldives	RUR	TSP	Feb-Apr2006	0.67 ± 0.03	-	'EC': 0.46 ± 0.08 'soot': 0.68 ± 0.06	EC also includes 'brown carbon'; 'soot' is a more recalcitrant component of EC
Huang et al. [26]	Lhasa, Tibet	URB	TSP	Aug 2006-Jul 2007	0.357-0.702	-	-	Higher f_c in winter c.f. in summer
Hodzic et al. [72]	Mexico City	URB, SUB	PM ₁	Mar 2006	URB 0.37-0.67; SUB 0.50-0.86			
Andersson et al. [83]	Stockholm, Sweden	URB, RUR	TSP	Aug – Oct 2006 Nov 2006 – Mar 2007	-	-	URB 0.38 (win), 0.45 (aut); RUR 0.43 (win), 0.35 (aut)	
Heal et al. [27]	Birmingham, UK	URB	PM _{2.5}	Jun-Aug 2007; Jan-May 2008	0.50 (range 0.27-0.66) (n =26)	f_M OC = 0.76 (n = 26)	f_M EC = 0.11 (n = 26)	No sig. difference with season. Enhanced contemporary OC with continental trajectories
El Haddad et al. [84;85]	Marseilles, France	URB	PM _{2.5}	Jun-Jul 2008	Not directly reported	-	-	Authors infer average f_c (OC) of 0.63, based on assumption that all EC is fossil
Gilardoni et al. [37]	Po Valley, Italy	RUR	PM _{2.5}	Jan-Dec 2007	0.73±0.16 (win) 0.59±0.26 (sum)	see notes	see notes	apportionment of TC into 8 sources of fossil-non-fossil carbon is described
Ceburnis et al. [86]	Mace Head, Ireland	COAST, MAR	PM _{1.5}	Jan-Nov 2006	0.86 (clean air mass); 0.63 (continental air mass)			Clean air mass: 0.79 marine biogenic, 0.07 continental non-fossil, 0.14 fossil; Polluted continental air mass: 0.32, 0.31, 0.37 resp.
Genberg et al. [38]	Vavihill, Sweden	RUR	PM ₁₀	Apr 2008-Apr2009	0.56 (win) 0.71 (spr) 0.85 (sum) 0.72 (aut)			These values for TC from source apportionment but some uncertain because not all TC accounted for
Yttri et al. [61]	Oslo, Norway	URB, RUR	PM ₁₀ & PM ₁	Jun-Jul 2006 Mar 2007	f_M values: URB PM ₁₀ 0.61 (win), 0.73 (sum); RUR PM ₁₀ 0.68 (win), 0.93 (sum); URB PM ₁ 0.64 (win), 0.65 (sum); RUR PM ₁ 0.70 (win), 0.83 (sum);			apportionment of TC into 7 sources of fossil-non-fossil carbon is described

Yttri et al. [60]	1 each Sweden, Norway, Finland, Denmark	RUR	PM ₁₀	Aug-Sep 2009	Averages across the 4 locations range 0.74-0.84.			apportionment of TC into 5 sources of fossil-non-fossil carbon is described
Fushimi et al. [54]	Kanto (Tokyo) Japan (2 sites)	SUB	PM _{2.5}	Aug 2007	0.37±0.15 & 0.37±0.15 for each site	-	-	f_c (TC) sig. higher at night
Glasius et al. [56]	5 European cities	KERB, URB, SUB, RUR	PM _{2.5}	2002-04	0.43±0.11 overall av.	-	-	Progression in f_c (TC) ranging from 0.36±0.07 (KERB) to 0.54±0.11 (RUR)
Minguillón et al. [39]	Barcelona, Spain	URB, RUR	PM ₁	Feb-Mar 2009 (win), Jul 2009 (sum)		URB 0.60 (win), 0.52 (sum); RUR 0.69 (win), 0.75 (sum)	URB 0.13 (win), 0.09 (sum); RUR 0.21 (win), 0.34 (sum)	f_c in EC and OC separately
Sun et al. [55]	Yufa (Beijing), China	RUR	PM _{2.5}	sum & win 2007	0.30-0.38 (win) ($n = 6$ day, $n = 6$ night) winter, 0.31-0.44 (sum) ($n = 6$ day, $n = 6$ night) winter,	-	Inferred f_c (EC) 0.13-0.20 in both seasons	f_c in TC only
Minoura et al. [87]	6 in Kanto area, Japan	URB, SUB, RUR	PM _{2.5}	sum 2008, win 2009	Overall mean: 0.51	0.58	0.39	Only 1 sample per site. In Tokyo f_c (TC) 0.29 (sum) & 0.48 (win). f_c (TC) higher by 10% for SUB & RUR
Dusek et al. [40]	Amsterdam & Petten, The Netherlands	URB, COAST	PM ₁₀ (URB), TSP (COAST)	Jan-Jun 2006 (URB) Jul-Sep 2009 (COAST)	-	URB 0.68 ±0.05 ($n=10$) COAST 0.83 ±0.04 ($n=8$)	-	f_c in OC only

Table 3: Estimation of primary and secondary splits to the OC_{fossil} and OC_{biogenic} source apportionment of TC provided by Heal et al. [27] for samples of $PM_{2.5}$ collected in Birmingham, UK. An estimation for scaling mass carbon to total mass within $PM_{2.5}$ is also provided. Table taken from AQEG [13].

Component	%	Mass C / $\mu\text{g m}^{-3}$	OM/OC factor	Mass OM / $\mu\text{g m}^{-3}$	%
Fossil EC	27	1.35	1.0	1.35	18
Fossil OC ^a	20	1.00			
- primary		0.47	1.25	0.59	8
- secondary		0.53	1.80	0.95	13
Biomass EC	2	0.10	1.0	0.10	1
Biomass OC	10	0.50	2.0	1.00	13
Biogenic OC ^b	41	2.05			
- primary		0.20	1.2	0.24	3
- secondary		1.85	1.80	3.33	44
TOTAL	100	5.00		7.56	100

^a Split of fossil OC into primary and secondary is based upon primary OC = 0.35 fossil EC [59].

^b Based upon average ratio of 0.10 between vegetative detritus and ‘other’ OC in Birmingham reported by Yin et al. [88].

Figure captions

Figure 1: Illustration of a ‘top down’ apportionment of particulate matter carbon into broad categories, first into elemental or organic carbon, with further sub-division into anthropogenic or contemporary sources and into direct primary emissions or in-situ secondary formation. The categories it is possible to quantify directly by ^{14}C determination by accelerator mass spectrometry are highlighted.

Figure 2: A general schematic of an accelerator mass spectrometer. Ions from the Cs^+ sputter source undergo rudimentary separation in the first electric and/or magnetic analyser before being accelerated to high energies to dissociate molecular ions and form multiply-charged elemental ions. Further electric and magnetic discrimination follows. Reproduced with permission from Litherland et al. [29].

Figure 3: Temporal change of observed atmospheric F^{14}CO_2 in the northern and southern hemispheres. A value of 1000 ‰ equates to a doubling of atmospheric ^{14}C compared with the modern standard. The 2010 value of F^{14}CO_2 is ~40 ‰ ($f_M = 1.04$). Figure reproduced from Levin et al. [89] (Creative Commons License).

Figure 4: Schematic of methodology of Szidat et al. [23;35] to isolate different categories of carbon within PM for contemporary-fossil apportionment. The ^{14}C values are directly measured in TC, OC, WINSOC, EC and the mixture ‘EC + polymerizable WSOC.’ The ^{14}C values in WSOC and ‘polymerizable WSOC’ are deduced from subtraction. Reproduced with permission from Szidat et al. [35].

Figure 5: Average ($n = 26$) % source apportionment of $\text{PM}_{2.5}$ from Birmingham (UK), from the work of Heal et al. [27]. $\text{OC}_{\text{biomass}}$ is POC from combustion of biofuels/biomass, $\text{OC}_{\text{fossil}}$ is both fossil-derived POC and any SOC from fossil-derived VOC, and $\text{OC}_{\text{biogenic}}$ is SOC formed from BVOC oxidation together with any other contemporary OC material not explicitly accounted for elsewhere, for example spores, plant detritus, tyre rubber, etc.

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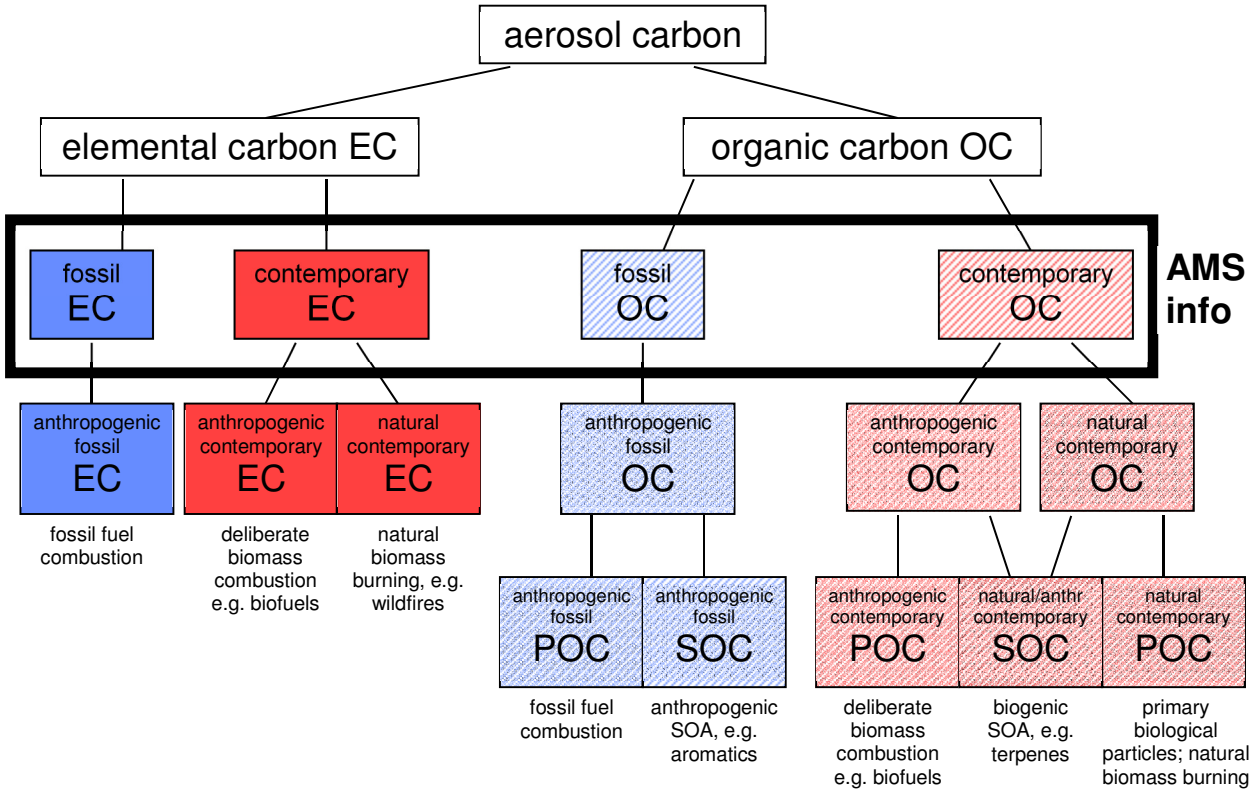


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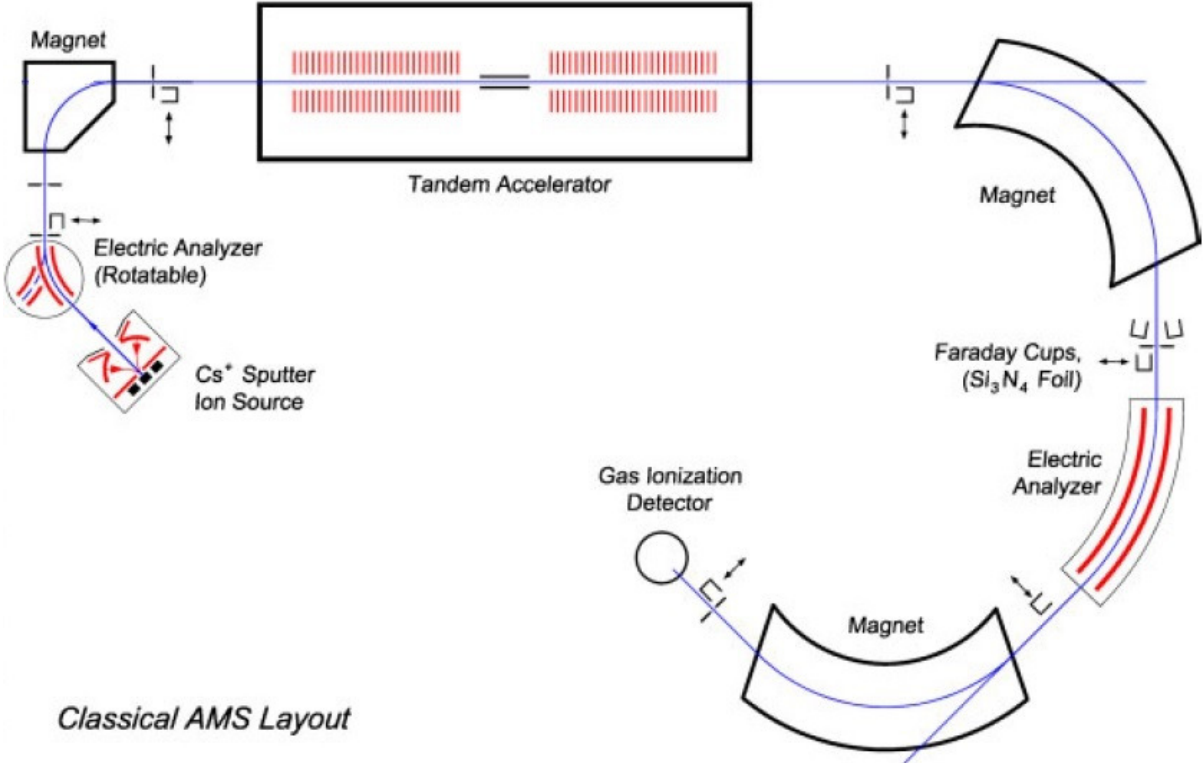


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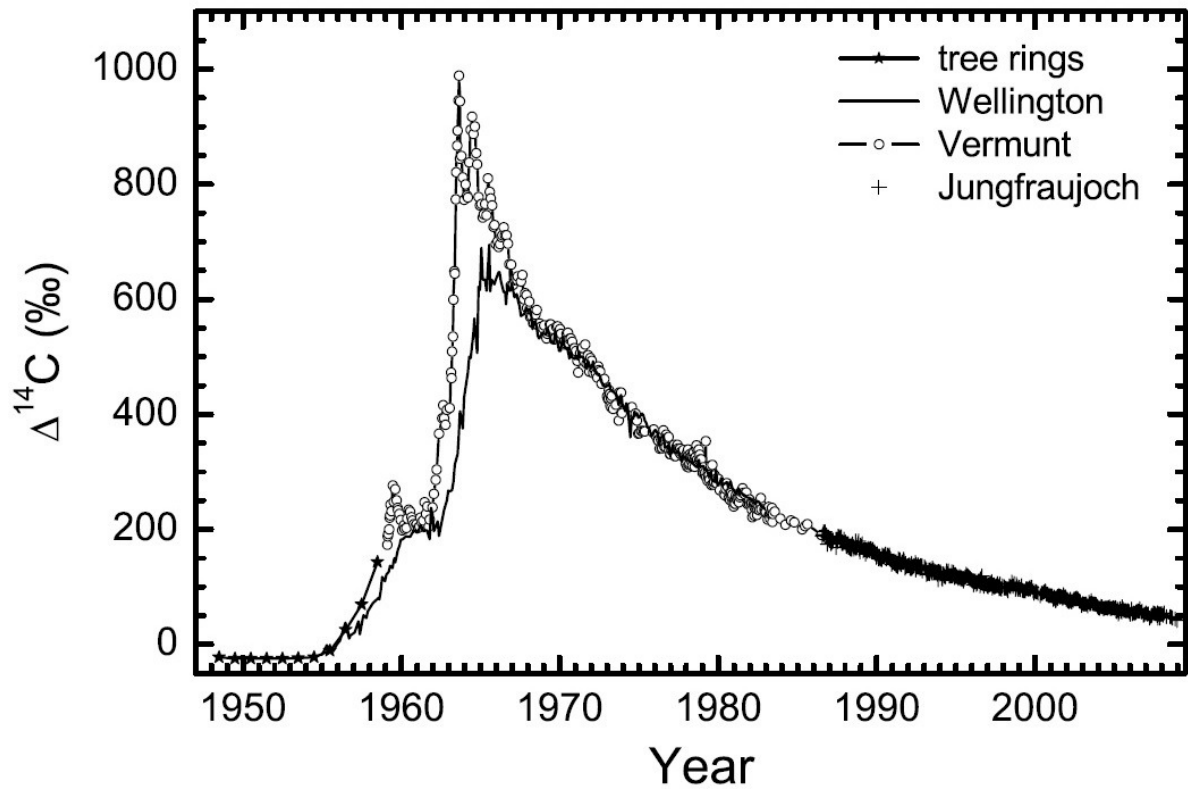


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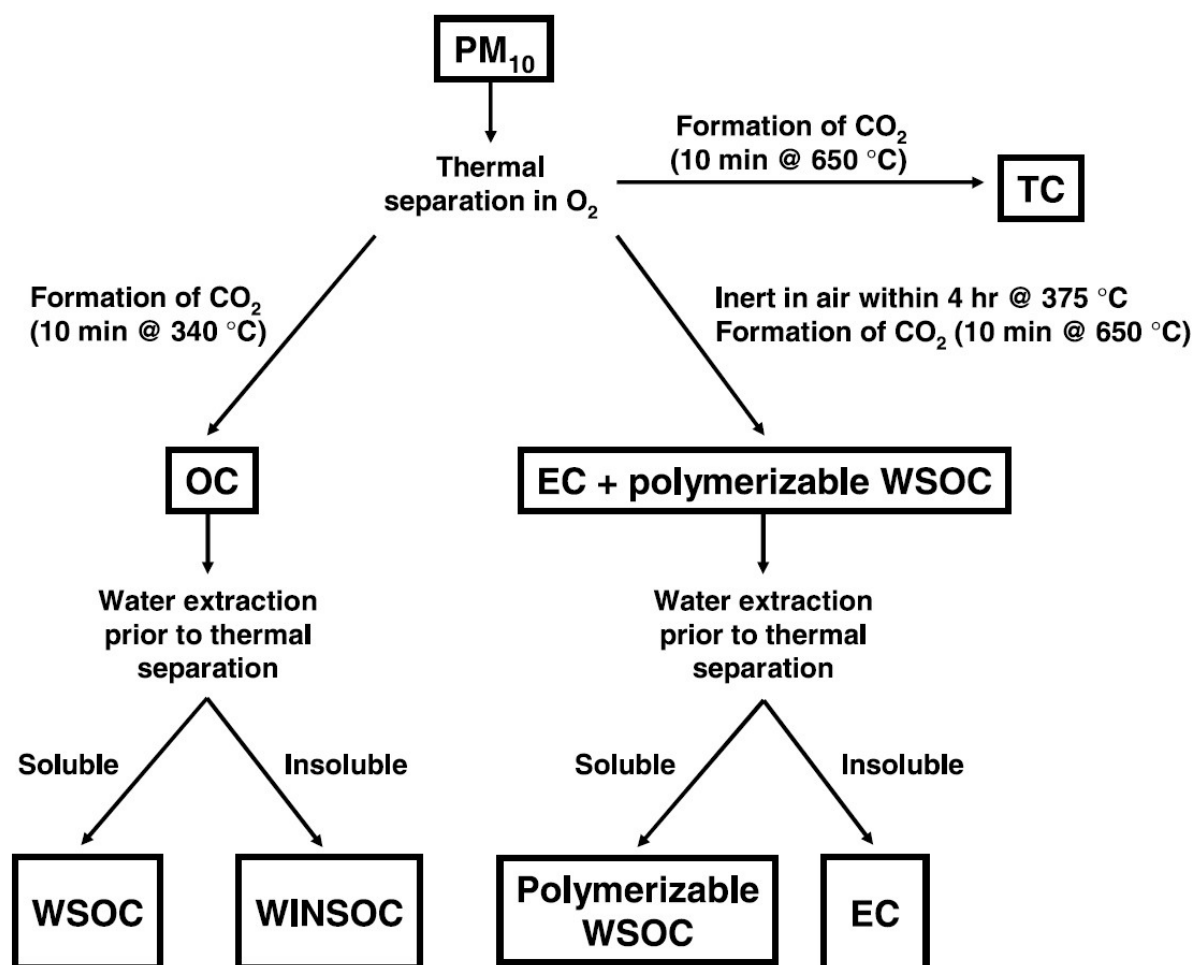


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