Source Apportionment of Elemental Carbon in Beijing, China: Insights from Radiocarbon and Organic Marker Measurements

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1. INTRODUCTION

Atmospheric aerosols adversely affect human health by causing respiratory and cardiopulmonary diseases associated with increased morbidity and mortality. Carbonaceous components are a major fraction of atmospheric aerosols and are often classified into the subfractions organic carbon (OC) and elemental carbon (EC) or black carbon (BC). In this study, BC is used as a qualitative and descriptive term not referring to measurement results of any specific properties, whereas BC mass quantified by thermal-optical methods is specified as EC. As the major light-absorbing part of carbonaceous material, BC exhibits the second largest anthropogenic radiative forcing after carbon dioxide (CO₂). Recently, it was estimated that 640–4900 premature human deaths could be prevented annually by utilizing available mitigation measures to reduce BC in the atmosphere. Due to a relatively short lifetime (~days) in atmosphere, reducing BC emissions may rapidly improve both climate and human health. Therefore, the identification and quantification of different BC sources and their emission source strengths is crucial for the implementation of effective mitigation strategies.

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contribution of these two sources still remains uncertain. In recent years, the radiocarbon (14C) measurement of EC has been proven to be a powerful tool for the differentiation between modern (i.e., biomass burning) and fossil (i.e., traffic and coal) sources. 14C is completely depleted in fossil fuel emissions due to its half-life (i.e., 5730 years), whereas 14C in nonfossil carbonaceous materials contains a similar composition as atmospheric CO2.9,10 Therefore, 14C measurement of the EC fraction directly enables the quantification of its biomass-burning and fossil sources.11 However, the 14C measurement of EC still remains challenging in comparison to total carbon (TC) due to its complex properties12 and since a clear physical separation remains challenging in comparison to total carbon (TC) due to a clear physical separation between OC and EC is necessary to avoid artifacts in the 14C signal. Nevertheless, recent developments and method adaptations from different groups show more consistent approaches and yield more robust 14C results.13,14

Beijing, the capital of China with about 19.6 million inhabitants in 2010, is one of the largest cities in the world and has become a heavily polluted area due to rapid urbanization and industrialization over the past two decades.15 In the past decade, many studies have reported the chemical composition and sources of aerosols in Beijing.20–23 Most of these studies have focused on source apportionment of organic aerosols (organic matter, OM or OC) by positive matrix factorization (PMF)24 and chemical mass balance (CMB) models21 from off-line organic markers measurement or online aerosol mass spectrometer measurement. However, only a few studies have reported year-round source apportionment results of BC. For example, Duan et al. (2004) demonstrated biomass burning and traffic and/or industry emissions are the major sources of both OC and EC during summer, while coal combustion is the dominant contributor during the winter heating period, although quantification of contributions from each source still remains uncertain. Based on PMF model analysis, about 50% of OC and EC in Beijing were associated with biomass-burning processes.25 In contrast, most recent source-diagnostic 14C studies suggested ~80% contribution from fossil fuels in winter for EC in China.15,23,26 A quantitative understanding of the temporal variations and source apportionment of EC in Beijing is still missing and thus crucially necessary. In this study, we determine fossil and biomass-burning contributions to year-round EC aerosols in Beijing by measuring 14C of EC and organic markers for fossil emissions (i.e., hopanics and picene).

2. EXPERIMENTAL SECTION

2.1. Sampling. Twenty four hour integrated PM4 samples (n = 155) were collected at the ground level on prebaked (650 °C, 4 h) quartz-fiber filters (diameter: 150 mm) using a high-volume sampler (Digitel DHA-80, Switzerland) at a flow rate of ~167 L/min during June 2010 to May 2011 at the campus of the China University of Geosciences, a residential area in North West of Beijing. It should be noted that during the whole campaign the actual sampling flow of ambient air was 167 instead of 500 L/min as a default setting due to an airflow shortcut from the interior of the sampler. As a consequence to the changed flow volume, the cut off of the sampler (original setting: 2.5 μm) had to be recalculated following the imopper design theory.27–29 It was found that particles smaller than 4 μm (i.e., PM4) were collected onto the filters. However, a comparison of 14C results obtained from the current study was not significantly different from those found for PM5.5 samples during winter 2013 (see Supporting Information (SI), Figure S1).30 Our previous work has also shown that there is no significant difference of EC source signatures (fossil vs nonfossil) between PM10, PM2.5, and PM10 at other locations (SI Table S1).30 Further, since EC almost exclusively derives from combustion sources, the size of EC particles from China’s source samples is mostly smaller than 1 μm31,32 and the majority of EC mass (~80%) in urban site of China resides in particles smaller than 3.2 μm in diameter and the fine mode peaks at around either 0.42 or 0.75 μm.33 As a result, the cut size present in our study generally would not affect the results of relative fossil and nonfossil contribution of EC of aerosols because EC is dominated in the fine particles. After sampling, filters were wrapped in aluminum foil and stored in a freezer at −20 °C before analysis. Every second week, one field blank was collected.

2.2. Elemental Carbon Measurement. A filter cut of 1.5 cm2 was used for EC measurement. The EC concentrations were measured using a thermo-optical OC/EC analyzer (model 4L, Sunset Laboratory Inc.), equipped with a nondispersive infrared (NDIR) detector following the thermal-optical transmittance protocol (TOT) EUSAAR2.34 A high uncertainty of 20% is considered for all measured EC concentrations to account for possible differences between different TOT protocols.35,36 It should be noted that only the absolute EC concentration is affected by this additional uncertainty, whereas the relative fossil and nonfossil contribution is only influenced by the combined uncertainty of the 14C measurement of EC and the bomb peak correction, which is on average 5% (see below). No EC was detected on blank filters and consequently no blank correction was necessary.

2.3. Radiocarbon (14C) Measurement of EC. A filter cut of 1–6 cm2 (corresponding to 5–30 μg C) was used for 14C analysis. The Swiss_4S protocol was applied for the EC isolation for the 14C analysis using a Sunset OC/EC analyzer connected to a gas preparation line as described by.14 This special protocol is optimized to minimize the bias in the 14C result of EC from OC charring or losses of the least refractory EC during the OC removal. In brief, to minimize possible artifacts from OC charring, water-soluble OC is first eliminated by a water-extraction pretreatment and the remaining water-insoluble OC is then removed using the Sunset OC/EC analyzer with a thermal treatment in three steps: (1) 375 °C for 150 s in pure oxygen (O2); (2) 475 °C for 180 s in O2; (3) 450 °C for 180 s followed by 180 s at 650 °C in helium. Finally, in step four EC is isolated by the combustion of the remaining carbonaceous material at 760 °C for 150 s in O2. EC recovery is estimated by the ratio ATN/ATN0, where ATN0 is the initial attenuation (ATN, see SI), which is related to the total amount of EC on the filter, and ATN is the attenuation at the time t, when the EC step (i.e., step 4) begins. By using the Swiss_4S protocol, OC charring is minimized to 4 ± 3% compared to EC (see SI), which may lead a negligible overestimation of nonfossil EC by less than 3%. This assures the accuracy of 14C measurement in EC. The EC recovery in this study was estimated as 85 ± 5%, thus presenting almost the entire continuum of EC. 14C results in EC were extrapolated to 100% EC recovery (fMEC,corrected = slope × (1 − EC recovery) + fMEC) to account for the less refractory EC, mainly from wood burning, which is removed during steps 1−3.34 The slope of 0.31 is deduced from linear regression of the EC recovery and fMEC.14 The uncertainty of the reported fMEC is obtained by an error propagation of all possible uncertainties including an assigned uncertainty of 10% for the slope, the measurement uncertainty of fMEC (2%) and an assigned uncertainty of 10% for the EC yield, which results to a total average uncertainty of 4%.
The evolving CO₂ in step 4 was separated from interfering gaseous products, cryo-trapped and sealed in glass ampules for 14C measurements. 14C measurements of the CO₂ was carried out with the mini radio carbon dating system, MICADAS37 using a gas ion source.38 The 14C results are presented as fraction of that of the reference year 1950.39 Oxalic acid (HOxII) decay between 1950 and the year of measurement.40 The 2.9 μg/m³ was obtained in the cold period (i.e., average from November to February is 4.8 μg/m³). It should be noted that the frequency of samples with EC concentrations >3 μg/m³ reported by 14 samples from different seasons were selected for the analysis of 14C of the EC fraction (Table 1). In order to address the air quality problems of Beijing,35 we characterized EC sources for days with medium and heavy air pollution during the warm and cold periods. Therefore, samples were selected for radiocarbon analysis with EC concentrations >3 μg/m³, which includes about 2/3 of all daily samples shown in Figure 1, representing ~82% of the integrated EC burden of all samples. However, EC sources of background days are not considered. The values for f(EC) ranged from 0.10 to 0.34 with a mean of 0.23 ± 0.06, indicating a dominance of fossil sources of EC in Beijing throughout the year. Since EC is only emitted as primary aerosol by combustion from either biomass or fossil fuels (i.e., coal and vehicle emissions), f(EC) particularly tracks the change of EC sources. The lowest f(EC) is found in summer (0.15), indicating the importance of vehicle emissions since the coal consumption is much reduced compared to other seasons. f(EC) is higher by 60% in the rest of the year than in summer, suggesting that EC from biomass burning becomes substantial during the other seasons. Further discussions of source apportionment of fossil EC will be presented in Section 3.4.

3.2. 14C Results of EC: Fraction of Modern. In order to further investigate the sources of EC, 14 samples from different seasons were selected for the analysis of 14C of the EC fraction (Table 1). In order to address the air quality problems of Beijing,35 we characterized EC sources for days with medium and heavy air pollution during the warm and cold periods. Therefore, samples were selected for radiocarbon analysis with EC concentrations >3 μg/m³, which includes about 2/3 of all daily samples shown in Figure 1, representing ~82% of the integrated EC burden of all samples. However, EC sources of background days are not considered. The values for f(EC) ranged from 0.10 to 0.34 with a mean of 0.23 ± 0.06, indicating a dominance of fossil sources of EC in Beijing throughout the year. Since EC is only emitted as primary aerosol by combustion from either biomass or fossil fuels (i.e., coal and vehicle emissions), f(EC) particularly tracks the change of EC sources. The lowest f(EC) is found in summer (0.15), indicating the importance of vehicle emissions since the coal consumption is much reduced compared to other seasons. f(EC) is higher by 60% in the rest of the year than in summer, suggesting that EC from biomass burning becomes substantial during the other seasons. Further discussions of source apportionment of fossil EC will be presented in Section 3.4.

3. RESULTS AND DISCUSSIONS

3.1. Temporal Variation of EC. Figure 1 shows EC concentrations during the whole sampling period. EC concentrations range from 0.8 to 11.8 μg/m³, and the average of 4.0 ± 2.2 μg/m³ is within the range (2.3–7.4 μg/m³) reported by previous studies for Beijing.31,42 The EC concentrations are significantly lower (t test with p < 0.05) during the warm period (i.e., average from March to October is 3.6 ± 1.5 μg/m³) than in the cold period (i.e., average from November to February is 4.8 ± 2.9 μg/m³). It should be noted that the frequency of samples with EC larger than 4.5 μg/m³ in the cold period is much larger than that in the warm period, indicating a higher primary particulate pollution from enhanced anthropogenic emissions during the cold period. A similar seasonal trend was also observed by ref 43. This seasonality is likely attributed to increased emissions from residential heating using coal or biofuel. The lower EC abundance in the warm period is mainly caused by reduced heating-related coal/biofuel emissions on the one hand and a higher mixing layer on the other hand. It should be pointed out that EC concentration in summer at the studied site is still higher than those observed in many other cities during summer such as Barcelona, Spain (1.2 μg/m³),44 Paris, France (1.4 μg/m³) or Pittsburgh, PA (0.89 μg/m³).46

Figure 1. Temporal variation of EC concentrations (μg/m³, n = 15S) in Beijing, China.

![Image](https://example.com/image.png)
of 79% ± 6% (ranging from 70% to 91%). The measured fossil contributions to EC are comparable to those previously reported with a similar 14C-based approach in Beijing during winter 2011.23 and winter 2013,23 but are higher than for an urban site in Guangzhou, China (winter 2012/2013: 71 ± 10%)56 and a background site on the Hainan Island, South China (annual average 2005/2006: 25–56%)57 as well as 16 urban and rural sites across Switzerland (winter 2007/2008–2011/2012: 13–88%).11 Higher ECFF concentrations were observed in the cold period, most probably associated with larger coal combustion for heating. However, relative contributions from fossil combustion are even lower in the cold season than in the warm season, implying that biomass-burning emissions are also considerably important for the EC increment in the cold season. It should be noted that it is common practice to burn maize and wheat residues especially in the rural areas without central space heating and gas supplying systems and a large fraction of this biomass burning is emitted as OC and EC.50 The contribution of these biomass-burning emissions to EC in cold seasons is likely very important due to lower combustion efficiency for residential biomass burning than for coal boilers. By subtracting mean values of ECBB and ECFF in the warm period from those in the cold period, the excess is estimated as 0.82 ± 0.40 μg/m^3 and 1.75 ± 0.52 μg/m^3 for ECBB and ECFF, respectively. Biomass burning accounted for on the average 32% of the excess during the cold period, which is significantly higher than the contribution of ECBB (19%) during the warm period, but lower than estimations from PMF model analysis (50%).25

3.4. Fossil EC from Coal Combustion and Vehicle Emissions. Hopanes are abundant in crude oils, coal and lubricants.51 They have been identified in emissions from heating oil burning,52 coal burning53 and vehicles.54 Table 2 presents hopane concentrations in the warm and cold periods and the difference between these two seasons. As shown in Figure 3 and Table 2, the total identified hopanes mass concentrations show a clearly seasonal trend with maximum in the cold period (68.6 ± 28.7 ng/m^3) and minimum in the warm period (17.9 ± 6.5 ng/m^3). The hopane molecular patterns differ substantially with the type of the fossil source, and therefore potentially allow a distinction of coal combustion and vehicle emissions.55,56 For example, the ab-hopane/(ab-hopane+ba-hopanes) ratio (i.e., 30ab/(30ab+30ba)) increases with increasing diagenesis and catagenesis of the sediments. This ratio, also called hopane index, is >0.9 in crude oil57 and 0.1–0.6 in different types of coal.53,55 In typical petroleum, the R/S-epimerization at C22 has an efficiency for residential coal burning was negligible or very small in summer in Beijing. In contrast, both ratios found in the cold period (0.57 ± 0.06 and 0.46 ± 0.07 for hopane index and the homohopane index, respectively) are between those of petroleum and coal-burning emissions, indicating additional fossil-fuel emissions from solid coal combustion. Moreover, picene (a specific marker of coal combustion) was also determined in our study (Figure 3 and Table 2) and considerable concentrations are observed during the cold period (i.e., ranging from 0.34 to 4.48 ng/m^3 with a mean of 1.82 ± 0.99 ng/m^3), in contrast to the warm period, when concentrations were often below the detection limit or very small. If we assume that meteorological factors (i.e., wind speed...
It should be pointed out that picene may not be stable in summer, however, the emission ratio estimated by our approach would only change by <3% if assuming 0–50% of picene in summer has decayed through photochemical transformations. This emission ratio is comparable to the calculated emission ratios for Chinese residential bituminous coal (0.8) combustion but much lower than those found in residential anthracite (2.7), and coal briquette (3.2) combustion. Similarly, the hopane and homohopane indexes for the excess between the cold and warm period is estimated as 0.49 and 0.35 (Table 2), respectively, which are very close to those in the calculation by Monte Carlo simulation which has been reported elsewhere.

The fraction of traffic and coal combustion to EC particles is further calculated by

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EC_{\text{coal}} = \text{picene}/(\text{picene}/EC)^{\text{coal}} \tag{6}
\]

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EC_{\text{traffic}} = EC_{\text{FF}} - EC_{\text{coal}} \tag{7}
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The “best estimate” and its associated uncertainty are obtained by Latin-hypercube sampling (LHS). This approach is comparable to Monte Carlo simulation which has been reported in many 14C-based source apportionment studies. The emission ratio of picene/EC for coal combustion or (picene/EC)coal may be overestimated by 25% or underestimated by 50% if the traffic EC in winter is actually lower or higher than that in summer, respectively. Considering the overall uncertainty of

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between the warm and cold season are substantial, though vehicle emissions are the most important source of EC in both the warm and cold periods with a mean contribution of 79 ± 6% and 50 ± 7%, respectively. However, the biomass-burning contribution slightly increased (from 19% to 24%) and the coal combustion contribution increased dramatically in the cold period. The excess of EC between the cold and warm seasons was shared by coal (68 ± 4%) and biomass burning combustion (32 ± 4%) sources. The importance of coal contribution in the cold period is also evident by the occurrence of picene and hopanes indices. The current results imply that wintertime aerosol pollution in Beijing is likely driven by increased coal combustion and possible secondary formation of other aerosol components such as nitrate, sulfate, and organic carbon coemitted with EC.

In summary, the sources of elemental carbon (EC) from ambient samples collected in Beijing were investigated based on both radiocarbon (14C) and organic marker measurements. The results demonstrate that EC is dominated by fossil emissions throughout the year with a mean contribution of 79% ± 6%. To further identify and quantify traffic-related emissions and coal combustion contributions to fossil EC, hopanes and picene were also measured. The concentrations of the total identified hopanes are 68.6 ± 28.7 ng/m³ and 17.9 ± 6.5 ng/m³ in the cold and the warm period, respectively. The seasonal molecular pattern of hopanes indicates that vehicle emissions are the most important fossil source in the warm period and coal combustion emission is increased significantly in the cold season. By combining the 14C and organic marker’s measurements, relative contributions from coal and biomass-burning to the excess of EC between the cold and warm seasons were estimated as 68% and 32%, respectively. Based on published data from source samples, the hopane and home-hopane indexes as well as the picene-to-EC ratios are compared among different kinds of coal types. The comparison shows that the residential bituminite is a dominant coal type used during winter in Beijing.

**ASSOCIATED CONTENT**

Supporting Information
Relevance of the charring reduction using the Swiss_4S protocol; table showing the fraction of modern (fM) of EC in PM1, PM2.5, and PM10 in Switzerland; figures describing the fraction of modern (fM) of EC in PM1 (winter, 2011) and PM2.5 (winter 2013) in Beijing, thermograms of water-extracted aerosol samples using Swiss_4S, integrated probability distributions of the averaged relative contributions to EC from different sources using the Latin-hypercube sampling (LHS) simulation, and the relative contribution to EC from coal combustion (ECcoal) as a function of the selected (picene/EC)coal. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01944.

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Notes
The authors declare no competing financial interest.

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