Source apportionment of elemental carbon in Beijing, China: insights from radiocarbon and organic marker measurements

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Abstract

Elemental carbon (EC) or black carbon (BC) in the atmosphere has a strong influence on both climate and human health. In this study, radiocarbon (^{14}C) based source apportionment is used to distinguish between fossil fuel and biomass burning sources of EC isolated from aerosol filter samples collected in Beijing from June 2010 to May 2011. The ^{14}C results demonstrate that EC is consistently dominated by fossil-fuel combustion throughout the whole year with a mean contribution of 79% ± 6% (ranging from 70% to 91%), though EC has a higher mean and peak concentrations in the cold season. The seasonal molecular pattern of hopanes (i.e. a class of organic markers mainly emitted during the combustion of different fossil fuels) indicates that traffic-related emissions are the most important fossil source in the warm period and coal combustion emissions are significantly increased in the cold season. By combining ^{14}C based source apportionment results and picene (i.e. an organic marker for coal emissions) concentrations, relative contributions from coal and vehicle to EC in the cold period were estimated as 25±4% and 50±7%, respectively, whereas the coal combustion contribution was negligible or very small in the warm period.

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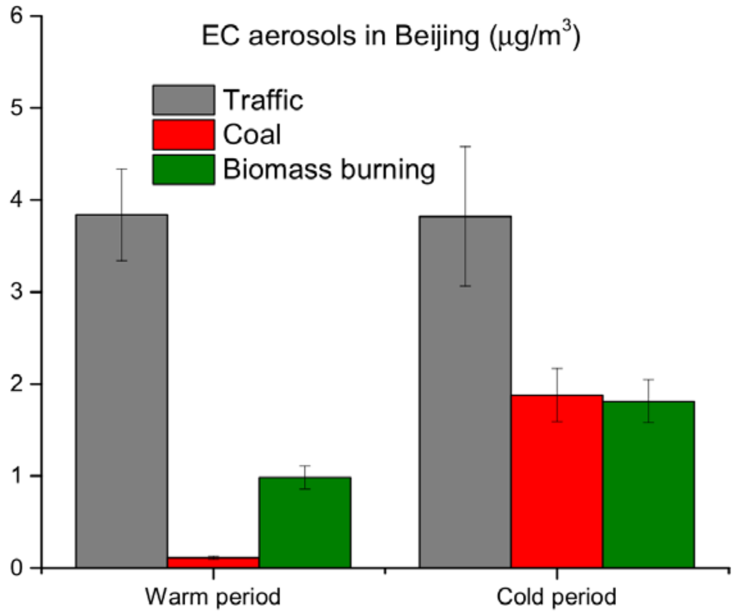

1 Introduction

Atmospheric aerosols adversely affect human health by causing respiratory and cardiopulmonary diseases associated with increased morbidity and mortality [1, 2]. Carbonaceous components are a major fraction of atmospheric aerosols and are often classified into the sub-fractions organic carbon (OC) and elemental carbon (EC) or black carbon (BC) [3]. 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 [4]. As the major light-absorbing part of carbonaceous material, BC exhibits the second largest anthropogenic radiative forcing after carbon dioxide (CO_2) [5]. 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 [6]. Due to a relatively short life time (~days) in atmosphere, reducing BC emissions may rapidly improve both climate and human health [7, 8]. Therefore, the identification and quantification of different BC sources and their emission source strengths is crucial for the implementation of effective mitigation strategies.

The emission sources of BC are exclusively combustion processes of fossil and non-fossil fuels, although the relative contribution of these two sources still remains uncertain. In recent years, the radiocarbon (^{14}C) 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. ^{14}C is completely depleted in fossil fuel emissions due to its half-life (i.e. 5730 years), whereas ^{14}C in non-fossil carbonaceous materials contains a similar composition as atmospheric CO_2 [9, 10]. Therefore, ^{14}C measurement of the EC fraction directly enables the quantification of its biomass-burning and fossil sources [11]. However, the ^{14}C measurement of EC still remains challenging in comparison to total carbon (TC) due to its complex properties [12] and since a clear physical separation between OC and EC is necessary to avoid artefacts in the ^{14}C signal. Nevertheless, recent developments and method adaptations from different groups show more consistent approaches and yield more robust ^{14}C 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 last decade, many studies have reported the chemical composition and sources of aerosols in Beijing [16-23]. 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) models [21] 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 ^{14}C 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 ^{14}C of EC and organic markers for fossil emissions (i.e. hopanes and picene).

2 Experimental

2.1 Sampling

24-h integrated PM4 samples (n=155) were collected at the ground level on pre-baked (650 °C, 4 h) quartz-fibre filters (diameter: 150mm) 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 impactor design theory [27, 28]. It was found that particles smaller than 4 μm (i.e., PM4) were collected onto the filters. However, a comparison of ^{14}C results obtained from the current study was not significantly different from those found for PM2.5 samples during winter 2013 (see Supplementary information, Figure S1) [29]. Our previous work has also shown that there is no significant difference of EC source signatures (fossil vs. non-fossil) between PM1, PM2.5 and PM10 at other locations (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 μm [31, 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 μm 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 non-fossil 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 cm^2 was used for EC measurement. The EC concentrations were measured using a thermo-optical OC/EC analyzer (Model 4L, Sunset Laboratory Inc, USA), equipped with a non-dispersive 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 non-fossil contribution is only influenced by the combined uncertainty of the ^{14}C 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 (^{14}C) measurement of EC

A filter cut of 1 to 6 cm^2 (corresponding to 5 to 30 µgC) was used for ^{14}C analysis. The Swiss_4S protocol was applied for the EC isolation for the ^{14}C 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 ^{14}C result of EC from OC charring or losses of the least refractory EC during the OC removal. In brief, to minimize positive artefacts from OC charring, water-soluble OC is first eliminated by a water-extraction pre-treatment 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 (O_2); (2) 475 °C for 180 s in O_2; (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 O_2. EC recovery is estimated by the ratio ATN_t/ATN_0, where ATN_0 is the initial attenuation (ATN, see Supporting Information), which is related to the total amount of EC on the filter, and ATN_t 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, which may lead a negligible overestimation of non-fossil EC by less than 3%. This assures the accuracy of ^{14}C measurement in EC (see Supporting Information). The EC recovery in this study was estimated as 85±5%, thus presenting almost the entire continuum of EC. ^{14}C results in EC were extrapolated to 100% EC recovery ($f_{M,EC,corrected}$ = slope * (1 – EC recovery) + $f_{M,EC}$) to account for the less refractory EC, mainly from wood burning, which is removed during steps 1 to 3 [14]. The slope of 0.31 is deduced from linear regression of the EC recovery and $f_{M,EC}$ [14]. The uncertainty of the reported $f_{M,EC}$ is obtained by an error propagation of all possible uncertainties including an assigned uncertainty of 10% for the slope, the measurement uncertainty of $f_{M,EC}$ (2%) and an assigned uncertainty of 10% for the EC yield, which results to a total average uncertainty of 4 %.

The evolving CO_2 in step 4 was separated from interfering gaseous products, cryo-trapped and sealed in glass ampoules for ^{14}C measurements. ^{14}C measurements of the CO_2 was carried out with the **MI**ni radio**CA**rbon **DA**ting **S**ystem, MICADAS [37] using a gas ion source [38]. The ^{14}C results are presented as fraction of modern (f_M) denoting the $^{14}C/^{12}C$ content of the sample related to that of the reference year 1950 [39]. Oxalic acid (HOxII) reference material (f_M=1.3407) and of ^{14}C-free materials (f_M=0) are used for normalization background correction. The f_M values were further corrected for $\delta^{13}C$ fractionation and for ^{14}C decay between 1950 and the year of measurement [40]. The f_M measurement uncertainty for the EC samples is ~2%.

2.4 Organic marker (hopanes and picene) measurements

A filter cut of 1-6 cm^2 was used for organic marker's measurement. The organic markers picene and hopanes (see Table 2) were quantified using in-situ derivatization thermal desorption gas-chromatography time of flight mass spectrometry (IDTD-GC-MS, Orasche et al. [41]). Briefly, the filter punches were placed into glass liners suitable for an automated thermal desorption unit. Isotope-labelled standard compounds were spiked directly onto the filter surface to account for influences of the matrix for later quantification. Derivatization was performed on the filter by adding of liquid derivatization reagent N-methyl-N-trimethylsilyl-tri fluoroacetamide (MSTFA, Macherey-Nagel, Germany). During 16 min of desorption time, in addition an in-situ derivatization with gaseous MSTFA was carried out. Desorbed molecules were trapped on a pre-column before separation by gas chromatography (BPX-5 capillary column, SGE, Australia). The detection and quantification of compounds was carried out on a Pegasus III time-of-flight mass spectrometer (TOF) using the ChromaTOF software package (LECO, St. Joseph, MI). The blank values of hopanes and picene were below the detection limit (0.02 ng/m^3).

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/m^3, and the average of 4.0±2.2 μg/m^3 is within the range (2.3~7.4 μg/m^3) reported by previous studies for Beijing [21, 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/m^3) than in the cold period (i.e. average from November to February is 4.8±2.9 μg/m^3). It should be noted that the frequency of samples with EC larger than 4.5 μg/m^3 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 [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/m^3) [44], Paris, France (1.4 μg/m^3) [45] or Pittsburgh, USA (0.89 μg/m^3) [46].

3.2 ^{14}C results of EC: fraction of modern

In order to further investigate the sources of EC, fourteen samples from different seasons were selected for the analysis of ^{14}C of the EC fraction (Table 1). In order to address the air quality problems of Beijing[15], 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/m^3, 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_M(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_M(EC) particularly tracks the change of EC sources. The lowest f_M(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_M(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 Sec. 3.4.

3.3 Fossil *vs.* biomass burning EC

The fraction of modern (f_M) is not identical to the fraction of non-fossil (f_{NF}) due to increased ^{14}C content of the atmosphere from the nuclear bomb test in the 1950s and 1960s. A reference value representing the modern ^{14}C content of biomass burning aerosols ($f_{M,bb}$) during the sampling period compared to 1950 before the bomb test is used to convert f_M to f_{NF}:

$f_{NF}(EC)=f_M(EC)/f_{M,bb}$ (Eq. 1)

The value of $f_{M,bb}$ is estimated as 1.12 ± 0.05 [47]. Since biomass burning (including biofuel combustion) is the only source of non-fossil EC, the fraction of non-fossil (f_{NF}) equals to the fraction of biomass burning (f_{BB}). The fraction of fossil fuels (f_{FF}) is determined by:

$f_{FF}=1-f_{BB}$ (Eq. 2)

Fossil-fuel and biomass-burning EC concentrations (i.e. EC_{FF} and EC_{BB}, respectively) are calculated as follows:

$EC_{FF}=EC*(1-f_{BB})$ (Eq. 3)

$EC_{BB}=EC*f_{BB}$ (Eq. 4)

Figure 2 shows the source apportionment results of EC. The EC_{FF} concentrations range from 2.5 to 7.5 μg/m^3, whereas the corresponding range for EC from biomass burning (EC_{BB}) was 0.4 to 2.4 μg/m^3. EC_{FF} values are on average 4.6 times higher than EC_{BB}, corresponding to a mean contribution of EC_{FF} to total EC of 79% ± 6% (ranging from 70% to 91%). The measured fossil contributions to EC are comparable to those previously reported with a similar ^{14}C-based approach in Beijing during winter 2011 [48] and winter 2013 [29], but are higher than for an urban site in Guangzhou, China (winter 2012/2013:

71±10%) [49] and a background site on the Hainan Island, South China (annual average 2005/2006: 25-56%) [47] as well as 16 urban and rural sites across Switzerland (winter 2007/2008–2011/2012: 13-88%) [11]. Higher EC_{FF} 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 EC_{BB} and EC_{FF} in the warm period from those in the cold period, the excess is estimated as 0.82±0.40 $\mu g/m^3$ and 1.75±0.52 $\mu g/m^3$ for EC_{BB} and EC_{FF}, respectively. Biomass burning accounted for on the average 32% of the excess during the cold period, which is significantly higher than the contribution of EC_{BB} (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 burning [53] 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 oil [57] and 0.1-0.6 in different types of coal [53, 58]. In typical petroleum, the R/S-epimerization at C22 has an equilibrium S/(S+R) ratio, the so-called homo-hopane index (i.e. 31abs/31abs+31abR) of ~0.6 [59], whereas this ratio ranges from about 0.1 for lignite coal to ~0.4 for bituminous coal. As seen in Table 2, both the hopane index (0.84 ± 0.11) and the homo-hopane index (0.56 ±0.04) in the warm period are very close to those in vehicle exhausts, suggesting that contribution of 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 homo-hopane 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 0.34-4.48 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 and boundary later height) equally affected both the EC_{FF} and picene concentrations then the difference between the cold and the warm periods for EC_{FF} and picene (i.e. ΔEC_{FF} and Δpicene, respectively) can be attributed only to additional coal combustion. This assumption is also supported by a recent study, in which primary organic aerosols from traffic-related emissions were only found to be ~10%, which was even smaller for high pollution events than for low pollution events in winter Beijing [15]. The emission ratio picene/EC for coal combustion is therefore estimated as 1.1 (ng/μg) by:

$(\text{picene}/EC)_{coal}=\Delta\text{picene}/\Delta EC_{FF}$ (Eq. 5)

The uncertainty of $(\text{picene}/EC)_{coal}$ is estimated to be 0.22 by an error propagation of possible uncertainties including by assigning 10% as the uncertainty of Δpicene and 20% as the uncertainty of ΔEC_{FF} associated with a overestimation of the EC_{coal} or $EC_{traffic}$ in winter.

It should be pointed out that picene may not be stable in summer [60], 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 [61]. Similarly, the hopane and homo-hopane 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 residential combustion of bituminous coal (0.52 and 0.37 for the hopane and homo-hopane indexes, respectively), but very different from typical emission ratios in mineral-oil-based sources (i.e. fuel oil consumption and vehicular emissions) (i.e. hopane index >0.9 and homohopane index in the range of 0.54-0.67) [53, 56, 59]. This suggests that the bituminite is a dominant contributor of the excess EC, which is associated with the highest EC emission factor from bituminous coals compared to other coal types on one hand and a larger percentage (78%) of bituminous coal in total raw coal in 2000 in China on the other hand [62].
The fraction of traffic and coal combustion to EC particles is further calculated by:

EC_{coal}= picene/(picene/EC)$_{coal}$ (Eq. 6)

$EC_{traffic}$=EC_{FF}-EC_{coal} (Eq. 7)

The “best estimate” and its associated uncertainty are obtained by Latin-hypercube sampling (LHS) [23]. This approach is comparable to Monte Carlo simulation which has been reported in many ^{14}C-based source apportionment studies [63-66]. 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 (picene/EC)$_{coal}$, a range from 0.75 to 1.5 with a central value of 1.0 is used as the input. The LHS simulation is conducted by generating 3000 random sets of variables. Simulations producing negative solutions are excluded and the median value from the remaining simulations is used as the best estimate, and the 10th and 90th percentiles of the solutions are used as uncertainties [23].

As shown in Figure 4, EC is divided into three major sources: EC_{BB}, $EC_{traffic}$ and EC_{coal}. The changes in the source pattern 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 co-emitted with EC [15, 29, 61, 67].

In summary, the sources of elemental carbon (EC) from ambient samples collected in Beijing were investigated based on both radiocarbon (^{14}C) 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/m^3 and 17.9 ±6.5 ng/m^3 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 ^{14}C 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 67% and 33%, 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 bituminite is a dominant coal type used during winter in Beijing.

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Table 1. Sampling dates and temperature (T) of the selected aerosol samples for ^{14}C measurements and their corresponding EC concentration, fraction of modern (f_M), fraction of biomass burning (f_{BB}), fraction of fossil-fuel (f_{FF}), biomass-burning EC (EC_{BB}) and fossil-fuel EC concentrations (EC_{FF}).

Date	T °C	EC (μg/m^3)	f_M	f_{BB}	f_{FF}	EC_{BB} (μg/m^3)	EC_{FF} (μg/m^3)
7/3/2010	30	4.30	0.15±0.02	0.14±0.02	0.86±0.02	0.59±0.07	3.7±0.46
7/5/2010	32	3.88	0.10±0.01	0.09±0.01	0.91±0.01	0.35±0.05	3.53±0.55
7/25/2010	30	4.38	0.18±0.01	0.17±0.01	0.83±0.01	0.73±0.06	3.65±0.29
7/27/2010	31	3.90	0.19±0.01	0.18±0.01	0.82±0.01	0.69±0.05	3.21±0.25
10/8/2010	17	9.50	0.25±0.02	0.23±0.02	0.77±0.02	2.19±0.21	7.31±0.7
11/28/2010	-1	7.30	0.34±0.02	0.31±0.02	0.69±0.02	2.26±0.15	5.04±0.33
11/30/2010	-1	7.64	0.28±0.02	0.25±0.02	0.75±0.02	1.95±0.13	5.7±0.39
2/15/2011	-6	5.55	0.25±0.02	0.23±0.02	0.77±0.02	1.27±0.09	4.28±0.31
2/16/2011	-3	7.75	0.25±0.02	0.23±0.02	0.77±0.02	1.77±0.13	5.98±0.45
2/21/2011	1	9.34	0.21±0.01	0.19±0.01	0.81±0.01	1.82±0.14	7.52±0.57
3/18/2011	8	4.27	0.23±0.02	0.21±0.02	0.79±0.02	0.91±0.08	3.36±0.29
3/20/2011	7	4.50	0.30±0.02	0.27±0.02	0.73±0.02	1.23±0.09	3.27±0.23
4/13/2011	17	6.61	0.26±0.02	0.24±0.02	0.76±0.02	1.59±0.13	5.02±0.4
4/30/2011	16	3.06	0.21±0.02	0.19±0.02	0.81±0.02	0.58±0.06	2.48±0.27

Table 2. Range and mean (± standard deviation) concentrations of hopanes (ng/m^3), picene (ng/m^3), total EC ($\mu g/m^3$), fossil-fuel EC (EC_{FF}) ($\mu g/m^3$) and picene-to-EC_{FF} emission ratio (ng/µg) in the warm and cold periods and the excess in the cold period.

Substance	Abbreviation	Warm period (n=22)		Cold period (n=15)		Excess	
		Range	Mean	Range	Mean	Mass	%
18α(H)-22,29,30-trisnorneohopane	Ts	0.39-3.80	1.52±1.18	0.93-3.69	2.21±0.85	0.69	46
17α(H)-22,29,30-trisnorhopane	Tm	0.58-2.68	1.12±0.49	2.13-13.14	7.58±3.38	6.46	577
17α(H),21β(H)-30-norhopane	29ab	0.87-6.01	3.68±1.45	4.92-33.66	16.13±7.61	12.45	339
17β(H),21α(H)-30-norhopane+17α(H),21α(H)-30-norhopane	29ba	0.33-2.84	1.27±0.77	1.68-16.31	10.41±4.75	9.13	718
17α(H),21β(H)-30-hopane	30ab	1.33-6.68	4.14±1.53	3.03-20.64	12.60±5.61	8.45	204
17β(H),21α(H)-30-hopane	30ba	0.49-2.21	1.02±0.51	1.7-16.43	9.67±4.54	8.65	847
17α(H),21β(H)-22S-homohopane	31abS	0.69-3.35	1.98±0.78	1.62-5.14	3.31±1.16	1.33	67
17α(H),21β(H)-22R-homohopane	31abR	0.5-2.28	1.54±0.50	0.95-7.49	3.99±1.63	2.45	159
17α(H),21β(H)-22S-bishomohopane	32abS	0.63-2.45	1.52±0.48	0.94-4.43	2.89±1.02	1.37	90
17α(H),21β(H)-22R-bishomohopane	32abR	0.35-4.30	1.46±0.92	0.83-3.81	2.48±0.91	1.03	70
Subtotal		2.49-24.36	17.88±6.45	17.79-120.98	68.63±28.7	50.75	284
hopane index: 30ab/(30ab+30ba)		0.61-1	0.84±0.11	0.49-0.66	0.57±0.06	0.49*	
homo-hopane index: 31abS/(31abS+31abR)		0.46-0.63	0.56±0.04	0.38-0.63	0.46±0.07	0.35*	
picene		0-0.17	0.02±0.05	0.34-4.48	1.82±0.99	1.79	7576
$EC^{\#}$		3.1-9.5	4.9±2.0	5.6-9.3	7.5±1.4	2.6	52
$EC^{\#}_{FF}$		2.5-7.3	3.9±1.4	4.3-7.5	5.7±1.2	1.7	43
(picene/EC_{FF})$^{\#}$		0-0.09	0.02±0.03	0.24-0.41	0.34±0.07	1.0*	

[*] These ratios are determined from the masses of the individual components for the excess in the cold period.

[#] The values are obtained from a subset of samples, which are measured for radiocarbon (n=9 and 5 for the warm and cold periods, respectively).

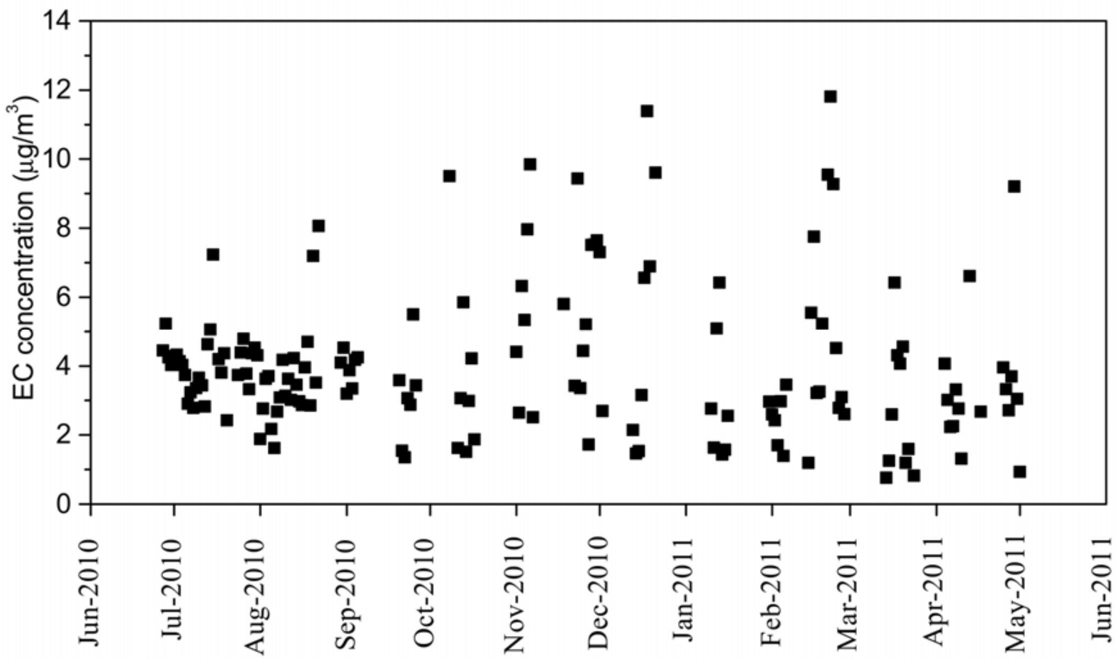

Figure 1. Temporal variation of EC concentrations (μg/m^3, n=155) in Beijing, China.

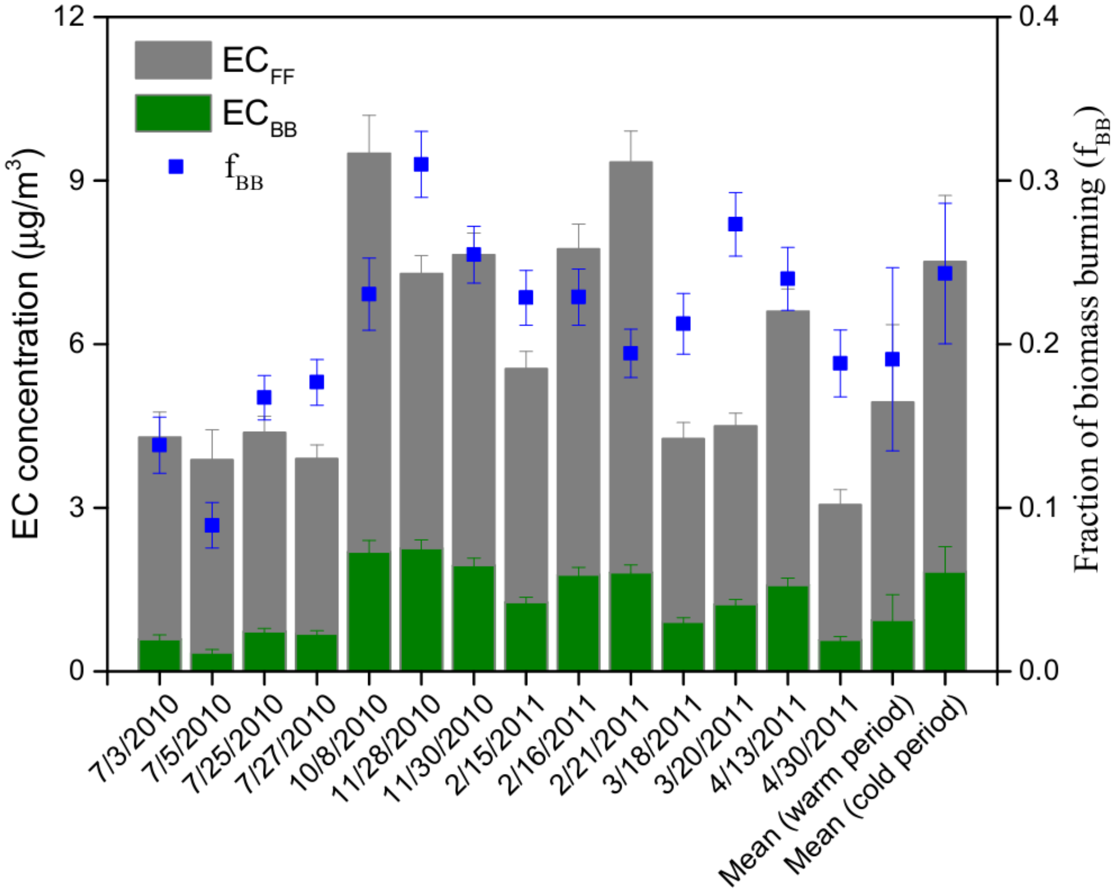

Figure 2. Mass concentrations (μg/m^3) of EC from biomass burning and fossil-fuel combustion (EC_{BB} and EC_{FF}, respectively) as well as fractions of biomass-burning EC to total EC (f_{BB}) in Beijing with 1σ uncertainties.

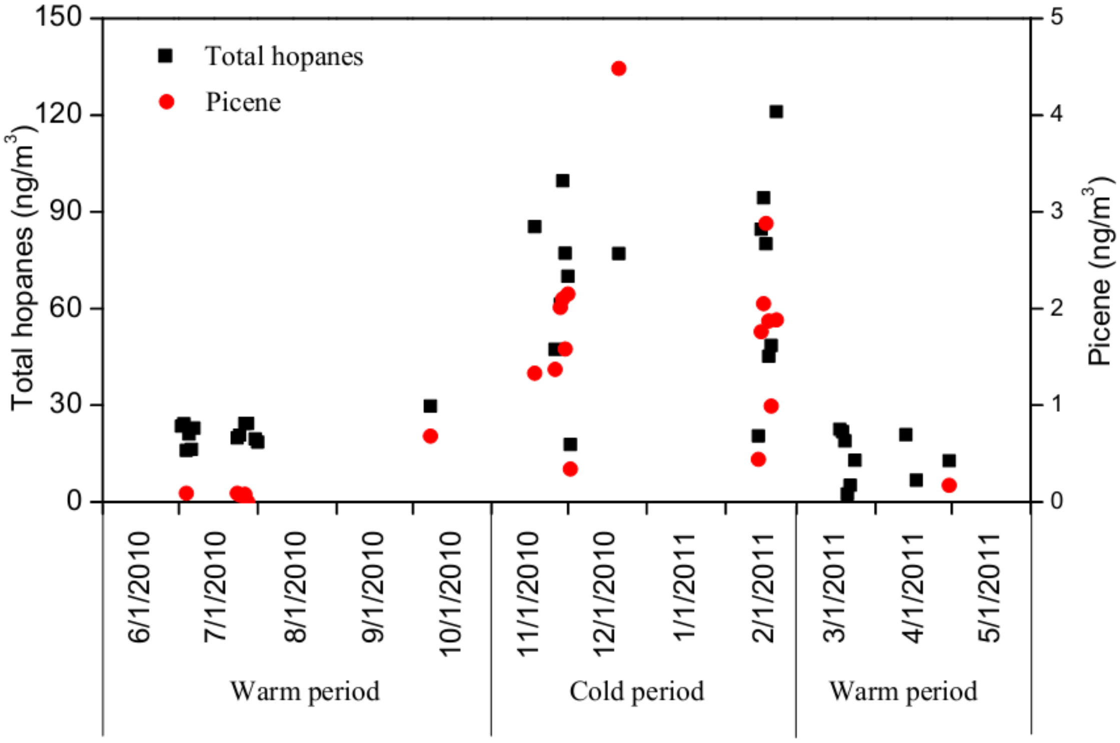

Figure 3. Temporal variation (n=35) of total identified hopanes (see in Table 2) and picene concentrations (ng/m^3) in Beijing, China. The interval of x-axis is 30 days.

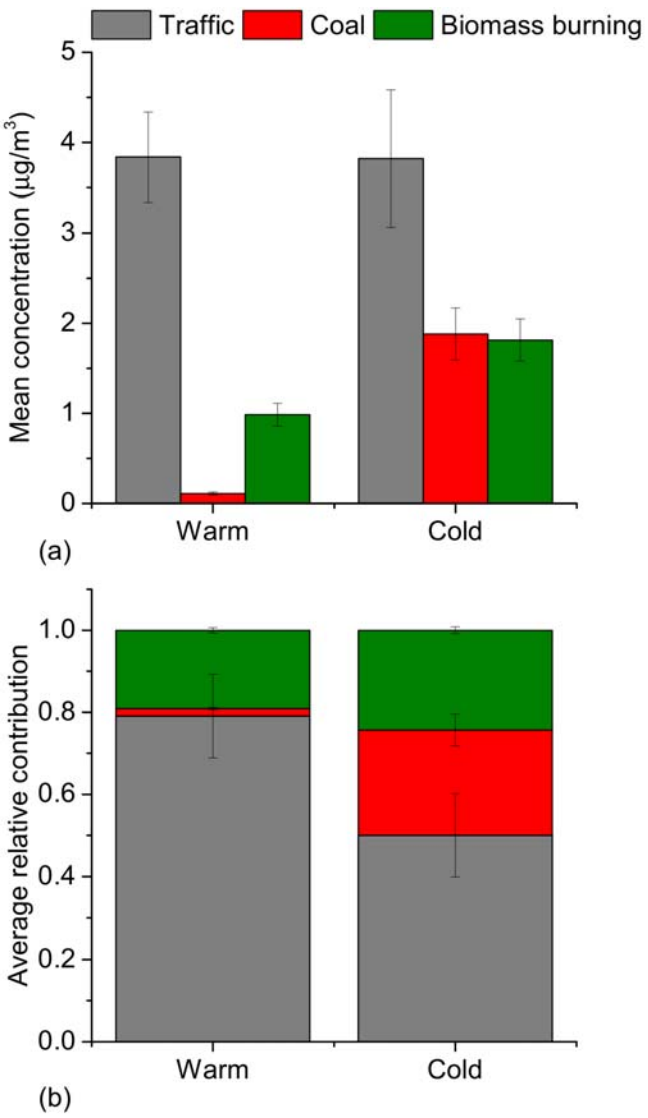

Figure 4. Average EC concentrations (a) and relative contributions (b) from traffic-related, coal and biomass-burning emissions in the warm (March to October) and cold (November to February) periods. Uncertainty bars represent 10th and 90th percentiles from LHS calculations. The integrated probability distribution from the LHS simulation is shown in the Figure S3 (see Supporting Information).