The Use of Levoglucosan and Radiocarbon for Source Apportionment of PM$_{2.5}$ Carbonaceous Aerosols at a Background Site in East China

Di Liu,[†,‖] Jun Li,[†,*] Yanlin Zhang,[†] Yue Xu,[†] Xiang Liu,[†] Ping Ding,[‡] Chengde Shen,[‡] Yingjun Chen,[§] Chongguo Tian,[§] and Gan Zhang[†]

[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

[‡]State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

[§]Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

[‖]Graduate University of the Chinese Academy of Sciences, Beijing 100039, China

S *Supporting Information*

ABSTRACT: Samples of fine particulate matter (PM$_{2.5}$) were collected during July 2009 to March 2010 at a regional background site in East China. The mass concentrations of organic carbon (OC) and elemental carbon (EC) were characterized by the highest levels in winter (December to February) and the lowest abundances in summer (June to August). Conversely, the concentrations of levoglucosan were higher in summer than in winter. The observations were associated to the anthropogenic air pollutions (predominantly fossil-fuel combustions) transport from the center and north China with the northwest winds in winter and large contribution of the open biomass burning activities in South China and East China in summer, which was evident by air-mass trajectories and MODIS satellite fire counts. To assign fossil and nonfossil contributions of carbonaceous

matters, the radiocarbon contents in water-insoluble OC (WINSOC) and EC in 4 combined samples representing four seasons were analyzed using the isolation system established in China. The results indicated that biomass burning and biogenic sources (59%) were the major contribution to the WINSOC, whereas fossil fuel (78%) was the dominant contributor to the refractory EC at this site. The source variation obtained by radiocarbon was consistent with other indicators, such as the OC/EC ratios and the levoglucosan concentration. Biomass burning and biogenic emissions were found to predominate in the summer and autumn, whereas fossil fuel emissions predominate in winter and spring.
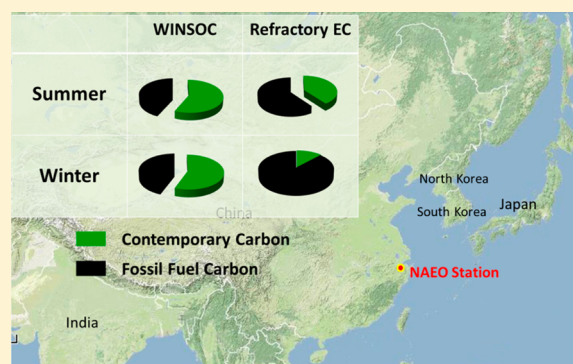
■ INTRODUCTION

Carbonaceous aerosol is one of the most abundant components (20−80%) of atmospheric fine particulates (PM$_{2.5}$)[1] and substantially affects both climate and human health. Many events, such as haze,[2] Himalayan glacier melting,[3] drought, and flood,[4] are strongly associated with carbonaceous aerosols. Moreover, these aerosols can cause respiratory and cardiovascular diseases.[5] Carbonaceous aerosols can be classified as organic carbon (OC) or elemental carbon (EC). In general, EC is a primary pollutant derived exclusively from the incomplete combustion of fossil fuels and biomass burning, whereas OC is a complex mixture of primary and secondary organic aerosols (POA and SOA, respectively). Carbonaceous aerosols are derived from a variety of sources that change over time and space, which makes it difficult to identify and quantify their sources.[6]

Several techniques have been developed to qualify and quantify the emission sources of carbonaceous aerosols.[7−9] Compared with other methods, such as the use of the OC/EC ratio, radiocarbon (^{14}C) analysis facilitates the direct differentiation of modern carbon sources from fossil fuel sources.[10,11] The ^{14}C/^{12}C ratio of carbonaceous particles is completely absent in fossil fuel sources (e.g., diesel exhaust, gasoline exhaust, and coal combustion) because it decays with a half-life of 5730 years, whereas modern materials (e.g., plant wax, pollen, and wild fire as natural origins; meat cooking, residential, and prescribed burning as anthropogenic origins) contain the contemporary or near contemporary radiocarbon

level.[10] Therefore, measuring the $^{14}C/^{12}C$ ratio in ambient $PM_{2.5}$ aerosols provides information on the influence of fossil fuel, biomass burning, and biogenic emissions on carbonaceous aerosols. To date, many ^{14}C studies have focused on the amount of total carbon (TC) in aerosols,[12−14] and only a few studies have separately analyzed both OC and EC due to limitations of the technique, the bulk samples required, and the high cost for ^{14}C measurement. Furthermore, due to their ambiguous artificial boundary, the identification of the individual OC and EC fractions in carbonaceous aerosols depends significantly on the method.[15] A two-step heating system for the EC/OC determination of radiocarbons in the environment (THEODORE)[16] was established based on a previously developed combustion system[17] and has been widely applied.[18,19] Because EC is emitted into the atmosphere solely from either fossil fuel combustion or biomass burning as primary particles, a clear distinction of the EC source between these two sources can be achieved.[20] As a result, the use of a combination of OC/EC separation and ^{14}C analysis for the identification of the source, regardless of whether its origin is fossil or nonfossil, is more effective than the analysis of the ^{14}C in the TC.

Due to the rapid economic growth and high population density in China, the aerosols and their precursor emissions have drawn significant attention in recent decades. As one of the three largest economic hubs in China, the Yangtze River Delta (YRD) experiences serious air pollution problems due to the resultant high energy consumption and large emissions of pollutants. In addition to fossil-fuel emissions, biomass burning is considered one of the major carbonaceous aerosol sources in East China. For example, many studies have investigated biomass burning in Southeast China,[21−23] and the results of these studies indicate that Southeast China has been significantly affected by the carbonaceous aerosols from South Asia. In addition to the method of radiocarbon (^{14}C) analysis, levoglucosan, which is a sugar anhydride produced during the combustion of cellulose,[24] is the most common marker used to indicate biomass burning, and the concentration of levoglucosan in aerosols is usually used to assess the contribution of biomass burning.[25−27] Recently, the combination of ^{14}C analysis and the concentration of levoglucosan has offered new insights into the detailed sources of carbonaceous aerosols.[10,28,29] Ningbo in the Zhejiang Province is located close to the East China Sea and in the southern part of the YRD and is a key site because it is the outlet for the aerosol transport routes from the Chinese subcontinent to the Pacific Ocean.

The objectives of this study were the following: (1) set up an off-line EC separation method and system for ^{14}C determination and (2) quantitatively apportion the contemporary and fossil fuel sources of OC and EC using this method and clarify their source seasonality at a regional background site in East China. In addition, the concentrations and seasonal variations of OC, EC, and levoglucosan in $PM_{2.5}$ were also investigated to substantiate the ^{14}C-based source apportionment results.

■ MATERIALS AND METHODS

Site Description and Regional Emission Sources. Ningbo Atmospheric Environment Observatory (NAEO) (29°40.8′N, 121°37′E, 550 m ASL) is located on a rural mountaintop in East China and is a regional background site (Figure 1). It is approximately 15 km west of the coast of the East China Sea (ECS), 20 km northeast of Ningbo, which is the
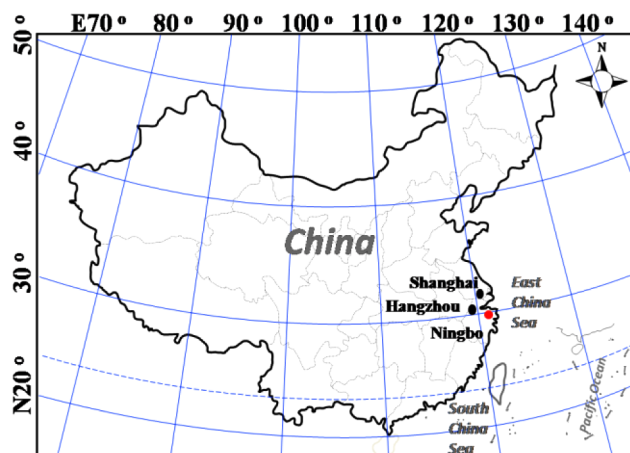

Figure 1. Ningbo Atmosphere Environment Observatory site (NAEO).

second largest city in the Zhejiang Province, approximately 150 km east of Hangzhou, and 150 km south of Shanghai. This sampling site is surrounded by forest, and there are several hills around the site with an elevation of less than 600 m. In addition to the above-mentioned cities around the NAEO, there are a number of smaller pollution sources located in the rural areas, including villages, small industrial plants, and agriculture-related biomass burning. The site has a subtropical monsoon climate, in which the weather is very hot and humid in the summer. In addition, during the summer, maritime air masses reach the sampling site by passing through the southern part of China under the influence of the Pacific anticyclone. In contrast, the sampling region is relatively cool and dry in the winter. The westerly or monsoon northwesterly winds caused predominantly by the Siberian anticyclone transport the air masses from the northern and the central parts of China to the NAEO.

Sampling Procedure. The $PM_{2.5}$ samples were collected at the rooftop of a building using high-volume (hi-vol.) samplers operating at 0.3 m^3 min^{-1}. A total of 36 24 h successive aerosol samples were collected once a week from July 2009 to March 2010. The air particles were collected on 8 × 10 in. quartz microfiber filters (PALL), and the filters were prebaked for 8 h at 450 °C to remove any contamination caused by carbonaceous material. Before and after the sampling, the filters were weighed using a balance (Sartorius, Analytic) with an accuracy of 0.1 mg, and the balance was treated in an electronic desiccator (RH = 50% and temperature = 25 °C) for 24 h before its use. After weighing, the loaded filters were stored at −20 °C in a refrigerator to prevent the evaporation of the volatile components before analysis.

Determination of ^{14}C in OC. The measurement of the ^{14}C in the OC was performed using the OC/EC separation system described previously[18] with slight modifications. In this study, the aerosol samples collected from the same season and wind direction were combined (up to mg of carbon) for the OC analysis. Therefore, there was only four samples combined for ^{14}C determination, and each one sample represented one season. The filters were all extracted with diluted hydrochloric acid and water to remove any interfering water-soluble inorganic and organic compounds prior to the thermal separation. As a result, it should be noted that the ^{14}C values in the OC obtained in this work only represent the water-insoluble OC (WINSOC) and do not include the water-soluble OC (WSOC). After pretreatment, the filter samples were

placed on a movable sample quartz boat at the modified elevated constant flow rate of approximately 40–45 mL min^{-1}, then placed in a tube oven at 650 °C for 45 s, and quickly moved to another tube oven at a temperature of 340 °C for 15 min to analyze the OC fraction. This flash heating can minimize the charring that is primarily produced by incomplete combustion of the OC.[17] The following third oven contains copper oxide to convert the incomplete combustion products, particularly carbon monoxide, into carbon dioxide at 850 °C. The water vapor was removed by a liquid nitrogen/ethanol trap at −70 °C. The carbon dioxide was trapped using a liquid nitrogen trap at −196 °C and was quantified using a manometer. The carbon mass of the produced carbon dioxide, which was expressed as M$_c$, was measured manometrically in a calibrated volume. The resulting carbon dioxide was frozen with liquid nitrogen and subsequently sealed in a quartz tube for AMS target preparation.

Determination of ^{14}C in EC. During the isolation of the OC, some of the OC is pyrolytically converted to EC (an artifact characterized as "charring"). As a result, the ^{14}C values of the EC fraction may be incorrect.[30] Although charring can be minimized by performing the water extraction step prior to the thermal treatment,[10,30,31] it is not adequate to separate all of the OC.[16,18] A longer separation duration for the elimination of the OC, for example, 12 and 24 h, was suggested at 375 °C in air.[20,32] In this study, the determination of the ^{14}C in the EC was performed by the evaporation of the OC at 375 °C in a muffle furnace in the presence of air[16,32,33] using a shorter separation time of 4 h to achieve the complete removal of the OC from the EC fraction (Supporting Information (SI)). The separation time was determined by investigating the behavior of the ^{14}C values in the EC (fraction of modern carbon, f_m) of standard reference material (SRM) 1649a, urban dust, and the EC/TC ratios at a fixed temperature of 375 °C in a muffle furnace. The standard was combusted for different times (2 h, 4 h, 8 h, and 12 h, respectively) at 375 °C in air for the determination of the ^{14}C in the EC. The result shows that the EC/TC ratios decrease with increasing separation time, but the f_m in the EC was almost constant for reaction times of 4 h or longer. As a result, 4 h was found to be an efficient separation time for a complete OC removal with a relatively higher EC yield.

In general, after the OC separation, the filters were removed from the system, placed into a muffle furnace at 375 °C, and combusted for 4 h, as described above. The controlled temperature of the muffle furnace was initially set to room temperature, increased to 350 °C at a rate of approximately 10 °C min^{-1}, and then increased to 375 °C at a rate of 0.5 °C min^{-1}. The filters were then quickly introduced back into the system and oxidized under a stream of pure oxygen at 650 °C for 10 min to analyze the EC fraction. The carbon dioxide from this fraction was cryogenically trapped and sealed in a quartz tube for AMS target preparation.

All of OC results were blank-corrected by subtracting an average field blank value (∼1.8 ± 0.3 µg, n = 3) from each sample. However, the EC results were uncorrected because the EC blanks were below the limit of detection. The EC yields obtained in this study were estimated to be approximately 20%, which may only represent the most refractory fraction of the EC.

Target Preparation and AMS Measurement. The preparation of graphite targets for accelerator mass spectrometry (AMS) a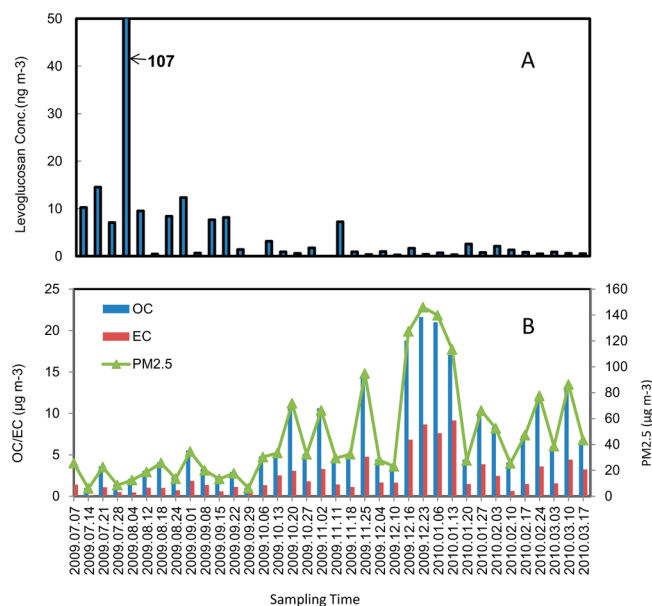nalysis was performed using the graphitization line at the Guangzhou Institute of Geochemistry, CAS through the hydrogen and zinc reduction method.[34] The ^{14}C/^{12}C ratios in the graphite samples were determined through NEC compact AMS at Peking University. The AMS calibration was performed using standards (Oxalic Acid Standard I and II) and blanks. The δ^{13}C value was obtained during the AMS measurements and applied to correct the ^{14}C measurements on the isotopic fractionation. The f_m was determined by comparing the measured ^{14}C/^{12}C in a sample with that in a modern standard (i.e., NBS Oxalic Acid I in AD 1950). All of the reported f_m values were corrected for δ^{13}C fractionation and for ^{14}C decay for the time period between 1950 and the year of measurement.

Determination of the OC, EC, and Levoglucosan Concentrations. The determaniation of OC, EC, and levoglucosan were described by the previous studies.[35,36] The details of the method are described in the SI.

■ RESULTS AND DISCUSSION

Seasonal Variation and Concentration levels of PM$_{2.5}$, OC, and EC. The concentrations of PM$_{2.5}$, OC, and EC ranged from 6.0 to 150 µg m^{-3}, 1.0 to 22 µg m^{-3}, and 0.1 to 9.1 µg m^{-3}, respectively. OC and EC were the important chemical components of PM$_{2.5}$ and contributed 15.8 ± 0.6% and 5.3 ± 1.7% of the total mass of fine particles, respectively. The average PM$_{2.5}$, OC, and EC concentrations were 46 ± 38 µg m^{-3}, 7.1 ± 5.6 µg m^{-3}, and 2.5 ± 2.3 µg m^{-3}, respectively. In comparison with other recent studies in China, the OC and EC concentrations in this study were higher than the values obtained at other CAWNET (China Atmosphere Watch Network) remote background stations, such as Mt. Waliguan (EC values in the range of 0.13 to 0.30 µg m^{-3}),[37] Shangri-La, Zhuzhang (average OC and EC concentrations of 3.1 ± 0.91 and 0.34 ± 0.18 µg m^{-3}, respectively), and Akdala (average OC and EC concentrations of 2.8 ± 1.2 and 0.36 ± 0.31 µg m^{-3}, respectively).[38] However, the values obtained in this study were similar to the reported values from Hok Tsui, which is located on the South China coast (average OC and EC concentrations of 8.7 ± 4.5 and 2.5 ± 1.9 µg m^{-3}, respectively),[21] and Changdao, which is an island at the demarcation line of the Bohai Sea and the Yellow Sea along the path of the Asian continental outflow,[39] and at the low end of the concentration ranges obtained for some rural sites in China (OC and EC concentration ranges of 11–30 µg m^{-3} and 2–5 µg m^{-3}, respectively).[38] The high values could be attributed to the anthropogenic emission sources from the northern part of China and the coastal area in Southeast China.

Figure 2B presents the temporal variations in the concentrations of PM$_{2.5}$, OC, and EC at NAEO. Although the concentrations varied significantly between samples, a seasonal variation with a maximum in the winter was observed. The means and ranges of the concentrations of PM$_{2.5}$, OC, and EC in the four seasons are summarized in Table 1. Seasonally, the highest concentration was found in the winter (December to February) and the lowest concentration was found in the summer (June to August). The topographic characteristics and the Asian monsoons make this sampling site a receptor of large amounts of pollutant emissions in the central and northern parts of China.[40] The 5-day back trajectory analysis demonstrated that the seasonal variations of carbonaceous materials were consistent with the changes in the winter and summer monsoons. Higher concentrations of OC and EC were observed during the Asian winter monsoon season, when the air masses originated from the northern or central part of

Figure 2. Temporal variation of (A) the levoglucosan concentrations and (B) the PM$_{2.5}$, OC, and EC mass concentrations from July 2009 to March 2010.
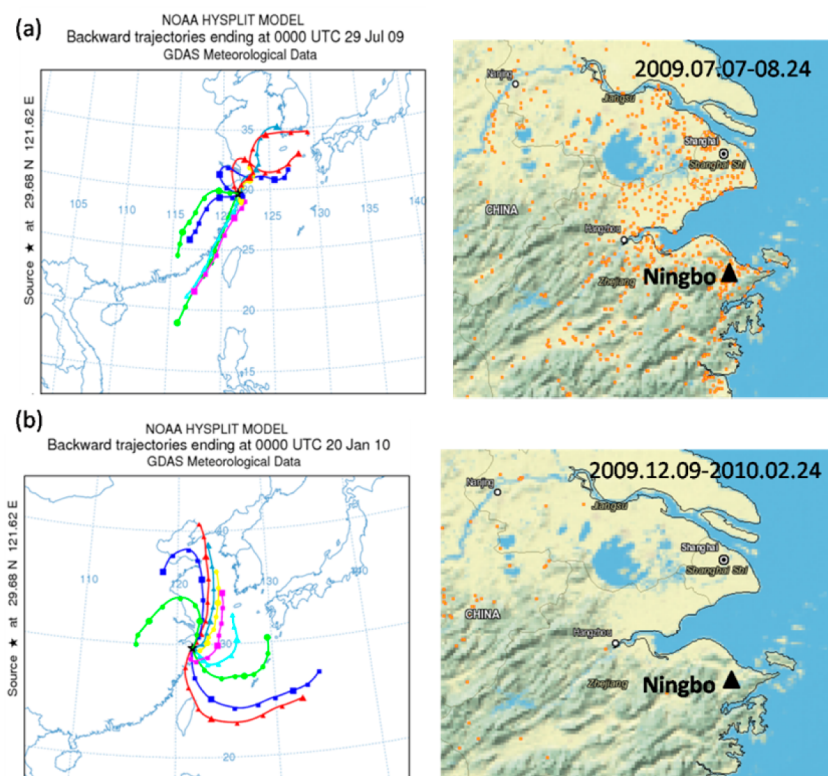
Philippine, and Malaysia, to the coastal areas of the eastern region of China. Thus, the levels of EC monitored during this season also reflected the regional background of EC in the South Asia region. Compared with the aerosols sampled during the winter monsoon season, the OC/EC ratios of the samples obtained in the summer were high, and the highest value of this ratio was 7.7. These higher OC/EC ratios can be attributed to the predominance of OC, which is mainly derived from biomass burning sources, and the SOC. For example, a previous study indicated that the OC/EC ratios for residential wood burning and mass burning are as high as 16.8−40.0 and 7.7, respectively.[42] In addition, the formation of SOC might be an additional source that induced the enhancement of OC.[35]

Seasonal Variation and Concentration Levels of Levoglucosan. The levoglucosan mass concentrations ranged from 0.28 to 110 ng m^{-3} with an average level of 6.4 ng m^{-3}. The average concentration of levoglucosan at NAEO was higher than that recorded at the Island of Chichi-jima in the western North Pacific (TSP, 0.017−15 ng m^{-3})[43] and comparable to that at other background sites in southeast China: Jianfengling and Hok Tsui (PM$_{2.5}$, 9.6−106 ng m^{-3} and 11.4−91.5 ng m^{-3}, respectively) .[23] However, the values obtained were lower than those observed at European background sites (PM$_{2.5}$, biannual average, 5.2−517 ng m^{-3}) .[36]

Figure 2A indicates the one-year temporal variation in the mass concentrations of levoglucosan at NAEO. The seasonal averages and ranges of the levoglucosan concentration throughout the four seasons are summarized in Table 1. The higher concentration of levoglucosan was observed during the summer, and the trends observed in the levoglucosan concentration were opposite from the OC and EC seasonal variations. The average concentration in the summer was approximately 20-fold higher than those observed in the other seasons. The seasonal characteristics of the levoglucosan concentration at background sites can be explained through the combined impact of climatic conditions and regional pollutant emissions. During the summer monsoon season, especially from July to August, the air masses and the abundant precipitation originated from marine areas. As a consequence of the precipitation washout, relatively lower concentrations of carbonaceous aerosols were monitored. However, during the summer, the fire counts map showed that intensive biomass burning activities took place in South China and South East Asia. The fire counts were detected by MODIS (Moderate Resolution Imaging Spectroradiometer) on NASA satellites (http://maps.geog.umd.edu/products.asp). One fire point in the map represents an active fire within a 1 × 1 km pixel

mainland China. For example, elevated OC and EC concentrations were observed from 16th December 2009 to 13th January 2010 at NAEO (see Figure 2B). During this episodic period, the OC and EC attained high concentrations of 17−22 and 6.8−9.1 μg m^{-3}, respectively. The back trajectory analysis suggested that the air mass in this period traveled in a south or southeast trajectory through continental inland areas of China, including the Zhejiang, Jiangsu, and Shandong provinces, to the sampling site. The OC/EC ratio can be used to determine the possible influences of the anthropogenic activity on the aerosol composition. A low OC/EC ratio generally indicates the presence of anthropogenic influences on the aerosol composition due to the combustion of the large fraction derived from EC.[41] In this episodic period, the OC/EC ratios of the carbonaceous matters were low (in the range of 1.9−2.8) and similar to those of industrial and vehicular emissions. Conversely, during the summer monsoon season, when the air masses originated from the west Pacific or the South China Sea, lower OC and EC concentrations were observed. In addition, during this season, the air mass mostly originated from the Indian Ocean and moved in a northeasterly direction through the South Asian countries, such as Vietnam,

Table 1. Summary of PM$_{2.5}$, OC, EC, OC/EC Ratio, Levoglucosan, f_c, and f_f in the WINSOC and the EC

season	spring ave (range)	summer ave (range)	autumn ave (range)	winter ave (range)
sampling time	Mar., 2010	Jul.−Aug., 2009	Sep.−Nov., 2009	Dec. 2009−Feb. 2010
number of samples	3	8	13	8
PM$_{2.5}$ (μg m^{-3})	56 (39−86)	17 (6.0−26)	37 (6.2−95)	73 (23−150)
OC (μg m^{-3})	8.6 (6.0−12.9)	2.7 (1.0−4.1)	5.8 (1.0−14)	11 (3.7−22)
EC (μg m^{-3})	3.1 (1.6−4.4)	0.8 (0.1−1.1)	1.9 (0.6−4.8)	4.1 (0.6−9.1)
OC/EC	2.9 (2.1−3.8)	3.9 (2.8−7.7)	3.0 (1.4−4.5)	3.2 (1.9−5.0)
levoglucosan (ng m^{-3})	0.65 (0.50−0.85)	21 (0.46−110)	2.9 (0.36−8.1)	1.1 (0.2−2.5)
f_c (WINSOC)	0.55	0.56	0.72	0.57
f_f (WINSOC)	0.45	0.44	0.28	0.43
f_c (EC)		0.40	0.18	0.12
f_f (EC)		0.60	0.82	0.88

Figure 3. Five-day backward air mass trajectories (http://ready.arl.noaa.gov/HYSPLIT.php) and MODIS fire counts (http://firefly.geog.umd.edu/firms/) at NAEO during the sampling periods in (a) the summer and (b) the winter.

resolution. The back trajectory showed that the air masses passed over the South East Asia continent or Southeast China. The open biomass burning in the southern inland areas of China could contribute to the enrichment of the levoglucosan concentration and the higher OC/EC ratios of carbonaceous aerosols at the sampling site through the long-range transport of air pollutants.[44] During the other seasons (especially in the winter), the fire count map showed that the biomass burning activities in the upwind direction was relatively small. The lower levoglucosan concentrations and the relatively lower OC/EC ratios during this season suggested that the carbonaceous aerosols from biomass burning contributed a lower proportion to the total carbonaceous aerosol masses (Figure 3).

Radiocarbon Results. *Analysis of Standard Reference Material.* In a previous study, three different standards (NBS Oxalic Acid I, NBS Oxalic Acid II, and ANU Sucrose) were used to confirm the quality of the OC measurement method, and the results were in good agreement (at a 95% confidence level) with the consensus values of the examined reference material.[18]

Table 2 shows the means of f_m in SRM 1649a, urban dust, which was used to check the quality of the EC measurement method compared to other procedures. The f_m results, in conjunction with the uncertainties obtained in this study, were greater than those reported by Szidat et al.,[16] who determined the EC fraction through the evaporation of the OC in a muffle furnace at 375 °C for 4 h. In addition, the $f_{m\ (EC)}$ value obtained in this study is similar to the value of 0.15 obtained by Heal et al.[45] Although the mean $f_{m\ (EC)}$ value varied between 0.065 and 0.15, the $f_{m\ (EC)}$ of 0.14 obtained in this study was in good agreement with these two values, which indicates considerable confidence in the consistency of the measurements.[46]

Table 2. Means of f_m in Urban Dust (SRM1649a) with the Uncertainties of the Mean^a

speciation	f_m	M_c (μg)	reference
OC	0.76 ± 0.03 ($n = 1$)	97	this work
EC	0.14 ± 0.05 ($n = 1$)	459	this work
OC	0.70 ± 0.05 ($n = 3$)	20−53	ref 16.
EC	0.066 ± 0.020 ($n = 4$)	37−70	ref 16.
OC	0.66 ± 0.02	not given	ref 45.
EC	0.15 ± 0.08	not given	ref 45.
OC	not given	not given	ref 46.
EC	0.065 ± 0.014	not given	ref 46.

$^a M_c$ refers to the carbon mass.

Source Apportionment of Carbonaceous Aerosols from ^{14}C in OC and EC. To perform the source apportionment of the organic aerosols, the term "fraction of contemporary" carbon (f_c), which is used to correct the ambient ^{14}C excess due to the atmospheric nuclear bomb tests in the 1950s, was used. In this study, a correction factor of 1.08 was chosen.[45] The f_c values in the samples were defined as $f_c = f_m/1.08$, and the fraction of fossil (f_f) was defined as $f_f = 1 - f_c$. Eight summer (July 7 to August 24) samples, 13 autumn (September 1 to November 25) samples, 8 winter samples (January 1 to February 24), and 3 spring samples (March 1 to March 21) were collected to determine the ^{14}C in the WINSOC and the EC. The samples collected in the same seasons were combined to ensure sufficient carbon to analyze the amount of radiocarbon in the WINSOC and the EC. Due to insufficient amounts of carbon, the determination of the ^{14}C in the EC from the spring samples failed.

The values of ^{14}C in the WINSOC and the EC for the four seasons are listed in Table 1. The f_c value of WINSOC ranged

from 0.55 to 0.72 with a mean value of 0.60 ± 0.08. This result implies that contemporary carbon sources (biogenic and biomass burning) were the dominant sources of WINSOC at NAEO. The average f_c value of WINSOC at this site was higher than that in other places, such as Göteborg (rural $f_c = 0.52$ and urban $f_c = 0.48$ in winter; urban $f_c = 0.56$ in summer).[10]

The f_c values of the EC ranged from 0.12 to 0.40 with an average of 0.23 ± 0.15. This finding indicates that fossil fuel combustion (e.g., vehicles exhaust and coal combustion) contributed a dominant portion of the EC at NAEO, which is attributed to particles emitted from fossil-fuel combustion and vehicular emissions in highly urbanized regions of East China. Seasonally, the f_c values of the EC at this site in the summer were higher than those in other cities, such as Göteborg (urban, $f_c = 0.36$)[10] and Beijing ($f_c = 0.17$).[14] In winter, the $f_{c\,(EC)}$ at NAEO was comparable to those in other cities, such as Göteborg (urban, $f_c = 0.12$) and Beijing ($f_c = 0.16$), but significantly lower than that obtained at a rural site in Göteborg ($f_c = 0.39$).[10]

The seasonal variations of $f_{c\,(EC)}$ were different from those of $f_{c\,(WINSOC)}$; however, the $f_{c\,(EC)}$ values agreed well with the levoglucosan concentrations. During the summer (June to August), the rain belt associated with the summer monsoon from the southeastern direction to northern China led to a heavy wet deposition of aerosols throughout the eastern part of China. As a result, the lowest carbonaceous particle concentrations were observed at the sampling site during this season. In contrast, the highest f_c values of the EC (0.40) and the highest levoglucosan concentrations (average value of 21 ng m^{-3}) were observed during this season, which indicates that biomass burning contributed substantially to the EC. In the harvesting period, which occurs during the summer season, many agricultural wastes were burnt in the upwind regions of East and South China and in Southeast Asia. As a result of this event, high EC concentrations traveled from the burning sites, and this hypothesis explains the results of the OC/EC ratios that demonstrate that the carbonaceous aerosols in the sampling site were significantly influenced by biomass burning in summer. During the winter, the prevailing monsoon wind flowed in a northerly direction from its high-altitude origin to bring cold and dry air containing pollutants from the northern and central parts of China to the eastern part of China. This hypothesis might explain the high carbonaceous particle concentrations found at NAEO during the winter. The highest EC concentration, in addition to the lower $f_{c\,(EC)}$ values and the lower levoglucosan concentrations, in the samples collected in the winter suggest that emissions from fossil fuel sources dominated the EC (88%) during this season. There is not a noticeable seasonal pattern with the $f_{c\,(WINSOC)}$ values. The $f_{c(WINSOC)}$ peaked in the autumn ($f_c = 0.72$), and the rest of the seasons, including the spring ($f_c = 0.55$), summer ($f_c = 0.56$), and winter ($f_c = 0.57$), had a similar ^{14}C signal. The highest f_c value of WINSOC in the autumn could be attributed to biogenic and/or biomass burning. It should be noticed that the $f_{c\,(WINSOC)}$ in the autumn at NAEO was surprisingly higher than that in the summer, although both primary biogenic and agricultural waste burning were higher during the summer period.

Based on the fractions of contemporary carbon, the WINSOC and the refractory EC could be divided into two components: contemporary carbon and fossil fuel carbon. The contemporary carbon concentrations of the WINSOC were 1.5, 4.2, and 6.2 μg m^{-3} in the summer, autumn, and winter,

respectively; similarly, the contemporary carbon concentrations of the refractory EC were 0.32, 0.34, and 0.49 μg m^{-3} in the summer, autumn, and winter, respectively. The fossil fuel carbon concentrations of the WINSOC were 1.2, 1.6, and 4.8 μg m^{-3} in the summer, autumn, and winter, respectively, whereas the fossil fuel carbon concentrations of the refractory EC were 0.48, 1.6, and 3.6 μg m^{-3} in the summer, autumn, and winter, respectively. The WINSOC/EC ratios of fossil fuel carbonaceous matter were 2.47 (summer), 1.05 (autumn), and 1.32 (winter). These low WINSOC/EC ratios were in agreement with the concentration of anthropogenic carbonaceous aerosols.[41] However, the WINSOC/EC ratios of the contemporary carbonaceous aerosol varied widely: 4.75 in the summer, 12.2 in the autumn, and 12.7 in the winter. The high OC/EC ratios for contemporary carbonaceous aerosols can be attributed to the predominance of organic carbon, which is mainly derived from biomass burning sources and biogenic emissions.[42]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Determination of the OC, EC, and levoglucosan concentrations; sampling site information; detailed information of PM$_{2.5}$, OC, EC, and levoglucosan concentrations; the measurement of f_m values in EC; and EC/TC ratios of SRM 1649a are available. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Phone: (86) 20 85291508; fax: (86) 20 85290706; e-mail: junli@gig.ac.cn.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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