Compound-Specific Stable Carbon Isotope Ratios of Terrestrial Biomarkers in Urban Aerosols from Beijing, China

Lujie Ren,‡ Wei Hu,† Juzhi Hou,§ Linjie Li,‡∥ Siyao Yue,‡∥ Yele Sun,‡ Zifa Wang,‡ Xiaodong Li,† Chandra Mouli Pavuluri,† Shengjie Hou,† Cong-Qiang Liu,‡ Kimitaka Kawamura,∥ Robert Mark Ellam,* and Pingqing Fu*†∥

†Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China
‡LAPC, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China
§Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100085, China
∥College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China
‡†Chubu Institute for Advanced Studies, Chubu University, Kasugai 487-8501, Japan
*Scottish Universities Environmental Research Centre, East Kilbride, G750QF, Scotland, United Kingdom

Supporting Information

ABSTRACT: Molecular compositions and stable carbon isotope ratios ($\delta^{13}C$) of n-alkanes and fatty acids (FA) were investigated in urban aerosols from Beijing, China. Seasonal trends for n-alkanes showed a higher carbon preference index (CPI) and $C_{\text{max}}$ at C29 in spring indicating the enhanced emission of higher plant waxes. Lower CPIs and $C_{\text{max}}$ at C21 were found in winter that should be associated with fossil fuel combustion. $^{13}$C-depletion in C29 n-alkane was observed during an extreme rainfall event, during which the inflow of air masses were originated from lower latitude regions. Higher concentrations of $^{13}$C-enriched C21 n-alkane in winter together with the air mass trajectories suggested that the Beijing aerosols were affected by the air masses transported from the southern regions. Fatty acids were abundant in fall and showed a bimodal pattern with $C_{\text{max}}$ at C16:0 and C18:0. Higher C24:0/FA ratios with $^{13}$C-enrichment occurred as in southwesterly air masses in fall and winter. These results suggested that C24:0 fatty acid was more abundantly transported from the southwestern air masses and may be a powerful tool to distinguish polluted aerosol source regions. Moreover, the $\delta^{13}C$ values of C24:0 fatty acid showed a positive correlation with levoglucosan, implying that the biomass-burning process may contribute $^{13}$C-enriched C24:0 fatty acid.

KEYWORDS: Urban aerosols, Compound-specific stable carbon isotopes, n-Alkanes, Fatty acids, Levoglucosan

1. INTRODUCTION

Organic aerosols are ubiquitous in atmospheric environments around the world, which contain thousands of identified and unidentified organic compounds. They have received increasing attention because of their important roles in the physicochemical properties of the atmosphere, biogeochemical cycles of nutrients, regional climate, and human health.1–3 Among the identified organic compounds, n-alkanes and fatty acids are the major compound classes and are important biomarkers in the biogeochemical cycle. Previous studies have reported a large number of fossil (e.g., coal combustion and vehicle exhaust) and nonfossil emissions (e.g., vegetation, biomass burning, and cooking)4–8 derived n-alkanes and fatty acids in aerosol samples. These studies have elucidated a number of modern geochemical processes, such as local and/or long-range atmospheric transport, circulation,6 and deposition of organic pollutants,7–9 as well as the relative contributions to lipid compounds from terrestrial vegetation emissions.10–12

Carbon isotope analysis of leaves from plants employing different pathways of photosynthetic carbon fixation, C3 (using C3 carbon metabolic pathway), C4 (using C4 carbon metabolic pathway), and Crassulacean acid metabolism (CAM) plants (using both C3 and C4 pathways), reveals characteristic differences in isotopic composition.4,11,14 Therefore, compound-specific isotope analyses (CSIA) can help to determine the plant types from which the lipids are derived and to further understand the physiological process in the leaf wax. Furthermore, the stable carbon isotopic compositions of lipids

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also show significant correlation with environmental parameters such as location and precipitation, resulting in isootope fractionation of bioelements prior to and during biosynthesis.13–17

Biomarkers in atmospheric aerosols are readily transported long distances by aeolian and/or photochemical processes from clean and remote areas (such as Mongolia, Russian Far East, Siberia) to East Asia,16,18 resulting in characteristic δ13C signatures for some specific compounds associated with biogenic input.10,19,20 High molecular weight (HMW) n-alkanes and fatty acids are representative biomarkers that originate from the epicuticular waxes of terrestrial higher plants and are indicators of their biogenic source. Low molecular weight (LMW) n-alkanes and fatty acids are the major components of anthropogenic sources, such as coal burning, vehicular exhaust, and cooking, resulting in a relatively narrow range of carbon isotope ratios.20,21 Advances in analytical chemistry enabling compound-specific isotope measurements have brought about a decade of exploration into the δ13C signatures of n-alkanes and fatty acids formed as important components of plant leaf waxes and organic aerosols.19,22–25 However, our knowledge of their sources and transport processes in heavily polluted urban aerosols in China is still limited.

According to Beijing Environmental Statements, concentrations of total suspended particles (TSP) and PM2.5 were 426 and 89.5 μg m−3, respectively, in 2013, indicating that Beijing is facing severe atmospheric particle pollution. The problem was exacerbated in winter due to adverse meteorological factors.26 Recently, extensive studies have been conducted to investigate seasonal variations in urban aerosols and thereby identify their sources and evolution processes and explore haze formation mechanisms.27,28 Nevertheless, there has been no CSIA of n-alkanes and fatty acids in aerosol samples collected throughout the year to investigate their molecular compositions and source characterization.

Here we investigate the seasonal variation in stable carbon isotopic composition of n-alkanes and fatty acids in urban aerosols from Beijing. To the best of our knowledge, this study is the first time incorporating compound-specific isotope measurements from all four seasons to characterize the sources of organic aerosols in urban Beijing. Our study provides a useful insight into the nonfossil and fossil sources of atmospheric aerosols in polluted regions.

2. MATERIAL AND METHODS

2.1. Sampling. Ambient TSP samples (n = 40) were collected on the rooftop of a three-story building (8 m above ground level) at the Institute of Atmospheric Physics, Chinese Academy of Sciences in urban Beijing (39°58′28″N, 116°22′13″E) from April 15, 2012 to January 27, 2013. Samples were collected onto prebaked (450 °C for 6 h) quartz fiber filters (20 cm × 25 cm, Pallflex) using a high-volume air sampler at a flow rate of 1.0 m3 min−1. For each season, 10 samples were collected continuously over 1–3 days. After sampling, each filter was stored separately in a precombusted glass jar with a Teflon-lined screw cap in a refrigerator at −20 °C until analysis.

2.2. Quantitative Determination. Our analytical method was identical to that reported previously.26 Briefly, a filter aliquot (about 25 cm2) was extracted three times with dichloromethane/methanol (2:1; v/v) under ultrasonication for 10 min. The supernatants were concentrated using a rotary evaporator and then were blown down to dryness under pure nitrogen gas. Derivatization was performed by reaction with 50 μL of N,O-bis(trimethylsilyl)trifluoroaceticamide (BSTFA) with 1% trimethylsilyl chloride and 10 μL of pyridine at 70 °C for 3 h. After that, 140 μL of n-hexane containing the internal standard (δ13C n-alkane, 1.43 ng μL−1) was added into the derivatives prior to gas chromatography/mass spectroscopy (GC-MS) analysis.

The compounds including n-alkanes, fatty acids, and levoglucosan were measured using an Agilent model 7890A GC coupled with an Agilent model 5975C mass-selective detector. The GC was equipped with an on-column injector and a DB-5 MS fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness). The GC oven temperature was held at 50 °C (2 min) to 120 °C at 15 °C min−1 and then followed from 120 to 300 °C at 5 °C min−1 with a final isotherm at 300 °C for 16 min. Mass spectral data were processed by the ChemStation software. Individual n-alkanes and fatty acids were identified by comparing mass spectra with authentic standards and by interpretation of mass fragmentation patterns. GC-MS response factors of individual compounds were obtained with authentic standards. Signal-to-noise ratios, limits of detection (LOD), and relative standard deviation were calculated for each compound based on duplicate analysis (Table S1). The result showed that LODs ranged from 0.017 to 0.139 ppm for n-alkanes and 0.004 to 0.262 ppm for fatty acids, respectively. The relative standard deviations of these detected compounds were less than 16% (Table S1). Recoveries for the authentic standards of compounds that were spiked onto precombusted quartz filters were better than 80%, while operation process can be found in our early report.29 The data reported here were corrected for field blanks but not for recoveries.

Organic carbon (OC) was analyzed using a thermal/optical carbon analyzer (model RT-4, Sunset Laboratory Inc., U.S.A.).30 The uncertainties from a duplicate analysis of each filter were within ±10%. The blank levels were in range of 1.54–2.43 μg C for OC.

2.3. Compound-Specific Stable Carbon Isotope Analyses. Each sample filter was extracted with 0.1 M KOH-methanol solution (70 °C, 2 h), and subsequent ultrasonication for 10 min with dichloromethane (DCM) three times at 25 °C. The extracts were combined and concentrated by a rotary evaporator and divided into neutral and acidic components with ultrapure water and a hexane/methylene chloride mixture (10:1; v/v). n-Alkanes were separated from the neutral fraction using a silica gel (230–400 mesh) column by elution with n-hexane. The acidic fraction was extracted with methylene chloride from the remaining solution after acidification with 6 M HCl (pH < 2). The acidic extracts were concentrated and then reacted with 14% BF3/methanol (90 °C, 1 h) to convert carboxylic acids to their methyl esters. Monocarboxylic acid methyl esters were then purified on a silica gel (230–400 mesh) column by elution with hexane/methylene chloride (1:2; v/v) mixture.

n-Alkanes and the fatty acid methyl esters (FAME) were analyzed using a Thermo Trace GC Ultra coupled with a gas isotope ratio MS (ThermoFisher Scientific MAT 253) via a combustion furnace maintained at a temperature of 1000 °C. The GC was equipped with a DB-5 MS fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness). The Trace GC oven temperature program was identical to the previously described GC-MS measurement protocol. Figure S1 shows a
typical isotope ratio gas chromatogram. Peaks were simultaneously detected in Faraday collectors at \(m/z 44\) (\(^{12}\text{C}\(^{16}\text{O}\)) and 45 (\(^{13}\text{C}\(^{16}\text{O}\)) and \(^{12}\text{C}\(^{17}\text{O}\)) and 46 (\(^{12}\text{C}\(^{16}\text{O}^{18}\text{O}\)), amplified, corrected for the presence of \(^{17}\text{O}\) at mass 45 using the Craig correction.\(^{31}\) The analytical error of the \(\delta^{13}\text{C}\) values of each compound based on duplicate analysis was \(<0.4\%e\). The carbon isotopic composition was reported as per mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard. The measured \(\delta^{13}\text{C}\) values of FAMEs were corrected for the contribution of carbon (\(\delta^{13}\text{C} = -21.1\%e\)) added during methyl esterification using the mass balance equation of Ren et al.\(^{21}\)

2.4. Meteorological Parameters and Backward Trajectory Analyses. The meteorological parameters, including temperature (T), relative humidity (RH), wind speed (WS), atmospheric pressure (P), and precipitation were obtained from a ground-based meteorological station at the sampling site. The time series of these meteorological parameters are presented in Figure S2. Pronounced seasonal variations were observed for all meteorological parameters. Temperature ranged from 11 to 28 °C in the warm seasons (spring, summer, and fall) and ranged from −8.5 °C to −3.5 °C in winter. Relative humidity averaged at 60% in summer and reached its minimum value (<30%) in winter. The temporal variations in WS were slightly higher in spring (1.82−4.41 m−1, average 2.74 m−1). Apart from an extreme rainfall event in July 2012, the other precipitation events were characterized by considerably lower amounts of precipitation (<100 mm). The July 2012 rainstorm was the largest rainfall event since 1951, and within 24 h the total precipitation reached 460 mm,\(^{32}\) causing multiple disasters, including urban/forest flooding, landslides, and debris flows, which claimed 79 lives.\(^{33}\)

Three-day air mass backward trajectory analyses were conducted for each of the samples (Figure 1). Air mass trajectories were sorted into four categories in terms of wind direction and the regions over which they passed. Trajectories of "Category A" were characterized by long-range transport from the northwestern region of Siberia, which were observed throughout the sampling period. "Category B" was associated with air masses also from the northern regions, which was only observed in summer. "Category C" represented air masses from the south of Beijing and was also observed within each sampling period. "Category D" was associated with the air masses derived from the marine environment and carried by southeast winds.

3. RESULTS AND DISCUSSION

3.1. Molecular Distributions of Organic Compounds and Their Stable Carbon Isotope Ratios. Table S2 is a summary of n-alkanes (\(\text{C}_{15}\)−\(\text{C}_{36}\)) and fatty acids (\(\text{C}_{12}\)−\(\text{C}_{36}\)) in the Beijing samples. Concentrations, compositions, distributions, and \(\delta^{13}\text{C}\) of the n-alkane homologues in the warm seasons were significantly different to those of winter aerosols. The concentrations of n-alkanes ranged from 34 to 360 ng m\(^{-3}\) (average 152 ng m\(^{-3}\)) with the highest abundance in winter (173−360 ng m\(^{-3}\), average 281 ng m\(^{-3}\)), followed by spring (155 ng m\(^{-3}\), fall (114 ng m\(^{-3}\)), and summer (57.8 ng m\(^{-3}\)). The concentrations of n-alkanes in Beijing were lower than those in coastal and inland megacities in China (42−1433 ng m\(^{-3}\))\(^{36−38}\) and 1−2 orders of magnitude higher than those (1.8 ng m\(^{-3}\)) in marine aerosols from the western north Pacific.\(^{7}\) HMW (\(\geq \text{C}_{25}\)) n-alkanes were the dominant species in warm seasons with \(C_{\text{max}}\) values at \(C_{29}\) whereas abundant LMW (<\(C_{25}\)) n-alkanes were detected in winter aerosols with \(C_{\text{max}}\) values at \(C_{23}\) (Figure 2).

The concentrations of fatty acids (\(\text{C}_{12}\)−\(\text{C}_{36}\)) ranged from 158 to 934 ng m\(^{-3}\) (average 382 ng m\(^{-3}\)) with the highest in fall (359−934 ng m\(^{-3}\), 553 ng m\(^{-3}\)), followed by spring (356 ng m\(^{-3}\)), winter (356 ng m\(^{-3}\)), and summer (263 ng m\(^{-3}\)). Lower concentrations of n-alkanes and fatty acids in summer were probably due to the meteorological condition. The elevated planetary boundary layer (PBL) influenced the distribution and transport of aerosols emitted to the higher troposphere in summer which increases the dilution of organic aerosols. Precipitation was also an important contributor to scavenger aerosol particles in summer; meteorological data indicated that more precipitation events occurred in summer resulting in lower concentrations of organic compounds (Figures S2 and S3). Higher concentrations in winter were mainly due to the lower mixing heights, increased carbon source emissions and poor ventilation (see Section 3.3). The concentrations of fatty acids were lower than those in coastal and inland megacities from China (155 to 3244 ng m\(^{-3}\))\(^{36−38}\) and 1−2 orders of magnitude higher than those (13.8 ng m\(^{-3}\)) in marine aerosols from the western north Pacific.\(^{7}\) Molecular distributions of fatty acids exhibited a strong even/odd carbon number predominance (CPI > 3.06) with \(C_{\text{max}}\) at \(C_{16}\) and \(C_{18}\) (Table S2; Figure 2). The average ratios of LMW/HMW fatty acids ranged from 1.1 to 13 with the highest ratios in summer (7.4 on average; Table S2), which were much higher than mountain aerosols (1.0 ± 0.8) in China\(^{29}\) but comparable to those (5.3 ± 1.8) reported in urban aerosols from Chennai, India\(^{39}\) where the contribution from biomass burning was significant.

The stable carbon isotope ratios (\(\delta^{13}\text{C}\)) of \(\text{C}_{23}\)−\(\text{C}_{34}\) n-alkanes ranged from −40.6‰ to −25.2‰ (Table S3; Figure 2). The \(\delta^{13}\text{C}\) values of odd-carbon numbered n-alkanes were generally lower in \(^{13}\text{C}\) by 1‰ relative to those of even-carbon numbered homologues (Figure 2a). LMW n-alkanes were relatively enriched in \(^{13}\text{C}\) in winter (average: −27.1‰), whereas HMW\(_{\text{odd}}\) n-alkanes exhibited consistently negative

![Figure 1. (a) Three-day backward air mass trajectories at 200 m height, using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (https://ready.arl.noaa.gov/HYSPLIT.php), which are grouped into four air mass categories (A is from the northwestern region; B is from the northern regions; C is from the southwestern region; D is extended to the marine environment and carried by southeast winds), and (b) three-day backward air mass trajectories at 500, 1000, 1500, and 2000 m AGL (above ground level) during the extreme rainfall events.](image-url)
δ¹³C values (−33.4‰) and showed a similar pattern to urban aerosols from Tokyo and Chichi-Jima (Table S4; Figure 3a). The δ¹³C values of C₁₄:0−C₂₈:₀ fatty acids ranged from −36.9‰ to −22.6‰ (Table S3; Figure 2), whereas HMW fatty acids exhibited systematic depletion in ¹³C as compared to the LMW fatty acids (average: 3.5‰; Figure 3b). Both HMW and LMW fatty acids displayed similar temporal variations in δ¹³C (Figure S4a). The HMW δ¹³C values were positively correlated with LMW values (n = 40, r² = 0.62; Figure S4b). The similar trends of variation between HMW and LMW fatty acids suggested that they might have similar sources and/or experienced similar atmospheric pathways and transport processes.

3.2. Characterization of Nonfossil Sources. 3.2.1. δ¹³C Signatures of HMW Compounds. The carbon preference indexes (CPIs) of terrestrial higher plant waxes are generally >5 when there is no significant input from anthropogenic emissions but the values tend to decrease down to 1.0 with increasing contribution from anthropogenic pollutants. In this study, the CPIHMW of n-alkanes showed relatively higher values (1.8 to 9.0, average: 3.5; Table S2). The percentage of plant wax derived n-alkanes (WNA%) represents the contribution of biogenic n-alkanes from higher plant waxes. The largest values of WNA% were observed in spring (31.6–74.8%, average 57.9%), which highlighted that the biogenic origin, such as terrestrial plant waxes, could be the main source for n-alkanes during spring when a large number of green leaves exist. HMWodd n-alkanes are important constituents of plant surfaces and are susceptible to environmental changes because of their location at the plant/atmosphere interface. The δ¹³C values of HMW_odd n-alkanes (−37.6‰ to −28.7‰) were in the typical range of C₃ and CAM plants, being similar to the values of urban aerosols from Tokyo and Chichi-Jima, where the contribution from C₃ plants was more significant (Table S4; Figure 3a). These results suggest that
HMW$_{alld}$ n-alkanes in the Beijing aerosols were probably dominated by materials derived from C$_3$ vegetation.

The C$_{20}$–C$_{32}$ even-carbon numbered n-fatty acids mainly originate from higher plant leaves, whereas terrestrial plants rarely contain odd-carbon numbered species. Odd-carbon numbered fatty acids are mainly derived from various geochemical reservoirs, such as soils, in which they are produced by microbial α-oxidation of even-carbon numbered fatty acids. The existence of odd-carbon-number species in the aerosols (Figure 2) suggested that fatty acids in the studied region were derived not only from higher plant leaves but also from soil organic matters which could be emitted into the atmosphere.

The C$_{22}$–C$_{32}$ even-carbon numbered n-fatty acids revealed relatively high concentrations in spring (92.9 ng m$^{-3}$), fall (91.6 ng m$^{-3}$), and winter (67.4 ng m$^{-3}$) compared with summer (28.3 ng m$^{-3}$; Figure 4). Figure 4a showed the variations in the distribution of air mass trajectory sectors. Different colors show different back-trajectories according to Figure 1a, (b) concentrations of C$_{22}$–C$_{32}$ even-carbon numbered n-fatty acids and the concentration ratios of C$_{24:0}$ and C$_{28:0}$ n-fatty acids against total concentrations of C$_{22}$–C$_{32}$ even-carbon numbered n-fatty acids (C$_{24:0}$/FA, C$_{28:0}$/FA, respectively), and (c) time series of δ$_{13}C$ values of C$_{24:0}$/n-fatty acids (C$_{24}$ FA).

Thus, the different seasonal trends of C$_{24}$/FA and C$_{28}$/FA ratios suggested that the relative abundance between the C$_{24}$,0 and C$_{28}$,0 fatty acids could be used to distinguish polluted aerosol source regions, and polluted air masses from the southwest could result in higher concentrations of $^{13}C$-enriched C$_{24:0}$ fatty acid.

The δ$_{13}C$ values of HMW fatty acids (−36.9‰ to −25.6‰) were within the typical range of terrestrial plants and combustion of C$_3$ and C$_4$ plants (Figure 3b), indicating the mixed sources of nonfossil input. The δ$_{13}C$ values of HMW fatty acids in spring varied from −36.9‰ to −28.5‰ and were depleted in $^{13}C$ by up to 4.1‰ compared to other seasons and marine aerosol samples (Table S3; Figure 3b). We speculate that they may originate from plenty of green leaves because of enhanced vegetation activities in the growing season, and pollen grains that contain HMW fatty acids abundantly as coating wax. Pollen grains can be emitted into the atmosphere in spring and are unlikely transported long distances because of their large particle sizes. Summer, fall, and winter aerosols had the similar patterns with those of marine aerosol samples from the Chichi-Jima Island and urban aerosols from Hokkaido, Japan (Table S4; Figure 3b). Those marine aerosol samples were characterized by significant contributions of nonfossil sources, such as higher plants, marine organisms, and loess deposits which could be in part transported long distances from the Asian continent when the westerlies prevail. Thus, HMW fatty acids in Beijing aerosols may originate from the combination of anthropogenic sources (such as biomass burning of C$_3$ and/or C$_4$ plants) and natural sources (such as the leaf waxes, pollen, and soil organic matter).

3.2.2. $\delta^{13}C$ Signatures of Biomass Burning. Levoglucosan is specifically formed by the pyrolysis of cellulose. Although levoglucosan is susceptible for photochemical degradation under strong oxidizing environment, its degradation is relatively low and its temporal trends could reflect the strength of the biomass burning contribution. Thus, it has been recognized as an excellent tracer of biomass burning. Higher concentrations of levoglucosan were observed in fall (281 ng m$^{-3}$) and winter (338 ng m$^{-3}$; Figure S5) and were much higher than those in spring (121 ng m$^{-3}$) and summer (40.8 ng m$^{-3}$). Interestingly, the concentrations of levoglucosan showed a positive correlation to C$_{24:0}$ fatty acid and their δ$_{13}C$ values (Figure S5), suggesting biomass-burning processes may contribute more C$_{24:0}$ fatty acid with less negative δ$_{13}C$ values in Beijing aerosols.

Compared to the δ$_{13}C$ values of fatty acids in C$_4$ plants, the δ$_{13}C$ values of fatty acids in aerosols showed an isotopic depletion of 2‰ to 6‰ during controlled laboratory burning of C$_4$ vegetation. However, the opposite relationship was observed for C$_3$ vegetation, with a carbon isotopic enrichment of 2‰ to 7‰ during biomass-burning processes compared with unburned C$_3$ plant matter. In this study, the δ$_{13}C$ values of HMW fatty acids in spring were in the range of C$_3$ plants (Figure 4b). Compared to the fatty acid homologues in spring, the δ$_{13}C$ values of fatty acids in fall and winter exhibited $^{13}C$ enrichment of 2.7‰ to 6.1‰ (except for C$_{16:0}$ fatty acid: 1‰ to 1.5‰), which were similar to the offsets in C$_4$ plants associated with biomass-burning (2‰ to 7‰). This suggested a dominant contribution from the combustion of C$_3$ plants in Beijing, which was consistent with previous studies.

3.2.3. δ$_{13}C$ Signatures of the Precipitation Effect. C$_{29}$ n-alkane is a representative lipid biomarker component of
terrestrial higher plants. The results of the stable isotopic measurements for the C29 n-alkane are given in Table S3. Abundant C29 n-alkane was observed in spring (45.8 ng m\(^{-3}\)) due to the enhanced emission of higher plant waxes and was about three times higher than the mean concentration for the other seasons (14.8 ng m\(^{-3}\); Figure 5b). The \(\delta^{13}C\) values of C29 n-alkane (\(\delta^{13}C_{C29}\)) in spring (−33.8 to −31.8\(^{\circ}\)) , summer (−36.8 to −30\(^{\circ}\)) , fall (−35.7 to −32.3\(^{\circ}\)) , and winter (−37.3 to −30.9\(^{\circ}\)) were in the range of C3 plants (−38.9 to −30\(^{\circ}\)) (Table S3; Figure 2), indicating a dominant contribution from C3 plants in the studied region.

\(\delta^{13}C_{C29}\) showed a significant fluctuation during the whole sampling period (up to 7.3\(^{\circ}\) offset; Figure 5b). The lowest \(\delta^{13}C_{C29}\) value (−36.8\(^{\circ}\)) in summer was observed during the extreme rainfall event; whereas there were no significant variations during the other precipitation events. Atmospheric transport is the main pathway for the terrestrial lipid compounds. Previous studies showed that the source of moisture at different elevations have a limited variation. Most moisture in the atmosphere is thought to be in the first 2000 m above ground level, so no higher levels were considered in this study (Figure 1b). The elevation was chosen at three different elevations: 500, 1000, and 2000 m above ground level in this study. Moisture pathways for the extreme precipitation events were clustered to the northwestern (accounting for 14.4\%) and southern regions at lower latitudes (85.6\%; Figures 1b and 4a). Atmospheric processes were capable of retaining the original isotope signal of moisture sources. Bendle et al. observed that different air masses may cause the shift of \(\delta^{13}C\) through the inflow of air mass from lower latitudes globally where vegetation provides lower isotopic values. A previous study described the global distribution of C3 and C4 plants using biosphere models to predict the biomass of C3 and C4 vegetation, which demonstrated the lower fractional C4 coverage (0% to 40%) in northeast China where southern air masses passed in this study. Previous studies also showed that C3 plants, such as Cinnamomum camphora, Cyperaceae, and Potentilla chinensis, were the main terrestrial vegetation and widely distributed in northeast China. C3 plants had lower carbon isotopic values compared with C4 plants in terms of n-alkanes (Figure 3a). The \(\delta^{13}C_{C29}\) value (−36.8\(^{\circ}\)) during the extreme rainfall event was in the range of C3 plants. Thus, lower isotopic values of C29 n-alkane may provide potential insight into the higher contribution of C3 plant and lipid materials transported from the lower latitudes to the observation site during the extreme rainfall event. However, \(\delta^{13}C_{C29}\) during other rainfall event did not show similar variations. This was because the air masses during the lower precipitation event did not involve regional transport from lower latitudes, but rather local transport and/or air masses from the marine environment played a major role in their sources. Substantial variations in \(\delta^{13}C\) during the extreme rainfall event suggested changes in the atmospheric environment could be recorded by the isotopic signatures of plant-derived n-alkanes in aerosols; and the \(\delta^{13}C_{C29}\) may reflect variability in the source areas and atmospheric transport pathways in a specific environment.

3.3. The Influence of Fossil Fuel Sources. Previous studies have demonstrated that organic aerosols were dominated by nonfossil sources throughout the year except winter when a higher fossil-derived contribution was observed associated with enhanced coal combustions for heating in Beijing. The winter aerosols showed the least WNA% (10.7\%) , implying a minor input from leaf epicuticular waxes. Low CPIs of n-alkanes (1.2) were detected in winter aerosols (Table S1), whereas abundant LMW n-alkanes (Figure S3) were relatively enriched in \(^{13}C\) in winter (average: −27.1\(^{\circ}\)) and within the range of those for fossil fuel sources (Figure 3a). Seasonal variations in the fossil fuel-derived marker, C23 n-alkane, showed high concentrations in winter (38.6 ng m\(^{-3}\)) (Figure 4a), which were more than 10 times higher than those in warm seasons (2.9 ng m\(^{-3}\)). The \(\delta^{13}C\) values of C18 n-alkane in winter (−27.2\(^{\circ}\)) were significantly enriched in \(^{13}C\) relative to those in warm seasons (−32\(^{\circ}\)) (Figure 4b). These values indicated that anthropogenic sources (such as vehicular exhausts and fossil fuel combustion residues) contributed more n-alkanes in cold seasons than in warm seasons. Floods of studies reported that Beijing experienced severe haze events in January 2013 due to unfavorable meteorological factors. The air masses on hazy days were from the south and southwest (category C) with a large number of anthropogenic pollutants. Unfavorable meteorological factors made the ground convergence stronger, thus preventing the diffusion of pollutants causing higher concentrations and \(^{13}C\)-enriched LMW n-alkanes. Thus, winter aerosols in Beijing were likely to be affected by southern air masses with abundant LMW n-alkanes and higher \(\delta^{13}C\) values.

Fossil fuel combustion (e.g., diesel truck exhaust) is an important source of fatty acids. C16:0 and C18:0 fatty acids as individual compounds are not source-specific but the C18:0/C16:0 fatty acid ratio is unique and can be used as a qualitative tool for source apportionments. The average ratios of C18:0/C16:0 values are lower than 0.25 in aerosols from nonfossil sources (such as vegetation combustion and waxy leaf surface abrasions); values in the interval 0.25 to 0.5 are typical of car and vehicle exhaust and values between 0.5 and 1.0 are characteristic of cooking and paved and unpaved road dust. The average ratio of C18:0/C16:0 in the present study were 0.31 to 0.47, indicating a strong and stable input of LMW fatty acids from vehicle emissions. Both the concentrations and \(\delta^{13}C\) values of C16:0 fatty acid showed a strong positive correlation with those of C18:0 fatty acid throughout the year (\(r^2 = 0.97\) and 0.66, respectively;
Figure S4c,d), suggesting that C_{16:0} and C_{18:0} fatty acids may have experienced similar atmospheric pathways and/or have similar sources.

3.4. Implications for Sources of Organic Aerosols. Average concentrations of OC in TSP were higher in winter (30.4 μg m⁻³ on average), followed by fall (24.3 μg m⁻³) and lower in summer (9.17 μg m⁻³), which are similar to those of n-alkanes. Interestingly, the temporal trends of OC (Figure S6) were also comparable to those of C_{20}−C_{32} even-carbon numbered fatty acids (Figure 4b). Such similarities in temporal and seasonal patterns of n-alkanes and fatty acids with that of OC imply that OC should have been mainly derived from the similar emission sources (coal burning, biomass burning, and higher plants) of n-alkanes and fatty acids and influenced by the meteorological conditions such as PBL and precipitation. Therefore, the main sources identified based on molecular composition and isotopic signatures of markers such as n-alkanes and fatty acids could be attributed to total organic aerosols. However, although n-alkanes and fatty acids could contribute 30% to 50% to carbon of detected organic compounds using GC-MS in urban aerosols,³⁹,⁶⁸ their contributions to OC were found to be very low (0.59% for n-alkanes and 1.41% for fatty acids; Table S2). Furthermore, their stable carbon isotopic characteristics for specific anthropogenic sources remain unclear due to a lack of sufficient isotopic data from emission sources such as coal combustion, vehicle exhaust, and cooking. Hence, the molecular and isotopic compositions of biomarkers could provide key insights for fossil and nonfossil sources of organic aerosols and add to a very limited base of information in the scientific literature on stable carbon isotope ratios of n-alkanes and fatty acids in atmospheric environment but it is difficult to apportion the specific sources, which require further studies.

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