Source forensics of $n$-alkanes and $n$-fatty acids in urban aerosols using compound specific radiocarbon/stable carbon isotopic composition

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Keywords: atmospheric aerosols, $n$-alkanes, $n$-fatty acids, compound-specific stable carbon isotopes, radiocarbon isotopes

Supplementary material for this article is available online

Abstract

$n$-Alkanes and fatty acids are important molecular markers for the source apportionment of organic matter in the atmosphere. Traditional approaches to date have mostly relied upon the source-specific differences in their molecular distributions and carbon preference index. Alternatively, we demonstrate here the use of stable carbon and radiocarbon isotopic composition ($\Delta^{13}C$ and $\Delta^{14}C$, respectively) of $n$-alkanes and $n$-fatty acids in aerosols from two urban receptor sites (Beijing and Tianjin) in Northeast China to assess their sources in autumn. The $\Delta^{14}C_{n}$-alkanes of C$_{19}$–C$_{24}$ and C$_{26}$–C$_{32}$ even-carbon homologs ($\sim$851to $\sim$708‰) indicate their dominance from fossil fuel combustion. In contrast, the $\Delta^{14}C$ of most abundant palmitic acid (C$_{16:0}$) and stearic acid (C$_{18:0}$) suggest a larger contribution from nonfossil sources ($\sim$91%–94%), mainly due to inputs from cooking, biomass burning and microorganisms. Compared with lower $\Delta^{14}C$ of C$_{27}$ and C$_{31}$ $n$-alkanes ($\sim$449‰), C$_{25}$ $n$-alkane ($\sim$241‰) and C$_{20}$–C$_{30}$ $n$-fatty acids ($\sim$263‰) showed more contemporary likely due to significant contribution from plant litter and biomass burning that contain more fresh biogenic material. Fossil character of C$_{27}$–C$_{31}$ $n$-alkanes (40%) and C$_{20}$–C$_{30}$ $n$-fatty acids (30%) could be from soil resuspension and/or loess deposits in upwind regions through long-range atmospheric transport.

1. Introduction

Airborne particle deposition is an important pathway for much of the terrestrial carbon transported to remote ocean setting. Lipid compounds (e.g. $n$-alkanes and fatty acids) in the continental outflows contribute to pelagic sediments and represent valuable organic geochemical tools for investigation and reconstruction of past environments. $n$-Alkanes and fatty acids are originally biosynthesized by different types of organisms, such as terrestrial plant epicuticular waxes (Collister et al. 1994, Bi et al. 2005, Nelson et al. 2018), marine phytoplankton, and bacteria (Matsumoto et al. 2007). Plant wax is characterized by odd-over-even carbon number preference for high molecular weight (HMW) $n$-alkanes ($\geq$25), and an even-over-odd carbon number preference for HMW $n$-fatty acids ($\geq$20), whereas low molecular weight (LMW) homologues are mainly produced by aquatic organisms (Makou et al. 2018) and anthropogenic emissions (Rogge et al. 1993a, 1994, Ballentine et al. 1996, 1998, Zhao et al. 2007b, Harvey et al. 2012).
Compound-specific stable carbon ($^{13}$C-) and radiocarbon ($^{14}$C-) isotopic analysis of n-alkanes and fatty acids is well-established for the quantitative apportionment of their origin from fossil and nonfossil sources (Tao et al. 2016). Owing to the slower turnover time of HMW compounds, their carbon isotopic compositions are well preserved in atmospheric and geological samples without suffering major modification. These biomarkers have been used successfully to further our understanding of biomarker sources and carbon cycling in soil (Matsumoto et al. 2007), marine and lake settings (Margoaan et al. 2014, Tao et al. 2015, 2016). One such revelation is that n-alkanes and fatty acids exhibit millennial-scale environmental change and transitions prior to sedimentary deposition. However, other anthropogenic sources such as coal burning (Rogge et al. 1993a, Harvey et al. 2012), vehicular exhaust (Rogge et al. 1994), biomass burning (Ballentine et al. 1996, 1998), and cooking (Zhao et al. 2007b) emit plenty of particles with abundant lipids into the air. Both wet scavenging and dryfallout are the major sink processes for these lipids and eventually deposited into modern and geological samples. Even the remotest regions on earth have significant contributions of these lipid biomarkers from anthropogenic activities besides the conventional sources (biogenic wax vs. fossil-fuel combustion). Hence, understanding of their fossil versus nonfossil sources contributions in urban aerosols using their molecular characterization is crucial for their ongoing use as paleo proxies in addition to information on their atmospheric transport processes.

Measurements of $^{14}$C of compound-specific compositions in aerosols focus on polycyclic aromatic hydrocarbons (PAHs) in fine particle (Reddy et al. 2002, Zencak et al. 2007, Xu et al. 2012b, Ya et al. 2018), dicarboxylic acids (Fahrni et al. 2010) and fatty acids in marine aerosols (Kawamura et al. 2010). For example, compound specific radiocarbon analysis (CSRA) was previously applied in studies to investigate the contributions of fossil fuel and biomass burning derived PAHs by isotopic mass balance model (Reddy et al. 2002, Zencak et al. 2007, Xu et al. 2012b, Ya et al. 2018). For fatty acids in aerosols, there are several publications about marine aerosols conducted by Matsumoto et al. (2004) and Kawamura et al. (2010), showing that the diversity of $\Delta^{14}$C in fatty acids varied significantly owing to the combined inputs of the marine sources, terrestrial plants, and loess deposit. However, comparatively few such radiocarbon investigations on individual n-alkanes and fatty acids are performed in urban aerosols which are influenced by anthropogenic emissions. To the best of our knowledge, rather limited (or no) studies in the literature have focused on the radiocarbon content of n-alkanes in urban aerosols.

In this study, we collected aerosol samples in Beijing and Tianjin (figure S1 (stacks.iop.org/ERL/15/074007/mmedia)), two megacities in which population, cooking, biomass burning, vegetation, gaseous pollutant, vehicle exhaust, and coal burning exerted the most significant effects (see publications for recent review (Chan and Yao 2008, Gao et al. 2018, Maji et al. 2018)). These samples were analyzed for the radiocarbon and stable carbon isotopic composition of individual n-alkanes and fatty acids along with their molecular composition to probe their applicability for the source appointment in urban aerosols. We interpreted these results in terms of potential sources and contribution of ancient and modern carbon to the aerosol n-alkanes and fatty acids alongside simultaneously highlighted the promising potential of CSRA to investigate their source appointment for urban aerosol applications.

2. Materials and methods

Beijing and Tianjin are located in the largest and most dynamic economic region in Northeast China (figure S1), where organic aerosols originate from both local anthropogenic/biogenic emissions (Chan and Yao 2008, Gao et al. 2018, Maji et al. 2018) and neighboring urban/rural/remote locations through long-range transport. For this study, eight total suspended particulate matter (TSP) samples were collected at two nearby urban sites (Beijing and Tianjin) during 13–25 October 2017; one site is on the rooftop of a three-story building (8 m above ground level) at the Institute of Atmospheric Physics, Chinese Academy of Sciences in Beijing, the other site is on the rooftop of a six-story building (16 m above ground level) in Tianjin University, Tianjin, China. The TSP samples were collected onto pre-baked (450 °C, 6 h) quartz filter fibers (20 cm × 25 cm, Pallflex™) using high-volume air samplers operated at a nominal flow rate of 1.0 m$^3$ min$^{-1}$. Each aerosol sample was collected continuously for 3 d to get enough carbon content required for the CSRA (table S1), wrapped in aluminum foil, and then sealed in zip-lock plastic bags and stored in refrigerator at $-20$ °C until analysis.

Our analytical method, including quantitative information and measurement of $\delta^{13}$C, is identical to previous studies (Yamamoto and Kawamura 2010, Ren et al. 2019). Detailed analytical protocols are presented in the supporting information (text S1). Figure S2 shows the typical gas chromatograms obtained for n-alkanes and fatty acid methyl esters (FAMEs) on the isotope ratio mass spectrometer. Monomer isolation and compound specific $^{14}$C analysis were done by the accelerator mass spectrometry (AMS) in the Laboratory for Ion Beam Physics, ETH Zürich. Individual homologues with similar characteristic were combined in cases where compound abundances were too low (i.e. <5 µg C) for reliable AMS measurement, with care to pool
homologues only of similar homologs (corresponding identification number for $^{14}$C analysis: BJ-1, BJ-2, TJ-1, TJ-2; table S1). The $^{14}$C measurement of $n$-alkanes consisted of four pooled aerosol filters corresponding to 9000 m$^3$ air (combination of BJ-1 and BJ-2 for Beijing aerosols; combination of TJ-1 and TJ-2 for Tianjin aerosols), whereas fatty acids consisted of 2 pooled aerosol filters corresponding to 4500 m$^3$ air (table S1). Compound-specific radiocarbon analyses and blank assessment were based on the approaches of Eglinton et al. (1996) and Tao et al. (2015). Details concerning sample analysis, data treatment and uncertainties of $^{14}$C measurement are provided in the supporting information (Text S1 and table S2).

3. Results and discussions

3.1. $n$-Alkanes

The molecular distributions of $n$-alkanes in ambient aerosols vary considerably among different source-emissions, that is, biogenic emissions, fossil-fuel combustion, biomass burning, and/or road dust (figure S3). Although having a lower abundance in total organic aerosols, $n$-alkanes serve as unambiguous tracers for the source apportionment because of their low reactivity and low volatility (Gelencs´er et al. 1998). Their applicability for the provenance studies, for instance, have relied upon the relative abundance of odd-C homologs over that of even-C homologs between C19 and C35, referred hereafter as carbon preference index (CPI$_{n}$-alkanes) (Gelencs´er et al. 1998). The CPI$_{n}$-alkanes are, thus, different for biogenic emissions (>5) (Schneider et al. 1983, Collister et al. 1994, Chikaraishi and Naraoka 2003, Fu et al. 2008a), biomass burning (2.1–3.9) (Fu et al. 2008a), road dust (~1.8) (Rogge et al. 1993b), and fossil-fuel combustion (~1) (Ren et al. 2016, Kang et al. 2018, Wang et al. 2006, Wu et al. 2007; Simonet 1984, Simonet et al. 1991, Yamamoto and Kawamura 2010). In our study, the CPI$_{n}$-alkanes in TSP samples collected during autumn period in Beijing (1.94–2.03) and Tianjin (1.89–2.29; table S3) are consistent with their dominant contribution from fossil-fuel combustion (~70%–90%; table S4). This is estimated based on the mass balance approach, where the CPI$_{n}$-alkanes in atmospheric particulate matter is a combination of their contributions from fossil versus biogenic/biomass burning times their source-specific CPI$_{n}$-alkanes values (table S4) (Yamamoto and Kawamura 2010). Air mass back trajectory calculations from the HYSPLIT model (figure S1) have revealed that TSP collected in Beijing and Tianjin had a mixture of $n$-alkanes, mostly from fossil sources of local origin (CPI$_{n}$-alkanes: ~1) (Wu et al. 2007, Wang et al. 2006, Ren et al. 2016, Kang et al. 2018) with some contributions from terrestrial vegetation in Mongolia and Russian Far East (CPI$_{n}$-alkanes: ~5) (Bendle et al. 2006).

Fossil-fuel combustion related emissions could generate abundant low molecular weight (LMW$_{n}$-alkanes, <C$_{25}$) and minor even-carbon $n$-alkanes from C$_{26}$ to C$_{32}$ (HMW$_{n}$-alkanes) (Rogge et al. 1993a, Harvey et al. 2012, Bai et al. 2014) whereas their lower concentrations (2.55–6.44 ng m$^{-3}$) were observed at both sites (figure 1). The $\Delta^{14}$C values for the LMW$_{n}$-alkanes (~851%o to ~708%o) and HMW$_{n}$-alkanes (~778%o to ~712%o), as well as the $\delta^{13}$C values (LMW$_{n}$-alkanes: ~33.1%o to ~30.7%o; HMW$_{n}$-alkanes: ~34.4% to ~31.3%o; figure 1), both of these are consistent with those reported for fossil fuel sources (figure 2(a)). $\Delta^{14}$C values were translated to the respective fractional contributions from fossil ($f^{\text{fossil}}$) and nonfossil ($f^{\text{nonfossil}}$) sources using a two-end member-mixing model ($\Delta^{14}$C$_{\text{fossil}}$ ≈ 1000‰ (Gustafsson et al. 2009); $\Delta^{14}$C$_{\text{nonfossil}}$ ≈ 50‰ (Graven et al. 2017; table 1). The $f^{\text{fossil}}$ of LMW$_{n}$-alkanes and HMW$_{n}$-alkanes in Beijing (~72% and 86%, respectively) and Tianjin (~73% and 79%, respectively) clearly indicate their major contribution from fossil source. Nevertheless, $f^{\text{nonfossil}}$ values for LMW$_{n}$-alkanes (27.8% for Beijing; 17.2% for Tianjin) and HMW$_{n}$-alkanes (27.4% for Beijing; 21.1% for Tianjin) could be associated with $n$-alkanes from biomass burning, cooking, and plant emissions (figure S3) (Oros et al. 2006, Zhao et al. 2007b).

The molecular distributions of $n$-alkanes in terrestrial higher plants have a characteristic predominance of odd-C homologs from C$_{27}$ to C$_{33}$ (HMW$_{odd}$-alkanes) (Eglinton and Hamilton 1967, Simonet et al. 1988). The $\Delta^{14}$C values for the HMW$_{odd}$-alkanes (~477‰o to ~209‰o; ~380‰o) are comparable to those reported for marine sediments from Yellow River (~288‰o) (Tao et al. 2015). $\delta^{13}$C values of abundant HMW$_{odd}$-alkanes (~36.0‰o to ~32.7‰o; table S3) reported here are consistent with those of Beijing aerosols (~36.8‰o to ~31.3‰o in autumn) (Ren et al. 2019) and C$_{3}$ plants (using C$_{3}$ carbon metabolic pathway) (figure 2(a)). Likewise, the $\Delta^{14}$C of individual HMW$_{odd}$-alkanes in Beijing and Tianjin had higher contributions from biogenic inputs (<75%; table 1). Among the three HMW$_{odd}$-alkanes fractions analyzed for $\Delta^{14}$C, the C$_{29}$ $n$-alkane showed higher abundance (figure 1) and more modern values (Beijing: ~209‰o; Tianjin: ~273‰o; figure 2(a)) compared to those for C$_{27}$ and C$_{31}$ at both sites. Here, the variability in $\Delta^{14}$C probably reflects differences in the type of terrestrial plant sources (such as growing leaves, dead leaf material, deciduous trees and coniferous trees). Alternatively, differing propensities for storage and mobilization could influence the abundance and carbon isotopic composition of specific plant wax lipids (Tao et al. 2016). Higher $\Delta^{14}$C of C$_{29}$ $n$-alkane suggests a greater reactivity or short residence time in the environment. This is consistent with the higher concentrations of C$_{29}$ $n$-alkane as compared with C$_{27}$ and...
Figure 1. Stable carbon isotope distributions ($\delta^{13}$C) and concentrations of individual $n$-alkanes (a)–(d) and $n$-fatty acids (e)–(h), respectively, collected from Beijing (BJ) and Tianjin (TJ).

Table 1. $^{14}$C analytical results for individual $n$-alkanes and $n$-fatty acids in urban aerosols from Beijing (BJ) and Tianjin (TJ).

| Lipid class  | Receptor site/identification number | $\Delta^{14}$C (%) | Error (%) | $f_{\text{nonfossil}}$ (%) | $f_{\text{fossil}}$ (%) |
|--------------|-----------------------------------|---------------------|-----------|-----------------------------|-------------------------|
| $n$-Alkanes   |                                   |                     |           |                             |                         |
| C_{27}        | BJ-1 and BJ-2                     | $-427$              | 27.2      | 54.6                        | 45.4                    |
|               | TJ-1 and TJ-2                     | $-477$              | 31.9      | 49.8                        | 50.2                    |
| C_{29}        | BJ-1 and BJ-2                     | $-209$              | 4.35      | 75.3                        | 24.7                    |
|               | TJ-1 and TJ-2                     | $-273$              | 10.2      | 69.2                        | 30.8                    |
| C_{31}        | BJ-1 and BJ-2                     | $-425$              | 29.6      | 54.8                        | 45.2                    |
|               | TJ-1 and TJ-2                     | $-468$              | 34.5      | 50.7                        | 49.3                    |
| C_{26+28+30+32}| BJ-1 and BJ-2                     | $-712$              | 56.8      | 27.4                        | 72.6                    |
|               | TJ-1 and TJ-2                     | $-778$              | 63.5      | 21.1                        | 78.9                    |
| C_{19+20+21+22+23}| BJ-1 and BJ-2                   | $-708$              | 63.2      | 27.8                        | 72.2                    |
|               | TJ-1 and TJ-2                     | $-851$              | 75.5      | 14.2                        | 85.8                    |
| $n$-Fatty acids|                                   |                     |           |                             |                         |
| C_{20+22+24+26+28+30}| BJ-1 and BJ-2               | $-261$              | 10.5      | 70.4                        | 29.6                    |
|               | TJ-1 and TJ-2                     | $-265$              | 10.6      | 70.0                        | 30.0                    |
| C_{16}        | BJ-1                              | $-8.52$             | 17.3      | 94.4                        | 5.57                    |
|               | BJ-2                              | $-3.27$             | 17.9      | 94.9                        | 5.07                    |
|               | TJ-1                              | $-6.67$             | 17.5      | 94.6                        | 5.40                    |
|               | TJ-2                              | $-18.4$             | 16.3      | 93.5                        | 6.52                    |
| C_{18}        | BJ-1                              | $-27.0$             | 16.6      | 92.7                        | 7.33                    |
|               | BJ-2                              | $-19.0$             | 17.4      | 93.4                        | 6.57                    |
|               | TJ-1                              | $-45.0$             | 15.8      | 91.0                        | 9.05                    |
|               | TJ-2                              | $-44.0$             | 14.9      | 91.0                        | 8.96                    |

$C_{31}$ in plant litter (Chikaraishi and Naraoka 2006, Wu et al 2019).

Because the aerosol sampling was conducted in autumn (October-November), it is implicit that contribution from epicuticular plant waxes to airborne $n$-alkanes could be much lower than other growing seasons (Wang et al 2018). Once a leaf falls from the growing plants, it forms the litter layer on top of the soil, with leaves comprising the majority of litterfall (Wu et al 2019). Organic compounds can be
blown up from decaying plant materials in soils by winds. It is, therefore, likely that plant litter in autumn could contribute to the atmospheric abundances of \( n \)-alkanes in Beijing and Tianjin. Consequently, the contribution of waxy-lipids from leaf litter and soil to the atmosphere could be greater in autumn than in other seasons (Nelson et al. 2018). Of HMW+\( n \)-alkanes, \( C_{29} \) is usually more active and abundant in plant litter (Chikaraishi and Naraoka 2006, Wu et al. 2019). Accordingly, we observed higher abundance and more contemporary biomass fraction based on the \( \Delta^{14}C \) for \( C_{29} \) \( n \)-alkane. In addition, smoldering and flaming phases of biomass burning (e.g. deciduous trees) mainly produce HMW+\( n \)-alkanes in which \( C_{29} \) as the dominant species contributing up to 40% of all paraffins (figure S3) (Oros and Simoneit 2001a). Hence, modern carbon that originated from leaf litter and biomass burning could contribute significantly to the terrestrial \( C_{29} \) \( n \)-alkane in ambient aerosols at both sites during autumn.

HMW+\( n \)-alkanes are abundant in soils and more refractory in nature (Smittenberg et al. 2006, Anokhina et al. 2018). If the post depositional changes of lipid compounds in soils and loess deposits contribute to airborne \( n \)-alkanes, we would expect them to have less contemporary \( \Delta^{14}C \) values of HMW+\( n \)-alkanes. Therefore, contribution from either pre-aged (i.e. several thousand-year-old) soil (Tao et al. 2016) or loess deposits from Mongolia and Russian Far East (i.e. inferred based on air mass back trajectories; figure S1) could result in lower \( \Delta^{14}C \) values of \( C_{27} \), \( C_{29} \) and \( C_{31} \) \( n \)-alkanes. Taken together of all these observations, we infer that HMW+\( n \)-alkanes in Beijing and Tianjin aerosols originate from fresh biological

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**Figure 2.** Cross plots of compound specific stable carbon and radiocarbon isotopic composition (i.e. \( \delta^{13}C-\Delta^{14}C \)) of \( n \)-alkanes (a) and \( n \)-fatty acids (b) in ambient aerosols collected during autumn season over two urban receptor sites (Beijing and Tianjin) in Northeast China. \( \delta^{13}C \) ranges of \( n \)-alkanes and \( n \)-fatty acids from \( C_3 \) plants are according to references Ballentine et al. (1998, 1996), Collister et al. (1994), Bi et al. (2005), Chikaraishi and Naraoka (2003). In panel (a), fossil-fuel combustion (i.e. crude oil and vehicle exhaust) are according to references Harvey et al. (2012), Bjoryøy et al. (1991) and Muhammad et al. (2015). In panel (b), \( \delta^{13}C \) values in \( n \)-fatty acids from biomass burning of \( C_3 \) plants are according to references Ballentine et al. (1996, 1998). Both the size and color of the symbols represent their ambient concentration levels in Beijing and Tianjin.
material (i.e. plant wax, plant litter and/or biomass burning), and pre-aged organic matter from soil suspension and/or losses deposits.

3.2. n-Fatty acids

The molecular distributions of fatty acids (FAs) exhibited a strong even-over-odd carbon number predominance (CPI > 3.03) with bimodal distributions with peaks at C_{16:0} and C_{18:0} at both sites (figure 1). Such distributions are also evident from inland megacities in China (Wang et al. 2006, Kang et al. 2017, Ren et al. 2018), lake sediments (Wang et al. 2014, Zhu et al. 2014), biomass burning (Simonite et al. 2002, Oros et al. 2006), as well as cooking (Zhao et al. 2007a, 2007b, Pei et al. 2016). LMW FAs (C_{12} to C_{19} fatty acids) showed higher δ^{13}C values (−30.7‰ to −26‰) than even-carbon numbered homologs from C_{20} to C_{30} FAs (HMW_{even-FAs} −35.6‰ to −31.6‰; figure 1), which were consistent with previous studies that were reported in urban aerosols (Ren et al. 2016), marine aerosols (Fang et al. 2002), soil samples (Matsumoto et al. 2007), dust aerosols (Kawamura et al. 2010), biomass burning (Ballentine et al. 1998), and cooking samples from China (table S5).

Higher ∆^{14}C values of C_{16:0} (−5.89‰ for Beijing; −12.5‰ for Tianjin; table 1) and C_{18:3} FAs (−23‰ for Beijing; −44.5‰ for Tianjin) in both cities indicated modern carbon corresponding to 1950−1955 (global and hemispheric average ∆^{14}C (Hua and Barbetti 2004, Graven et al. 2017), when nuclear bomb tests were carried out. Chinese cooking could emit abundant LMW_{FAs}, while C_{16:0} and C_{18:0} FAs constituted 70% to 90% of the quantified compounds (figure S3) (Zhao et al. 2007a, 2007b, Pei et al. 2016). This is attributed to the larger consumption of ingredients with high fat content (e.g. seed oil). Relative abundance of even-C homologs over that of odd-C homologs between C_{12} and C_{30}, referred as carbon preference index (CPI_{FAs}). The CPI_{FAs} of LMW_{FAs} in Beijing (29.2–35.1) and Tianjin (32.8–56.3), as well as δ^{13}C of C_{16:0} and C_{18:0} FAs (−29.2‰ to −27.5‰; table S3), both of these are consistent with those reported for Chinese cooking (Zhao et al. 2007b) (CPI_{FAs}: 26–47 for LMW_{FAs}; δ^{13}C: −31.9‰ to −25.7‰ for LMW_{FAs}; table S5 and figure S3). This observation suggests that Chinese cooking could be the principal modern carbon sources of LMW_{FAs} in urban aerosols.

LMW_{FAs} are also abundant in airborne fungal spores as well as in soil detritus. Therefore, these source-emissions could contribute to the atmospheric abundances of LMW_{FAs} (Kramer and Gleixner 2006). Microbial activities can enhance the emission of sugar alcohols at a certain level during autumn (Kramer and Gleixner 2006, Li et al. 2018). We observed higher concentrations of arabitol (ave., 24.3 ng m^{-3}; table S3) and mannitol (60.2 ng m^{-3}), tracers for airborne fungal spores (Burshtein et al. 2011), implying that abundant microorganism existed in the atmosphere. Hence, microorganism could be an important modern source of LMW fatty acids in autumn in both cities. Lipid-rich pollen also contains abundant even-carbon numbered n-fatty acids (Kawamura et al. 2010). However, the pollen period lasts from August to September in Northeast China (Xu et al. 2012a); and pollen is easily scavenged from the atmosphere by dry/wet deposition and is unlikely transported long distances owing to their large particle sizes. Thus, pollen probably contributed little fatty acids during this period (October) at both sites.

Biomass-burning is active during sampling period in and around the both receptor sites (Beijing and Tianjin). Accordingly, we observed high concentrations of levoglucosan (ave., 145 ng m^{-3}; table S3), a tracer of biomass burning (Ren et al. 2019). Likewise, biomass burning also contributes to higher abundances of even-carbon numbered n-fatty acids (figure S3) (Oros and Simonite 2001a, 2001b; Oros et al. 2006). The CPI_{FAs} for the TSP samples collected in Beijing (3–4) and Tianjin (3.36–3.69) overlap with those typical biomass burning emissions (−5.5) in Northeast China (Fu et al. 2008b). Likewise, δ^{13}C values of FAs (−35.6‰ to −26.0‰) are also comparable to those reported for biomass burning (figure 2b). Therefore, biomass burning could be an important contemporary carbon source of even-carbon numbered fatty acids in autumn at both sites.

Compared to high contribution of modern organic carbon (91‰−94.9‰; table 1) to LMW_{FAs}, HMW_{even-FAs} showed relatively older carbon characterized by negative 14C values (−261‰ for Beijing and −265‰ for Tianjin; figure 2(b)) at both sites, corresponding to relatively higher contributions from fossil sources (29.6% for Beijing and 30% for Tianjin; table 1). Such differences in 14C between LMW_{FAs} and HMW_{even-FAs} were documented previously in marine sediments from marginal sea around China (Tao et al. 2015, 2016), surface soil from northern Japan (Matsumoto et al. 2007), and marine aerosols (marine algal sources for LMW_{FAs}, but terrestrial higher plants for HMW_{even-FAs}) from Northwest Pacific (Matsumoto et al. 2001, Kawamura et al. 2010).

HMW_{even-FAs} showed similar ∆^{14}C values with the C_{29} n-alkane (−209‰ to −273‰), implying their similar transport times. There are compositional differences between green and dead leaves due to either seasonal transition or the effect of variations in leaf age wax (Rogge et al. 1993c, Chikaraishi and Naraoka 2006). Concentrations of HMW_{odd-n-alkanes} are much higher than those of HMW_{even-FAs} in green leaf wax (Rogge et al. 1993c, Chikaraishi and Naraoka 2006). In contrast, n-alkanols and n-alkanen could be oxidized to HMW_{even-FAs}. In the dead leaves resulting in four times higher HMW_{even-FAs} than those of green leaves (Rogge et al. 1993c). Accordingly, we observed that total concentrations of HMW_{even-FAs} (49 ng m^{-3} for Beijing and 41 ng m^{-3} for Tianjin) was roughly two times higher than those of HMW_{odd-n-alkanes}. 
(23.1 ng m\(^{-3}\) for Beijing and 21.9 ng m\(^{-3}\) for Tianjin; table S3) in autumn aerosols. Thus, dead leaves abrasion products existing in soil detritus or road dust could be in part responsible for the modern carbon in HMW\(_{\text{even-FA}}\) during autumn periods at both sites.

The leaf litter with abundant fatty acids could undergo selective microbial degradation on the soil surfaces, such as odd-carbon numbered fatty acids produced by microbial \(\alpha\)-oxidation of even-carbon numbered fatty acids (Matsumoto et al. 2007). The prevalence of odd-carbon numbered fatty acids (figure 1), further suggests that soil organic matters could contribute to fatty acids in both cities. Besides, LMW\(_{\text{FA}}\) in leaf litters could be more easily transported downward by precipitation and utilized by soil microorganisms due to their hydrophilicity. In contrast, HMW\(_{\text{even-FA}}\) are less water-soluble and are not efficiently transported via a stem down to the roots in soils resulting in higher concentrations in surface soil. Hence, HMW\(_{\text{even-FA}}\) are more likely retained in the soils and/or loess deposit for hundreds to thousands of year and mobilized by winds to be emitted to the air from upwind regions (i.e. Mongolia and Russian Far East), resulting in biogenic but old HMW\(_{\text{even-FA}}\) carbon in urban aerosols from Beijing and Tianjin.

4. Implications

As this is one of the first reports on \(^{14}\)C signals of atmospheric \(n\)-alkanes and fatty acids in China, we could only compare our data with the existing atmospheric \(\Delta^{14}\)C data for organic carbon (OC). The \(\Delta^{14}\)C of OC in Beijing showed their origin from nonfossil sources (60% to 80%) in autumn (Zhang et al. 2017), mainly due to relatively high contribution from biomass-burning, cooking and plant. These are consistent with our results of fatty acids. Our previous observation suggested that temporal trend of OC and HMW\(_{\text{even-FA}}\) was similar throughout the year (Ren et al. 2019), indicating that the main sources identified based on abundances, \(^{13}\)C and \(^{14}\)C of fatty acids may be attributed to total organic aerosols. Likewise, other studies focusing on \(\Delta^{14}\)C of OC in wintertime aerosols (2013 and 2014, respectively) from Beijing and Tianjin have revealed significant contributions from fossil-fuel sources (Yan et al. 2017, Fang et al. 2017). The \(\Delta^{14}\)C of OC from these studies (−800‰ to −600‰) overlapped with our results of fossil-derived LMW\(_{\text{n-alkanes}}\) and HMW\(_{\text{even-alkanes}}\) (−850‰ to −708‰). The agreement of \(^{14}\)C signal of fossil-fuel compounds during different period and different sites may indicate \(\Delta^{14}\)C approximately ranging from −850‰ to −600‰ as a lower limit in Beijing and Tianjin.

Terrestrial organic carbon is significantly influenced by a variety of anthropogenic sources, and is an important contributor to marine and terrestrial basins via atmospheric transport and deposition. Considering the OC exchange between the atmosphere and sediments, there is a possibility that old organic carbon in continent could be sporadically transported from exposed marginal sea sediments (such as Bohai Sea; figure S1) with abundant deposition of ancient but biogenic fossil OC, through aeolian sediment accumulations associated with marine-level variation. However, the contribution of OC from pre-aged plant-derived litter in soil, ancient loess deposits and/or exposed sediments are diluted by modern material (i.e. cooking, biomass burning, microorganism, and contemporary plant litter in soils). The sites where this study was conducted are highly urbanized in terms of its population, industrial structure and environmental setting. Since particles could be long-range transported, results from their \(^{14}\)C content, thus, could draw broad generalization to support reliability of CSRA on \(n\)-alkanes and fatty acids in other areas, especially for coastal region focused on marine sediments. In general, application of CSRA technique to get the radiocarbon content of \(n\)-alkanes and fatty acids in urban aerosols will broaden our knowledge of their source appointment, atmospheric transport processes and the transformation mechanism of aerosol OC to marine and terrestrial basins.

Acknowledgments

The authors declare no competing financial interest. This study was financially supported by the National Key R&D Program of China (Grant No. 2017YFC0212700), the National Natural Science Foundation of China (Grant Nos. 41807303 and 41625014) and State Key Laboratory of Organic Geochemistry, GIGCAS (Grant No. SKLOG-201747).

Data availability

The data that support the findings of this study are available upon request from the authors.

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